Solubility / Retention Relationships in Supercritical-Fluid Chromatography

Z. SERMIN GONENC[1], *UGUR AKMAN*[1] *and AYDIN K. SUNOL**

Department of Chemical Engineering, University of South Florida, Tampa, FL 33620, USA
[1]***Department of Chemical Engineering, Bogazici University, Bebek 80815, Istanbul, Turkey***

The effects of temperature, pressure and supercritical fluid density on solubility-retention relationship of solutes in supercritical fluid partition chromatography are investigated. New retention data for naphthalene and phenanthrene are obtained as a function of pressure at different temperatures. The mobile-phase partial molar volumes of the solutes are determined from infinite-dilution fugacity coefficients and used to model the pressure dependence of solute retention that reveals the nature of interactions between the stationary phase and the solute. Relationships between pressure and temperature dependence of solubility and retention of solutes are also illustrated.

On a étudié les effets de la température, de la pression et de la masse volumique du fluide supercritique sur la relation de solubilité-rétention de solutés en chromatographie de partage en phase fluide supercritique. Les nouvelles données de rétention pour le naphtalène et le phénanthrène sont obtenues en fonction de la pression à différentes températures. Les volumes molaires partiels de la phase mobile des solutés sont déterminés à partir des coefficients de fugacité de dilution infinie et servent à modéliser la piézodépendance de la rétention des solutés qui révèle la nature des interactions entre la phase stationnaire et le soluté. Les relations entre la dépendance en pression et en température de la solubilité et de la rétention sont également illustrées.

Keywords: supercritical partition chromatography, solubility/sorption/retention relationships.

Supercritical Fluid Chromatography (SFC) is a rather recent tool that continues to receive considerable attention for chemical analysis and physico-chemical property estimation. Given the existing difficulties in physico-chemical property measurement and estimation under supercritical conditions, any SFC-based approach deserves a special attention, in part due to its promise in high data turnaround. Although the area is quite new, there is some foundation, from similar GC and HPLC work, to build upon. The retention of a solute in the chromatographic column in SFC is dependent on the strength of sorption of the solute on (and within) the stationary phase, as well as the solubility of the solute in the supercritical mobile phase. Since many physico-chemical properties can be related to the retention in SFC, a thorough investigation of the characteristics of retention including its relation to solubility in SFC, is essential.

The effects of temperature, pressure, mobile-phase (almost exclusively CO_2) density and stationary-phase material (in capillary or packed columns) on the behavior of solute retention in SFC have been subject to extensive experimental and theoretical research (Van Wasen et al., 1980; Gere et al., 1982; Yonker et al., 1987; Yonker and Smith, 1988a, b; Shim and Johnston, 1989; Bartle et al., 1990; Kelley and Chimowitz, 1990; Roth, 1990; Shim and Johnston, 1991; Gonenc and Sunol, 1992; Gonenc et al., 1992).

The literature data for retention-pressure and corresponding analysis lack due weighing of the anomalities near the critical region. Therefore, two different solutes were used at different temperatures to study the pressure dependence of $\overline{V}_s^{\infty}$, particularly near the critical point of the mobile phase. A thermodynamic framework derived through integration of pressure rentetion relation is used, along with infinite dilution fugacity coefficients, to model the solubility retention behavior.

