Molecular Thermodynamics of Solute-Polymer-Supercritical Fluid Systems

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The distribution coefficients of the solutes (toluene, naphthalene, and phenanthrene) are reported at infinite dilution between silicone rubber and supercritical-fluid carbon dioxide. A new technique is described in which a thin film of polymer is coated and cross-linked onto silica, and the distribution coefficient is measured rapidly by elution supercritical-fluid chromatography. Because CO_2 significantly enhances the solute's volatility and its diffusion coefficient in the polymer, it is possible to study solute-polymer interactions at room temperature for nonvolatile compounds which would be difficult to study by conventional techniques such as gas chromatography. These infinite dilution data are used to determine solute-polymer interaction parameters to calculate phase diagrams over a wide concentration range. The residual, combinatorial, and cross-link contributions to the solute activity coefficient in the polymer are discussed as a function of concentration. In addition, pronounced pressure and temperature effects are described in terms of experimentally measured solute partial molar volumes (to -14 L/mol) and partial molar enthalpies (to -850 kJ/mol) in the fluid phase.

Introduction

Several recent studies in supercritical fluid (SCF) science and technology have focused on the influence of a fluid on a polymeric condensed phase (Liau and McHugh, 1985; Fleming and Koros, 1986; Wissinger and Paulaitis, 1987; Ziger, 1987; Berens and Huvard, 1989; Shim and Johnston, 1989, 1991). Often the polymer is insoluble in SCF CO_2. At supercritical conditions where the activity of CO_2 is large, it swells certain polymers significantly and can depress glass transition temperatures. Because CO_2 is a small linear molecule, it diffuses more quickly than conventional liquid solvents in polymers, so that the swelling is more rapid. Swelling facilitates the diffusion of a solute, which in a practical application may be an impurity to be extracted from or an additive to be impregnated into a polymer (Berens et al., 1988). Other desirable features of CO_2 are that it is released rather rapidly and fully from the polymer after depressurization, and it is less toxic than most liquid solvents. Potential applications include impregnation of polymers for controlled release, extraction of pollutants from adsorbents (Roop et al., 1989; King et al., 1988), purification of specialty polymers, for example, for biomedical or electronic applications and the UNICARB spray process (Hoy and Donohue, 1990). However, the development has been hindered by a lack of understanding of the phase behavior and transport properties in these systems.

The concept of polymer impregnation was advanced markedly by Berens et al. (1988) who measured solubility and transport data for an additive in polymer-CO_2 systems by a gravimetric method. For this purpose, it was necessary to measure the degree of solubilization only in the polymer phase. Since composition was not reported in the other phase or phases, the phase equilibria were unknown.

Studies of phase equilibria at supercritical conditions have examined low-molecular-weight components to a much greater extent than those of polymers. This is due in part to experimental challenges. Our objective has been to develop efficient experimental techniques and predictive theoretical models to determine distribution coefficients of solutes between polymers and CO_2. In this article, distribution coefficients at infinite dilution are reported for the determination of interaction parameters which are then used to calculate phase diagrams over wide concentration ranges.

In our first article in this series (1989), distribution coefficients of toluene between CO_2 and 250-μm-thick spiral-wound strips of silicone rubber were measured at finite concentration

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by supercritical fluid chromatography (SFC). This was done with a frontal analysis technique, in which the polymer is saturated with a known concentration of solute in CO_2, and the amount of solute is determined accurately during desorption with pure CO_2. Because the polymer was neat and not coated on a support, errors due to adsorption were minimal; however, rates were slow due to the large thickness of the polymer strips. An important result is that the distribution coefficient may be varied over a wide range with temperature and pressure because of the adjustable nature of the solvent strength of the supercritical fluid (SCF). This variability is due primarily to pronounced solute partial molar volumes (Eckert et al., 1986) and enthalpies (Shim and Johnston, 1991), a result of the large compressibility of the fluid. Simple linear correlations have been developed for $\ln K$ vs. $\ln \rho$ at constant T and vs. $1/T$ at constant ρ (Shim and Johnston, 1991).

A more rapid method for determining solute thermodynamic properties is supercritical-fluid chromatography by an elution technique. The solute must be infinitely dilute, otherwise the interpretation of the data may be expected to be quite complex at supercritical-fluid conditions (Conder and Young, 1979). Here, the polymer in the stationary phase is saturated with CO_2, and a small pulse of solute is injected. Mostly, all of the previous SFC studies have reported results in terms of the capacity factor of a solute, $k_i = (t_i - t_o)/t_o$, where t_i and t_o are the retention times of the solute and an unretained species, respectively. Unfortunately, the distribution coefficient is unknown because the volumes of the mobile and stationary phases were not measured. An exception is the work of Shim and Johnston (1991), performed with a commercial octadecylsilica column, in which the swelling and thus the phase volumes were determined. Another limitation is that the retention mechanism is typically an unknown combination of adsorption on the support and partitioning into the bulk liquid phase. This study corrected the retention to remove the unwanted contribution due to adsorption on the silica support.

The purpose of this study is to utilize the above experimental advancements to study molecular interactions between a solute and a polymer of interest, instead of a commercially prepared stationary phase. This may be called inverse SFC (ISFC) by analogy with inverse gas chromatography (Lloyd et al., 1989). Here, inverse means that the attention is focused on the polymer liquid stationary phase, not on peak separation. The stringent test of Conder and Young (1979) is used to distinguish between adsorption vs. partitioning, by varying the amount of liquid (polymer) loading on the support. Silicone rubber was chosen since it is a relatively inert material; and unlike glassy polymers, it is at equilibrium which facilitates theoretical analysis (Fleming and Koros, 1986). Also, this allows for comparison with previous data at finite concentration (Shim and Johnston, 1989). A new coating method is introduced, in which the polymer is cross-linked on the silica. A variety of thermodynamic properties are reported: the polymer-solute interaction parameter, other solute properties in the polymer phase including the equilibrium distribution coefficient, activity coefficient, and Henry's constant, and finally the solute partial molar volume and partial molar enthalpy at infinite dilution in the fluid phase. The experimental results are utilized in a phase equilibria model to calculate ternary-phase diagrams over a wide concentration range.

Recently, SFC has been used to study sorption at finite concentration with isotope tracers (Strubinger et al., 1990; Yonker and Smith, 1990). This technique provides a powerful means to investigate multicomponent systems over wide concentration ranges; however, there are differences in the results compared with other methods which will be discussed.

