Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

EFFECTS OF CHEMICAL IMPURITIES ON GAS SORPTION IN POLYMERIC MEMBRANES. I. POLYCARBONATE AND POLYSULFONE

Bryan Pereira[a]; Wudneh Admassu[a]
[a] Department of Chemical Engineering, University of Idaho, Moscow, Idaho, U.S.A.

To cite this Article Pereira, Bryan and Admassu, Wudneh(2001) 'EFFECTS OF CHEMICAL IMPURITIES ON GAS SORPTION IN POLYMERIC MEMBRANES. I. POLYCARBONATE AND POLYSULFONE', Separation Science and Technology, 36: 2, 177 — 197

To link to this Article: DOI: 10.1081/SS-100001074

URL: http://dx.doi.org/10.1081/SS-100001074

SEPARATION SCIENCE AND TECHNOLOGY, 36(2), 177–197 (2001)

EFFECTS OF CHEMICAL IMPURITIES ON GAS SORPTION IN POLYMERIC MEMBRANES. I. POLYCARBONATE AND POLYSULFONE

Bryan Pereira and Wudneh Admassu*

Department of Chemical Engineering, University of Idaho,
Moscow, Idaho

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 N_2, O_2, CH_4 and CO_2 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

---

*Corresponding author. E-mail: wadmassu@uidaho.edu

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 1960's 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 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 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 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:

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

where C_D is the sorbed population in the densified regions that is described by Henry's law, and C_H is the Langmuir term that accounts for sorption in the microvoids. This is mathematically expressed as

$$C_D = k_D p \tag{2}$$

$$C_{\mathrm{H}} = \frac{C'_{\mathrm{H}} bp}{1 + bp} \tag{3}$$

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, like that used by Jolley and Hilderbrand (14) in the case of liquids. The expression derived for k_{D} at 35°C is

$$k_{\mathrm{D}} = \exp\left(\frac{-1 - \chi + 0.0255\,\varepsilon/\kappa}{V}\right) \tag{4}$$

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,

$$\chi = \left(\frac{\delta_{\mathrm{p}} - \delta_{\mathrm{g}}}{RT}\right)^2 \tag{5}$$

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, $(V_{\mathrm{g}} - V_{\mathrm{l}})$

$$C'_{\mathrm{H}} = \frac{(V_{\mathrm{g}} - V_{\mathrm{l}})}{V_{\mathrm{g}}} \frac{22414}{V} \tag{6}$$

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. This 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:

$$C'_{\mathrm{H}} = \frac{\left(\frac{dv}{dT}\right)_{\mathrm{l}} - \left(\frac{dV}{dT}\right)_{\mathrm{g}}}{V_{\mathrm{g}}} (T_{\mathrm{g}} - T_{\mathrm{l}}) \frac{22414}{V} \tag{7}$$

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 CO_2 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

$$b = b_o \exp(q/kT) \tag{8}$$

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 isoteric heat of sorption, to establish a relationship between "b" and ε/κ at 25°C, shown following:

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

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 Equation (1), describing the overall sorption of gases in glassy polymers, the following asymptotic limits are approached:

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

$$C = (k_D + C'_H b)p \tag{10}$$

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

$$C = k_D p + C'_H \tag{11}$$

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 applies to any condensable gas and glassy polymer that 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. It is in this context that this paper will address the effects of chemical impurities such as compressor oils on gas sorption in polymeric membranes.

EXPERIMENTAL PROCEDURE

Materials

The following polymers were used for fabricating dense membranes:

Polycarbonate (cat. no. 18,162-5) supplied by Aldrich Chemical Company, Inc.

Polysulfone (cat. no. 18,244-3) supplied by Aldrich Chemical Company, Inc.

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. Dopants were used in concentrations of 10^3, 10^4, and 10^5 ppm based on the polymer weight. These levels of doping concentrations were used to observe performance changes in the membrane similar to those typically exhibited in field modules. At oil concentrations above 10^5 ppm, it was difficult to fabricate defect free membranes. Below 10^3 ppm oil level, the observed effects on the membrane were within margins of experimental error and therefore not deemed significant.

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 methylene chloride, and the resulting solution was used in casting dense homogeneous films. The films were dried at room temperature and were used as is or annealed 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.