Experimental

The experiments were carried out on a Lee Scientific (Salt Lake City, UT) supercritical fluid chromatograph Series 600. The chromatograph was fitted with 5-m long, 100-μm ID capillary column coated with poly-dimethylsiloxane of 0.25 μL film thickness. The detections were made with the aid of a flame ionization detector. Column temperature and mobile-phase pressure were controlled to an accuracy of ± 0.1 K and ± 0.01 MPa, respectively. Retention times were measured using the computer system of the chromatograph with an accuracy of 0.02 seconds. Carbon dioxide (supplied by Matheson Gas Products, East Rutherford, NJ) was used as the carrier fluid. The samples (dissolved in *n*-pentane) were introduced into the column by means of an automatic injection system. The samples were at infinite dilution in *n*-pentane. Methane (supplied by Tampa Oxygen, Tampa, FL) was used as the inert material to determine the retention time of a compound which is sorbed negligibly (if at all) on the column material. Retention data were taken for naphthalene and phenanthrene at various pressures and at isothermal conditions. Naphthalene and HPLC-grade *n*-pentane were supplied by Fisher Scientific Company (Pittsburgh, PA) and phenanthrene was supplied by Aldrich Chemicals (Milwaukee, WI). Some details of the experiments can be found in a previous publication (Gonenc and Sunol, 1992).

Results and discussion

In SFC literature, naphthalene-CO_2 is one of the more popular solute-solvent systems studied for various stationary-phases over a wide ranges of pressure and temperature. Figure 1 shows the solubility of naphthalene in CO_2 as a function of pressure and fluid-phase density at different temperatures. Calculations were performed with the Peng-Robinson (1976) equation of state using the van der Waals

*Author to whom correspondence should be addressed.

