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EFFECTS OF CHEMICAL IMPURITIES ON GAS SORPTION IN POLYMERIC MEMBRANES. II. PC-1 AND PC-2

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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. It has, however, been observed that impurities in the feed stream (such as vapors from compressor oils) affect the productivity of the membrane module even at parts per million (ppm) levels.

In order 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. Solubilities of N₂, O₂, CH₄, and CO₂ were measured in dense homogeneous films at 35°C. Two types of compressor oils were used in doping the polymers at three concentration levels. Results from the solubility data were well described by the dual-mode model for glassy polymers that consists of a

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Henry's solubility term k_D , Langmuir sorption capacity C'_H , and an affinity constant "b." The effect of the oil on each of the model parameters is presented. The effect of annealing on sorption in clean and doped samples of the polymers was also examined. Such thermal treatment affected the Langmuir sorption capacity C'_H more than any of the other dual-mode parameters. Annealing lowered C'_H because of the ensuing densification of the glassy structure. This effect was common to both clean and doped films. A good understanding of the effects of such trace chemicals on gas solubility in synthetic membranes will assist in examining effects of impurities on the overall membrane productivity and 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 processes like cryogenic distillation and pressure swing adsorption. Discoveries by Loeb and Sourirajan in the early 1960s of a 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 low energy requirements as opposed to the conventional processes mentioned earlier (3).

Therefore, in recent years this 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 airstreams (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 like compressor oils affect the membrane performance in concentrations on the order of parts per million (ppm). Although a survey of fouling in microporous and ultrafiltration membranes has been carried out to some extent (6), there has not been any significant research in the area of fouling in gas separation membranes. Because the performance of a module is based on a clean system, often the actual membrane performance differs significantly from that of the manufacturer's. 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 sorption in two 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 first two mechanisms are used in porous membranes, and 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. The mechanism of permeation in such membranes is, therefore, usually considered to consist of three steps:

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

Several authors have shown that the sorption of gases in glassy polymers over a moderate pressure range (0 to 30 atmospheres) is described by means of a dual-mode sorption model (8,9,10,11). 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:

$$C = C_D + C_H = k_D p + \frac{C'_H b p}{1 + b p} \quad (1)$$

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. This is mathematically expressed as

$$C_D = k_D p \quad (2)$$

$$C_H = \frac{C'_H b p}{1 + b p} \quad (3)$$



Solubility in the Henry's region of polymers has been shown to be comparable to dissolution of gases in organic liquids. Michaels and Bixler (13) used a thermodynamic approach to correlate solubility with the Lennard-Jones force constant of the gas ϵ/κ , such as that used by Jolley and Hildebrand (14) in the case of liquids. The expression derived for k_D at 35°C is

$$k_D = \exp\left(\frac{-1 - \chi + 0.0255\epsilon/\kappa}{V}\right) \quad (4)$$

where χ is the polymer-gas interaction parameter as defined in the Flory-Huggins theory (15) and V is the molar volume of the penetrant as it exists in the polymer. The term involving ϵ/κ accounts for the condensibility of the gas. The interaction parameter χ can be estimated using solubility parameter theory,

$$\chi = \left(\frac{\delta_p - \delta_g}{RT}\right)^2 \quad (5)$$

where δ_p and δ_g are solubility parameters for the polymer and penetrant, respectively. 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 (8). Koros and Paul (16) proposed the following expression, which relates C'_H to the unrelaxed volume of the glassy polymer relative to the equilibrium liquid state, that is $(V_g - V_l)$,

$$C'_H = \frac{(V_g - V_l)}{V_g} \frac{22414}{V} \quad (6)$$

Here, V_g and V_l are the specific volumes of the glass and the equilibrium liquid at temperature T , whereas V is the molar volume of the gas sorbed into this unrelaxed volume. The above expression can also be written in terms of the glass transition temperature and the thermal expansion coefficients of the rubbery and glassy states of the polymer as follows.

$$C'_H = \frac{\left(\frac{dV}{dT}\right)_l - \left(\frac{dV}{dT}\right)_g}{V_g} (T_g - T_l) \frac{22414}{V} \quad (7)$$

As before, V_g corresponds to the specific volume of the polymer in the glassy state at temperature T . The sorption capacity is found to be 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. They found C'_H decreased considerably as the duration of annealing was increased whereas k_D and b were not affected. Erb



and Paul (18) obtained similar results with CO₂ sorption in polysulfone. It is therefore established that such thermal treatment causes reduction in the free volume through densification of the microvoids in the glassy region of the polymer.

The hole affinity constant, b , is an equilibrium constant equal to the ratio of rate constants of sorption and desorption of penetrants in the holes and is therefore a measure of the tendency of a given penetrant to sorb in the Langmuir mode.

Brunauer (19) has shown that it can be written as

$$b = b_o \exp(q/kT) \quad (8)$$

The heat given off when a molecule enters the sorbed state, q , is shown to be related to the Lennard-Jones potential ε/κ . Vieth et al. (20) used a thermodynamic analysis, based on the isotheric heat of sorption, to establish a relationship between b and ε/κ at 25°C, shown following:

$$\ln b = 0.026 \frac{\varepsilon}{\kappa} + \ln \frac{\theta}{1 - \theta} - I' \quad (9)$$

where $\theta = C_H/C'_H$ is the fraction of surface area bounding the free volume occupied by gas molecules and I' is a system constant dependent on the choice of the reference state for the gas-polymer system.

In analyzing Eq. (1), describing the overall sorption of gases in glassy polymers, the following asymptotic limits are approached.

At low pressures, where the product $(b^*p) \ll 1$, Eq. (1) reduces to a linear form:

$$C = (k_D + C'_H b)p \quad (10)$$

At sufficiently high pressures, where the product $(b^*p) \gg 1$, the microvoids become saturated and Eq. 1 becomes:

$$C = k_D p + C'_H \quad (11)$$

Thus, the dual-mode model predicts that an isothermal plot of C vs. p will consist of a low-pressure linear region (Eq. 10) and a high-pressure linear region (Eq. 11) connected by a nonlinear region in the intermediate pressure range.

The theoretical background discussed above applies to any condensable gas and glassy polymer, which is typically free of any additives. It has, however, been speculated that trace chemicals affect the productivity of gas separation polymeric membrane. Because the overall gas transport is a combination of solution and diffusion of the gas in the polymer, it would be worthwhile to study the effects of such impurities on each step independently. Results from such a study with polycarbonate and polysulfone have been presented in a separate paper (21). This paper describes a similar study with two substituted polycarbonates.



