JOURNAL REVIEW

Phase Equilibria for Supercritical Fluid Process Design

Supercritical fluids (SCF's) are powerful solvents with many unique properties. They have great potential for many extraction processes, but reliable and versatile mathematical models of the phase equilibrium thermodynamics are needed for their use in process design and economic feasibility studies. This paper reviews existing experimental data and analytical methods and attempts to delineate their strengths and limitations. Also discussed are new data needs and possible new directions for a better fundamental understanding of the molecular processes in SCF solutions.

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Introduction

In recent years the advent of supercritical fluid extraction (SCFE) has been hailed by researchers as a solution for many of the challenging separation problems of the 21st century. Designers, however, have been apprehensive about the high capital costs coupled with the safety problems of both high-pressure and (sometimes) flammable solvents. Above all, they are uneasy about what appears to them to be a relatively untried technology with relatively limited mathematical models for design and scaleup.

In truth, SCFE is neither a panacea nor a hazard. Although it has often appeared to be a solution in search of problems, there are in fact many important areas where it can solve important, practical separation problems. It has been used in the petroleum industry with CO_2 for tertiary oil recovery and SCF pentane for heavy ends processing. Unfortunately, many of the best successes are proprietary, such as the applications in foods, flavors, and fragrances, not to mention the difficult separations of thermally labile pharmaceuticals; for the most part, information on these are not yet available in the open literature. Reviews of applications are available elsewhere (Williams, 1981; Paulaitis et al., 1982; Ely and Baker, 1983; Rizvi et al., 1986; Larson and King, 1986; Eckert et al., 1986b; McHugh and Krukonis, 1986).

SCFE probably is employed best for difficult separations, especially on relatively low-volume, high-value products. It should never be the first technique tried for any separation problem, but more often the last. Certainly if liquid-liquid extraction or any type of distillation can do an adequate job, it is almost always cheaper. Notable exceptions exist in processes where environmental concerns or governmental regulations make supercritical extraction with carbon dioxide more attractive than conventional separations.

The hazards of SCFE are probably due most to its application by people in industries not accustomed to dealing with moderate pressures and/or flammable solvents. For example, much more danger is perceived in the food industry than in the petroleum industry.

Nonetheless, any really widespread applications of SCFE in the future are highly dependent on the ability of engineers to model and predict phase equilibria in the complex systems represented. Only then will designers be able to choose the situations where this unique process will realize its full economic benefit. Equally important, they will be able to identify and reject many of the speculative schemes with little promise of economic success, on the basis of valid process designs and economic feasibility studies. Thus, design reliability may assuage the apprehension of many engineers to use SCFE and further its economical application. To open such doors for SCFE, we need first to achieve a sufficiently detailed understanding of the actual molecular process in SCF mixtures, and then to use this knowledge to transcend empirical correlations and develop reliable, versatile, theoretically-based predictive models.

There are some special properties of SCF systems that make them both very interesting for extractions and yet especially challenging to characterize. Figure 1 presents a density-pressure plot of a typical SCF solvent, and the shaded region is the area where most extractions would take place. Note two features: 1. the solvent density is high, nearly that of the normal liquid, and this gives the fluid a high capacity for solutes; 2. the slope of the isotherm (the compressibility) is very high, going to infinity at the critical point itself. This factor means that very small pressure changes give large density variations. Generally solubilities

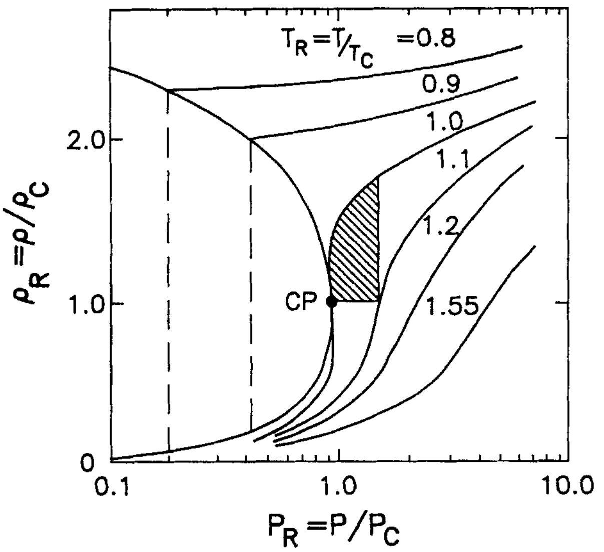

Figure 1. Pure component phase diagram in the vicinity of its critical point.

Shaded region indicates where most SCFE occurs.

are too low and control problems are too difficult to operate an extraction very near the critical point (within a very few degrees celsius). To take advantage of the desirable physical properties, however, the range T_R = 1.01–1.10 and P_R = 1.01–1.5 would typically be most attractive.

Figure 2 shows a typical plot of solute loading as a function of solvent density, and the solubility is virtually exponential. This means that very small pressure changes have enormous effects on solubility. Finally, SCF's typically have solute molecular diffusivities much higher than those of liquids (Tsekhanskaya, 1968, 1971; Swaid and Schneider, 1979; Saad and Gulari, 1984a, b) and viscosities that are almost as low as those of gases (Reichenberg, 1975; Stephan and Lucas, 1979). In all, they are virtually ideal fluids for enhancing mass transfer across a boundary.

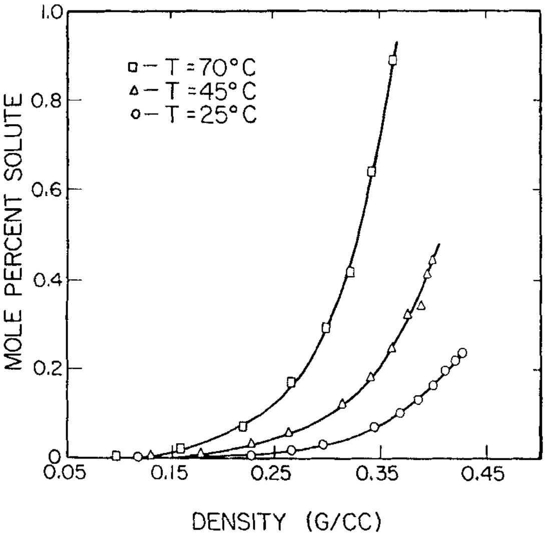

Figure 2. Typical exponential solubility behavior: phenanthrene in SCF ethylene.

Thus, the important characteristics of SCF's for extraction are then:

1. They have a very high capacity for solutes. It is not unusual for the solubility to be 10^3–10^6 or even 10^8 greater than one would expect in an ideal gas.
2. They offer the advantages of both distillation and extraction, in that they separate compounds not only by differences in vapor pressure, but also by specific interactions with well-chosen solvent components. (See Entrainers, discussed later.)
3. They are readily adapted to very difficult separations. Not only do they permit facile separation of thermally-labile materials at low temperatures, but, because of the high compressibility and exponential solubility, they can give good separations with very small pressure variations. (See, for example, the virtually monochromatic separation of polydispersed styrene oligimers, Klesper, 1978.)

There are, however, two aspects of SCF behavior that render them especially difficult to model. The first is the proximity to the critical point itself, and the second is the great asymmetry of most SCF systems of interest. The term "asymmetry" refers to systems with large differences in both size and force constant (or attractive forces) of the molecules involved, such as for the phenanthrene-ethylene system shown in Figure 2. Most equations of state (EOS's) and corresponding states treatments were originally developed to deal with petroleum fractions, usually not near the critical point, involving mixtures of similar molecules as found in a typical cut. Most EOS's, such as the common cubic forms, are least precise in the region of interest for extractions near the critical point (within 1 to 10% in temperature and 1 to 50% in pressure, as discussed above). Most EOS's, of course, are completely inapplicable right at the critical point, which is mathematically singular. The mixing rules to determine the characteristic constants of the mixture for the EOS also become suspect, and the ubiquitous k_{12} (adjustable parameter that should be close to zero, customarily added to the standard mixing rule to obtain the solute/solvent energy interaction parameter) becomes even larger and more variable. Finally, because of both the high pressures and difficulties in sampling a system with exponential solubility relationships, the acquisition of extensive high-quality data becomes more exacting.

The very early work studying phase equilibria in SCF's consisted mostly of Edisonian extraction experiments, reported primarily in the patent literature (for example, Zosel, 1963, 1978). In the past decade or so, significant progress has been made both in experiment and analysis. Much more careful measurements of solubilities, including both solvent and solute mixtures, are now available, and semiempirical thermodynamic models, as, for example, cubic equations of state (EOS's) or perturbation models have been adapted to the correlation of solubilities in well-characterized binary SCF systems. More recently, investigators have probed more deeply, measuring thermodynamic derivative properties and molecular phenomena, as well as using computer simulations and more advanced EOS's. These promise to lead to a more fundamental understanding.

The purpose of this paper is to review these experimental and analytical efforts in phase equilibrium thermodynamics of SCF systems. We attempt to delineate what data are currently available and what data are needed for further development. Also we wish to show both the capabilities and limitations of current correlative and predictive methods. Finally we emphasize the need for a better appreciation at a molecular level of the unique processes occurring, so that we might improve our models and extend them to new compounds, more severe thermodynamic conditions and to more complex, realistic situations.

SCF: Solid/Fluid Equilibria

The bulk of research with SCF's has been the measurement and modeling of the phase equilibria between heavy organic solutes and the SCF's. We not only review the results of solubility studies for a wide range of solutes, but discuss the use of "entrainers" to enhance solubility and improve selectivity, special considerations necessary with solute mixtures, and how separations can be made with SCF's. Discussed also are the numerous models and modeling methods that have been developed for solid/fluid equilibria.

Solid/fluid solubilities

Most of the early experimental studies are tabulated in the review by Paulaitis et al. (1982). The solutes generally fall into two classes: the first comprises a series of simple, mostly aromatic hydrocarbons; the second is a wide variety of solutes of practical importance, ranging from coal tar (Wise, 1970) to pharmaceutical products such as morphine (Stahl and Willing, 1980). The experimental studies and applications for these natural products are discussed in more detail in a review by Ely and Baker (1983).

The most commonly used solvent continues to be CO_2, which is attractive because of a convenient critical point of 304.2 K and 73.8 bar, low cost, nontoxicity, and nonflammibility. Other interesting SCF's investigated in the early studies include water, methane, fluoroform, ethylene, and ethane.

Recent investigations have included studies of solutes containing interesting and specific functional groups, more natural products, and to a wider variety of solvents with higher critical temperatures and pressures. More importantly, solute and solvent *mixtures* have been investigated to yield information on the possibility of separations using SCF's.

Recent research has demonstrated the applications of SCF technology to natural products and systems of immediate practical importance. For example, there has been a significant effort to determine the feasibility of extracting toxins from soil, activated charcoal, and other environmental solids (DeFilippi and Robey, 1983; Brady et al., 1987; Dooley et al., 1987; Schantz and Chesler, 1986; Hawthorne and Miller, 1987a, b), as well as model compounds (Kander and Paulaitis, 1983; Eckert et al., 1987). Unfortunately, the attractiveness of the extractions seems to be dependent strongly on the particular properties of the solid samples, which are variable and unpredictable. In many cases, however, it has been demonstrated that solid samples can be cleaned by SCFE with good overall removal.

The high cost and lack of reliability of our energy sources have evoked interest in better utilization of our nation's own resources. As a result, SCFE has been targeted as a means of upgrading coal, tar sands, lignite, and other fuels, mostly by pretreatment (Vasilakos et al., 1985; Pang and McLaughlin, 1985; Monge and Prausnitz, 1983; Scarrah, 1983; Chen and Kazimi, 1985). In these cases, higher-temperature fluids, such as tetrahydrofuran, toluene, benzene, the higher (up to dodecane) *n*-paraffins, methanol, acetone or water, are required (Fong et al., 1983; Eisenbach et al., 1983; Amestica and Wolf, 1985; Penninger, 1985; Wilhelm and Hedden, 1985; Ross et al., 1987; Deshpande et al., 1987; Kershaw and Bagnell, 1987; Triday and Smith, 1988). At these elevated temperatures, frequently above 400°C, both extraction and pyrolysis take place. Coal retains most of its heating value after extraction, and organic sulfur can be selectively removed by using polar solvents that are capable of hydrogen bonding with the sulfur. This suggests that understanding specific chemical interactions (for example, hydrogen bonding, acid/base interactions, and charge-transfer complexation) in order to tailor solvent mixtures will be important in the optimization of coal extraction processes. While these systems are important for evaluation of actual processes, it is again difficult to make generalizations or derive information about intermolecular interactions due to the wide variability of the samples. Therefore, careful choice and investigation of model compounds are required.

Since the early model compounds studied were nonfunctional polycyclic aromatics, the logical extension was to polycyclic aromatic solutes containing oxygen, nitrogen and bromine functional groups. These were investigated in both nonpolar and polar solvents to examine the effect of solvent size and polarity on the solubilities (Hansen, 1985). The solutes were acridine, dibenzofuran, 9-fluorenone, and carbon tetrabromide. The solvents were nonpolar CO_2, ethane, ethylene, sulfur hexafluoride, a relatively large solvent molecule, and the polar solvent fluoroform. The general conclusions were that the solubility was dominated in most cases by dispersion forces, such that ethylene was a better solvent than CO_2, except for nonpolar solutes, for which CO_2 was as good as ethylene. In general, fluoroform, the polar solvent, was a poor solvent for nonpolar compounds, but approached the solvent power of ethylene for polar solutes due to the added dipole/dipole interactions which augmented the dispersion interactions.