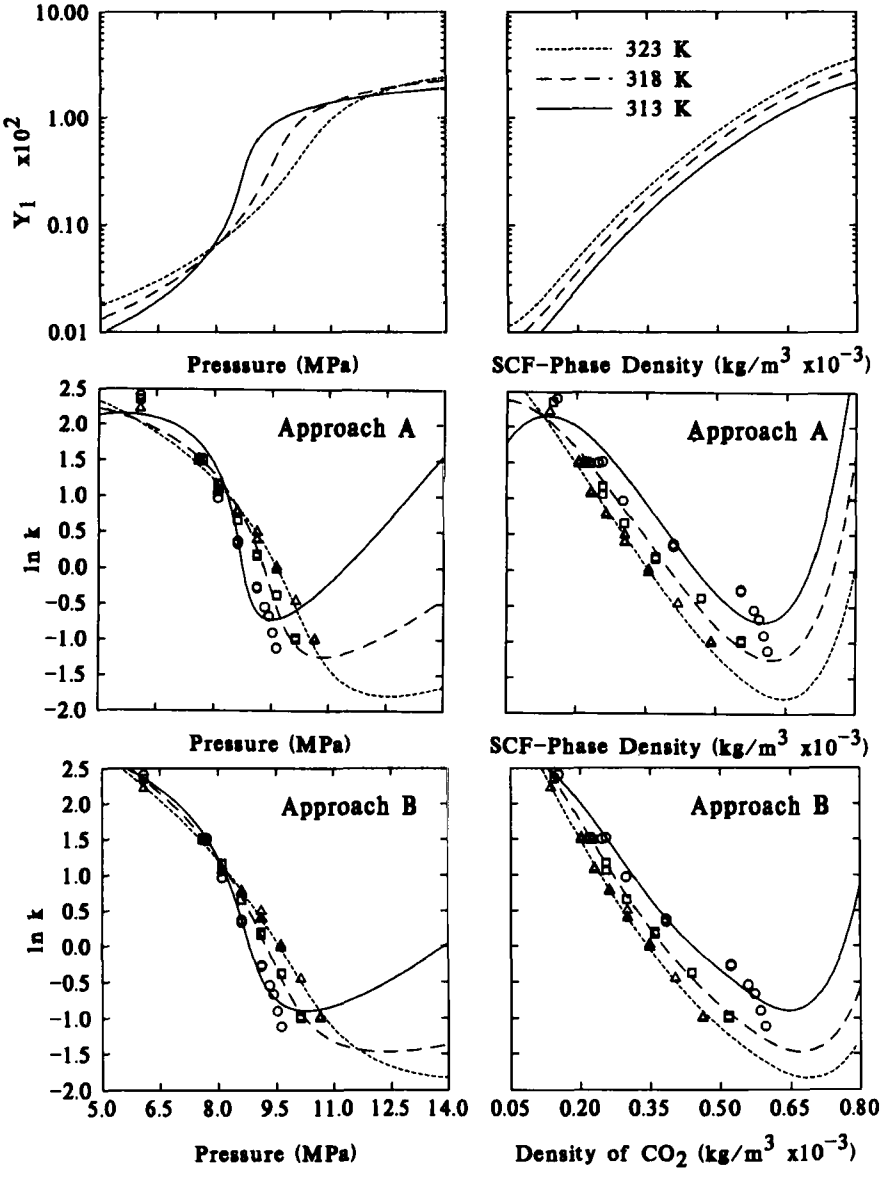


Figure 1 — Solubility and retention coefficient of naphthalene.

one-fluid mixing rules and the non-quadratic combining rule of Panagiotopoulos and Reid (1986). Pure component parameters were obtained from the usual acentric-factor correlation. Binary interaction parameters for naphthalene-CO_2 were regressed as temperature dependent from a bulk solubility data (McHugh and Paulaitis, 1980). In order to show both temperature and pressure effects, in this work, the retention data for naphthalene-CO_2-polydimethylsiloxane system (capillary column) were used. Figure 1 shows the experimental and theoretical retention coefficient of naphthalene as a function of pressure and density of pure CO_2. The model was fitted to retention data through linear regression by assuming constant $\overline{V}_s^{\infty}$values. Molar density of pure CO_2 was obtained from an accurate correlation. Infinite dilution fugacity coefficient of naphthalene in CO_2 was calculated from the Peng-Robinson equation of state as explained above. The calcualted $\overline{V}_s^{\infty}$data are given in Table 1. The procedure for the calculations is summarized in Figure 2. Unlike in most of the previous research (Yonker and Smith, 1988a,b),

TABLE 1
Infinite Dilution Partial Molar Volumes of Solutes in Stationary Phase

	$\overline{V}_s^{\infty}$		
Solute	40°C	45°C	50°C
Naphthalene	−1166 ± 22%	−650 ± 11%	−422 ± 18%
Phenanthrene	2031 ± 13%	n.e.	133 ± 250%

n.e. — no experiment

infinite dilution fugacity coefficient (approach B) as opposed to solubility data (approach A) is used. In the calculation of $\hat{\phi}_m^{\infty}$, one has the option to utilize data (solubility) to obtain the interaction parameters of the equation of state. However, this approach avoids the necessity for solubility data. Futhermore, as can be seen from Figure 1, our approach (approach B) better predicts the data both qualitatively and quantitatively.

Since the values of $\overline{V}_s^{\infty}$ are quite different than molar volume of solid naphthalene (110 cm^3/mol), even though

