

## Distribution of Solutes Between Polymer and Supercritical Fluid by Inverse Supercritical Fluid Chromatography

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(Received 22 June 2001 • accepted 18 July 2001)

**Abstract**—Two methods of inverse supercritical fluid chromatography (ISFC), frontal analysis supercritical fluid chromatography (SFC) and elution SFC, have been compared for the determination of distribution coefficients of solutes between a polymer and a supercritical  $\text{CO}_2$ . The logarithm of the distribution coefficient showed monotonic decrease with the density of the supercritical fluid (SF). The abnormal-maximum behavior of solute sorption in the polymer phase was explained by the fluid and solute properties,  $\phi_1 P/P_1^{\text{ext}}$ . Interesting open-elliptic shapes of sorption and volume-fraction curves were obtained and explained with the fugacity coefficient. Correction to the capacity factor was employed to eliminate the retention due to the adsorption on the surface of the silica support. A model based on the Flory equation and the Peng-Robinson equation of state (EOS) successfully predicted the phase behavior of the ternary solute-supercritical fluid-polymer systems using only interaction parameters obtained from the binary systems. The solute distribution coefficient at infinite dilution was used to calculate the phase equilibrium at finite concentration using a ternary-phase diagram.

Key words: Distribution Coefficient, Supercritical Fluid, Polymer, Solute, Sorption, Supercritical Fluid Chromatography, Phase Equilibrium

### INTRODUCTION

Supercritical fluids received only little attention until the 1970's when they began to be considered as solvents for low-cost processing of food and pharmaceutical products. In the mid-1980's, the scope of supercritical fluid technology widened to include separations, reactions, and material processing of complex substances such as polymers, surfactants, and bio-molecules [McHugh and Krukonis, 1994]. An impetus for this expansion was the need to respond to the increased performance demands on the materials that conventional techniques could not meet. Polymer processing with supercritical fluids includes fractionation, impregnation and purification of polymers, formation of porous or powdery polymers [McHugh and Krukonis, 1994], and dispersion polymerization [Shim et al., 1999, 2001]. Since they have solvent strengths adjustable continuously with temperature and pressure, the SFs are more advantageous in polymer processing than the conventional liquid solvents whose strengths are only modestly adjustable with temperature.

Supercritical fluids also swell polymers so that they may be impregnated rapidly (8 orders of magnitude for glassy polymers) with additives such as pharmaceuticals, flavors, fragrances, insecticides, etc., for controlled release applications [Berens et al., 1988; Sand, 1986], or with additives such as dyes [Saus et al., 1993; Chang et al., 1996], pigments, stabilizers, plasticizers, electrically conductive agents, and toughness-improving agents. Polymers may be purified by extraction of oligomers, monomers, residual solvent, and other impurities with pure supercritical fluids [Paulaitis et al., 1983].

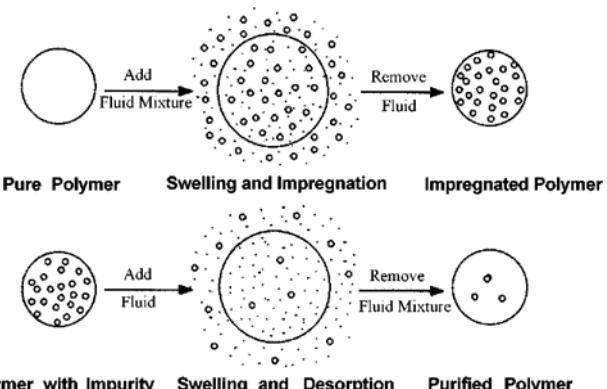


Fig. 1. A schematic diagram describing the polymer impregnation- and purification processes. The purification process is reverse of the impregnation process.

(●) additive or impurity; (•) supercritical fluid

Purification may be considered as a reverse process of the impregnation but uses the same concept of phase equilibrium (Fig. 1). For both processes the supercritical fluid penetrates and swells the polymer fast [Chang et al., 1998], promoting the diffusion of the larger solute molecules into or out of the polymer.

An important factor required in designing the polymer impregnation and purification processes is the equilibrium distribution coefficient of a solute between a polymer and a supercritical fluid. The distribution coefficient is also used in determining other thermodynamic properties. The polymer-solute Flory interaction parameters are fundamental thermodynamic relations that are necessary to calculate the distribution coefficient. However, these thermodynamic parameters are scarce in ternary systems containing polymers and

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supercritical fluids. Conventional pressure-volume-temperature measurement (for example, partial molar volume measurement by Eckert et al., 1986) or gravimetric sorption measurement [Berens and Huvard, 1989] is difficult to apply at elevated pressures. Those are very time-intensive and may not be appropriate when the solute is at infinite dilution. Without these restrictions the SFC has become an attractive technique to determine those thermodynamic properties.

