

Equation of State Predictions of Sorption Isotherms in Polymeric Materials

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SYNOPSIS

The ability of the Sanchez–Lacombe equation of state to predict the solubility of small penetrants in rubbery polymer matrices, over a wide range of ambient pressures, is examined critically. The solute chemical potential and, in turn, the resulting predicted isotherms are found to depend strongly on solute equation of state parameter values and on the mixing parameter for polymer–penetrant interactions. The isotherms are less sensitive to polymer equation of state parameters. In the sorption of organic vapors into polymers, the model does not describe well the sorption isotherms at high values of penetrant activity. The model appears to describe sorption isotherms most accurately when both polymer and penetrant equation of state parameters are determined from pure component properties, in the same temperature and pressure range as the sorption data, and when a mixing parameter is used to adjust the fit of the model to the data. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The Sanchez–Lacombe (SL) lattice–fluid model^{1,2} has been used to describe the properties of low molecular weight pure fluids,² mixtures of low molecular weight fluids,¹ pure polymers in the liquid state,³ polymer solutions,⁴ and gas–polymer mixtures.⁵ Pope et al.⁶ compared measured absorption isotherms for several gaseous penetrants in silicon rubber to predictions by the SL model. Pope et al.⁶ concluded that the model well described the sorption isotherms of these gases in silicone rubber, using only pure component parameter values, that is, without recourse to experimental sorption data. The same conclusion was reached by Sanchez and Rodgers,⁷ after calculations of sorption isotherms of hydrocarbons and chlorinated hydrocarbons into non-polar polymers were performed. After judiciously selecting pure penetrant parameters and fitting one mixture interaction parameter, Kiszka et al.⁸ concluded that this model was capable of describing quantitatively gas sorption into rubbery polymers. These compelling results, suggesting that gas sorp-

tion isotherms might be predicted accurately *a priori*, using the Sanchez–Lacombe model, have stimulated the present study, which is directed towards exploring the sensitivity of calculated sorption isotherms to the mixture interaction parameter and to pure polymer and penetrant parameters. The resultant sorption isotherms, calculated using the SL model, are found to be sensitive to the values of the penetrant parameters and to the value of the mixture interaction parameter.

THEORY

In the Sanchez–Lacombe model, polymer chains are treated as a connected set of interacting beads on a lattice. The so-called “Van der Waals” interaction potential, which assumes that the potential energy of interaction scales as the inverse of the volume, is used to describe interactions between components on neighboring lattice sites.⁹ Like the Flory–Huggins model, the Sanchez–Lacombe model assumes that polymer chains and penetrant molecules mix together randomly on a lattice (the so-called mean field approximation). Unlike the Flory–Huggins model, the Sanchez–Lacombe model permits some

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lattice sites to be empty, which allows holes or free volume in the fluid. The addition of free volume to the lattice permits, for example, volume changes upon mixing the polymer and penetrant.¹

Each component of the mixture is characterized by three independent parameters:⁵

1. P_i^* , the characteristic pressure, which is the hypothetical cohesive energy density of component i in the close packed state.
2. T_i^* The characteristic temperature, which is proportional to the potential energy well depth, associated with component i .
3. ρ_i^* The characteristic density, which is the hypothetical mass density of component i at closest packing.

Within these parameters, $i = 1$ corresponds to the penetrant and $i = 2$ corresponds to the polymer. As described in more detail below, these parameters may be determined from pure component experimental PVT data.⁶ A dimensionless size parameter, r_1 , which corresponds to the number of lattice sites occupied by a penetrant molecule, is related to the other three parameters and the molecular weight M_1 of pure penetrant by⁴

$$r_1 = \frac{P_1^* M_1}{RT_1^* \rho_1^*} \quad (1)$$

where R is the gas constant. For polymers, r_2 is typically set to infinity and does not, therefore, appear in the chemical potential or equation of state expressions.

The SL model provides equations of state and chemical potential expressions for both pure components and mixtures. The amount of penetrant gas sorbed into a polymer is determined by equating the chemical potential of the penetrant in both the penetrant and polymer phases and by satisfying the equation of state properties of the pure penetrant phase and the polymer-penetrant mixture. As in osmotic equilibrium, the solute (polymer) does not partition into the contiguous pure solvent (penetrant) phase and, consequently, no polymer chemical potential equilibration constraint is applied. At fixed temperature and pressure, these conditions are met by solving the following three nonlinear algebraic equations for $\tilde{\rho}_1$: the reduced density of the pure penetrant in contact with the polymer, $\tilde{\rho}$, the reduced density of the polymer-penetrant mixture, and Φ_1 , the close-packed volume fraction of gas in the polymer,⁴

1. Equation of state for pure penetrant in penetrant phase:

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

2. Equation of state for penetrant-polymer mixture:

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

3. Equilibration of penetrant chemical potential between the pure penetrant phase and the penetrant-polymer mixture:

$$\begin{aligned} & \left[-\frac{\tilde{\rho}_1}{\tilde{T}_1} + \frac{\tilde{P}_1}{\tilde{T}_1 \tilde{\rho}_1} + \frac{(1 - \tilde{\rho}_1) \ln(1 - \tilde{\rho}_1)}{\tilde{\rho}_1} \right. \\ & \left. + \frac{\ln \tilde{\rho}_1}{r_1} \right] r_1 = \ln \Phi_1 + 1 - \Phi_1 + \tilde{\rho} \frac{M_1}{\rho_1^*} \\ & \times \chi(1 - \Phi_1)^2 + \left[-\frac{\tilde{\rho}}{\tilde{T}_1} + \frac{\tilde{P}_1}{\tilde{T}_1 \tilde{\rho}} \right. \\ & \left. + \frac{(1 - \tilde{\rho}) \ln(1 - \tilde{\rho})}{\tilde{\rho}} + \frac{\ln \tilde{\rho}}{r_1} \right] r_1 \quad (4) \end{aligned}$$

In eq. (4), the parameter χ is given by

$$\chi = \frac{\Delta P^*}{RT} \quad (5)$$

where

$$\Delta P^* = P_1^* + P_2^* - 2P_{12}^* \quad (6)$$

The parameter P_{12}^* is related to the pure component reduced pressures, P_1^* and P_2^* , through the relationship,

$$P_{12}^* = \psi \sqrt{P_1^* P_2^*} \quad (7)$$

The mixing parameter, ψ , is a measure of the deviation of the mixture from the empirical geometric mean combination rule, and is commonly assumed to be unity when the mixture components are non-polar.^{6,7} The calculated sorption isotherms are found to be sensitive to ψ , so a judicious choice of this parameter is a critical step in predicting isotherms.

The reduced variables are related to the actual

density, pressure, and temperatures by the expressions

$$\tilde{\rho}_1 \equiv \rho_1/\rho_1^* \quad (8)$$

$$\tilde{\rho} \equiv \rho/\rho^* \quad (9)$$

$$\tilde{P}_1 \equiv P/P_1^* \quad (10)$$

$$\tilde{P} \equiv P/P^* \quad (11)$$

$$\tilde{T}_1 \equiv T/T_1^* \quad (12)$$

$$\tilde{T} \equiv T/T^* \quad (13)$$

The mixture parameters are obtained using the following, previously established mixing rules⁶

$$P^* = \Phi_1 P_1^* + \Phi_2 P_2^* - \Phi_1 \Phi_2 \Delta P^* \quad (14)$$

and

$$T^* = \frac{P^*}{\frac{\Phi_1 P_1^*}{T_1^*} + \frac{\Phi_2 P_2^*}{T_2^*}} \quad (15)$$

The weight fraction of penetrant in the polymer, ω_1 , may be calculated⁶ from the close packed volume fraction of penetrant in the polymer, Φ_1

$$\omega_1 = \frac{\Phi_1}{\Phi_1 + (1 - \Phi_1) \frac{\rho_2^*}{\rho_1}} \quad (16)$$

and the concentration of gas in the polymer, C (cc STP/cc polymer), may be calculated from

$$C = \frac{\omega_1}{1 - \omega_1} \frac{\rho_2^0}{M_1} V_{id} \quad (17)$$

where ρ_2^0 is the penetrant-free polymer density, M_1 is the penetrant molecular weight, and V_{id} is the ideal gas molar volume at standard temperature and pressure (i.e., 22,414 cm³/mol).