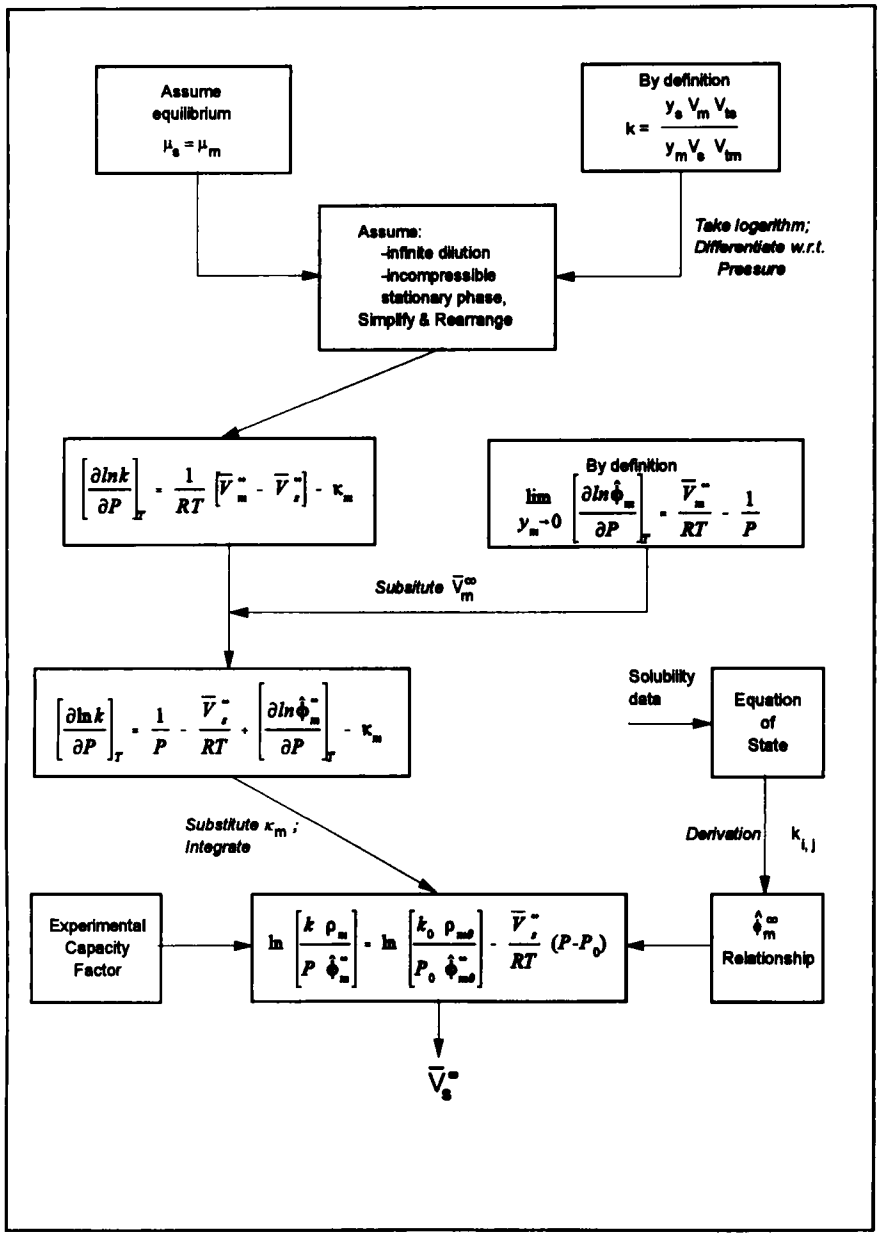


Figure 2 — Procedure for calculation of infinite-dilution partial-molar volume.

effects of possible swelling of polydimethylsiloxane by supercritical CO_2 cannot be assessed, it can be concluded that naphthalene partitions into the polydimethylsiloxane phase. With an assumption of constant $\bar{V}_s^{\infty}$ the model cannot adequately describe the retention behavior at 40°C (close to the critical temperature of CO_2) above approximately 9 MPa. The model also wrongly predicts temperature-dependent retention minima both in retention-pressure and retention-density planes. Retention minima cannot be explained phsyically since one expects the retention of the solute to decrease to a constant level (asymptotic approach to zero) as the solvent power of the mobile phase increases with pressure/density. Even though the bulk solubility of naphthalene in CO_2 is as high as 10^{-2} (highly concentrated compared to infinite-dillution conditions in SFC), it is interesting to notice the strong relationship between solubility and retention coefficient. The crossover of both the solubility and retention isotherms occur within approximately the same pressure range. Also, the retrograde temperature effects in the solubility-pressure and retention-pressure planes both disappear in the density plane. However, the theoretical retention isotherms do cross around 6 MPa, whereas there is only one crossover region of the solubility isotherms.