APPARATUS

A schematic of the apparatus used in performing sorption measurements is shown in Figure 1. The design is similar to the one used by Sanders and co-workers (21) for performing sorption measurements with mixed gases. Cells 3 and 4 are reservoirs for holding the gas prior to its introduction into the sample cell, that is, cell 2, which contains the polymer sample of interest. 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

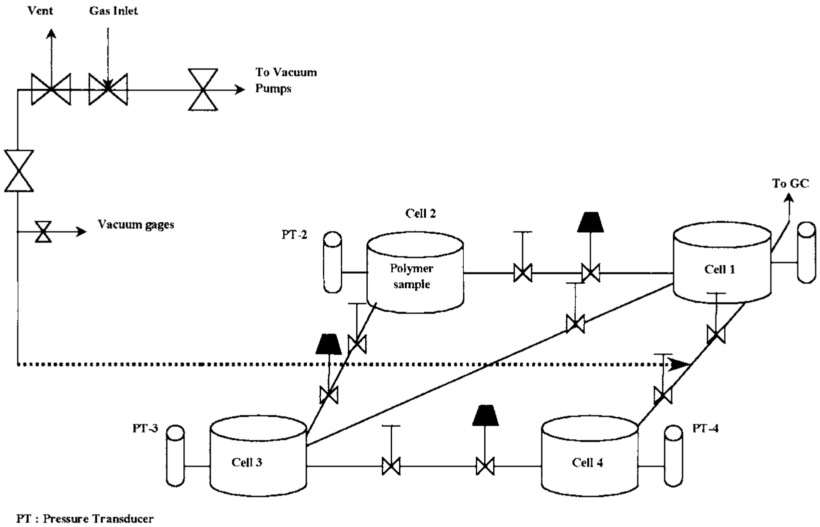

Figure 1. Gas sorption apparatus.

system with the reservoir volume (cell 3) and the polymer sample cell (cell 2). The volumes for the system were determined by initially evacuating the entire system, closing off each of the four cells shown in Figure 1 and then expanding a known volume of gas (at a given pressure) into each of the cells in succession. Nitrogen and helium were used in measuring the system volumes. The average difference between the two gases was 0.41%. The volumes determined were as follows: $V_1 = 18.45\,\mathrm{cm}^3$, $V_2 = 19.28\,\mathrm{cm}^3$, $V_3 = 18.45\,\mathrm{cm}^3$, and $V_4 = 18.41\,\mathrm{cm}^3$.

The sorption apparatus is placed in a water bath in order to regulate the temperature. Temperature control was accomplished using a baseload heater (795 W) to compensate for the evaporative losses or the heat losses from the surface of the water bath due to free convection. A Dyna-Sense mercury thermoregulator ($\pm 0.1^\circ$C) and relay controlled heater (450 W) supplied the remainder of the heat required and were 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 Figure 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 $1.90\,\mathrm{cm}^3$ was used for conducting sorption experiments.

The gas was initially introduced in the reservoir (cell 3) and then expanded into the polymer sample cell (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 polymer sample cell, the equation of state shown below can be used to calculate the initial and final moles of gas in cell 2, thereby permitting

Table 1. ε/κ Values for Gases (23)

Gas	ε/κ(°K)
CO_2	190
CH_4	136.5
O_2	113
N_2	91.5

calculation of the amount of gas sorbed by the polymer.

$$n = \frac{pv}{zRT} \tag{12}$$

n = Number of moles of gas
p = Pressure
R = Gas constant
T = Temperature
v = Polymer sample cell volume
z = Compressibility factor

The moles sorbed can be correlated to volume of gas (in cm^3 at STP conditions) using a conversion factor of 22,400 cm^3 gas (STP) per mole of gas.

RESULTS AND DISCUSSION

Experiments with polycarbonate and polysulfone 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 obtain estimates of the dual-mode model parameters listed in Tables 2 through 5 with confidence intervals for each parameter determined at a 90% confidence level. This assisted in determining whether the impact of oil on each of the model parameters was statistically significant or not. 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 presence and absence of oil was compared against an independent set of experimental measurements. The data is based on triplicate measurements with a different membrane sample used in each of the experiments. 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 polycarbonate for a clean sample as well as with 10^5 ppm SH-46. The agreement between the data and the dual-mode model was similar at all other concentrations of oil as well as with SH-100 as a dopant. Results for polysulfone