RESULTS AND DISCUSSION

Evaluation of Polymer Parameters

Sanchez and Lacombe,³ Pottiger and Laurence,¹⁰ Dee and Walsh,⁹ and Zoller¹¹ have fit the SL model to experimental density data for several polymers. Pottiger and Laurence found that two sets of polymer parameters, one determined at low pressures,

0–20 MPa, and the other determined at high pressures, 170–200 MPa, yielded significantly better fits to the experimental data in those pressure ranges than the fit obtained when average parameters were determined using data from the entire pressure range. The other investigators provided average values for the polymer parameters which best fit the polymer density data over a wide range of pressures and temperatures.

Figure 1 (a) presents a comparison of the best fit of the Sanchez–Lacombe model, using constant values of the pure polymer parameters ($P_2^* = 2980$ atm, $T_2^* = 476$ K, and $\rho_2^* = 1.104$ g/cm³) obtained from Sanchez and Lacombe,³ to the specific volume of poly(dimethylsiloxane) (PDMS) at 29°C and 60°C. The specific volume at ambient pressure is determined from the experimental data reported by Lichtenthaler et al.¹² and the change in specific volume with pressure is from the experimental data of Kubota and Ogino.¹³ Using constant parameters, the SL model was found to describe the experimental polymer specific volume data within 1.2% over wide ranges of temperature and pressure.³

In Figure 1 (a), the ability of the empirical Tait equation to describe the experimental data is also presented. The Tait equation is given by:

$$V(P, T) = [A_0 + A_1 T + A_2 T^2] \times \left\{ 1 - C \ln \left[1 + \frac{P}{B_0 \exp(-B_1 T)} \right] \right\} \quad (18)$$

where V is the specific volume at a specified temperature T and pressure P . The Tait equation parameters in Figure 1 are for a sample of PDMS, of a number average molecular weight of 7860, from Zoller:¹⁴ $B_0 = 88.5$ MPa, $B_1 = 6.1 \times 10^{-3} \times ^\circ\text{C}^{-1}$, $C = 0.089$, $A_0 = 1.006$ cm³/g, $A_1 = 0.9931 \times 10^{-3}$ cm³/g \times $^\circ\text{C}$, and $A_2 = -0.078 \times 10^{-6}$ cm³/g \times $^\circ\text{C}^2$.

When the SL parameters are treated as constants over a wide pressure range, the SL equation of state predictions of the pressure dependence of other polymer thermodynamic properties, such as the isothermal compressibility, α ,

$$\alpha \equiv \left(\frac{\partial \ln V}{\partial T} \right)_P \quad (19)$$

and the thermal expansion coefficient, β ,

$$\beta \equiv - \left(\frac{\partial \ln V}{\partial P} \right)_T \quad (20)$$

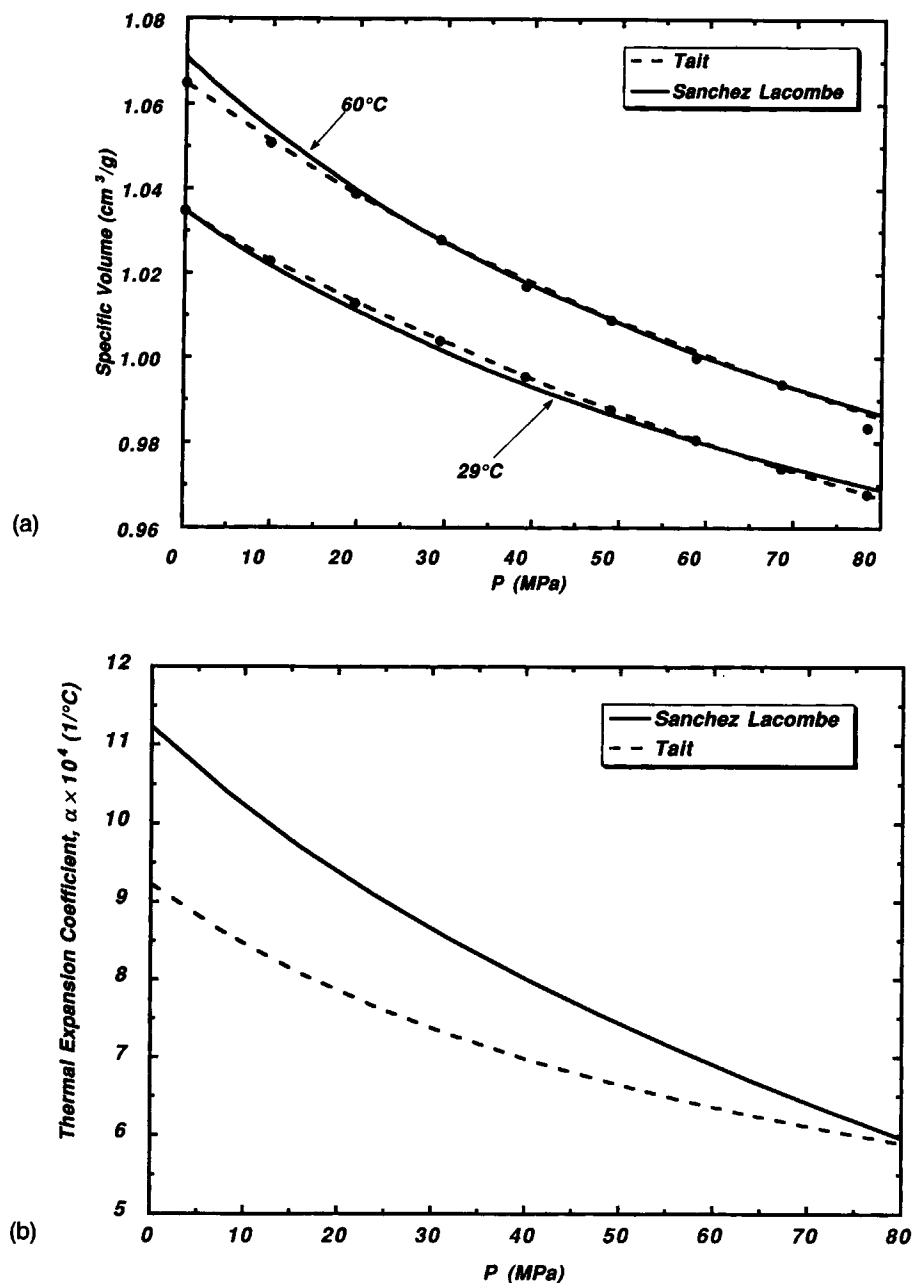


Figure 1 (a) Comparison of Sanchez-Lacombe and Tait equation predictions of specific volume of poly(dimethylsiloxane) at 29°C and 60°C, with experimental data. (b) Comparison of Sanchez-Lacombe and Tait equation predictions of thermal expansion coefficient of poly(dimethylsiloxane) at 60°C. (c) Comparison of Sanchez-Lacombe and Tait equation predictions of isothermal compressibility of poly(dimethylsiloxane) at 60°C. The Tait equation prediction is from the work of Zoller.¹⁴ The SL model results were calculated using parameters from Sanchez and Lacombe.³

can show strong deviations from values of these properties determined from experimental data. For example, Figures 1 (b) and 1 (c) present comparisons

of the compressibility and expansion coefficient of PDMS at 60°C calculated from the SL model with those calculated using the Tait equation, which pre-