The qualitative simulation for the solubility retention seen for naphthalene-CO_2 system could not be extrapolated to all other systems. The phenanthrene-CO_2 system is an example for which retention behavior significantly deviates from solubility behavior. Figure 3 shows the solubility of phenanthrene in CO_2 as a function of pressure and fluid-phase density at different temperatues. Calculations were performed with the Peng-Robinson (1976) equataion of state, as explained before, and the binary interaction coefficients for phenanthrene-CO_2 were regressed as temperature dependent from bulk solubility data (Kurnik et al., 1981; Dodds et al.,

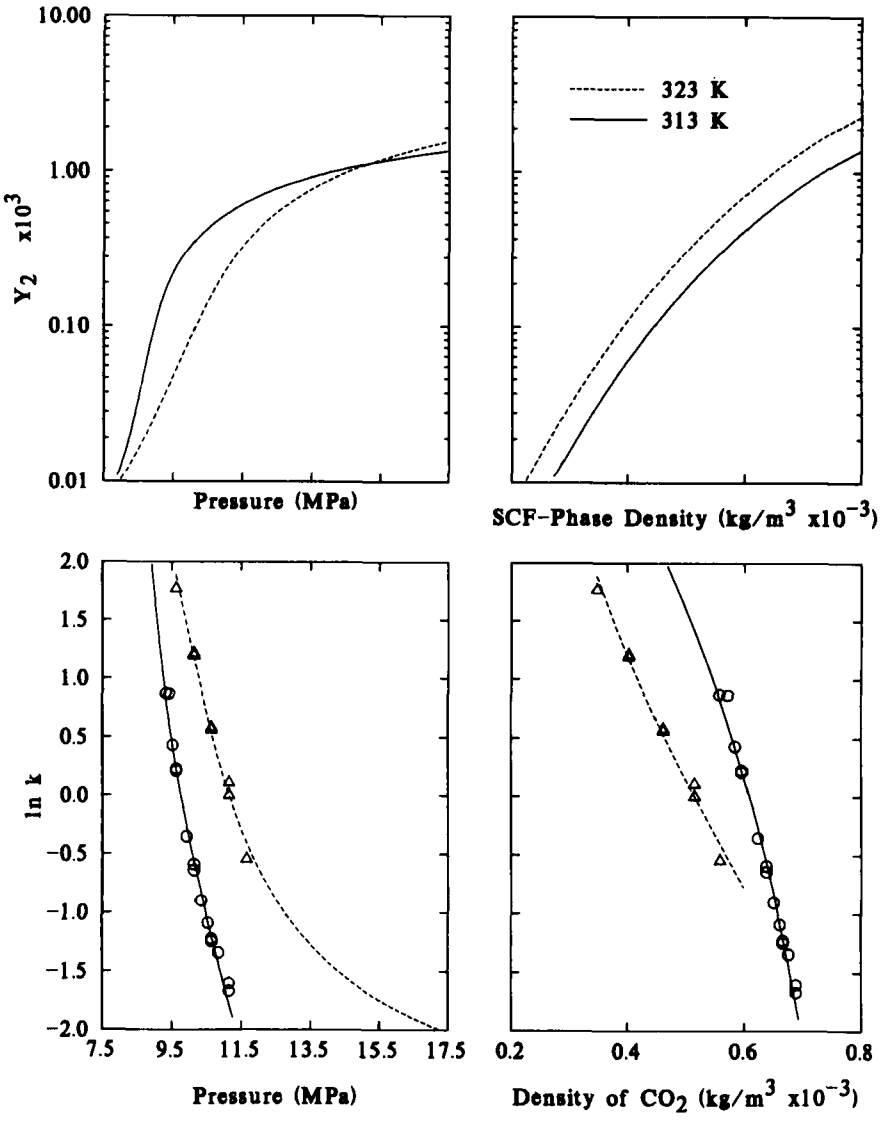


Figure 3 — Solubility and retention coefficient of phenanthrene.

