Hydrocarbon and Fluorocarbon Solubility and Dilation in Poly(dimethylsiloxane): Comparison of Experimental Data with Predictions of the Sanchez–Lacombe Equation of State

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ABSTRACT: Sorption and dilation isotherms are reported for a series of gases (N_2, O_2, CO_2), hydrocarbon vapors (CH_4, C_2H_6, C_3H_8), and their fluorocarbon analogs (CF_4, C_2F_6, C_3F_8) in poly(dimethylsiloxane) (PDMS) at 35°C and pressures up to 27 atmospheres. The hydrocarbons are significantly more soluble in hydrocarbon-based PDMS than their fluorocarbon analogs. Infinite dilution partial molar volumes of both hydrocarbons and fluorocarbons in PDMS were similar to their partial molar volumes in other hydrocarbon polymers and in organic liquids. Except for C_2H_6 and C_3H_8, partial molar volume was independent of penetrant concentration. For these penetrants, partial molar volume increased with increasing concentration. The Sanchez–Lacombe equation of state is used to predict gas solubility and polymer dilation. If the Sanchez–Lacombe model is used with no adjustable parameters, solubility is always overpredicted. The extent of overprediction is more substantial for fluorocarbon penetrants than for hydrocarbons. Very good fits of the model to the experimental sorption and dilation data are obtained when the mixture interaction parameter is treated as an adjustable parameter. For the hydrocarbons, the interaction parameter is approximately 0.96, and for the fluorocarbons, it is approximately 0.87. These values suggest less favorable interactions between the hydrocarbon-based PDMS matrix and the fluorocarbon penetrants than between PDMS and hydrocarbons. © 1999 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 37: 3011–3026, 1999

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INTRODUCTION

The Sanchez–Lacombe (SL) lattice-fluid model[1–4] has been used previously to describe thermodynamic properties and predict gas solubility in poly(dimethylsiloxane), (PDMS). Using only pure polymer and pure penetrant pressure–volume–temperature data to determine the three model parameters characteristic of each component in the gas/polymer mixture, the solubility of the gas in the polymer can be calculated. Then, for each polymer/penetrant pair the model contains only one parameter, which characterizes interactions between the gas and polymer. This mixture interaction parameter can either be estimated *a priori,* using the first-order approximation based on the geometric mean rule, or determined by fitting the parameter to experimental gas sorption data. In the first case, gas sorption isotherms are calculated based only on pure polymer and gas properties, and this is the so-called zero-parameter

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model. In the second case, which we call the one-parameter model, the gas–polymer interaction parameter is empirically selected to provide the best fit of the model to the experimental data.

Pope et al.[5] compared experimental sorption isotherms for several light gases in PDMS to predictions by the SL model. Satisfactory agreement between experimental and calculated sorption isotherms was obtained with no adjustable parameter to characterize the gas–polymer mixture (zero-parameter model). Good agreement between measured and predicted values of partial molar volumes of the penetrants was also noted. Kiszka et al.[6] analyzed sorption and dilation behavior of many polymer–penetrant mixtures. They observed that the SL model could predict both sorption and dilation isotherms if the mixture interaction parameter was adjusted to give the best fit to the sorption isotherm. Sanchez and Rodgers[7] compared gas and vapor solubility in a large number of polymers with the zero-parameter prediction of the SL model. They concluded that gas solubilities could be quantitatively predicted for hydrocarbon and chlorinated hydrocarbon vapors in nonpolar polymers and for polar gases in polar polymers. The difference between predicted and experimentally measured solubility was substantially greater for polar penetrant sorption in nonpolar polymers and nonpolar penetrant sorption in polar polymers. Deviations between calculated and measured solubilities were systematic and of the same order of magnitude for a homologous series of penetrants, suggesting a correlation between the mixture interaction parameter and the chemical structures of the gas and polymer. Therefore, when the polymers and penetrants are chemically dissimilar, the geometric mean rule commonly used for the estimation of the mixture interaction parameter in the zero-parameter modeling is inaccurate.

In the present work, the sorption and dilation properties of two homologous series of penetrants, hydrocarbons and fluorocarbons, in PDMS are compared with predictions of the SL model. In addition to the fundamental interest in studying the sorption properties of fluorocarbon penetrants and their hydrocarbon analogs in polymers, a growing practical issue also motivated the choice of penetrants. Separation of organic vapors from permanent gases is emerging as an important commercial application of polymer membrane technology.[8,9] The recovery of greenhouse gases such as CF_4 and C_2F_6 from industrial semiconductor waste gas streams may become an environmentally important and economically viable application of membrane separation technology.[10] To evaluate membrane materials for this application, fundamental studies of sorption, diffusion, and transport of fluorinated penetrants in model polymers such as PDMS are required.

BACKGROUND

The Sanchez–Lacombe model treats polymer chains as a set of connected beads on a lattice and, like the Flory–Huggins model, polymer chains are mixed randomly with penetrant molecules.[4] However, unlike the Flory–Huggins model, the Sanchez–Lacombe model permits the presence of empty sites in the lattice, so that free volume exists in the polymer–penetrant mixture, and volume changes upon mixing penetrant and polymer molecules are allowed.[2] Each component of the mixture is completely characterized by three independent parameters.[11] (1) P_i^*, the characteristic pressure, which is the hypothetical cohesive energy density of component i in the close-packed state (liquid at 0 K), (2) ρ_i^*, which is the corresponding mass density in the close-packed state, and (3) the characteristic temperature T_i^*, which is related to the depth of the potential energy well. These three parameters can be determined from experimental PVT data of pure components. A dimensionless size parameter, r_i, also appears in the following equations, and it is defined as follows[4]:

$$r_i = \frac{P_i^* M_i}{R T_i^* \rho_i^*} \tag{1}$$

where R is the gas constant, and M_i is the molecular weight. Because r_i represents the number of lattice sites occupied by a molecule, it is usually set to infinity for the polymer. The SL model provides equations of state for both pure components and mixtures as well as chemical potential expressions for each species. The chemical potential of the pure penetrant in the gaseous state could alternatively be expressed by other models, possibly more appropriate for a noncondensed phase. For simplicity, we use the SL model both for gaseous and polymeric phases. The solubility of a gas in a polymer is determined, at fixed temperature and pressure, by satisfying the equation of state properties of the pure penetrant gas phase and the polymer–penetrant mixture [eqs.

(2) and (3) below], and by equating the chemical potential of penetrant in both the penetrant and polymer phases. In the following equations, variables with subscript 1 or 2 refer to the penetrant or the polymer, respectively.

$$\tilde{\rho}_1 = 1 - \exp\left[-\frac{\tilde{\rho}_1^2}{\tilde{T}_1} - \frac{\tilde{P}_1}{\tilde{T}_1} - \left(1 - \frac{1}{r_1^0}\right) \cdot \tilde{\rho}_1 \right] \qquad (2)$$

$$\tilde{\rho} = 1 - \exp\left[-\frac{\tilde{\rho}^2}{\tilde{T}} - \frac{\tilde{P}}{\tilde{T}} - \left(1 - \frac{\Phi_1}{r_1}\right) \cdot \tilde{\rho} \right] \qquad (3)$$

$$\left[-\frac{\tilde{\rho}_1}{\tilde{T}_1} + \frac{\tilde{P}_1}{\tilde{T}_1 \tilde{\rho}_1} + \frac{(1-\tilde{\rho}_1)\ln(1-\tilde{\rho}_1)}{\tilde{\rho}_1} + \frac{\ln \tilde{\rho}_1}{r_1^0} \right] \cdot r_1^0$$

$$= \ln \Phi_1 + (1 - \Phi_1) + \tilde{\rho} \cdot \frac{M_1}{\rho_1^*} \frac{\Delta P^*}{RT} \cdot (1 - \Phi_1)^2$$

$$+ \left[-\frac{\tilde{\rho}}{\tilde{T}_1} + \frac{\tilde{P}_1}{\tilde{T}_1 \cdot \tilde{\rho}} + \frac{(1-\tilde{\rho})\ln(1-\tilde{\rho})}{\tilde{\rho}} + \frac{\ln \tilde{\rho}}{r_1} \right] \cdot r_1 \qquad (4)$$

