Adjustable Solute Distribution between Polymers and Supercritical Fluids

The sorption of toluene, dilute in CO_2, and likewise the distribution coefficient of toluene between silicone rubber and CO_2 have been explored from gaseous to supercritical fluid conditions. Sorption and desorption isotherms were determined by frontal analysis using a new inverse supercritical fluid chromatography technique at 35 and 70°C up to 250 bar. Complementary swelling data are presented for pure CO_2 in silicone rubber up to 315 bar. A new result is that the sorption of toluene goes through a maximum and is highly adjustable over a continuum in the highly compressible region of carbon dioxide. This behavior is explained physically and predicted quantitatively with the Flory equation and the Peng-Robinson equation of state using only information from binary systems. These results are useful for a wide variety of applications including impregnation of polymers with pharmaceuticals, fragrances and other additives, and polymer purification.

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Introduction

The concept of using supercritical fluids (SCF's) such as carbon dioxide in polymer processing is beginning to receive significant attention (Paulaitis et al., 1983; McHugh and Krukonis, 1986; Seckner et al., 1988; Ziger, 1987). One branch of the field deals with the fractionation of certain polymers by extraction at elevated temperatures and pressures (McHugh and Krukonis, 1986; Kumar et al., 1986). The present study focuses on the other branch, that is the influence of the fluid on the polymer phase, for an insoluble cross-linked polymer. SCF's such as $CO_2 (T_c = 31.05°C, P_c = 73.8$ bar) are so small that they diffuse quickly into glassy as well as rubbery polymers to produce a significant degree of swelling. There are a variety of interesting opportunities for processing polymers in the swollen state. They may be purified by the removal of oligomers, monomers, or residual solvent (Paulaitis et al., 1983), or may be impregnated with a wide variety of additives (Sand, 1986; Berens et al., 1988). A key factor which dictates the feasibility of the process is the equilibrium distribution coefficient of the solute which is either being extracted or impregnated. Distribution coefficients have not been reported previously for ternary systems, which consist of a polymer, a SCF and a dilute solute, except for a study which was performed using capillary column chromatography (Olesik et al., 1987). The objective of this work is to determine distribution coefficients experimentally and to predict the behavior as a function of pressure, temperature, and composition theoretically using molecular thermodynamics.

In order to maximize the understanding gained from the thermodynamic analysis of the data, we chose to study silicone rubber rather than glassy polymers which are much more complicated because they are not at equilibrium. Carbon dioxide was used as the swelling agent, while the concentration of the solute, toluene, was maintained near infinite dilution in the fluid phase in order to test the model at the most nonideal conditions.

A unique feature of a SCF is that the solvent strength, for example the solubility parameter or the solvatochromic polarity parameter (Kim and Johnston, 1987), is highly adjustable with respect to temperature or pressure in the highly compressible critical region. Therefore, the fugacity or alternatively the chemical potential of a solute in the fluid is highly variable (Kim et al., 1985). This adjustability is the basis of SCF extraction, and recently has been shown to have a large influence on reaction rate constants (Johnston and Haynes, 1987; Alexander and Paulaitis, 1987) and equilibrium constants (Peck et al., 1989; Flarsheim et al., 1989). Our hypothesis is that this adjustability also has a large influence on distribution coefficients in polymer-fluid systems. The additional variable of pressure could be used to select the degree of loading during impregnation, or for a purification process, to influence the selectivity and degree of extraction.

Several recent studies of the sorption of a pure SCF in poly-

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mers provide a basis for the present study. Fleming and Koros (1986) investigated silicone rubber and polycarbonate up to 60 bar at 35°C using subcritical CO_2. The sorption behavior for silicone rubber was described using the Flory equation, while that for polycarbonate was described successfully using a dual-mode theory, which treats both Langmuir sorption as well as Henry's Law-type sorption. Liau and McHugh (1985) investigated the phase behavior of polymethylmethacrylate and SCF CO_2 to 270 bar at temperatures from 41 to 68°C. Berens and Huvard (1989) studied sorption kinetics and equilibria in a wide variety of polymers at pressures up to 100 bar at 25°C. Glass transition temperatures may be lowered significantly as a function of pressure, which causes a large increase in diffusion coefficients of solutes. Wissinger and Paulaitis (1987) examined the glass transition pressures of several polymers as a function of temperature. King (1987, 1988) examined the adsorption of benzene, heptane, and a variety of other organic compounds on polymeric resins chromatographically.

A variety of impregnation applications may be developed using polymers swollen at SCF conditions. It is possible to impregnate polymers with pharmaceuticals, flavors, fragrances, insecticides, etc. for controlled release (Berens et al., 1988; Sand, 1986; Langer, 1980), or with additives such as pigments, stabilizers, plasticizers, electrically-conductive agents, and toughness-improving agents. Membrane separations, which are influenced in part by the solubility of gases in the membrane, are being investigated at higher pressures approaching the critical pressure, for example, in the separation of CO_2 and methane (Jordan et al., 1987). SCF's could be used for the regeneration of certain sorbents such as activated carbon and polymeric resins. Finally, polymer sorbents could play an important role in the selective recovery of products from SCF reaction or extraction processes (King, 1988). There are some potential benefits in using a SCF in these applications. SCF CO_2 is a particularly desirable solvent since it is nonflammable, nontoxic, inexpensive and easy to dispose of. The recovery of the solvent is efficient using either pressure or temperature changes, and solvent residue is not left in the polymer. The rates of polymer swelling, the ensuing impregnation or purification, and solvent recovery are all accelerated with a SCF solvent compared with a liquid. Finally, pressure and temperature may be used as new tools to adjust the solute loading or degree of polymer purification.

Experimental Methods

Swelling

Silicone rubber films approximately 0.254 mm (10 mil) thick were prepared by mixing 10 parts by weight of silicone rubber compound (General Electric RTV 615A) with one part of curing agent (General Electric RTV 615B). The films were cured in a vacuum oven at 150°C for 2 days. Impurities including oligomers were extracted with 100 cm^3 cyclohexane for about 5 days, and the films were dried at 100°C to reduce the polymer weight by 3%. The final purification was done using flowing CO_2 at 40°C and 60 bar for about 15 hours to reduce the weight of the polymer by another 0.6%.