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

Gas	Reported*	Clean	10^3 ppm	10^4 ppm	10^5 ppm
			k_D (cc/cc polymer-atm.)		
N_2	0.0909	0.112 ± 0.011	0.132 ± 0.006	0.161 ± 0.004	0.180 ± 0.013
O_2	No data	0.152 ± 0.004	0.167 ± 0.005	0.177 ± 0.004	0.186 ± 0.003
CH_4	0.1473	0.163 ± 0.008	0.21 ± 0.010	0.258 ± 0.010	0.289 ± 0.010
CO_2	0.6852	0.414 ± 0.009	0.476 ± 0.008	0.547 ± 0.014	0.615 ± 0.009
			C'_H (cc/cc polymer)		
N_2	2.109	1.494 ± 0.062	0.974 ± 0.031	0.856 ± 0.067	0.705 ± 0.061
O_2	No data	1.626 ± 0.048	1.082 ± 0.034	0.988 ± 0.021	0.724 ± 0.057
CH_4	8.382	3.015 ± 0.283	2.045 ± 0.157	1.769 ± 0.103	1.266 ± 0.207
CO_2	18.805	9.38 ± 0.260	7.592 ± 0.225	7.017 ± 0.241	6.379 ± 0.275
			b (atm^{-1})		
N_2	0.0564	0.067 ± 0.034	0.403 ± 0.035	0.397 ± 0.050	0.409 ± 0.067
O_2	No data	0.090 ± 0.032	0.375 ± 0.042	0.384 ± 0.044	0.386 ± 0.052
CH_4	0.0841	0.104 ± 0.032	0.287 ± 0.064	0.291 ± 0.081	0.295 ± 0.070
CO_2	0.2618	0.159 ± 0.034	0.255 ± 0.027	0.258 ± 0.033	0.260 ± 0.035

*Sample conditioned in 20 atmospheres of CO_2 for 4 h (11).

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

Gas	Reported*	Clean	10^3 ppm	10^4 ppm	10^5 ppm
			k_D (cc/cc polymer-atm.)		
N_2	0.0753	0.147 ± 0.009	0.171 ± 0.007	0.203 ± 0.012	0.221 ± 0.003
O_2	No data	0.191 ± 0.005	0.212 ± 0.003	0.220 ± 0.003	0.247 ± 0.003
CH_4	0.161	0.203 ± 0.009	0.257 ± 0.004	0.319 ± 0.008	0.351 ± 0.005
CO_2	0.664	0.563 ± 0.014	0.654 ± 0.008	0.711 ± 0.010	0.845 ± 0.009
			C'_H (cc/cc polymer)		
N_2	9.98	1.563 ± 0.086	1.082 ± 0.058	0.969 ± 0.028	0.860 ± 0.041
O_2	No data	1.830 ± 0.084	1.509 ± 0.021	1.458 ± 0.015	1.373 ± 0.046
CH_4	9.86	2.312 ± 0.113	1.289 ± 0.063	1.151 ± 0.051	0.828 ± 0.087
CO_2	17.9	8.295 ± 0.202	6.423 ± 0.165	6.051 ± 0.154	5.392 ± 0.189
			b (atm^{-1})		
N_2	0.0156	0.101 ± 0.027	0.501 ± 0.032	0.497 ± 0.045	0.507 ± 0.043
O_2	No data	0.136 ± 0.033	0.437 ± 0.046	0.440 ± 0.063	0.443 ± 0.067
CH_4	0.0698	0.149 ± 0.033	0.298 ± 0.050	0.309 ± 0.061	0.306 ± 0.036
CO_2	0.326	0.171 ± 0.017	0.262 ± 0.020	0.269 ± 0.024	0.269 ± 0.031

*Sample conditioned in 20 atmospheres of CO_2 for 24 h (17).

Table 4. Dual-Mode Sorption Parameters for Polycarbonate (Annealed) with SH-46

Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
k_D (cc/cc polymer-atm.)				
N_2	0.101 ± 0.007	0.126 ± 0.011	0.156 ± 0.009	0.170 ± 0.004
O_2	0.146 ± 0.005	0.157 ± 0.004	0.165 ± 0.004	0.18 ± 0.007
CH_4	0.160 ± 0.013	0.193 ± 0.006	0.244 ± 0.011	0.281 ± 0.008
CO_2	0.410 ± 0.006	0.454 ± 0.007	0.535 ± 0.011	0.609 ± 0.022
C'_H (cc/cc polymer)				
N_2	1.240 ± 0.056	0.794 ± 0.031	0.716 ± 0.021	0.607 ± 0.048
O_2	1.252 ± 0.086	0.886 ± 0.035	0.808 ± 0.038	0.578 ± 0.074
CH_4	2.412 ± 0.102	1.606 ± 0.081	1.440 ± 0.071	1.040 ± 0.084
CO_2	7.037 ± 0.205	5.814 ± 0.204	5.441 ± 0.144	5.117 ± 0.171
b (atm^{-1})				
N_2	0.067 ± 0.023	0.401 ± 0.048	0.403 ± 0.044	0.398 ± 0.037
O_2	0.089 ± 0.036	0.377 ± 0.031	0.381 ± 0.037	0.379 ± 0.044
CH_4	0.103 ± 0.039	0.282 ± 0.026	0.289 ± 0.044	0.291 ± 0.031
CO_2	0.155 ± 0.032	0.253 ± 0.023	0.256 ± 0.036	0.255 ± 0.030