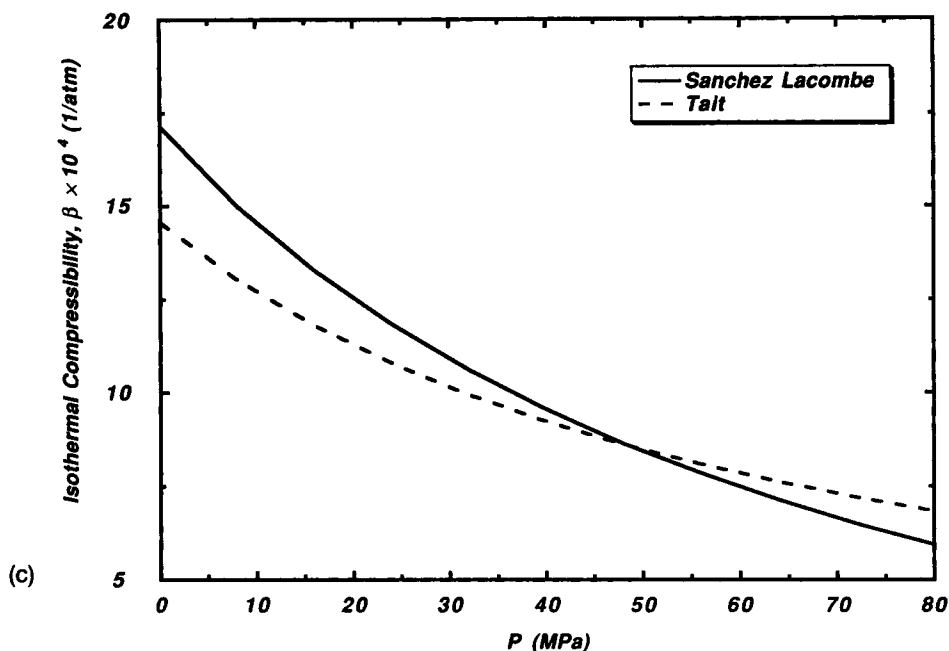


Figure 1 (Continued from the previous page)

sumably accurately describes the experimental data. Over this limited pressure range, the deviation between the experimental data and SL model estimates of the polymer expansivity and compressibility can be as large as 20%, even though the largest deviation between the observed and calculated specific volume is less than 1%. Therefore, if derivatives of polymer volume are required for a particular application, it is best to use SL parameter values determined from density, compressibility, and expansivity data over the desired pressure range.

Values of P_2^* , T_2^* , and ρ_2^* may be determined at any temperature and pressure by fitting the SL model to polymer density, expansivity, and compressibility values at the particular temperature and pressure.³ Figures 2(a), (b), and (c) present the pressure and temperature dependence of the parameters P_2^* , T_2^* , and ρ_2^* , respectively, of PDMS determined by this method. As illustrated in Figure 2, the parameters can be strong functions of pressure and temperature. The constant values of the parameters reported by Sanchez and Lacombe³ are also shown in Figure 2 for comparison. Similar variations in parameter values with pressure and temperature were found by using data for 14 different polymer systems.¹⁵

In subsequent calculations of the sorption isotherms, constant values of the polymer parameters

were chosen which best fit the PVT, α , and β data over the pressure range of the available sorption data and at the temperature at which the sorption data were measured. These values, along with parameter values for PDMS reported by Pope et al.,⁶ are presented in Table I. The effect of polymer parameters on predicted sorption isotherms is discussed below.

Evaluation of Penetrant Parameters

Pope et al.⁶ estimated penetrant parameters using experimental values of vapor and liquid density of the pure penetrant at the saturation temperature (boiling point) at 1 atm, the critical temperature of the fluid and the enthalpy of vaporization. Following this procedure, parameter values for nitrogen, methane, and cyclohexane were evaluated and are presented in Table I. The gas parameter values reported by Pope et al.⁶ are not completely converged, which results in a small difference between the parameter values for CH_4 in Table I and those presented by Pope et al.⁶

Since the triple point pressure of CO_2 is 5.115 atm, this gas does not have a boiling point at 1 atm. It is not clear, therefore, how CO_2 parameters were determined by Pope et al. The CO_2 parameters for this study were determined using a CO_2 vapor pressure of 5.716 atm at -53.89°C . At this temperature