The enhancement factor is a dimensionless measure of solvent power, defined as the measured solubility divided by the ideal gas solubility. While enhancement factors of $10^4 - 10^6$ are quite common, values as high as 10^{12} have been recorded (McKinley et al., 1961). It was observed that the logarithm of the enhancement factor was generally a linear function of the solvent density. In fact, in a common nonpolar solvent, CO_2, the solubilities of both polar and nonpolar solutes with different functional groups varied only as a result of different vapor pressures. As a result, all these compounds have similar enhancement factors, as shown in Figure 3 (Van Alsten, 1986). The enhancement is relatively insensitive to the solute structure but very dependent on the polarity and density of the solvent.

Another study looked systematically at the solubility of solutes that were chosen to represent different chemical functionalities in supercritical CO_2, ethane, fluoroform, and chlorotrifluoromethane (Schmitt and Reid, 1986). The solutes were either simple polycyclic hydrocarbons or monofunctional derivatives of those hydrocarbons, chosen on the basis of their relatively similar critical temperatures but greatly different structures. Ethane was the best solvent for the simple hydrocarbons; CO_2 was nearly as good; and both fluoroform and $CClF_3$ were poorer solvents for these solutes. The trends, however, were significantly different for solutes containing various functional groups. CO_2 was significantly better for benzoic acid, and fluoroform (which had been a poor solvent for the simple hydrocarbons) was a good solvent for molecules like 2-aminofluorene and 1,4-naphthoquinone. This confirms the previously-mentioned findings that polar solvents are poor for simple nonpolar hydro-

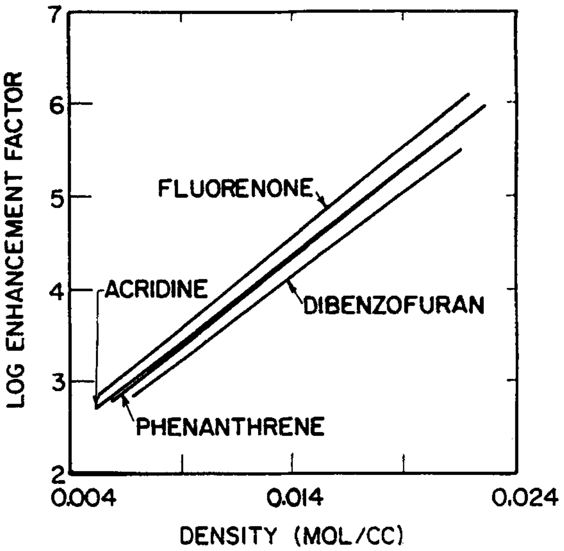

Figure 3. Enhancement factors for three-ring aromatics in supercritical CO_2 at 50°C.

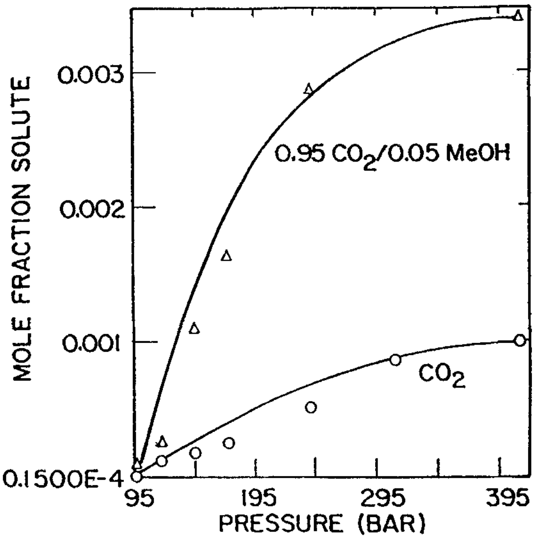

Figure 4. Solubility increase of acridine at 50°C with an entrainer-doped solvent.

carbons, but exhibit great potential for polar molecules and those containing functional groups that can hydrogen-bond with the acidic proton of the solvent.

A later study extended the SCF database to three additional higher-temperature solvents: butane, ammonia, and ethanol (Hess, 1987). The researchers studied solutes with higher melting points that contained sulfur as well as oxygen and nitrogen. These included dibenzothiophene, thianthrene, thioxanthone, xanthone, dodecahydrotriphenylene, and 6,13-dihydrodibenzo[b,i]phenazine. While this study greatly expanded the solubility database, the general conclusion was that the only differences in solubility were due to differences in vapor pressure.

A study of three hydroxybenzoic acid isomers and three dihydroxybenzene isomers in supercritical carbon dioxide corroborated the above observations (Krukonis and Kurnik, 1985). The authors concluded that the solubility could be correlated with the melting point (or vapor pressure) of the isomer and that a separation with supercritical fluids could be facilitated if there were significant differences in the melting points (or, subsequently, vapor pressures) of the isomers. While separations based on differences in vapor pressure are useful, it also would be desirable to separate compounds on the basis of chemical properties. Consequently, it has been proposed that separations and enhanced solubilities would be achieved best by using solvent mixtures, or "entrainer" mixtures that target specific interactions between the solute and the solvent or entrainer.

Entrainers

Solubilities of heavy organic solutes can be greatly increased by adding entrainers to the SCF solvent, as shown in Figure 4. An entrainer, or cosolvent, is a small amount (1–5%) of an additional component, usually of intermediate volatility, added to the SCF that does not change significantly the critical properties or density of the solvent mixture. The entrainer may be selected to interact more strongly with one component to facilitate separations. The use of entrainers has improved selectivity while maintaining the sensitivity of the solubility to small changes in temperature and pressure, which has made SCFE such an attractive alternative to conventional separation methods.

Brunner presented the use of entrainers to enhance the solubility of low-volatility *liquids* in SCF's (Brunner, 1983). Although the analysis of the phase equilibria is complicated by the solubility of the entrainer and SCF in the liquid phase, the solubilities of the low-volatility liquids were several times greater with the entrainer present. More importantly, the *separation factor* (ratio of hexadecanol solubility to octadecane solubility) was also increased by using methanol or acetone as the entrainer, because the entrainer was capable of hydrogen-bonding with hexadecanol.

Solid solutes are also enhanced in many entrainer systems. In general, nonpolar cosolvents or entrainers increase the solubility of nonfunctional aromatic hydrocarbons up to several hundred percent. For *n*-alkane entrainers the solubility enhancement is a linear function of the solubility parameter: i.e., the longer the chain, the greater the enhancement. Also, the greater the concentration of entrainer, the greater the solubility is enhanced. For nonpolar solutes and entrainers, however, there is no indication of increased selectivity. The solubility isotherms are uniformly shifted upwards for the solutes studied. The ratio of solute mole fraction (y_2) in the entrainer system to y_2 in the pure solvent system is relatively independent of density, so no real improvement in selectivity could be anticipated by temperature and pressure manipulation (Dobbs et al., 1986).

Johnston and coworkers obtained similar results for polar cosolvents with polar solutes (Dobbs et al., 1987). The additional dipole/induced dipole interactions shifted the isotherms upward by a relatively constant factor. The enhancements for systems with the possibility of hydrogen bonding or strong dipole/dipole interactions, however, were frequently greater than those found for the nonpolar solutes. For 2-aminobenzoic acid, the addition of 3.5 mol % methanol increased the solubility 620%. These findings suggested that entrainers could facilitate separations if the solutes were of *differing polarities*. As a result, when Wong and Johnston (1986) measured the solubilities of three sterols of similar polarity—cholesterol, stigmasterol, and ergosterol, they found that the separation factors would be about the same with or without entrainers added to the CO_2. In this case, however, entrainers might be useful even though they do not improve selectivity. The solubilities of these sterols are so low that adding the entrainer to enhance all the solubilities by about an order of magnitude may be essential to the economics of the process. Interestingly, the cholesterol/ethanol system formed a solid complex that lowered its activity. As a result, solid complex formation may be an additional means of improving separations in some specific systems.

An extreme example of an entrainer effect was reported very recently by Johnston (1988), who observed increases of solubility of two to three *decades* for hydroquinone in carbon dioxide with the addition of small amounts of tributyl phosphate entrainer, as shown in Figure 5.

Besides dipole/dipole and dipole/induced dipole interactions, hydrogen bonding is an important and distinct mechanism for solubility enhancement. Extremely polar compounds like 9-fluorenone (3.4 D) are enhanced more greatly by acetone as an entrainer, since it is more polar than methanol. Methanol, however, is capable of hydrogen bonding, so less polar solutes like acridine (2.1 D) are more greatly enhanced by methanol (Van Alsten, 1986). This suggests that careful choice of entrainers could be used to separate compounds, not just on the basis of polarity, but also on the basis of functionality and ability to have specific interactions.

Mixed solutes

An important consideration in separation processes that must be addressed is the effect of solute/solute interactions. In most models of supercritical solubilities discussed later, investigators assume infinite dilution of all solutes: i.e., no solute/solute interactions, because the mole fractions are generally below 10^{-2} or 10^{-3} (Dobbs et al., 1987; Johnston and Eckert, 1981; Johnston et al., 1982; Schmitt and Reid, 1986; Ziger and Eckert, 1983). However, there is significant experimental evidence to suggest that solute/solute interactions are important even in dilute solutions.

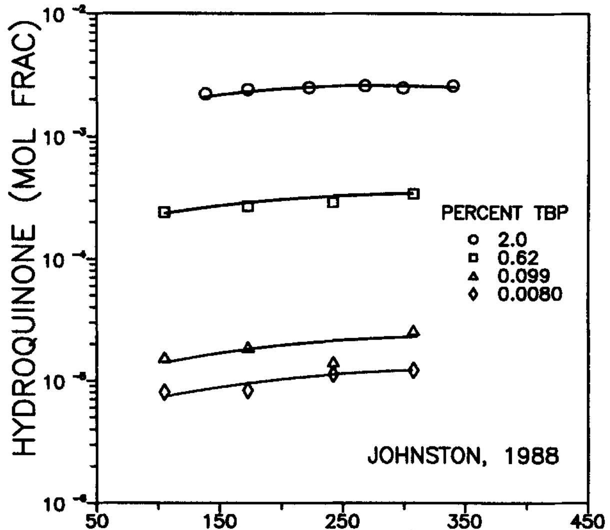

Figure 5. Extreme entrainer enhancement: the effect of tributyl phosphate on the solubility of hydroquinone in SCF CO_2.

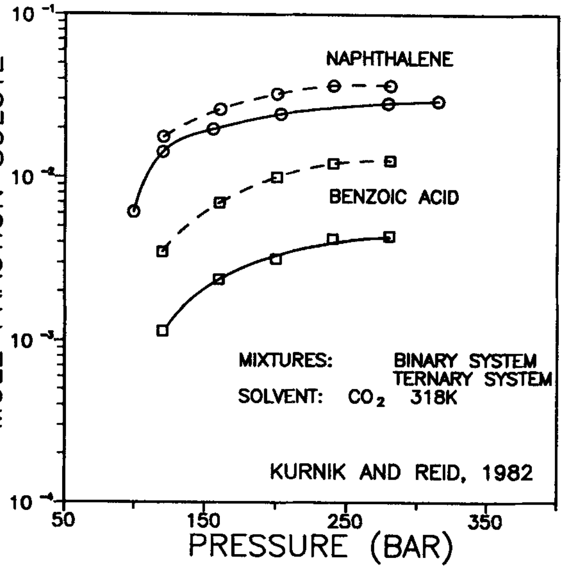

Figure 6. Synergistic solubility behavior in a mixed solute system.

Kurnik and Reid (1982) compared the ternary (two solutes) solubilities to the corresponding binary solubilities and found that in many cases the solubilities of both components were increased by as much as 100%. This is shown for the benzoic acid/naphthalene/CO_2 system in Figure 6. With solubilities on the order of 10^{-2}–10^{-3} mol fraction, attractive interactions appear to pull both solute species into solution, resulting in the synergistic behavior.

A study of the phenanthrene/anthracene/CO_2 by Kwiatkowski et al. (1984) provided additional and complimentary information. They found that the solubility of anthracene (about 10^{-5} mol fraction) increased, while that of phenanthrene (about 10^{-3} mol fraction) decreased slightly relative to the binary pairs. This suggests that anthracene sees attractive forces from the more concentrated phenanthrene but that the anthracene is sufficiently dilute not to effect the phenanthrene.

Fluorescence spectroscopy experiments have verified the existence of solute/solute interactions at low concentrations in SCF solutions in terms of excimer formation (Brennecke and Eckert, 1988, 1989). Excimers are excited state dimers that result in a broad structureless band at significantly longer wavelengths than the normal fluorescence. While they are not dimers in the sense of a ground state complex, their existence does indicate that there is sufficient interaction in the short lifetime ($\approx 10^{-6}$ s) of the excited state to form the excited state complex. For example, the spectra of pyrene in SCF CO_2 show significant excimer formation at a mole fraction of less than 10^{-5}, indicating solute/solute interactions even at that low concentration.

