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EFFECTS OF CHEMICAL IMPURITIES ON GAS PERMEATION AND DIFFUSION IN POLYMERIC MEMBRANES

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ABSTRACT

In recent years, polymeric membranes have been increasingly used in key unit operations such as gas separations. In theory, the performance of a polymeric membrane module depends solely on the chemical structure of the polymer and the feed gas composition. However, impurities in the feed stream (such as vapors from compressor oils) have been found to affect the productivity of the membrane module even at parts per million (ppm) levels.

To understand the fundamental effects of such trace chemicals, commercial polymers were studied for their solubility and permeability characteristics in the presence and absence of such impurities. Two types of compressor oils were used in doping the polymers at three concentration levels. Permeabilities of N_2, O_2, CH_4, and CO_2 were measured in dense homogeneous films at 35°C. Selectivities of O_2/N_2 and CO_2/CH_4 were also calculated in the presence and absence of oil. The permeability data were used in conjunction with the sorption results as reported in previous pa-

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pers to calculate diffusivities in the Henry's (D_D) and Langmuir (D_H) regions of the polymer.

The effect of annealing on permeability and diffusivity in clean and doped samples of the polymers was also examined. Such thermal treatment reduced the diffusivity and permeability due to densification of the glassy structure. The effect was common to both clean and doped films.

A good understanding of the effects of such trace chemicals on the permeability characteristics of the membrane will aid in designing effective polymeric membrane modules in the future.

INTRODUCTION

The earliest recorded developments in the field of membranology date back as far as 1846 when Schoenbein studied cellulose nitrate, the first synthetic polymer. Early attempts to control and vary porosity in synthetic membranes were largely empirical. As a result, fluxes obtained were low and made membrane technology uneconomical in relation to conventional separation processes, such as cryogenic distillation and pressure swing adsorption. Discoveries by Loeb and Sourirajan in the early 1960s of means to produce the first asymmetrically skinned membrane for reverse osmosis (1) was finally applied to gases in 1970 (2). Separation of gas mixtures using polymer membranes offers the advantage of lower energy requirements compared to those of conventional processes (3).

Therefore, in recent years this membrane technology has either replaced or supplemented conventional processes as an important industrial unit operation. Some of the common applications of this technology have been generation of nitrogen from air (4), SO_2 removal from smelter gas streams, and H_2S and water removal from natural gas and air streams (5).

In theory, the polymer and feed gas mixture are the only factors that determine the sorption and diffusion processes in a given membrane. However, in actual commercial operations, additional factors, such as organic impurities, influence the performance of the membrane module. Although filters are used upstream of the membrane unit to mitigate the problem, impurities such as compressor oils affect the membrane performance in concentrations on the order of parts per million (ppm). While a survey of fouling in microporous and ultrafiltration membranes has been completed to some extent (6), no significant research in the area of fouling in gas separation membranes has been reported. Because the performance of a module is based on a clean system, the actual membrane performance often differs significantly from that reported by the manufacturer. The overall transport of gas through a membrane is comprised of two independent processes, namely, sorption and diffusion. This paper addresses the effect of the impurity on gas permeability and diffusion in a series of polymers.

THEORY

In general, gas separation can be performed using synthetic membranes based on one of three general transport mechanisms (7):

Knudsen-diffusion
Molecular sieving
Solution-diffusion

The Knudsen-diffusion and molecular-sieving mechanisms are used in porous membranes while the solution-diffusion mechanism is the governing transport mode in nonporous (dense) membranes. In nonporous membranes, the gas molecules actually dissolve and diffuse in the dense membrane matrix. Therefore, the mechanism of permeation in such membranes consists of three steps:

1. Sorption at the upstream boundary.
2. Diffusion through the membrane.
3. Desorption from the downstream boundary.

Several authors have described the sorption of gases in glassy polymers over a moderate pressure range (0–30 atm) that is achieved by means of a dual-mode sorption model (8–11). Inherent in the dual-mode sorption model is the concept of sorption into two idealized environments (8,11,12). One population of sorption is viewed as arising from uptake into a dissolved environment similar to sorption in low molecular-weight liquids and rubbery polymers and is described by Henry's law. The second population of sorbate is considered to occupy the unrelaxed volume or "microvoids" present in glassy polymers and is described by a Langmuir isotherm. The total sorption for a single gas is given as the sum of these two populations as follows:

$$C = C_D + C_H = k_D p + \frac{C'_H bp}{1 + bp} \tag{1}$$

where, C_D is the sorbed population in the densified regions that is described by Henry's law while C_H is the Langmuir term that accounts for sorption in the microvoids. Solubility in the Henry's region of polymers is comparable to dissolution of gases in organic liquids (13–15).

The Langmuir sorption capacity C'_H is a measure of the sorption capacity of the unrelaxed volume, and its magnitude increases as the temperature decreases below the glass transition temperature (T_g) (8,16). The sorption capacity is strongly dependent on the history of the polymer sample. Chan and Paul (17) demonstrated that in the case of polycarbonate, annealing the sample in the sub-T_g region decreased the sorption capacity of the sample. The researchers found that C'_H decreased considerably as the duration of annealing was increased while k_D and b (the hole affinity constant) were not affected by annealing. Erb and Paul (18) obtained similar results with CO_2 sorption in polysulfone. These works established that thermal treatment causes reduction in the free volume through densification of the microvoids in the glassy region of the polymer.

The b is an equilibrium constant equal to the ratio of rate constants of penetrant sorption and desorption in the holes and is therefore a measure of the tendency of a penetrant to sorb as measured in the Langmuir model (19,20).