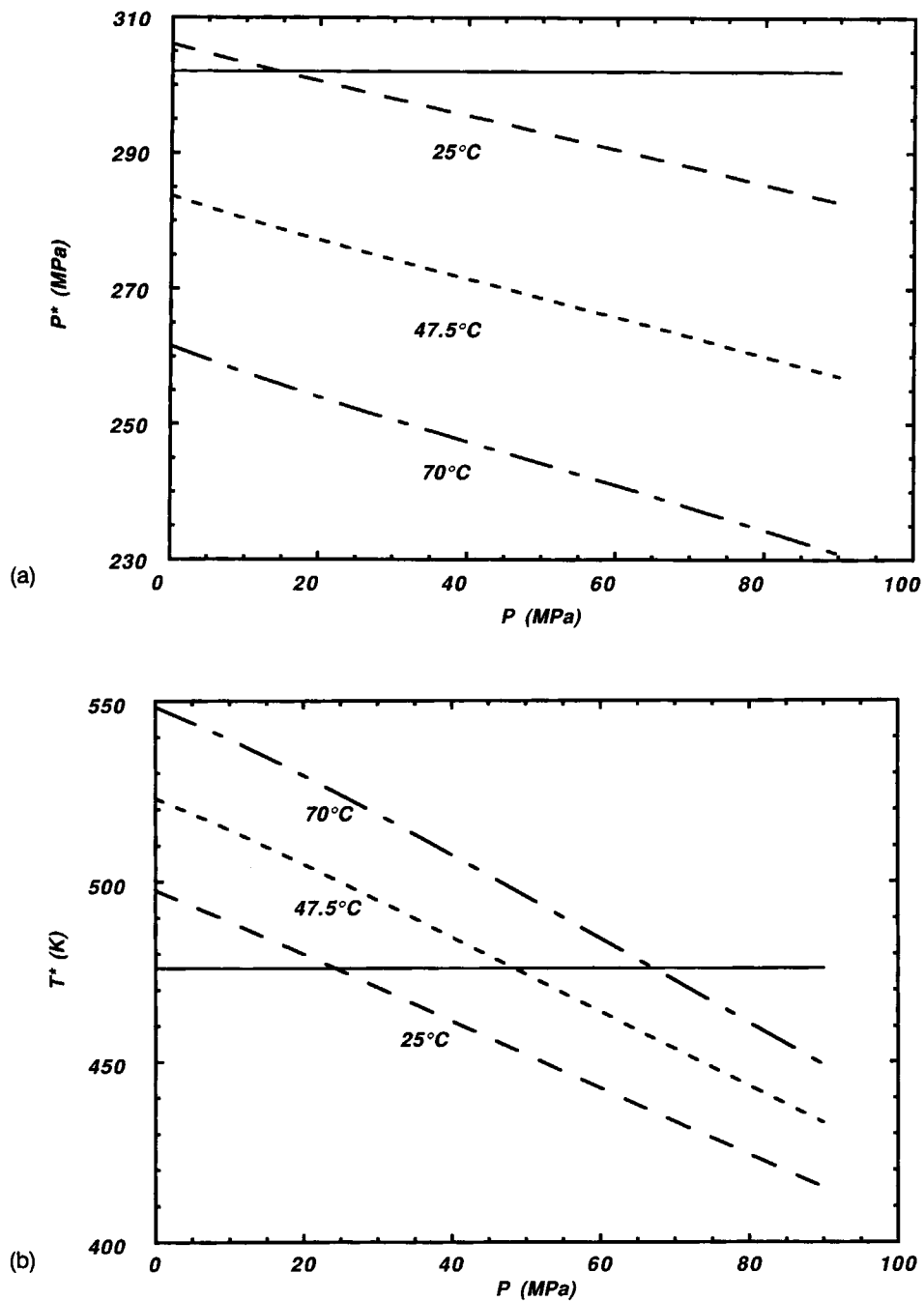


Figure 2 (a) The effect of pressure on P_2^* of PDMS at 25, 47.5, and 70°C. (b) The effect of pressure on T_2^* of PDMS at 25, 47.5, and 70°C. (c) The effect of pressure on ρ_2^* of PDMS at 25, 47.5, and 70°C. The horizontal line represents the values reported by Sanchez and Lacombe.³

and pressure, CO₂ exists as a vapor–liquid mixture, even though this pressure and temperature pair are arbitrary. Kiszka et al.⁸ have suggested that gas parameters should be determined based upon the fits

of the vapor–liquid equilibrium data in the pressure and temperature range where sorption predictions are desired. Kilpatrick and Chang¹⁶ determined CO₂ parameters by fitting experimental vapor liquid

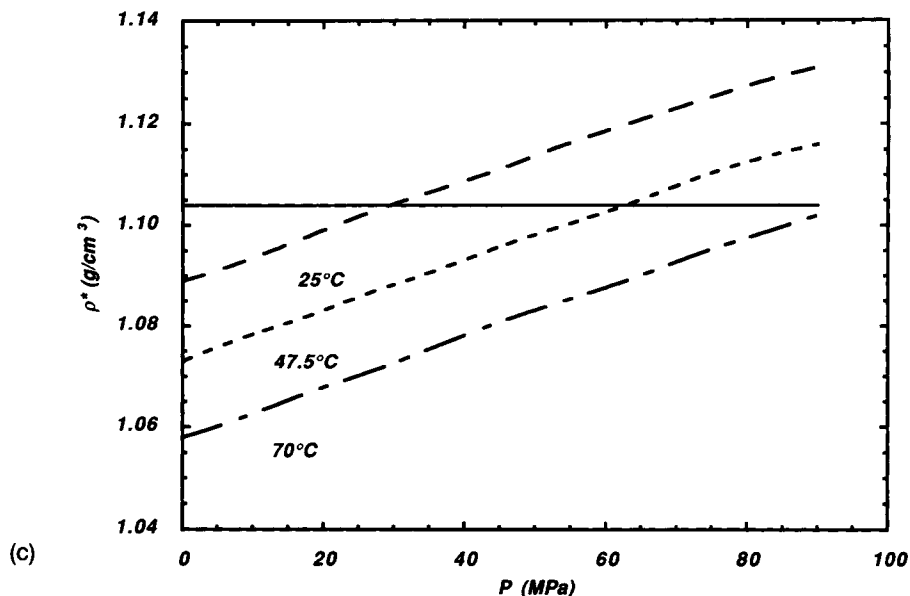


Figure 2 (Continued from the previous page)

equilibrium density data at temperatures from -56.6°C to 31°C (i.e., the critical temperature) and pressures ranging from 0.51 MPa to 7.4 MPa (i.e., the critical pressure).

As illustrated in Table I, the parameter values are sensitive to the parameter determination strategy. This result is consistent with the observation by Kiszka et al. that the SL model cannot accurately

Table I Parameter Values

| Material | P^* (atm) | T^* (K) | ρ^* (g/cm^3) | r |
|--------------------------|-------------|-----------|-------------------------------------|------|
| PDMS | 2913 | 506 | 1.0835 | — |
| PDMS ^a | 2914 | 506 | 1.0835 | — |
| PDMS ^b | 2887 | 498 | 1.0805 | — |
| PDMS ³ | 2980 | 476 | 1.104 | — |
| PDMS ⁶ | 3500 | 560 | 1.2 | — |
| SBR (23% S) | 3290 | 608 | 0.9867 | — |
| N_2^c | 1698 | 134 | 0.9018 | 4.80 |
| CO_2^d | 4126 | 316 | 1.369 | 5.11 |
| CO_2^6 | 6510 | 283 | 1.62 | 7.6 |
| CO_2^8 | 5670 | 305 | 1.510 | 6.60 |
| CO_2^{16} | 7101 | 280 | 1.6177 | 8.40 |
| CH_4^c | 2221 | 206 | 0.4675 | 4.50 |
| CH_4^8 | 2448 | 224 | 0.500 | 4.27 |
| Cyclohexane ^c | 3168 | 543 | 0.9184 | 6.52 |

^a PDMS parameters, determined by fitting experimental density, α , and β over a pressure range of 1–68 atm.

^b PDMS parameters, determined by fitting experimental density, α , and β over a pressure range of 1–250 atm.

^c Nitrogen, methane, and cyclohexane parameters were determined by fitting the SL model to the critical temperature and to liquid and gas phase densities and the heat of vaporization at the normal boiling point (i.e., where the saturated vapor pressure was 1 atmosphere).

^d Carbon dioxide parameters were determined by fitting the SL model to the critical temperature and to liquid and gas phase densities and the heat of vaporization at 5.716 atm.

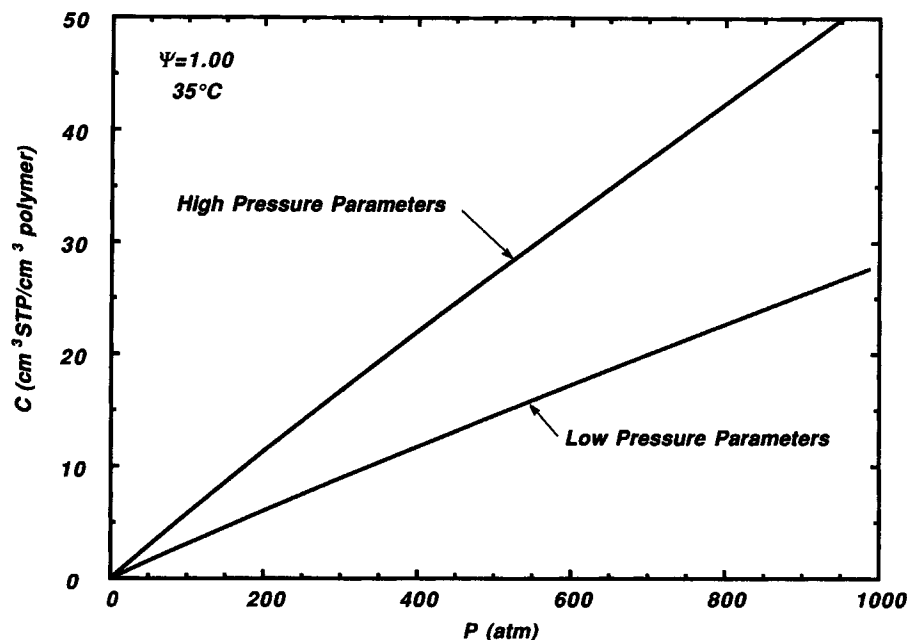


Figure 3 The effect of polymer parameters on predicted nitrogen sorption isotherm in PDMS. Low pressure parameters are $P_2^* = 296.2$ MPa, $T_2^* = 509$ K, and $\rho_2^* = 1.081$ g/cm³. High pressure parameters are $P_2^* = 271.4$ MPa, $T_2^* = 423.4$ K, and $\rho_2^* = 1.125$ g/cm³.