These results emphasize that we must reconsider the concept of infinite dilution for SCF solutions and take solute interactions into consideration in the investigation and design of separation processes.

Separations

Although binary and entrainer system solubilities suggest that separations are possible with careful selection of solvent and possibly entrainer, very few experimental verifications of these separations exist.

Chrastil (1982) reported that α-tocopherol could be selectively extracted from a mixture of α-tocopherol and tripalmitin with SCF CO_2, especially at higher temperatures and pressures. The $\ln y_2$ vs. density isotherms for these two compounds are characteristically linear but have different slopes, leading to the greatest difference in solubilities at higher pressures.

The only test of entrainer-induced selectivity changes is a carefully designed one in which a mixture of anthracene and acridine were extracted with a 1% CH_3OH in CO_2 mixture. Anthracene and acridine do not exhibit synergism in the binary solute mixture (as discussed above) and the acridine should be highly interactive with the methanol through dipole interactions and hydrogen bonding, while the anthracene should be relatively unaffected. While the solubility of both components increased, which is undesirable from a separations point of view, the selectivity increased dramatically, as shown in Figure 7 (Van Alsten, 1986). Thus, this constitutes an experimental verification of a system in which specific interactions between an entrainer and a solute enhanced separation in a SCF.

Alternate separation methods

The number of stages required for SCFE may be reduced drastically according to a scheme taking advantage of the inverse temperature relationship of the solubility in certain regions of pressure-temperature space. This method may give a highly purified product in a single step (Chimowitz and Pennisi, 1986), and requires that both solutes exhibit "crossover" points at distinctly different pressures. The "crossover" point is the pressure at which two isotherms cross on a y_2 vs. pressure diagram, as shown in Figure 8, and many solutes exhibit this behavior in the region near the critical point. Below the crossover point, the solubility drops as the temperature is increased. This behavior is not unusual but is simply the result of competition between the temperature and density effects in a near-critical fluid. Raising the temperature increases the vapor pressure and correspondingly increases the solubility. The solubility, however, is also a strong function of the density. Raising the temperature *decreases* the density and decreases solubility. Below the crossover point, the density effect dominates and lowers the solubility with increasing temperature. The method proposed is a two-stage isobaric cascade system with temperature cycling. At a pressure intermediate between the two crossover pressures, one can lower the temperature from T_2 to T_1 and pure solute B should drop out since the solubility of A would theoretically increase. Then one can increase the temperature from T_1 to T_2 and precipitate out pure solute A.

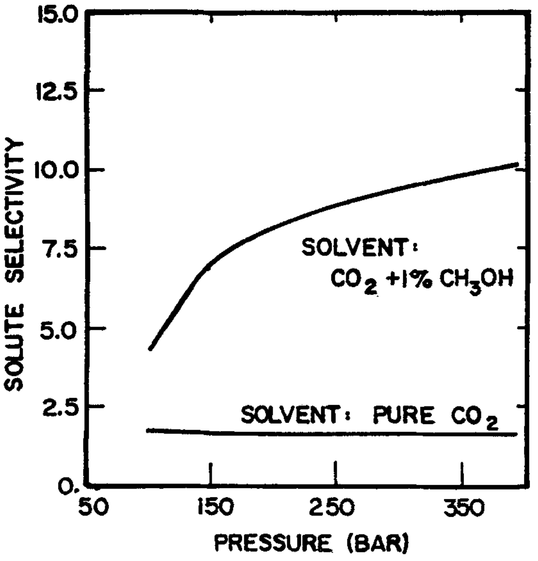

Figure 7. Increase in selectivity for acridine from an acridine/anthracene mixture using entrainer-doped SCF CO_2 at 50°C.

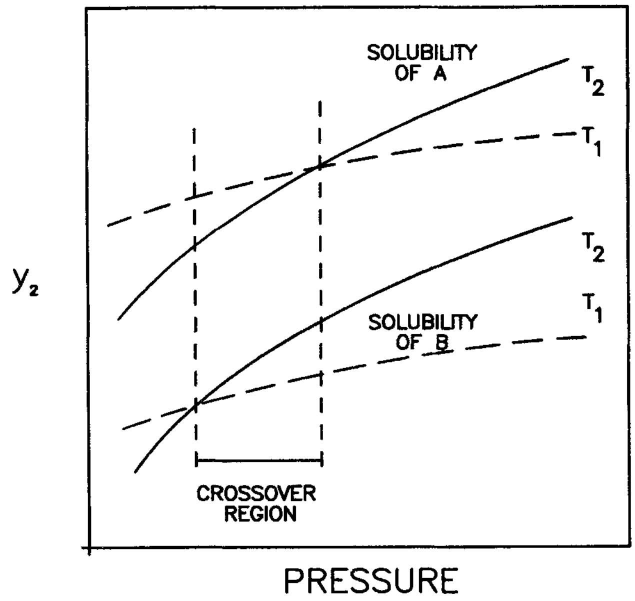

Figure 8. Typical solubility behavior of two compounds exhibiting a crossover region for separation.

While Chimowitz and Pennisi (1986) found the process to be quite successful in the separation of benzoic acid from a benzoic acid and 1,10 decanediol system, other systems are more difficult, due to nonexistent, narrow or poorly-defined crossover regions (Johnston et al., 1987a). For example, Johnston and coworkers achieved only 79% purity from a 50/50 solute mixture in the separation of the 2,3- and 2,6-dimethylnaphthalene isomers using CO_2.

Modeling phase equilibria

The design and evaluation of SCF separation processes relies heavily on the ability to model the phase behavior. Several major difficulties particular to the modeling of the SCF-phase equilibria were mentioned earlier, including the asymmetry of the systems, the high compressibility, and the mathematically singular nature of the critical point.

The goals of the modeling efforts are both to correlate existing data and to attempt *prediction* of phase equilibria in regions where experimental results are not available. Correlations often contain a large number of regressed parameters, contain a varying amount of theoretical basis, and may succeed in fitting the data with some accuracy. Conversely, models developed for the purpose of prediction attempt to minimize the number of parameters and link those parameters closely to real physical phenomena while maintaining theoretical justification for the form of the equation. Both methods serve distinct and useful purposes. In reality, however, the distinction between the two methods is often lost, as theoretically-based models are forced to fit the data better by the introduction of additional adjustable parameters.

Models for supercritical-phase equilibria fall into several categories. The most common method treats the SCF phase as a dense gas and uses an equation of state to calculate the fugacity coefficient of the solute in the fluid phase. In this approach, the results are frequently very sensitive to the interaction energies and size factors, necessitating the need to develop improved mixing rules to estimate the mixture size and energy parameters needed in the EOS. Another modeling strategy treats the SCF phase as an expanded liquid (Mackay and Paulaitis, 1979). There are also a large number of semiempirical correlations, as well as models that have been developed for computer simulations. We discuss these topics with emphasis on the equation of state approach.

EOS-Cubic Equations of State. The most common method to model SCF-phase equilibria is with an equation of state. For a system consisting of a solid phase in equilibrium with the SCF, the solubility of the solid in the fluid phase is given by

$$y_2 = \frac{P_2^{sat}\phi_2^{sat}\exp\left[\dfrac{v_2^s(P - P_2^{sat})}{RT}\right]}{\phi_2 P}$$

where

P_2^{sat} = saturation pressure

ϕ_2^{sat} = fugacity coefficient at saturation (usually very nearly unity)

v_2^s = solid volume

P = system pressure

ϕ_2 = fugacity coefficient of the solute in the fluid phase

The reasonable assumptions that have been made in this equation are that the solid phase is pure and that the solid volume is constant. The term in the exponent is the Poynting correction factor and is generally less than 2 or 3 (Prausnitz et al., 1986). The solubility in an ideal gas would be $y_2 = P_2^{sat}\,\phi_2^{sat}/P$. Therefore, the large solubility enhancements in SCF's relative to an ideal gas are due to exceptionally small values of ϕ_2. An equation of state determines the values of the solute fugacity coefficient in the SCF phase.

The first efforts to model SCF-phase behavior attempted to use the virial equation (Ewald et al., 1953; King and Robertson, 1962; Najour and King, 1970; Rössling and Franck, 1983). Even with the inclusion of the third virial coefficient, the virial equation cannot model the dense fluid region at densities near the critical; fourth or higher virial coefficients would be required and these are certainly not available (Prausnitz et al., 1986).

Many equations used more recently are based on a perturbation about a spherical hard-sphere reference. Simplifying assumptions lead to what will be called the "perturbation" equations, and, with certain assumptions, the cubic equations (like the van der Waals equation) result. Finally, lattice gas models have been developed and refined that have shown some success for modeling SCF-phase behavior.

Cubic equations of state are exceedingly simple, have been remarkably successful in modeling SCF-phase behavior, and are probably the most widely used in analyzing experimental data. Moreover, the cubic EOS must be the equation of choice for process design of any very complex system, because the interactions are too involved to justify the use of a more fundamentally-based equation. However, due to their approximate and somewhat empirical nature, mixing rules are extremely important in determining the quality of the model.

Most simple cubic EOS's can be derived from a first-order perturbation about a hard-sphere reference state. One can obtain the van der Waals EOS by assuming that the integral of the perturbing intermolecular potential for a pair of molecules is a constant: this is the mean field approximation (Jonah et al., 1983). The Redlich-Kwong (RK) equation and the Peng-Robinson (PR) equation (1976) are obtained by introducing a temperature and density dependence into the perturbing intermolecular potential. The Peng-Robinson equation and the Soave modification of the Redlich-Kwong (SRK) equation have been used widely to model solid/SCF phase equilibria. Kurnik et al. (1981) successfully reproduced solubility data for aromatic hydrocarbons in SCF ethylene and CO_2 by including a regressed binary interaction parameter to determine the cross energy parameter. Most workers have found that the binary interaction parameters are temperature-dependent, which introduces more fitting of parameters. Schmitt and Reid (1986) obtained good results by eliminating the binary interaction parameter and regressing the solute size and energy parameters rather than obtaining them from estimated critical properties. Although limitations clearly exist, the Peng-Robinson equation gives a good qualitative picture of all types of SCF-phase behavior (Hong and Modell, 1983) and reasonably good quantitative fits for a wide variety of systems. In fact, in a comprehensive com-

Table 1. Equations of State

Carnahan-Starling-van der Waals (CSVDW)

$$P = RT\frac{\xi}{b_o}\frac{(1 - \xi + \xi^2 - \xi^3)}{(1 - \xi)^3} - \frac{a}{V^2} \qquad \xi = b/V$$

Augmented van der Waals (AVDW)

$$P = RT\frac{\xi}{b_o}\frac{(1 - \xi + \xi^2 - \xi^3)}{(1 - \xi)^3} - \frac{1}{b}\sum_{m=1}^{6} m\,A_{1m}\,\xi^{m+1}\,\epsilon + \frac{\beta}{RTb\beta^{max}}\sum_{m=1}^{9} m\,A_{2m}\xi^{m+1}\,\epsilon^2$$

A_{nm} = Alder constants

ϵ = energy term

$\beta = -(1/V)\,(\partial V/\partial P)$

β^{max} = maximum β at given temperature

Carnahan Starling-Redlich Kwong (CSRK)

$$P = RT\frac{\xi}{b_o}\frac{(1 - \xi + \xi^2 - \xi^3)}{(1 - \xi)^3} - \frac{a}{T^{1/2}V(V + b)}$$

Hard Sphere-van der Waals

$$P = \frac{RT}{V}\frac{[(1 + \xi + \xi^2) - 3\xi(y_1 + y_2\xi) - \xi^3 y_3]}{(1 - \xi)^3} - \frac{a}{V^2}$$

where

$\xi, y_1, y_2, y_3 = f$(hard-sphere diameters and mole fractions) parison with several other equations, the Peng-Robinson performed almost as well as more complicated perturbed hard-sphere equations for a wide variety of solutes in a diverse field of SCF solvents (Ellison, 1986; Hess, 1987).

EOS-Perturbation Equations. Use of the Carnahan-Starling (1972) repulsive term, instead of the VDW version, significantly improves the EOS's representation of SCF equilibria. The VDW $V/(V - b)$ repulsive term is replaced by $(1 + \xi + \xi^2 - \xi^3)/(1 - \xi)^3$ where $\xi = b/V$. This is the approach taken by Johnston and his coworkers (Johnston and Eckert, 1981; Johnston et al., 1982) in the development of the Carnahan-Starling-van-der-Waals (CSVDW) model and the augmented van der Waals (AVDW) equation. The form of these equations is shown in Table 1. With the CSVDW, the solubility of nonpolar aromatics in SC ethylene was represented quite well, especially in the higher-density regions. The interaction energy, a_{12}, was the parameter fit and was found to be only slightly temperature-dependent. In addition, a_{12}'s correlated well with the enthalpy of vaporization of the solute. A Carnahan-Starling-Redlich-Kwong (CSRK) equation, which incorporates both the better repulsive and attractive terms, gave improved results as well. A later study, which included polar solutes and SCF solvents, found the CSVDW equation to give equally reasonable results for the more complicated systems. Bertucco et al. (1986) applied the same approach to a wider variety of systems and found similar results. In addition, if one is willing to introduce a second adjustable parameter for the combining rule of the volumes, one can improve the fits further.