Table 5. Dual-Mode Sorption Parameters for Polysulfone (Annealed) with SH-46

Gas	Clean	10^3 ppm	10^4 ppm	10^5 ppm
k_D (cc/cc polymer-atm.)				
N_2	0.139 ± 0.006	0.158 ± 0.010	0.196 ± 0.010	0.213 ± 0.008
O_2	0.185 ± 0.004	0.200 ± 0.002	0.204 ± 0.002	0.232 ± 0.006
CH_4	0.202 ± 0.009	0.242 ± 0.008	0.292 ± 0.012	0.335 ± 0.009
CO_2	0.559 ± 0.009	0.617 ± 0.008	0.679 ± 0.007	0.779 ± 0.008
C'_H (cc/cc polymer)				
N_2	1.250 ± 0.088	0.892 ± 0.043	0.750 ± 0.027	0.702 ± 0.021
O_2	1.373 ± 0.071	1.199 ± 0.031	1.108 ± 0.041	1.037 ± 0.027
CH_4	1.872 ± 0.102	0.976 ± 0.054	0.886 ± 0.041	0.664 ± 0.059
CO_2	5.797 ± 0.114	4.776 ± 0.097	4.326 ± 0.121	4.076 ± 0.109
b (atm^{-1})				
N_2	0.103 ± 0.021	0.496 ± 0.051	0.499 ± 0.039	0.505 ± 0.034
O_2	0.130 ± 0.028	0.432 ± 0.063	0.435 ± 0.041	0.430 ± 0.051
CH_4	0.148 ± 0.033	0.293 ± 0.047	0.302 ± 0.053	0.307 ± 0.041
CO_2	0.169 ± 0.020	0.256 ± 0.027	0.263 ± 0.033	0.262 ± 0.039

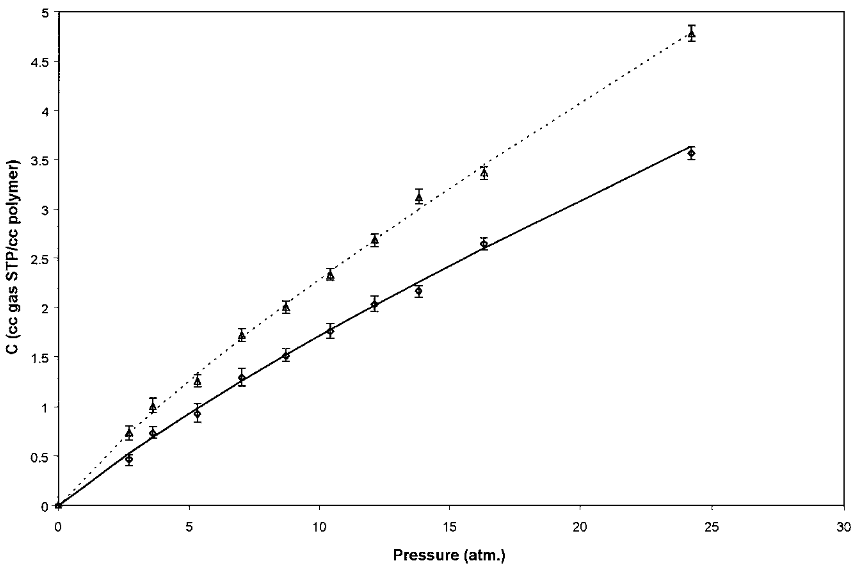

Figure 2. Sorption in polycarbonate (clean; nonannealed).

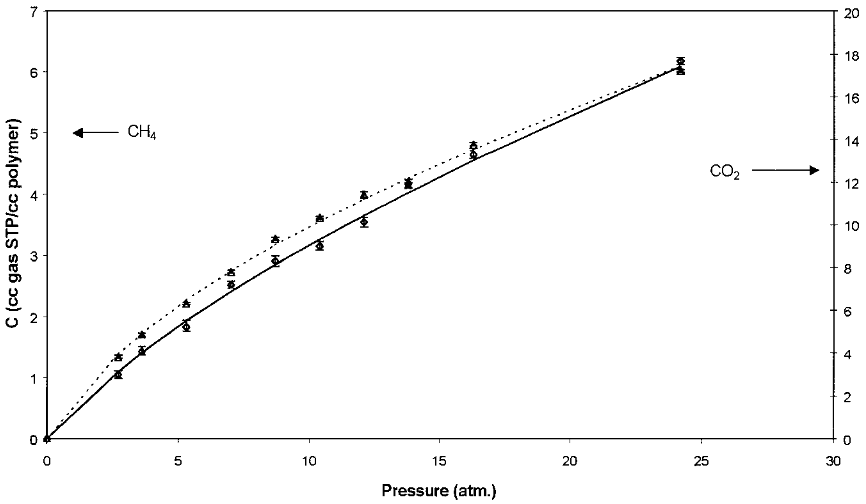

Figure 3. Sorption in polycarbonate (clean; noneanneled).