Based on the assumption that the gas sorbed in the Langmuir mode is completely immobilized, Vieth and Sladek developed the unsteady-state transport model for single gas diffusion (10). Petropoulos (21) noted that the sorbed gas molecules, as described by Langmuir isotherms, may not be completely immobilized and derived the unsteady-state transport model based on separate diffusion coefficients for molecules in the "dissolved" region and those sorbed in the microvoids. Paul and Koros (22) extended Petropoulos's work by deriving the partial immobilization or dual mobility model by considering concentration instead of chemical potential as the driving force for diffusion. The dual mobility transport of a gas in a glassy polymer can be described by Fick's law:

$$J = J_D + J_H = -D_D \frac{\partial C_D}{\partial x} - D_H \frac{\partial C_H}{\partial x} \tag{2}$$

where J is the total diffusional flux; J_D and J_H are the respective fluxes of two populations, C_D (Henry's) and C_H (Langmuir); and D_D and D_H are the corresponding diffusion coefficients. The activation energy tends to be larger for D_H than for D_D (11,22,23). Therefore, due to the differences in the energetics of diffusional jumps in the 2 environments, D_D is typically much larger than D_H except for noncondensable gases such as helium or hydrogen.

For the case in which the downstream pressure is effectively zero, Koros and Paul (24) showed that the appropriate expression derived from the dual-mode sorption and transport models for steady-state permeability of a pure component in a glassy polymer is given by:

$$P = k_D D_D \left(1 + \frac{FK}{1 + bp}\right) \tag{3}$$

where P is the permeability in barrers; $F = D_H/D_D$ and $K = (C'_H b)/k_D$ are convenient dimensionless groups; and p is the upstream driving pressure. Based on Eq. (3), diffusivities of the gas molecules in the dense (D_D) and Langmuir (D_H) regions of the polymer can be obtained through linear regression of permeability versus pressure if the sorption parameters k_D, C'_H, and b are known. The intercept of the line will yield D_D while D_H is determined using the slope. The sorption parameters k_D, C'_H, and b are derived by means of a nonlinear regression of gas sorption data obtained through Eq. (1). The sorption parameters estimated for clean and doped membranes were reported in separate articles (25,26).

Arguments similar to those presented above for single gases have been extended to generalize the expressions in Eqs. (1) and (3) to account for mixed penetrants as shown below (27):

$$C_A = k_{DA}p_A + \frac{C'_{HA}b_A p_A}{1 + b_A p_A + b_B p_B} \tag{4}$$

and

$$P_A = k_{DA}D_{DA}\left(1 + \frac{F_A K_A}{1 + b_A p_A + b_B p_B}\right) \tag{5}$$

In the above expressions, A refers to the component of primary interest while B refers to the secondary component.

The theoretical background discussed above was developed for a condensable gas and glassy additive-free polymer. However, trace chemicals may affect the productivity of the gas-separation polymeric membrane. Because overall gas transport combines a solution and diffusion process, the effects of such impurities on each process were studied independently. Studies on the effects on gas sorption have been reported in separate papers (25,26). In this paper we address the effects of impurities, such as compressor oils on the permeability characteristics of the membrane as well as diffusivities in the Henry's (D_D) and Langmuir (D_H) regions of the polymer.

EXPERIMENTAL PROCEDURE

Materials

The following four polymers were used for fabricating dense homogeneous membranes:

polycarbonate and polysulfone supplied by Aldrich Chemical Company Inc. (Milwaukee, Wisconsin), and substituted polycarbonates, PC-1 and PC-2, supplied by MG Generon (Pittsburg, California).

Typical compressor oils SH-100 and SH-46 (Summit Oil Company, Inc, Tyler, Texas) were used as dopants. Both compressor oils are synthetic hydrocarbons (poly α-olefin) with the molecular weight of SH-100 being higher than that of SH-46. However, because the effects on membrane performance of both compressor oils were similar, only results pertaining to SH-46 are reported in this manuscript.

Dopants were used in concentrations of 10^3, 10^4, and 10^5 ppm based on polymer weight. At oil concentrations greater than 10^5 ppm, fabrication of a defect-free membrane was not feasible, and therefore, this doping level constituted the upper limit for exploring effects of impurities on membrane performance. N_2, O_2, CH_4, and CO_2 were used as single gases to determine permeabilities of clean and doped membranes.

Film Preparation

The polymer of interest was dissolved in a solvent and the resulting solution was used to cast dense homogeneous films. The films were dried at room temperature and were used without further modification or were annealed at 20°C below the respective T_g of the virgin polymer for 2 hours. The effective cross-sectional area of membrane sample used in permeability studies was 9.6 cm^2. The average thickness of the sample used was 30 microns. Doped films were prepared through the same protocol as that for clean membranes with the exception that the dopant was introduced in the casting solution at the predetermined concentrations of 10^3, 10^4, and 10^5 ppm.

APPARATUS

A schematic of the apparatus used in performing permeation measurements is shown in Fig. 1. The membrane modules are the primary elements in the permeation apparatus. These modules are high-pressure Millipore filter holders. The membrane sample was placed in these filter holders. A filter paper was used as support for the membrane sample. The pressures were monitored by Ashcroft pressure gauges (0–600 psig). Bubble flowmeters were employed to measure the gas flow rates through the membrane because the flow rates were too small (10^{-3} to 10^{-4} cc/s) to be measured with rotameters. Permeabilities of N_2, O_2, CH_4, and CO_2 in the 4 polymers were measured at 35°C and feed pressures of 50, 100, 150, 200, and 250 psig.