Theory

Theoretical models have been developed to calculate capacity factors in SFC (for an adsorption mechanism) over a wide range including the interesting retrograde region (Kelley and Chimowitz, 1990; Grover and Chimowitz, 1990). In the present study, the inverse problem is investigated: the determination of thermodynamic properties from SFC. The equilibrium-phase behavior may be calculated in terms of the relevant intermolecular interaction parameters. At equilibrium, the fugacity of the solute, f_2, is equal in each phase. For the fluid phase, we choose the ideal gas reference, thus

$$f_2^F = y_2 \phi_2 P \tag{1}$$

The Peng-Robinson equation of state, with quadratic mixing rules for both the size and attractive parameters, is used to calculate ϕ_2, based on a large number of investigations reviewed elsewhere (Brennecke and Eckert, 1989; Johnston et al., 1989b). For the liquid phase which contains the polymer, we consider two standard states. For the pure solute standard state, the fugacity may be expressed as:

$$f_2^L = \Phi_2 \Gamma_2 P_2^{\text{sat}} \phi_2^{\text{sat}} \exp\left[\frac{\bar{v}_2^L (P - P_2^{\text{sat}})}{RT}\right] \tag{2}$$

where Φ_2 is the volume fraction, Γ_2 is the activity coefficient and $\bar{v}_2^L$ is the partial molar volume of the solute in the liquid phase. For the infinite dilution standard state,

$$f_2^L = \Phi_2 H_2(P^o) \exp\left[\frac{\bar{v}_2^L (P - P^o)}{RT}\right] \tag{3}$$

where $H_2(P^o)$ is the Henry's constant defined at the reference pressure, 1.013 bar (1 atm). Here, the solute is at infinite dilution, although CO_2 is at finite concentration. This standard state is useful particularly for low concentrations and for solids with high melting points, since their vapor pressures may be unknown.

A key challenge in applying Eq. 2 is the determination of Γ_2 in a ternary system. This may be accomplished with the Flory equation (1 = fluid, 2 = solute and 3 = cross-linked polymer)

$$\ln \Gamma_2 = (1 - \Phi_2) - \Phi_1 (v_2/v_1) + (\chi_{21}\Phi_1 + \chi_{23}\Phi_3)(\Phi_1 + \Phi_3) - \chi_{13}(v_2/v_1)\Phi_1\Phi_3 + v_2(\nu_e/V_0)(\Phi_3^{1/3} - \Phi_3/2) \tag{4}$$

where v is the molar volume, χ is the Flory interaction parameter, ν_e is the effective number of chains in the network expressed in moles, and V_0 is the volume of the unswollen polymer. For a solute at infinite dilution, Φ_2 approaches zero and this equation is reduced to

$$\ln \Gamma_2^{\infty} = 1 - \Phi_1 (v_2/v_1) + \chi_{21}\Phi_1 + \chi_{23}\Phi_3 - \chi_{13}(v_2/v_1)\Phi_1\Phi_3 + v_2(\nu_e/V_0)(\Phi_3^{1/3} - \Phi_3/2) \tag{5}$$

A similar a relationship may be written for the fluid solvent, CO_2.

The chromatographic data may be used to determine Γ_2, given the Peng-Robinson equation for the nonidealities in the fluid phase, i.e., ϕ_2. The capacity factor of the solute, k_2, is defined as the molar ratio of solute between the liquid (stationary) and fluid (mobile) phases,

$$k_2 = \frac{n_2^L}{n_2^F} = \frac{C_2^L}{C_2^F} \cdot \frac{V^L}{V^F} = \frac{t_2 - t_0}{t_0} \tag{6}$$

where V^L and V^F are the volumes of the liquid and fluid phases, respectively, t_2 is the retention time of the solute, t_0 is that of a marker that has minimal retention. This equation may be derived from chromatographic theory for a single-species partitioning between the phases at infinite dilution. However, it is also applicable to the case where the carrier fluid concentration is at steady state in both phases and the solute is at infinite dilution (Haydel and Kobayashi, 1967; Conder and Young, 1979). The distribution coefficient of a solute is given by

$$K_2 = c_2^L / c_2^F = k_2 V^F / V^L \tag{7}$$

It is important to note that it is necessary to know the phase ratio to calculate the intensive property K_2 from the extensive property k_2. Unfortunately, almost all of the SFC literature gives only k_2, since the effect of swelling on the phase ratio was neglected.

The distribution coefficient may be expressed in terms of volume fraction units instead of concentration units if it is assumed that the volume of mixing is zero in the liquid phase. The resulting expression

$$K_2 = \frac{\Phi_2 / v_2^L}{y_2 / v^F} \tag{8}$$

is used to relate the chromatographically measured property K_2 to the phase equilibria equations. For example, the combination of Eqs. 1, 2 and 8 yields:

$$\Gamma_2 = \frac{v^F}{v_2^L} \frac{\phi_2 P}{K_2 P_2^{sat} \phi_2^{sat} \exp\left[\frac{\bar{v}_2^L (P - P_2^{sat})}{RT}\right]} \tag{9}$$

and of Eqs. 1, 3 and 8 yields

$$H_2(P^0) = \frac{v^F \phi_2^\infty P}{K_2 v_2^L \exp\left[\frac{\bar{v}_2^{L\infty}(P - P^0)}{RT}\right]} \tag{10}$$

The chemical potential of a solute is a strong function of pressure and temperature in a highly compressible supercritical fluid, as described by solute partial molar volumes and enthalpies, respectively. These properties may be obtained quantitatively from SFC by the relationships (Shim and Johnston, 1991)

$$\bar{v}_2^{F,\infty} = \bar{v}_2^{L,\infty} + \kappa RT \{1 + \rho(\partial \ln K_2 / \partial \rho)_T\} \tag{11}$$

and

$$\bar{h}_2^{F,\infty} - h^{IG} = -\Delta h_2^{vap} - RT^2 [(\partial \ln K_2 / \partial T)_\rho - \beta\{1 + \rho(\partial \ln K_2 / \partial \rho)_T\}] \tag{12}$$

which are a refined version of earlier expressions based on the slopes of k_2. Better accuracy can be obtained from slopes of K_2 than k_2 since the phase ratio, V^F/V^L, changes with swelling, particularly in the highly compressible near critical region.

Experimental Technique

The experimental technique, which used a modified supercritical fluid chromatograph (Lee Scientific Inc., Model 501), has been described in detail (Shim, 1990; Shim and Johnston, 1991). The variation in k_2 was less than ±4% for flow rates from 0.05 to 0.4 mL/min (at column conditions), with a reproducibility in k_2 better than ±1%. The carrier gas, CO_2, containing a small amount of methane as a marker was used as the injection solvent. If a liquid were used as the injection solvent, errors would occur due to solvent-solute interactions in the column and to the large concentration perturbation (Conder and Young, 1979).