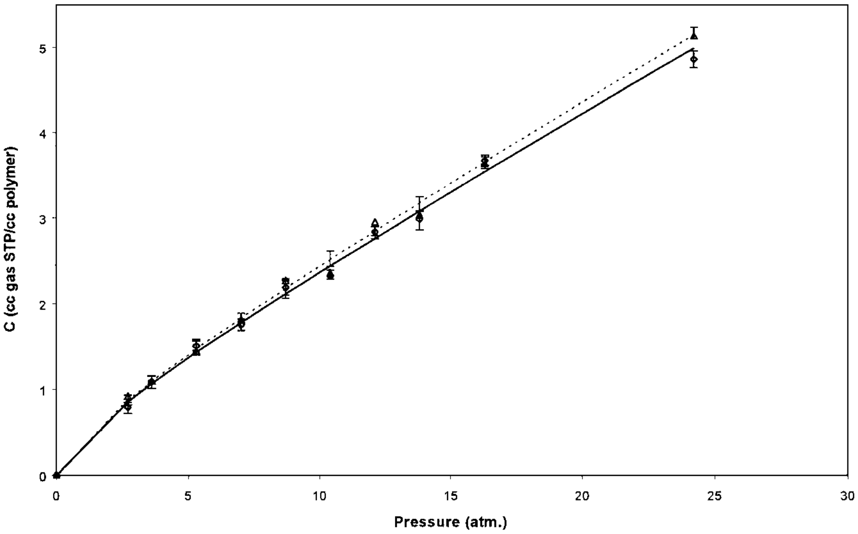

Figure 4. Sorption in polycarbonate (10^5 ppm SH-46; nonannealed).

indicated similar agreement between the experimental data and dual-mode sorption model.

The presence of compressor oil increased the overall sorption of each of the four gases. The polycarbonate based films and polysulfone samples were affected

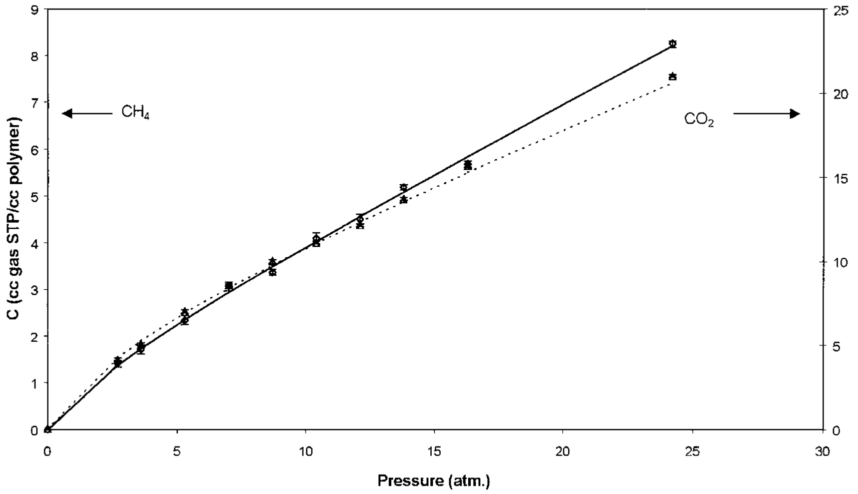

Figure 5. Sorption in polycarbonate (10^5 ppm SH-46; nonannealed).

to a similar degree by the presence of the oil. Therefore, it is less likely that the chemical composition of the polymer is a key element in how the oil affects gas dissolution. Also, SH-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.