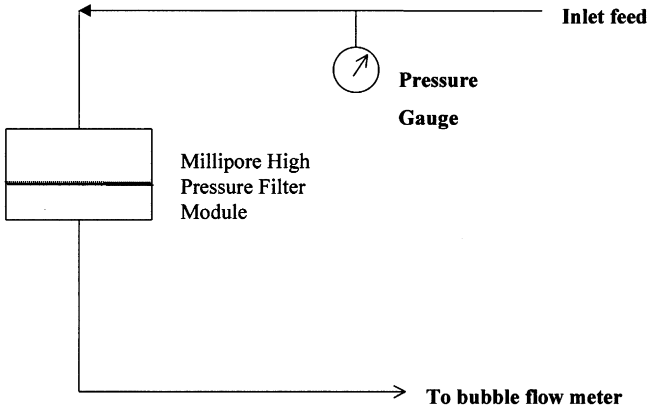

Figure 1.

The T_g values of the clean and doped polymer samples were measured with a Perkin-Elmer DSC 7 differential scanning calorimeter attached with a TAC 7/3 instrument controller. The instrument was calibrated with indium (melting point = 156.6°C) and zinc (melting point = 419.47°C). Samples sizes of approximately 3 mg were used and heated at a rate of 20°C/min under a N_2 atmosphere.

RESULTS

Permeability

The model parameters were computed using the dual-mode sorption (Eq. 1) and permeability (Eq. 3) expressions for a single gas in glassy polymers. The sorption parameters, describing the effects of compressor oils on the dissolution of N_2, O_2, CH_4, and CO_2 in the 4 polymers, were reported in separate papers (25,26).

Tables 1–4 list permeabilities to N_2, O_2, CH_4, and CO_2 in the presence and absence of oil for each of the 4 polymers prior to and after annealing of the

Table 1. Permeability and Ideal Selectivity for Polycarbonate

	Permeability (Barrers) (Nonannealed)			
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N_2	0.365 ± 0.004	0.308 ± 0.005	0.300 ± 0.004	0.252 ± 0.005
O_2	1.894 ± 0.008	1.706 ± 0.011	1.686 ± 0.01	1.454 ± 0.007
CH_4	0.289 ± 0.006	0.257 ± 0.005	0.212 ± 0.007	0.207 ± 0.005
CO_2	6.878 ± 0.013	6.812 ± 0.009	6.531 ± 0.007	6.443 ± 0.008
	Ideal Selectivity			
O_2/N_2	5.19 ± 0.04	5.54 ± 0.02	5.62 ± 0.02	5.77 ± 0.03
CO_2/CH_4	23.8 ± 0.11	26.51 ± 0.09	30.81 ± 0.07	31.13 ± 0.05
	Permeability (Barrers) (Annealed)			
N_2	0.277 ± 0.004	0.229 ± 0.003	0.212 ± 0.006	0.18 ± 0.006
O_2	1.483 ± 0.009	1.273 ± 0.008	1.25 ± 0.008	1.069 ± 0.01
CH_4	0.176 ± 0.003	0.155 ± 0.002	0.117 ± 0.001	0.106 ± 0.002
CO_2	4.815 ± 0.009	4.603 ± 0.008	4.188 ± 0.007	3.901 ± 0.011
	Ideal Selectivity			
O_2/N_2	5.35 ± 0.03	5.56 ± 0.01	5.9 ± 0.01	5.96 ± 0.02
CO_2/CH_4	27.36 ± 0.07	29.7 ± 0.07	35.79 ± 0.03	36.8 ± 0.04

Table 2. Permeability and Ideal Selectivity for Polysulfone

Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
Permeability (Barrers) (Nonannealed)				
N_2	0.37 ± 0.004	0.317 ± 0.002	0.293 ± 0.002	0.286 ± 0.003
O_2	1.86 ± 0.003	1.73 ± 0.004	1.64 ± 0.003	1.623 ± 0.002
CH_4	0.396 ± 0.006	0.341 ± 0.006	0.31 ± 0.003	0.26 ± 0.005
CO_2	5.67 ± 0.007	5.247 ± 0.008	5.176 ± 0.006	5.106 ± 0.005
Ideal Selectivity				
O_2/N_2	5.03 ± 0.03	5.46 ± 0.03	5.6 ± 0.02	5.69 ± 0.02
CO_2/CH_4	14.32 ± 0.05	15.39 ± 0.06	16.7 ± 0.07	19.64 ± 0.05
Permeability (Barrers) (Annealed)				
N_2	0.278 ± 0.005	0.236 ± 0.003	0.213 ± 0.004	0.19 ± 0.005
O_2	1.52 ± 0.006	1.324 ± 0.005	1.259 ± 0.003	1.147 ± 0.006
CH_4	0.242 ± 0.002	0.196 ± 0.004	0.172 ± 0.003	0.148 ± 0.003
CO_2	4.994 ± 0.004	4.656 ± 0.007	4.387 ± 0.006	4.294 ± 0.007
Ideal Selectivity				
O_2/N_2	5.47 ± 0.04	5.61 ± 0.03	5.91 ± 0.02	6.04 ± 0.05
CO_2/CH_4	20.64 ± 0.07	23.76 ± 0.04	25.51 ± 0.06	29.01 ± 0.08

respective membrane samples. The listed permeability values were deduced at 150 psig feed pressure, which is the typical operating pressure for commercial gas-separation modules. Data obtained at other feed pressures (50, 100, 200, and 250 psig) were used in conjunction with the 150-psig permeability data to compute diffusion coefficients for a given polymer-gas pair in the presence and absence of oil.

The data indicate that permeability decreases with increased oil concentration in the membrane film. The permeability reductions were observed in annealed samples as well as samples that were not thermally treated. Because both oils (SH-46 and SH-100) affected the membrane performances to an equal degree, the molecular weight of the oil may not be a variable in the impact of oil on membrane productivity. Also, the polycarbonate-based films and polysulfone samples were affected to a similar degree by the presence of oil. This result suggests that the chemical composition of the polymer is also not likely to be a factor governing the effect of oil on membrane permeability. In other words, the oil may interact with the polymer on a physical rather than chemical basis.