The swelling was observed in a steel Jerguson gauge with glass windows, which had a maximum pressure rating of 340 bar, using a method similar to those in the literature (Fleming and Koros, 1986; Liau and McHugh, 1985). A 11 cm by 0.3 cm silicone rubber strip was placed in an aluminum guide to prevent distortion during swelling. The gauge was immersed in a water bath which was controlled to ±0.1°C. The pressure was raised to 200 bar using CO_2 (Big Three Industries, 99.99%) to remove any constraining forces on the polymer strip, such as adhesion to the guide. The pressure was reduced slowly, and the system was evacuated to determine the unswollen length. The pressure was increased using 5 to 20 bar increments, and the length of the strip was measured to within ±0.05% using a cathetometer (Gaertner Scientific Corp.). The amount of swelling was calculated from the change in length by assuming isotropic volume dilation (Fleming and Koros, 1986). After reaching the maximum pressure, 315 bar, the polymer was depressurized using 5 to 20 bar decrements to determine the swelling during desorption. The equilibration required 10 minutes to 1 hour. The longest times were observed for the increments or decrements with the largest changes in swelling. The experimental error due to distortion of the polymer was less than 0.5%.

Sorption

Silicone rubber films were prepared as described above for the swelling experiments. A 13 mm × 15 mm polymer film with a weight of 30–40 mg was laid upon a 200 mesh stainless steel screen cloth (Argus Steel Products, 13 mm × 20 mm), and the combination was rolled into a spiral. The purpose of the screen was to maximize polymer surface area/volume by preventing the polymer film from sticking together. Each spiral assembly (13 mm long by 2.8 mm diameter) was weighed to ±0.1 mg, and three such assemblies were deposited into a microsorption cell.

Using a modified supercritical fluid chromatograph (SFC), toluene at a constant concentration in CO_2 was sorbed into silicone rubber, and then desorbed using pure SCF CO_2 at the same pressure (see Figure 1). The SFC (Lee Scientific Model 501) consisted of a 175 mL computer-controlled syringe pump, a temperature-controlled oven, a microsorption cell, a flame ionization detector, and an integrator (Spectraphysics, Model 4270). All of the lines between the SFC pump and the oven were traced, insulated and heated to 70°C to prevent condensation of toluene. A 100 mL manual syringe pump (Ruska Laboratories, Inc.) was used as a supply reservoir of pure CO_2 for the desorption cycle. The sorption and desorption of toluene took place in a microsorption cell which was composed of two 6.35 mm to 1.59 mm Swagelok reducing unions attached to a short stainless steel tube (40 mm long, 6.35 mm o.d. and 3.05 mm i.d.). The inlet line to the cell was 1.59 mm o.d. by 127 μm i.d. stainless steel

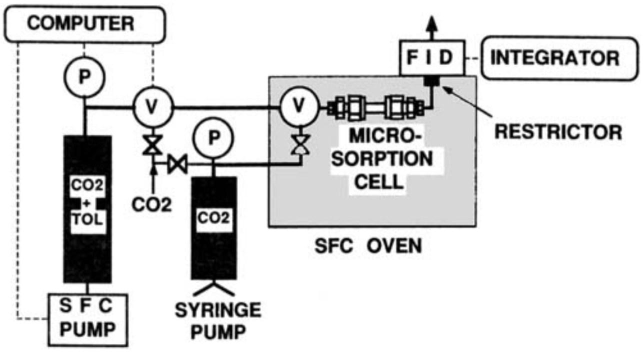

Figure 1. High-pressure sorption-desorption flow apparatus using a modified supercritical fluid chromatograph.

P = pressure transducer; *V* = rotary switching valve tubing and the outlet line was 250 μm o.d. by 100 μm i.d. capillary tubing which had a ceramic frit flow restrictor built into the downstream end (Lee Scientific, Inc.). The flame ionization detector was heated to 300°C to prevent condensation of the solute during depressurization which would upset the flow rate. It was calibrated by flowing a measured volume (at atmospheric pressure) of SCF solution of known concentration.

The pressure control in the SFC pump was accurate to ±0.1% as verified using a digital gauge (Heise, Model 710B). The maximum design pressure of the apparatus was 400 bar. The pumps were thermostatted to within ±0.2°C. Because the manual pump was heated, the pressure dropped only about 3 bar over a period of 2 hours, as determined using a Sensotec TJE pressure transducer which was calibrated to within 0.05%. The pressure was readjusted every 2 hours. One of the rotary chromatographic switching valves was a standard part of the SFC system, while the other one provided a means to switch between the sorption mode (SFC pump) and the desorption mode (manual syringe pump).

A known weight of carbon dioxide, typically 150 ± 0.1 g, was added to a known weight of toluene (Aldrich, glass distilled HPLC grade 99.9%) in the SFC pump to prepare a mixture with a toluene concentration known to within ±1%. Pure carbon dioxide was passed through the cell to swell the polymer at the experimental pressure. The flow was switched to the CO_2-toluene mixture at the same pressure to start the sorption of toluene. The resulting sigmoidal sorption curve (toluene concentration vs. time as determined by the FID) was integrated until about 99.9% of the inlet concentration was attained. The integration was stopped and the flow rate was measured at the outlet of the FID. The valve was switched to flow pure CO_2, and the desorption curve was integrated. Three restrictors were used, each with a different length of frit, so that typical flow rates were 1 to 4 standard mL/min. The time for either sorption or desorption of toluene varied from 2 days at the lower flow rates to 10 hours at the higher flow rates. In the future, higher flow rates could be used to improve mass transfer in the fluid phase and thus provide a more sensitive measure of diffusion rates in the polymer phase. The flow rates were too low in the present experiments to determine the kinetics accurately.

The measurement of sorption from the desorption mode is inherently more accurate than from the sorption mode. In the latter, it is necessary to measure a small difference between the inlet and outlet mass flow rates of toluene over time. The accuracy was limited because the inlet total mass flow rate was assumed to be constant, even though it fluctuated about 1%. This limitation is not present for the desorption model. The sorption values calculated from the sorption mode were 1 to 10% smaller than those calculated from the desorption mode. The uncertainties in the values from the desorption mode were less than ±3%.

Experimental Results

The experimental results may be placed in perspective with a global description of the phase behavior over composition space for various pressures. After discussing the global phase behavior, we will focus on swelling and sorption isotherms for particular fluid phase compositions. In Figure 2, the phase equilibria is represented as a prism, which is a collection of ternary triangular diagrams, each at constant pressure and temperature. The temperature is 35°C and concentrations are in units of weight fraction. At 200 bar, the triangular diagram does not include a three-phase region, since carbon dioxide and toluene are fully miscible. For low concentrations of CO_2 and/or toluene, only one polymer phase is present, while at higher concentrations a fluid phase appears. The solubility of the cross-linked silicone rubber in the fluid is so negligible that the tie lines extend all the way to the carbon dioxide-toluene side of the triangle. As the pressure is lowered, the fluid phase splits into a carbon dioxide-rich fluid phase and a liquid phase with a higher toluene concentration. The area of this three-phase region increases with decreasing pressure, as more carbon dioxide vaporizes from the liquid phase and more toluene precipitates from the fluid (gas-like) phase. To the left of this three-phase region, two-phase fluid-polymer equilibria is present, where the fluid is gas-like. The other two-phase region, in which liquid-polymer equilibria exists at higher toluene concentrations, has been explored both experimentally and theoretically by Seckner et al. (1988) for the polystyrene-toluene-ethane system.