In principle, a variety of interesting physical and chemical properties can be obtained by inverse gas chromatography (IGC) and inverse high performance liquid chromatography (IHPLC). However, IGC is restricted due to the limited volatility and thermal stability of many organic compounds, and IHPLC, due to the limitations of the solute diffusion in the mobile phase, causing long analysis time. ISFC overcomes these difficulties and permits high resolution at low temperatures with short analysis time [Bartle, 1988]. ISFC has been used to measure thermodynamic properties of solutes [van Wassen et al., 1980; Olesik et al., 1987; Yonker and Smith, 1988; Shim and Johnston, 1989, 1991a, b]. This chromatographic method is often called elution chromatography. The basic parameter for ISFC is the capacity factor,  $k$ , which is defined by the mole ratio of the solute between a polymer and a fluid phase, and is determined by the retention times of the solute and an unretained marker. The distribution coefficient of a solute is calculated from this capacity factor and the phase-volume ratio of the mobile phase to the stationary phase in the column.

The phase equilibrium is considerably more complex in the elution SFC than in IGC because the interactions in the dense-fluid (mobile) phase are highly nonideal, and because the carrier fluid swells the liquid (stationary) phase. Therefore, it is challenging to understand this behavior and to determine thermodynamic properties by the ISFC. An important factor influencing the properties from the ISFC is the swelling of the stationary phase. By including the swelling data of polymers, more accurate properties can be determined from the distribution coefficient [Shim and Johnston, 1991a, b]. It is also important to eliminate the contribution of surface adsorption to the solute retention, so that only the absorption into the bulk polymer phase is considered in the determination of thermodynamic properties. This can be accomplished by subtracting the capacity factor on the bare silica support from the capacity factor in the polymer-coated silica. The resulting net capacity factor is due primarily to bulk absorption into the stationary-liquid coating [Card et al., 1985; Shim and Johnston, 1991a, b].

While most chromatographic studies have been done at conditions of infinite dilution, measurement of thermodynamic properties at finite solute concentration is also possible [Shim and Johnston, 1989]. In the frontal analysis technique, a stream of pure carrier fluid is equilibrated with the stationary phase of the column and then replaced by a continuous stream of carrier mixed with solute vapor at a constant concentration [Conder and Young, 1979]. The resulting frontal boundary may be used to calculate the total number of moles of the solute absorbed in the stationary phase and the distribution coefficient of the solute. In this study, the distribution coefficients of solutes that were measured by the above ISFC were compared with those predicted theoretically by a model. Prediction of the phase behavior at finite concentration from the data at infinite dilution will also be discussed. To obtain more meaningful results than obtained previously, an additional retention correction

was included in the calculation. A thermodynamic model based on the Flory equation and the Peng-Robinson equation was employed to explain the behavior and to predict thermodynamic properties that are relevant to polymer processing with supercritical fluids.

## THEORY

### 1. The Frontal Analysis SFC

Since rubbery polymers behave as highly viscous liquids, the partitioning of a solute between a polymer and a SF may be described by the following simple vapor-liquid phase equilibrium suggested by Prausnitz et al. [1999]. Here, the fluid phase is considered as a vapor phase and the rubbery polymer phase, as a liquid phase. An ideal gas reference state and a (hypothetical) pure liquid standard state are, therefore, chosen for the supercritical fluid and for the solvent in the polymer, respectively.

$$y_i \phi_i P = \Phi_i \Gamma_i P_i^{\text{sat}} \phi_i^{\text{sat}} \exp\left(\frac{V_i^P (P - P_i^{\text{sat}})}{RT}\right) \quad (1)$$

where  $y_i$  is the mole fraction of  $i$  in the fluid phase (unity for a pure solvent);  $\phi_i$  is the fugacity coefficient;  $\Phi_i$  is the volume fraction in the polymer;  $\Gamma_i$  is the activity coefficient in the polymer;  $P_i^{\text{sat}}$  is the vapor pressure which may be extrapolated above the critical pressure if necessary;  $\phi_i^{\text{sat}}$  is the fugacity coefficient at the vapor pressure; and  $V_i^P$  is the partial molar volume of  $i$  in the polymer phase. Note that the activity coefficient  $\Gamma_i$  is defined as  $a_i / \Phi_i$  based on the volume fraction, where  $a_i$  is the activity of  $i$  in the polymer phase.  $\Gamma_i$  is particularly useful for polymer systems, as it does not require the molecular weight or the molecular weight distribution of the polymer.