In the equations above, $\tilde{\rho}_1$, $\tilde{P}_1$, and $\tilde{T}_1$ are the reduced density, temperature, and pressure of the pure penetrant, and $\tilde{\rho}$, $\tilde{P}$, and $\tilde{T}$ are the corresponding variables for the mixture. Φ_1 is the close-packed volume fraction of gas in the polymer,[4] which is related to the mass fraction of the gas through eq. (5).[5] The parameters r_1^0 and r_1 are the number of lattice sites occupied by a gas molecule in the pure gas and in the mixture, respectively. Penetrant solubility is determined by solving eqs. (2), (3), and (4) simultaneously for the three variables $\tilde{\rho}_1$, $\tilde{\rho}$, and Φ_1; the equilibrium penetrant mass fraction in the polymer, ω_1, is then calculated as follows:

$$\omega_1 = \frac{\Phi_1}{\Phi_1 + (1 - \Phi_1) \cdot \dfrac{\rho_2^*}{\rho_1^*}} \qquad (5)$$

The reduced variables are related to the actual density, pressure and temperature by the following expressions

$$\tilde{\rho}_1 = \frac{\rho_1}{\rho_1^*} \qquad \tilde{P}_1 = \frac{P}{P_1^*} \qquad \tilde{T}_1 = \frac{T}{T_1^*} \qquad (6)$$

$$\tilde{\rho} = \frac{\rho}{\rho^*} \qquad \tilde{P} = \frac{P}{P^*} \qquad \tilde{T} = \frac{T}{T^*} \qquad (7)$$

where ρ_1 and ρ are the actual densities of the pure penetrant phase and of the mixture, respectively. P and T are the temperature and pressure of the two phases in equilibrium. The mixture parameters are given by the following previously established mixing rules[4,5]:

$$P^* = \Phi_1 P_1^* + \Phi_2 P_2^* - \Phi_1 \Phi_2 \Delta P^* \qquad (8)$$

$$T^* = \frac{P^*}{\dfrac{\Phi_1 P_1^*}{T_1^*} + \dfrac{\Phi_2 P_2^*}{T_2^*}} \qquad (9)$$

and

$$P^* v^* = RT^* \qquad (10)$$

where v^* is the close-packed volume of the mixture.

In eqs. (4) and (8), the parameter ΔP^* is representative of the mixture energetic interactions. Specifically, it is the net change in cohesive energy density upon mixing at 0 K[4]:

$$\Delta P^* = P_1^* + P_2^* - 2P_{12}^* \qquad (11)$$

If ΔP^* is positive, which is true for many gas–polymer mixtures, then gas–polymer (i.e., 1–2) interactions are energetically less favored than the average of the gas–gas (1–1) and polymer–polymer (2–2) interactions. P_{12}^* is characteristic of the mixture and, as a first approximation, P_{12}^* is often equated to the geometric mean of P_1^* and P_2^*.

At finite temperatures, the cohesive energy density in the SL model is nearly equal to $(\tilde{\rho}^2 P^*)$.[4] Thus, P^* is a measure of strength of intermolecular interactions in the polymer, penetrant, or polymer–penetrant mixture. Therefore, the geometric mean approximation used to estimate P_{12}^* is analogous to a similar approximation used to estimate interaction energy in regular solution theory,[12] and in the most common cubic equations of state (e.g., Soave–Redlich–Kwong and Peng–Robinson).[13] Indeed, the geometric mean for the energetic interaction parameter can be derived as a consequence of a frequently used approximate expression for the intermolecular potential.[14,15] The geometric mean was first introduced to model energetic interactions between two nonpolar molecules of different species, and it is obeyed when the ionization potentials of the two different molecules have similar values.[14]

Moreover, using this approximation, the value of ΔP^* can be estimated *a priori* without using any gas–polymer mixture data. This approximation forms the basis of the zero-parameter SL model. The physical basis of this assumption is discussed below, and is used later in the discussion of the energetics of interactions of various penetrants with PDMS. To account for deviations of the actual value of P^*_{12} from the geometric mean, an empirical mixing parameter, Ψ, is introduced[4]:

$$P^*_{12} = \Psi \sqrt{P^*_1 P^*_2} \tag{12}$$

The mixing parameter is a measure of the deviation of the cohesive energy density of the mixture from that given by the geometric mean rule. When $\Psi = 1$, P^*_{12} is the geometric mean of P^*_1 and P^*_2. In this case, ΔP^* values are positive [cf. eq. (11)], because the geometric mean of two real numbers is always less than the arithmetic mean.

The mixture interaction energy can be represented either by ΔP^* or by Ψ, because they are related through eqs. (11) and (12). The value of Ψ can, in principle, be determined from a single gas–polymer mixture data point, and it is taken by Sanchez and Lacombe to be independent of temperature and pressure.[2,4] Practically, however, Kiszka has found that significantly better fits of the SL model to experimental sorption isotherms are obtained if Ψ is allowed to vary with temperature.[6]

Studies of the solubility of mixtures of small molecule liquids provide some insight into the value of Ψ for gas–polymer systems. Hildebrand and Scott[12] suggested that the geometric mean rule, i.e., $\Psi = 1$, should be confined to mixtures whose components have equal hydrogen bond strength or, rather, equal interactions between molecules of the same species (1–1 or 2–2). Based on their studies, the experimental mixture interaction energy (and, therefore, solubility) is overestimated by the geometric mean rule for liquids that associate with themselves (i.e., 1–1 and/or 2–2 interactions are favored over 1–2 interactions), and underestimated when complexation between the components occurs (i.e., 1–2 interactions are favored over like molecule interactions). Another source of error inherent to the geometric mean rule is that ionization potentials sometimes have very different values. For example, Reed[16] reported that the ionization potentials of hydrocarbons and fluorocarbons differ greatly from one another, and that the geometric mean overestimates hydrocarbon–fluorocarbon interaction energy. These observations are consistent with prior experimental results that good predictions of gas solubility in polymers using the SL theory are obtained when the SL mixing parameter, Ψ, is set to unity in systems where both components of the mixture are chemically similar (e.g., both are nonpolar).[7] Poor predictions of penetrant solubility in polymers are obtained for mixtures that are chemically dissimilar (e.g., polar–nonpolar mixtures) unless the proper value of the mixing parameter is used.

EXPERIMENTAL

Materials

The polymer film used in this study was kindly prepared by Dr. Ingo Pinnau of Membrane Technology and Research, Inc. (Menlo Park, CA) using poly(dimethylsiloxane) supplied by Wacker Silicones Corp. (Adrian, MI). Crosslinking of the dense 250 μm-thick PDMS film was performed at 100°C using a proprietary crosslinker-catalyst system supplied by Wacker Silicones Corp. The density of the sample was 0.98 g/cm^3 at 35°C.[17] The crosslink density, 7.8×10^{-5} mol/cm^3, was estimated by measuring the amount of liquid cyclohexane sorbed by a dry PDMS film of known weight.[17]

Gas Sorption

Sorption measurements were performed using a high pressure barometric sorption apparatus.[18] The PDMS film was first exposed to a vacuum overnight to remove air gases, then penetrant gas was introduced into the chamber. Once the chamber pressure was constant and sorption equilibrium was attained, more penetrant was introduced and allowed to come to equilibrium. In this manner, penetrant uptake as a function of pressure was determined. Sorption equilibrium for all gases was reached within a few hours. After measuring each isotherm, polymer samples were degassed overnight. The experimental temperature was 35°C, and was controlled using a constant temperature water bath.

Dilation

Dilation measurements were conducted using equipment similar to that described by Fleming and Koros.[19] This device monitors one coordinate dimension of the sample during sorption and desorption. Because the dilation of silicone rubber is isotropic,[19] only elongation of the sample was measured. The sample was a strip of polymer 106 mm long. It was placed in a Jerguson gauge (model 23-TL-10), and it was unconstrained in its ability to elongate. The sample was suspended in the gauge, and the length of the sample was monitored using a Cohu CCD camera that stored digital images of the sample on a computer as a function of time. More details regarding the digital image capture and analysis protocols are reported by McDowell et al.[20] Length change was calculated by measuring the distance of the end of the sample from a fixed reference rod. This apparatus permits measurements of length changes to within ±0.02%. After evacuating the sample chamber for 24 h, the gas pressure was increased in regular steps and the equilibrium length of the sample was recorded. The temperature was maintained at 35°C using a water circulator bath with an accuracy of ±0.05°C.