EXPERIMENTAL PROCEDURE

Materials

Substituted (halogenated) polycarbonates PC-1 and PC-2, supplied by MG Generon (Pittsburg, California) were used for fabricating dense membranes. These polymers are characterized by high glass transition temperatures ($T_g > 200^\circ\text{C}$), have an average molecular weight of more than 100,000, and are employed in gas separation including air. The halogen substitutions on the polycarbonate backbone are unique for each polymer. Typical compressor oils SH-100 and SH-46 (Summit Oil Company, Inc., Tyler, Texas) were used as dopants. Both compressor oils are synthetic hydrocarbon (poly α -olefin) with the molecular weight of SH-100 being higher than SH-46. The oils have a boiling point greater than 600°F and specific gravity of less than 1. These oils were used as dopants in concentrations of 10^3 , 10^4 , and 10^5 ppm based on the polymer weight. N_2 , O_2 , CH_4 , and CO_2 were used as single gases to measure sorption in 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 as is or annealed at 20°C below the respective glass transition temperatures (T_g) of the virgin polymer. Doped films were prepared using the same protocol as for clean membranes with the exception that the dopant was introduced in the casting solution at the predetermined concentrations mentioned earlier. The doped films varied in appearance from almost transparent (clean membranes) to largely opaque (10^5 ppm oil doped).

APPARATUS

A schematic of the apparatus used in performing sorption measurements is shown in Fig. 1. The design is similar to the one used by Sanders and coworkers (22) for performing sorption measurements with mixed gases. Cells 3 and 4 are reservoirs for holding the gas prior to its introduction into the sorption cell, that is, cell 2 containing the polymer. Cell 1 was used for providing samples of mixed gas to the gas chromatograph for analysis. For the work reported here with single gases, the apparatus was reduced to essentially a dual-volume system with the reservoir volume (cell 3) and the reactor (cell 2) that contained the polymer sample. The volumes for the system were determined by performing expansions with



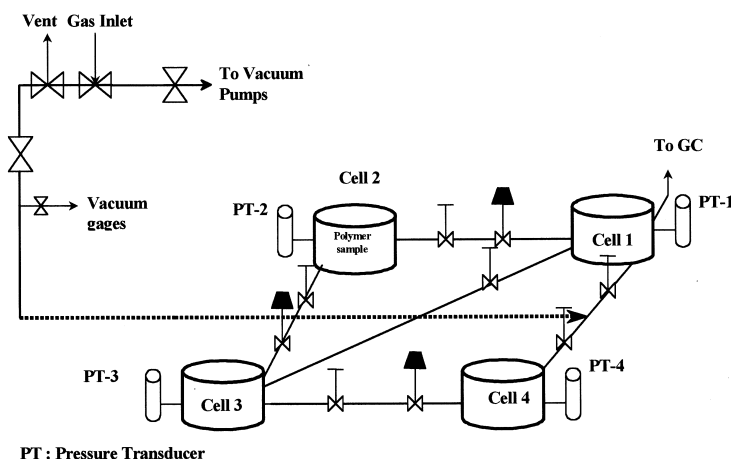


Figure 1. Gas sorption apparatus.

N_2 and He. The average difference between the two gases was 0.41%. The volumes determined were as follows: $V_1 = 18.45 \text{ cm}^3$, $V_2 = 19.28 \text{ cm}^3$, $V_3 = 18.45 \text{ cm}^3$, and $V_4 = 18.41 \text{ cm}^3$.

Temperature control was accomplished using a baseload heater to compensate for the evaporative loss. A Dyna-Sense mercury thermoregulator ($\pm 0.1^\circ\text{C}$) and relay controlled heater supplied the remainder of the heat required and are responsible for the actual temperature control. All measurements were made at 35°C . The pressures were monitored by means of four Setra Model 212 transducers. Transducers 2, 3, and 4 indicated in Fig. 1 have a range of -14.7 to 500 psig whereas transducer 1 has a range of 14.7 to 100 psig. A polymer sample of 1.90 cm^3 was used for conducting sorption experiments.

The gas was initially introduced in the reservoir (cell 3) and then expanded into the reactor (cell 2). Sorption of the gas was then allowed to proceed until a final equilibrium pressure was reached. Based on the initial and final pressures in the reactor, the equation of state can be used to calculate the initial and final moles of gas in the reactor, thereby permitting calculation of the amount of gas sorbed by the polymer.

RESULTS AND DISCUSSION

Experiments with PC-1 and PC-2 indicate that the dual-mode sorption model provides a satisfactory description of solubility of all four gases in clean as well as doped films. A nonlinear regression of the sorption data was performed to



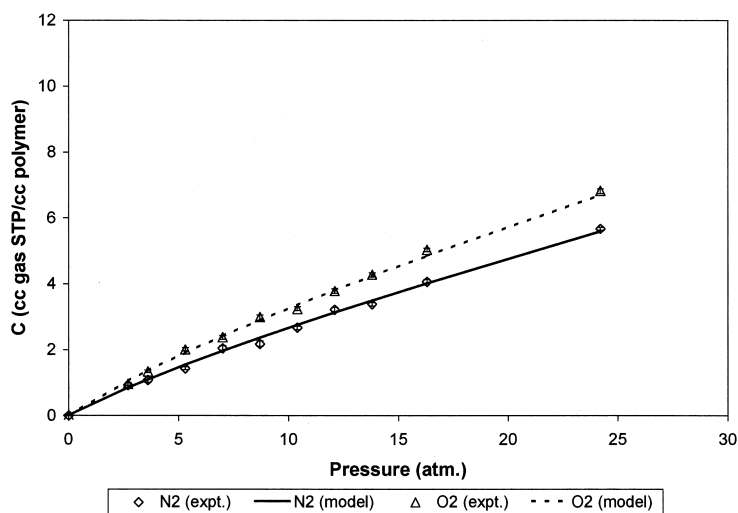


Figure 2. Sorption in PC-1 (clean; nonannealed).

obtain estimates of the dual-mode model parameters. This permitted a comparison of each model parameter in the presence and absence of oil. It also allowed for an interpretation of each parameter in terms of analyses that have been done for pure polymers by other researchers. The model for each gas-polymer pair in the pres-