In Eq. (1) the two governing factors describing the nonideality are  $\phi_i$  for the fluid phase and  $\Gamma_i$  for the polymer phase. The Peng-Robinson EOS [1976] may be used to obtain the fugacity coefficient and to describe the binary mixture in the fluid phase (since there is no polymer molecule in the fluid phase for any crosslinked polymer).

$$\ln \phi_i = \frac{b}{b} (Z - 1) - \ln (Z - B) - \frac{A}{2\sqrt{2}B} \left( \frac{2 \sum_i y_i a_i}{a} - \frac{b}{b} \right) \ln \left( \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \quad (2)$$

On the contrary, the simple Flory theory [1969] may be adopted to describe the polymer phase, where the free energy of mixing of a crosslinked polymer with a solvent consists of an entropic term, an enthalpic term that includes the Flory interaction parameter,  $\chi$ , and the elastic free energy term for the expansion of the network structure. For a binary system the activity coefficient of the solvent 1 in a crosslinked polymer 3 is obtained by differentiating the free energy of mixing with the result

$$\ln \Gamma_1 = (1 - 1/\chi) \Phi_3 + \chi_{13} \Phi_3^2 + v_1 (v_e/v_0) (\Phi_3^{1/2} - \Phi_3/2) \quad (3)$$

where  $\Phi_3$  is the volume fraction of polymer;  $\chi$  is the ratio of the molar volumes of polymer to solvent;  $v_1$  is the molar volume of solvent;  $v_e$  is the effective number of chains in the network expressed in moles; and  $V_0$  is the volume of the original unswollen polymer.

For a ternary system, the activity coefficients of the two pene-

trants, 1 and 2, in the crosslinked polymer, 3, are provided by the following equations [Flory, 1969; Shim and Johnston, 1991b]

$$\ln \Gamma_1 = (1 - \Phi_1) - \Phi_2 (v_1/v_2) + (\chi_{12} \Phi_2 + \chi_{13} \Phi_3) (\Phi_2 + \Phi_3) - \chi_{13} (v_1/v_2) \Phi_2 \Phi_3 + v_1 (v_2/V_0) (\Phi_3^B - \Phi_3/2) \quad (4)$$

$$\ln \Gamma_2 = (1 - \Phi_2) - \Phi_1 (v_2/v_1) + (\chi_{21} \Phi_1 + \chi_{23} \Phi_3) (\Phi_1 + \Phi_3) - \chi_{13} (v_2/v_1) \Phi_1 \Phi_3 + v_2 (v_1/V_0) (\Phi_3^B - \Phi_3/2) \quad (5)$$

These equations may be used to predict the 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 the characteristic binary constant  $k_{12}$  for the fluid phase.

The equilibrium distribution coefficient of the penetrant may be defined as the ratio of the concentration in the polymer phase to that in the fluid phase [Shim and Johnston, 1989],

$$K_2 = \frac{C_2^P}{C_2^F} = \frac{\Phi_2/v_2^P}{y_2/v^P} \quad (6)$$

where  $C_2^P$  and  $C_2^F$  are the concentrations of the solute in the liquid-like polymer phase and in the fluid phase, respectively;  $v_2^P$  is the molar volume of the solute in the polymer phase which is approximated as that of pure (hypothetical) liquid; and  $v^P$  is the molar volume of the fluid phase. Combining Eqs. (1) and (6) yields:

$$K_2 = \frac{v^P}{v_2^P} \frac{\phi_2 P}{\Gamma_2 P_2^{\text{sat}} \phi_2^{\text{sat}} \exp\left(\frac{V_2^P (P - P_2^{\text{sat}})}{RT}\right)} \quad (7)$$

## 2. The Elution SFC

The capacity factor of the solute,  $k_2$ , is defined as the molar ratio of solute between the liquid-like polymer (stationary) and fluid (mobile) phases and is obtained directly from the retention time data of the solute and a marker [Conder and Young, 1979]

$$k_2 = \frac{n_2^P}{n_2^F} = \frac{t_2 - t_0}{t_0} \quad (8)$$

where  $n_2^P$  and  $n_2^F$  are the number of moles of the polymer phase and of the fluid phase, respectively;  $t_2$  is the retention time of the solute; and  $t_0$  is that of a marker which has the minimal retention. The molar ratio is written as the product of the concentration ratio and the phase volume ratio as [Shim and Johnston, 1991a]

$$\frac{n_2^P}{n_2^F} = \frac{C_2^P V^P}{C_2^F V^P} \quad (9)$$

where  $V^P$  and  $V^F$  are the volumes of the polymer- and the fluid phases in the column, respectively. From Eqs. (6), (8) and (9),  $K_2$  is related to  $k_2$  as follows:

$$K_2 = k_2 \frac{V^P}{V^F} \quad (10)$$

As the phase ratio varies upon the swelling of the stationary (liquid) phase at high pressures, Eq. (10) may be modified to include the swelling effect as

$$K_2 = k_2 \frac{V_0^P/V_0^F - \Delta V^P/V_0^F}{1 + \Delta V^P/V_0^F} \quad (11)$$

where  $V_0^P/V_0^F$  is the phase ratio at zero pressure;  $\Delta V^P/V_0^F$  is the swelling of the liquid phase; and F and P designate the fluid and liquid

phases, respectively.

