Macromolecules **2005,** *38,* 1899−1910

Sorption and Transport Properties of Propane and Perfluoropropane in Poly(dimethylsiloxane) and Poly(1-trimethylsilyl-1-propyne)

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Received September 23, 2004; Revised Manuscript Received November 8, 2004

ABSTRACT: The effect of pressure on solubility and the influence of temperature on solubility, permeability, and diffusivity of C_3F_8 and its hydrocarbon analogue, C_3H_8, are reported in rubbery poly(dimethylsiloxane) (PDMS) and glassy poly(1-trimethylsilyl-1-propyne) (PTMSP). The solubility of C_3F_8 is lower than that of C_3H_8 in both polymers at all temperatures and pressures investigated. The isosteric enthalpy of mixing C_3F_8 with PDMS and PTMSP is higher than that of C_3H_8 due to less favorable polymer−fluorocarbon interactions in the case of C_3F_8, and it decreases with increasing C_3F_8 concentration. Assuming a coordination number of 10, the energy associated with mixing C_3F_8 molecules and PDMS segments is 4.5 kJ/mol more than that required to mix C_3H_8 molecules with PDMS segments, in the limit of infinite dilution. The isobaric activation energy of permeation (E_P) for C_3F_8 is positive for both polymers, and that for C_3H_8 is negative in both polymers. This result is particularly interesting for PTMSP since all previous studies of activation energy of gas permeation in PTMSP report values that are near zero or negative; this study provides the first report of a positive E_P value in PTMSP. In PDMS, differences in both activation energy of diffusion (E_D) and enthalpy change on sorption contribute significantly to the difference in E_P values of C_3H_8 and C_3F_8. For PTMSP, the difference in E_P values for C_3F_8 and C_3H_8 stems mainly from a substantially larger E_D value for C_3F_8 than for C_3H_8.

Introduction

Perfluorocarbons (PFCs) are industrially important compounds with very long atmospheric lifetimes (3000−5000 years) and enormous global warming potentials (5000−10 000 times greater than that of CO_2).[1] Because of the potentially deleterious effect of these materials on the environment, U.S. federal regulations have restricted their use to "high-performance, precision-engineered applications only, where reasonable efforts have been made to ascertain that other alternatives are not technically feasible due to performance or safety requirements."[2]

The separation of PFCs from permanent gases using membranes has been the subject of several investigations.[3−10] Relative to their hydrocarbon analogues, PFCs exhibit low solubility in hydrocarbon-based polymers such as poly(dimethylsiloxane) (PDMS),[7,11] poly(1-trimethylsilyl-1-propyne) (PTMSP),[5,7] and polyethylene.[11] This behavior has been ascribed to less favorable interactions between fluorinated penetrants and hydrocarbon-based polymers than between hydrocarbon penetrants and hydrocarbon-based polymers.[7,9,10] Similar observations of low fluorocarbon solubility in hydrocarbon liquids have also been reported.[12−14] For example, the mole fractions of C_3F_8 and C_3H_8 dissolved in cyclohexane at 25 °C and 1 atm are 0.006 532 and 0.095 578, respectively;[14] that is, C_3F_8 is almost 15 times less soluble in cyclohexane than C_3H_8.

This report provides quantitative, experimental evidence of the less favorable interactions between fluorocarbon penetrants and hydrocarbon-based polymers that influence the energetics of gas sorption and transport. Perfluoropropane was selected as a model penetrant, and its sorption, diffusion, and permeation properties are compared with those of its hydrocarbon analogue, propane, in two very different hydrocarbon-based polymers, PDMS and PTMSP. PDMS is a rubbery polymer (its glass transition temperature, T_g, is −123 °C).[15] As such, it presents a mobile, liquidlike environment to penetrant molecules. PTMSP, on the other hand, is a stiff chain, glassy polymer (T_g > 250 °C) exhibiting very poor chain packing in the solid state.[16,17] It is the most permeable polymer known, and it has the lowest density and highest fractional free volume of all known hydrocarbon-based polymers.[9] Permeability coefficients of N_2 and H_2 in these polymers are also provided because separation of PFCs from mixtures with these permanent gases has been the focus of industrial interest.[18−26]

Background

Permeability. The permeability of a polymer film to a pure penetrant is given by[27]

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

where P is the permeability coefficient, N is the steady-state gas flux through the polymer membrane, l is film thickness, p_2 is the feed or upstream pressure, and p_1 is the permeate or downstream pressure. Penetrant

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10.1021/ma048032k CCC: $30.25

transport through a polymer film is commonly described by a three-step solution-diffusion mechanism.[27] According to this mechanism, when penetrant flux obeys Fick's law

$$P = \frac{C_2 - C_1}{p_2 - p_1} D \tag{2}$$

where D is the effective concentration-averaged diffusion coefficient, and C_2 and C_1 are the penetrant concentrations at the upstream and downstream faces of the membrane. If the downstream pressure is negligible compared to the upstream pressure, eq 2 can be simplified:[27]

$$P = SD \tag{3}$$

where the solubility coefficient, S, is defined as follows:

$$S = \frac{C}{p} \tag{4}$$

In eq 3, S should be evaluated at the upstream conditions. The effective concentration-averaged diffusivity is defined by

$$D = \int_{C_1}^{C_2} \frac{D_{\mathrm{loc}}}{1 - \omega}\, \mathrm{d}C = \int_{C_1}^{C_2} D_{\mathrm{eff}}\, \mathrm{d}C \tag{5}$$

where D_{loc} is the local concentration-dependent diffusion coefficient, ω is the penetrant mass fraction in the polymer at concentration C, and D_{eff} is the so-called local effective diffusion coefficient.

Selectivity. The ideal selectivity, $\alpha_{\mathrm{A/B}}$, of component A over B is a measure of the potential separation ability of the membrane material. The ideal selectivity can be written as the ratio of the pure gas permeabilities:[27]

$$\alpha_{\mathrm{A/B}} \equiv \frac{P_{\mathrm{A}}}{P_{\mathrm{B}}} \tag{6}$$

or

$$\alpha_{\mathrm{A/B}} = \frac{S_{\mathrm{A}}}{S_{\mathrm{B}}} \frac{D_{\mathrm{A}}}{D_{\mathrm{B}}} \tag{7}$$

where the first term on the right-hand side is the solubility selectivity and the second is the diffusivity selectivity. In addition to operating conditions (i.e., temperature, pressure, and gas composition), penetrant solubility depends on condensability and polymer−penetrant interactions.[27] In the absence of specific interactions (e.g., hydrogen bonding), the first effect is dominant, and solubility increases as penetrant condensability, characterized by critical temperature, normal boiling point, or Lennard-Jones force constant, increases.[27] Thus, solubility selectivity increases as the difference in condensability between two penetrants in a mixture increases. Often, larger penetrants are more condensable and therefore more soluble than smaller penetrants. However, larger penetrants have lower diffusion coefficients than smaller penetrants, and as the difference in penetrant size increases, so does the diffusivity selectivity.[27] Thus, a tradeoff often exists between solubility selectivity and diffusivity selectivity, with the overall selectivity depending on the relative magnitudes of these two terms.