The liquid stationary phase, poly(dimethyl siloxane) (General Electric RTV 615 Silicone Rubber) was coated onto Vydac TP wide pore silica (300A pore size, 20–30 μm particle size). The silanol groups on the silica were deactivated with dimethylchlorosilane. Known amounts of two parts of the silicone rubber mixture (90 wt. % of part A and 10 wt. % of part B as a curing agent) were dissolved separately into toluene to make about a 1 wt. % polymer solution. To prevent cross-linking in the toluene solution, the solution was maintained at room temperature. A small amount of polymer solution was applied drop by drop onto the VYDAC TP silica while agitating the silica particles to help coat the silica uniformly. The silica particles were then dried at about 110°C for 20 minutes to evaporate toluene and to cross-link the polymer. These steps were repeated 15 to 20 times until the entire solution was consumed. Finally, the particles were baked at 110°C overnight to evaporate the remaining toluene and to complete the cross-linking. The stationary phase was packed into a stainless steel tubing of 25-cm-long and 1-mm inside diameter by gravity. Three columns were prepared with 8.0, 13.6 and 26.4 wt. % silicone rubber. Any remaining uncross-linked polymer was extracted with a continuous stream of high-pressure carbon dioxide at 250 bar and 110°C.

The amount of polymer on the silica support was analyzed with a Thermogravimetric Analyzer (Perkin-Elmer Model TGA 7). Weight reductions occurred in two different temperature ranges: from 30 to 200°C and from 250 to 900°C for all of the polymer loadings. The first weight loss was due to moisture, and the second to combustion of the coated polymer and unknown materials inside the silica. It was necessary to compensate for the fact that one of the combustion products SiO_2 is not volatilized. Finally, the swelling of the silicone rubber was measured at 50°C with a previously described visual technique (Shim and Johnston, 1989), and the uncertainty in V^F/V^L was 1%.

The solutes toluene (Aldrich Chemicals, glass-distilled HPLC grade 99.9%), naphthalene (Aldrich Chemicals, 99+%) and phenanthrene (Aldrich Chemicals, 98+%), and the marker, methane (Liquid Carbonic Inc., 99.97%) were used as received.

Table 1. Retention Time of Hydrocarbons on 13.6% Silicone Rubber/VYDAC TP Silica at 35.2°C and 78.3 atm

Hydrocarbons	Retention Time (min)
CH_4	3.81
C_2H_6	4.40
C_3H_8	4.81
$n-C_4H_{10}$	4.97
CH_2Cl_2	6.40

Results and Discussion

Experimental requirements for determining thermodynamic properties by inverse SFC

Several precautions must be taken to obtain reliable thermodynamic properties from SFC. To determine the capacity factor, it is important that the retention of the marker by the stationary phase is negligible. Since only combustible markers are appropriate for a flame ionization detector, retention times were measured for methane, ethane, propane, *n*-butane, and methylene chloride for a packed column containing 13.6% silicone rubber at 35.2°C and 78.3 atm. As shown in Table 1, methane is retained much less than the rest and was chosen for this study. It has only about half the retention of methylene chloride, which is consistent with a previous GC study (Parcher and Johnson, 1980). Although methylene chloride is used commonly as a marker as well as an injection solvent, this can lead to large errors, especially at high pressures where capacity factors are the smallest.

The unwanted contribution of adsorption to the capacity factor was removed by subtracting k_2 for bare deactivated silica from the k_2 for the polymer-coated, deactivated silica (Shim and Johnston, 1989). The correction was significantly larger for silicone rubber than C_{18} in the previous study, which decreases the experimental accuracy. For naphthalene, the contribution of bare silica was a little above half of the total retention (Shim, 1990). The values of k_2 and K_2 for toluene, naphthalene, and phenanthrene and listed in Tables 2–4.

Table 2. Thermodynamic Properties of Toluene at Infinite Dilution from SFC (Liquid Phase: 13.6% Silicone Rubber, Fluid Phase: CO_2)

P (bar)	k	K	$\bar{v}^{F\infty}$ (L/mol)	$\bar{h}^{F\infty}$(kJ/mol)
		at 35.2°C		
70.2	2.79	24.6	−0.942	−44.0
73.2	2.06	17.5	−1.36	−63.9
75.3	1.63	13.5	−1.87	−85.5
77.8	1.12	9.07	−3.31	−148.0
79.3	0.796	6.36	−5.20	−246.0
80.3	0.563	4.47	−6.19	−324.0
82.4	0.264	2.07	−3.54	−254.0
85.5	0.192	1.49	−1.16	−124.0
95.6	0.132	0.996	−0.200	−64.0
		at 50.1°C		
75.3	2.44	23.9	−0.486	−32.1
80.3	1.92	18.3	−0.631	−37.3
85.5	1.45	13.4	−0.817	−45.2
90.6	1.06	9.58	−1.04	−57.4
95.6	0.738	6.50	−1.28	−74.2
105.9	0.348	2.91	−1.15	−94.0
116.0	0.201	1.62	−0.569	−75.7
126.2	0.146	1.14	−0.249	−58.3
		at 70.0°C		
75.3	2.03	21.3	−0.148	−13.8
80.3	1.79	18.5	−0.202	−16.5
85.5	1.50	15.3	−0.257	−16.9
90.6	1.31	13.1	−0.312	−20.8
95.6	1.11	10.9	−0.367	−23.4
105.9	0.808	7.69	−0.475	−33.4
126.2	0.395	3.51	−0.555	−52.2
141.4	0.252	2.14	−0.417	−59.0
156.7	0.169	1.37	−0.245	−51.0

Table 3. Thermodynamic Properties of Naphthalene at Infinite Dilution from SFC (Liquid Phase: 8.0% Silicone Rubber, Fluid Phase: CO_2)