RESULTS AND DISCUSSION

Evaluation of Polymer Parameters

Typically, SL equation of state parameters are determined by a least-squares regression of the SL model to experimental values of polymer density as a function of pressure and temperature.[21] Often, a single set of parameters cannot accurately describe experimental pressure–volume–temperature PVT data over wide ranges of temperature and pressure. For example, Pottiger and Laurence[22] found that two sets of polymer parameters, one determined at low pressures, and the other determined at high pressures, gave significantly better fits to experimental PVT data in those pressure ranges than a single set of parameters determined by a best fit over the entire pressure range. Hariharan et al.[23] observed substantial variations in the values of the SL parameters for PDMS as a function of temperature and pressure.[23]

As the solubility values calculated using the SL model are rather sensitive to the values of the polymer parameters,[23] it is important to choose a set of parameters that accurately describes the pure polymer volumetric properties. When a comparison between experimental and predicted data is required at a specific temperature and over a narrow range of pressure, the most appropriate choice of polymer parameters is the set that provides the best description of the experimental PVT data of the polymer over the range of temperature and pressure of interest. For PDMS, we use PVT data from the compilation of Zoller and Walsh.[24] As the polymer used in our present study is crosslinked, experimental PVT data for a high molecular weight sample ($M_w = 1.5 \times 10^6$ g/mol) were selected. However, experimental data for samples of lower molecular weight also gave essentially the same parameter values as those used in this study.

Table I. Lattice Fluid Parameters for the Sanchez–Lacombe Model for PDMS

Set	Ref.	P^* (MPa)	T^* (K)	ρ^* (kg/L)
A	23	292.5	498	1.0805
B	23	295.2	506	1.0835
C	4	301.9	476	1.104
D	5	354.6	560	1.2

A list of previously reported SL parameters for PDMS is displayed in Table I. Sets A and B were obtained from the same experimental PVT data, but over different ranges of pressure.[23] Set D in Table I, which is significantly different from the other sets, was determined using the experimental density, isothermal compressibility, and thermal expansion coefficient at a single temperature (308 K).[5] Set A in Table I ($P^* = 292.5$ MPa, $T^* = 498$ K, $\rho^* = 1.0805$ kg/L) yields the most accurate prediction of the experimental polymer density within the range of temperatures and pressures (300–400 K, 0–1000 atm) encompassing our sorption and dilation data ($T = 308$ K, $P = 0$–30 atm). A comparison between the SL model of polymer specific volume using parameter set A and experimental data is presented in Figure 1. The SL model predictions of polymer specific volume are within less than ±1% of the experimental values over the range of pressure and temperature corresponding to our sorption and dilation experiments. Also, the predicted density of the polymer at ambient pressure and 35°C (0.95 g/cm^3) is similar to the experimental value (0.98 g/cm^3) of the sample used in this study. This figure also shows that the specific volume predicted by parameter set D in Table I is significantly lower than the experimental data. Moreover, the density at 35°C and ambient pressure predicted by parameter set D is 1.1 g/cm^3, which

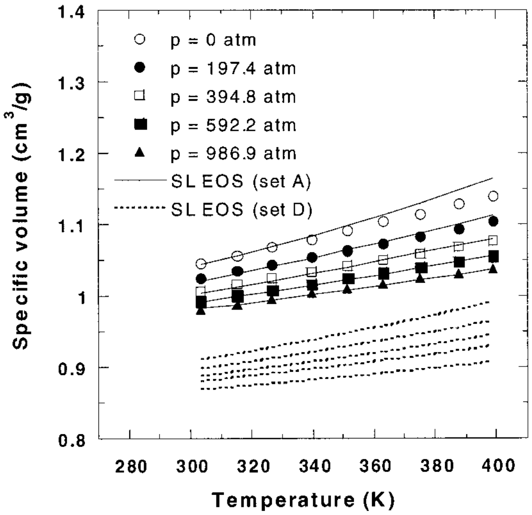

Figure 1. Comparison of Sanchez–Lacombe equation prediction of specific volume of poly(dimethylsiloxane) with experimental data. The SL parameters used are: $P^* = 292.5$ MPa, $T^* = 498$ K, $\rho^* = 1.0805$ kg/L (set A in Table I) for the solid line; $P^* = 354.6$ MPa, $T^* = 560$ K, $\rho^* = 1.2$ kg/L (set D in Table I) for the dashed line.

is significantly higher than the experimentally determined density for the sample used in this study.

Evaluation of Penetrant Parameters

The SL model parameters for the penetrants used in this study have been determined through least-squares fits of the model to experimental PVT data.[25–27] For light gases, such as N_2, O_2, CO_2, and CH_4, the SL parameters were determined by fitting the model to experimental gas densities as a function of temperature at various pressures. The experimental data were taken from the work of Vargaftik.[28] For propane, the parameters were determined by fitting the model to vapor pressure and saturated liquid densities as a function of temperature from the experimental data given by Vargaftik.[28] For ethane and the fluorinated gases, the parameters were determined from the best fit of the model to experimental values of vapor pressure and saturated liquid density as a function of temperature, from the experimental data by Daubert and Danner.[29] The SL parameters for all penetrants are listed in Table II.

Sorption and Dilation Isotherms for Light Gases (N_2, O_2, CO_2)

Experimental sorption isotherms of oxygen, nitrogen, and carbon dioxide in PDMS at 35°C are presented in Figure 2. Penetrant in the polymer is C. The corresponding dilation isotherms are presented in Figure 3, where ΔV is the absolute change in polymer volume during sorption, and V_0 is the volume of penetrant-free polymer at the same temperature and pressure. For both O_2 and N_2, the dilation and sorption isotherms are linear functions of pressure. For CO_2, the sorption and dilation isotherms are slightly convex to the pressure axis, consistent with previous reports of CO_2 sorption and dilation in PDMS.[5] A comparison with previously published values of Henry's law coefficients (i.e., infinite dilution solubility coefficients) for N_2, CO_2, and CH_4 in PDMS is shown in Table III. Our experimental values are in good agreement with previously reported values.

The lines in Figures 2 and 3 represent SL model predictions of sorption and dilation behavior, respectively. For the sorption isotherms with Ψ equal to unity (dashed lines in Fig. 2), the SL model systematically overestimated solubility. The deviations were more than 100% for N_2 and

Table II. Lattice Fluid Parameters for the Sanchez–Lacombe Model for Penetrants

Penetrant	P^* (MPa)	T^* (K)	ρ^* (kg/L)	Ref.	Source of PVT Data
N_2	160	145	0.943	25	Vargaftik (1983)[28]
O_2	214	180	1.250	26	Vargaftik (1983)[28]
CO_2	630	300	1.515	27	Vargaftik (1983)[28]
CH_4	250	215	0.500	25	Vargaftik (1983)[28]
C_2H_6	330	320	0.640	26	Daubert and Danner (1989)[29]
C_3H_8	320	375	0.690	26	Vargaftik (1983)[28]
CF_4	265	230	1.920	26	Daubert and Danner (1989)[29]
C_2F_6	227	296	1.950	26	Daubert and Danner (1989)[29]
C_3F_8	225	335	2.050	This work	Daubert and Danner (1989)[29]

O_2, while the CO_2 sorption isotherm prediction was more satisfactory (maximum error of 13% with $\Psi = 1$). This overestimation in penetrant concentration when $\Psi = 1$ is observed for all penetrants in this study. For the CO_2–PDMS mixture, these results diverge from those obtained by Pope et al.[5] As shown in Table III, they found the sorption levels to be underestimated by the zero-parameter model. Our results are more consistent with those of Kiszka[6] for the CO_2–PDMS system. For the N_2–PDMS system, there is a large difference between the calculated sorption levels in this study and those of Pope et al.[5] These discrepancies are mainly due to differences in the SL parameters for PDMS. The calculated sorption levels are very sensitive to the values of these parameters.[23] As previously mentioned, the parameters used by Pope (set D) are quite different from those used in this study and from other sets taken from the literature. Therefore, one should expect differences in the resulting calculated sorption isotherms. We used parameter set A from Table I rather than set D because set A provides a much better fit to the experimental PVT data than set D, as indicated in Figure 1. Table III shows that rather good Henry's law coefficients can be obtained by using parameter set A in Table I and treating Ψ as an adjustable parameter; it is also shown that, by using parameter set D, one can obtain acceptable estimates of the Henry's law coefficients, albeit not as good as in the former case. However, the reasonable fit of the sorption data by the SL model obtained by Pope et al. is generated using pure polymer parameters that give polymer density values that are inconsistent with our experimental density. This comparison demonstrates the challenge faced in determining the "best" set of pure component parameters to use for gas solubility predictions.