Solubility. The sorption of sparingly soluble gases in rubbery polymers is qualitatively similar to the sorption of gases in low molecular weight liquids, and the gas concentration in the polymer, C, often obeys Henry's law:[27]

$$C = k_{\mathrm{D}} p \tag{8}$$

where k_{D} is the Henry's law constant and p is the gas pressure in contact with the polymer. The uptake of more soluble vapors in a cross-linked rubbery polymer is frequently described using the Flory−Rehner expression:[28]

$$\ln a = \ln \phi_2 + (1 - \phi_2) + \chi(1 - \phi_2)^2 + V_2\left(\frac{\nu_{\mathrm{e}}}{V_0}\right)\left[(1 - \phi_2)^{1/3} - \left(\frac{1 - \phi_2}{2}\right)\right] \tag{9}$$

where a is penetrant activity in the vapor phase, ϕ_2 is the volume fraction of sorbed penetrant, χ is the Flory−Huggins interaction parameter, V_2 is the penetrant molar volume, and ν_{e}/V_0 is the effective number of cross-links per unit volume of penetrant-free polymer (expressed in moles of cross-links per unit volume of penetrant-free polymer). In this study, penetrant activity is set equal to the relative pressure, p/p_{sat}, where p_{sat} is the saturation vapor pressure of the penetrant. The volume fraction of sorbed penetrant, ϕ_2, is calculated from the equilibrium penetrant concentration in the polymer, C, as follows:

$$\phi_2 = \left[1 + \frac{22414}{C\bar{V}_2}\right]^{-1} \tag{10}$$

where $\bar{V}_2$ is the penetrant partial molar volume and is estimated as described previously.[10] In this equation, C and $\bar{V}_2$ have units of cm^3 (STP)/cm^3 polymer and cm^3/mol, respectively. 22414 is a conversion factor (cm^3 (STP)/mol).

Sorption isotherms for gases in glassy polymers are usually concave to the pressure axis at low pressures and linear at higher pressures.[27] Such isotherms are often described using the dual-mode sorption model.[29] In this model, penetrant molecules are viewed as being partitioned into two populations which are in dynamic equilibrium with each other: (i) penetrant molecules sorbed by a dissolution mechanism in the dense polymer matrix (Henry's law population) and (ii) penetrant molecules filling unrelaxed, molecular-scale gaps (microvoids) frozen into the glassy state (Langmuir population).[29] The dual-mode model is expressed analytically as a sum of these two contributions to penetrant sorption:

$$C = k_{\mathrm{D}} p + \frac{C'_{\mathrm{H}} b p}{1 + bp} \tag{11}$$

where C is the total concentration of penetrant in the polymer, k_{D} is the Henry's law constant, C'_{H} is the hole saturation constant or Langmuir sorption capacity parameter, and b is the Langmuir affinity parameter.

Temperature Dependence. The temperature dependence of permeability, diffusivity, and solubility at temperatures far removed from polymer thermal transitions is described as follows:[27]

$$P = P_0 \exp\left(-\frac{E_P}{RT}\right) \tag{12}$$

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \tag{13}$$

$$S = S_0 \exp\left(-\frac{\Delta H_s}{RT}\right) \tag{14}$$

where P_0, D_0, and S_0 are preexponential constants, E_P is the activation energy of permeation, E_D is the activation energy of diffusion, and ΔH_s is the enthalpy of sorption. Because permeability is the product of solubility and diffusivity (eq 3), the activation energies of permeation and diffusion and the enthalpy of sorption are related:

$$E_P = E_D + \Delta H_s \tag{15}$$

Equation 15 is a consequence of eqs 3, 12, 13, and 14 and is, therefore, subject to the assumptions inherent in these equations. For example, eq 15 does not hold if the downstream pressure cannot be neglected in comparison to the upstream pressure due to the assumptions underlying eq 3. Also, if the penetrant transport properties (i.e., P, D, and S) are functions of concentration, eq 15 is expected to be a simplified form of a more general model.[30] Nevertheless, eqs 12−15 are the standard model for describing the temperature dependence of gas solubility, diffusivity, and permeability in polymers, and we will use them in this study.

Experimental Section

Materials. *PDMS*. Poly(dimethylsiloxane) (PDMS) composite membranes were used for pure gas permeation experiments. These membranes, composed of a filler-free PDMS film on a highly microporous support, were kindly provided by Dr. Ingo Pinnau of Membrane Technology and Research, Inc. (Menlo Park, CA). The poly(dimethylsiloxane) was from Wacker Silicones Corp. (Adrian, MI) and was cross-linked at 100 °C using a proprietary cross-linker/catalyst system supplied by them.

A dense filler-free PDMS film of thickness approximately 250 μm was used for the sorption measurements. Cross-linking was achieved using the same method described above. The cross-link density of this film was estimated to be 7.8×10^{-5} mol/cm^3.[31] Since the film for the permeation measurements was cross-linked under the same conditions, it should have a similar cross-link density to that of the dense film.

PTMSP. PTMSP was kindly provided by Permea, Inc. (St. Louis, MO). Isotropic poly(1-trimethylsilyl-1-propyne) films, approximately 50 μm thick, were prepared from a 2 wt % solution of the polymer in toluene as described previously.[32] After casting and drying, the samples were stored in liquid methanol at ambient conditions to mitigate physical aging. The films were removed from methanol and dried at ambient conditions for 24 h before using them for experiments. These films were utilized for both sorption and permeation measurements.

Gases. The gases and vapors used in the permeation and sorption experiments had a purity of at least 99.5%. N_2 and H_2 were obtained from National Specialty Gases (Durham, NC) while C_3H_8 and C_3F_8 were purchased from Machine Welding (Raleigh, NC). All gases were used as received.

Characterization. *Sorption.* Solubility coefficients were determined using a high-pressure barometric apparatus.[33] Initially, a polymer film was placed in the sample chamber and exposed to vacuum overnight to remove the air gases. A known amount of penetrant gas was introduced into the chamber, and the pressure was allowed to equilibrate. Once the chamber pressure was constant, the amount of gas sorbed by the polymer was determined by mass balance. Then additional penetrant was introduced, and the procedure was repeated. In this incremental manner, penetrant uptake was determined as a function of pressure. The maximum pressure was 3−25 atm depending on the penetrant. Sorption equilibrium for all gases was reached within, at most, a few hours. After measuring each isotherm, the polymer samples were degassed under vacuum overnight. The system temperature was controlled to ±0.1 °C using a constant temperature water bath. For PDMS, the sorption experiments were performed in the following order: N_2, H_2, C_3H_8, and C_3F_8. For the last two gases, solubility was measured at different temperatures in the order of increasing temperature, i.e., 25, 35, 45, and then 55 °C. The orders of gases and temperatures for PTMSP were also the same, except that sorption of H_2 in PTMSP was not measured.

Permeation. Pure gas permeability coefficients were determined using a constant pressure/variable volume apparatus.[34] The membrane area was 13.8 cm^2. The upstream pressure was varied from 2 to 17.4 atm for N_2 and H_2 while for C_3H_8 and C_3F_8 it was kept constant at 2.36 atm. In all cases, the downstream pressure was atmospheric. Gas flow rates were measured with a soap-film bubble flowmeter. The system temperature was controlled to ±0.5 °C using a DYNA-SENSE temperature control system. Prior to each experiment, the upstream and downstream sides of the permeation cell were purged with penetrant gas. Permeability coefficients of the gases and vapors were determined in the following order: N_2, H_2, C_3H_8, and C_3F_8 where, for each gas, measurements at different temperatures were made in the order of increasing temperature. For PTMSP, to minimize conditioning effects, a fresh film was used for each gas. The variation in nitrogen permeability from film to film, at all temperatures measured, was less than 10%. When pseudo-steady-state conditions were attained, the following expression was used to evaluate permeability:

$$P = \frac{22414}{A} \frac{l}{p_2 - p_1} \frac{p_1}{RT} \frac{dV}{dt} \tag{16}$$

where A is the membrane area (cm^2), l is the membrane thickness (cm), p_2 is the upstream pressure (atm), p_1 is the downstream pressure (atmospheric pressure in this case), R is the universal gas constant (6236.56 cm^3 cmHg/(mol K)), T is the absolute temperature (K), and dV/dt is the volumetric displacement rate of the soap film in the bubble flowmeter (cm^3/s).