The AVDW equation also contains the improved CS repulsive term but uses the molecular dynamics square well results of Alder (1969, 1972) to include second-order perturbation effects and improve the attractive term. This significantly improved the representation in the region of reduced densities from 1.0 to 1.5.

Subsequently, Johnston and coworkers have used a hard-sphere van der Waals (HSVDW) equation which incorporates an accurate repulsive expression for the hard-sphere mixture (Mansoori et al., 1971) with the standard VDW attractive term to correlate solute/SCF/entrainer data (Dobbs et al., 1986; Dobbs and Johnston, 1987; Dobbs et al., 1987). The representations are good when the solute/cosolvent interaction parameter is fit, but only comparable to the other equations when the parameter is predicted from physical properties.

Another perturbation method that has been applied to SCF is the perturbed hard-chain theory (PHCT) (Mart et al., 1986) and its variations (Vimalchand and Donohue, 1985; Jin et al., 1986; Ikonomou and Donohue, 1987; Morris et al., 1987; Walsh et al., 1987). This model addresses the asymmetry of the size of the molecules, taking into consideration the ability of the solvent to interact with only part of the solute. Like the AVDW, the PHCT includes the CS repulsive expression and an extension of the second-order Alder functions for the attractive term. However, its mixture properties are based on surface or volume fractions, and it uses mixing rules based on a nonrandom approach, which we discuss in more detail in the mixing rule section. Although different mixing rules are derived for each perturbation, there is only one adjustable binary interaction parameter. The model yields good results for the solubility of nonfunctional polycyclic aromatics in nonpolar SCF solvents, using relatively small values of the binary interaction parameter.

There are a variety of other perturbation methods (Jonah et al., 1983; Teja and Smith, 1983). These include a method which uses the Padé approximant, a mean field approximation like the van der Waals equation discussed earlier in the cubic EOS section, except that higher-order perturbations are included and a corresponding states treatment called the shape factor approach that involves a perturbation about a nonspherical reference. While these methods show promise for the limited systems presented, they would have to be analyzed for a wider range of systems to draw any conclusions.

EOS-Lattice Gas and Scaling Forms. A different approach has been the use of lattice gas models or those including scaling laws (like the model of Leung and Griffiths, 1973), which are nonanalytic. These approaches address the fact that behavior in the *immediate* vicinity of the solution critical point is nonclassical and cannot be described correctly by a classical equation of state like the VDW equation or its modifications. In fact, the limiting values of the partial molar volume, enthalpy, and heat capacity approach negative or positive infinity and, for some properties, the limiting values are path-dependent (Rozen, 1976; Chang et al., 1984; Chang and Levelt Sengers, 1986; Levelt Sengers et al., 1986). This unusual behavior suggests the need for a nonclassical EOS, which, if scaled properly, can describe thermodynamic properties in terms of the "distance" from the critical point, as governed by the universal "critical exponents." This is the essence of scaling law models. In this spirit, lattice gas models and the Leung-Griffiths model impose the correct asymptotic behavior at the critical point. Fortunately, most extraction and separation processes will take place sufficiently removed (several degrees Kelvin) from the critical point that consideration of the nonclassical nature of this region is not generally necessary. However, complete understanding of the critical region is of continued interest and a lattice gas model or other scaled models seem to be the best approach.

A lattice gas model is based on the idea of the distribution of molecules over the sites in a three-dimensional lattice. Trappeniers et al. (1970) used a mean-field, two-component lattice gas model, which introduces vacant lattice sites, to explore the phenomenon of "gas-gas equilibria" observed for some noble gas mixtures at high pressures. Vezzetti (1982) extended the two-component lattice gas concept to model solubilities of solutes in SCF's, and asymmetric mixtures (1984) by allowing the solvent and the solute to occupy different numbers of sites in the lattice. Vezzetti obtained good fits for slightly asymmetric mixtures using only one adjustable parameter. Kleintjens and coworkers extended the mean-field lattice gas treatment of Trappeniers by including an empirical entropy correction parameter (Kleintjens and Koningsveld, 1980). With two mixture parameters, in addition to several pure-component parameters determined from limited experimental data, they were able to reproduce quantitively the phase diagrams of a number of systems as asymmetric as naphthalene/ethylene (Kleintjens, 1983; Koningsveld et al., 1984; Kleintjens and Koningsveld, 1983). The model has recently been extended to multicomponent systems (Kleintjens et al., 1988).

A decorated lattice gas superimposes an additional set of lattice sites at the midpoints of the regular lattice, and this is applicable particularly to asymmetric systems. Wheeler (1972) first applied this to describe limiting behavior of dilute solutions near the critical point. Gilbert (1987) developed a decorated lattice gas model that incorporates the Ising model to allow for full development of the critical region. With this decorated lattice gas model, he was able to fit solubility and partial molar volume data, which is a more stringent test of any model because it requires the pressure derivative of the model to be correct (as discussed in the section on partial molar volumes), for highly asymmetric mixtures with two adjustable parameters. Nielson and Levelt Sengers (1987) concurrently developed a decorated lattice gas model for supercritical solutions and were able to reproduce portions of solubility curves. Although they use a more complex nonclassical description of the pure solvent and include the temperature and pressure dependence of the additional (solute) phase, they were unable to represent the partial molar volume data at all quantitively with the same parameters, perhaps due to a somewhat different interpretation of Mermin's decorated lattice gas. Kumar et al. (1987) also presented a lattice-gas-based model that was able to reproduce the solubilities of polycyclic aromatics in SCF's outside the critical region with only one temperature-independent interaction parameter. They did not attempt to predict partial molar volumes.

Leung and Griffiths (1973) developed a scaling law equation, not based on a lattice gas, that used "field" variables as the independent parameters. Field variables are those that remain constant across a phase boundary, like temperature, pressure, and chemical potential. These are in contrast to "density" variables like mole fraction that are different in the two phases. Leung and Griffiths were successful in reproducing the phase behavior for He^3-He^4 mixtures. An attractive feature of this equation is that the constants in the equation should be universal for all components or obtained from physical data for that compound. Unfortunately, when Rainwater and Moldover (1983) attempted to extend the model to slightly more asymmetric mixtures, they could obtain adequate fits only when they adjusted several of the parameters.

Fox presented one alternate method of dealing with the problem in which he suggested a way to modify classical EOS to improve their performance in the nonclassical region, i.e., to make them nonclassical in the region very close to the critical (Fox, 1983). This was accomplished with a switching function to change from the use of the nonclassical scaling equation close to the critical point to a normal EOS further from the critical region. Although it might be useful in practice, it does lead to internal inconsistencies in the model.

While all these developments provide poorer representations than cubic EOS or perturbation equations with the same number of parameters, they do provide a more theoretically-based approach with potential for further development.

Expanded Liquid Treatment. The alternate method to the dense gas approach is to describe the phenomena as expanded liquid/solid equilibria. The disadvantage of this method is that, instead of one thermodynamic variable (ϕ_2) to be correlated or predicted, two are needed (γ^∞ and $\bar{v}_2$). Mackay and Paulaitis (1979) took this approach with two adjustable parameters—the infinite dilution activity coefficient and a binary interaction parameter—to calculate the infinite dilution partial molar volume from the Redlich-Kwong EOS. They obtained very large ($\approx$1,000) activity coefficients but observed good representations for naphthalene in CO_2 and ethylene.

Instead of being used as adjustable parameters, the activity coefficients could be estimated from a solution model. In a study of dense gases for chromatographic separations, Giddings (1969) suggested the use of the Hildebrand solubility parameter and correctly observed that the solubility parameter and subsequently the solubility should be proportional to the fluid density. Unfortunately, most attempts to include regular solution theory have resorted to at least semiempirical formulations. Pang and McLaughlin (1985) resorted to fitting the solubility as a function of the solubility parameter and pressure with *four* parameters to model several aromatics in CO_2 and ethylene.

The most successful use of the solubility parameter in a semiempirical correlation was that of Ziger and Eckert (1983). Using regular solution theory and the VDW equation, they developed an equation for the enhancement factor, which they modified slightly with two empirical parameters. They successfully reproduced the solubilities of a variety of functional and nonfunctional solutes in SCF CO_2, ethylene, and ethane.

Empirical. Although they are not capable of predicting unknown phase equilibria, empirical models serve a useful purpose in correlating existing solubility data. The most successful of these has been a very simple three-parameter equation suggested by Chrastil (1982)

$$C = d^k \exp (a/T + b)$$

where

C = concentration of the solute in a gas, g/L
d = density of the fluid, g/L
k, a, b = empirical constants

The form of the equation is based on the idea of complex formation between the solute and the solvent molecules. We shall discuss this concept in more detail in the sections on intermolecular interactions. Chrastil fit successfully a variety of unusual solutes, including acids, sterols, and water, in SCF CO_2, as well as a few other systems. Tan and Weng (1987) used this equation to correlate their naphthol isomer data. Adachi and Lu (1983) extended the correlation to a total of 37 systems, but at the price of making the k density-dependent and adding two more parameters.

Mixing Rules. All of the EOS models are extremely sensitive to the interaction energy and size factor of dissimilar components in a mixture (Mart et al., 1986; Šerbanović and Djordjević, 1987). These are the parameters characteristic of the mixture that are needed in the EOS. Therefore, the form of the mixing rules to obtain these mixture parameters becomes very important, and improving these mixing rules has been the object of extended research. In most cases, the improved mixing rules involve one or more additional adjustable parameters. The results, however, are still extremely sensitive to the value (or values) of the interaction parameter so it is unclear whether the added complexity is entirely justified.

Won (1983) proposed an empirical nonquadratic mixing rule that represented the naphthalene/CO_2 system better than conventional combining rules, but failed to meet the theoretical requirement of a quadratic mixing rule at the limit of low pressures. Another mostly empirical attempt (Mart and Papadopoulous, 1985) tried to include multibody effects. In a comparison in which only a single adjustable parameter was used for each method, their new mixing rules did perform better than normal VDW mixing or the conformal solution mixing rules (discussed later) using either mole or surface fractions for polycyclic aromatics in SCF's.

Mansoori and coworkers made an interesting advance when they showed that the VDW mixing rules (VDW1) were not theoretically suited for use with other cubic EOS's and derived the appropriate rules for the RK and PR equations (Benmekki et al., 1987; Kwak and Mansoori, 1986). Park et al. (1987) also showed how the new mixing rules (VDW2) conformed to conformal solution theory. While the new rules may be theoretically satisfying, they include more adjustable parameters: three for the PR equation instead of the usual one. As a result, it is not surprising that these new rules yield much improved results for asymmetric SCF solutions.

Another approach has been the use of local composition and, subsequently, density-dependent mixing rules. Mollerup pioneered the local composition concept to bridge the gap between solution models and EOS (Mollerup, 1981). He used the nonrandom two-liquid approach, which yields a significant improvement over the normal one fluid theory because it recognizes the ordering around a solute due to the interaction energies between molecules rather than trying to view the mixture as an "averaged" pure fluid. Mollerup derived local composition (LC) versions of the CSVDW, SRK and PR equations. Whiting and Prausnitz (1982) used the same concept but different details to show that the effect of the local composition consideration was to include a density dependence in the mixing rules. As a result, the mixing rules can maintain quadratic form at low densities, but take on the more complicated forms at higher densities with a smooth transition between the two extremes.

Mathias and Copeman (1983) applied the density-dependent, local-composition (DDLC) form of the PR to liquids with some success. Vidal (1984) showed the usefulness of the Mollerup LC model for asymmetric SCF solutions by fitting the naphthalene/CO_2 system remarkably well. He also used Whiting and Prausnitz's DDLC model to reproduce the phase diagram for the H_2O/ethanol/CO_2 system. While the DDLC models give a better intuitive description of the physical situation, these attempts also require the evaluation of a number of system-specific parameters. By contrast, Johnston and coworkers attempted to correlate the unknown parameters with physical properties in their use of the DDLC concept for SCF solutions (with entrainer) in the development of the augmented van der Waals density-dependent local composition (AVDW-DDLC) model (Johnston et al., 1987b; Kim and Johnston, 1987a). This will be discussed in more detail in the section on modeling intermolecular interactions.

A variation of the density-dependent mixing rule concept was presented by Mansoori and Ely (1985) who derived density expansion mixing rules that are functions of composition, density and temperature. They yield better results than the VDW1 mixing rules but perform almost identically to the VDW2 mixing rules, even though they are significantly more complex.

In summary, the new mixing rules present an improvement only if they can improve solubility and, perhaps, derivative property representations without introducing new adjustable parameters or by introducing parameters that can be predicted from known physical properties. While the local composition concept describes the experimental observations of clustering in SCF's (discussed in the section on Intermolecular Interactions) more accurately than conventional models, its successful application to SCF solutions remains a challenge.