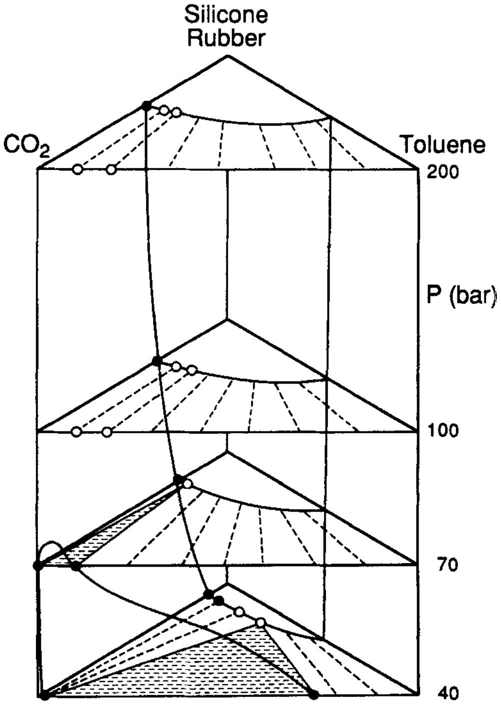

Figure 2. Phase equilibria of the ternary CO_2-toluene-silicone rubber system at 35°C based on weight fractions.

● experimental; O predicted; ●----● experimental tie-line; O----O, ●-----O, ●———O predicted tie-line; ---- schematic tie-line

The experimental data points on the ternary diagram are indicated by solid black circles. The weight fraction of pure carbon dioxide in silicone rubber, which was determined from the swelling data, is plotted against pressure on the binary carbon dioxide-silicone rubber surface of the prism. Notice that the sorption of CO_2 increases with pressure up to 200 bar. For the binary toluene-silicone rubber system, the weight fraction of toluene is 0.51 at room temperature and at atmospheric pressure, based on a swelling measurement. The effect of pressure on the sorption of pure toluene was not determined, although it would be expected to be much smaller for a liquid than for a SCF. The vapor-liquid equilibria data of Ng and Robinson

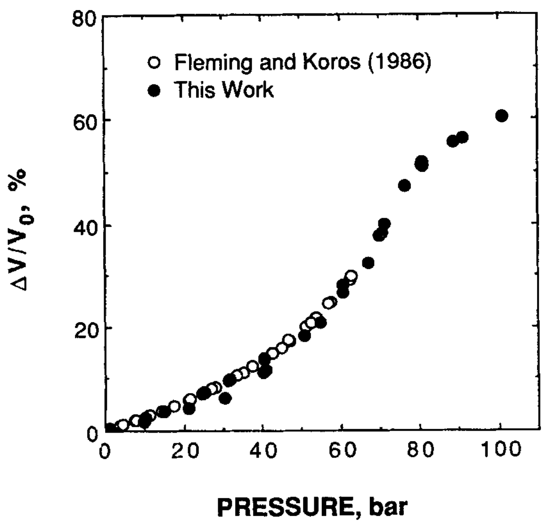

Figure 3. A comparison of the two studies of the swelling of silicone rubber in pure CO_2 at 35°C.

Each data set contains swelling data for both sorption and desorption cycles.

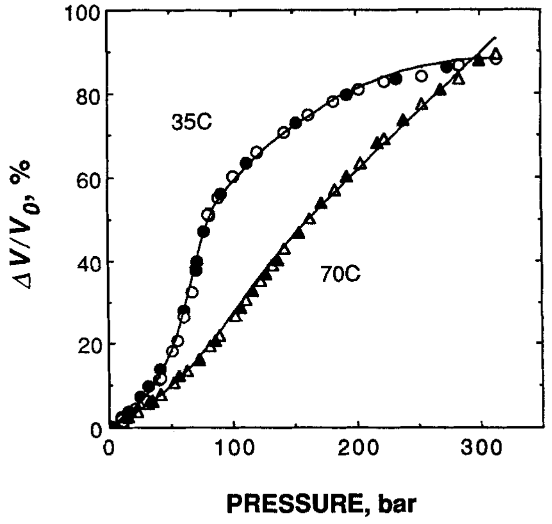

Figure 4. Experimental and correlated swelling isotherms for silicone rubber in carbon dioxide.

○△ swelling during sorption; ●▲ swelling during desorption; —— correlated using Eqs. 2 and 3

(1978) are shown for the CO_2-toluene binary. The calculated points on the diagram will be treated later in the discussion section.

The major emphasis of the study was to determine tie-lines (shown by dashed lines) for the ternary system in the fluid-polymer two-phase region. A particular tie-line was measured as each pressure with a toluene concentration close to 0.0014 mole fraction in the fluid, which is near infinite dilution. This tie-line is visible at 40 bar in Figure 2 (solid black circle endpoints), but is too close to the CO_2-polymer edge of the triangle to be noticeable at higher pressures. At each pressure studied, the polymer phase was in equilibrium with only a single fluid phase, as is evident from the vapor-liquid equilibria data for CO_2 and toluene. The measured toluene concentrations at the FID provided further evidence that only one fluid phase was present, since the steady-state signal (per flow rate) was the same at high and low pressures. Given this global description of the phase behavior, we will now present detailed results for particular fluid compositions.

The amount of swelling of silicone rubber by pure CO_2, $\Delta V/V_0$, was calculated from the measured length dilation with the assumption of isotropic volume dilation (Fleming and Koros, 1986) using the relationship

$$\frac{\Delta V}{V_0} = \left(\frac{l}{l_0}\right)^3 - 1 \qquad (1)$$

where ΔV is the volume change of the polymer, V_0 is the volume of unswollen polymer, l is the length of swollen polymer, and l_0 is the length of unswollen polymer. The results agree well with those of Fleming and Koros (1986) at pressures up to 60 bar as shown in Figure 3. As shown in Figure 4, the swelling data exhibit a sigmoidal shape versus pressure up to 310 bar, both at 35 and 70°C. There was no evidence of hysteresis between the sorption and the desorption cycles, although hysteresis would be expected for glassy polymers, as shown by Fleming and Koros (1986). At 35°C, the swelling is a strong function of pressure in the region where the fluid is highly compressible, but levels off at higher pressures where the fluid density becomes less variable. At 70°C, the slope is smaller up to about 100 bar, and the change in the concavity is much less pronounced. These observations will be explained in terms of the activity of carbon dioxide in the discussion section.