Henry's Solubility Constant, k_D

Tables 2 and 3 show the effect of SH-46 on the solubility of the gas in the densified regions of polycarbonate and polysulfone films respectively. The solubility in the Henry's region as described in Equation (4) is equivalent to gas dissolution in rubbery polymers and low molecular weight organic liquids. In the doped polymers, k_D showed an increase 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 with the difference between the two oils being at the most 5% or less. The effect was also very comparable in both polymers that were studied. Therefore, it seems that the chemical nature of the polymer or the substituents present on its backbone may not be factors in determining how the solubility in the densified region of the polymer 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 Equation (4). χ can be estimated from the individual polymer and gas solubility parameters δ_p and δ_g (22) as shown in Equation (5). Based on the 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 Equation (5) is a net result of the polymer-gas ($\chi_{p\text{-}g}$) interaction as well as oil-gas ($\chi_{o\text{-}g}$) interaction. For N_2, O_2, and CO_2, 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. CH_4 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 Equations (4) and (5), it can be hypothesized that CH_4 being a hydrocarbon interacts more strongly with the hydrocarbon based oil, resulting in a larger $\chi_{o\text{-}g}$ 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 Equation (6) as $(V_g - V_l)$ is lowered with the presence of oil in the polymer. Subsequently, the Langmuir sites available for gas sorption is reduced. Tables 2 and 3 show the decrease in C'_H for polycarbonate and polysulfone, with increasing concentration of SH-46. This trend was observed in both polymers in the presence of either compressor oil viz. SH-46 or SH-100. The difference in molecular weight of the oils is most likely not a factor because the reduction in the magnitude of C'_H was observed to be similar for both oils. 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, N_2, O_2, and CH_4 suffer losses in their respective C'_H values on the order of 30% to 50%, as the level of doping increases. CO_2, 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 CO_2, 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 N_2, O_2, and CH_4.

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 appreciable change with increasing oil concentration as illustrated in Tables 2 and 3. It can be postulated that the oil enhances the condensibility of the gas in the polymer, but the effect is not a function of the oil concentration in the polymer, unlike in the case of k_D and C'_H. For a two-component polymer-gas system, the exponential dependence of "*b*" on ε/κ is shown in Equation (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 in the clean and doped polymer. In the clean membrane, the magnitude of "*b*" follows the trend in ε/κ values that are listed in Table 1. Thus, CO_2 has the highest affinity constant followed by CH_4, O_2, and N_2. Upon introduction of the oil, N_2 shows the largest increase in the value of "*b*" followed by O_2, CH_4, and CO_2. Because the increase in "*b*" is more pronounced in the case of less condensible gases like N_2 and O_2 compared to CO_2 and CH_4, it can be hypothesized that in the case of oil doped films the affinity constant is not entirely a function of ε/κ of the gas. Data obtained also showed both oils had similar effects on the behavior of the affinity constant "*b*," which again is indicative of the fact that the differing molecular weight of the oils is most likely not a factor in how the oil affects "*b*." The affinity constant is, therefore, a function of only the specific polymer-gas interaction and is affected by the introduction of oil in the polymer. However, the exact mechanism by which the affinity constants of the less condensible species (N_2 and O_2) are enhanced by the presence of oil is not clear at this time.

To illustrate the effect of oil on the overall solubility of gas in the polymer, models for sorption of N_2 (less condensible) and CO_2 (highly condensible) at three levels of SH-46 doping are compared against that for the corresponding clean samples. Figures 6 and 7 depict this for polycarbonate with N_2 and CO_2, respectively. As mentioned earlier, the presence of oil increases the overall sorption of gas in the polymer. The enhancement in solubility is the greatest in the low-pressure region (∼2 atmospheres) and for N_2 this increase was around 70% for polycarbonate and 60% for polysulfone. However, CO_2 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 Equation (10). Because the increase in magnitude of "*b*," with doping, is much greater for N_2 than CO_2 (Tabs. 2 and 3), the solubility of N_2 is also enhanced more than that of CO_2 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 N_2 and CO_2 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 Equation (11) describes the overall gas solubility. In the intermediate pressure range (10 through 15 atmospheres) N_2 exhibits increase of

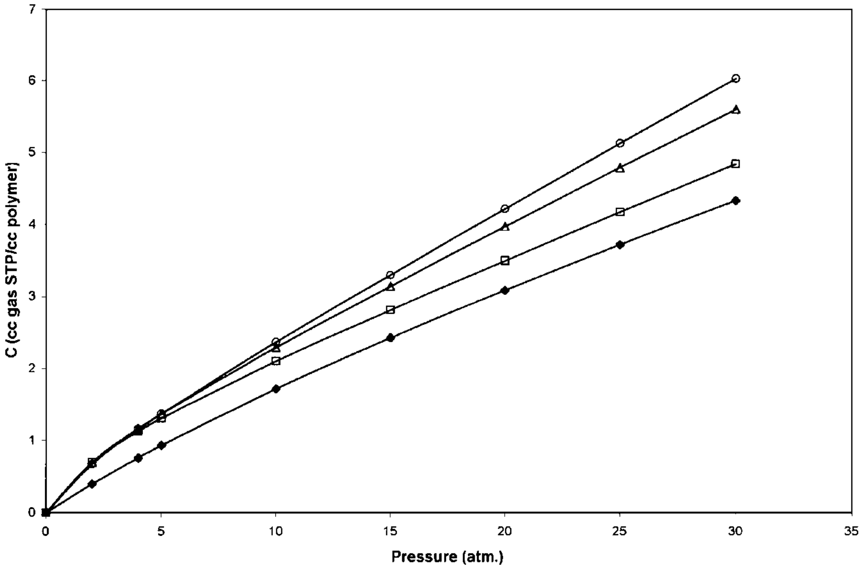

Figure 6. N_2 sorption in polycarbonate.