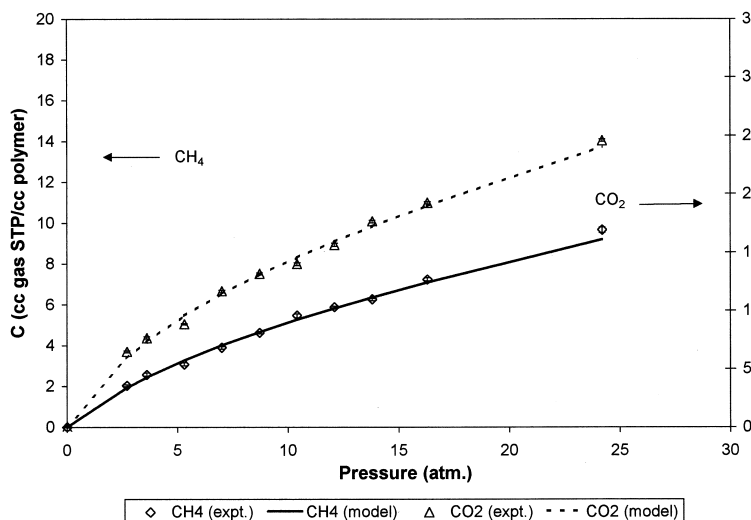


Figure 3. Sorption in PC-1 (clean; nonannealed).



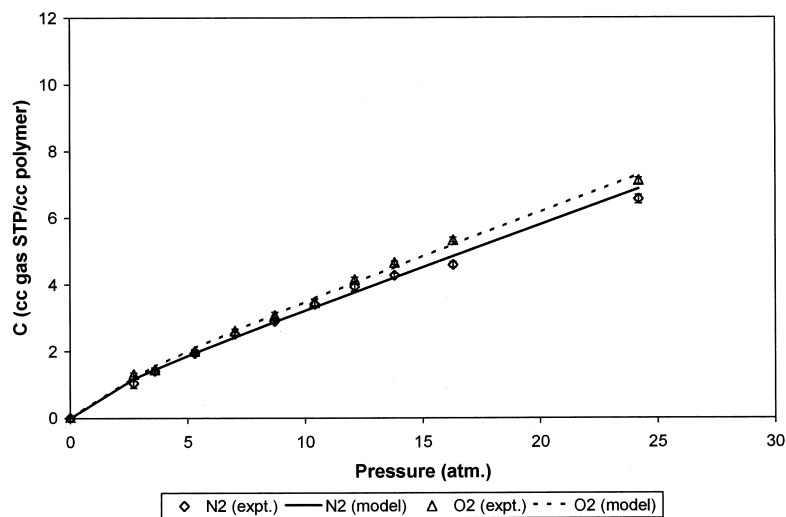


Figure 4. Sorption in PC-1 (10^5 ppm SH-46; nonannealed).

ence and absence of oil was compared against an independent set of experimental measurements. Figures 2 through 5 show the close agreement between the model and independent data collected over a pressure range of 0 to 25 atmospheres for PC-1 in the presence and absence of oil. Figures 6 through 9 show a similar comparison for PC-2.

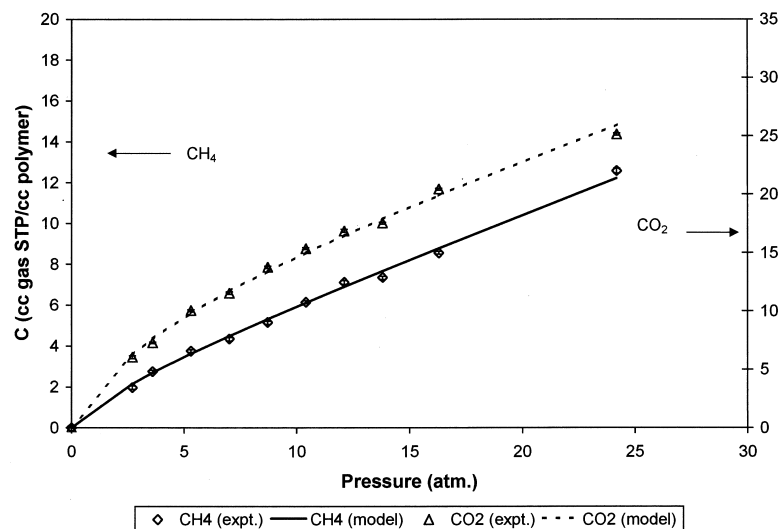


Figure 5. Sorption in PC-1 (10^5 ppm SH-100; nonannealed).



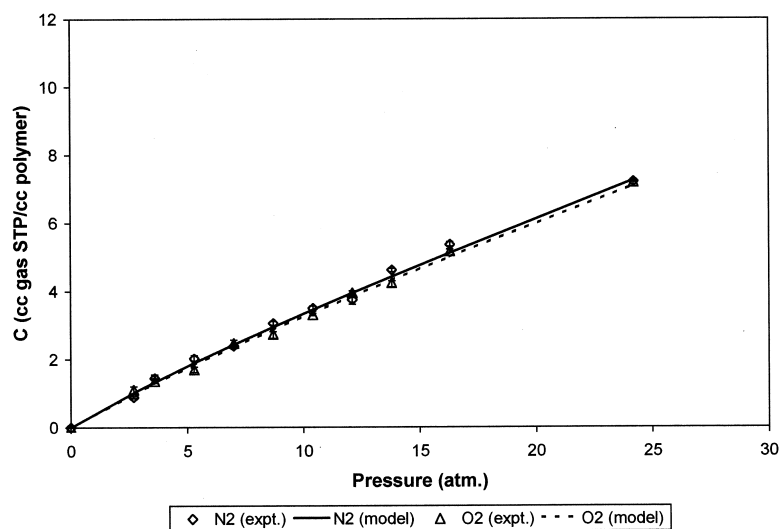


Figure 6. Sorption in PC-2 (clean; annealed).