The solid lines in Figures 2 and 3 were calculated by adjusting the mixture interaction parameter, Ψ, to give the best fit to the sorption isotherm. Then, using this optimized value of the interaction parameter, the dilation isotherm was predicted as follows:

$$\frac{\Delta V}{V_0} = \frac{1}{\tilde{\rho}\rho^*(1-\omega_1)\hat{v}_2^0} - 1 \qquad (13)$$

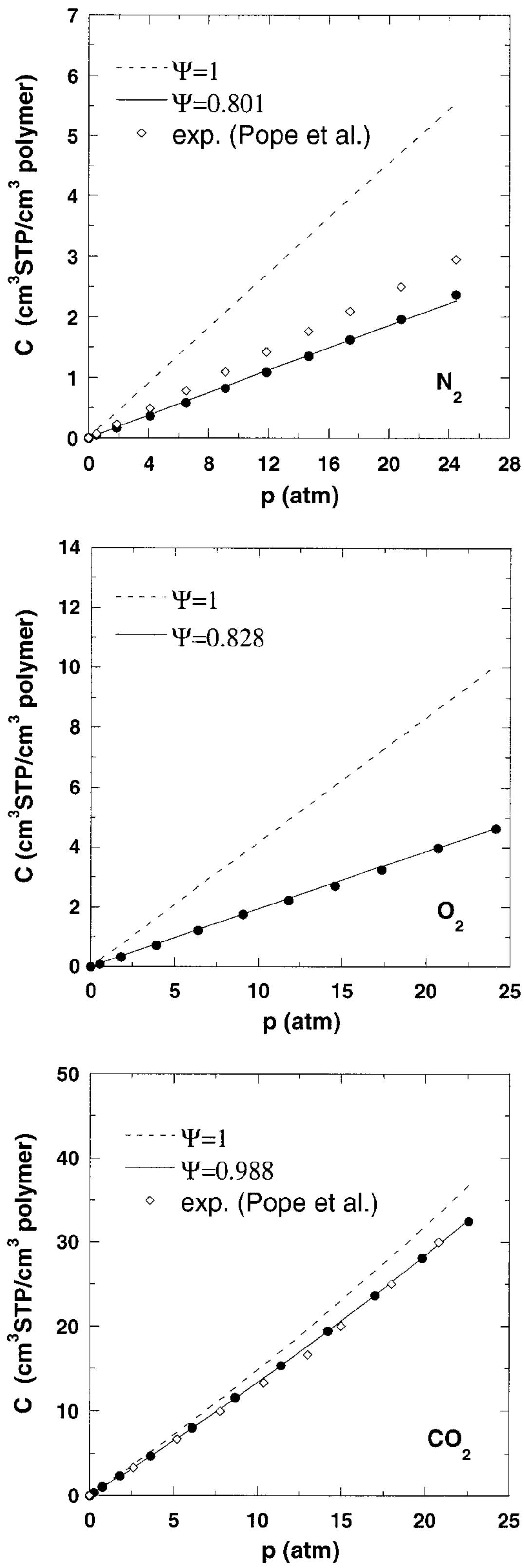

Figure 2. Comparison of experimental and predicted sorption isotherms of (a) N_2, (b) O_2, and (c) CO_2 in PDMS using the SL model with $\Psi = 1$ (dashed line) and Ψ adjusted (solid line). Experimental data by Pope et al.[5] for the N_2–PDMS and the CO_2–PDMS systems are also shown.

where $\tilde{\rho}$ and ρ^* are the mixture reduced and characteristic density, respectively, at a fixed temperature, pressure, and composition; $\hat{v}_2^0$ is the specific volume of the pure polymer at the same temperature and pressure. For each penetrant, when Ψ is adjusted, there is excellent agreement between the model and experimental sorption and dilation isotherms. Ψ is always less than 1, which indicates that the interaction energy of a gas molecule–polymer segment pair is less than the value predicted by the geometric mean rule.

Sorption Isotherms of Hydrocarbons and Their Fluorocarbon Analogs

Figures 4, 5, and 6 present predicted and experimental sorption isotherms for hydrocarbons and fluorocarbons. At all pressures, the concentration of hydrocarbon is substantially greater than that of the analogous fluorocarbon. At a given pressure, the concentration of gas dissolved in the polymer increases with increasing carbon number. The zero-parameter SL model prediction of sorption, shown as the dashed lines in these figures, is systematically higher than the observed sorption level. For example, the average deviation, calculated as the relative difference between predicted and experimental gas concentration averaged over all pressures, is 35% for CH_4 and approximately 200% for CF_4 [cf. Fig. 4(a) and 4(b)]. At 15 atm, the sorption level of CH_4 predicted by the zero-parameter model is 8.5 cm^3 (STP)/cm^3 and for CF_4 it is somewhat higher, 9.2 cm^3 (STP)/cm^3. In contrast, the experimental values of methane and perfluoromethane concentration at 15 atm are 6.2 and 2.7 cm^3 (STP)/cm^3, respectively. Thus, the experimental sorption levels are lower than those predicted by the model, and the observed order of penetrant sorption (CH_4 concentration > CF_4 concentration) is incorrectly predicted by the zero-parameter model. As shown in Figures 5 and 6, the situation is similar for the other fluorocarbon/hydrocarbon pairs. In the case of C_2H_6/C_2F_6 and C_3H_8/C_3F_8, the model correctly predicts that the hydrocarbon solubility is higher than that of the analogous fluorocarbon, but it dramatically overpredicts the sorption level of fluorocarbon while only moderately overpre-

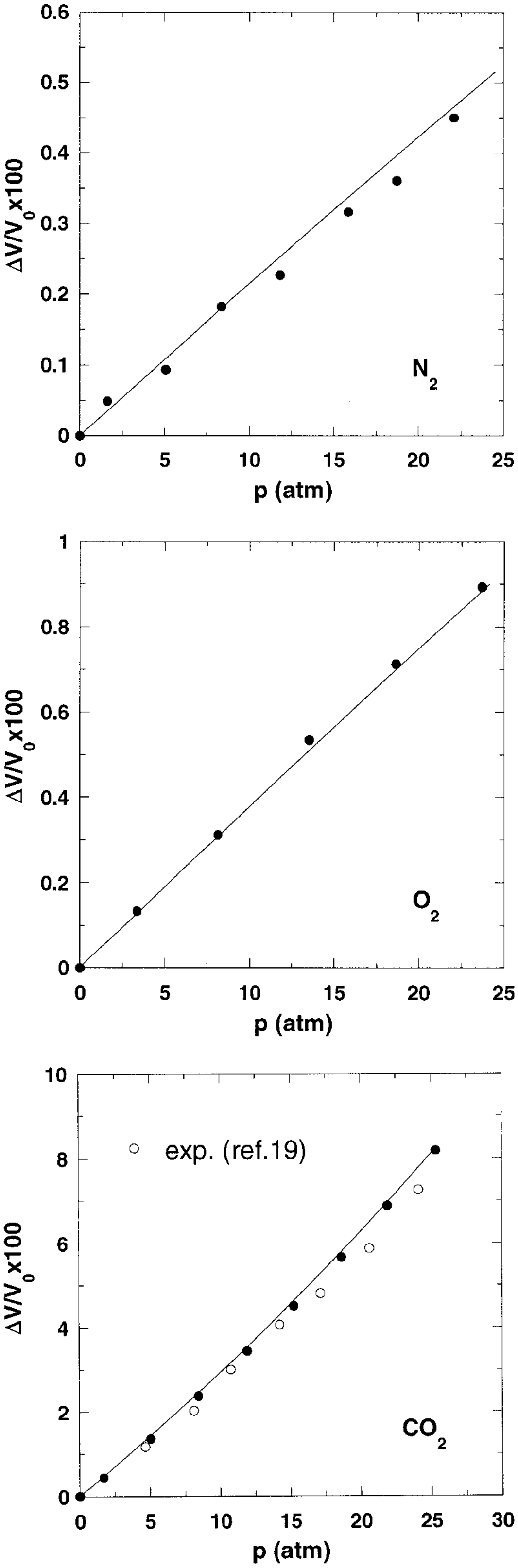

Figure 3. Comparison of experimental data to predicted dilation isotherm of PDMS in the presence of (a) N_2, (b) O_2, and (c) CO_2. Predicted values are calculated using SL Model with the best fit value of Ψ. Experimental data by Fleming and Koros[19] for the CO_2–PDMS systems are also shown.