A careful analysis of the data presented indicates that the permeability of the polymer to the different gases is affected in a discriminating manner based on the kinetic diameters of the gas species. Therefore, CH_4 is affected the most followed by N_2, O_2, and CO_2. This type of sieving of the gas molecules follows their respective kinetic sizes (Table 5). This selective discrimination based on molecular size of the gas species translates to enhanced selectivities of O_2/N_2 and CO_2/CH_4. Increase in O_2/N_2 separation ranged from approximately 5% at the 10^3-ppm oil concentration to approximately 15% at the 10^5-ppm level of oil. CO_2/CH_4 selectivity increased from around 15% at 10^3-ppm concentrations of oil to approximately 30% at the 10^5-ppm impurity level. This increase in selectivities is within the same order of magnitude for all polymers. This type of selectivity enhancement at the expense of loss in productivity has the potential of being a desired trade-off if the separation factor for a pair of gases, such as O_2 and N_2 or CO_2 and CH_4, needs to be increased without substituting the membrane material with an entirely new polymer. However, depending on the desired throughput of the module and the end use for the specific gas components, the benefit of the higher separation must be weighed against the loss in membrane productivity.

Maeda and Paul (28) described the effect of certain low molecular-weight diluents on polymer permeability and selectivity. In their study, the presence of

Table 3. Permeability and Ideal Selectivity for PC-1

Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
	Permeability (Barrers) (Nonannealed)			
N_2	0.34 ± 0.005	0.298 ± 0.006	0.279 ± 0.003	0.228 ± 0.004
O_2	2.24 ± 0.003	2.141 ± 0.004	2.038 ± 0.006	1.709 ± 0.007
CH_4	0.26 ± 0.005	0.224 ± 0.003	0.211 ± 0.003	0.205 ± 0.002
CO_2	6.77 ± 0.008	6.467 ± 0.006	6.422 ± 0.009	6.344 ± 0.007
	Ideal Selectivity			
O_2/N_2	6.59 ± 0.06	7.18 ± 0.05	7.3 ± 0.03	7.5 ± 0.04
CO_2/CH_4	26.04 ± 0.07	28.87 ± 0.06	30.44 ± 0.06	30.95 ± 0.05
	Permeability (Barrers) (Annealed)			
N_2	0.23 ± 0.002	0.193 ± 0.003	0.18 ± 0.004	0.145 ± 0.006
O_2	1.69 ± 0.006	1.522 ± 0.005	1.45 ± 0.005	1.206 ± 0.003
CH_4	0.17 ± 0.006	0.139 ± 0.006	0.126 ± 0.002	0.114 ± 0.004
CO_2	6.099 ± 0.01	5.616 ± 0.005	5.522 ± 0.007	5.278 ± 0.009
	Ideal Selectivity			
O_2/N_2	7.35 ± 0.03	7.89 ± 0.08	8.06 ± 0.04	8.32 ± 0.05
CO_2/CH_4	35.88 ± 0.1	40.4 ± 0.04	43.83 ± 0.09	46.3 ± 0.11

Table 4. Permeability and Ideal Selectivity for PC-2

Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
Permeability (Barrers) (Nonannealed)				
N_2	0.969 ± 0.005	0.844 ± 0.008	0.799 ± 0.006	0.719 ± 0.007
O_2	5.897 ± 0.007	5.33 ± 0.01	5.179 ± 0.009	4.978 ± 0.008
CH_4	0.73 ± 0.004	0.649 ± 0.004	0.607 ± 0.007	0.528 ± 0.006
CO_2	12.61 ± 0.009	12.491 ± 0.007	12.388 ± 0.006	12.278 ± 0.007
Ideal Selectivity				
O_2/N_2	6.09 ± 0.07	6.32 ± 0.06	6.48 ± 0.06	6.92 ± 0.09
CO_2/CH_4	17.27 ± 0.09	19.25 ± 0.05	20.41 ± 0.07	23.25 ± 0.1
Permeability (Barrers) (Annealed)				
N_2	0.692 ± 0.009	0.567 ± 0.008	0.496 ± 0.003	0.454 ± 0.006
O_2	4.5 ± 0.009	3.889 ± 0.006	3.566 ± 0.009	3.36 ± 0.005
CH_4	0.473 ± 0.003	0.441 ± 0.006	0.408 ± 0.007	0.359 ± 0.008
CO_2	9.587 ± 0.007	9.488 ± 0.008	9.421 ± 0.008	9.387 ± 0.005
Ideal Selectivity				
O_2/N_2	6.50 ± 0.09	6.86 ± 0.07	7.19 ± 0.06	7.40 ± 0.04
CO_2/CH_4	20.27 ± 0.06	21.51 ± 0.08	23.09 ± 0.09	26.15 ± 0.09

such compounds in the polymer reduced the permeability and enhanced the selectivity of the gas separation membrane. These compounds, present in concentrations at 10 to 20% of the polymer weight, retarded the segmental motions in the polymer thereby reducing chain flexibility. Such additives are commonly termed "antiplasticizers" as an antithesis to plasticizers, which typically increase chain mobility in the polymer. In addition to mechanical stiffening of the chains, antiplasticization is also characterized by a depression in the T_g. Shuster and Narkis

Table 5. Kinetic Diameters of Gases

Gas	Kinetic Diameter (Å)
CH_4	3.80
N_2	3.64
O_2	3.46
CO_2	3.30

Data from (4).