Since the concentrations of the fluid and polymer phases are extremely small, we may introduce Henry's law to describe the phase equilibrium in the column. The Henry's constant may be obtained when  $K_2$  is known. On the other hand, when the Henry's constant is available,  $K_2$  may be calculated from the following equation [Shim and Johnston, 1991a]:

$$K_2 = \frac{v^P}{v_2^P} \frac{\phi_2^{\text{sat}} P}{H_2(P^0) \exp\left[\frac{V_2^P (P - P^0)}{RT}\right]} \quad (12)$$

where  $H_2(P^0)$  is the Henry's constant at the reference pressure ( $P^0$ ). The infinite dilution fugacity coefficient of the solute,  $\phi_2$ , is obtained from Eq. (2) derived from Peng-Robinson EOS. While the activity coefficient of a solute at infinite dilution can be reduced from Eq. (5) with negligible  $\Phi_2$  as

$$\ln \Gamma_2^{\text{sat}} = 1 - \Phi_1 (v_2/v_1) + \chi_{21} \Phi_1 + \chi_{23} \Phi_3 - \chi_{13} (v_2/v_1) \Phi_1 \Phi_3 + v_2 (v_1/V_0) (\Phi_3^B - \Phi_3/2) \quad (13)$$

## RESULTS AND DISCUSSION

### 1. Solute Sorption and Distribution by the Frontal Analysis SFC

The equilibrium sorption of toluene in silicone rubber in the presence of  $\text{CO}_2$  was measured by the frontal analysis SFC in our previous study [Shim and Johnston, 1989], while the concentration of toluene in the fluid phase was maintained constant (0.14 mole%) throughout the experiment. The amount of sorption showed maximum behavior at around 40 bar, but the sorption isotherms at two different temperatures intersected each other in the pressure plot. When the sorption was drawn as a function of density, the two isotherms did not cross each other (Fig. 2). At 308.15 K, the sorption curve had a maximum of 0.065 g/g  $\text{CO}_2$  at density 0.08 g/ml and then decreased rather rapidly to about 0.005 g/g  $\text{CO}_2$  as the density increased to 0.5 g/ml, thereafter it decreased slowly. Because the

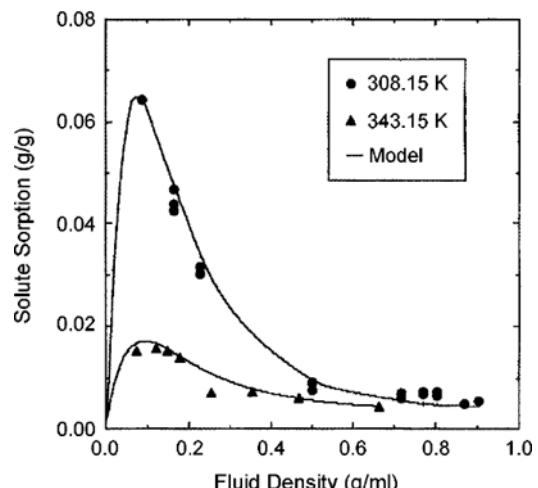


Fig. 2. The amount of sorption of toluene in silicone rubber expressed versus the density of  $\text{CO}_2$ .

— sorption predicted with the Flory/Peng-Robinson model using  $\chi_{ij}$ 's in Shim and Johnston [1989].

solvent strength and thus the extraction power of the fluid increased rapidly over the absorbing power of the polymer at densities larger than 0.08 g/ml, the amount of solute in the polymer decreased with increasing pressure. The overall shape of the sorption curve at 343.15 K was similar to that at 308.15 K, except for the fact that the height was reduced to 1/4th.

At densities lower than 0.08 g/ml, the sorption measurement would take tremendous time. So I tried to predict the sorption quantitatively using a theoretical model (solid lines in Fig. 2). It can be easily recognized that the gas phase is nearly ideal and therefore the sorption increases almost linearly with density. As the density of the gas further increases, the sorption goes through a maximum, and then decreases rapidly as the solvent strength becomes significant. It has been widely known that the solubility is nearly proportional to the density of the fluid. In this study, as the solute loading was fixed to 0.14 mol%, the fluid  $\text{CO}_2$  at high densities must have extracted the solute that had already penetrated into the polymer phase, showing a maximum at the density of 0.08 g/ml. Therefore, the density representation may be better for explaining the sorption behavior than the pressure representation.