1986). Figure 3 shows the experimental and theoretical retention coefficient of phenanthrene as a function of pressure and density of pure CO_2. As opposed to naphthalene, for phenanthrene the values of $\overline{V}_s^{\infty}$ are positive and at 50°C, $\overline{V}_s^{\infty}$ is very close to the molar volume of solid phenanthrene (173 cm^3/mol). Therefore, without considering the effects of possible swelling of polydimethylsiloxane, it can be concluded that phenanthrene does not partition into the polydimethylsiloxane phase as much as naphthalene does at 50°C. Even though the bulk solubility of phenanthrene in CO_2 is about ten times lower than that of naphthalene (more closely approximates the infinite-dilution conditions in SFC), neither experimental data nor theory, with constant $\overline{V}_s^{\infty}$, show a crossover region of the retention isotherms comparable to that of the solubility isotherms. When the theoretical retention isotherms are extrapolated to pressures higher than those shown in Figure 3, the retention isotherm for 40°C does not show a retention minimum, whereas retention isotherm for 50°C does.

As can be understood from the above discussion, interactions among solute, solvent and stationary-phase material, characterized by $\overline{V}_s^{\infty}$, play key roles in the mechanism of retention. These interactions are temperature and pressure dependent. The assumption of constant $\overline{V}_s^{\infty}$ should be used with caution, particularly around the critical region. Furthermore, the location of the minimum observed with the model strongly depends on the data range and, therefore, the approach should be used with care for extrapolation, especially since this minimum is not experimentally verified (Yonker and Smith, 1988b).

Conclusions

The use of infinite-dilution fugacity coefficient instead of bulk solubility data in determining the partial molar volume of the solute in the mobile phase improves the correlation ability of the retention values of the solutes, especially around the critical pressure and for solutes with appreciable bulk solubility in the mobile phase. However, the probably more significant contribution of the approach is in providing the means of estimating $\overline{V}_s^{\infty}$ in the absence of solubility data.

Models which neglect the interaction of stationary phase and the mobile phase do not represent the experimental retention of solutes very well. This is particularly true in the vicinity of the critical point where $\overline{V}_s^{\infty}$ is shown to be pressure dependent.

In estimating physico-chemical properties such as solubility, one should either use adsorption chromatography as opposed to partition or start with a model that does not neglect stationary-phase/mobile-phase interactions. In supercritical adsorption chromatography, the relationships among solubility retention are not confounded by the effects (pressure dependence) of $\overline{V}_s^{\infty}$ and stationary phase swelling. Therefore, the direct inverse relationship present between solubility and sorption under supercritical conditions also exists between solubility (solvent power) and retention, but as weighed by the molar volume of the mobile phase.

Nomenclature

k = capacity ratio
k_{ij} = binary interaction parameter
P = pressure, MPa
R = universal gas constant, MPa·cm^3/mol·K
T = temperature, °C or K
V_m = molar volume of mobile phase, cm^3/mol
V_s = molar volume of stationary phase, cm^3/mol
V_{tm} = total volume of mobile phase, cm^3/mol
V_{ts} = total volume of stationary phase, cm^3/mol
$\overline{V}_m^{\infty}$ = partial molar volume of solute at infinite dilution in mobile phase, cm^3/mol
$\overline{V}_s^{\infty}$ = partial molar volume of solute at infinite dilution in a stationary phase, cm^3/mol
y_m = mole fraction of solute in mobile phase
y_s = mole fraction of solute in stationary phase
Y_1 = solubility of naphthalene in CO_2, mole fraction
Y_2 = solubility of phenanthrene in CO_2, mole fraction

Greek letters

$\hat{\phi}_g^{\infty}$ = infinite-dilution fugacity coefficient of solute in mobile phase
κ_m = isothermal compressibility of mobile phase, MPa^{-1}
μ_m = chemical potential of mobile phase, MPA·cm^3/mol
μ_s = chemical potential of stationary phase, MPa·cm^3/mol
ρ_m = molar density of mobile phase, mol/cm^3

References

Bartle, K. D., A. A. Clifford and B. A. Jafar, "Relationship Between Retention of a Solid Solute in a Liquid and Supercritical Fluid Chromatography and its Solubility in the Mobile Phase", J. Chem. Soc. Faraday Trans. **86**, 855–860 (1990).