The presence of compressor oil increased the overall sorption of each of the four gases. The PC-1 and PC-2 samples were affected to a similar degree by the presence of the oil. Therefore, it is less likely that the substituents on the polymer backbone are factors in how the oil affects gas dissolution. Also, SH-

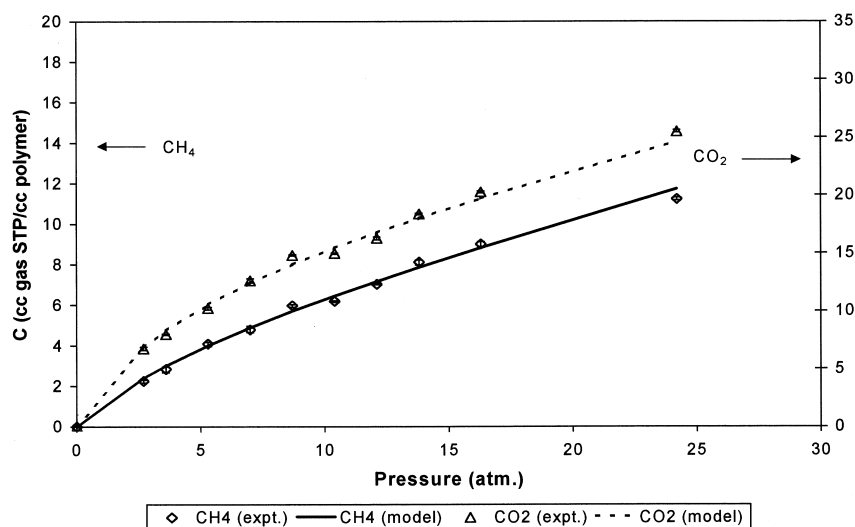


Figure 7. Sorption in PC-2 (clean; annealed).



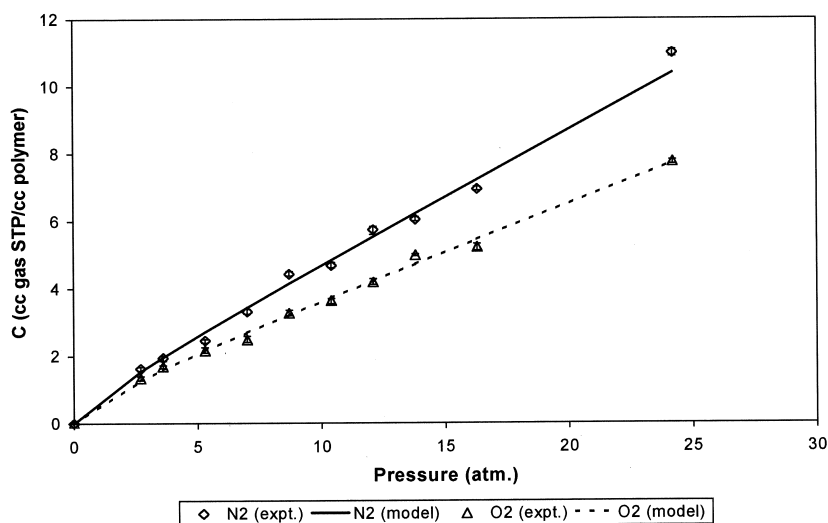


Figure 8. Sorption in PC-2 (10^5 ppm SH-46; annealed).

46 and SH-100 exhibited similar effects on the solubilities of the four gases in the polymers that were examined. Therefore, it is likely that the difference in molecular weight of the oils does not play a significant role in governing gas sorption in the polymer.

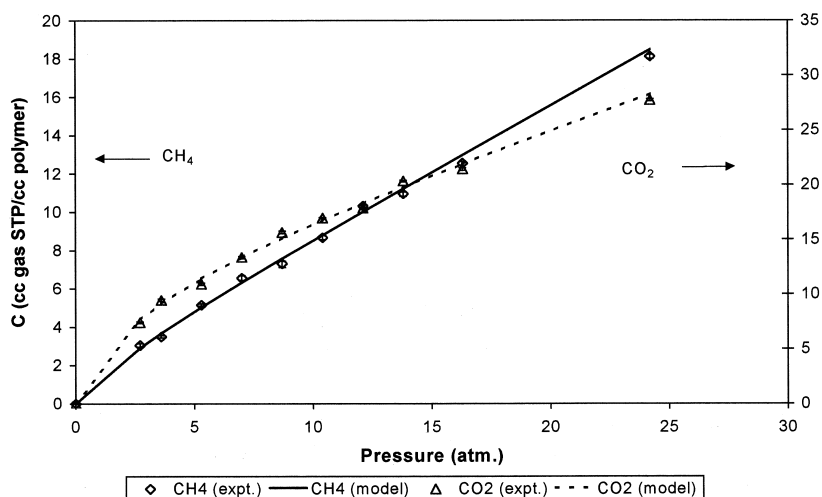


Figure 9. Sorption in PC-2 (10^5 ppm SH-100; annealed).



Table 1. ε/κ Values for Gases (24)

Gas	ε/κ ($^{\circ}\text{K}$)
CO_2	190
CH_4	136.5
O_2	113
N_2	91.5

Henry's Solubility Constant, k_D

Tables 2 through 9 show the effect of the oil on the solubility of the gas in the densified regions of PC-1 and PC-2 films. The solubility in the Henry's region as described in Eq. (4) is equivalent to gas dissolution in rubbery polymers and low-molecular-weight organic liquids. In the doped polymers, k_D showed an in-

Table 2. Dual-Mode Sorption Parameters for PC-1 (Nonannealed) with SH-46

k_D (cc/cc polymer-atm)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N_2	0.177	0.2	0.231	0.251
O_2	0.206	0.229	0.243	0.258
CH_4	0.212	0.27	0.329	0.387
CO_2	0.511	0.573	0.653	0.734
C'_H (cc/cc polymer)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N_2	1.962	1.214	1.066	0.851
O_2	2.497	1.669	1.494	1.195
CH_4	5.418	3.726	3.074	2.431
CO_2	14.493	12.156	11.383	10.357
b (atm^{-1})				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N_2	0.0821	0.502	0.508	0.498
O_2	0.0912	0.312	0.307	0.303
CH_4	0.123	0.28	0.285	0.286
CO_2	0.169	0.262	0.258	0.26



Table 3. Dual-Mode Sorption Parameters for PC-2 (Nonannealed) with SH-46

k_D (cc/cc polymer-atm)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	0.273	0.315	0.383	0.429
O ₂	0.263	0.287	0.308	0.316
CH ₄	0.445	0.566	0.713	0.777
CO ₂	0.596	0.656	0.748	0.853
C'_H (cc/cc polymer)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	2.565	1.738	1.338	1.199
O ₂	2.498	1.704	1.394	1.246
CH ₄	6.967	4.936	4.357	2.91
CO ₂	19.636	16.012	15.047	14.271
b (atm ⁻¹)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	0.0991	0.402	0.4	0.403
O ₂	0.0877	0.439	0.442	0.437
CH ₄	0.174	0.357	0.354	0.358
CO ₂	0.24	0.368	0.369	0.373

crease in magnitude when compared against the corresponding clean polymer sample for all four gases. The magnitude of increase was approximately similar in the presence of either SH-46 or SH-100. The effect was also very comparable in both polymers that were studied. Therefore, it seems that the substituents present on its backbone may not be factors in determining how gas solubility in the Henry's region is affected by the presence of oil.