Table 6. Glass Transition Temperatures for All Polymers

		T_g (°C)		
Polymer	Clean	10^3 ppm SH-46	10^4 ppm SH-46	10^5 ppm SH-46
Polycarbonate	146.4	143.1	141.1	133.4
Polysulfone	184.6	181.4	180.8	171.0
PC-1	256.9	242.1	235.5	227.3
PC-2	—	—	—	—

— Data not available.

(29) observed a depression in the T_g of polycarbonate upon adding polycaprolactone to it in varying amounts. Their findings also supported the reduction or elimination of the secondary relaxation process in the polymer thereby confirming the antiplasticizing effect of polycaprolactone on polycarbonate. A DSC analysis of doped samples of the polymers (Table 6) shows a depression in the T_g with increased oil concentration in the membrane. In fact, both oils used affected (SH-100 not shown in the table) T_g comparably, which offers further support to the notion that the molecular weight of the oil is not a key variable in the effect of oil on membrane performance. The oil may be imparting changes similar to what Maeda and Paul (28) observed with the low molecular-weight diluents. The lowering in T_g of the various polymers through doping is indicative of the increased chain mobility within the polymer. The increased chain mobility causes a general relaxation of the previously stressed polymer chain. This relaxation causes a reduction of microvoids or free volume (25,26). This lesser volume decreases the amount of permeating gas species and consequently overall permeability is reduced. The oil likely acts as an "antiplasticizer" because the resulting permeabilities of CH_4, N_2, O_2, and CO_2 are reduced through doping, despite the increased mobility of the individual polymer chains.

Diffusion

The permeability data were used in conjunction with the sorption data reported on these polymers (25,26) to obtain the diffusivities in the Henry's (D_D) and Langmuir (D_H) regions. The diffusivities for the four polymers are shown in Tables 7–10. Typically, D_D has a higher value than D_H due to the larger activation energy associated with diffusion in the holes. This diffusion-effect has been shown in studies with clean polycarbonate (11,22) and polysulfone (17) films by other investigators. In the case of doped samples, the data indicate that D_D is larger than D_H in our experiments as well. Therefore, the doped samples follow a simi-

Table 7. Diffusivities for Polycarbonate

<table>
<tr><th colspan="6">D_D (1×10^8 cm^2/s) (Nonannealed)</th></tr>
<tr><th>Gas</th><th>Reported *</th><th>Clean</th><th>10^3 ppm</th><th>10^4 ppm</th><th>10^5 ppm</th></tr>
<tr><td>N_2</td><td>1.76</td><td>2.05 ± 0.017</td><td>1.43 ± 0.022</td><td>1.19 ± 0.020</td><td>0.959 ± 0.025</td></tr>
<tr><td>O_2</td><td>No data</td><td>7.98 ± 0.034</td><td>6.31 ± 0.016</td><td>5.97 ± 0.020</td><td>5.34 ± 0.027</td></tr>
<tr><td>CH_4</td><td>1.09</td><td>1.13 ± 0.017</td><td>0.837 ± 0.024</td><td>0.569 ± 0.017</td><td>0.508 ± 0.019</td></tr>
<tr><td>CO_2</td><td>6.22</td><td>10.6 ± 0.026</td><td>9.19 ± 0.022</td><td>7.93 ± 0.022</td><td>7.16 ± 0.015</td></tr>
<tr><th colspan="6">D_H (1×10^8 cm^2/s) (Nonannealed)</th></tr>
<tr><td>N_2</td><td>0.509</td><td>0.866 ± 0.009</td><td>0.577 ± 0.008</td><td>0.532 ± 0.011</td><td>0.374 ± 0.008</td></tr>
<tr><td>O_2</td><td>No data</td><td>3.2 ± 0.012</td><td>2.97 ± 0.008</td><td>2.84 ± 0.005</td><td>2.18 ± 0.007</td></tr>
<tr><td>CH_4</td><td>0.1258</td><td>0.258 ± 0.006</td><td>0.149 ± 0.007</td><td>0.117 ± 0.005</td><td>0.107 ± 0.003</td></tr>
<tr><td>CO_2</td><td>0.485</td><td>1.65 ± 0.004</td><td>1.54 ± 0.01</td><td>1.36 ± 0.012</td><td>1.17 ± 0.008</td></tr>
<tr><th colspan="6">D_D (1×10^8 cm^2/s) (Annealed)</th></tr>
<tr><td>N_2</td><td>No data</td><td>1.71 ± 0.014</td><td>1.14 ± 0.018</td><td>0.878 ±0.012</td><td>0.708 ± 0.022</td></tr>
<tr><td>O_2</td><td>No data</td><td>6.6 ± 0.023</td><td>5.06 ± 0.014</td><td>4.9 ± 0.019</td><td>3.99 ± 0.018</td></tr>
<tr><td>CH_4</td><td>No data</td><td>0.676 ± 0.011</td><td>0.512 ± 0.019</td><td>0.321 ± 0.015</td><td>0.263 ± 0.015</td></tr>
<tr><td>CO_2</td><td>No data</td><td>7.59 ± 0.018</td><td>6.48 ± 0.021</td><td>5.18 ± 0.016</td><td>4.37 ± 0.013</td></tr>
<tr><th colspan="6">D_H (1×10^8 cm^2/s) (Annealed)</th></tr>
<tr><td>N_2</td><td>No data</td><td>0.829 ± 0.007</td><td>0.545 ± 0.012</td><td>0.411 ± 0.011</td><td>0.342 ± 0.008</td></tr>
<tr><td>O_2</td><td>No data</td><td>3.11 ± 0.009</td><td>2.84 ± 0.011</td><td>2.14 ± 0.008</td><td>2.09 ± 0.013</td></tr>
<tr><td>CH_4</td><td>No data</td><td>0.228 ± 0.008</td><td>0.15 ± 0.007</td><td>0.111 ± 0.011</td><td>0.095 ± 0.011</td></tr>
<tr><td>CO_2</td><td>No data</td><td>1.42 ± 0.013</td><td>1.32 ± 0.006</td><td>1.2 ± 0.009</td><td>0.913 ± 0.015</td></tr>
</table>

* Sample conditioned in 20 atm of CO_2 for 4 hours (11).

lar pattern as the clean samples in terms of the energetics associated with diffusivities in the Henry's and Langmuir regions of the polymer.