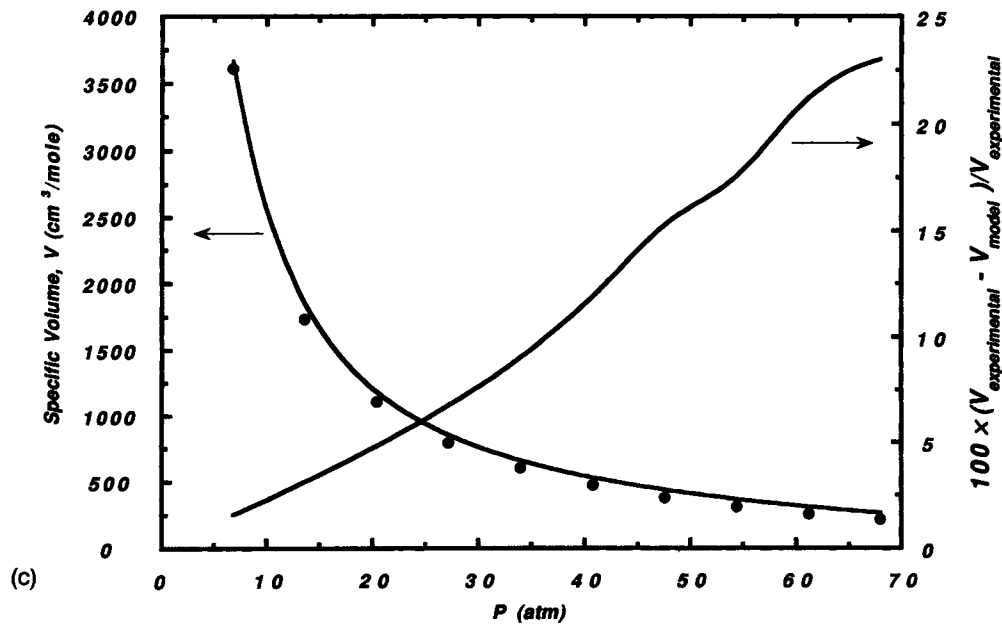
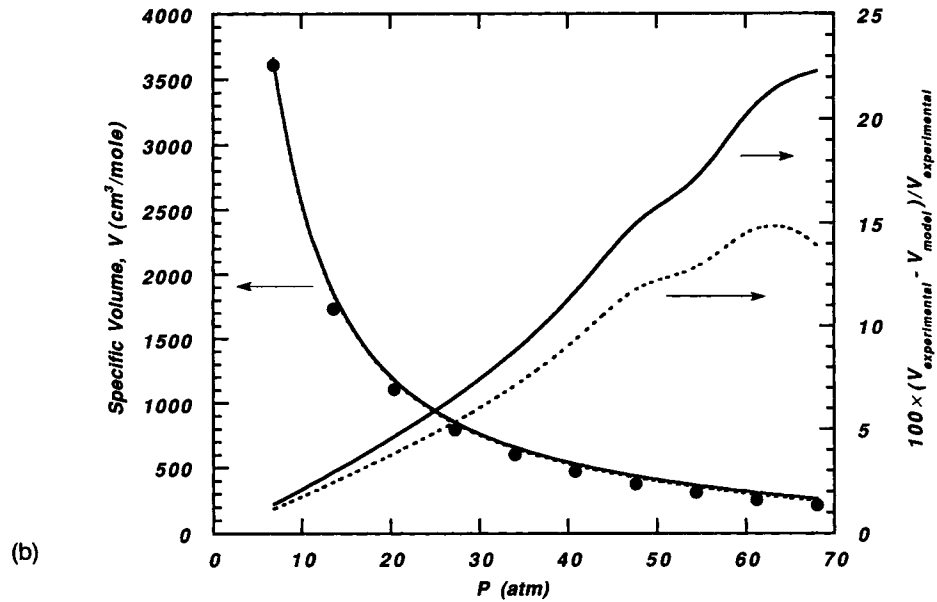
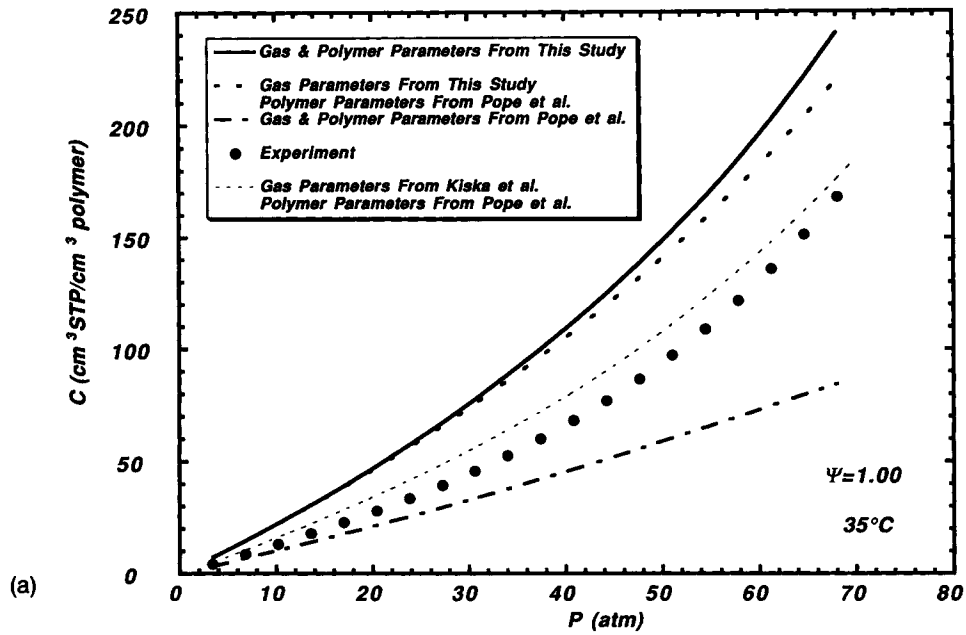
describe gas phase data over wide ranges of temperature and pressure using constant values for the model parameters.⁸

Effect of Polymer Parameters on Predicted Sorption Isotherms of Nitrogen in PDMS

The effect of polymer parameters on sorption isotherm predictions, using the SL model, are illustrated in Figure 3, which presents calculations of the sorption of nitrogen into PDMS at pressures up to 1000 atm. Polymer parameters were chosen from two different pressure ranges. The low pressure parameters correspond to PDMS parameters, obtained

using density, expansivity, and compressibility data at ambient conditions, while the high pressure parameters were determined by fitting polymer data at 90 MPa. The nitrogen parameters used for Figure 3 are from Table I. Since the resulting isotherms are nearly linear, Henry's Law coefficients (i.e., isotherm slopes) were calculated. They are 0.0279 cm³ (STP)/cm³ polymer · atm for the low pressure parameters, and 0.0523 cm³ (STP)/cm³ polymer × atm for the high pressure parameters. Thus, the choice of polymer parameters can influence substantially the calculated sorption isotherm, and the effect becomes more pronounced with increasing pressure.