P (bar)	k	K	$\bar{v}^{F\infty}$ (L/mol)	$\bar{h}^{F\infty}$(kJ/mol)
		at 34.2°C		
75.3	4.57	66.0	−3.09	−135.0
77.8	2.28	32.3	−7.77	−354.0
79.4	0.919	12.8	−11.2	−632.0
80.4	0.500	6.95	−7.37	−502.0
82.4	0.309	4.25	−3.08	−280.0
85.5	0.238	3.23	−1.44	−176.0
95.6	0.157	2.07	−0.463	−108.0
105.8	0.133	1.72	−0.240	−88.4
126.2	0.104	1.29	−0.085	−75.3
		at 49.1°C		
90.6	2.82	44.4	−1.54	−88.4
95.6	1.77	27.2	−1.92	−114.0
105.8	0.570	8.31	−1.73	−141.0
116.0	0.277	3.91	−0.930	−117.0
126.2	0.206	2.82	−0.495	−98.1
156.7	0.120	1.53	−0.133	−73.1
		at 69.0°C		
95.6	3.77	64.2	−0.698	−51.5
105.8	2.19	36.2	−0.854	−61.6
126.2	0.766	11.8	−0.949	−83.6
141.4	0.416	6.16	−0.714	−86.0
156.7	0.261	3.71	−0.447	−79.1
207.6	0.122	1.54	−0.105	−65.2
		at 99.0°C		
95.6	3.12	56.6	−0.270	−27.1
105.8	2.40	42.5	−0.333	−31.8
126.2	1.40	23.9	−0.431	−42.9
156.7	0.584	9.43	−0.469	−56.2
177.1	0.364	5.69	−0.405	−63.8
207.6	0.206	3.07	−0.262	−66.1
258.5	0.107	1.49	−0.087	−57.0

Various techniques have been developed to measure the swelling of the stationary phase, which is needed to determine V^F/V^L. The swelling of a stationary phase in a capillary column may be measured on column, but this technique is only qualitative as discussed elsewhere (Strubinger and Parcher, 1989). Another possibility is to measure the weight change of the coated stationary phase with a quartz spring. Although this technique is appropriate for a pure polymer condensed phase (Wissinger and Paulaitis, 1987), we found it to be inaccurate for determining sorption into a coating that makes up only about 10% of the condensed phase. Perhaps the best way to determine the sorption of CO_2 into the polymer is tracer pulse chromatography. The weight percent sorption of CO_2 was measured in SE-30 for various pressures and temperatures including the critical region (Strubinger et al., 1990). Each isotherm went through a maximum which is expected for the Gibbs sorption, but not for absolute absorption. As pressure increases over this range, the fugacity of CO_2 increases mon-

Table 4. Thermodynamic Properties of Phenanthrene at Infinite Dilution from SFC (Liquid Phase: 8.0% Silicone Rubber, Fluid Phase: CO_2)

P (bar)	k	K	$\bar{v}^{F\infty}$ (L/mol)	$\bar{h}^{F\infty}$(kJ/mol)
		at 34.2°C		
75.3	34.2	495.0	−5.35	−230.0
77.8	11.6	165.0	−11.8	−547.0
79.4	33.49	55.9	−14.8	−850.0
80.4	1.88	26.1	−9.17	−636.0
82.4	1.05	14.4	−3.72	−348.0
85.5	0.754	10.2	−1.72	−220.0
95.6	0.453	5.98	−0.559	−136.0
105.8	0.353	4.56	−0.297	−113.0
126.2	0.267	3.32	−0.116	−97.2
156.7	0.207	2.48	−0.022	−86.6
207.6	0.147	1.68	0.040	−81.7
258.5	0.123	1.37	0.069	−78.0
		at 49.1°C		
90.6	21.8	343.0	−2.50	−144.0
95.6	10.0	153.0	−2.96	−179.0
105.8	2.38	34.8	−2.48	−209.0
116.0	0.946	13.3	−1.33	−171.0
126.2	0.582	7.95	−0.736	−139.0
156.7	0.270	3.45	−0.202	−102.0
207.6	0.170	2.01	−0.016	−86.2
258.5	0.116	1.31	0.043	−76.6
		at 69.0°C		
105.8	17.4	287.0	−1.49	−100.0
126.2	4.04	62.3	−1.42	−127.0
141.4	1.61	23.8	−1.02	−128.0
156.7	0.853	12.1	−0.661	−119.0
207.6	0.296	3.74	−0.179	−98.5
258.5	0.178	2.09	−0.033	−88.0
		at 99.0°C		
105.8	21.5	382.0	−0.755	−49.8
126.2	9.40	160.0	−0.784	−63.1
156.7	2.89	46.6	−0.686	−80.5
177.1	1.49	23.3	−0.544	−87.5
207.6	0.715	10.6	−0.342	−92.1
258.5	0.317	4.41	−0.149	−91.3

otonically, which would increase the sorption. Based on visual experiments of neat polymer strips, the swelling does not go through a maximum for CO_2 in silicone rubber (Shim and Johnston, 1989). It is also known that swelling and sorption are closely related for this system. The reason for the different behavior in these studies is unknown.

To determine the volumes of the phases, the swelling of a strip of neat polymer, without a support present, was measured. Given this, and the amount of polymer on the support determined using TGA, the amount of swelling in the column was determined. If the swelling effect is not included, significant errors may result in the thermodynamic properties. For example, for silicone rubber at 35°C and 310 bar, the distribution coefficient and Henry's constant of each solute would be 90% larger and 45% smaller, respectively, than the actual values. Also, $\bar{v}_2^{F,\infty}$ of phenanthrene at 35°C and 75 bar would be in error by 17%, and in considerably greater error at higher pressures where the swelling is larger.

The distribution coefficient was calculated from k_2 along with the polymer swelling data shown in Figure 1. The swelling was estimated at 100°C by extrapolating the values at 35, 50 and 70°C on a plot of the activity vs. swelling. It has been shown that temperature effects on swelling are small on this type of plot, although they are large on a plot of pressure vs. swelling (Berens and Huvard, 1989; Shim and Johnston, 1989).

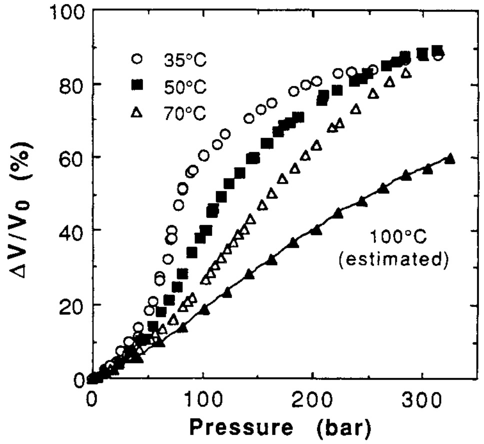

Figure 1. Swelling ($\Delta V/V_0$) of silicone rubber in the presence of high-pressure carbon dioxide.