Table III. Comparison of Experimental Henry's Law Constant Values in PDMS for Light Gases

	Henry's Law Constant, Experimental $cm^3(STP)/(cm^3\ atm)$		Henry's Law Constant, Calculated $cm^3(STP)/(cm^3\ atm)$	
Penetrant	This Study	Pope et al.[5]	This Study[a]	Pope et al.[5] [b]
N_2	0.094	0.120	0.093	0.088
CO_2 [c]	1.30	1.28	1.24	0.98
CH_4	0.43	0.43	0.43	0.33

[a] Parameter set A in Table I plus adjustable Ψ.
[b] Parameter set D in Table I with $\Psi = 1$.
[c] Infinite dilution.

dicting the hydrocarbon sorption level. As shown by the solid lines in Figures 4, 5, and 6, the experimental sorption levels are accurately represented when Ψ is treated as an adjustable parameter. The best values for the interaction parameters are recorded in Table IV. The mixture interaction parameters are systematically smaller for the fluorocarbons, suggesting stronger (i.e., more unfavorable) deviations from the geometric mean rule for fluorocarbons than for hydrocarbons in PDMS. Because the interaction parameter is related to the cohesive energy of the mixture, lower values of this parameter indicate less favorable interactions between the fluorocarbon penetrants and the PDMS matrix than between the hydrocarbons and the PDMS matrix. This result is consistent with the systematically lower sorption level of fluorocarbons in PDMS.

For hydrocarbon–PDMS mixtures, the zero-parameter model predictions of solubility are similar in magnitude to the measured solubility values, so gas–polymer interactions are very close to the estimates offered by the geometric mean approximation. In this case, the deviations in gas–polymer interactions that are not described by the geometric mean approximation for the gas–polymer interaction energy play a secondary role. For these mixtures, the binary interaction parameter is adjusted to refine the prediction of solubility.

The situation is quite different for the fluorocarbon–PDMS systems. In these cases, the zero-parameter model yields a large overestimation of fluorocarbons solubility in PDMS. Thus, the gas–polymer interaction energy is not well represented by the geometric mean, and cannot be obtained from the pure component parameters alone; indeed, in the present case, a proper value of the parameter Ψ is required. This behavior resembles that obtained by Sanchez and Rodgers[7] for polar–nonpolar mixtures, while, on the contrary, the hydrocarbons solubility in PDMS follows the trends observed by the same authors for nonpolar–nonpolar components, for which solubility can be quantitatively predicted by the zero-parameter model. That is, the large overestimation of fluorocarbon solubility in PDMS by the zero-parameter model is qualitatively similar to the overestimation of polar penetrant solubility in nonpolar polymers and the overestimation of alkane solubility in polar polymers reported by Sanchez and Rodgers.[7] Because PDMS is a nonpolar polymer and both hydrocarbons and fluorocarbons are nonpolar, the reason for the weaker interactions of fluorocarbons with PDMS relative to hydrocarbons is not related to the presence of polar forces. The reason for the higher solubility of the hydrocarbons in PDMS and the more accurate predictions by the SL model is likely related to similarities between the molecular structure of the hydrocarbons and the repeat unit of PDMS. These findings confirm and extend the result obtained by Sanchez and Rodgers that the geometric mean approximation provides a satisfactory description of the binary energy interactions when the gas–polymer pairs have chemically similar structures.

Dilation Isotherms of Hydrocarbons and Their Fluorocarbon Analogs

Dilation isotherms are presented in Figures 7, 8, and 9 for the hydrocarbons and fluorocarbons. The dilation of PDMS by fluorocarbons is less than the dilation by hydrocarbons at all pressures, consistent with the substantially lower solubility of the fluorocarbons in PDMS. The amount of dilation at a given pressure increases with increasing carbon number, consistent with the in-

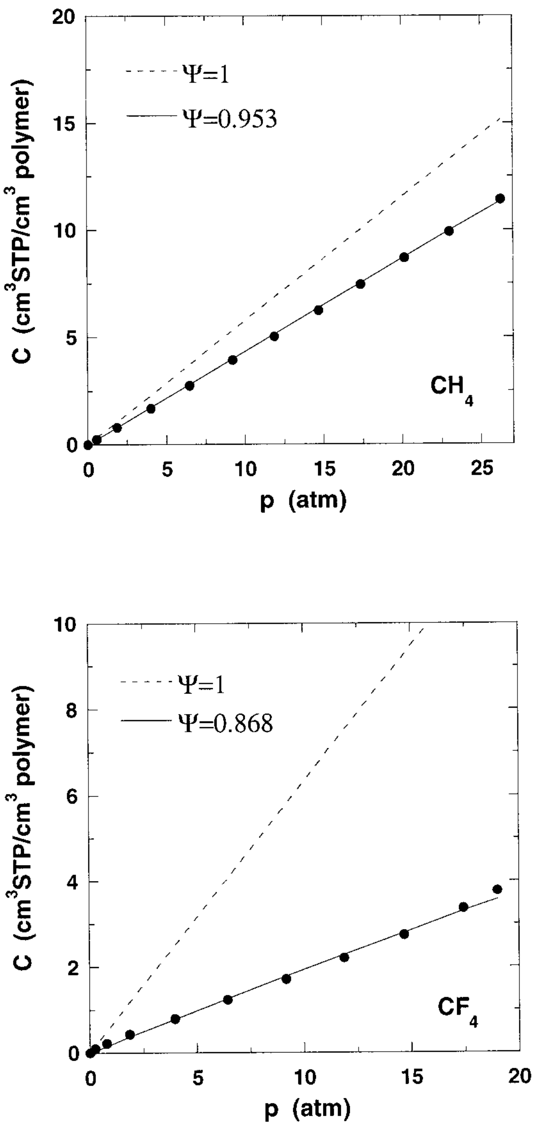

Figure 4. Comparison of experimental and predicted sorption isotherms of (a) CH_4 and (b) CF_4 in PDMS using the SL model with $\Psi = 1$ (dashed line) and Ψ adjusted (solid line, cf. Table IV).

crease in penetrant concentration at a fixed pressure with increasing carbon number. The solid lines in these figures represent predictions of the SL equation using values of Ψ (cf. Table IV) that best fit the solubility isotherm. For CF_4 and CH_4, the SL prediction of dilation is in very good agreement with the experimental data. For C_2H_6, C_2F_6, C_3H_8, and C_3F_8, the experimentally measured dilation is smaller than the calculated swelling. The difference between calculated and measured swelling increases at higher pressures. The deviation of the calculated dilation values from the experimental data is approximately 20% at 25 atm for C_2H_6 and is somewhat larger, 35%, for C_2F_6. The difference between the calculated swelling of PDMS in the presence of C_3H_8 and the experimental value is about 11% at 5.8 atm and approximately 38% for C_3F_8 at 6.3 atm. The results of the comparison between predicted and measured dilation isotherms suggest that the deviation between the experimental and predicted dilation level increases with the molecular size. The reason for these deviations is not well understood.