Computer Simulations. Molecular dynamics and Monte Carlo simulations have also been used to model SCF-phase behavior, although they have been extended to include even slightly asymmetric mixtures only recently. Hoheisel et al. (1983) compared the results of the van der Waals *n*-fluid approximations and the mean density approximation to essentially exact mixture data for a *L-J* (12-6) system using molecular dynamics. The VDW1 fluid approximation worked best for SCF mixtures but only for slightly asymmetric size ratios. In a later paper (Vogelsang and Hoheisel, 1984), they attempted to compare a supercritical fluid to a liquid, but the simulations were at different densities so one cannot make any real comparisons. Likewise, Monte Carlo simulations are capable of predicting the phase equilibria of somewhat nonideal fluid mixtures, for example, acetone/CO_2 (Panagiotopoulos et al., 1986) and naphthalene/CO_2 (Shing and Chung, 1987; Nouacer and Shing, 1989). As computing technology continues to advance, the use of these techniques presents a unique and challenging way to simulate SCF phenomena and highly nonideal solutions. The simulation results can be used to evaluate various approximate techniques and differentiate between errors in the methods and errors in the *potentials*.

SCF: Liquid/Fluid Equilibria

Solid/fluid extraction processes possess the potential for the largest solubility enhancements and, consequently, the largest commercial implementation. However, there also exists the potential for low-volatility liquids. Unfortunately, the investigation and analysis of liquid/fluid or solid/liquid/fluid systems are complicated by the solubility of the fluid in the liquid phase, which can often be quite high, so that one is far removed from the Henry's Law region. For example, at 35°C and 2,000 psia (14 MPa) the solubility of CO_2 in the liquid *n*-hexadecane phase is nearly 85% (Charoensombut-Amon, 1986). This is especially true near the upper critical end point (UCEP), which ends the LLV curve by one of the liquid phases becoming identical to the vapor phase.

An extremely useful application, where this problem becomes important, is the use of SCF's for chromatographic separations. Recent development of this technology has shown its benefit in separating high-molecular-weight compounds and thermally-labile compounds that cannot be separated by gas chromatography. SCF chromatography has the added feature of pressure or density programming, in addition to temperature variation, because solubilities are so sensitive to both temperature and density in SCF's. Several reviews are available on the subject (Gouw and Jentoft, 1972; Klesper, 1978; van Wasen et al., 1980; Peaden and Lee, 1982). Because of the complex nature of the stationary phase, little fundamental understanding of phase behavior in SCF chromatography has appeared yet.

The difficulty in investigating liquid/fluid and other multiphase systems is the need to sample or otherwise determine the compositions of all phases. Removing even small samples can seriously disturb the equilibrium, unless the vessel is very large and obtaining representative samples is fraught with hazards! Despite this limitation, there have been a number of studies of both subcritical- and supercritical-phase behavior based on clever modifications of this technique (Reamer and Sage, 1962, 1963, 1964; Tsang and Streett, 1981; Charoensombut-Amon et al., 1986; Radosz, 1986; Nagarajan and Robinson, 1987; Adams et al., 1988). However, there are several examples of low-volatility liquid/fluid or solid/liquid/fluid equilibria, in which only the *fluid phase* composition was measured (Van Leer and Paulaitis, 1980; Brunner, 1983; Chang and Morrell, 1985; Gopal et al., 1985).

Mixed or pure solutes in the presence of a high-pressure fluid can experience significant freezing point depressions, and the SCF dissolved in the liquid phase can have a pronounced effect on the composition of the fluid phase. Brunner found that, the greater the dissolution of the fluid in the liquid, the higher the solubility of the liquid in the SCF phase. Van Leer and Paulaitis (1980) observed that the solubility vs. pressure isotherms of liquids in SCF's had a different qualitative form than those for solids. The liquids do not exhibit the precipitous decrease in solubility in the vicinity of the fluid critical point. While modeling these types of systems is more complicated than solid/fluid systems, Hess (1987) has shown for systems sufficiently removed from a critical end point that standard methods for normal liquids can be used for the liquid phase. In this way the solubility of the fluid in the liquid, the solubility of the solid in the liquid, and the freezing point temperature of the solute can be modeled for solid/liquid/fluid systems. He reproduced the experimental SLG curves for naphthalene/CO_2, biphenyl/CO_2, and octacosane/CO_2 with remarkable accuracy.

A more complete picture of the phase equilibria, especially the phase diagram, can be obtained with high-pressure view cells, sometimes equipped with sampling valves for all phases (Rodrigues et al., 1968; Lee and Kohn, 1969; Kalra et al., 1978; Tiffin et al., 1978; Kohn et al., 1980; Legret et al., 1980; Li et al., 1981; Meskel-Lesavre et al., 1981; Gasem and Robinson, 1985; Hsu et al., 1985; Nagarajan and Robinson, 1986; Anderson et al., 1986; Bufkin et al., 1986). A very early study (Chappelear and Elgin, 1961) examined seven organic liquids in SCF Freon 13. Several investigators have used this technique to study the equilibrium between polymers or copolymers and their SCF reactants or solvents (Luft and Subramanian, 1987; McClellan et al., 1985; Seckner et al., 1988). These systems include ethylene/methyl acrylate and copolymers, polystyrene/toluene/CO_2, and polystyrene/toluene/ethane. Other popular techniques include high-pressure chromatography and flow gas saturation techniques (Czubryt et al., 1970; Chen et al., 1976; Sebastian et al., 1980; Kragas et al., 1984; Inomata et al., 1986a, 1986b).

The view cell experiment was simplified when it was shown that a three-phase/three-component system could be fully determined without sampling by measuring the phase volumes with merely three different starting compositions (Paulaitis et al., 1984, 1985; DiAndreth et al., 1987). In this way the researchers determined phase diagrams of the two-and three-phase regions of alcohol/H_2O/CO_2 systems. McHugh et al. (1983) used a similar method to investigate the ethanol/H_2O/ethane system. The alcohol systems were also of interest to Brignole et al. (1984, 1985, 1987), who suggested the use of supercritical fluids for the extraction of alcohols from water and presented entire processes for the recovery systems.

Derivative Properties

While developing an equation of state that can model volume and solubility data is a challenge, concurrently modeling a derivative property is an even more demanding endeavor. Not only does one have to develop an equation that accurately reproduces the solubility, but the compositional dependence must also be correct. Two properties exhibit anomalous behavior in the vicinity of the solution critical point: the excess enthalpy of mixing and the solute partial molar volume. In fact, a fundamental relationship exists between these two quantities; Wheeler (1972) has shown that in the context of the decorated lattice gas model, the infinite dilution partial molar volume should scale as the infinite dilution partial molar enthalpy (see relationship to h^E_m below) arbitrarily close to the solvent's critical point. In addition, Debenedetti and Kumar (1988) have analyzed these quantities in terms of the formation of solvent clusters around the solute (this will be discussed in detail in the next section on Intermolecular Interactions) and used that information to describe the regions of inverse solubility behavior of many systems, in which an increase in temperature causes a decrease in solubility.

Excess enthalpies of mixing

The excess enthalpy of mixing of SCF solutions can be measured efficiently by flow calorimetry. The excess enthalpy of a binary mixture is related to the partial molar enthalpies of both components by:

$$h^E_m = x_1(\bar{h}_1 - h_1) + x_2(\bar{h}_2 - h_2)$$

Therefore, unusual behavior of either component's partial molar enthalpy will be reflected in the excess enthalpy of mixing. Christensen and coworkers have studied a number of systems and presented an excellent review of the subject (Christensen et al., 1987). The common characteristics of these systems are shown for the propane/Freon-12 system in Figure 9. The critical temperature of propane is 370.0 K and that of Freon-12 is 385.2 K. At temperatures below the more volatile component's critical temperature h^E_m consists of small positive values, characteristic of a regular solution. As the temperature is raised, h^E_m becomes extremely large and negative. At even higher temperatures, near the critical temperature of the heavier component, the values are extremely large and positive. Finally, above the critical temperature of the less volatile component, h^E_m returns to small positive deviations from ideality. Additional data are available for the $CO_2 + N_2$ and CO_2 + *n*-hexane + toluene systems (Wormald and Eyears, 1988; Faux et al., 1988). This phenomenon is explained as the more volatile component being in a

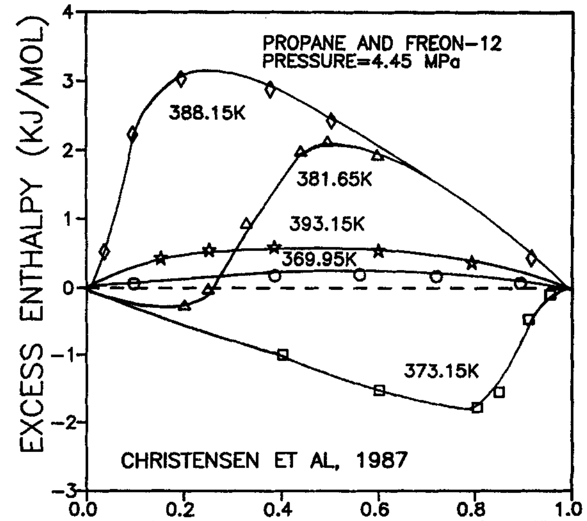

Figure 9. Excess enthalpies of mixing of SCF propane and Freon-12.

more dense state in the mixture than it would be as a pure component when the mixture is near but above the critical point of that component (the lower T_c), resulting in a lower partial molal enthalpy in the mixture. Therefore, if the system were at a pressure below the critical locus, condensation into the mixture would occur. Conversely, near the higher T_c the less volatile component is in a less dense state than it would be as a pure component, resulting in a higher partial molal enthalpy in the mixture (Christensen et al., 1987). This is termed an "equation-of-state" effect, whereby the two components are more or less expanded relative to the pure components, depending on their respective reduced temperatures, resulting in the changing h_m^E (and, correspondingly, v_m^E) values. Morrison et al. (1985) used thermodynamic stability arguments to explain the general shape of the excess enthalpy curves. These arguments with the necessary condition that $(\partial H/\partial x)_{P,T}$ diverges at the pure-component critical point are used to justify all the qualitative features of this complex behavior. A variety of EOS models, some with binary interaction parameters, have been used in an attempt to reproduce the h_m^E data. While most EOS's give the qualitative form, none has been very successful at quantitative modeling.

Partial molar volumes

Another property of interest is the partial molar volume. Of the derivative properties it is the most fundamental macroscopic thermodynamic property that can be used to analyze supercritical solution phenomena (Kim and Johnston, 1985). The partial molar volume is related directly to the solubility through the fugacity coefficient of the solute in the fluid phase. Yonker and Smith (1988a) pointed out the importance of the partial molar volume in determining the density dependence of the retention time in SCF chromatography.

As pointed out earlier, the variation in the fugacity coefficient accounts for the large changes in the solubility and enhancement factors. The integral in determining the fugacity coefficient is "forgiving" in that errors in $\bar{v}_2$ can be averaged out over the pressure range. Therefore, one can have an EOS that may model solubilities but does not represent well $\bar{v}_2$ data; thus it does not really represent the molecular interactions. Unfortunately, until recently partial molar volume data in the supercritical region were extremely scarce. However, a handful of investigators reported values obtained by taking the compositional derivative of volume data for mixtures in the critical region (Bensen et al., 1953; Chappelear and Elgin, 1961; Tsekhanskaya et al., 1966; Ehrlich and Fariss, 1969; Ehrlich, 1971; Wu and Ehrlich, 1973; Abraham and Ehrlich, 1975). All these values were at finite concentrations, and the common observation was that the partial molar volumes of the solute became very large and negative (≈ -100 to $-1{,}000$ cm^3/mol) in the vicinity of the solvent critical point. The systems studied were very diverse, including organic liquids in SCF ethane and Freon-13, polymers in SCF ethylene, and NaCl in SCF water. Even with these limited data, suggestions of "molecular cluster" formation, solute-solvent bond formation, and the collapse of the solvent about the solute abounded.

The dearth of $\bar{v}_2$ data is undoubtedly due to the difficulty in obtaining it, especially near the critical point where small changes in temperature and pressure can cause large errors in the measured values. Van Wasen and Schneider (1980) proposed a chromatographic method to calculate the solute partial molar volume at infinite dilution from the isothermal pressure dependence of the experimentally-determined solute retention time. Paulaitis et al. (1981), however, pointed out that, through the assumption of Henry's law solution behavior, the method assumed that $(\partial \bar{v}_2^\infty/\partial y_2)_{P\to P_c, T\to T_c}$ approached zero. Unfortunately, the partial molar volume is both predicted and observed to be a strong function of the solute concentration. Eckert et al. (1983, 1986a) proposed a novel method to measure infinite dilution partial molar volumes of solutes in SCF's, which involved the use of a high-precision densitometer so that measurements could be made as close as 2°C from the critical point of the solvent. They reported values for several organic solutes in SCF CO_2 and ethylene as large as $-20{,}000$ cm^3/mol. A typical isotherm is shown in Figure 10. Biggerstaff and Wood (1988) have used the precision densitometer method as well to determine the partial molar volumes of argon, ethylene and xenon in subcritical and supercritical water. While these measurements were at somewhat higher solute concentrations, they are interesting because the solutes exhibit large *positive* partial molar volumes in the vicinity of the solvent critical point. In contrast to the work of Eckert et al. (1983, 1986), in these systems the solutes have lower critical temperatures than the solvent, so that the solute/solvent interactions are more repulsive than the solvent/solvent interactions.