The sorption of toluene in silicone rubber at low pressures was predicted by using the Flory/Peng-Robinson model suggested in the previous section. The fugacity coefficients of  $\text{CO}_2$  and toluene were obtained by Eq. (2) derived from Peng-Robinson EOS with the  $\text{CO}_2$ -toluene characteristic binary constant,  $k_{12}=0.090$ . The Flory interaction parameters were determined from binary data in the literature [Shim and Johnston, 1989]. The fugacity coefficients of toluene and  $\text{CO}_2$  were substituted into Eq. (1), and then combined with Eqs. (4) and (5). The resulting equations were solved and optimized to find suitable values for  $\Phi_1$  and  $\Phi_2$ . Assuming that the sorption of  $\text{CO}_2$  was not affected by the presence of dilute toluene, the amount of sorption  $S_2$  was calculated by Eq. (14).

$$\Phi_2 = \frac{S_2(\rho_2/\rho_1)}{\Delta V/V_0 + S_2(\rho_2/\rho_1) + 1} \quad (14)$$

where  $\rho_2$  and  $\rho_1$  are densities of solute and polymer, respectively, and  $\Delta V/V_0$  represents the amount of swelling of silicone rubber. Fig. 3 shows that the product of the fugacity coefficient and pressure

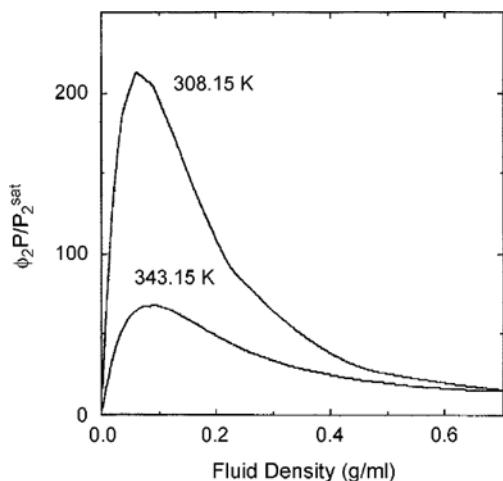


Fig. 3. The fugacity coefficient times pressure divided by the saturation pressure of toluene versus the density of  $\text{CO}_2$ .

divided by the saturation pressure of solute,  $\phi_2 P / P_2^{\text{sat}}$ , has a shape similar to the sorption curves in Fig. 2. Because it does not contain any polymer-phase-related properties but the fluid-phase fugacity coefficient, the polymer phase is governed by the fluid phase. In other words, the abnormal behavior of the sorption curve is explained by the change of the solvent power of the fluid with density. The behavior was explained previously by the activity of solute in the polymer phase [Shim and Johnston, 1989]. Since this activity varies mainly with the interactions between the fluid and solute molecules, the total pressure of the system and the saturation pressure of the solute [Eq. (1)],  $\phi_2 P / P_2^{\text{sat}}$  is a better tool than the activity to understand the behavior.

When I plotted the sorption or the volume fraction of toluene against the activity of toluene in the polymer phase, some interesting open-elliptic shape sorption curves were obtained (Figs. 4 and 5). The higher the system temperature was, the smaller became the ellipses. Along the bottom-half of the curve, the sorption and the volume fraction increased with increasing activity of solute at low densities, while along the top-half, they decreased with decreasing

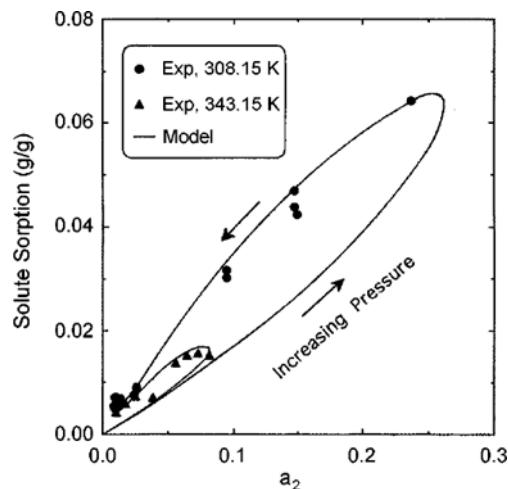


Fig. 4. Open-elliptic shape sorption curves versus the activity of toluene. The open ends are located at the low activity sides of the ellipses.