Estimated from extrapolation of a plot of swelling vs. activity of CO_2 (Shim and Johnston, 1989)

Even though the distribution coefficient is calculated from the corrected capacity factor, which is hopefully free from retention by adsorption, it is necessary to test this assumption more rigorously as suggested by Conder and Young (1979). If K_2 is free of adsorption, it should not vary with the degree of loading of polymer on the support. This test was performed for a series of polymer loadings and pressures at 35.2°C, as shown in Figure 2. There is only a 1% variation in K_2 for silicone rubber loadings of 8.0 and 13.6 wt. %. For a higher loading of 26.4 wt. %, however, K_2 decreases by 27%, which may be caused by blocking the pores of the silica support by the large amount of polymer. Here, the solute likely did not equilibrate with all of the polymeric stationary phase. Therefore, we may conclude that there is a minimal effect of adsorption for polymer loadings from 8 to 15% over this pressure range.

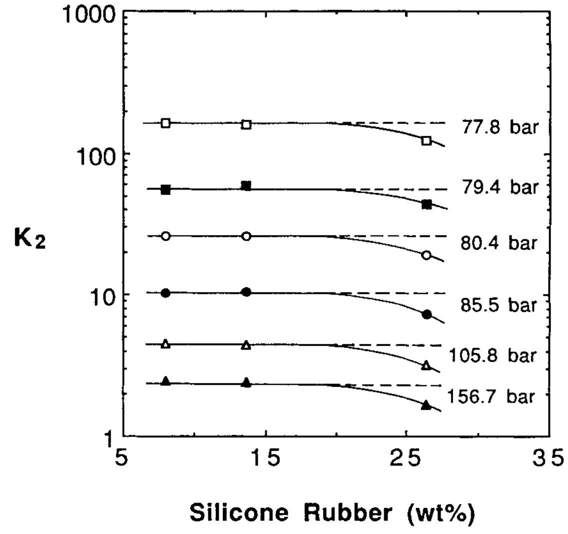

Figure 2. Effect of stationary-phase polymer loading on the distibution coefficient of phenanthrene at 35°C.

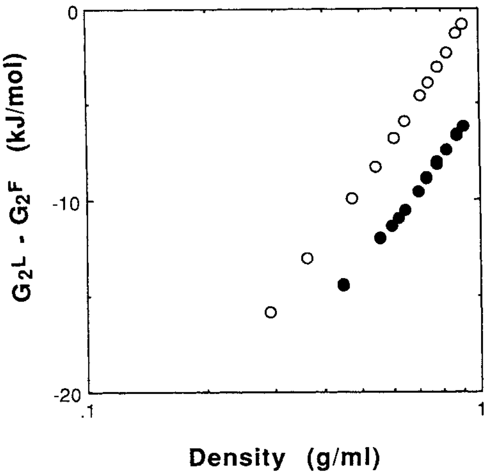

Figure 3. Gibbs free energy of transfer of phenanthrene from the fluid phase to the stationary phase.

Silicone rubber, ○, or C_{18}, ●, at 35°C

Discussion

Comparison of liquid polymeric phases by supercritical-fluid chromatography

The solute free energy of transfer may be defined in terms of the distribution coefficient by the relationship (Luffer and Novotny, 1990).

$$G_2^L - G_2^F = -RT \ln K_2 \qquad (13)$$

In Figure 3, $G_2^L - G_2^F$ for phenanthrene in C_{18} and in silicone rubber is plotted vs. log density at 35°C. The approximate linearity in plots of $\ln K_2$ (and likewise the free energy of transfer) vs. log ρ has been observed experimentally and been explained theoretically (Shim and Johnston, 1991). The free energy of transfer for C_{18} is more negative than that for silicone rubber, which indicates more favorable interactions in the polymer phase. This is consistent with the solubility parameters of silicone rubber, C_{18}, naphthalene and phenanthrene, which are 14.9, 16.4, 20.3 and 20.0 $(J/mL)^{1/2}$, respectively. Since δ of C_{18} is closer to those of the solutes than δ of silicone rubber, the interactions are stronger.

The Henry's constants of toluene, naphthalene, and phenanthrene in silicone rubber and C_{18} were calculated from the data with Eq. 10 (see Figure 4). The Henry's constants for toluene in the silicone rubber phase are about one order of magnitude larger than those of naphthalene and three orders of magnitude larger than those of phenanthrene. These differences are due primarily to the differences in their vapor pressures. Also, the Henry's constants of both naphthalene and phenanthrene generally are larger in the silicone rubber phase than in the C_{18} phase, except for naphthalene at 100°C. As is evident from Eq. 3, the nonidealities in the liquid phase have been included in the Henry's constant. Based on the solubility parameters, the enthalpic interactions are less favorable for each solute with silicone rubber than C_{18}, thus the Henry's constants are larger. This analysis of the free energies of transfer and Henry's constants provides a framework for comparing interactions of solutes with a variety of polymers.

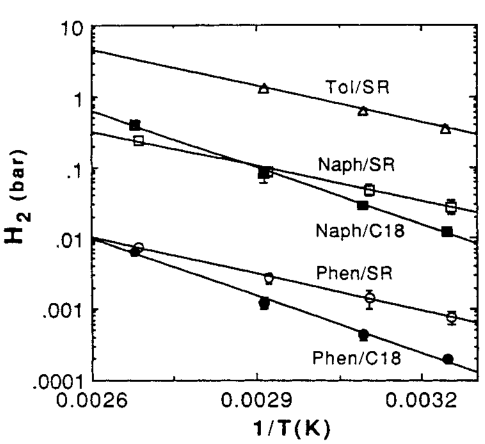

Figure 4. Henry's constants for toluene, naphthalene, and phenanthrene in silicone rubber and C_{18}, determined by SFC and Eq. 10.

Predicted ternary-phase behavior at finite concentration from interaction parameters at infinite dilution

The distribution coefficients of toluene at infinite dilution may be compared with literature values at finite concentration as shown in Figure 5. They were also calculated with Eqs. 4 and 9. In a previous study, the Flory interaction parameters were regressed from binary data (Shim and Johnston, 1989). The agreement is good at finite concentration, although for infinite dilution, the calculated values are 71% and 35% larger at 35° and 70°C, respectively, than the data. This could be due to errors in the models for Γ_2, for ϕ_2, or to errors in the infinite dilution data. More accurate correlations could be obtained by adjusting the Flory parameters with ternary data; however, we chose to use only binary data. The calculated results may be explained in terms of the nonidealities in each phase. In the fluid phase, the variation in ϕ_2 with concentration is small over this range. However, in the polymer phase, Γ_2 decreases modestly with an increase in Φ_2 over this range, which would increase K_2. Thus, the trends in the theory and data are consistent.