The Henry's solubility constant k_D has been correlated to an interaction parameter χ , as described by Eq. (4). χ can be estimated from the individual polymer and gas solubility parameters δ_p and δ_g (23), as shown in Eq. (5). Based on experimental results obtained thus far, it can be postulated that the oil reduces the polymer-penetrant interaction parameter χ , which results in a larger k_D . This can be possible if the oil competes with the polymer to a certain degree during the dissolution of the gas in the densified regions, such that the interaction parameter χ that appears in Eq. (5) is a net result of the polymer-gas (χ_{p-g}) interaction as well as oil-gas (χ_{o-g}) interaction. If χ_{o-g} were less than χ_{p-g} , because the oil is a liquid, then the overall χ would decrease with increasing oil concentration thereby increasing k_D .



Table 4. Dual-Mode Sorption Parameters for PC-1 (Nonannealed) with SH-100

k_D (cc/cc polymer-atm)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	0.177	0.193	0.244	0.248
O ₂	0.206	0.242	0.253	0.267
CH ₄	0.212	0.267	0.323	0.421
CO ₂	0.511	0.551	0.628	0.694
C'_H (cc/cc polymer)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	1.962	1.242	1.126	0.841
O ₂	2.497	1.637	1.469	1.222
CH ₄	5.418	3.892	2.979	2.312
CO ₂	14.493	12.327	11.637	10.61
b (atm ⁻¹)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	0.0821	0.503	0.509	0.502
O ₂	0.0912	0.312	0.302	0.31
CH ₄	0.123	0.286	0.289	0.286
CO ₂	0.169	0.255	0.253	0.262

For N₂, O₂, and CO₂, the increase in k_D is typically in the range of about 15% at the 10^3 ppm doping level to around 50% at the 10^5 ppm level of oil concentration in the polymer. CH₄ shows a larger increase in k_D with doping, ranging from approximately 30% at the 10^3 ppm level to around 75% with 10^5 ppm of oil. On the basis of Eq. (4) and (5), it can be hypothesized that CH₄ being a hydrocarbon interacts more strongly with the hydrocarbon-based oil, resulting in a larger χ_{o-g} and consequently a greater k_D value.

Langmuir Capacity, C'_H

The effect of the oil on the Langmuir sorption capacity C'_H is more intuitive in terms of the direct relation of C'_H to the nonequilibrium free volume that characterizes glassy polymers. This "excess" volume represented in Eq. (6) as $(V_g - V_l)$ is lowered with the presence of oil in the polymer. Subsequently, the Langmuir sites available for gas sorption are reduced. Tables 2 through 9 show the decrease in C'_H for PC-1 and PC-2 with increasing oil concentration. This trend was observed in



Table 5. Dual-Mode Sorption Parameters for PC-2 (Nonannealed) with SH-100

k_D (cc/cc polymer-atm)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	0.273	0.299	0.392	0.439
O ₂	0.263	0.281	0.299	0.334
CH ₄	0.445	0.568	0.729	0.775
CO ₂	0.596	0.696	0.769	0.91
C'_H (cc/cc polymer)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	2.565	1.73	1.359	1.243
O ₂	2.498	1.761	1.349	1.278
CH ₄	6.967	5.203	4.35	3.061
CO ₂	19.636	15.622	15.394	13.779
b (atm ⁻¹)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	0.0991	0.41	0.404	0.413
O ₂	0.0877	0.431	0.431	0.426
CH ₄	0.174	0.363	0.367	0.362
CO ₂	0.24	0.372	0.374	0.377

both polymers in the presence of either compressor oil. Therefore, the difference in molecular weight of the oils is most likely not a factor the reduction of C'_H . Because C'_H is a measure of the unrelaxed free volume, it can be inferred that the oil reduces the available free volume in the polymer. The magnitude of reduction in this free volume is related to the concentration of oil in the polymer. Interestingly, N₂, O₂, and CH₄ suffer losses in their respective C'_H values on the order of 30% to 50%, as the level of doping increases. CO₂, on the other hand, loses only 20% to 30% of its Langmuir sorption capacity with the increasing oil concentration in the polymer. This difference may be due to the ability of CO₂, in particular, to plasticize the polymer to a certain degree, thereby making the effect of the oil on C'_H slightly less pronounced than in the case of N₂, O₂, and CH₄.

Hole Affinity Constant, b

The hole affinity constant b shows a significant increase in value when 10^3 ppm of oil is introduced in the polymer. However, its value does not show any ap-



Table 6. Dual-Mode Sorption Parameters for PC-1 (Annealed) with SH-46

k_D (cc/cc polymer-atm)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	0.168	0.188	0.21	0.232
O ₂	0.192	0.209	0.22	0.242
CH ₄	0.191	0.245	0.288	0.359
CO ₂	0.47	0.537	0.618	0.67
C'_H (cc/cc polymer)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	1.494	0.97	0.869	0.727
O ₂	1.926	1.376	1.253	1.037
CH ₄	4.038	2.901	2.456	2.053
CO ₂	10.966	10.18	9.396	9.055
b (atm ⁻¹)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	0.0818	0.498	0.506	0.501
O ₂	0.0906	0.311	0.303	0.299
CH ₄	0.121	0.274	0.283	0.281
CO ₂	0.166	0.257	0.26	0.257

preciable change with increasing oil concentration as illustrated in Tables 2 through 9. It can be postulated that the oil, residing in the microvoids, enhances the condensibility of the gas in the polymer by providing a surface that the gas molecules can readily adsorb onto. However, unlike in the case of k_D and C'_H , the effect on condensibility is not a function of the oil concentration in the polymer. For a two-component polymer-gas system, the exponential dependence of b on ϵ/κ is shown in Eq. (9). The presence of a third component such as oil in all likelihood alters the form of dependence of b on ϵ/κ . This is evident from a comparison of the affinity constants for clean and doped polymers. In the clean membrane, the magnitude of b follows the trend in ϵ/κ values that are listed in Table 1. Thus, CO₂ has the highest affinity constant followed by CH₄, O₂, and N₂. Upon introduction of the oil, N₂ shows the largest increase in the value of b followed by O₂, CH₄, and CO₂. Because the increase in b is more pronounced in less condensible gases like N₂ and O₂ compared to CO₂ and CH₄, it can be hypothesized that for oil-doped films the affinity constant is not entirely a function of ϵ/κ of the gas. From the data obtained, it can also be inferred that both oils have similar effects on the behavior of the affinity constant b , which again is indicative of the fact that