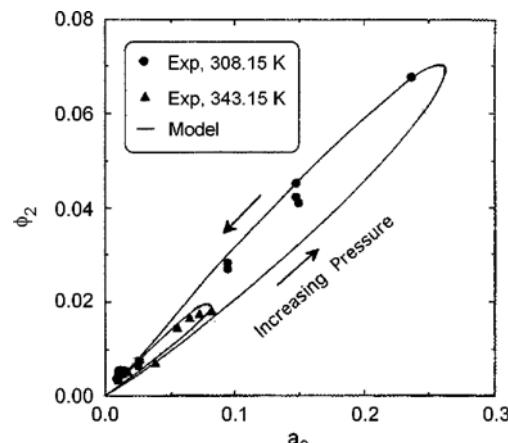


Fig. 5. Open-elliptic shape volume-fraction curves versus the activity of toluene.

activity at high densities. Shim and Johnston [1989] showed previously that the activity increases at low pressures but decreases at high pressures. The activity at constant temperature depends mainly upon both pressure and the fugacity coefficient of solute. At low pressures, the system pressure primarily influences the activity since the fugacity coefficient does not decrease much. At high pressures, however, the fugacity coefficient decreases dramatically as the interaction between the solute and fluid molecules becomes significant. In this region, the fugacity decrease overcomes the increase of pressure and thus the activity decreases. Therefore, the sorption varies with increasing pressure (density) along the elliptic curve, forming a maximum near the activity of 0.27.

For a given volume fraction of toluene I obtained two different activities: the larger one at lower density and the smaller one at higher density. We have seen in Fig. 2 that we may get the same volume fraction of toluene,  $\Phi_2$ , at two different densities. In Eq. (15), the values for  $\Phi_1$  and  $\Phi_3$  at the higher density must be different from those at the lower density, resulting in different values for  $a_2$ .

$$a_2 \equiv \Phi_2 \Gamma_2 = \Phi_2 \exp[(1 - \Phi_2) - \Phi_1(v_2/v_1) + (\chi_{12}\Phi_1 + \chi_{23}\Phi_3)(\Phi_1 + \Phi_3) - \chi_{13}(v_2/v_1)\Phi_1\Phi_3 + v_2(v_2/V_0)(\Phi_1^{1/2} - \Phi_2/2)] \quad (15)$$

Also, for a given activity of toluene, we have two different volume fractions of toluene as they are at different fluid densities. Because the activity coefficient of toluene  $\Gamma_2$  decreases with increasing pressure [Shim and Johnston, 1989] or density,  $\Phi_2$  should be larger at the higher density for the same  $a_2$ . For the impregnation of polymer, a medium pressure and any lowest possible temperature corresponding to the maximum activity of toluene are preferred, as it allows the largest amount of sorption. For purification of polymer, a high pressure and a highest possible temperature corresponding to the lowest activity may be chosen, as the least amount of solute can exist in the polymer at this condition.

In the pressure plot, we can see the complex behavior of the distribution coefficient that is defined by Eq. (6). The lines have at least one inflection point and are very steep downwards near the highly-adjustable critical range for the solute [Shim and Johnston, 1989]. When the distribution coefficient  $K_2$  calculated by Eq. (7) was plotted

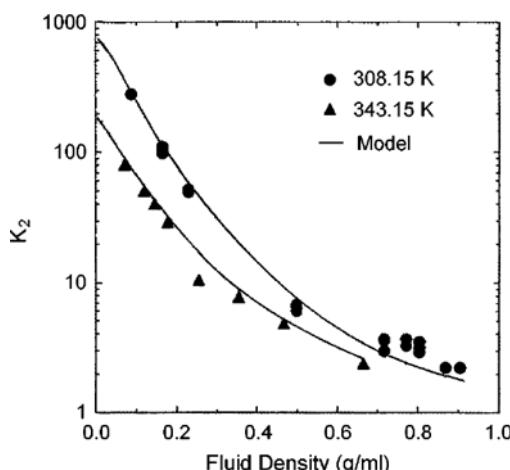


Fig. 6. The logarithm of the distribution coefficient of toluene (0.14 mole% in the fluid phase) decreases almost linearly with fluid density.

as a function of density, however, the plot appeared much simpler (Fig. 6). The logarithm of the distribution coefficient decreased monotonically but slightly concaved upward. The distribution coefficient (solid-line) was calculated from the Flory/Peng-Robinson model using the binary interaction parameters. In this model, the fluid phase nonideality was corrected with the fugacity coefficient calculated by Peng-Robinson EOS. The polymer phase nonideality was corrected with the activity coefficient calculated by the Flory equation. The figure shows that the model predicts the distribution coefficients very well. I confirmed again that density is a tool much better than pressure to explain the supercritical fluid behavior.