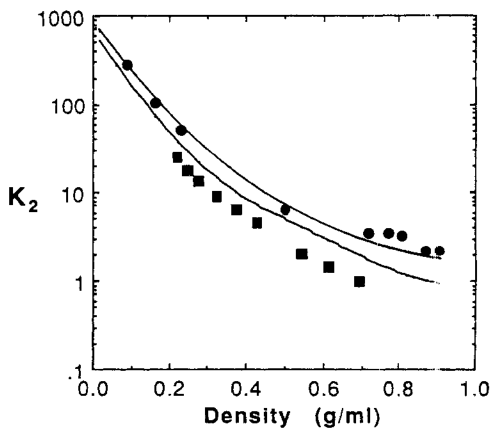

Figure 5. Distribution coefficients of toluene at 35°C.

●, finite concentration, experimental; ■, infinite dilution, experimental; ——— , calculated with Eq. 9 using χ_{ij}'s in Shim and Johnston (1989)

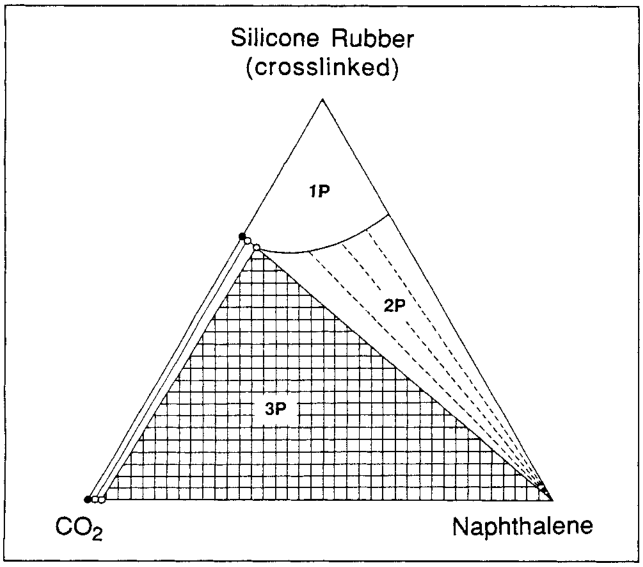

Figure 6. Calculated phase diagram at 34.2°C and 100 bar in weight fraction units, using a naphthalene-silicone rubber χ_{ij} regressed from the experimental infinite dilution distribution coefficient.

Naphthalene is a solid at this condition; o , calculated points on tie line; ---, schematic tie line

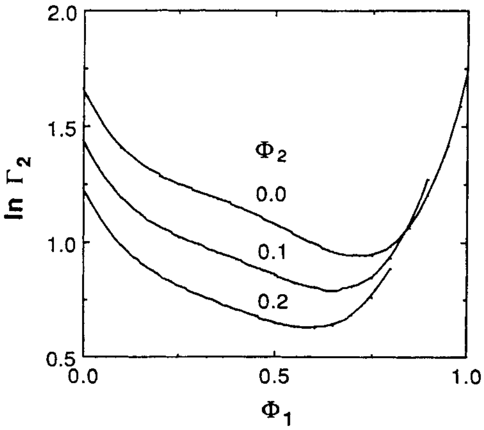

Figure 7. Logarithm of activity coefficient of toluene as a function of volume fraction of CO_2 for various volume fractions of toluene from Eq. 4.

The ternary-phase behavior of the CO_2-toluene-silicone rubber (cross-linked) system has been studied as a function of composition and pressure (Shim and Johnston, 1989). At pressures typically above 100 bar, two phases are present: a fluid phase and a swollen polymer phase. At lower pressures, the fluid phase separates into gaseous and liquid phases to form a three-phase mixture.

The phase diagram somewhat differs for the CO_2-naphthalene-silicone rubber system, as shown in Figure 6. Tie lines on the phase diagram were calculated by equating fugacities of solute and of CO_2, with Eqs. 1, 2, and 4 and the analogous equations for CO_2. The CO_2–silicone rubber Flory interaction parameter was regressed from binary data as described above, the naphthalene-CO_2 parameter from solubility parameters, and the silicone rubber-naphthalene parameter from the experimental distribution coefficient at infinite dilution. Consider the naphthalene-CO_2 binary. Solid naphthalene is soluble in CO_2, but CO_2 is essentially insoluble in the crystalline solid phase, at temperatures below the binary solid-liquid gas curve (McHugh and Krukonis, 1986). The calculated solubility of naphthalene in CO_2 is 0.01 mol fraction at these conditions, in agreement with the literature (McHugh and Krukonis, 1986). The silicone rubber is not soluble in CO_2 because it is cross-linked; this is a reason why it is used in supercritical-fluid chromatography. Although the nonpolar solid naphthalene may be expected to be soluble in silicone rubber (as is liquid toluene), it would take an extremely long time for the solid to diffuse into the polymer.

There is a large three-phase solid (naphthalene-rich)-liquid (silicone-rubber-rich)-vapor (CO_2-rich) region, which shrinks gradually as pressure increases. Calculated tie-lines are shown on the left side of the three-phase region. These lines intersect the CO_2 naphthalene axis since the polymer is cross-linked and insoluble. Examples of tie lines that extend to a binary axis are described by Walas (1985). Schematic tie lines are shown to the right of the three-phase region, although such lines could be calculated with a model in the literature (Lemert and Johnston, 1989). These tie lines emanate from the pure naphthalene vertex as described previously (Koningsveld and Diepen, 1983). For phenanthrene, the phase diagram is similar. The important conclusion is that SFC may be used to measure distribution coefficients at infinite dilution, which provide a basis for calculating ternary-phase diagrams at concentrations orders of magnitude above infinite dilution.

In order to more fully understand the effect of solute composition on phase behavior, it is useful to examine the activity coefficient of the solute, Γ_2, in the liquid polymer phase. Equation 4 was used to calculate Γ_2 as a function of CO_2 volume fraction, Φ_1, for various values of Φ_2 (see Figure 7). In the limit of infinite dilution of solute and solvent ($\Phi_1 = \Phi_2 = 0$), ln Γ_2^∞ is 1.66. As Φ_1 increases, ln Γ_2^∞ decreases, i.e., the solute encounters a more ideal environment as the polymer is swollen with solvent. Likewise, it decreases with Φ_2 at a given Φ_1, as the solute interacts with itself more favorably than with the other components. As the concentration of solvent increases above 0.7, Γ_2 stops decreasing and increases sharply; however, the solvent usually is not this soluble in the cross-inked polymer.