Table 7. Dual-Mode Sorption Parameters for PC-2 (Annealed) with SH-46

k_D (cc/cc polymer-atm)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	0.249	0.285	0.355	0.395
O ₂	0.246	0.264	0.29	0.284
CH ₄	0.326	0.516	0.617	0.695
CO ₂	0.518	0.598	0.661	0.739
C'_H (cc/cc polymer)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	1.798	1.286	1.008	0.911
O ₂	1.698	1.216	1.006	0.933
CH ₄	4.759	3.529	3.186	2.167
CO ₂	14.277	12.297	11.753	11.29
b (atm ⁻¹)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	0.088	0.397	0.395	0.401
O ₂	0.0869	0.438	0.44	0.442
CH ₄	0.173	0.358	0.352	0.357
CO ₂	0.229	0.372	0.364	0.37

the differing molecular weight of the oils is most likely not a factor in how b is affected. The affinity constant is therefore a function of only the specific polymer-gas interaction and is altered by the introduction of oil in the polymer. However, the exact mechanism by which the affinity constants of the less condensable species (N₂ and O₂) are enhanced by the presence of oil is not clear at this time.

To illustrate the effect of the oil on the overall solubility of gas in the polymer, models for sorption of N₂ (less condensable) and CO₂ (highly condensable) at three levels of SH-46 doping are compared against that for the corresponding clean samples. Figures 10 and 11 depict this for PC-1 with N₂ and CO₂ respectively. Figures 12 and 13 illustrate a similar case for PC-2. As mentioned earlier, the presence of oil increases the sorption of gas in the polymer. The enhancement in solubility is the greatest in the low-pressure region (~2 atmospheres), and for N₂ this increase was around 60% for PC-1 and 45% for PC-2. However, CO₂ solubility increased by only about 10% in both polymers in this pressure regime. This signifies the role of the hole affinity constant b in gas sorption at low pressures, which is consistent with Eq. (10). Because the in-



Table 8. Dual-Mode Sorption Parameters for PC-1 (Annealed) with SH-100

k_D (cc/cc polymer-atm)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	0.168	0.19	0.206	0.217
O ₂	0.192	0.216	0.228	0.256
CH ₄	0.191	0.239	0.294	0.375
CO ₂	0.47	0.519	0.63	0.64
C'_H (cc/cc polymer)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	1.494	1.003	0.859	0.743
O ₂	1.926	1.369	1.224	1.064
CH ₄	4.038	2.772	2.538	1.985
CO ₂	10.966	9.828	9.054	9.022
b (atm ⁻¹)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	0.0818	0.501	0.503	0.506
O ₂	0.0906	0.306	0.31	0.305
CH ₄	0.121	0.295	0.291	0.285
CO ₂	0.166	0.251	0.257	0.257

crease in magnitude of b , with doping, is much greater for N₂ than CO₂ (Tables 2 and 3), the solubility of N₂ is also enhanced more than that of CO₂ at low pressures where the effect of b is more pronounced. Moreover, b does not change appreciably between 10^3 ppm and 10^5 ppm level of doping, and consequently, the increase in the overall solubility of N₂ and CO₂ was fairly constant across the three levels of oil concentration in the low-pressure region. With increasing pressure, the effect of b becomes less significant until the point is reached where Eq. (11) describes the overall gas solubility. In the intermediate pressure range (10 through 15 atmospheres) N₂ exhibits increase of about 15% through 20% for PC-1 and 15% through 30% for PC-2. This increase is less than that observed at lower pressures. In the intermediate region, the isotherm is increasingly nonlinear (Eq. 1) and the affinity constant b plays a less-significant role. The overall solubility of both gases in this pressure regime increased with oil concentration in the polymer. Because the Henry's solubility constant k_D increases with the level of doping as indicated in Tables 2 and 3, it most likely is the governing parameter in the overall gas sorption at the intermediate pressure levels. At higher



Table 9. Dual-Mode Sorption Parameters for PC-2 (Annealed) with SH-100

k_D (cc/cc polymer-atm)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	0.249	0.301	0.343	0.404
O ₂	0.246	0.265	0.281	0.3
CH ₄	0.326	0.537	0.638	0.686
CO ₂	0.518	0.618	0.654	0.751
C'_H (cc/cc polymer)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	1.798	1.315	1.019	0.88
O ₂	1.698	1.211	1.016	0.986
CH ₄	4.759	3.463	3.175	2.094
CO ₂	14.277	12.587	12.016	11.249
b (atm ⁻¹)				
Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
N ₂	0.088	0.407	0.409	0.406
O ₂	0.0869	0.423	0.426	0.419
CH ₄	0.173	0.368	0.374	0.374
CO ₂	0.229	0.374	0.371	0.373

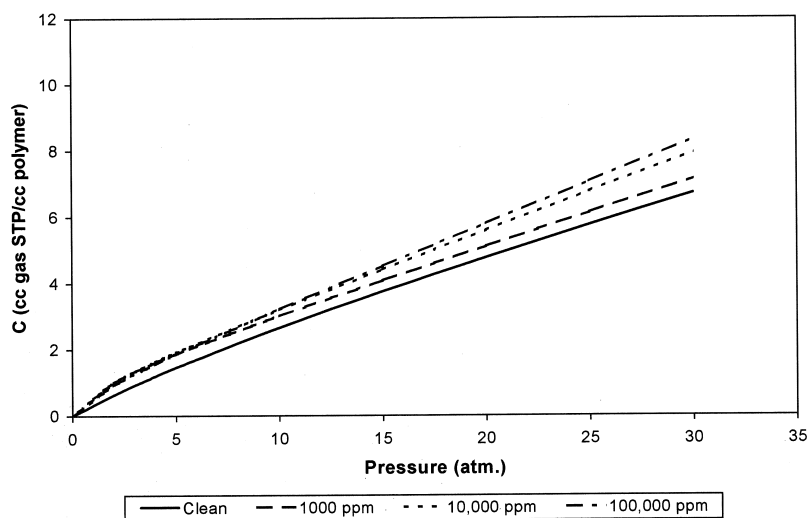


Figure 10. Model comparisons for N₂ sorption in PC-1.