Results and Discussion

Solubility. *PDMS.* Sorption isotherms for nitrogen and hydrogen in PDMS at 35 °C are presented in Figure 1. The isotherms obey Henry's law, and our experimental data are in good agreement with previously published data for nitrogen sorption in PDMS at 35 °C.[35] From Figure 1, the ratio of nitrogen to hydrogen solubility is approximately 1.6. The value of this ratio in a wide variety of liquids lies between 1.2 and 2.2.[36] For example, the N_2/H_2 solubility ratio is 1.4 in carbon disulfide, around 1.7 in alcohols, and in the range 1.9−2.2 in hydrocarbon liquids at 25 °C and 1 atm.[36] Thus, the N_2/H_2 solubility ratio in PDMS lies in the same range as that in liquids, and this is one simple method for ensuring that the data are reasonable, since this ratio is expected to be comparable among rubbery polymers and liquids.

Sorption isotherms for propane and perfluoropropane in PDMS at 25, 35, 45, and 55 °C are presented in parts a and b of Figure 2, respectively. Perfluoropropane solubility in PDMS is enormously lower than that of propane. For example, at 35 °C and 3 atm the sorbed

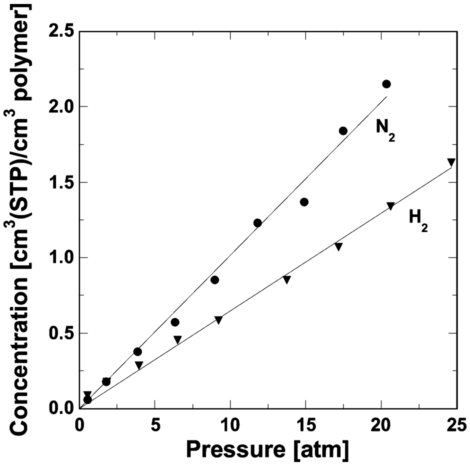

Figure 1. N_2 and H_2 sorption in PDMS at 35 °C.

concentrations of C_3H_8 and C_3F_8 are 23 and 2.3 cm^3 (STP)/(cm^3 polymer), respectively, a difference of 1 order of magnitude. For both penetrants, solubility decreases with increasing temperature at a given pressure, indicating that the sorption process is exothermic.

Propane sorption isotherms are convex to the pressure axis, which is consistent with the behavior of highly sorbing penetrants in rubbery polymers.[27] The curvature of the isotherms decreases with increasing temperature, suggesting a weaker dependence of solubility on pressure at higher temperatures. This is consistent with the findings of Shah et al.,[37] who observed a decrease in the pressure dependence of propane solubility in PDMS as temperature increased. They obtained an infinite dilution solubility of 6.45 cm^3 (STP)/(cm^3 polymer atm) at 35 °C, which is in excellent agreement with our value of 6.5 ± 0.06 cm^3 (STP)/(cm^3 polymer atm). If the propane sorption isotherms are plotted as a function of activity (i.e., p/p_{sat}) instead of pressure (cf. Figure 2c), the four isotherms collapse to a single curve. This result suggests that the change in the curvature of the isotherms with temperature is a result of exploring a smaller activity range at higher temperatures, since the maximum pressure in these experiments is almost the same but the value of p_{sat} increases substantially with temperature.

Perfluoropropane sorption isotherms are linear (cf. Figure 2b). When the amount of perfluoropropane sorbed in PDMS is plotted against penetrant activity (cf. Figure 2d), which should account for variability in C_3F_8 condensability with temperature, the C_3F_8 sorbed concentration increases with temperature. This behavior is qualitatively unlike that of C_3H_8 and suggests less favorable interactions between C_3F_8 and the PDMS matrix than between C_3H_8 and PDMS.

In the absence of specific interactions between penetrant molecules and the polymer matrix, solubility coefficients usually scale with measures of penetrant condensability such as critical temperature, T_c.[27] Such relationships often utilize solubility coefficients in the limit of zero pressure (called infinite dilution solubility, S^∞) to compare solubilities of penetrants on a consistent basis:

$$S^\infty = \lim_{p\to 0} S = \lim_{p\to 0} \frac{C}{p} \tag{17}$$

Suwandi and Stern[38] observed a linear correlation of the logarithm of infinite dilution solubility, S^∞, with $(T_c/T)^2$ for a large number of penetrants in PDMS. This result has been reproduced in Figure 3 (the numerical data have been tabulated previously[10]) along with the S^∞ values of propane and perfluoropropane determined in this study (filled symbols). The data for propane obey this correlation, but perfluoropropane solubility coefficients fall well below the trendline, consistent with our previous isothermal study of hydrocarbon and fluorocarbon solubility in PDMS.[10] This result suggests that the fluorinated penetrant experiences less favorable interactions with PDMS than its hydrocarbon analogue.

From sorption data such as those presented in Figure 2a,b, the effect of temperature on solubility can be determined. Solubility values from these figures, calculated either at constant penetrant pressure or at a constant penetrant concentration in the polymer, can be fitted to the van't Hoff equation (eq 14) to obtain enthalpies of penetrant sorption. Thus, two enthalpies of sorption can be calculated viz. the enthalpy of sorption at constant pressure (isobaric), ΔH_s^P, or the enthalpy of sorption at constant concentration (isosteric), ΔH_s^C. The relationship between the isobaric and isosteric enthalpies of sorption is derived in the Appendix. In this document, ΔH_s will be used in equations which apply to both isosteric and isobaric enthalpies of sorption, while the superscripts "*C*" and "*P*" will be used to denote the particular types of enthalpies when it is necessary to make this distinction.

Isosteric enthalpies of sorption were calculated for C_3H_8 and C_3F_8 in PDMS from the data in Figure 2a,b. Since sorption is typically viewed as a two-step process involving penetrant condensation from a gaslike density to a liquidlike density followed by mixing condensed penetrant molecules with polymer segments, the enthalpy of sorption can be viewed as a sum of the enthalpy changes for these two steps:[39]

$$\Delta H_s = \Delta H_{\mathrm{cond}} + \Delta H_m \tag{18}$$

where ΔH_{cond} and ΔH_m are the enthalpy changes associated with penetrant condensation and mixing, respectively.[39] To estimate ΔH_m, a value of ΔH_{cond} must be supplied. However, ΔH_{cond} varies somewhat over the temperature range of study. For example, ΔH_{cond} for C_3H_8 and C_3F_8 changes by 2.7 and 4.5 kJ/mol, respectively, over the temperature range investigated. For the present calculation, ΔH_{cond} values have been taken at 40 °C, which is the midpoint of the experimental temperature range. The ΔH_{cond} values are −13.6 and −12.7 kJ/mol for C_3H_8 and C_3F_8, respectively, at this temperature.[40] These values were used in eq 18 to calculate the isosteric enthalpy of mixing in PDMS, and the results are presented in Figure 4a. Basing the calculation of ΔH_m on the ΔH_{cond} value at 40 °C is an arbitrary choice, and the values of ΔH_m in Figure 4a will vary somewhat depending on the value of ΔH_{cond} used. However, there is no qualitative change in the order of the data presented in Figure 4a or its dependence on concentration if other reasonable reference temperatures are used for determining ΔH_{cond}, so the discussion and conclusions below are not affected by this choice.