The equilibrium sorption of toluene in silicon rubber in the presence of CO_2 is shown as a function of pressure in Table 1 and Figure 5. The concentration of toluene in CO_2 is constant for each experiment, but varies slightly for different experiments as shown in Table 1. Because the mole fraction of CO_2 approaches unity, its partial pressure approaches the total pressure. At 35°C, the sorption decreases rapidly with pressure from

Table 1. Sorption of Toluene in the Carbon Dioxide–Toluene–Silicone Rubber System*

35°C			70°C		
P bar	y_{toluene}	Sorption g/g Polymer	*P* bar	y_{toluene}	Sorption g/g Polymer
40.5	0.00137	0.06427	40.5	0.00139	0.01535
60.8	0.00137	0.04390	60.8	0.00139	0.01580
60.8	0.00137	0.04694	70.9	0.00139	0.01534
60.8	0.00139	0.04245	81.0	0.00139	0.01381
70.9	0.00141	0.03012	101.3	0.00139	0.00706
70.9	0.00141	0.03159	121.6	0.00139	0.00735
81.0	0.00141	0.00910	141.8	0.00139	0.00601
81.0	0.00141	0.00871	202.6	0.00139	0.00421
81.0	0.00132	0.00762			
101.3	0.00132	0.00662			
101.3	0.00141	0.00583			
101.3	0.00141	0.00683			
121.6	0.00141	0.00680			
121.6	0.00132	0.00718			
141.8	0.00132	0.00715			
141.8	0.00141	0.00634			
141.8	0.00141	0.00664			
202.6	0.00139	0.00490			
253.3	0.00139	0.00537			

*Determined using inverse supercritical fluid chromatography (frontal analysis)

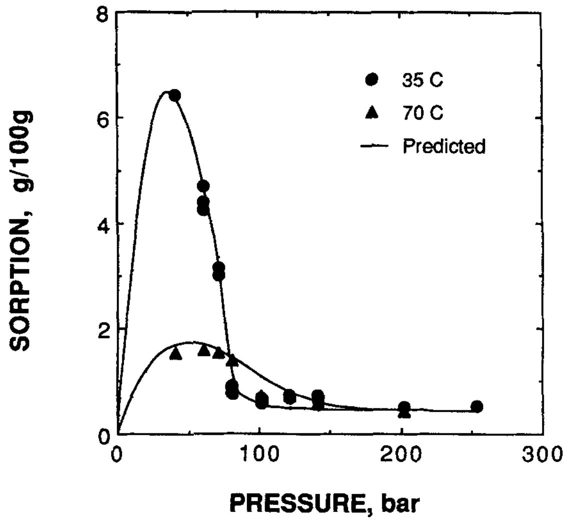

Figure 5. Pronounced pressure effect on sorption of toluene in silicone rubber, expressed in g of toluene/100 g of polymer.

In each case, the toluene concentration is approximately 0.14 mol % in the fluid phase (Table 1) so that the pressure in the system is very close to the partial pressure of CO_2.
—— predicted using $\chi_{12} = 1.30$, $\chi_{13} = f(T, \Phi_1)$ (Eqs. 17 and 18), and $\chi_{23} = 0.65$.

40 to 100 bar where the fluid is highly compressible. The variable solvent density (and thus solvent strength) of the SCF causes this interesting adjustability of the sorption. At higher pressures where the variation in fluid density with pressure is small, the sorption is relatively constant. This adjustability is also present for the adsorption of benzene and *n*-hexane on styrene/divinylbenzene resins (King, 1987). At 70°C, the pressure effect is significantly smaller, which may be expected since the change in the density of the fluid with pressure is also much smaller. A phase equilibria model will be developed in order to explain these results more fully.

Theory

The phase equilibria may be described conveniently by choosing an ideal gas reference state for the SCF and a pure liquid (or hypothetical pure liquid) standard state for the solvent in the polymer. The activity of component i in the polymer is defined as follows (Prausnitz et al., 1986):

$$\mathcal{A}_i = \Gamma_i \Phi_i = \frac{y_i \phi_i P}{P_i^{sat} \phi_i^{sat} \exp\left(\dfrac{\bar{v}_i^P (P - P_i^{sat})}{RT}\right)} \tag{2}$$

where

Φ_i = volume fraction of component i
Γ_i = activity coefficient based on volume fraction units
y_i = mole fraction in the fluid phase (unity for a pure solvent)
ϕ_i = fugacity coefficient
P_i^{sat} = vapor pressure which may be extrapolated above the critical pressure if necessary
ϕ_i^{sat} = fugacity coefficient at the vapor pressure
$\bar{v}_i^P$ = partial molar volume of i in the polymer phase

The determination of the nonidealities in the fluid phase, as described by ϕ_i, and in the polymer phase by Γ_i is the key challenge, while the other properties are relatively straightforward.

To describe the polymer phase, we adopted Flory's (1969) theory for the free energy of mixing of a cross-linked polymer with a solvent. It consists of an entropic term, an enthalpic term which includes a Flory interaction parameter, χ, and the elastic free energy for the expansion of the network structure. For a binary system, the activity of the solvent, 1, in a cross-linked polymer, 3, (component designation 2 is reserved for ternary systems containing two penetrants) is obtained by differentiating the free energy of mixing with the result

$$\ln \mathcal{A}_1 = \ln(1 - \Phi_3) + (1 - 1/x)\Phi_3 + \chi_{13}\Phi_3^2 + v_1(\nu_e/V_0)(\Phi_3^{1/3} - \Phi_3/2) \tag{3}$$

where

Φ_3 = volume fraction of polymer
x = ratio of the molar volumes of polymer to solvent
v_1 = molar volume of solvent
ν_e = effective number of chains in the network, mol
V_0 = volume of unswollen polymer