Figure 4 (a) Comparison of experimental data to predicted CO₂ isotherm in PDMS, using the Sanchez-Lacombe model with various parameter sets. Experimental sorption data are from Fleming and Koros.²² The polymer parameters were chosen so as to best fit the PVT, α , and β data over the pressure range (1–68 atm) at the temperature of the experiment. This fit yielded the following parameters: $P_2^* = 2914$ atm, $T_2^* = 506$ K, and $\rho_2^* = 1.0835$ g/cm³. (b) Sanchez-Lacombe model predictions and experimental values of specific volume of carbon dioxide at 37.8°C (100°F), using parameters obtained in this study (solid lines) and parameters from Kiszka et al.⁸ (dashed lines). (c) Comparison of experimental and predicted CO₂ specific volume, using parameters from Pope et al.⁶ at 37.8°C (100°F).



Effect of Penetrant Parameters on Model Predictions

Predictions of CO₂-PDMS Sorption Isotherm and CO₂ Specific Volume

An example of the sensitivity of the calculated sorption isotherm of CO₂ in PDMS to the choice of penetrant parameters is shown in Figure 4(a). CO₂ parameters from three sources were used in calculating the isotherms shown in Figure 4. When compared to the experimental data, the isotherm predicted that using the gas and polymer parameters reported by Pope et al.⁶ significantly underpredicts the concentration of absorbed CO₂ over the entire pressure range. The isotherm calculated using parameters from this study overpredicts the CO₂ concentration in the polymer, and the isotherm computed using Kiszka et al.'s parameters overpredicts the sorption, but provides better predictions than the other two parameter sets. A change in PDMS parameters from those determined for this study to those reported by Pope et al., leads to relatively small changes in the absorption isotherm. Therefore, most of the difference between the absorption predictions is due to the difference in CO₂ parameter values. Clearly, the parameter selection strategy of Kiszka et al.⁸ provides the best agreement with the experimental data.

The CO₂ parameter values obtained in this study and those of Kiszka et al. were used to compute the specific volume of CO₂ as a function of pressure, and the results are shown in Figure 4(b). The computed specific volumes are compared to experimental data¹⁷ in the same figure. A temperature of 37.8°C was chosen for this comparison, since the experimental specific volume data were available at this temperature. The agreement between theory and experiment is excellent at the lower pressures, and there is a 23% error near 70 atm. A similar curve, computed using the CO₂ parameters from Pope et al.,⁶ is shown in Figure 4(c), and it is nearly indistinguishable from Figure 4(b). These results suggest that density data alone are not a good predictor of P_1^* , T_1^* , and r_1^* values, which lead to accurate calculations of absorption isotherms. Figure 4(a) presents examples in which drastically different absorption isotherms are obtained from different sets of CO₂ parameters, which yield a nearly identical fit to the gas phase pure component PVT data.

As might be expected, the calculated absorption isotherms are different, because the gas phase chemical potential is sensitive to the penetrant parameters, as shown in Figure 5(a). The chemical potential, computed using the parameters from this study, is uniformly higher than that calculated using Pope et al.'s parameters. The CO₂ chemical poten-

tial, calculated using Kiszka et al.'s parameters, lies between that calculated in this study and the results of Pope et al. The left side of eq. (3), the expression for the gas phase chemical potential, is directly proportional to the value of r_1 . Table I shows that the estimation procedure used in this study produced a value of $r_1 = 5.107$ for CO₂, while Pope et al.⁶ reported a value of $r_1 = 7.6$, and Kiszka et al. found r_1 to be 6.602. In Figure 5(b), the pressure dependence of the CO₂ chemical potential, divided by r_1 , is presented. These normalized chemical potential values lie closer together, but this simple procedure does not lead to a single universal curve for all three parameter sets. Thus, the disparate CO₂ parameters in Table I provide similar predictions of specific volume, but lead to chemical potential values which are different. These differences in chemical potential, in turn, lead to predicted sorption levels which vary considerably depending on the parameter values chosen for the penetrant.

Effect of Mixing Parameter on Calculated Sorption Isotherms

Figure 6 shows the effect of a small change in the value of the interaction parameter ψ on the calculated sorption isotherm of CO₂ in PDMS. Changing ψ from 1 to 0.942 causes a large decrease in the predicted isotherm. This result is consistent with the findings of Kiska et al.,⁸ who found that a value of ψ of 0.953 was needed to describe adequately the experimental sorption data of CO₂ in PDMS. The requirement of accurate values of binary interaction parameters to describe phase equilibria is not unique to the Sanchez-Lacombe model, but is, rather, typical of most equations of state.¹⁸ If quantitative agreement is desired between the SL theory and experimental isotherms, there seems to be little choice but to fit ψ to the isotherm. In most cases, a value of $\psi = 1$ will not provide a sufficiently accurate estimate of the amount of absorption for quantitative purposes.

Sorption Isotherms in Supercritical vs. Subcritical Fluids

There is a consistent trend in the results obtained for absorption isotherms, using the SL equation of state, for fluids that are in supercritical and subcritical conditions. These effects are illustrated by the following two examples: Figure 7(a) shows the computed absorption isotherm for methane in PDMS at 308 K, using the parameter values in Table I. The comparison between the calculated absorption values, when $\psi = 0.989$, and the experimental⁶ values is excellent. The calculated methane specific volume,