As indicated in Figure 4a, the enthalpy of mixing perfluoropropane with PDMS segments is much greater than that of propane. For example, at infinite dilution the enthalpies of mixing for C_3F_8 and C_3H_8 are 2.5 and −2.8 kJ/mol, respectively. In both cases, the enthalpy

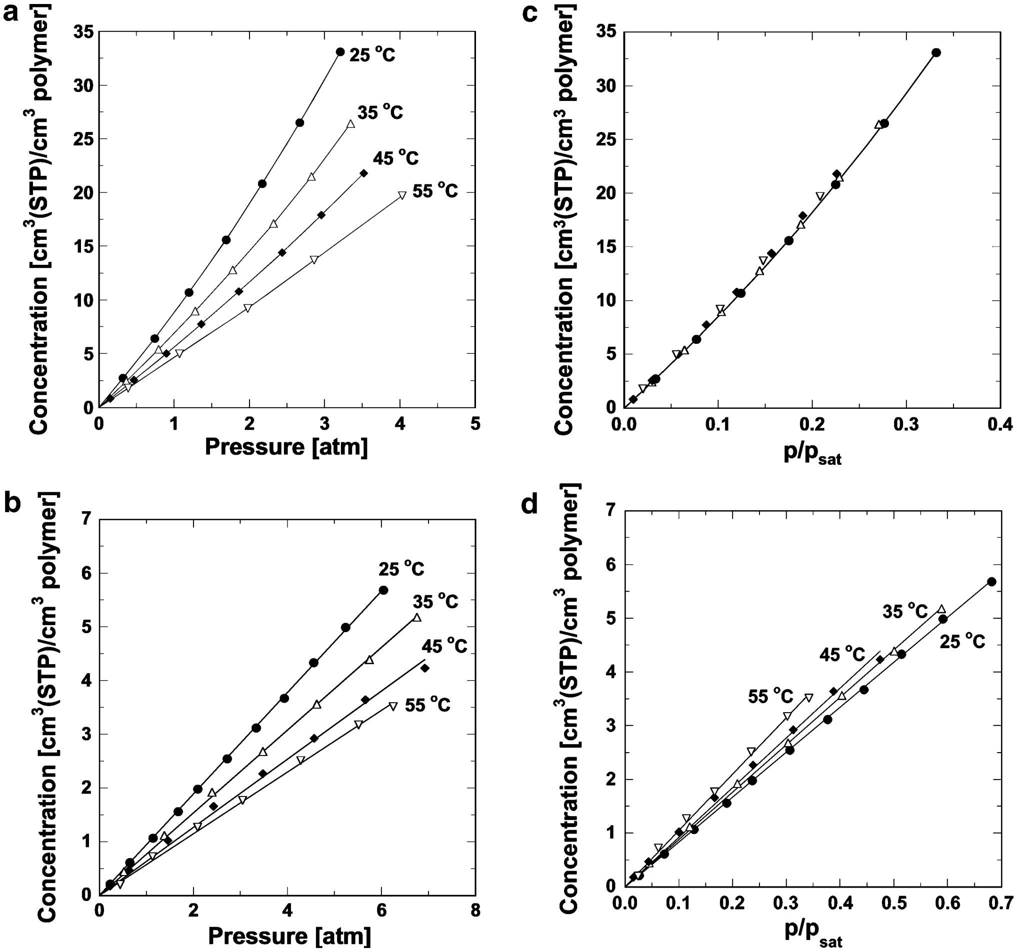

Figure 2. (a) C_3H_8 and (b) C_3F_8 sorption in PDMS as a function of temperature. (c) C_3H_8 and (d) C_3F_8 sorption in PDMS as a function of penetrant activity (p/p_{sat}) at four temperatures: (●) 25, (△) 35, (◆) 45, and (▽) 55 °C. p_{sat} values are from the correlations in Appendix A of Reid et al.[52]

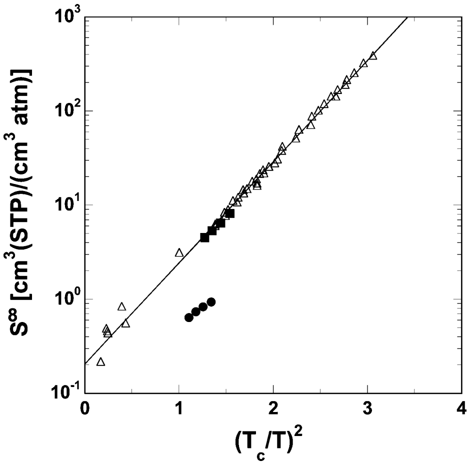

Figure 3. Correlation of infinite dilution solubility, S^∞, in PDMS with reduced critical temperature: (■) propane data of this study; (●) perfluoropropane data of this study; (△) data of Suwandi and Stern,[38] Barrer et al.,[53] and Robb.[54] The correlation line is S^∞ [cm^3 (STP)/(cm^3 atm)] = $0.0245 \times 10^{1.075(T_c/T)^2}$.

of mixing decreases with concentration, implying that the process of mixing becomes more favorable in the presence of greater amounts of penetrant. Typically, if the polymer matrix and the penetrant molecules are chemically dissimilar and do not have specific interactions with each other, interactions among penetrant molecules are more favorable than those between penetrant molecules and polymer chains. At low penetrant concentrations, mixing these penetrant molecules with the polymer is a less favorable process than at higher concentrations. As penetrant concentration increases, the environment into which the penetrant is dissolving becomes more like that of the penetrant, and the mixing process becomes more favorable. The enthalpy of mixing of propane depends much less on penetrant concentration than that of perfluoropropane. This result is reasonable because, from a structural viewpoint, propane and PDMS are much more similar than perfluoropropane and PDMS.

The difference in interaction energy of PDMS with perfluoropropane and propane can be estimated from polymer–polymer, penetrant–penetrant, and polymer–penetrant interaction energies. Based on the regular solution and Flory–Huggins theories[10]

$$z(\Gamma_{FP} - \Gamma_{HP}) = \frac{RT}{N_A}\left[(\chi_F - \chi_H) - \frac{1}{RT}(\Delta H_{condH} - \Delta H_{condF})\right] \quad (19)$$

where Γ_{FP} is the potential energy required to separate a perfluoropropane molecule and a PDMS segment to infinite distance, Γ_{HP} is the potential energy required to separate a propane molecule and a PDMS segment to infinite distance, z is the coordination number, N_A is Avogadro's number, χ_F and χ_H are the Flory–Huggins interaction parameters for perfluoropropane and pro-

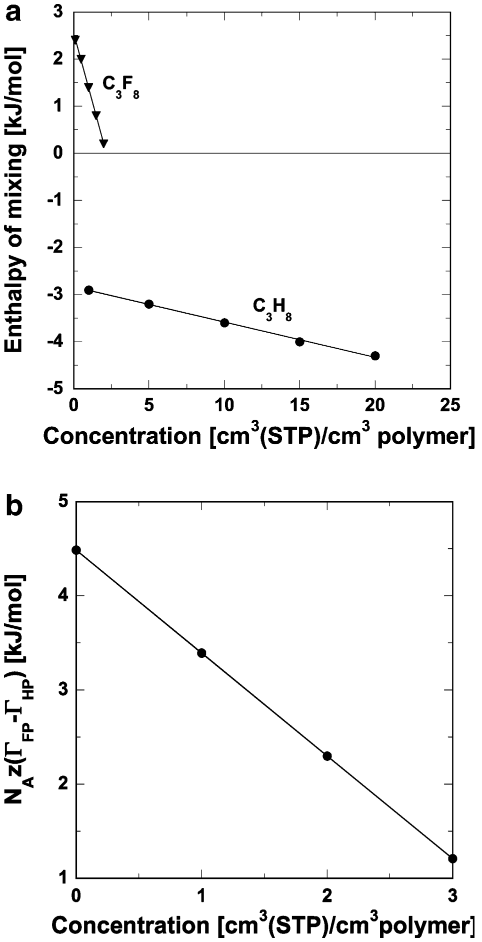

Figure 4. (a) Isosteric enthalpy of mixing of C_3H_8 and C_3F_8 in PDMS. (b) Difference in potential energies associated with insertion of C_3F_8 and C_3H_8 in PDMS.

pane, respectively, and $\Delta H_{\mathrm{condF}}$ and $\Delta H_{\mathrm{condH}}$ are the molar enthalpies of condensation of perfluoropropane and propane, respectively. The product $z(\Gamma_{\mathrm{FP}} - \Gamma_{\mathrm{HP}})$ is the difference in potential energy associated with inserting a C_3F_8 molecule and a C_3H_8 molecule in PDMS. Also[41]

$$\Delta H_{\mathrm{m}} = RT\chi(1 - \phi_2) \tag{20}$$

where ΔH_{m} is the enthalpy of mixing and ϕ_2 is the penetrant volume fraction (which is $\ll 1$ in this study). Combining eqs 19 and 20 yields

$$\begin{aligned} N_{\mathrm{A}}z(\Gamma_{\mathrm{FP}} - \Gamma_{\mathrm{HP}}) &= (\Delta H_{\mathrm{mF}} - \Delta H_{\mathrm{mH}}) - \\ &\qquad (\Delta H_{\mathrm{condH}} - \Delta H_{\mathrm{condF}}) \\ &= \Delta H_{\mathrm{sF}}^{\mathrm{C}} - \Delta H_{\mathrm{sH}}^{\mathrm{C}} \end{aligned} \tag{21}$$

where $\Delta H_{\mathrm{sF}}^{\mathrm{C}}$ and $\Delta H_{\mathrm{sH}}^{\mathrm{C}}$ are the isosteric enthalpies of mixing the fluorocarbon and hydrocarbon penetrants, respectively, with the polymer segments. The left-hand side of eq 21 is the difference in energy associated with inserting a mole of C_3F_8 molecules and a mole of C_3H_8 molecules in PDMS.