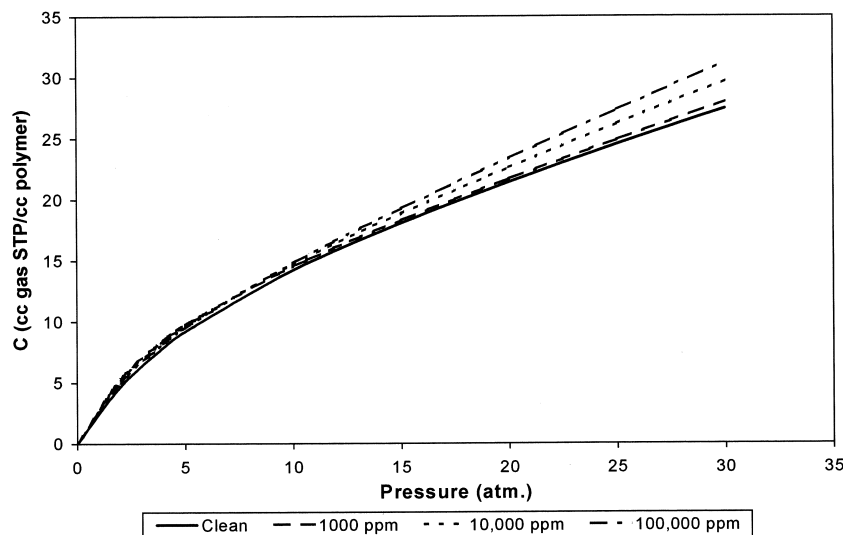


Figure 11. Model comparisons for CO₂ sorption in PC-1.

pressures (>20 atmospheres), the microvoids become saturated and the isotherm approaches the asymptotic limit described by Eq. (11). Here, k_D and C'_H are the key parameters in the dual mode model. The presence of oil increases k_D but reduces C'_H . Because the overall solubility of the two gases (N₂ and CO₂) in-

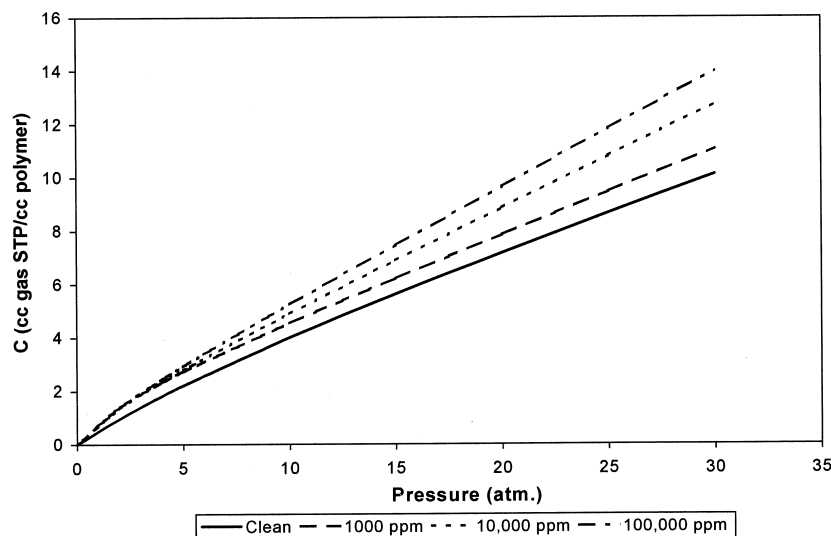


Figure 12. Model comparisons for N₂ sorption in PC-2.



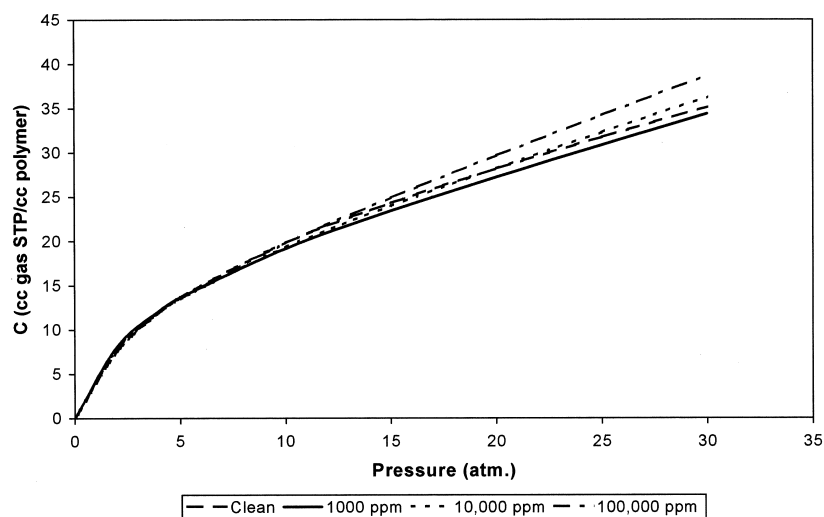


Figure 13. Model comparisons for CO₂ sorption in PC-2.

creased with doping of the polymer as shown in Figs. 10 through 13, k_D in all likelihood overrides the effect of C'_H at the higher pressure levels.

ANNEALING

Annealing of gas separation membranes is typically done to accelerate relaxation of the polymer chains such that they pack together closely. Without annealing, the membrane would ideally suffer loss in productivity over time due to the collapsing pore structure in the polymer. This is more commonly referred to as "aging" of the membrane. In our study, in addition to the clean films, we were interested in examining the effects of annealing on the oil-doped samples as well. It is observed that the overall solubility of all gases was lowered with annealing. A nonlinear regression routine was used to obtain parameters of the dual-mode model, which are listed in Tables 6 through 9 for PC-1 and PC-2. A careful comparison of the data in Tables 6 through 9 against corresponding parameters in Tables 2 through 5 indicates that the most pronounced effect of annealing was on the Langmuir sorption capacity term C'_H . Other researchers (17,18) that have studied the effect of sub- T_g annealing on CO₂ sorption in clean polycarbonate and polysulfone have found C'_H to be highly susceptible to thermal treatment of the polymer film. In our work, the loss in Langmuir sorption capacity through annealing is demonstrated with all four gases viz. N₂, O₂, CH₄, and CO₂ in clean and



doped films. The effect was similar in films cast from both types of polymers with either type of compressor oil. In clean membranes the reduction in C'_H is attributed mainly to the loss of free volume, represented as $(V_g - V_l)$ in Eq. (6). This occurs due to the densification of the glassy structure caused by thermal treatment of the polymer sample. In the case of doped films, even at the highest level of oil concentration a certain amount of free volume still exists and, therefore, when the sample is annealed a loss in this residual volume occurs. This translates to a decrease in C'_H .