Further physical insight may be gained by examining various contributions to ln Γ_2^∞ in Eq. 5 (Patterson et al., 1971), i.e.,

$$\ln \Gamma_2^\infty \text{ (combinatorial)} = 1 - \Phi_1 (v_2/v_1) \tag{14}$$

$$\ln \Gamma_2^\infty \text{ (residual)} = \chi_{21}\Phi_1 + \chi_{23}\Phi_3 - \chi_{13}(v_2/v_1)\Phi_1\Phi_3 \tag{15}$$

$$\ln \Gamma_2^\infty \text{ (cross-link)} = v_2 (\nu_e / V_0)(\Phi_3^{1/3} - \Phi_3/2) \tag{16}$$

These contributions to ln Γ_2^∞ were calculated at 35°C with the same Flory parameters as used above (see Figure 8), and the cross-link density was obtained from the literature (Shim and Johnston, 1989). The total ln Γ_2^∞, indicated by a solid line, is the same as in Figure 7 for $\Phi_2 = 0$. Near $\Phi_1 = 0$, the com-

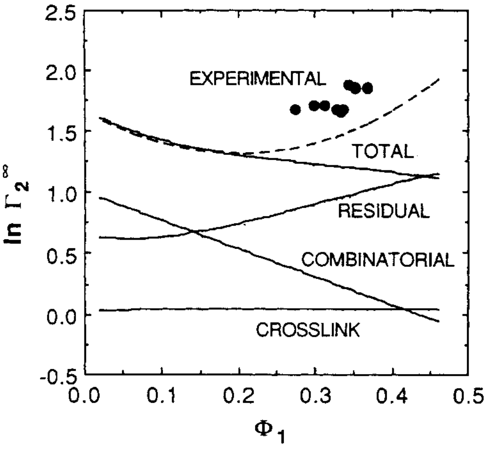

Figure 8. Comparison of combinatorial, residual and crosslinking contributions to the infinite dilution activity coefficient of toluene at 35°C.

———, $\ln\Gamma_2^\infty$ using $\chi_{12} = 1.3$; ---, $\ln\Gamma_2^\infty$ using $\chi_{12} = 1.155 + 7.227\Phi_1 + 4.125\Phi_1^2$

binatorial term is dominant and decreases linearly with increasing Φ_1, while the residual contribution becomes dominant at larger Φ_1. As the volume fraction of solvent increases, the polymer swells and allows the solute molecules to become more disordered. This makes the combinatorial term smaller.

In contrast, the increase in ln Γ_2^∞ (residual) is related to the difference in solubility parameters (Prausnitz et al., 1986, p. 312). Since toluene [$\delta = 18.2$ $(J \cdot cm^{-3})^{1/2}$] is more dissimilar to CO_2 ($\delta = 12.3$) than to silicone rubber ($\delta = 14.9$), the residual contribution to ln Γ_2^∞ increases as the fraction of CO_2 in the polymer increases. The ln Γ_2^∞ (cross-link) term is small, since the influence of the infinitely dilute solute on the expansion of the polymer network is minor. The resulting total ln Γ_2^∞ decreases slightly with increasing Φ_1, as the change in the combinatorial contribution is a little larger than the residual one.

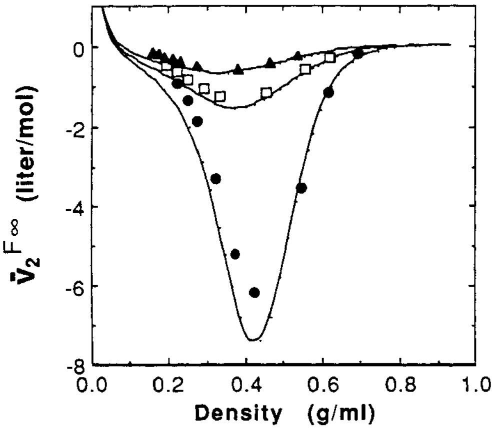

Figure 9. Partial molar volume of toluene at infinite dilution in CO_2.

●, 35.2°C; □, 50.1°C; ▲, 70°C

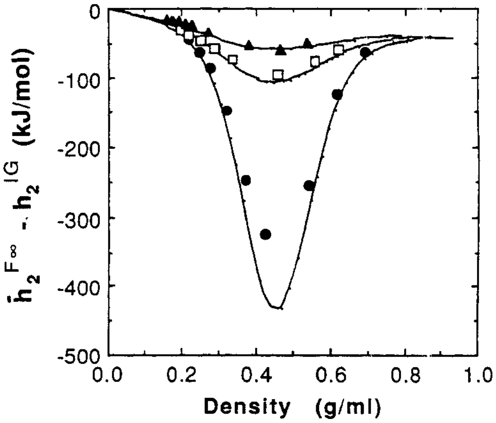

Figure 10. Partial molar enthalpy of toluene at infinite dilution in CO_2.

●, 35.2°C; □, 50.1°C; ▲, 70°C

The values of Γ_2^∞ from experiment based on Eq. 9 (along with ϕ_2 from the equation of state) are compared with the theoretical values from Eq. 5 in Figure 8. The theoretical values were predicted with constant values of χ_{12} and χ_{23} from binary data, and a composition-dependent χ_{13} reported previously (Shim and Johnston, 1989). The difference between the theoretical and experimental results may be due to errors in the calculation of ϕ_2, to errors in the experiment, or to the assumption of composition-independent Flory parameters. For example, if χ_{12} is correlated as a function of volume fraction from binary data, better agreement is observed as shown. Eichinger and Flory (1968) measured χ for a natural rubber-benzene system at 25°C by vapor sorption and high-pressure osmometry and found, as is often the case, that it varied with composition. Perhaps the use of an equation of state such as the Sanchez-Lacombe equation could improve the calculation over wider ranges in composition.

Solute partial molar volumes and enthalpies at infinite dilution

The large pressure and temperature effects on the phase diagrams reflect the pronounced values of the solute partial molar properties in the highly compressible fluid. These partial molar properties were calculated from slopes of distribution coefficients for toluene, naphthalene, and phenanthrene in CO_2 according to Eqs. 11 and 12 (see Figures 9-10 and Tables 2-4). The term $\rho(\partial \ln K_2/\partial\rho)$ is always significant compared to unity; for example, it is -2.1 to -73 for densities of 0.1 and 0.9 g/mL, respectively. An advantage of this technique is that the shapes of the infinite dilution partial molar properties follow those of κ and the volume expansivity of the pure fluid, as expected from theoretical investigations (Debenedetti, 1987; Kim et al., 1985). The properties κ and β were calculated from analytical derivatives of a highly accurate equation of state for CO_2 (Reynolds, 1979). The results were in good agreement with those calculated from another highly accurate equation of state (Ely, 1986).