The diffusivity of the Henry's law species (D_D) of the various gases correlated well with their respective kinetic diameters, listed in Table 5, for clean and doped polymer samples. Therefore, CO_2 had the highest D_D followed by O_2, N_2, and CH_4. On the contrary, in the frozen "holes" or microvoids, the diffusivity (D_H) of O_2 was higher than CO_2 for both polymers irrespective of whether the sample was doped or not. However, the D_H values for CH_4 and N_2 followed the correlation with their corresponding kinetic diameters. We do not know why O_2 exhibits a greater D_H than does CO_2. However, one possible cause may be the aging history of the polymer where a highly condensable gas such as O_2 induces a relaxation in the microvoid region of the polymer, thereby decreasing the diffusivity D_H of subsequent gases such as CO_2. However, because no data for O_2 was reported in the literature, comparisons cannot be made against values measured by other investigators.

The effect of oil on gas diffusion was similar in all the polymers. Tables 7–10 indicate a decrease in gas diffusivities with increasing oil concentration for all polymers. Typically, CH_4 and N_2 are affected to a higher degree than O_2 and CO_2 by the presence of oil in the polymer. Like in the case of clean films, D_H for O_2 is higher than it is for CO_2 in doped polymer samples. This result can be attributed to the relaxation induced in the Langmuir region when permeation experiments with O_2 are followed by those with CO_2, D_D, and D_H are affected to about the same extent; although in some cases, at the lower oil concentrations, the effect on D_H is more pronounced than it is on D_D. This situation may arise from the relaxation induced by the oil in the highly stressed glassy region of the poly-

Table 8. Diffusivities for Polysulfone

Gas	Reported *	Clean	10^3 ppm	10^4 ppm	10^5 ppm
		D_D (1×10^8 cm^2/s) (Nonannealed)			
N_2	1.03	1.47 ± 0.016	1.12 ± 0.012	0.913 ± 0.008	0.855 ± 0.008
O_2	No data	5.77 ± 0.017	4.70 ± 0.016	4.43 ± 0.007	4.00 ± 0.011
CH_4	0.444	1.24 ± 0.011	0.931 ± 0.013	0.687 ± 0.013	0.534 ± 0.008
CO_2	4.4	5.98 ± 0.007	5.16 ± 0.015	4.73 ± 0.022	4.03 ± 0.014
		D_H (1×10^8 cm^2/s) (Nonannealed)			
N_2	0.468	0.871 ± 0.010	0.541 ± 0.008	0.503 ± 0.007	0.425 ± 0.012
O_2	No data	3.02 ± 0.014	2.51 ± 0.012	2.38 ± 0.007	2.15 ± 0.006
CH_4	0.155	0.381 ± 0.013	0.233 ± 0.013	0.203 ± 0.008	0.163 ± 0.012
CO_2	0.462	1.83 ± 0.019	1.47 ± 0.017	1.38 ± 0.008	1.32 ± 0.009
		D_D (1×10^8 cm^2/s) (Annealed)			
N_2	No data	1.25 ± 0.007	0.933 ± 0.011	0.715 ± 0.009	0.618 ± 0.011
O_2	No data	5.41 ± 0.013	4.25 ± 0.008	3.91 ± 0.016	3.37 ± 0.017
CH_4	No data	0.79 ± 0.006	0.559 ± 0.013	0.421 ± 0.009	0.323 ± 0.004
CO_2	No data	5.71 ± 0.018	4.92 ± 0.023	4.23 ± 0.006	3.83 ± 0.008
		D_H (1×10^8 cm^2/s) (Annealed)			
N_2	No data	0.607 ± 0.009	0.458 ± 0.013	0.384 ± 0.012	0.247 ± 0.018
O_2	No data	2.2 ± 0.007	2.03 ± 0.016	1.98 ± 0.012	1.14 ± 0.013
CH_4	No data	0.241 ± 0.010	0.197 ± 0.008	0.122 ± 0.007	0.0921 ± 0.011
CO_2	No data	1.71 ± 0.015	1.48 ± 0.02	1.17 ± 0.010	0.896 ± 0.014

* Sample conditioned in 20 atm of CO_2 for 24 hours (18).

mer, which would tend to lower the diffusivity (D_H) of the permeating gas. However, at the highest doping level, D_D and D_H are affected comparably.

The selective manner in which the diffusivity of these gases is affected is very similar to the trend in permeability reductions. This would suggest that the kinetic diameters of the gas molecules are a factor in how the oil affects the diffusivities of the Henry's and Langmuir species. The sorption results (25,26) indicate a slight enhancement in gas solubilities with the presence of the oil. However, the permeabilities to all gases are reduced. Because the permeability is a combined outcome of the solution and diffusion processes, our study suggests that the oil is limiting the diffusion step in the overall gas-transport mechanism in the membrane. The oil may be physically blocking available transport routes within the polymeric membrane, thereby creating a barrier to diffusion of the gas molecules. The sorption results presented evidence that the oil is distributed in both the