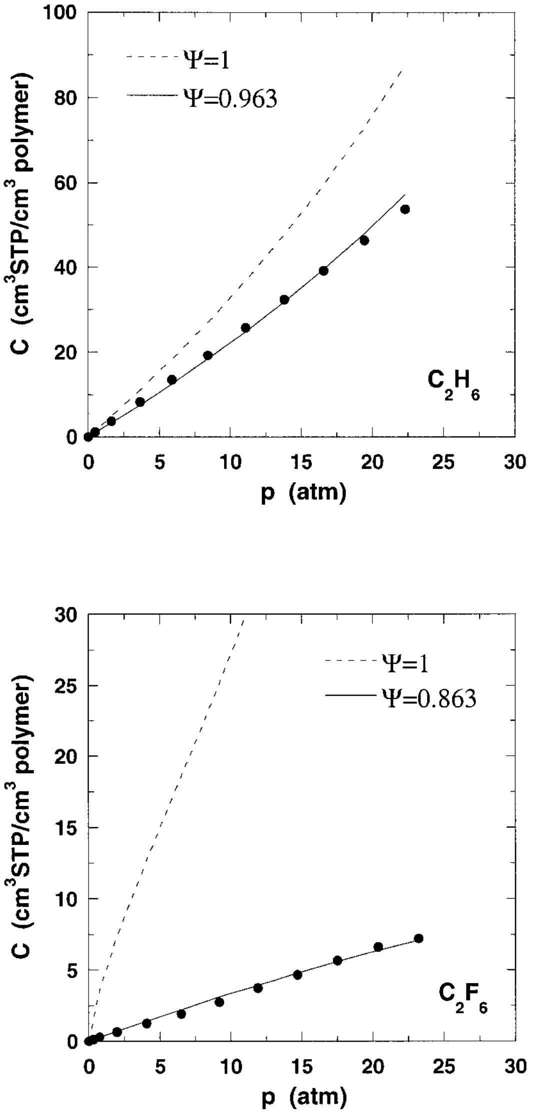

Figure 5. Comparison of experimental and predicted sorption isotherms of (a) C_2H_6 and (b) C_2F_6 in PDMS using the SL model with $\Psi = 1$ (dashed line) and Ψ adjusted (solid line, cf. Table IV).

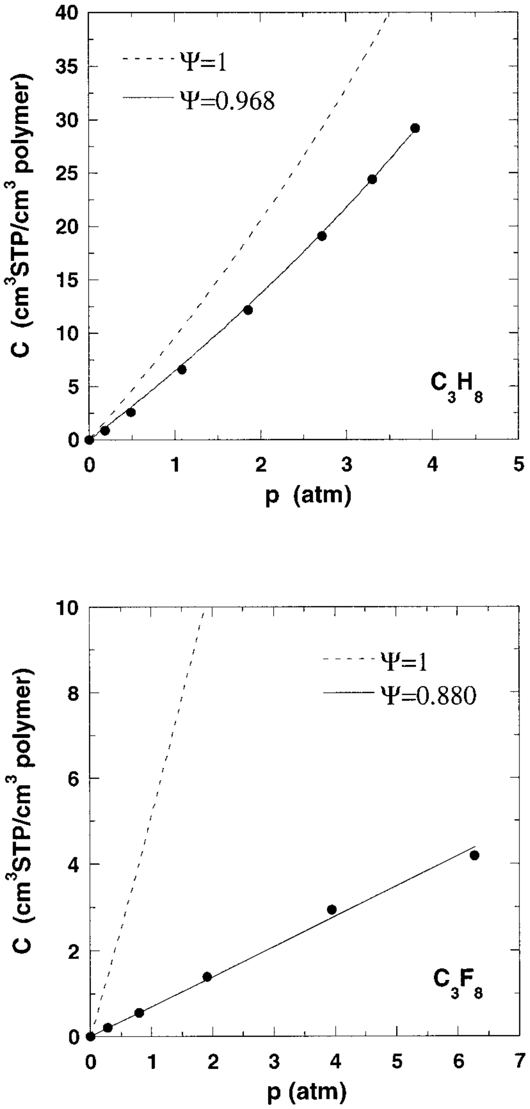

Figure 6. Comparison of experimental and predicted sorption isotherms of (a) C_3H_8 and (b) C_3F_8 in PDMS using the SL model with $\Psi = 1$ (dashed line) and Ψ adjusted (solid line, cf. Table IV).

Partial Molar Volumes

The experimental sorption and dilation data can be combined to determine the partial molar volumes for penetrants in silicone rubber. The partial molar volume of a component in a mixture is defined by[14]:

$$\bar{v}_i \equiv \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{14}$$

where n_i is the number of moles of component i in the mixture, and V is the total mixture volume. For a gas–polymer mixture, the partial molar volume of the penetrant can be given by[30]:

$$\bar{v}_i = v_{\mathrm{STP}}\left[\frac{d}{dP}\left(\frac{\Delta V}{V_0}\right) + \beta\right]\frac{dP}{dC} \tag{15}$$

where v_{STP} is the molar volume of an ideal gas at standard temperature and pressure ($v_{\mathrm{STP}} = 22414$ cm^3/mol), V_0 is the volume of the pure polymer at the temperature of the experiment, and β is the isothermal compressibility of the mixture, which is defined as follows[14]:

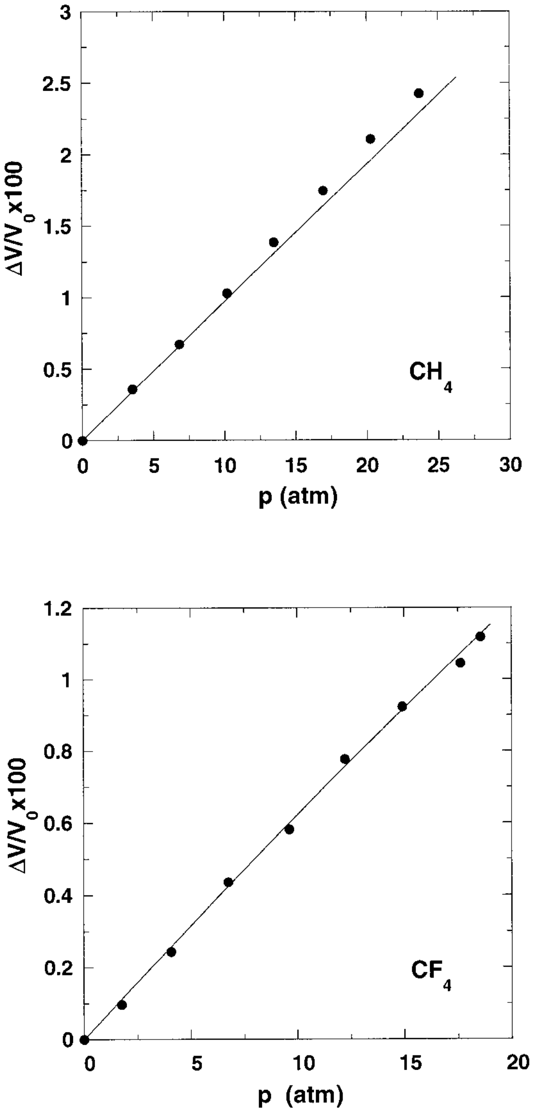

Figure 7. Comparison of experimental data to predicted dilation isotherm of PDMS in the presence of (a) CH_4 and (b) CF_4. Predicted values are calculated using SL model with the best fit value of Ψ (cf. Table IV).