All these observations are in agreement with the classical arguments of Wheeler (1972), who used the decorated lattice gas theory to show that the infinite dilution partial molar volume of the solute should diverge to negative infinity at the solvent critical point if there are attractive interactions between the solute and the solvent and to positive infinity if there are repulsive interactions. The infinite dilution partial molar volume data, extremely near the solvent critical point, show unusual behavior because they can have different limiting values dependent on the pathway of approach (Rozen, 1976). Levelt Sengers and coworkers (Chang et al., 1984; Chang and Levelt Sengers, 1986) explained this phenomenon in terms of the Leung-Griffiths model. As the solute concentration goes to zero (infinite dilution) the mixture critical point is changing with the change in composition. Dependent on the path of approach to the pure

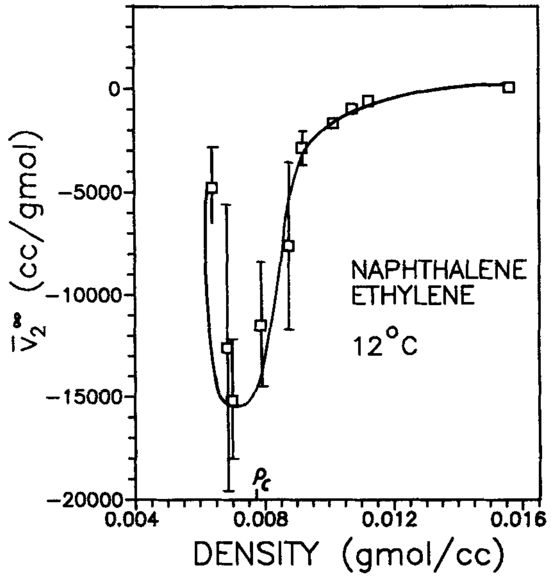

Figure 10. Partial molar volume at infinite dilution of naphthalene in ethylene at 12°C.

solvent critical point (such as along an isobar or isotherm), the system will be at varying distances from that changing *mixture* critical point resulting in different values of the partial molar volume and other limiting properties.

Intermolecular Interactions

Evidence of clustering

The observed $\bar{v}_2^\infty$ values provided the main impetus for a whole new realm of investigations seeking to better understand the intermolecular interactions between the solute and the other species in SCF solutions.

The extremely large negative infinite dilution partial molar volumes measured by Ziger suggest the clustering or agglomeration of many solvent molecules when a molecule of solute is added to solution, perhaps somewhat akin to electrostriction about a center of force in solutions. This can be envisioned as the collapse of the solvent shell about the solute or the formation of solute/solvent clusters in solution. Benson and coworkers made this suggestion of some type of clustering, complex formation, or strong solute/solvent interactions as early as 1953 when they looked at the $\bar{v}_2$ of NaCl in SCF H_2O (Bensen et al., 1953). More recently, Eckert et al. (1983) showed that the extremely large values of $\bar{v}_2^\infty$ measured by Ziger corresponded to the disappearance in volume of as many as 100 moles of solvent per mole of solute: i.e., a solvent partial molar volume of $-10{,}000$ cm^3/mol at a solution density of 100 cm^3/mol. The composition and density around the solute could be very different from the bulk solution due to the strong solute/solvent interactions. This may account for some of the success of the LC and DDLC mixing rule models.

These data, however, also indicate such strong phenomena that perhaps *specific* interactions, which may account for the difference in the bulk density and the local density of solvent or entrainer around a solute, may be important in modeling SCF-phase equilibria. In such a case, a chemical-type model of cluster or aggregate formation may be a useful representation of the molecular structure and may be superior to strictly EOS treatments. This is especially important in entrainer systems, where the cosolvent may be chosen specifically to hydrogen bond or have acid/base interactions with the solute to pull it into solution. In these systems, one is concerned about the composition in the region about the solute, which is likely to be enriched with entrainer, as well as changes in the local density resulting from unusual solute/SCF solvent interactions.

Both experimental and modeling efforts to better understand the clustering phenomenon are extremely limited. Nevertheless, they will be presented here in some detail due to their significance in trying to understand the molecular interactions that govern SCF solubilities, enhancements and separations.

Experimental studies

An excellent way to study solute/solvent and solute/entrainer interactions is with nonintrusive spectroscopic methods. In this way, the systems can be examined on a microscopic level without perturbing the molecular interactions.

The earliest studies were not motivated so much by interest in clustering as by a need to quantify the solvent power of SCF's for chromatographic applications. A common method of classifying solvents is the Kamlet-Taft equation (Kamlet et al., 1977, 1983). This is a linear solvation energy relationship that relates some observed quantity (reaction rate constant, position of the maximum absorption peak in the IR, UV-visible, NMR, ESR, etc.) to three scales of chemical characteristics by:

$$XYZ = XYZ_o + a\alpha + b\beta + s\pi^*$$

where α, β, and π^* are *solvent*-specific and represent the solvent's ability to be a hydrogen bond donor, ability to be a hydrogen bond acceptor, and its polarity/polarizability, respectively. The *a*, *b*, and *s* are *solute*-specific and have been tabulated for a wide variety of chromophores. In this case, the quantity measured was the wavelength of maximum absorbance of a dilute chromophore in solution, which will be different with different solvents due to varying degrees of solvent-induced stabilization of the electronic states. For CO_2, the π^* values are negative, indicating very weak interaction (Hyatt, 1984; Sigman et al., 1985). Subsequently, data became available for Xe, SF_6, C_2H_6, and NH_3 (Yonker et al., 1986; Smith et al., 1987), that indicated somewhat changing values of π^* through the SC region, but no marked changes in the immediate vicinity of the critical point.

In a more detailed study, Kim and Johnston (1987b) found that the actual local solvent densities were greater than those predicted for a uniform bulk SCF solution by the standard solvent shift theory of McRae (1957). They compared the predicted and observed values to obtain estimates of the actual local density. In addition, they showed that the estimated local density could be correlated with the solvent isothermal compressibility: i.e., the solvent became more tightly packed around the solute when the solvent was very compressible near the critical point. They used only one dye and it is unknown whether the results are solute-specific.

The fluorescence spectra of solutes are particularly sensitive to the solvent environment. Kajimoto et al. (1988) used this technique, coupled with absorption, to study (N,N,dimethylamino)benzonitrile in SCF fluoroform. Fluoroform is highly polar and, as a result, is likely to cause large shifts in the spectra. In addition, this benzonitrile forms a charge-transfer complex so that both the normal and the charge transfer peaks could be studied. In the slightly SC region, the shifts were greater than those predicted by the McRae (1957) theory in both the absorption and fluorescence spectra. Once again, this was explained as the aggregation of the solvent molecules around the solute in the low-density SCF. The authors describe the aggregation with a Langmuir-type adsorption equilibria, but this required significant assumptions about the relative contributions of the solvent molecules to the shift.

Nonetheless, these experiments do point out that there is significant evidence of aggregation of the solvent molecules around the solute, at least in these systems involving rather polar and highly functional solutes.

Strong solute/solvent interactions or clustering is also important nearer the critical point in nonpolar systems (Brennecke and Eckert, 1988, 1989). The ratio of the intensity of the first peak to the intensity of the third peak in the fluorescence spectrum of pyrene is an excellent measure of the strength of these interactions. The transition corresponding to the first peak is not allowed by symmetry arguments. If there is strong interaction between the solute and the solvent, however, the symmetry is disrupted and that transition takes place with greater intensity. The intensity of the third peak is relatively insensitive to the sol-

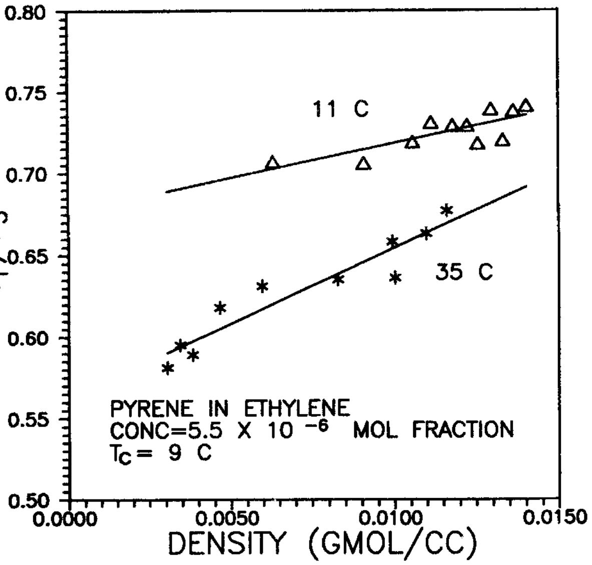

Figure 11. Fluorescence spectroscopy results indicating clustering near the critical point.

vent environment. Figure 11 shows this ratio of intensity for two isotherms of pyrene in supercritical ethylene at a common mole fraction. The 11°C isotherm, which is nearer the critical point, has much higher values for I_1/I_3 than the isotherm further away, indicating much stronger solute/solvent interaction nearer the critical point. The decrease in I_1/I_3 along either isotherm at lower densities is a result of the decreased density, not the proximity to the critical point.

The next obvious step was to try to understand and quantify the clustering of entrainers about solutes. Kim and Johnston (1987a) measured the υ_{max} of phenol blue in several CO_2/entrainer systems. Using an approach based on the dielectric enrichment arguments of Nitsche and Suppan (1982), they calculated local entrainer compositions. In all cases, the local compositions exceeded the bulk concentrations because the entrainers interacted more strongly with the solute than with the SCF solvent. For the phenol blue/acetone/CO_2 system, the entrainer concentration is as much as four times the bulk concentration near the solvent critical point but approaches that bulk concentration at high pressures. In a slightly varied approach, Yonker and Smith (1988b) estimated the local compositions by assuming a linear contribution of the entrainer and the solvent to the observed π^* value. Their results for the 2-nitroanisole/2-propanol/CO_2 system were in complete agreement with those of Kim and Johnston (1987a).

Modeling

The spectroscopic experiments and the $\bar{v}_2^\infty$ data lead to two conclusions: First, even with nonpolar SCF solvents, there is an unusually strong interaction between the solute and the solvent that results in a local density about the solute that is greater than the bulk. Second, in entrainer systems, the local *composition* is indeed enriched with the entrainer. In both cases, the effects are most significant in the region of high compressibility near the critical point.

One approach to model this behavior is chemical theory, which hypothesizes the formation of aggregates in solution and treats them by the law of mass action. (See for example, Alger, 1982.) Chemical theory has frequently been used for systems known to form strong hydrogen bonds. It was used to describe high-pressure, light-hydrocarbon/methanol systems, but only included complex formation of the methanol molecules with each other (Peschel and Wenzel, 1984).

A very rough model of the clusters in SCF's was made using ideal chemical theory, which assumes that all nonidealities in solution are due to complex formation. While this is an unrealistic model since SCF's are far from ideal gases, ideal chemical theory predictions do show good qualitative agreement with Ziger's infinite dilution partial molar volume date for naphthalene in CO_2 at 35°C. A plot of these predictions with cluster sizes of $n = 10$ and $n = 50$ is shown in Figure 12 (Eckert et al., 1983). An equation of state could be used to obtain fugacity coefficients to produce a model containing both chemical and physical contributions.

Donohue and coworkers (Walsh et al., 1987) recognized the formation of complexes between solutes in SCF's and entrainers added to the SCF. In the associated perturbed anisotropic chain theory (an extension of the PHCT discussed in the section on Perturbation EOS), only the ideal gas term is affected by association by changing the number of molecules present. Both association between alcohol molecules and solvation of the solute by the alcohol are taken into account. However, no complex formation is assumed to occur between the solute and the SCF solvent.

By contrast, Debenedetti (1987) has used a fluctuation analysis to derive an expression for the solute infinite dilution partial molar volume in terms of an actual cluster size of solvent molecules around the solute. While this cluster size is numerically a measure of the statistical correlations between solute and solvent concentration fluctuations at infinite dilution, it is presented as taking on the mechanistic significance of the number of SCF solvent molecules surrounding the solute. Cluster sizes are calculated from $\bar{v}_2^\infty$ data by using literature data for solvent density and compressibility. These calculated cluster sizes indicate as many as 100 molecules of CO_2 surrounding a molecule of

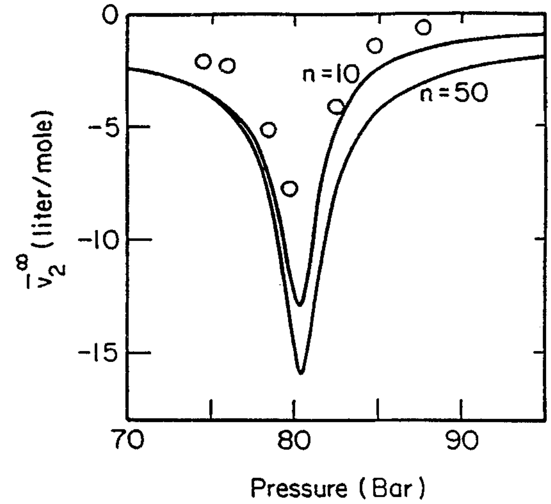

Figure 12. Ideal chemical theory predictions of the partial molar volume of naphthalene in CO_2 at 35°C.

n = cluster size.