Figure 4b presents the calculated difference in potential energy associated with inserting C_3F_8 molecules and C_3H_8 molecules in PDMS. In the limit of infinite dilution, this difference is 4.5 kJ/mol while at the highest concentration considered, 3 cm^3 (STP)/(cm^3 polymer), it is 1.2 kJ/mol. The result at infinite dilution is in excellent agreement with that previously estimated from isothermal sorption data (4.6 kJ/mol at infinite dilution).[10]

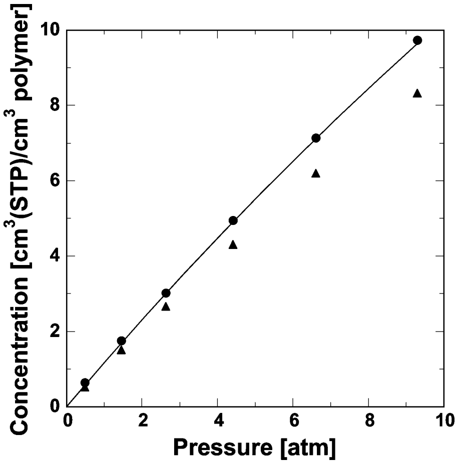

Figure 5. N_2 sorption in PTMSP at 35 °C. Data of Ichiraku et al.[42] (▲) are provided for comparison.

PTMSP. A nitrogen sorption isotherm in PTMSP at 35 °C is presented in Figure 5 along with previously published data for comparison.[42] Our data are in good agreement with the literature data. Sorption isotherms for propane and perfluoropropane in PTMSP at 25, 35, and 45 °C are presented in parts a and b of Figure 6, respectively. The isotherms are concave to the pressure axis, which is typical for gas sorption in glassy polymers.[27] There is a substantial difference in the solubilities of the hydrocarbon and fluorocarbon analogues, with propane being more soluble in PTMSP at all temperatures and pressures tested. As noted previously,[9] this difference in hydrocarbon and perfluorocarbon solubilities is smaller in high free volume PTMSP than in liquidlike PDMS. For example, at 35 °C and 3 atm, the sorbed concentrations of C_3H_8 and C_3F_8 in PTMSP are 68 and 26 cm^3 (STP)/(cm^3 polymer), respectively, which is significantly smaller than the order of magnitude difference observed in PDMS.

Isosteric enthalpies of sorption were calculated for C_3H_8 and C_3F_8 in PTMSP from the data in Figure 6a,b. The enthalpies of condensation for C_3H_8 (−14 kJ/mol) and C_3F_8 (−13.4 kJ/mol) were taken at 35 °C, the midpoint of the experimental temperature range.[40] The isosteric enthalpies of mixing in PTMSP were then calculated from eq 18 and are presented in Figure 7a as a function of penetrant concentration. Similar to PDMS, the enthalpy of mixing of C_3F_8 in PTMSP is generally more positive (i.e., endothermic) than that of C_3H_8 in PTMSP. However, unlike PDMS, the enthalpies of mixing of the two penetrants show opposite trends in PTMSP; the enthalpy of mixing C_3F_8 with PTMSP decreases with concentration while the enthalpy of mixing C_3H_8 with PTMSP increases with concentration.

The trend of the enthalpy of mixing of propane can be rationalized by considering the additional mode of sorption available in glassy polymers, i.e., the Langmuir microvoids. A glassy polymer such as PTMSP contains nonequilibrium microvoids (so-called Langmuir sites) dispersed throughout the equilibrium matrix. These microvoids represent sorption sites that, from an energetic perspective, are easily accessible to penetrant

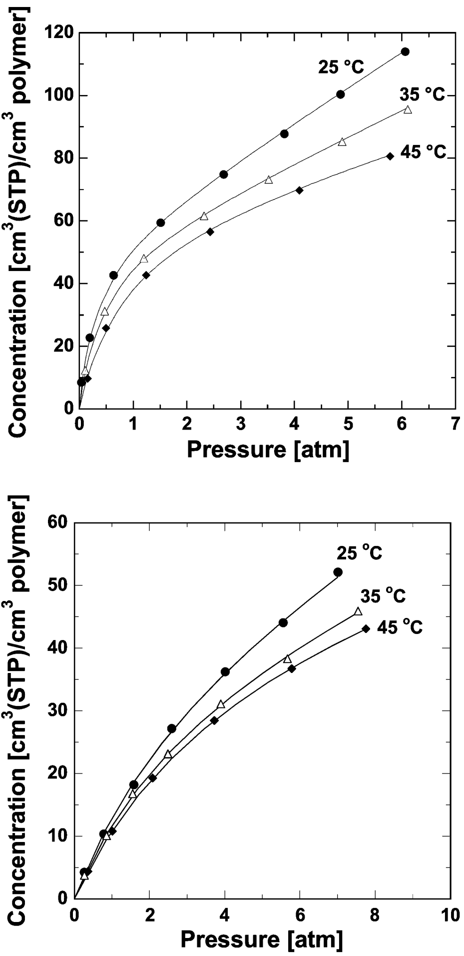

Figure 6. (a) C_3H_8 and (b) C_3F_8 sorption in PTMSP as a function of temperature.

molecules. At low penetrant concentrations, the microvoids are relatively unoccupied and can accommodate penetrant molecules with little or no distortion (i.e., swelling) of the polymer matrix. As penetrant concentration in the polymer increases, these sites become progressively more saturated, resulting in a larger fraction of the sorption occurring in the densified regions of the polymer (i.e., the so-called Henry's law region). Penetrant sorption in the Henry's law region is energetically more expensive than sorption in a Langmuir microvoid, since this process involves the creation of a gap large enough to accommodate the penetrant (i.e., the polymer swells[43]). Thus, the enthalpy of mixing increases with concentration. At high concentrations, it reaches a limiting value determined by the enthalpy of sorption of the penetrant in the densified matrix. A similar trend has been reported for CO_2 sorption in a high barrier, glassy polymer, poly(ethylene terephthalate).[44]

The concentration dependence of the enthalpy of mixing of perfluoropropane in PTMSP is similar to that in PDMS. This result suggests that the less favorable interactions between the fluorinated penetrant and the hydrocarbon matrix are more important than the dual-mode effects in determining sorption energetics.

An interesting example of mixing behavior that follows the same logic is displayed in Figure 7b for isosteric enthalpies of mixing C_3H_8 and C_3F_8 with a fluorinated copolymer of 87 mol % 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole and 13 mol % tetrafluoroethylene, called Teflon AF2400.[8] In this case, the penetrants encounter a fluorinated environment, and the concentration dependence of the enthalpies of mixing as well as their relative magnitudes reflect this fact. Propane has a less exothermic enthalpy of mixing, and ΔH_m decreases with concentration, both of which signify less favorable polymer–penetrant interactions. On the other hand, the concentration dependence of perfluoropropane's enthalpy of mixing suggests that Langmuir microvoid filling is the dominant factor affecting the energetics of the dissolution process.