For a ternary system, the activities of the two penetrants, 1 and 2, in cross-linked polymer, 3, are described as follows (Flory, 1969)

$$\begin{aligned}\ln \mathcal{A}_1 = {} & \ln \Phi_1 + (1 - \Phi_1) - \Phi_2(v_1/v_2) \\ & + (\chi_{12}\Phi_2 + \chi_{13}\Phi_3)(\Phi_2 + \Phi_3) \\ & - \chi_{23}(v_1/v_2)\Phi_2\Phi_3 + v_1(\nu_e/V_0)(\Phi_3^{1/3} - \Phi_3/2)\end{aligned} \tag{4}$$

$$\begin{aligned}\ln \mathcal{A}_2 = {} & \ln \Phi_2 + (1 - \Phi_2) - \Phi_1(v_2/v_1) \\ & + (\chi_{21}\Phi_1 + \chi_{23}\Phi_3)(\Phi_1 + \Phi_3) \\ & - \chi_{13}(v_2/v_1)\Phi_1\Phi_3 + v_2(\nu_e/V_0)(\Phi_3^{1/3} - \Phi_3/2)\end{aligned} \tag{5}$$

The χ_{ij}'s are related by

$$\chi_{ji} = \chi_{ij}(v_j/v_i) \tag{6}$$

To describe a binary mixture in the fluid phase, we chose the Peng-Robinson equation of state (1976) where

$$\ln \phi_i = \frac{b_i}{b}(Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B}\left(\frac{2\sum_j y_j a_{ji}}{a} - \frac{b_i}{b}\right) \ln\left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B}\right) \tag{7}$$

and

$$A = \frac{aP}{R^2T^2} \tag{8}$$

$$B = \frac{bP}{RT} \tag{9}$$

$$Z = \frac{Pv}{RT} \tag{10}$$

The mixture parameters are defined by the mixing rules

$$a = \sum_i \sum_j y_i y_j a_{ij} \tag{11}$$

$$b = \sum_i y_i b_i \tag{12}$$

where

$$a_{ij} = (1 - k_{ij})(a_{ii}a_{jj})^{1/2} \tag{13}$$

These equations may be used to predict volume fractions and thus the degree of sorption of each penetrant in the polymer, given the three binary Flory interaction parameters for the polymer phase and k_{12}.

The equilibrium distribution coefficient of a penetrant may be defined as a ratio of the concentration in the polymer phase to that in the fluid phase,

$$K_i = \frac{C_i^p}{C_i^f} = \frac{\Phi_i \rho_i^p}{y_i \rho^f} \tag{14}$$

where ρ_i^p is the molar density of i in the polymer phase which is approximated as that of pure (hypothetical) liquid i, and ρ^f is the molar density of the fluid phase. The distribution coefficient may be expressed by substituting Eq. 2 into Eq. 14 to give

$$K_i = \frac{\rho_i^p}{\rho^f} \frac{\phi_i P}{\Gamma_i P_i^{\text{sat}} \phi_i^{\text{sat}} \exp\left(\dfrac{\bar{v}_i^p (P - P_i^{\text{sat}})}{RT}\right)} \tag{15}$$

Discussion

CO_2-silicone rubber system

The silicone rubber swelling data in Figure 4 are represented accurately over the entire pressure range by the above theory. The phase equilibria is described by Eq. 2; the nonidealities in the polymer phase by the Flory equation (Eq. 3); and the nonidealities in the vapor phase by the Peng-Robinson equation of state (Eq. 7). The ϕ of pure CO_2 was also calculated using a more rigorous equation of state (Ely, 1986); however, there was only a minor difference, typically 1%. In order to describe the standard state fugacity of pure hypothetical liquid CO_2 in the polymer phase, the vapor pressure was extrapolated beyond the critical temperature, 31°C, up to 70°C using a linear relationship for ln P^{sat} vs. $1/T$. The density of the clear silicone rubber was 1.1 g/cm^3. The effective molar cross-link density of the silicone rubber, $v_e/V_0 = 4.79 \times 10^{-4}$ gmol/cm^3, was determined by Eq. 3 (where the subscript 2 is substituted for 1), a swelling measurement for silicone rubber in toluene, and a χ_{23} measured by Kuwahara et al. (1968). Given the assumption that the excess volume of mixing is zero in the polymer phase (Fleming and Koros, 1986), the relationship between volume fraction of CO_2 and swelling, $\Delta V/V_0$, is

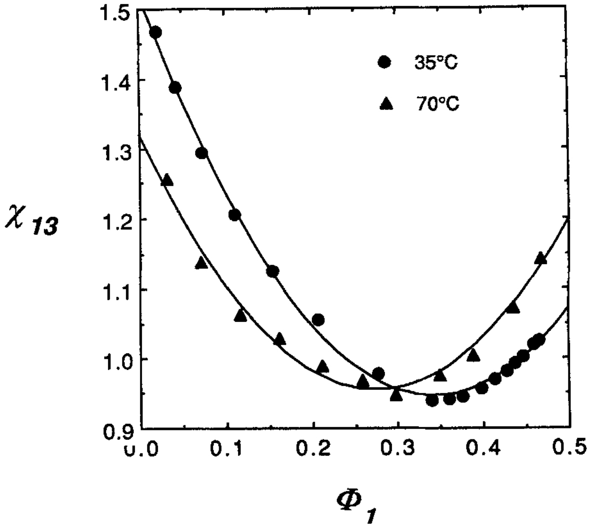

Figure 6. CO_2-silicone rubber Flory interaction parameter as a function of volume fraction for the crosslinked silicone rubber-carbon dioxide system.

$$\Phi_1 = \frac{\Delta V/V_0}{\Delta V/V_0 + 1} \tag{16}$$

The Flory interaction parameters, χ_{13}'s, were regressed from the data and are given by the quadratic functions (see Figure 6)

$$\chi_{13}(35°\text{C}) = 1.525 - 3.380\Phi_1 + 4.935\Phi_1^2 \tag{17}$$

and

$$\chi_{13}(70°\text{C}) = 1.320 - 2.656\Phi_1 + 4.816\Phi_1^2. \tag{18}$$

The swelling data in Figure 4 are complex in that the isotherms are sigmoidal and have different curvatures. They may be represented in a much simpler manner as a function of CO_2 activity (see Eq. 2) as shown in Figure 7. Not only does this activity representation eliminate the complex sigmoidal behavior, but it also removes temperature effects. At a given carbon dioxide activity, the swelling is relatively temperature-insensitive, as was observed in the case of glassy polymers (Berens and Huvard, 1989). Since the volume fraction, Φ_1, does not change with temperature for a given value of a_1, the activity coefficient, Γ_1, is independent of temperature (see Eq. 2). Consequently, the excess enthalpy vanishes. This simple activity representation of swelling is clearly more useful for interpolating and extrapolating data with respect to temperature and pressure than the pressure representation. For this reason, as well as the fact that it is straightforward to calculate the activity of a pure hypothetical liquid, we recommend the activity representation highly.