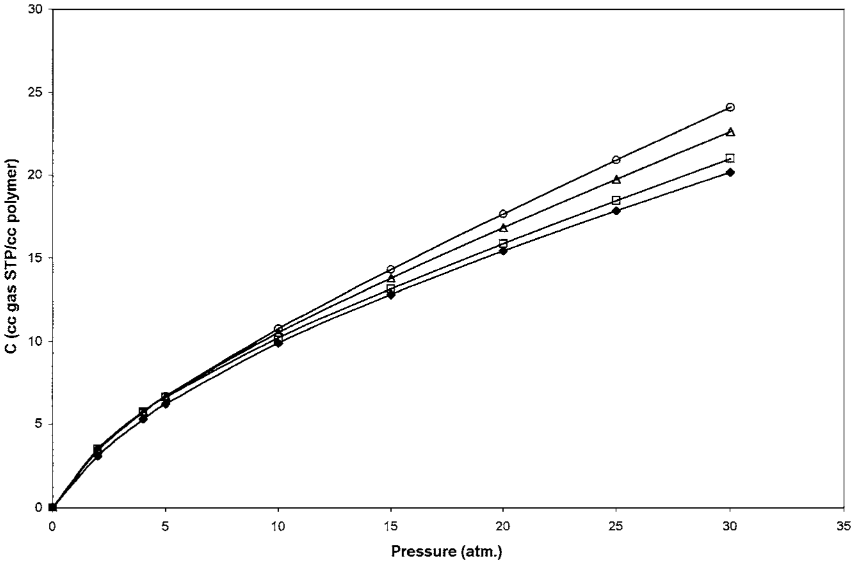

Figure 7. CO_2 sorption in polycarbonate.

about 18% through 40% for polycarbonate and 15% through 30% for polysulfone. 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 pressures (>20 atmospheres), the microvoids become saturated and the isotherm approaches the asymptotic limit described by Equation (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 (N_2 and CO_2) increased with doping of the polymer as shown in Figures 6 and 7, 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 so 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 4 and 5 for polycarbonate and polysulfone respectively with SH-46. SH-100 yielded exhibited similar effects in both polymers at all levels of doping. A careful comparison of the data in Tables 4 and 5 against corresponding parameters in Tables 2 and 3 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 CO_2 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. N_2, O_2, CH_4, and CO_2 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 Equation (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 Equation (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 Equation (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 ($\chi_{\text{p-g}}$) as well as oil-gas ($\chi_{\text{o-g}}$) as postulated earlier. The decrease in k_d in the doped films can then likely be attributed to an increase in $\chi_{\text{p-g}}$ and $\chi_{\text{o-g}}$, which most probably results from an increase in $(\delta_p - \delta_g)$ and $(\delta_o - \delta_g)$.

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 polycarbonate and polysulfone 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 non annealed 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 Equation (9) for clean membranes breaks down with the introduction of oil in the polymer, which is similar to the observations made in the case of the nonannealed films as well.

CONCLUSIONS

The dual-mode model that has been widely used to describe solubility of gases in glassy polymers by several investigators (8,9,10,11) 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 manner that reduces the interaction parameter χ that appears in Equation (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 a show a significant change thereafter with higher oil concentrations. The oil, however, enhanced the condensibility of N_2 and O_2 relative to CH_4 and CO_2, as indicated by the increase in "b." Therefore, unlike with the clean polymer samples, the affinity constants of gases in the doped sample is 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 ($\sim$2 atmospheres), the effect of oil on the affinity constant "b" assumes considerable importance as illustrated by comparing solubility models for N_2 and CO_2 with the presence of SH-46. In the intermediate pressure region (10 to 15 atmospheres), "b" becomes less significant and instead the Henry's solubility constant k_D determines the overall gas solubility. At the higher pressures ($>$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 solubility of gases in the polymers in the presence and absence of oil.

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 concurrent mechanisms viz. sorption or diffusion is retarded in the overall transport of gas through the membrane.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support provided by MG Generon, Pittsburg, California, and wish to thank Mr. Fred Coan, Mr. John Jensvold, and Mr. Tom Jeanes for their suggestions and help during the experimental phase of the project. We would also like to express our deep appreciation and gratitude to Mr. Tom Breese for his invaluable technical assistance through the course of this project. A special thanks to Dr. Roger Korus for the helpful suggestions offered during the preparation of this manuscript.