With regard to the effect of annealing on the sorption in the densified region of the polymer, it is observed that there is a small decrease in the value of k_D as well, although it is less than what is observed in the case of C'_H . The reduction in k_D is common to clean and doped samples. Because k_D is a function of the interaction parameter χ as shown in Eq. (4), it is plausible that annealing increases χ . For clean films, this could most likely be ascribed to an increase in $(\delta_p - \delta_g)$ based on Eq. (5). In the case of samples doped with impurities (oils), the interaction parameter χ is a net result from the interaction of the polymer-gas (χ_{p-g}) as well as oil-gas (χ_{o-g}) as postulated earlier. The decrease in k_D in the doped films can then likely be attributed to an increase in χ_{p-g} and χ_{o-g} , which most probably results from an increase in $(\delta_p - \delta_g)$ and $(\delta_o - \delta_g)$. This increase, in turn, may be due to the fact that previously rubbery nature of the amorphous region is partly densified into a more rigid phase.

The hole affinity constant b that characterizes the ratio of sorption to desorption in the microvoids, is not affected by such thermal treatment of the sample. Chan et al. (16) and Erb and Paul (18) found this to be true for CO_2 sorption in polycarbonate and polysulfone, respectively. In our case, we were able to illustrate a similar effect on b in clean as well as doped samples of PC-1 and PC-2 with four gases viz. N_2 , O_2 , CH_4 , and CO_2 . Thus, the condensibility of the gas species is not affected by physical stresses such as thermal effects. However, as in the case of the nonannealed films, the introduction of oil in the polymer in the annealed samples increased the affinity constants of N_2 and O_2 to a greater degree than that of CH_4 and CO_2 . Therefore, the exponential dependence of b on ε/κ value of the gas that has been shown in Eq. (9) for clean membranes breaks down with the introduction of oil in the polymer. This is similar to the observations made in the case of the nonannealed samples.

CONCLUSIONS

The dual-mode model that has been widely used to describe solubility of gases in glassy polymers by several investigators (8–11) was applied to our work with doped membranes. The model provided a satisfactory description for the solubility of gases in the presence of the dopant (oil). The parameters that



were obtained by a nonlinear regression of the solubility data provided a means of comparing k_D , C'_H , and b of the doped samples against those of the clean films. These parameters provide a basis for understanding the effect of the oil on the gas dissolution process in the Henry's (dense) and Langmuir (microvoids) regions of the polymer. The Henry's solubility constant k_D increased with the presence of oil, which suggests that the oil may be competing with the polymer during gas dissolution in the densified region in a manner that reduces the interaction parameter χ that appears in Eq. (4). The Langmuir sorption capacity C'_H , which is a direct measure of the unrelaxed free volume that characterizes glassy polymers, decreased in the doped films. This implies that the oil is most likely occupying some of the residual free volume that would have ordinarily been available for gas sorption. As the oil concentration in the polymer increased, C'_H decreased suggesting that more of the residual free volume was being occupied by the oil. On the contrary, the hole affinity constant b increased with introduction of 10^3 ppm of oil in the polymer and does not show a significant change thereafter with higher oil concentrations. The oil, however, enhanced the condensibility of N_2 and O_2 to a greater degree than for CH_4 and CO_2 , as indicated by the increase in b . Therefore, unlike with the clean polymer samples, the affinity constants for gases in the doped samples are not proportional to the ϵ/κ value of the gas.

In summary, the presence of oil in the polymer increases k_D and b , but lowers C'_H . The overall solubility though of all gases is enhanced with doping. At the lower pressures (~ 2 atmospheres) the effect of oil on the affinity constant b assumes considerable importance as illustrated by comparing solubility models for N_2 and CO_2 with the presence of SH-46. In the intermediate pressure region (10 to 15 atmospheres), b becomes less significant and instead the Henry's solubility constant k_D determines the overall gas solubility. At the higher pressures (> 20 atmospheres) the microvoids become saturated and the overall sorption is governed by k_D . Commercial membrane-based gas separators typically operate at about 10 atmospheres. From our earlier discussion, at this pressure level k_D is most likely to have a bigger effect than C'_H and b on how the overall gas solubility is affected in the presence of compressor oil impurities. Annealing was carried out with clean and doped samples. The most pronounced effect of this thermal treatment was the reduction of the free volume as indicated by the decrease in C'_H . This loss resulted from the densification process in the polymer by such treatment and was observed in clean and doped films. There was also a decrease in k_D , although it was less than in the case of C'_H . The hole affinity constant b was not affected to any significant degree by annealing. The net result, therefore, was the lowering of the overall gas solubility of gases in clean and doped polymer samples. Although the solubility of the gas increased in the presence of oil, it would be of tremendous interest to evaluate the permeability of the polymer to the various gases of interest in the presence and absence of oil.



This would serve a two-fold objective. First, it would demonstrate how the oil affects the productivity and permselectivity of the membrane. Secondly, it would permit obtaining independent diffusivity values and thereby assist in determining which of the two steps viz. sorption or diffusion is retarded in the overall transport of gas through the membrane.

NOMENCLATURE

b	Hole affinity constant (atm^{-1})
C	concentration of gas sorbed ($\text{cm}^3 \text{ STP}/\text{cm}^3 \text{ polymer}$)
C'_H	Langmuir sorption capacity ($\text{cm}^3 \text{ STP}/\text{cm}^3 \text{ polymer}$)
k_D	Henry's solubility constant ($\text{cm}^3 \text{ STP}/\text{cm}^3 \text{ polymer-atm}$)
p	pressure (atm)
R	Universal Gas constant
T	temperature
V	molar volume of gas sorbed in the unrelaxed volume
V_g	specific volume of the glassy region at temperature T
V_l	specific volume of the equilibrium liquid at temperature T

Greek Letters

ε/κ	Lennard-Jones potential ($^\circ\text{K}$)
χ	polymer-gas interaction parameter
δ_p	polymer solubility parameter (cal/cm^3) ^{1/2}
δ_g	penetrant solubility parameter (cal/cm^3) ^{1/2}
θ	fraction of surface area bounding the free volume occupied by gas molecules

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