Table 9. Diffusivities for PC-1

D_D (1 × 10^8 cm^2/s) (Nonannealed)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N_2	1.22 ± 0.011	0.938 ± 0.009	0.794 ± 0.013	0.629 ± 0.013
O_2	6.87 ± 0.006	5.86 ± 0.007	5.48 ± 0.018	4.41 ± 0.012
CH_4	0.797 ± 0.005	0.562 ± 0.013	0.443 ± 0.009	0.382 ± 0.011
CO_2	8.54 ± 0.008	7.35 ± 0.016	6.5 ± 0.017	5.96 ± 0.015
D_H (1 × 10^8 cm^2/s) (Nonannealed)				
N_2	0.511 ± 0.006	0.423 ± 0.004	0.389 ± 0.010	0.276 ± 0.005
O_2	2.58 ± 0.009	2.3 ± 0.012	2.21 ± 0.013	2.11 ± 0.011
CH_4	0.106 ± 0.009	0.089 ± 0.009	0.068 ± 0.004	0.049 ± 0.007
CO_2	0.924 ± 0.013	0.85 ± 0.007	0.826 ± 0.01	0.639 ± 0.011
D_D (1 × 10^8 cm^2/s) (Annealed)				
N_2	0.876 ± 0.009	0.663 ± 0.011	0.557 ± 0.007	0.423 ± 0.008
O_2	5.65 ± 0.010	4.62 ± 0.015	4.26 ± 0.013	3.27 ± 0.007
CH_4	0.57 ± 0.005	0.378 ± 0.009	0.301 ± 0.009	0.227 ± 0.012
CO_2	8.46 ± 0.015	7.04 ± 0.017	6.11 ± 0.013	5.43 ± 0.013
D_H (1 × 10^8 cm^2/s) (Annealed)				
N_2	0.447 ± 0.008	0.337 ± 0.006	0.314 ± 0.005	0.263 ± 0.004
O_2	2.45 ± 0.009	2.17 ± 0.014	1.97 ± 0.006	1.9 ± 0.012
CH_4	0.102 ± 0.007	0.081 ± 0.005	0.062 ± 0.010	0.040 ± 0.007
CO_2	0.92 ± 0.011	0.811 ± 0.016	0.749 ± 0.013	0.625 ± 0.007

Table 10. Diffusivities for PC-2

Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
D_D (1×10^8 cm^2/s) (Nonannealed)				
N_2	2.13 ± 0.013	1.64 ± 0.008	1.35 ± 0.014	1.16 ± 0.014
O_2	13.1 ± 0.021	10.9 ± 0.016	10.3 ± 0.013	9.99 ± 0.017
CH_4	1.08 ± 0.008	0.798 ± 0.011	0.602 ± 0.005	0.496 ± 0.012
CO_2	13.8 ± 0.011	12.7 ± 0.016	11.4 ± 0.013	10 ± 0.011
D_H (1×10^8 cm^2/s) (Nonannealed)				
N_2	1.29 ± 0.009	0.94 ± 0.012	0.869 ± 0.015	0.573 ± 0.005
O_2	9 ± 0.018	6.75 ± 0.011	6.5 ± 0.009	6.19 ± 0.020
CH_4	0.171 ± 0.011	0.128 ± 0.007	0.094 ± 0.014	0.063 ± 0.007
CO_2	1.07 ± 0.006	0.957 ± 0.013	0.743 ± 0.015	0.654 ± 0.019
D_D (1×10^8 cm^2/s) (Annealed)				
N_2	1.54 ± 0.008	1.22 ± 0.013	0.908 ± 0.013	0.783 ± 0.009
O_2	11.2 ± 0.014	8.84 ± 0.016	7.75 ± 0.016	7.63 ± 0.018
CH_4	0.969 ± 0.015	0.61 ± 0.014	0.48 ± 0.011	0.381 ± 0.015
CO_2	12.5 ± 0.007	10.9 ± 0.013	9.83 ± 0.019	8.93 ± 0.018
D_H (1×10^8 cm^2/s) (Annealed)				
N_2	1.19 ± 0.016	0.839 ± 0.013	0.762 ± 0.014	0.559 ± 0.017
O_2	8.91 ± 0.023	6.68 ± 0.017	6.19 ± 0.019	5.6 ± 0.021
CH_4	0.155 ± 0.008	0.092 ± 0.012	0.068 ± 0.006	0.044 ± 0.007
CO_2	0.89 ± 0.010	0.751 ± 0.007	0.626 ± 0.009	0.546 ± 0.014

Henry's and Langmuir regions of the polymer. Thus, in the densified region of the polymer, the oil may act as a plugging agent within the minute pores distributed in the region. These blockages would act as a resistance to the diffusion of the gas molecules in this region.

The presence of oil also decreased the "excess" or free volume available to the gases as was deduced from the reduction of Langmuir sorption capacity C'_H. This type of reduction is likely to be produced by relaxation of the glassy region through increased mobility of the polymer chains caused by the presence of oil in the membrane. This loss of "free volume" can in part explain the decrease in gas diffusivity (D_H) in the Langmuir region.

The more plausible scenario is that the pore-blocking action of the oil is synergistic with the relaxation of the glassy or "free-volume" region of the polymer in retarding diffusion of the permeating gas species. The reduction in diffusivities is related to the kinetic sizes of the gas molecules with smaller species such as O_2

and CO_2 experiencing a lower resistance than the larger molecules N_2 and CH_4. This translates to higher O_2/N_2 and CO_2/CH_4 permselectivities described in the discussion on permeability.

ANNEALING

In previous papers (25,26), in which descriptions on the effect of the oil on gas solubility were presented, annealing reportedly lowered sorption in both regions (Henry's and Langmuir) of the glassy polymer to a greater extent than it did in the nonannealed samples. In terms of the dual-mode parameters, the Henry's solubility constant k_D and the Langmuir sorption capacity C'_H were reduced by thermal treatment of both clean and doped samples of the polymer; the effect was more pronounced in the case of C'_H. The diffusivities in the Henry's region (D_D) and the Langmuir region (D_H) for the annealed samples of the polymers with SH-46 are shown in Tables 7–10. Comparison among the corresponding diffusivities for the nonannealed samples shows a reduction in D_D and D_H.