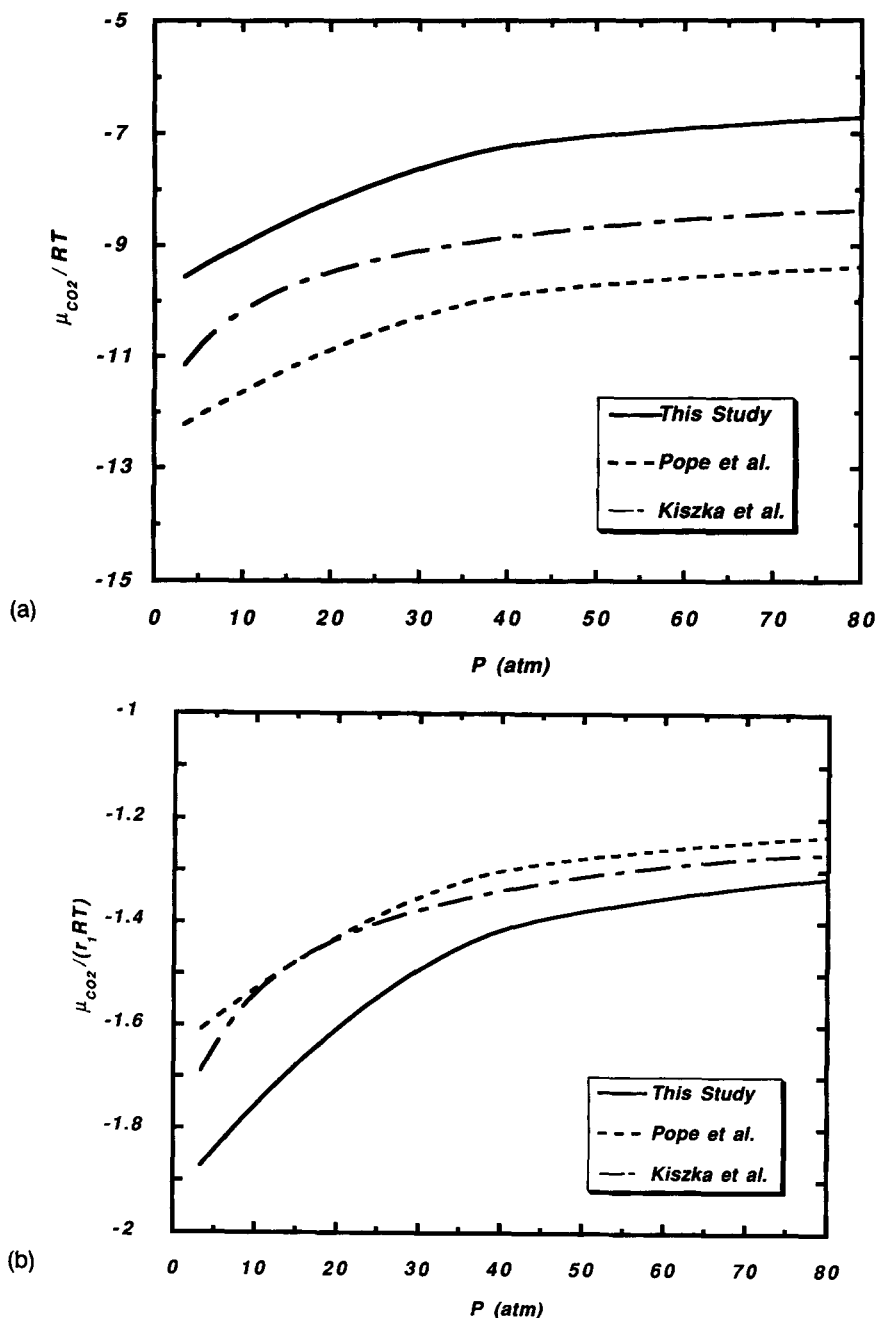


Figure 5 (a) The effect of gas phase equation of state parameters on the predicted chemical potential of carbon dioxide at 35°C. (b) The effect of normalizing predicted chemical potential of carbon dioxide at 35°C by the size parameter, r_1 .

presented in Figure 7(b), shows good agreement with the experimental data, with errors less than 3.5% over the entire pressure range. This type of agreement is typical of the predictions of the SL equation of state for the absorption of fluids that are in supercritical conditions. The critical temperature of methane is 190.6 K, thus the absorption isotherm in Figure 7(a) was measured at 117 K above the critical temperature. Systems far above

the critical point are more ideal, and since the SL theory reduces to the ideal gas law at low densities, it provides good estimates of gas phase specific volumes for highly supercritical systems. By comparison, the critical temperature of CO_2 is 304.2 K. The isotherm described in Figure 4(a) was measured at only 4 K above the critical temperature. The deviations in the specific volume calculations, shown in Figure 4(b), may be related to the inability of the

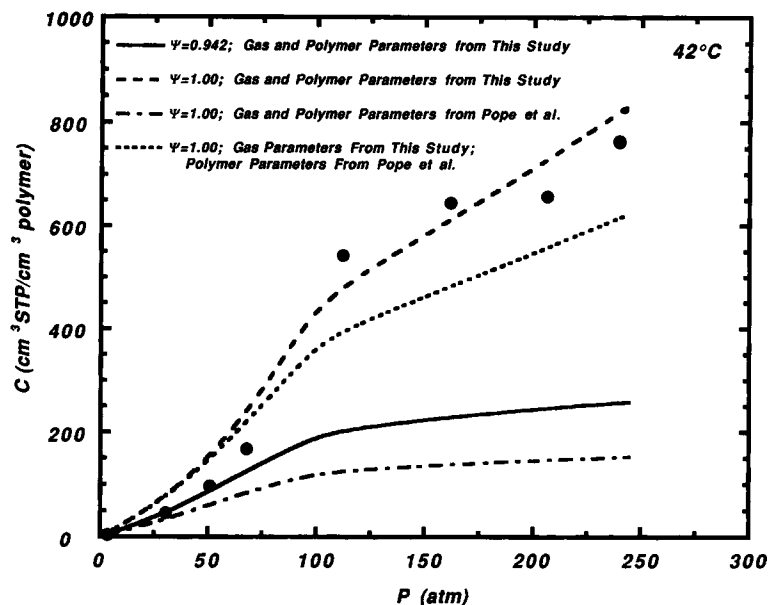


Figure 6 The effect of the mixing interaction parameter, ψ , on predicted CO_2 sorption isotherm in PDMS, using the Sanchez–Lacombe model with various parameter sets. The experimental sorption data, denoted by the filled circles, are from the study of Briscoe and Zakaria.²³ The polymer parameters were chosen so as to best fit density, α , and β data over the pressure range (1–250 atm), at the temperature of the experiment. This fit yielded the following parameters: $P_2^* = 2887$ atm, $T_2^* = 497.5$ K, and $\rho_2^* = 1.0805$ g/cm³.

SL model and, in fact, of many equation of state models, to describe accurately the phase behavior of fluids near the critical point.

The computed and experimental¹⁹ absorption isotherms for cyclohexane vapor in styrene–butadiene rubber (23%) (SBR) at 40°C are shown in Figure 8(a). The computations were performed using values of vapor and polymer parameters indicated in Table I. Because cyclohexane is subcritical at 40°C under these pressure conditions, the pressure axis is expressed in terms of the activity of the penetrant, namely, the ratio of the pressure to the saturation pressure at 40°C (0.2421 atm). At values of activity less than 0.5, it is possible to find a value of ψ that fits the data extremely well at low pressure. However, as the pressure increases and the activity values rise above 0.5, significant deviations are seen between the predicted and experimental absorption isotherms. The SL theory tends to underpredict significantly the absorption. The reason for this is probably not due to any failure in the ability of the SL theory to predict the thermodynamic properties of the vapor. For example, the vapor phase parameter values in Table I allow an excellent prediction of the specific volume of cyclohexane as a function of pressure, as shown in Figure 8(b). The deviation between theory and experiment is never more than 0.6% over the entire pressure range. This is typical

of the types of fits seen with the SL theory for fluids well below the critical point. The SL equation was originally developed for condensed phases, and it tends to give good results when the fluid is well below the critical point, as well as when the fluid is well above the critical point. It is more likely that the mixing rule for the solute and penetrant parameters, in a binary mixture, fails when the activity of the solute is high, and that this is responsible for the deviations seen in subcritical fluids, such as those in Figure 8(b). The search for adequate mixing rules to use in the prediction of thermodynamic properties is not restricted to the SL model; much current research is directed toward defining the mixing rules in order to allow equations of state to better describe experimental data.^{20,21}

CONCLUSIONS

The ability of the Sanchez–Lacombe model to provide quantitative predictions of gas and vapor sorption isotherms in polymers has been explored. While the model provides good fits to experimental polymer density over wide ranges of temperature and pressure, compressibility and expansivity may be poorly predicted. Sorption isotherms can be sensitive to the choice of polymer parameters, particularly at