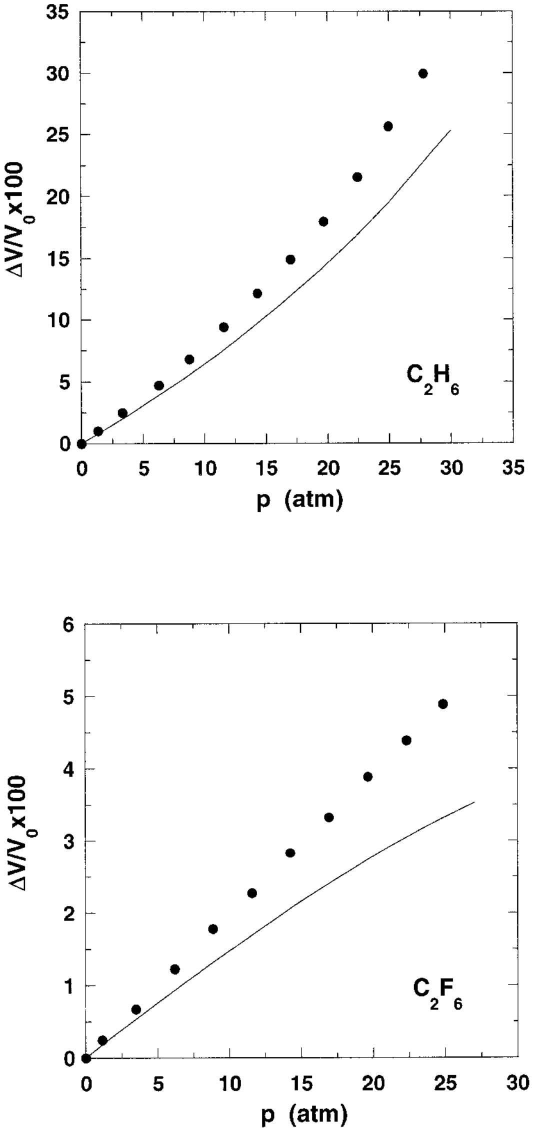

Figure 8. Comparison of experimental data to predicted dilation isotherm of PDMS in the presence of (a) C_2H_6 and (b) C_2F_6. Predicted values are calculated using SL model with the best fit value of Ψ (cf. Table IV).

$$\beta \equiv -\frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_{T,n_1,n_2} \tag{16}$$

The isothermal compressibility of PDMS is obtained from the volumetric data reported by Zoller and Walsh.[24] At 35°C, β is 1.0×10^{-4} atm^{-1} for PDMS with a molecular weight (M_w) of 1.5×10^6 g/mol, and is practically independent of M_w. As indicated in eq. (15), from the measured dilation and solubility data and from the above compressibility value, one may calculate partial molar volume. These values are reported in Table V at infinite dilution. Similar to previous reports,[31] the polymer compressibility term usually introduces a negligible contribution to eq. (15) for more soluble gases and vapors (e.g., CO_2, C_2H_6, C_3H_8, etc.). For the less soluble light gases (e.g., O_2, N_2, and CF_4), the compressibility term represents a more significant contribution to the calculated partial molar volume value.

For the penetrants considered in this study, the partial molar volume values were, in most cases, essentially independent of concentration,

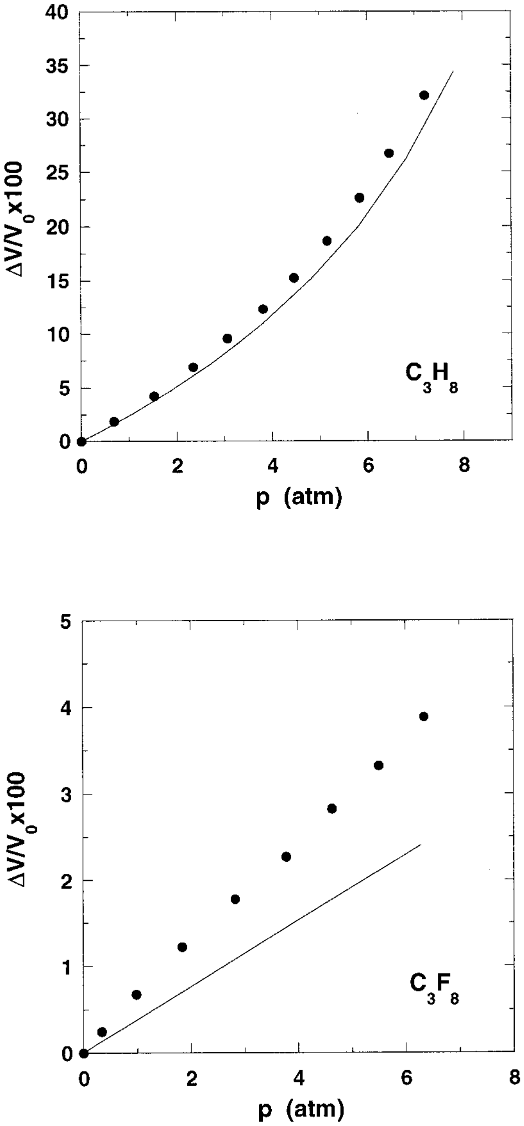

Figure 9. Comparison of experimental data to predicted dilation isotherm of PDMS in the presence of (a) C_3H_8 and (b) C_3F_8. Predicted values are calculated using SL model with the best fit value of Ψ (cf. Table IV).

Table IV. Values of Ψ Adjusted on Solubility for Penetrant–PDMS Mixtures

Penetrant	Ψ	Penetrant	Ψ	Penetrant	Ψ
N_2	0.801	CH_4	0.953	CF_4	0.868
O_2	0.828	C_2H_6	0.963	C_2F_6	0.862
CO_2	0.987	C_3H_8	0.968	C_3F_8	0.880

i.e., the behavior is consistent with volume additivity in the mixture. For ethane and propane, however, an appreciable concentration dependence is observed as shown in Figure 10, so that for these penetrants, volume additivity does not hold. Based on the data presented in Table V, the light gas and hydrocarbon partial molar volumes are similar to values for these penetrants measured in other PDMS samples (either liquid or crosslinked rubber), in polybutadiene, and in other hydrocarbon-based organic liquids.[32] This result suggests that the environment into which the penetrants dissolve in PDMS is rather similar to the environment experienced by the penetrants when they dissolve in other hydrocarbon-based polymers and organic liquids. This result also underscores the similarity between penetrant dissolution in rubbery polymers such as PDMS and penetrant dissolution in liquids.

Generally, larger penetrants have higher partial molar volumes. This trend is demonstrated in Figure 11, where the hydrocarbon and fluorocarbon partial molar volume data from Table V for our PDMS sample are presented as a function of van der Waals volume, a convenient measure of penetrant size. Consistent with the results of Kamiya et al.,[32] the partial molar volume of both hydrocarbons and fluorocarbons increase with increasing penetrant size. Similarly, the molar volumes of pure liquid hydrocarbon and fluorocarbon penetrants at 20°C and 1 atmosphere total pressure increase linearly with van der Waals volume. Extrapolation of these pure component data to sizes consistent with those of the penetrants considered in this study suggests that the partial molar volume values of the penetrants in PDMS are consistent with the corresponding pure liquid molar volumes. This result suggests a strong similarity in the mechanism of penetrant dissolution in polymers and in liquids. Our hydrocarbon partial molar volume data in PDMS are very similar to the values reported by Kamiya et al.[32] for polybutadiene and poly(ethyl-

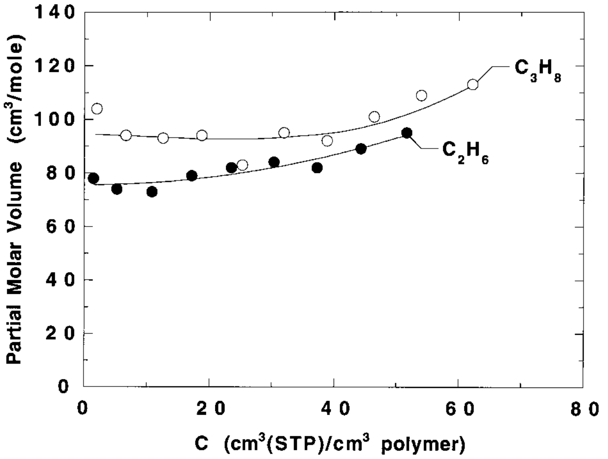

Figure 10. Partial molar volumes of ethane and propane in PDMS, at 35°C, as a function of concentration.