## 2. Capacity Factors and Distribution Coefficients by the Elution SFC

From the definition in Eq. (8), the capacity factors can be easily obtained from the experimental retention times of a marker and a solute that were measured by the fast elution SFC. Unfortunately, the capacity factors include additional retention due to the adsorption on the bare silica that causes an experimental error. By the definition of the capacity factor in Eq. (8) we can write the following relation between the capacity factors:

$$k_2^P = \frac{n_2^P + n_2^S}{n_2^P} = \frac{n_2^P}{n_2^P} + \frac{n_2^S}{n_2^P} = k_2^P + k_2^S \quad (16)$$

where  $k_2^S$  is the capacity factor of solute in the polymer-coated silica;  $k_2^P$  is the net capacity factor in polymer;  $k_2^S$  is the capacity factor in the bare silica;  $n_2$  is the number of moles of the solute; and the superscripts t, P, F, and s designate "total (polymer+silica)," "polymer," "fluid," and "silica," respectively. From Eq. (16) the net capacity factor of solute can be obtained by subtracting  $k_2^S$  from  $k_2^P$ .

$$k_2^P = k_2^P - k_2^S \quad (17)$$

This net capacity factor may be free of retention due to the adsorption on the silica surface. The average deviation of the amount of correction was 2%. Fig. 7 shows that the logarithm of the net capacity factors for phenanthrene decreases linearly with density for all temperatures. At higher densities, the solvent strength of the fluid

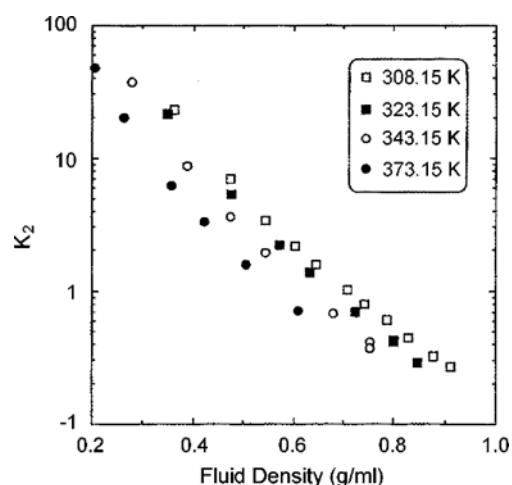
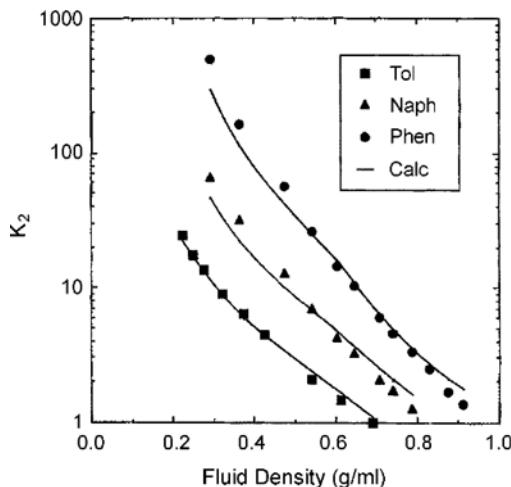


Fig. 7. The linear behavior of the capacity factors of phenanthrene measured with 7% silicone rubber-coated silica column. These factors were corrected for adsorption on the silica surface.



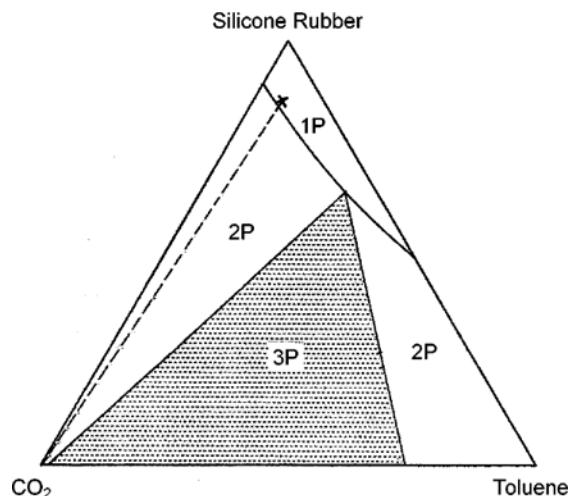
**Fig. 8.** The distribution coefficients of toluene, naphthalene, and phenanthrene at 308.15 K versus the density of  $\text{CO}_2$ . Solid lines are calculated by Eq. (12).

phase is larger and the retention becomes shorter than at lower densities. The factors also decrease with temperature. At higher temperatures, we have shorter retention time than at lower temperatures due to the higher energy and thus faster molecular motion of solute molecules. The phase equilibrium favors the fluid phase and the solute molecules easily desorb at this condition.