Dobbs, J. M., J. M. Wong and K. P. Johnston, "Non-polar Co-solvents for Solubility Enhancement in Supercritical Fluid Carbon Dioxide", J. Chem. Eng. Data **31**, 303–308 (1986).

Gere, D. R., R. Board and D. McManigill, Supercritical Fluid Chromatography with Small Particle Diameter Packed Columns", Anal. Chem. **54**, 736–740 (1982).

Gonenc, Z. S. and A. K. Sunol, "Pressure Dependence of the Partition Coefficient as Measured by Supercritical Fluid Chromatography", Doga: Tr. J. Chem. **16**, 151–157 (1992).

Gonenc, Z. S., U. Akman and A. K. Sunol, "The Relationships Among Solubility, Equilibrium Adsorption from Supercritical CO_2 and Supercritical Fluid Chromatography", presented at the AIChE Annual Meeting, Paper No. 44c, Miami, FL, (Nov., 1992).

Kelley, F. D. and E. H. Chimowitz, "Near-Critical Phenomena and Resolution in Supercritical Fluid Chromatography", AIChE J. **36**, 1163–1175 (1990).

Kurnic, R. T., S. J. Holla and R. C. Reid, "Solubility of Solids in Supercritical Carbon-dioxide and Ethylene", J. Chem. Eng. Data **26**, 47–51 (1981).

McHugh, M. and M. E. Paulatis, "Solid Solubilities of Naphthalene an Biphenyl in Supercritical Carbon Dioxide", J. Chem. Eng. Data **25**, 326-329 (1980).

Panagiotopoulos, A. Z. and R. C. Reid, "New Mixing Rule for Cubic Equation of State for Highly Polar, Asymmetric Systems", in "Equations of State: Theories and Applications", ACS Symp. Ser. **300** (1986), pp. 571–582.

Peng, D. Y. and D. B. Robinson, "A New Two-Constant Equation of State", Ind. Eng. Chem. Fundam, **15**, 59–64 (1976).

Roth, M., "Thermodynamics of Retention in Supercritical Fluid Chromatography: A Refined Model", J. Phys. Chem. **94**, 4309–4314 (1990).

Shimm, J. and K. P. Johnston, "Adjustable Solute Distribution between Polymers and Supercritical Fluids", AIChE J. **35**, 1097–1106 (1989).

Shimm, J. and K. P. Johnston, "Phase Equilibria, Partial Molar Enthalpies and Partial Molar Volumes Determined by Supercritical Fluid Chromatography", J. Phys. Chem. **95**, 353–360 (1991).

Van Wasen, U. I. Swaid and G. M. Schneider, "Physicochemical Principles and Application of Supercritical Fluid Chromatography", Angew. Chem. Int. Ed. Engl. **19**, 575–587 (1980).

Yonker, C. R. and R. D. Smith, "Effect of the Partial Molar Volume of the Solute in the Stationary Phase on Retention in Supercritical Fluid Chromatography", J. Chromatogr. **459**, 183–191 (1988a).

Yonker, C. R., and R. D. Smith, "Retention in Supercritical Fluid Chromatography: Influence of the Partial Molar Volume of the Solute in the Stationary Phase", J. Phys. Chem. **92**, 1664–1667 (1988b).

Yonker, C. R., R. W. Wright, S. L. Frye and R. D. Smith, "Mechanism of Solute Retention in Supercritical Fluid Chromatography", in "Supercritical Fluids", T. G. Squires and M. E. Paulatis, Ed., ACS Symp. Ser. **329** (1987), pp. 172–188.

Manuscript received May 28, 1993; revised manuscript received November 14,1994; accepted for publication November 20, 1994.