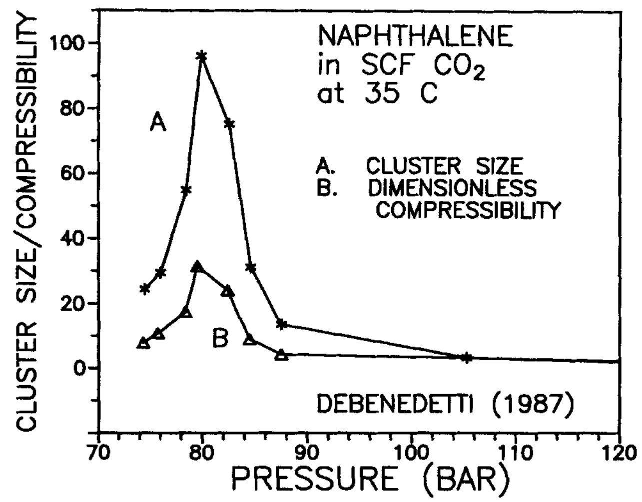

Figure 13. Fluctuation calculations of cluster sizes.

naphthalene or tetrabromomethane in the region of highest CO_2 compressibility; examples for the naphthalene/CO_2 system are shown in Figure 13.

Lee and coworkers have been successful in solving the integral equations and calculating the direct pair correlation functions for asymmetric SCF systems such as naphthalene/CO_2 and pyrene/CO_2 (Lee and Cochran, 1988; Lee, 1989). They find that clustering is evident as long-range correlations in the fluctuations of solvent molecules around the solute.

There have also been attempts to modify the purely physical EOS models to permit them to describe without chemical theory the very strong solute/solvent or solute/entrainer interactions. Johnston and coworkers (Kim and Johnston, 1987a; Johnston et al., 1987b) modeled the phenol blue/entrainer/CO_2 systems, by modifying the already very good AVDW equation with the DDLC of Mollerup (1981) and Whiting and Prausnitz (1982). They correlated the cross interaction energy with the total configurational internal energy, which can be calculated from literature solubility parameter values, so no new adjustable parameters were introduced. The qualitative agreement they obtained suggests some possibilities for this method.

Conclusions

- SCF extraction is often inappropriate for separations because easier methods are available, but when it is needed it is a very powerful tool.
- The applicability of SCFE is highly dependent on our ability to model and predict phase equilibria in complex systems. SCF systems are especially challenging because of the high compressibility and the asymmetry of the systems encountered.
- Many good data exist, especially for solid solutes in SCF's, including entrainer effects and a few data for mixed solutes. Fewer good data exist for liquid solutes, and especially for the solubility of SCF's in equilibrium liquids.
- Cubic EOS's and perturbation models have enjoyed some success in the correlation of solubilities. They are less successful either in representing derivative properties or in prediction.
- A better fundamental understanding of molecular behavior in SCF's is needed to develop predictive models. Present studies that show promise are spectroscopic investigations and perhaps models of solution behavior incorporating specific interactions. Computer simulation also provides a powerful tool, especially when used in conjunction with experiment.

Acknowledgment

The authors gratefully acknowledge funding support for this work: from the U.S. Environmental Protection Agency, through the Advanced Environmental Control Technology Research Center at the University of Illinois, supported under Cooperative Agreement CR-806819; from the U.S. Department of Energy, under grants DE-FG22-88PC88922 and DE-FG22-84PC70801; from the Hazardous Waste Research Information Center of the State of Illinois, under grant SENR HWR 89-062; and from the National Science Foundation and the E.I. DuPont de Nemours Co., for fellowship support.

Literature Cited

Abraham, K. P., and P. Ehrlich, "Partial Molar Volume of a Polymer in Supercritical Solution," *Macromol.*, **8**(6), 944 (1975).

Adachi, Y., and B. C.-Y. Lu, "Supercritical Fluid Extraction With Carbon Dioxide and Ethylene," *Fluid Ph. Equil.*, **14**, 147 (1983).

Adams, W. R., J. A. Zollweg, W. B. Streett, and S. S. H. Rizvi, "New Apparatus for Measurement of Supercritical Fluid-Liquid Phase Equilibria," *AIChE J.*, **34**(8), 1387 (Aug., 1988).

Alder, B. J., and C. E. Hecht, "Studies in Molecular Dynamics: VII. Hard-Sphere Distribution Functions and an Augmented van der Waals Theory," *J. Chem. Phys.*, **50**(5), 2032 (1969).

Alder, B. J., D. A. Young, and M. A. Mark, "Studies in Molecular Dynamics: X. Corrections to the Augmented van der Waals Theory for the Square Well Fluid," *J. Chem. Phys.*, **56**(6), 3013 (1972).

Alger, M. M., "The Thermodynamics of Highly Solvated Liquid Metal Solutions," PhD Thesis, Univ. of Illinois, Urbana (1982).

Amestica, L. A., and E. E. Wolf, "Catalytic Liquefaction of Coal in Supercritical Tetralin," *Supercritical Fluid Technology*, J. M. L. Penninger et al., ed., Elsevier, New York, 331 (1985).

Anderson, J. M., M. W. Barrick, and R. L. Robinson, Jr., "Solubilities of Carbon Dioxide in Cyclohexane and trans-Decalin at Pressures to 10.7 MPa and Temperatures from 323 to 423 K," *J. Chem. Eng. Data*, **31**, 172 (1986).

Benmekki, E. H., T. Y. Kwak, and G. A. Mansoori, "Van der Waals Mixing Rules for Cubic Equations of State," *Supercritical Fluids*, T. G. Squires and M. E. Paulaitis, eds., ACS, Washington, DC, 101 (1987).

Benson, S. W., C. S. Copeland, and D. Pearson, "Molal Volumes and Compressibilities of the System NaCl-H_2O above the Critical Temperature of Water," *J. Chem. Phys.*, **21**(12), 2208 (1953).

Bertucco, A., M. Fermeglia, and L. Kikic, "Modified Carnahan-Starling-van der Waals Equation for Supercritical Fluid Extraction," *Chem. Eng. J.*, **32**(1), 21 (1986).

Biggerstaff, D. R., and R. H. Wood, "Apparent Molar Volumes of Aqueous Argon, Ethylene, and Xenon from 300 to 716 K," *J. Phys. Chem.*, **92**, 1988 (1988).

Brady, B. O., C.-P. C. Kao, K. M. Dooley, F. C. Knopf, and R. P. Gambrell, "Supercritical Extraction of Toxic Organics from Soils," *Ind. Eng. Chem. Res.*, **26**, 261 (1987).

Brennecke, J. F., and C. A. Eckert, "Molecular Interactions from Fluorescence Spectroscopy," *Proc. Int. Symp. on Supercritical Fluids*, Nice, France (Oct., 1988).

———, "Fluorescence Spectroscopy Studies of Intermolecular Interactions in Supercritical Fluids," *Supercritical Fluid Science and Technology*, K. P. Johnston and J. M. L. Penninger, eds., ACS, Washington, DC, in press (1989).

Brignole, E. A., P. M. Andersen, and Aa. Fredenslund, "Supercritical Fluid Extraction of Alcohols from Water," *Ind. Eng. Chem. Res.*, **26**, 254 (1987).

Brignole, E. A., S. Skjold-Jørgensen, and Aa. Fredenslund, "Application of a Local Composition Equation of State to Supercritical Fluid Phase Equilibrium Problems," *Ber. Bunsenges. Phys. Chem.*, **88**, 801 (1984).

———, "Application of the Group Contribution Equation of State to Supercritical Fluid Extraction," *Supercritical Fluid Technology*, J. M. L. Penninger et al., eds., Elsevier, New York, 87 (1985).

Brunner, J., "Selectivity of Supercritical Compounds and Entrainers with Respect to Model Substances," *Fluid Ph. Equil.*, **10**, 289 (1983).

Bufkin, B. A., R. L. Robinson, Jr., S. s. Estrera, and K. D. Luks, "Solubility of Ethane in n-Decane at Pressures to 8.2 MPa and Temperatures from 278 to 411 K," *J. Chem. Eng. Data*, **31**, 421 (1986).

Carnahan, N. F., and K. E. Starling, "Intermolecular Repulsions and the Equation of State for Fluids," *AIChE J.*, **18**(6), 1184 (Nov., 1972).

Chang, R. F., and J. M. H. Levelt Sengers, "Behavior of Dilute Mixtures Near the Solvent's Critical Point," *J. Phys. Chem.*, **90**, 5921 (1986).

Chang, H., and D. G. Morrell, "Solubilities of Methoxy-1-tetralone and Methyl Nitrobenzoate Isomers and Their Mixtures in Supercritical Carbon Dioxide," *J. Chem. Eng. Data*, **30**, 74 (1985).

Chang, R. F., G. Morrison, and J. M. H. Levelt Sengers, "The Critical Dilemma of Dilute Mixtures," *J. Phys. Chem.*, **88**(16), 3389 (1984).

Charoensombut-Amon, T., R. J. Martin, and R. Kobayashi, "Application of a Generalized Multiproperty Apparatus to Measure Phase Equilibrium and Vapor Phase Densities of Supercritical Carbon Dioxide in n-Hexadecane Systems up to 26 MPa," *Fluid Ph. Equil.*, **31**, 89 (1986).

Chappelear, D. C., and J. C. Elgin, "Phase Equilibria in the Critical Region," *J. Chem. Eng. Data*, **6**(3), 415 (1961).

Chen, R. J. J., P. S. Chappelear, and R. Kobayashi, "Dew-Point Loci for Methane-n-Hexane and Methane-n-Heptane Binary Systems," *J. Chem. Eng. Data*, **21**(2), 213 (1976).

Chen, W.-Y., and F. Kazimi, "Coal Liquefaction with Supercritical Ammonia and Amines," *Supercritical Fluid Technology*, J. M. L. Penninger et al., eds., Elsevier, New York, 281 (1985).

Chimowitz, E. H., and K. J. Pennisi, "Process Synthesis Concepts for Supercritical Gas Extraction in the Crossover Region," *AIChE J.*, **32** (10), 1665 (1986).

Chrastil, J., "Solubility of Solids and Liquids in Supercritical Gases," *J. Phys. Chem.*, **86**, 3016 (1982).

Christensen, J. J., R. M. Izatt, and D. M. Zebolshy, "Heats of Mixing in the Critical Region," *Fluid Ph. Equil.*, **38**, 163 (1987).

Czubryt, J. J., M. N. Myers, and J. C. Giddings, "Solubility Phenomena in Dense Carbon Dioxide Gas in the Range 270–1900 Atmospheres," *J. Phys. Chem.*, **74**(24), 4260 (1970).

Debenedetti, P. G., "Clustering in Dilute, Binary Supercritical Mixtures: A Fluctuation Analysis," *Chem. Eng. Sci.*, **42**, 2203 (1987).

Debenedetti, P. G., and S. K. Kumar, "The Molecular Basis of Temperature Effects in Supercritical Extraction," *AIChE J.*, **34**(4), 645 (Apr., 1988).

DeFilippi, R. P., and R. J. Robey, "Supercritical Fluid Regeneration of Adsorbents," EPA Project Summary, EPA-600, S2-83-038 (1983).

Deshpande, G. V., G. D. Holder, and Y. T. Shah, "Effect of Solvent Density on Coal Liquefaction Kinetics," *Supercritical Fluids*, T. G. Squires and M. E. Paulaitis, eds., ACS, Washington, DC, 251 (1987).

DiAndreth, J. R., J. M. Ritter, and M. E. Paulaitis, "Experimental Technique for Determining Mixture Compositions and Molar Volumes of Three or More Equilibrium Phases at Elevated Pressures," *Ind. Eng. Chem. Res.*, **26**, 337 (1987).

Dobbs, J. M., and K. P. Johnston, "Selectivities in Pure and Mixed Supercritical Fluid Solvents," *Ind. Eng. Chem. Res.*, **26**, 1476 (1987).

Dobbs, J. M., J. M. Wong, and K. P. Johnston, "Nonpolar Co-Solvents for Solubility Enhancement in Supercritical Fluid Carbon Dioxide," *J. Chem. Eng. Data*, **31**(3), 303 (1986).

Dobbs, J. M., J. M. Wong, R. J. Lahiere, and K. P. Johnston, "Modification of Supercritical Fluid Phase Behavior Using Polar Cosolvents," *Ind. Eng. Chem. Res.*, **26**, 56(1987).

Dooley, K. M., C.-P. Kao, R. P. Gambrell, and F. C. Knopf, "The Use of Entrainers in the Supercritical Extraction of Soils Contaminated with Hazardous Organics," *Ind. Eng. Chem. Res.*, **26**, 2058 (1987).

Eckert, C. A., J. G. Van Alsten, and T. Stoicos, "Supercritical Fluid Processing," *Environ. Sci. Technol.*, **20**(4), 319 (1986b).