The reason why the pressure and activity representations of swelling are so different may be understood by examining pressure effects on the activity of CO_2. The activity of CO_2 is plotted against pressure for two temperatures in Figure 8. At low pressures below about 20 bar, ϕ is very close to unity and the Poynting correction is essentially constant, so that the activity is essen-

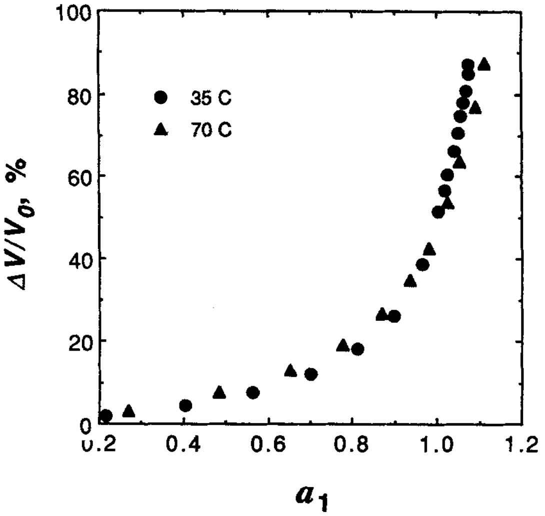

Figure 7. Swelling of silicone rubber vs. activity of pure carbon dioxide.

tially linear in pressure (see Eq. 2). Most previous studies of swelling examined this linear region. At higher pressures, the slope of the activity decreases because of a decrease in ϕ (see Figure 9) and an increase in the Poynting correction. In summary, swelling is quite different in gases and SCF's as a function of pressure, but is very similar as a function of activity. For glassy polymers, it will be necessary to treat additional factors, such as depressions in glass transition temperatures due to sorption of the SCF.

CO_2-toluene-silicone rubber system

The sorption of toluene and likewise its distribution coefficient between silicone rubber and CO_2 are quite different at gaseous and SCF conditions. Although the sorption data appear to be quite complex, they may be predicted quantitatively using the Flory model, along with a suitable description of the SCF phase, for example, the Peng-Robinson equation of state. The calculation procedure begins with the determination of a_1 and a_2 derived from Eq. 2. Assuming that the sorption of CO_2 is not affected by the presence of dilute toluene, the volume fractions of CO_2 and toluene are given by

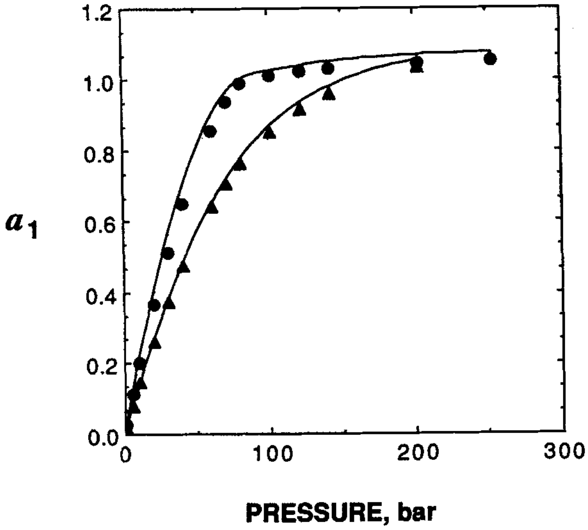

Figure 8. Calculated activities of CO_2 as a function of pressure.

● 35°C, Eq. 4; ▲ 70°C, Eq. 4; ——— Eq. 2.

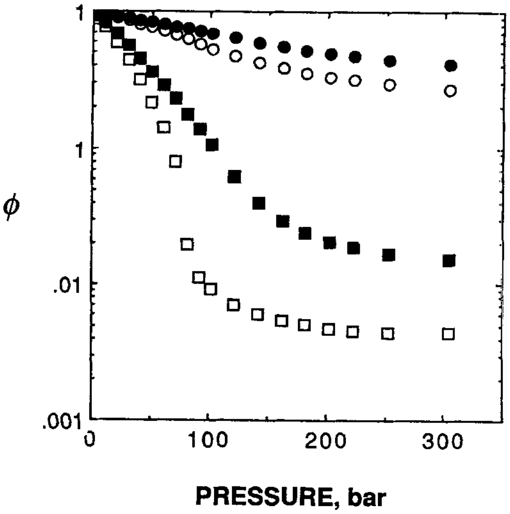

Figure 9. Fugacity coefficients of CO2 and toluene calculated using Peng-Robinson equation of state.

○ Pure CO_2, 35°C; ● Pure CO_2, 70°C; □ Toluene (y_2 = 0.0014), 35°C; ■ Toluene (y_2 = 0.0014), 70°C

$$\Phi_1 = \frac{\Delta V/V_0}{\Delta V/V_0 + S_2(\rho_3/\rho_2) + 1} \tag{19}$$

and

$$\Phi_2 = \frac{S_2(\rho_3/\rho_2)}{\Delta V/V_0 + S_2(\rho_3/\rho_2) + 1} \tag{20}$$

where S_2 is the sorption in grams of toluene per gram of polymer, ρ_2 is the density of toluene, and ρ_3 is the density of silicone rubber. Equations 19 and 20 are substituted into Eqs. 4 and 5 along with the molar volume of CO_2, which is approximated at its average partial molar volume in organic liquids, 46.2 cm^3/mol (Fleming and Koros, 1986). The experimental values of $\Delta V/V_0$ for the binary CO_2-silicone rubber system are used in Eqs. 19 and 20. The value of S_2 is optimized based on the intersection of Eqs. 4 and 5.

The Flory parameters were determined from binary data in the literature. The CO_2-toluene interaction parameter, χ_{12} = 1.30, was optimized from VLE data of Ng and Robinson (1978) using their value of k_{12}, 0.090. The value of χ_{21} was determined by Eq. 6. The experimental data of Kuwahara et al. (1968) were used to determine the optimum value of χ_{23}, which is 0.65. The value of χ_{13} is the same as above for the CO_2-silicone rubber binary system.

The model predicts the complex sorption behavior of toluene remarkably well using the above three binary Flory interaction parameters, without any ternary data (Figure 5). The average absolute deviations for the model are 16% and 11% at 35°C and 70°C, respectively. Since ternary and multicomponent data are rarely available, this predictive approach requiring only binary data is highly useful.