The large negative value of $\bar{h}_2^{F,\infty}$ in the near-critical region indicates an increase in the number of exothermic interactions between CO_2 and the solute molecules, producing clusters that extend over many coordination shells. Here, the word cluster means that there are more solvent molecules about each solute molecule in a given volume than would be present for pure solvent in the same volume. It does not mean that there is a tightly bound entity such as a stoichiometric complex. The increase in solute-solvent interactions occurs over many coordination shells since each layer of solvent is somewhat denser than the bulk and can attract more solvent molecules. Spectroscopic probes have been used to determine average increases in the local density of about 50 to 150% (Johnston et al., 1989a). The spectroscopic probe may be influenced by direct solute-solvent interactions and indirect solute-solvent-solvent interactions over many coordination shells. Therefore, the radius that defines the local volume increases as the compressibility and the correlation length increase. This clustering over many coordination shells about the solute is also apparent from $\bar{v}_2^{F,\infty}$, as about 100 solvent molecules cluster about each solute molecule in the highly compressible near-critical region (Eckert et al., 1986; Debenedetti, 1987).

The magnitudes of the partial molar enthalpies and volumes vary among the solutes. For example, at 35°C, the minimum in $\bar{h}_2^{F,\infty} - h_2^{IG}$ for phenanthrene and toluene are 1,100 and 440 kJ/mol, respectively. Because the former is more polarizable, it interacts more strongly with CO_2 with a greater number of exothermic interactions and also a more negative $\bar{v}_2^{F,\infty}$.

It is interesting to compare the experimental $\bar{h}_2^{F,\infty}$ values for each solute obtained for the two different liquid (stationary) phases, C_{18} (Shim and Johnston, 1991), and silicone rubber. If the stationary-phase interactions are ideal, $\bar{h}_2^{F,\infty}$ of a given solute should be the same for each polymeric stationary phase. Since $\bar{h}_2^{F,\infty}$ differs slightly for the two polymers, it is likely that there is a small heat effect in the stationary phase. To estimate this effect, we begin by writing the partial molar enthalpy of transfer as:

$$\bar{h}_2^{L,\infty} - \bar{h}_2^{F,\infty} = (h_2^L - h_2^{IG}) + (\bar{h}_2^{L,\infty} - h_2^L) - (\bar{h}_2^{F,\infty} - h_2^{IG}) \quad (17)$$

where h_2^L is the enthalpy of pure (hypothetical) liquid solute. The difference in enthalpies of transfer for silicone rubber and C_{18} is

$$(\bar{h}_2^{L,\infty} - \bar{h}_2^{F,\infty})_{C_{18}} - (\bar{h}_2^{L,\infty} - \bar{h}_2^{F,\infty})_{SR} = (\bar{h}_2^{L,\infty} - h_2^L)_{C_{18}} - (\bar{h}_2^{L,\infty} - h_2^L)_{SR} \quad (18)$$

The partial molar enthalpies of mixing, $\bar{h}_2^{L,\infty} - h_2^L$, of naphthalene and phenanthrene were calculated with Eqs. 12, 17 and 18. In both silicone rubber and C_{18}, they are endothermic, and are about 20 and 40 kJ/mol larger for naphthalene and phenanthrene, respectively, in silicone rubber, except for the highly compressible region at 35°C. This indicates more favorable energetic interactions of each solute with C_{18} than with silicone rubber, which is consistent with the solubility parameters.

The agreement is good between the experimental values of $\bar{v}_2^{F,\infty}$ and $\bar{h}_2^{F,\infty}$ and those calculated with the Peng-Robinson equation of state with quadratic mixing rules (see Shim and Johnston, 1991). The k_{12} is 0.09 as reported by Ng and Robinson (1978). In general, the equation of state is of limited accuracy in highly compressible supercritical fluids. However, the density and compressibility of pure CO_2 were calculated with a highly accurate equation of state (Reynolds, 1979), and the Peng-Robinson equation was used only for mixture properties. Similar agreement was observed for naphthalene and phenanthrene.

Conclusions

The chromatographic technique provides a rapid and convenient means to measure solute distribution coefficients at infinite dilution between a supercritical fluid and a polymer. Precautions are required to minimize errors due to unwanted adsorption on the silica support. These include deactivation of the bare silica support, subtraction of the retention on the bare silica, and variation of the film thickness. It is important to measure swelling to obtain the distribution coefficient from the capacity factor to accurately determine thermodynamic properties. Although swelling can be measured visually for the neat polymer, it would be convenient in the future to determine swelling chromatographically, possible with tracer pulse techniques.

A variety of solutes and polymers may be studied with the experimental technique to develop a database to understand the molecular interactions and phase behavior. The solutes toluene, naphthalene, and phenanthrene interact more strongly with C_{18} than silicone rubber because of C_{18}'s larger solubility parameter. This is evident in the solute free energies of transfer, Henry's constants, and activity coefficients. As the CO_2 sorption in the polymer increases thus lowering the solubility parameter, the residual contribution to the solute activity coefficient Γ_2 becomes more nonideal. The solute becomes more disordered and the combinatorial entropy contribution becomes more ideal. Ternary-phase diagrams may be calculated semiquantitatively over a wide concentration range with the Flory and Peng-Robinson equations along with solute-polymer interaction constants obtained from the infinite dilution SFC data. Future improvement could be achieved with an equation of state for the polymer phase such as the Sanchez-Lacombe equation. These phase diagrams provide a basis for the evaluation and design of polymer impregnation and purification processes with supercritical fluids.

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Notation

C = concentration, mol/mL
f = fugacity, bar
G = Gibbs free energy, J/mol
h = molar enthalpy, J/mol
$\bar{h}$ = partial molar enthalpy, J/mol
H = Henry's constant, bar
k = capacity factor
K = distribution coefficient
n = number of moles of a component(s), mol
P^o = reference pressure (1.013 bar)
v = molar volume, mL/mol
$\bar{v}$ = partial molar volume, mL/mol
V = volume of a phase, mL
y = mole fraction in the fluid

Greek letters

β = isobaric volume expansivity
χ = Flory interaction parameter
ϕ = fugacity coefficient
Φ = volume fraction in the liquid (stationary) phase

Γ = activity coefficient in the liquid phase based on volume fraction
κ = isothermal compressibility, 1/bar
ν_e = effective number of chains in the network polymer, mol
ρ = density of the fluid, g/mL

Superscripts

F = fluid (mobile) phase
IG = ideal gas state
L = liquid (stationary or polymer) phase
sat = saturated state
∞ = infinite dilution state

Subscripts

0 = unswollen state of polymer
1 = fluid (CO_2)
2 = solute (toluene, naphthalene, or phenanthrene)
3 = stationary phase material (silicone rubber or C_{18})

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