In the Langmuir region, the loss of free volume that occurs due to the densification of the glassy structure, with annealing, increases the resistance to the diffusing species in this region. Hence, a lower D_H is observed in annealed doped and clean polymer films. In the Henry's region, annealing likely causes the polymer chains to pack more tightly thereby increasing the resistance to the diffusing species. As a consequence, a decrease in D_D occurs in clean and doped samples of the various polymers. A combination of reduction in the solubility parameters for each population of gas species (i.e. k_D and C'_H) as well as their corresponding transport parameters, namely D_D and D_H, results in lower permeabilities in the annealed samples. This is illustrated by a comparison of permeability data in Tables 1–4 for annealed films against samples that received no thermal treatment. The enhancement in selectivities of O_2/N_2 and CO_2/CH_4, in clean and doped films, obtained by annealing suggests that the smaller species (O_2 and CO_2) are affected less than the larger molecules (N_2 and CH_4). This would be indicative of the smaller gas species being able to traverse the available transport routes with greater ease than could the larger components. In practice, annealing of gas separation membranes is done typically to accelerate relaxation of the polymer chains without which the membrane would be susceptible to "aging" (loss in productivity) over a period of time. In the work reported here, this type of relaxation of the polymer chains induced by thermal annealing occurred in the oil doped films as well as those not annealed.

CONCLUSIONS

The results presented here allow one to compare the transport parameters in homogeneous polymeric membranes in the presence and absence of a chemical impurity (compressor oil). The presence of oil reduced the membrane permeability to all four gases. Because all polymers were affected to about the same extent by the oil, the chemical composition of the polymer (backbone of the polymer structure or the substituents present on it) likely determines how the oil affects gas transport through the membrane. The molecular weight of the oil itself does not seem to play a significant role in affecting membrane productivity. The losses in fluxes of all gases through the membrane were accompanied by an enhancement in O_2/N_2 and CO_2/CH_4 selectivities. Doping the polymer with the oil also resulted in a depression in the T_g of the polymer. In practice, the reduction in T_g of the polymer is achieved by blending a plasticizer with it. This addition increases the segmental mobility in the polymer chains and would have typically enhanced the permeability of the gas species through the membrane. Based on the results obtained, i.e. permeability reduction accompanied by an enhancement in selectivities, we postulate that the oil may have an "antiplasticizing" effect on the polymer. Although polymer chain mobility is enhanced by the oil presence, as indicated by the reduction in T_g, subsequent relaxation in the glassy or Langmuir region of the polymer reduces the sorption and diffusion of the permeating species thereby decreasing the overall gas permeability. The results with sorption experiments (25,26) showed a slight increase in gas solubilities in the presence of such oils. However, the results indicated that the permeabilities of all gases were reduced. This implies that gas diffusion in the polymeric membrane is likely the limiting step in the overall gas transport (solution-diffusion) mechanism.

The diffusivities in Henry's and Langmuir regions of the polymer are both decreased with doping. The molecules with smaller kinetic diameters, such as O_2 and CO_2, are affected to a lesser degree than the larger species, such as N_2 and CH_4. This observation would most likely explain the enhancement in selectivities of O_2/N_2 and CO_2/CH_4 with doping. This type of behavior can be explained on the basis of the oil physically blocking available transport routes such that the smaller species are affected to a lesser extent than are the larger ones. In addition, the reduction in physical dimensions of the microvoids through polymer relaxation constitutes another source of resistance to gas diffusion.

The effect of annealing on the doped samples was similar to the effect observed with clean films and CO_2 by other investigators (17,18). Our work expanded this study to include N_2, O_2, and CH_4 with the presence and absence of oil in the polymer. The sorption results showed a loss in free volume, denoted by a decrease in the Langmuir sorption capacity term C'_H, to be the significant effect of this type of thermal treatment. This result occurs due to the densification of the glassy structure. Intuitive reasoning allows one to suppose that the ensuing densification would affect the diffusivity of the gas species in the microvoids. This change is observed as a reduction in D_H. In the Henry's region, annealing collapses the pores, which consequently leads to a decrease in the solubility constant

k_D and the diffusivity D_D. Therefore, the combined result of decrease in solubility and diffusivity in either region of the glassy polymer translates to an overall decrease in permeability. However, because the smaller species are affected to a lesser degree than the kinetically larger ones, the resultant selectivities of O_2/N_2 and CO_2/CH_4 are enhanced through doping.

NOMENCLATURE

b	hole affinity constant (atm^{-1})
C	concentration of gas sorbed (cm^3 STP/cm^3 polymer)
C'_H	Langmuir sorption capacity (cm^3 STP/cm^3 polymer)
D_D	diffusivity of Henry's species (cm^2/s)
D_H	diffusivity of Langmuir species (cm^2/s)
F	D_H/D_D
K	$(C'_H b/k_D)$
k_D	Henry's solubility constant (cm^3 STP/cm^3 polymeratm)
J	total diffusive flux of gas species (cm^3 STP/$cm^2 \cdot s$)
J_D	diffusive flux of Henry's species (cm^3 STP/$cm^2 \cdot s$)
J_H	diffusive flux of Langmuir species (cm^3 STP/$cm^2 \cdot s$)
P	permeability of the gas species (barrer); 1 barrer = 10^{-10} cm^3 STP·cm/cm^2·s·cm Hg
p	pressure (atm)

Greek Letters

α	selectivity of gas species A relative to gas species B

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