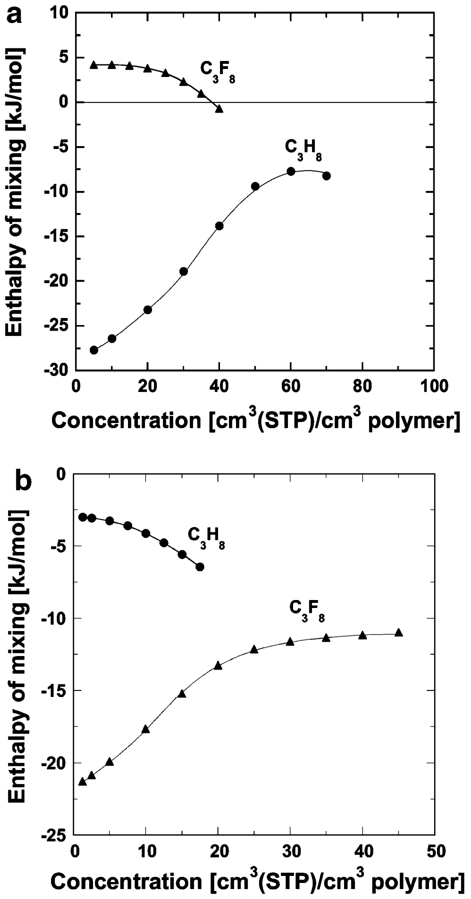

Figure 7. Isosteric enthalpies of mixing of C_3H_8 and C_3F_8 in (a) PTMSP and (b) Teflon AF2400.[8]

Permeability. *PDMS.* The permeabilities of PDMS to nitrogen and hydrogen in PDMS as a function of the pressure difference across the polymer film at 25, 35, 45, and 55 °C are shown in parts a and b of Figure 8, respectively. The permeabilities of both penetrants increase with increasing temperature at a given pressure, indicating a positive activation energy of permeation. This result is typical for the permeation of supercritical gases in PDMS. For example, Bixler and Sweeting[45] reported an E_P value for nitrogen in PDMS of 10.9 kJ/mol, which is similar to the value of 9.3 kJ/mol obtained from the data in Figure 8a.

Parts a and b of Figure 9 present the effect of temperature on the permeability of PDMS to propane and perfluoropropane, respectively, at an upstream pressure of 2.36 atm. The data can be fit to the Arrhenius equation (eq 12), and the activation energy of permeation, E_P, can be calculated. Since the permeability values are at a constant upstream pressure, the E_P value thus calculated is an isobaric (i.e., constant pressure) activation energy of permeation. In a similar

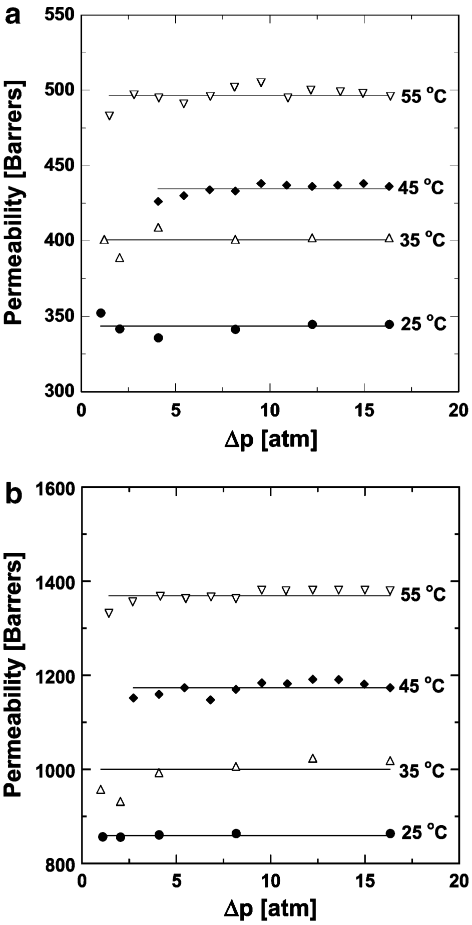

Figure 8. (a) N_2 and (b) H_2 permeation in PDMS as a function of temperature and pressure difference across the membrane. The downstream pressure is 1 atm.

Table 1. Activation Energies of Permeation and Diffusion, and Enthalpy of Sorption at 2.36 atm (i.e., Isobaric) for C_3H_8 and C_3F_8 in PDMS and PTMSP[a]

polymer	penetrant	E_P (kJ/mol)	ΔH_s^p (kJ/mol)	E_D (kJ/mol)
PDMS	C_3H_8	−13 ± 1.2	−20 ± 0.2	7 ± 1.2
	C_3F_8	3 ± 3	−13 ± 1.8	16 ± 3
PTMSP	C_3H_8	−8 ± 1.2	−9 ± 0.7	1 ± 1.4
	C_3F_8	7 ± 4.0	−7 ± 2.0	14 ± 4.5

[a] Note: E_P, ΔH_s, and E_D values have been calculated using eqs 12, 14, and 15, respectively.

fashion, isobaric enthalpies of sorption can be calculated for the two penetrants at a pressure of 2.36 atm, from eq 14 and the data in Figure 2a,b. The calculated values are presented in Table 1. The errors in the table have been calculated by the method of propagation of errors.[46] These E_P and ΔH_s^P values have been used to calculate E_D values according to eq 15. As indicated earlier, the use of eq 15 is subject to restrictions on the concentration or pressure dependence of the permeability, solubility, and diffusion coefficients. However, since the permeability data have been measured at a single pressure, it is not possible to evaluate the pressure (or concentration) dependence of the permeability coefficients. Therefore, the activation energy of diffusion has been calculated by assuming the validity of eq 15, as is practically always done in the literature.

Usually, the permeability of relatively condensable gases in PDMS decreases with increasing temperature (i.e., E_P is negative).[47] This is because, in weakly size sieving PDMS, the solubility of condensable gases decreases with increasing temperature more rapidly than diffusion coefficients increase (i.e., $|\Delta H_s| > E_D$). The propane data in PDMS are consistent with this trend. However, perfluoropropane displays markedly different behavior. Its permeability coefficient increases slightly with temperature, indicating a positive E_P value. From Table 1, the different effect of temperature on the permeation behavior of the C_3 analogues is related to differences in both the dissolution and diffusion of these penetrants. Larger penetrants require more energy to execute a diffusive jump in a polymer matrix than smaller penetrants.[48] In this regard, perfluoropropane is substantially larger than its hydrocarbon analogue. The critical volumes of C_3F_8 and C_3H_8 are 300 and 203 cm^3/mol, respectively. Consequently, the activation energy of diffusion is much larger for C_3F_8 (16 kJ/mol) than for C_3H_8 (7 kJ/mol). Additionally, a difference in polymer−penetrant interactions contributes to the difference in the temperature dependence of permeability of C_3F_8 and C_3H_8. From Table 1, the magnitude of the isobaric enthalpy of sorption is lower for C_3F_8 than for C_3H_8. The enthalpies of condensation for C_3F_8 and C_3H_8 are similar (−12.7 and −13.6 kJ/mol, respectively, at 40 °C[40]), so the mixing of propane with PDMS is more favorable than mixing perfluoropropane with PDMS. The combination of less favorable mixing and hindered diffusion causes C_3F_8 to have a substantially larger activation energy of permeation than C_3H_8 in PDMS.

PTMSP. Figure 10a,b presents N_2 and H_2 permeability in PTMSP as a function of temperature and pressure. For these penetrants, permeability coefficients decrease with increasing temperature, which is opposite to the behavior in PDMS. This temperature dependence of permeability is consistent with the high free volume and poor size-sieving ability of PTMSP.