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)
k_D	Henry's solubility constant (cm^3 STP/cm^3 polymer-atm.)
n	number of moles of gas
p	pressure (atm.)
R	Universal Gas constant
T	temperature
V	molar volume of gas sorbed in the unrelaxed volume
v	polymer sample cell volume
V_g	specific volume of the glassy region at temperature T
V_l	specific volume of the equilibrium liquid at temperature T
z	compressibility factor

Greek Letters

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

REFERENCES

1. Loeb, S.; Sourirajan, S. Sea Water Demineralization by Means of an Osmotic Membrane. Advan. Chem. Ser. **1962**, *38*, 117.
2. Gantzel, P.K.; Merten, U. Gas Separation with High-Flux Cellulose Acetate Membranes. Ind. Eng. Chem., Proc. Res. Dev. **1969**, *8*, 84.
3. Alexander Stern, S. Polymers for Gas Separations: The Next Decade. J. Memb. Sci. **1994**, *94*, 1.
4. Kesting, R.E.; Fritzsche, A.K. *Polymeric Gas Separation Membranes*; John Wiley & Sons: New York, 1993.
5. Haggin, J. Nitrogen for Blanketing Seen as Growth Area for Gas Separations. Chem.& Eng. News **1989**, *67*, 14.
6. Bootsveld, C.; Wienk, I. *Membrane Fouling and Concentration Polarization*; Soc. of Chem. Tech., Univ. of Twente: Twente, The Netherlands, 1988.
7. Koros, W.J.; Fleming, G.K. Membrane-Based Gas Separation. J. Memb. Sci. **1993**, *83*, 1.
8. Barrer, R.M.; Barrie, J.A.; Slater, J. Sorption and Diffusion in Ethyl Cellulose. Part III. J. Polymer Sci. **1958**, *27*, 177.
9. Michaels, A.S.; Vieth, W.R.; Barrie, J.A. Solution of Gases in Polyethylene Terephthalate. J. Applied Phys. **1963**, *34*, 1.
10. Vieth, W.R.; Sladek, K.J. A Model for Diffusion in a Glassy Polymer. J. Colloid Sci. **1965**, *20*, 1014.
11. Koros, W.J.; Chan, A.H.; Paul, D.R. Sorption and Transport of Various Gases in Polycarbonate. J. Memb. Sci. **1977**, *2*, 165.
12. Assink, R.A. Investigation of the Dual-Mode Sorption of Ammonia in Polystyrene by NMR. J. Polymer Sci., Phys. Ed. **1975**, *13*, 1665.
13. Michaels, A.S.; Bixler, H.J. Solubility of Gases in Polyethylene. J. Polymer Sci. **1961**, *50*, 393.
14. Jolley, J.E.; Hildebrand, J.H. Solubility, Entropy and Partial Molal Volumes in Solutions of Gases in Non-Polar Solvents. J. Am. Chem. Soc. **1958**, *80*, 1050.
15. Flory, P.J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, New York, 1953.

16. Koros, W.J.; Paul, D.R. CO_2 Sorption in Poly(ethylene terephthalate) above and below the Glass Transition. J. Polymer Sci., Polymer Phys. Ed. **1978**, *16*, 1947.
17. Chan, A.H.; Paul, D.R. Effect of Sub-T_g Annealing on CO_2 Sorption in Polycarbonate. Polymer Eng. and Sci. **1980**, *20*, (1), 87.
18. Erb, A.J.; Paul, D.R. Gas Sorption and Transport in Polysulfone. J. Memb. Sci. **1981**, *8*, 11.
19. Brunauer, S. *The Adsorption of Gases and Vapors*; Princeton Univ. Press: Princeton, N.J., 1943; vol. 64, 419–422.
20. Vieth, W.R.; Tam, P.M.; Michaels, A.S. Dual Sorption Mechanisms in Glassy Polystyrene. J. Colloid and Interface Sci. **1966**, *22*, 360.
21. Sanders, E.S.; Koros, W.J.; Hopfenberg, H.B.; Stannett, V.T. Mixed Gas Sorption in Glassy Polymers: Equipment Design Consideration and Preliminary Results. J. Memb. Sci. **1983**, *13*, 161.
22. Barton, A.F.M. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, FL, 1985.
23. Welty, J.R.; Wicks, C.E.; Wilson, R.E. *Fundamentals of Momentum, Heat, and Mass Transfer*, 3rd Ed.; John Wiley and Sons: New York, 1984.

Received October 21, 1999
Revised May 2000

Downloaded At: 10:52 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS100001074