A physical picture will be developed to describe the unusual shape of the sorption vs. pressure isotherms, by examining the phase equilibrium relationship, Eq. 2. The analysis is simplified by the constraint that the toluene mole fraction in the fluid phase, y_2, is constant. In summary, the sorption increases linearly with pressure at ideal gas conditions, but decreases at higher pressures as the fugacity coefficient of toluene in the fluid phase is decreased dramatically by interactions with the dense solvent.

The activity of toluene $\mathcal{A}_2$ is a convenient function for understanding the shape of the sorption isotherm. As shown in Figure 10, the shape of $\mathcal{A}_2$ vs. P resembles closely that of sorption vs. pressure. The pressure dependence of $\mathcal{A}_2$ is due to the factor $\phi_2 P$ in the fluid phase, and the Poynting correction in the liquid phase (Eq. 2). The effect of the Poynting correction is minor, that is a factor of about two over the entire pressure range. The fugacity coefficient of toluene, ϕ_2, is plotted against pressure in Figure 9. At low pressures below 20 bar, both ϕ_2 and the Poynting correction are close to unity. Here the activity of toluene increases linearly with the partial pressure. As pressure increases, the interactions between toluene and CO_2 become progressively more important so that ϕ_2 decreases rapidly. The decrease in ϕ_2 becomes more rapid than the increase in P, so that the activity goes through a maximum and then decreases. Eventually at the highest pressures, the decrease in ϕ_2 and thus in $\mathcal{A}_2$ become relatively small. Because ϕ_2 is a key property that influences the activity, it will be examined in greater detail.

The pressure effect on toluene's fugacity coefficient in the fluid phase, ϕ_2, is described thermodynamically by the partial molar volume $\bar{v}_2^f$. The pressure derivative of ln ϕ_2 (Prausnitz et al., 1986) is:

$$(\partial \ln \phi_2/\partial P)T, y = \bar{v}_2^f/RT - 1/P \qquad (21)$$

It has been demonstrated experimentally and explained theoretically (Eckert et al., 1986; Kim et al., 1985; Debenedetti, 1987; Kumar and Johnston, 1988) that $\bar{v}_2^f$ for a solute such as naphthalene at infinite dilution in ethylene reaches thousands of mL/mol negative in the highly compressible region of the solvent. It reaches negative infinity at the critical point. This explains the huge decrease in ϕ_2 with respect to pressure in the critical region at 35°C (Figure 9). Here the density increases strongly with pressure, which increases the number of solute-solvent interactions. At 70°C, the isothermal compressibility and the magnitude of $\bar{v}_2^f$ are smaller (Eckert et al., 1986; Kim et al., 1985), thus the changes in ϕ_2 and $\mathcal{A}_2$ are less pronounced.

The maximum in the activity of toluene may be determined by differentiating Eq. 2 and substituting Eq. 21 with the result

$$(\partial \ln a_2/\partial P)_{T,y_2} = \frac{\bar{v}_2^f - \bar{v}_2^p}{RT} \qquad (22)$$

The partial molar volume of toluene in the polymer phase $\bar{v}_2^p$ is relatively constant. In the limit of zero pressure, $\bar{v}_2^f$ is positive infinity, but it decreases sharply with pressure not far below the critical pressure (Eckert et al., 1986), intersecting the point where $\bar{v}_2^f = \bar{v}_2^p$. Here the activity goes through a maximum (Figure 10). For similar reasons, the solubility of a pure solid in a SCF goes through a minimum in this pressure range at the point where $\bar{v}_2^f$ equals the molar volume of the solid (Kurnik and Reid, 1981). Because $\bar{v}_2^f$ is such a strong function of pressure in this region, the activity decreases rapidly on each side of the maximum. At higher pressures where the fluid becomes much less compressible, the magnitude of $\bar{v}_2^f$ becomes so small that ϕ_2 and thus a_2 become much less pressure-sensitive.

The remaining property in Eq. 2 which needs to be addressed is the activity coefficient of toluene, Γ_2. The Flory model, Eq. 5, may be used to calculate Γ_2 ($=\mathcal{A}/\Phi_2$) as shown in Figure 11. Γ_2 is defined at the vapor pressure, so that it is not an explicit function of pressure (see Prausnitz et al., 1986, Ch. 10). However, Γ_2 does change with pressure, because the volume fractions are a function of pressure. As the volume fraction of toluene goes to zero at zero pressure, Γ_2 is the furthest from unity. The effect of pressure on Γ_2 is not nearly as dramatic as that on ϕ_2. As a result, the shapes of the $\mathcal{A}_2$ and Φ_2 ($=\mathcal{A}_2/\Gamma_2$) isotherms are similar as a function of pressure. This characteristic shape is found also for the sorption isotherm since sorption is related closely to Φ_2 (Eq.

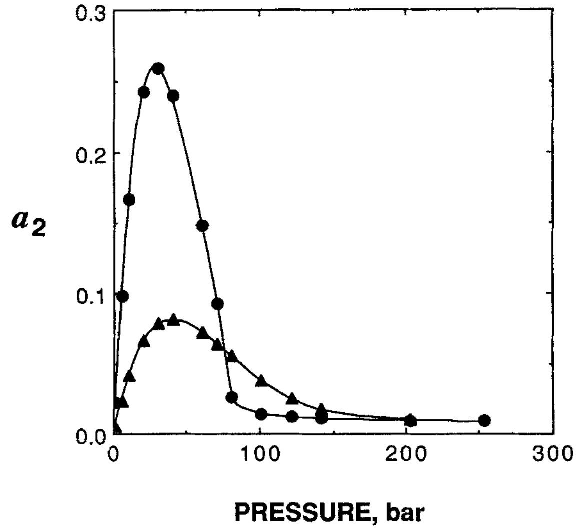

Figure 10. Calculated activity of toluene as a function of pressure.

● 35°C, Eq. 5; ▲ 70°C, Eq. 5; ——— Eq. 2.

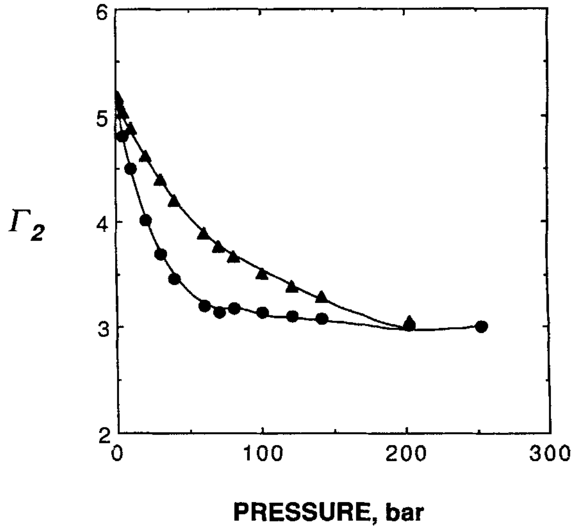

Figure 11. Calculated activity coefficient of toluene vs. pressure.