Parts a and b of Figure 11 present Arrhenius plots of C_3H_8 and C_3F_8 permeability coefficients, respectively, in PTMSP at 2.36 atm. For C_3H_8, permeability increases as temperature decreases, which is qualitatively similar to the trend in PDMS. On the other hand, C_3F_8 permeability decreases as temperature decreases, and this is the first report of permeability coefficients decreasing with decreasing temperature in PTMSP. Isobaric activation energies of permeation for these penetrants are tabulated in Table 1 along with enthalpies of sorption and calculated activation energies of diffusion. Similar to PDMS, E_P for C_3F_8 in PTMSP is positive and opposite in sign to that of propane. This result reflects the larger size of perfluoropropane (larger E_D) and its less favorable interactions with PTMSP (larger ΔH_m and, therefore, more positive ΔH_s relative to propane). The relative contributions of these two effects to the difference in E_P between C_3H_8 and C_3F_8 in PTMSP are shown in Table 1. For PTMSP, the difference in C_3H_8 and C_3F_8 activation energies of permeation (15 kJ/mol) is mostly due to the large difference in E_D values (13 kJ/mol) with a small contribution from the ΔH_s difference (2 kJ/mol). Thus, for PTMSP, it is primarily the difference in penetrant size and the associated effect on the diffusion process that causes the dramatic difference in C_3 analogue transport properties. In contrast, in PDMS the difference in E_P values between C_3H_8 and C_3F_8 (16 kJ/mol) is due to nearly equal contributions from the difference in E_D (9 kJ/mol) and ΔH_s (7 kJ/mol). This result suggests that hydrocarbon−fluorocarbon interac-

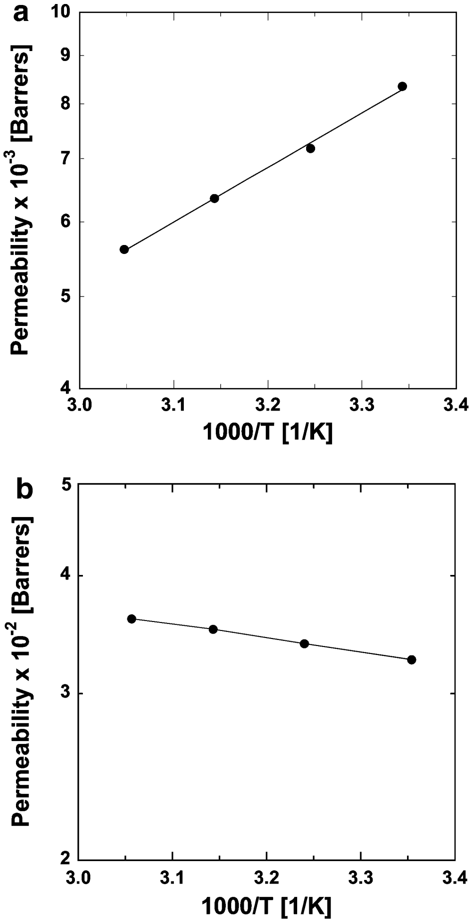

Figure 9. Effect of temperature on (a) C3H8 and (b) C3F8 permeation in PDMS at 2.36 atm upstream pressure and 1 atm downstream pressure.

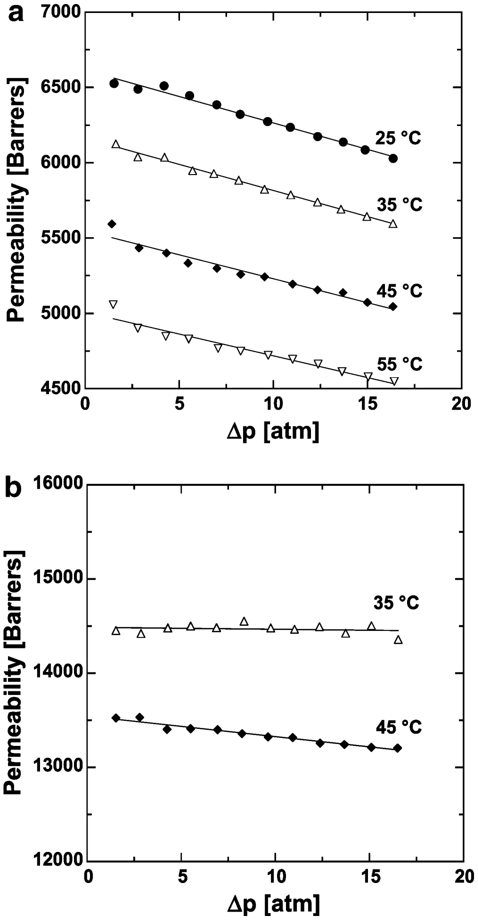

Figure 10. (a) N_2 and (b) H_2 permeation in PTMSP as a function of temperature and pressure difference across the membrane. The downstream pressure is 1 atm.

tions have a stronger effect on penetrant transport properties in liquidlike PDMS than in high free volume, glassy PTMSP.

The unusual nature of C_3F_8's positive activation energy of permeation in PTMSP is highlighted in Figure 12, which presents E_P values as a function of penetrant critical temperature for this polymer. The data of Masuda et al.[49] are included in Figure 12 for comparison. Excluding our data for C_3F_8, E_P values in PTMSP are negative for all penetrants and decrease (i.e., increase in absolute value) with increasing penetrant critical temperature. This behavior is consistent with a solubility selective polymer where E_P is significantly influenced by ΔH_s (because $|\Delta H_s| > E_D$) and where the enthalpy of sorption decreases with increasing penetrant condensability (T_c). The activation energy of permeation for C_3F_8 deviates substantially from the empirical trendline through the other penetrants. In fact, based on C_3F_8's critical temperature and the best fit line through the rest of the data, its expected E_P value would be −9.8 kJ/mol as compared to the measured value of 7 kJ/mol. As mentioned previously, this difference appears to be primarily due to C_3F_8's large size and its effect on the diffusion process.

It has been suggested[5,50] that PTMSP contains a network of quasi-permanent, interconnected free volume elements spanning the polymer through which the majority of penetrant transport occurs. Transport in these interconnected free volume elements may be similar to that in zeolites, where the critical penetrant diameter, or the smallest size window through which a given molecule can fit, governs the transport. Transport through such interconnected free volume elements should be an energetically inexpensive process compared to transport through the densified polymer matrix. The kinetic diameter of C_3F_8 (5.4 Å) is much larger than that of C_3H_8 (4.3 Å).[51] Thus, it is possible that C_3F_8 is larger than the critical free volume element diameter for transport in the interconnected free volume elements, which may restrict its access to this energetically inexpensive mode of transport.

Conclusions

C_3F_8 solubility is lower than that of its hydrocarbon analogue, C_3H_8, in both PDMS and PTMSP due to less favorable polymer−fluorocarbon interactions as indicated by a higher ΔH_m for the fluorocarbon as well as a decrease in ΔH_m with increasing penetrant concentration. Unlike PDMS, ΔH_m of C_3H_8 in PTMSP increases with penetrant concentration, which is due to the different energy requirements for dissolution in the two types of sorption sites present in a glassy polymer viz. the Langmuir sites and the Henry's law sites.