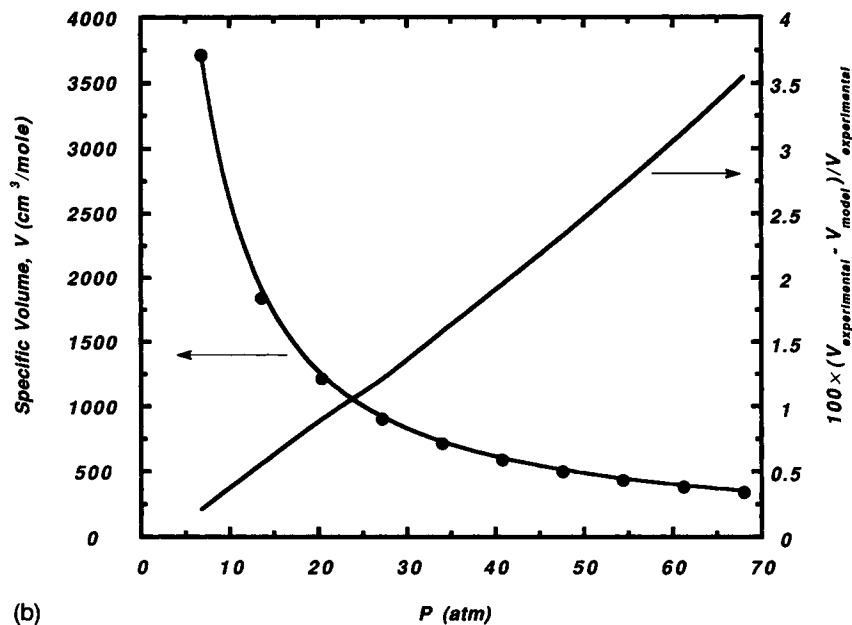
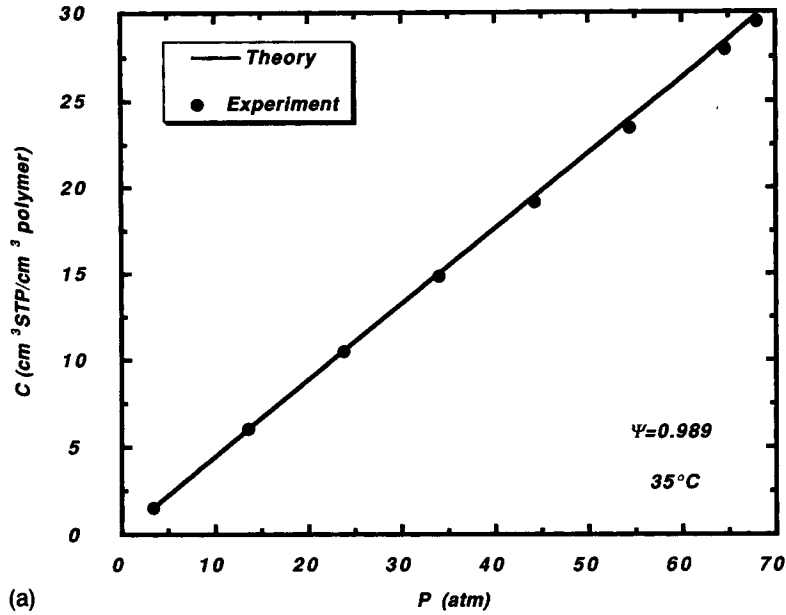


Figure 7 (a) Comparison of predicted methane sorption isotherm in PDMS with experimental data from the study of Pope et al.⁶ (b) Comparison of predicted and experimental methane specific volume at 35°C . The experimental data are from the work of Canjar and Manning.¹⁷

elevated pressures, and the best choice seems to be to determine parameters by fitting the polymer specific volume, expansivity, and compressibility over the range of temperature and pressure of interest in the sorption experiment. The results of this study suggest that a judicious selection of penetrant parameters is required to achieve good agreement with

the experimental sorption data for penetrants that are near their critical point. The predicted sorption isotherms are sensitive to the value of the mixture interaction parameter. Moreover, in the sorption of organic vapors into polymers, it appears that the mixing rule describing polymer-penetrant interactions should be improved.

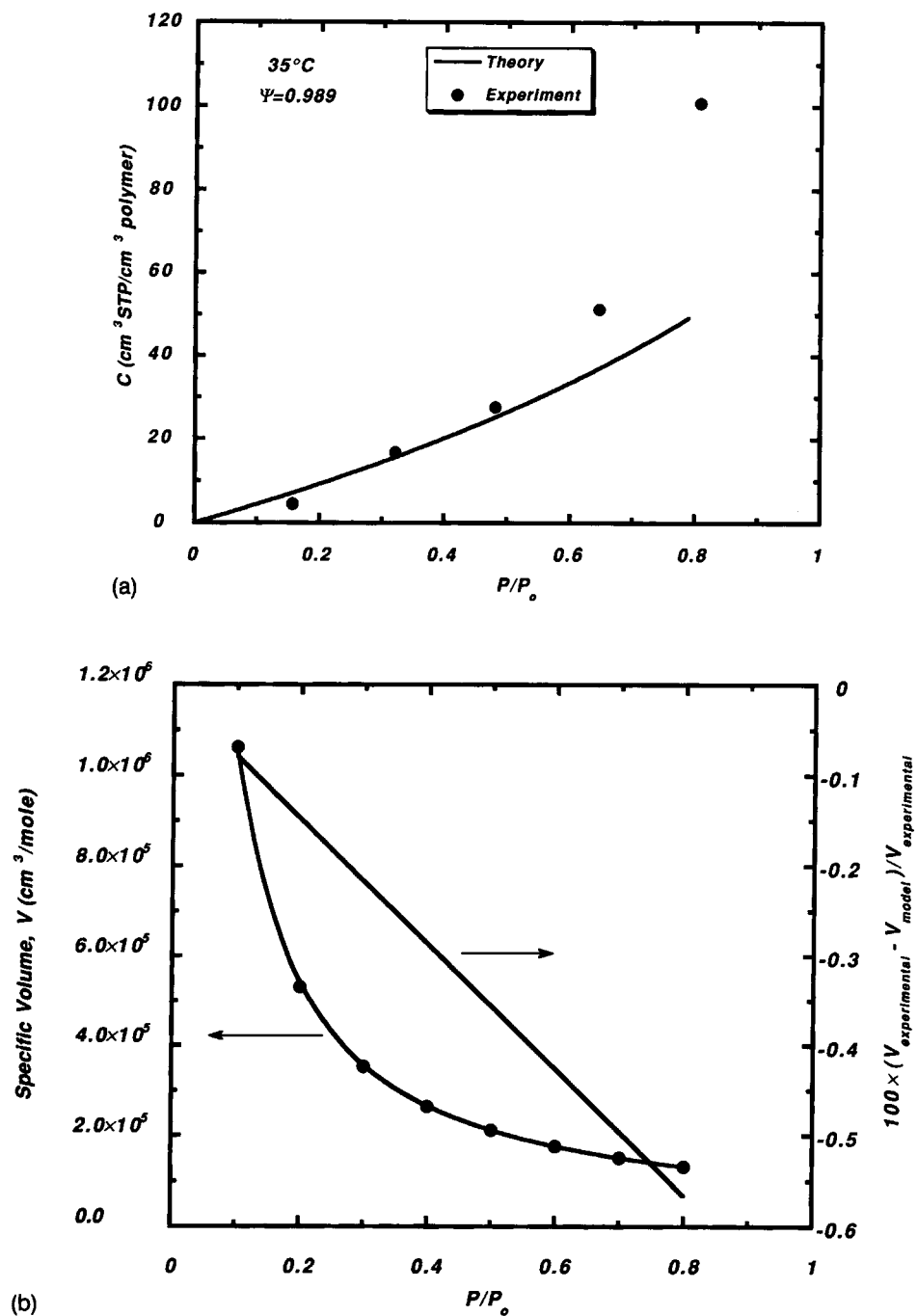


Figure 8 (a) Comparison of predicted cyclohexane sorption isotherm in SBR rubber with experimental data. (b) Comparison of predicted (line) and experimental (filled circles) cyclohexane specific volume at 313 K. Experimental data are calculated, using the Peng-Robinson equation of state.

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