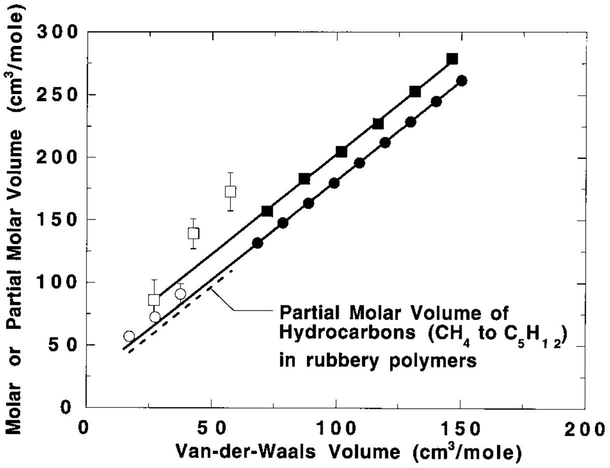

Figure 11. Effect of penetrant size on partial molar volumes in PDMS and molar volumes of pure liquid linear hydrocarbons and perfluorocarbons. Infinite dilution partial molar volumes of hydrocarbons (○) and perfluorocarbons (□) in PDMS at 35°C are compared with the molar volumes (at 1 atmosphere and 20°C) of hydrocarbons (●)[39] and fluorocarbons (■).[39] The infinite dilution partial molar volumes at 25°C of CH_4 to C_5H_{12} in polybutadiene and poly(ethylene-*co*-vinyl acetate) reported by Kamiya et al.[32] are represented by the dashed line. Van der Waals volumes were estimated using the group contribution method reported in Van Krevelen.[38]

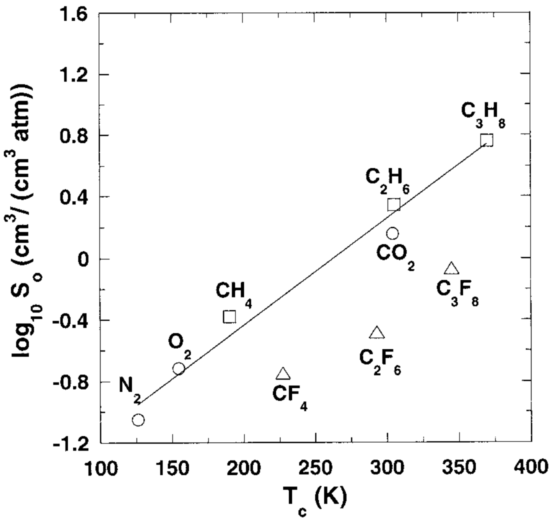

Figure 12. Experimental infinite dilution solubility coefficients, S_0, as a function of penetrant critical temperature, T_c.

ene-*co*-vinyl acetate) at 25°C. The line for the fluorocarbons lies above that for the hydrocarbons; that is, at the same equivalent van der Waals volume, the molar volume or partial molar volume values for the fluorocarbons are higher than those of the hydrocarbons. One finds a single correlation for each family of components (hydrocarbons or fluorocarbons). The correlation lines do not coincide, suggesting differences in condensed phase volumes of hydrocarbons and fluorocarbons that are not simply related to molecular size as characterized by Van der Waals volume.

Infinite Dilution Solubility Coefficients Prediction

The infinite dilution solubility coefficient, S_0, is defined by:

$$S_0 = \lim_{P \to 0} \left(\frac{C}{P} \right) \tag{17}$$

Figure 12 presents experimental infinite dilution solubility coefficients as a function of penetrant critical temperature, T_c, a common measure of penetrant condensability.[33] Based on the data in this figure, penetrant solubility generally increases as critical temperature increases. This trend is commonly observed in both glassy and rubbery polymers.[34] A model of penetrant solubility in amorphous polymers, developed from classical thermodynamics, predicts a linear relationship between the logarithm of gas solubility and critical temperature when strong polymer–penetrant interactions are absent.[35,36] For a variety of liquids, rubbery polymers, and glassy polymers the slope of a plot of $\log_{10}(S)$ vs. T_c is 0.0074 K^{-1}.[37,38] For our data, the slope of the best fit line of $\log_{10}(S)$ vs. T_c is 0.0069 ± 0.0005 K^{-1} when the fluorocarbons are not included in the regression, and 0.0058 ± 0.0010 K^{-1} when they are included. Within the limits of uncertainty of the measurements, the slope obtained when only hydrocarbon and light gas penetrants are considered is in agreement with the literature value. Figure 12 clearly shows that the solubility of the fluorocarbon penetrants is low relative to their critical temperatures and the solubility of the other penetrants. Indeed, penetrant condensability alone does not account for differences in the energetic interactions between the polymer matrix and different families of penetrants. Therefore, it is not surprising to observe that for hydrocarbons, which interact more favorably with the PDMS matrix, the solubility coefficient at any T_c is higher than for the corresponding fluorocarbons, which interact less favorably with the polymer. The observed differences for the solubility–condensability relationship of hydrocarbons and fluorocarbons further support the conclusion that specific energetic interactions between penetrant and polymer must be taken properly into account to accurately predict solubility when the penetrants and polymer are chemically dissimilar.

Effect of Penetrant Properties on Polymer–Penetrant Interaction Parameter, Ψ

The best-fit values of the interaction parameters determined from the sorption isotherms are recorded in Table V. The interaction parameter is nearly constant for each homologous series of penetrants in PDMS. For the hydrocarbons, it is approximately 0.962, and for fluorocarbons, the average value is 0.870, which is substantially lower. Similar values of Ψ imply similar deviations of P^*_{12} from $(P^*_1 P^*_2)^{1/2}$. The binary interaction parameter influences the characteristic pressure of the mixture, P^*. For pure alkanes, for example, in a fixed volume there are almost the same number of —CH_2— units. The characteristic pressures of alkanes, as calculated by Sanchez and Rodgers,[7] from propane to undecane, are very similar. Their values fall within the range of 308 ± 5% MPa, and they appear to approach a constant asymptotic value as carbon number in-

Table V. Infinite Dilution Partial Molar Volumes of Penetrants[a]

Penetrant ⇒	N_2	O_2	CO_2	CH_4	C_2H_6	C_3H_8	CF_4	C_2F_6	C_3F_8
PDMS, this study[b]	64	48	48	57	73	91	86	139	173
PDMS, liquid[32]	56	53	48	51	59				
PDMS, rubber[32]	51	39	43	41	56				
Polybutadiene[32]	45	47	44	44	57				
Other media[32] [c]	55	48	53	46	67				
Cyclohexane[12]							86	108	140

[a] Partial molar volume values are in cm^3/mol at 25°C, with the exception of the values in PDMS reported in this study, which are at 35°C.

[b] Partial molar volumes estimated using eq. (15).

[c] Averaged values for five organic liquids.

creases. In this regard, Sanchez and Lacombe[4] suggested that, for a homologous series of fluids, T^* and P^* are expected to be constant. For alkanes, for example, each —CH_2— unit contributes a nearly constant amount to the total molecular interaction energy and to the molecular close-packed volume. Therefore, their ratio, which is P^*, is nearly constant for all alkanes. If different penetrants, belonging to the same series, are characterized by similar energetic interactions in the pure state, they are expected to undergo similar interactions with a polymer.

CONCLUSIONS

The sorption and dilation properties of a series of light gases, hydrocarbons, and fluorocarbons in PDMS have been determined at 35°C and pressures up to 27 atmospheres. Based on these results, the sorption of hydrocarbons is markedly higher than that of the analogous fluorocarbons, and sorption levels increase in both hydrocarbons and fluorocarbons as carbon number increases. Consistent with the sorption data, the dilation of PDMS by fluorocarbons was much less than the dilation resulting from contacting PDMS with hydrocarbon penetrants, even though the fluorocarbons are substantially larger than their hydrocarbon analogs. The fluorocarbons exhibit a partial molar volume that is larger than the corresponding hydrocarbon analogs. These composite results suggest less favorable interactions between fluorocarbons and the PDMS matrix than between hydrocarbons and the PDMS matrix.

The ability of the Sanchez–Lacombe model to describe these experimental results was also evaluated. With no adjustable parameters, the SL model consistently overpredicts sorption levels of all penetrants. When the mixture interaction parameter, Ψ, is adjusted based on a fit to the sorption isotherms, excellent agreement between the model and the experimental sorption data is observed. Moreover, using these fitted mixture interaction parameters in the model resulted in excellent predictions of dilation isotherms for all penetrants except the higher hydrocarbons here considered (ethane and propane) and their fluorinated analogs, where swelling is moderately underestimated. Values of the mixture interaction parameter, required to obtain accurate estimates of gas solubility in PDMS, were approximately 0.962 for the hydrocarbon penetrants and 0.870 for the fluorocarbons, and were approximately independent of carbon number. The lower values of the interaction parameters in the fluorocarbons signal weaker or less energetically favorable interactions between the fluorocarbons and the PDMS matrix than between the hydrocarbons and PDMS.

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