The distribution coefficients were more easily and quickly obtained from the corrected (net) capacity factors and the phase ratio than those from the sorption measurement (the frontal analysis SFC). The net capacity factor and the phase ratio used here were corrected for polymer swelling by Eq. (11) with the data of Shim [1990]. Fig. 8 shows the distribution coefficients for toluene, naphthalene, and phenanthrene at 308.15 K. The solid lines were calculated by Eq. (12) using the Henry's constants in Shim and Johnston [1991b]. The distribution coefficients for the three solutes were nearly parallel each other. Phenanthrene had 7 to 25 times larger values than toluene, and naphthalene had 2 to 5 times larger values. The distribution coefficients by the elution SFC showed near linear behavior similar to those from the frontal analysis SFC.

### 3. Prediction of the Ternary Phase Behavior

The ternary-phase behavior of a  $\text{CO}_2$ -liquid solute(toluene)-silicone rubber system was fairly simple since the rubber is crosslinked and is essentially insoluble in both fluid  $\text{CO}_2$  and liquid toluene. There were a liquid(1)-liquid(2)-vapor three-phase region for this ternary system at 308.15 K and 40 bar (Fig. 10). Here, "Liquid(1)" is the silicone rubber-rich phase; "liquid(2)" is the toluene-rich phase; and "vapor" is the  $\text{CO}_2$ -rich fluid phase. The concentrations of  $\text{CO}_2$  and toluene at the three-phase boundary were 6.7 and 29.4 wt%, respectively. The right-hand side of this three-phase region is the liquid(1)-liquid(2) two-phase region and the left-hand side is the liquid(1)-vapor two-phase region. The experimental distribution coefficient data at finite concentration may be used to construct a tie-line on the left edge of this region, allowing us to predict tie-lines at higher concentrations. The tie-line in Fig. 9 was the one thus obtained. At pressures higher than 75 bar, there exists only a liquid(1)-vapor two-phase region and a silicone rubber-rich one-phase region. The advantage of high pressure is that there is no restriction



**Fig. 9.** The triangular phase-diagram for the silicone rubber(cross-linked)- $\text{CO}_2$ -toluene ternary system at 308.15 K and 40 bar, which is based on weight fraction. The dashed line is a tie-line and the shaded area is a 3-phase region.

on the concentration of toluene in the fluid phase. It is possible to impregnate large amounts of liquid solute into the polymer from a fluid.

For a ternary system containing a solid solute such as naphthalene and phenanthrene, the phase diagram has a somewhat different shape [Shim and Johnston, 1991b]. These solutes are soluble in  $\text{CO}_2$ , but  $\text{CO}_2$  is essentially insoluble in the crystalline solid phase. The equilibrium tie-lines between the fluid mixture and the polymer are predicted by the Flory/Peng-Robinson model with Flory binary interaction parameters. The sorption of solid solute may occur slowly and inefficiently if it directly contacts the polymer. The supercritical fluid accelerates sorption by swelling the polymer, even if the concentration of the solute is not so high. This kind of phase diagram has practical importance for the application of the supercritical fluid polymer processing and can be calculated from the binary solubility data and the infinite dilution distribution coefficient data. These ISFC experimental methods provide a rapid and efficient tool for determining distribution coefficients at infinite dilution as discussed above.

## CONCLUSIONS

Two ISFC methods, frontal analysis SFC and elution SFC, have been found to be useful in measuring the equilibrium distribution coefficients of solutes (either liquid or solid) between a polymer and a supercritical fluid. The abnormal-maximum behavior of solute sorption in the polymer phase could be explained by the fluid and solute properties,  $\phi_2 P/P_2^{\text{ext}}$ , that are closely related to the solvent strength of the fluid. An interesting open-elliptic shape sorption curve is due to the change of fugacity coefficient upon pressure. The volume-fraction curve had a similar shape to the sorption curve but was a little flatter. Elution SFC proved to be easier and faster for measuring the sorption and the distribution coefficients than the frontal analysis SFC, without mentioning the conventional methods. However, a correction on the capacity factor was necessary to eliminate the retention due to the adsorption on the surface of the silica

support. The logarithm of the distribution coefficient shows a monotonic decrease with the density of the supercritical fluid.

The Flory/Peng-Robinson model was useful to predict the phase equilibria of solute-polymer-supercritical fluid ternary systems. It predicted very well the distribution coefficients at finite concentration and fairly well at infinite dilution with only binary interaction parameters in the literature. Another important result is that the distribution coefficient obtained at finite concentration or at infinite dilution could be used to predict the phase equilibria at much higher concentrations. The information on the phase equilibria was plotted on a ternary-phase diagram of a system containing a solute. These phase equilibria are useful in understanding and designing the polymer impregnation and purification processes.

### ACKNOWLEDGMENT

This research has partly been supported by the R&D Management Center for Energy and Resources (96-E-ID02-P-19) and by the Basic Research Program of the Korea Science & Engineering Foundation (Grant No. 2000-2-30700-001-3).

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