● 35°C, Eq. 5; ▲ 70°C, Eq. 5; ——— Eq. 2.

20). Even though the shape of the sorption isotherm is influenced primarily by the nonidealities in the fluid phase, it is important to have a reliable model for Γ_2, such as the Flory equation, in order to predict the magnitude with good accuracy.

The distribution coefficient for toluene, K_2, defined by Eqs. 14 and 15, is shown as a function of pressure in Figure 12. At 35°C, the distribution coefficient decreases about two orders of magnitude for a pressure increase from 40 to 100 bar. As discussed previously, this may be attributed to the large decrease in ϕ_2 in the fluid phase caused by the large increase in density (Eq. 15). In contrast, the distribution coefficient of CO_2 is rather invariant up to 250 bar, since ϕ_1 is less variable. The distribution coefficients are much higher for toluene, primarily because its saturation pressure is about 1,000 times smaller than CO_2's. This difference in the K's diminishes at the higher pressures (densities) as ϕ_2 decreases, because of an increase in the number of toluene-CO_2 interactions.

It is reasonable to use the model to extrapolate to higher toluene concentrations, since the infinite dilution state is the most nonideal. This philosophy is practiced commonly for vapor-liquid equilibria. Equilibrium tie-lines are predicted for other toluene concentrations in Figure 2, which are indicated as dashed lines with at least one open-circle endpoint. For example, at 100 bar the toluene concentrations are 13.1 wt. % in the polymer and 18.9 wt. % in the fluid phase. The model may also be used to predict the composition of the polymer phase in the three-phase region at a given pressure. Since the fluid and liquid phases do not contain the cross-linked polymer, their compositions are governed by binary liquid-fluid equilibria as shown. The composition of the polymer phase was predicted given the composition of toluene in the fluid phase at saturation. This point on the three-phase boundary represents the maximum loading of the solute into the polymer from a single SCF phase. At 40 bar, the predicted concentrations of toluene and CO_2 at the three-phase boundary are 29.4 wt. % and 6.7 wt. %, respectively. At 70 bar, the magnitude of these concentrations are reversed, that is 3.5 wt. % and 24.1 wt. %. These kinds of changes occur in SCF's because of large pressure effects on density and fugacity.

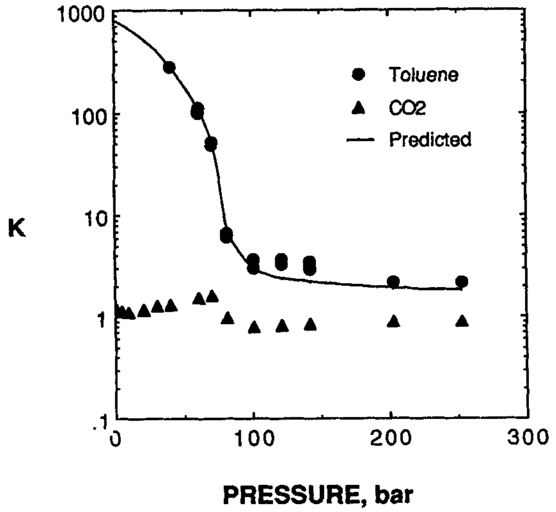

Figure 12. Pronounced pressure effect on the distribution coefficients, $K_i = C_i^{polymer}/C_i^{fluid}$, of CO_2 and toluene.

—— predicted using Eqs. 2–14

Conclusions

The sorption of pure carbon dioxide in silicone rubber may be represented more simply and accurately against CO_2 activity than pressure. The swelling behavior of silicone rubber in the presence of SCF carbon dioxide may be correlated from 0 to 315 bar using the Flory equation for the polymer phase and an appropriate equation of state for the fluid phase.

For systems consisting of a dilute solute in CO_2, the inverse supercritical fluid chromatography technique provides accurate sorption data particularly in the desorption mode. The results are novel and interesting in that the degree of sorption and likewise the distribution coefficient are extremely sensitive with respect to pressure. At low pressures, the gas phase is nearly ideal and the sorption increases linearly with the partial pressure. As the gas density increases, the sorption goes through a maximum and then decreases rapidly as the solvent strength becomes significant, so that the fugacity coefficient of toluene decreases sharply with pressure. This is another manifestation of the pronounced partial molar volumes of solutes which occur in the critical region of the solvent. It is evident that the unusual shape of the sorption curve is due primarily to pronounced pressure effects in the fluid phase, and to a much lesser extent to interactions in the polymer phase. Nevertheless, it is important to use an appropriate model for the polymer phase in order to obtain the correct magnitude of the sorption. The model, which consists of the Flory equation for the polymer phase and the Peng-Robinson equation for the fluid phase, predicts quantitatively the sorption of toluene over a considerable range in pressure, temperature, and composition using only binary interaction parameters.

These results indicate that pressure as well as temperature may be used to adjust the level of impregnation of a solute. For solutes with low solubilities in carbon dioxide, the pressure may have to be optimized to achieve significant solubility in the fluid phase while maintaining a desirable value of the sorption. An alternative, which has been explored elsewhere (Berens et al., 1988), would be to use a SCF to swell a polymer which is submerged in a pool of liquid containing the impregnant without the need to solubilize the impregnant into the fluid phase. For the removal of volatile impurities such as toluene, it is not necessary to increase the pressure much above 100 bar since the distribution coefficient becomes relatively constant.

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Notation

a = intermolecular attraction parameter
$\mathcal{A}$ = activity
b = intermolecular repulsion parameter
C = concentration
k = binary interaction parameter
l = length of polymer
S_2 = sorption of toluene, g/g of silicone rubber
V = volume of polymer

$\bar{v}$ = partial molar volume
x = molar volume ratio of polymer to solvent
y = mole fraction in the fluid phase
Z = compressibility factor

Greek letters

χ = Flory interaction parameter
Φ = volume fraction
ϕ = fugacity coefficient
Γ = activity coefficient of the solvent or solute based on volume fraction
ν_e = effective number of chains in the network polymer, mol

Superscripts

f = fluid phase
p = polymer phase
sat = saturated state

Subscripts

0 = unswollen state
1 = solvent (CO_2)
2 = solute (toluene)
3 = polymer (silicone rubber)
i, j = component designations

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