The activation energy of permeation for C_3F_8 is positive and opposite in sign to that of C_3H_8 in both polymers. This is the first report of a penetrant having a positive activation energy of permeation in PTMSP. In PDMS, the difference in E_P values between propane and perfluoropropane is due to the difference in penetrant sizes as well as the difference in polymer−penetrant interactions. For PTMSP, however, it is primarily the larger size of C_3F_8 and its associated effect

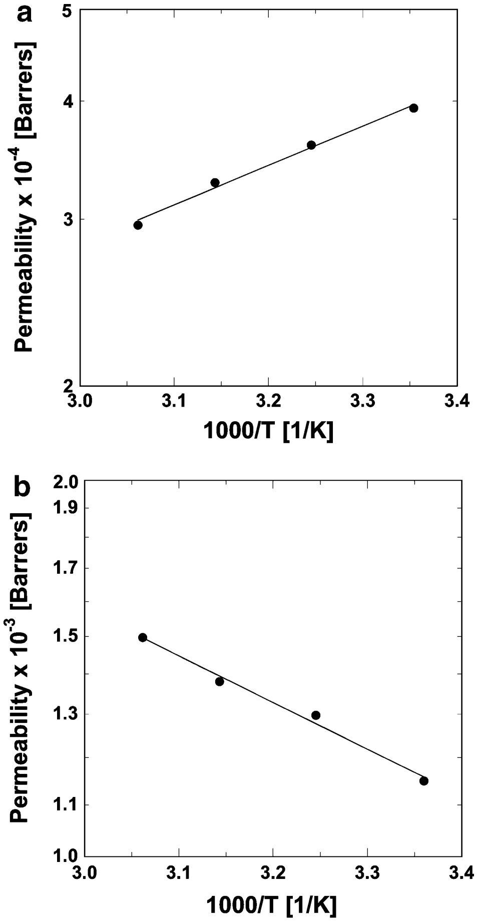

Figure 11. Effect of temperature on (a) C_3H_8 and (b) C_3F_8 permeation in PTMSP at 2.36 atm upstream pressure and 1 atm downstream pressure.

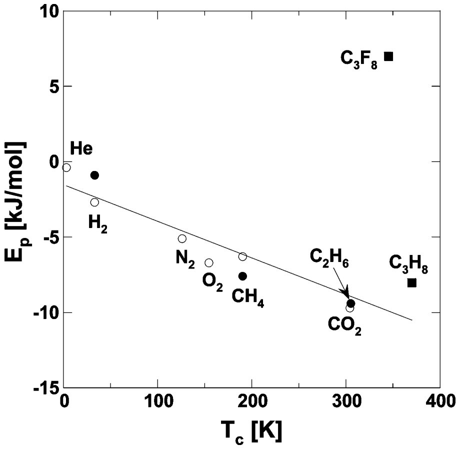

Figure 12. Activation energy of permeation of various penetrants in PTMSP: (●) data from Masuda et al.;[49] (○) unpublished data of T. C. Merkel and Z. He at Membrane Technology and Research, Inc. (Menlo Park, CA); (■) data of this study. The straight-line in the figure is the least-squares fit to the data for all the penetrants except C_3F_8 and is given by E_P [kJ/mol] = −1.52 − 0.024 × T_c [K].

on diffusion that is responsible for the difference in E_P values. Thus, polymer−penetrant interactions have more of an effect on gas transport properties in liquid-like PDMS than in high free volume, glassy PTMSP.

Acknowledgment. The authors gratefully acknowledge partial support of this study by the United States Department of Energy under Grant DE-FGO2-99ER14991. This research was also partially supported with funding from the United States Department of Energy's National Energy Technology Laboratory under a subcontract from Research Triangle Institute through their Prime Contract DE-AC26-99FT40675. The authors are also indebted to Zhenjie He for allowing us to utilize her data.

Appendix

The activation energy of permeation provides information about the temperature dependence of the permeability coefficient of a penetrant in a polymer. This parameter is usually determined from permeability data measured over a range of temperatures and at a fixed pressure. To assess the contributions of sorption and diffusion to the temperature dependence of the permeation process, the activation energy of permeation is compared with the enthalpy of sorption and the activation energy of diffusion. To make this comparison in a consistent manner, these parameters must also be determined from data at similar conditions of temperature and pressure. Specifically, for the enthalpy of sorption, gas solubility must be determined at the same fixed pressure as the permeability data and over the same range of temperatures. The enthalpy of sorption, thus determined, is an isobaric enthalpy. From eq 14

$$\Delta H_s^P = -R\left(\frac{\mathrm{d}\ln S}{\mathrm{d}(1/T)}\right)_p \tag{A1}$$

Using eq 4, eq A1 can be rewritten as

$$\Delta H_s^P = -R\left(\frac{\mathrm{d}\ln C}{\mathrm{d}(1/T)}\right)_p \tag{A2}$$

On the other hand, if the energetics of the sorption process are used to obtain information about differences in interactions of various gas molecules with the polymer matrix, it might be of interest to compare enthalpies of sorption at the same penetrant concentration in the polymer rather than at the same pressure in the gas phase surrounding the polymer. This enthalpy of sorption at constant concentration is the isosteric enthalpy of sorption, which is defined as

$$\Delta H_s^C = -R\left(\frac{\mathrm{d}\ln S}{d(1/T)}\right)_C = +R\left(\frac{\mathrm{d}\ln p}{\mathrm{d}(1/T)}\right)_C \tag{A3}$$

The isobaric and isosteric enthalpies of sorption defined by eqs A2 and A3, respectively, are related, and this relationship is derived below.

To maintain equilibrium between penetrant in a pure gas phase (α) and in a sorbed phase (β) as a result of a change in temperature and/or pressure, the change in penetrant chemical potential, μ, in both phases must be equal:[44]

$$\mathrm{d}\mu^{\alpha} = \mathrm{d}\mu^{\beta} \tag{A4}$$

Dividing by the absolute temperature T and expanding the resulting differentials for μ/T in the two phases gives[44]

$$\left(\frac{\partial\mu^{\alpha}/T}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial\mu^{\alpha}/T}{\partial p}\right)_T \mathrm{d}p = \left(\frac{\partial\mu^{\beta}/T}{\partial T}\right)_{P,C} \mathrm{d}T + \left(\frac{\partial\mu^{\beta}/T}{\partial p}\right)_{T,C} \mathrm{d}p + \left(\frac{\partial\mu^{\beta}/T}{\partial C}\right)_{P,T} \mathrm{d}C \tag{A5}$$

At constant concentration C, eq A5 simplifies to

$$\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_C = \frac{\left(\dfrac{\partial \mu^{\alpha}/T}{\partial T}\right)_P - \left(\dfrac{\partial \mu^{\beta}/T}{\partial T}\right)_{P,C}}{\left(\dfrac{\partial \mu^{\beta}/T}{\partial p}\right)_{T,C} - \left(\dfrac{\partial \mu^{\alpha}/T}{\partial p}\right)_T} \tag{A6}$$

Substituting for the various partial derivatives[44]

$$\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_C = \frac{-H^{\alpha} + H^{\beta}}{T(V^{\beta} - V^{\alpha})} \tag{A7}$$

where H^{β}, H^{α}, V^{β}, and V^{α} refer to the partial molar enthalpies and volumes in phases β and α, respectively. If phase α is a gas phase and phase β is the sorbed gas in a polymer in equilibrium with phase α, then typically $V^{\alpha} \gg V^{\beta}$. Substituting $(V^{\beta} - V^{\alpha}) \approx -zRT/p$ and rearranging[44]

$$\left(\frac{\mathrm{d}\ln p}{\mathrm{d}(1/T)}\right)_C = \frac{H^{\beta} - H^{\alpha}}{zR} \tag{A8}$$

Alternatively, at constant pressure, eq A5 simplifies to

$$\left(\frac{\mathrm{d}C}{\mathrm{d}T}\right)_p = \frac{H^{\beta} - H^{\alpha}}{T\left(\dfrac{\partial \mu^{\beta}}{\partial C}\right)_{P,T}} \tag{A9}$$

Now[39]

$$\mu^{\beta} = \mu_0^{\beta} + RT\ln a \tag{A10}$$

where a is the penetrant activity. Combining eqs A9 and A10 and rearranging

$$\left(\frac{\mathrm{d}\ln C}{d(1/T)}\right)_p = \frac{H^{\beta} - H^{\alpha}}{-R\left(\dfrac{\partial \ln a}{\partial \ln C}\right)_{P,T}} \tag{A11}$$

From eqs A2, A3, A8, and A11

$$\Delta H_{\mathrm{s}}^{C} = \frac{1}{z}\left(\frac{\partial \ln a}{\partial \ln C}\right)_{P,T}\Delta H_{\mathrm{s}}^{P} \tag{A12}$$

Equation A12 provides the relationship between the isobaric and isosteric enthalpies of sorption.

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MA048032K