Eckert, C. A., H. C. Yang, J. F. Brennecke, and S. R. Alferi, "Chemical Engineering Applications in Environmental Technology," *Proc. Mediterranean Cong. on Chemical Engineering*, Barcelona, Spain (Nov., 1987).

Eckert, C. A., D. H. Ziger, K. P. Johnston, and T. K. Ellison, "The Use of Partial Molal Volume Data to Evaluate Equations of State for Supercritical Fluid Mixtures," *Fluid Ph. Equil.*, **14**, 167 (1983).

Eckert, C. A., D. H. Ziger, K. P. Johnston, and S. Kim, "Solute Partial Molal Volumes in Supercritical Fluids," *J. Phys. Chem.*, **90**(12), 2738 (1986a).

Ehrlich, P., "Partial Molar Volume Anomaly in Supercritical Mixtures and the Free Radical Polymerization of Ethylene," *J. Macromol. Sci.-Chem.*, **A5**(8), 1259 (1971).

Ehrlich, P., and R. H. Fariss, "Negative Partial Molal Volumes in the Critical Region. Mixtures of Ethylene and Vinyl Chloride," *J. Phys. Chem.*, **73**(4), 1164 (1969).

Eisenbach, W. O., K. Niemann, and P. J. Göttsch, "Supercritical Fluid Extraction of Oil Sands and Residues from Oil and Coal Hydrogenation," *Chemical Engineering at Supercritical Fluid Conditions*, M. E. Paulaitis et al., eds., Ann Arbor Science, Ann Arbor, MI, 419 (1983).

Ellison, T. K., "Supercritical Fluids: Kinetic Solvent Effect and the Correlation of Solid-Fluid Equilibria," PhD Thesis, Univ. of Illinois, Urbana (1986).

Ely, J. F., and J. K. Baker, "A Review of Supercritical Fluid Extraction," *NBS Technical Note 1070* (1983).

Ewald, A. H., W. B. Jepson, and J. S. Rowlinson, "The Solubility of Solids in Gases," *Disc. Farad. Soc.*, **15**, 238 (1953).

Faux, P. W., J. J. Christensen, R. M. Izatt, C. Pando, and J. A. R. Renuncio, The Excess Enthalpies of (carbon dioxide + n-hexane + toluene) at 470.15 K and 7.5 and 12.5 MPa," *J. Chem. Thermody.*, **20**, 1297 (1988).

Fong, W. S., P. C. F. Chan, P. Pichaichanarong, W. H. Corcoran, and D. D. Lawson, "Experimental Observations on a Systematic Approach to Supercritical Extraction of Coal," *Chemical Engineering at Supercritical Fluid Conditions*, M. E. Paulaitis et al., eds., Ann Arbor Science, Ann Arbor, MI, 377 (1983).

Fox, J. R., "Method for Construction of Nonclassical Equations of State," *Fluid Ph. Equil.*, **14**, 45 (1983).

Gasem, K. A. M., and R. L. Robinson, Jr., "Solubilities of Carbon Dioxide in Heavy Normal Paraffins (C_{20}-C_{44}) at Pressures to 9.6 MPa and Temperatures from 323 to 423 K," *J. Chem. Eng. Data*, **30**, 53 (1985).

Giddings, J. C., M. N. Myers, and J. W. King, "Dense Gas Chromatography at Pressures to 2000 Atmospheres," *J. Chrom. Sci.*, **7**, 276 (1969).

Gilbert, S. W., "Experimental and Theoretical Studies of Supercritical Fluid Behavior," PhD Thesis, Univ. of Illinois, Urbana (1987).

Gopal, J. S., G. D. Holder, and E. Kosal, "Solubility of Solid and Liquid Mixtures in Supercritical Carbon Dioxide," *Ind. Eng. Chem. Proc. Des. Dev.*, **24**(3), 697 (1985).

Gouw, T. H., and R. E. Jentoft, "Supercritical Fluid Chromatography," *J. Chromat.*, **68**, 303 (1972).

Hansen, P. C., "Binary Supercritical Fluid Enhancement Factors for Separation Processes," PhD Thesis, Univ. of Illinois, Urbana (1985).

Hawthorne, S. B., and D. J. Miller, "Extraction and Recovery of Polycyclic Aromatic Hydrocarbons from Environmental Solids Using Supercritical Fluids," *Anal. Chem.* **59**(13), 1705 (1987a).

———, "Directly Coupled Supercritical Fluid Extraction—Gas Chromatographic Analysis of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls from Environmental Solids," *J. Chromat.*, **403**, 63 (1987b).

Hess, B. S., "Supercritical Fluids: Measurement and Correlation Studies of Model Coal Compound Solubility and the Modeling of Solid-Liquid-Fluid Equilibria," PhD Thesis, Univ. of Illinois, Urbana (1987).

Hoheisel, C., U. Deiters, and K. Lucas, "The Extension of Pure Fluid Thermodynamic Properties to Supercritical Mixtures," *Molecular Phys.*, **49**(1), 159 (1983).

Hong, G. T., and M. Modell, "Binary Phase Diagrams from a Cubic Equation of State," *Chemical Engineering at Supercritical Fluid Conditions*, M. E. Paulaitis et al., eds., Ann Arbor Science, Ann Arbor, MI, 263 (1983).

Hsu, J. J.-C., N. Nagarajan, and R. L. Robinson, Jr., "Equilibrium Phase Compositions, Phase Densities, and Interfacial Tensions for CO_2 + Hydrocarbon Systems 1. CO_2 + n-Butane," *J. Chem. Eng. Data*, **30**, 485 (1985).

Hyatt, J. A., "Liquid and Supercritical Carbon Dioxide as Organic Solvents," *J. Org. Chem.*, **49**, 5097 (1984).

Ikonomou, G. D., and M. D. Donohue, "COMPACT: A Simple Equation of State for Associated Molecules," *Fluid Ph. Equil.*, **33**, 61 (1987).

Inomata, H., K. Arai, and S. Saito, "Measurement of Vapor-Liquid Equilibria at Elevated Temperatures and Pressures Using a Flow Type Apparatus," *Fluid Ph. Equil.*, **29**, 225 (1986b).

Inomata, H., K. Tuchiya, K. Arai, and S. Saito, "Measurement of Vapor-Liquid Equilibria at Elevated Temperatures and Pressures Using a Flow Type Apparatus," *J. Chem. Eng. Japan*, **19**(5), 386 (1986a).

Jin, G., J. M. Walsh, and M. D. Donohue, "A Group-Contribution Correlation for Predicting Thermodynamic Properties with the Perturbed-Soft-Chain Theory," *Fluid Ph. Equil.*, **31**, 123 (1986).

Johnston, K. P., personal communication (1988).

Johnston, K. P., S. E. Barry, N. K. Read, and T. R. Holcomb, "Separation of Isomers Using Retrograde Crystallization from Supercritical Fluids," *Ind. Eng. Chem. Res.*, **26**, 2372 (1987a).

Johnston, K. P., and C. A. Eckert, "An Analytical Carnahan-Starling-van der Waals Model for Solubility of Hydrocarbon Solids in Supercritical Fluids," *AIChE J.*, **27**(5), 773 (Sept., 1981).

Johnston, K. P., S. Kim, and J. M. Wong, "Local Composition Models for Fluid Mixtures over a Wide Density Range," *Fluid Ph. Equil.*, **38**, 39 (1987b).

Johnston, K. P., D. H. Ziger, and C. A. Eckert, "Solubilities of Hydrocarbon Solids in Supercritical Fluids. The Augmented van der Waals Treatment," *Ind. Eng. Chem. Fund.*, **21**, 191 (1982).

Jonah, D. A., K. S. Shing, V. Venkatasubramanian, and K. E. Gubbins, "Molecular Thermodynamics of Dilute Solutes in Supercritical Solvents," *Chemical Engineering at Supercritical Fluid Conditions*, M. E. Paulaitis et al., eds., Ann Arbor Science, Ann Arbor, MI, 221 (1983).

Kajimoto, O., M. Futakami, T. Kobayashi, and K. Yamasaki, "Charge-Transfer-State Formation in Supercritical Fluid: (N,N-Dimethylamino) benzonitrile in CF_3H," *J. Phys. Chem.*, **92**, 1347 (1988).

Kalra, H., H. Kubota, D. B. Robinson, and H.-J. Ng, "Equilibrium Phase Properties of the Carbon Dioxide-n-Heptane System," *J. Chem. Eng. Data*, **23** (4), 317 (1978).

Kamlet, M. J., J. L. Abboud, M. H. Abraham, and R. W. Taft, "Linear Solvation Energy Relationships: 23. A Comprehensive Collection of the Solvatochromic Parameter, π^*, α, β, and Some Methods for Simplifying the Generalized Solvatochromic Equations," *J. Org. Chem.*, **48**, 2877 (1983).

Kamlet, M. J., J. L. Abboud, and R. W. Taft, "The Solvatochromic Comparison Method. 6. The π^* Scale of Solvent Polarities," *J. Amer. Chem. Soc.*, **99**(18), 6027 (1977).

Kander, R. G., and M. E. Paulaitis, "The Adsorption of Phenol from Dense Carbon Dioxide onto Activated Carbon," *Chemical Engineering at Supercritical Fluid Conditions*, M. E. Paulaitis et al., eds., Ann Arbor Science, Ann Arbor, MI, 461 (1983).

Kershaw, J. R., and L. J. Bagnell, "Extraction of Australian Coals with Supercritical Aqueous Solvents," *Supercritical Fluids*, T. G. Squires and M. E. Paulaitis, eds., ACS, Washington, DC, 266 (1987).

Kim, S., and K. P. Johnston, "Clustering in Supercritical Fluid Mixtures," *AIChE J.*, **33**(10), 1603 (Oct., 1987a).

———, "Molecular Interactions in Dilute Supercritical Fluid Solutions," *Ind. Eng. Chem. Res.*, **26**, 1206 (1987b).

———, "Theory of the Pressure Effect in Dense Gas Extraction," AIChE Meeting, San Francisco (1985).

King, Jr., A. D., and W. W. Robertson, "Solubility of Naphthalene in Compressed Gases," *J. Chem. Phys.*, **37**(7), 1453 (1962).

Kleintjens, L. A., "Mean-Field Lattice Gas Description of Vapour-Liquid and Supercritical Equilibria," *Fluid Ph. Equil.*, **10**, 183 (1983).

Kleintjens, L. A., and R. Koningsveld, "Lattice-Gas Treatment of Supercritical Phase Behavior in Fluid Mixtures," *J. Electrochem. Soc.*, **25**, 2352 (1980).

———, "Mean-Field Lattice-Gas Description of Fluid-Phase Equilibria," *Chemical Engineering at Supercritical Fluid Conditions*, M. E. Paulaitis et al., eds., Ann Arbor Science, Ann Arbor, MI, 245 (1983).

Kleintjens, L. A., R. Van der Haegen, L. van Opstal, and R. Koningsveld, "Mean-Field Lattice-Gas Modelling of Supercritical Phase Behavior," *J. Supercrit. Fluids*, **1**, 23 (1988).

Klesper, E., "Chromatography with Supercritical Fluids," *Angew. Chem. Int. Ed. Engl.*, **17**, 738 (1978).

Kohn, J. P., E. S. Andrle, K. D. Luks, and J. D. Colmenares, "Phase Equilibria of Ethylene and Certain Normal Paraffins," *J. Chem. Eng. Data*, **25**, 348 (1980).

Koningsveld, R., L. A. Kleintjens, and G. A. M. Diepen, "Solubility of Solids in Supercritical Solvents: I. General Principles," *Ber. Bunsenges. Phys. Chem.*, **88**, 848 (1984).

Kragas, T. K., J. Pollin, R. J. Martin, and R. Kobayashi, "A High-Pressure-High-Temperature Chromatographic Apparatus for the Measurement of Vapor-Liquid Equilibria," *Fluid Ph. Equil.*, **16**, 205 (1984).

Krukonis, V. J., and R. T. Kurnik, "Solubility of Solid Aromatic Isomers in Carbon Dioxide," *J. Chem. Eng. Data*, **30**, 247 (1985).

Kumar, S. K., U. W. Suter, and R. C. Reid, "A Statistical Mechanics Based Lattice Model Equation of State," *Ind. Eng. Chem. Res.*, **26**, 2532 (1987).

Kurnik, R. T., S. J. Holla, and R. C. Reid, "Solubility of Solids in Supercritical Carbon Dioxide and Ethylene," *J. Chem. Eng. Data*, **26**, 47 (1981).

Kurnik, R. T., and R. C. Reid, "Solubility of Solid Mixtures in Supercritical Fluids," *Fluid Ph. Equil.*, **8**, 93 (1982).

Kwak, T. Y., and G. A. Mansoori, "Van der Waals Mixing Rules for Cubic Equations of State. Applications for Supercritical Fluid Extraction Modelling," *Chem. Eng. Sci.*, **41**(5), 1303 (1986).

Kwiatkowski, J., Z. Lisicki, and W. Majewski, "An Experimental Method for Measuring Solubilities of Solids in Supercritical Fluids," *Ber. Bunsenges. Phys. Chem.*, **88**, 865 (1984).

Larson, K. A., and M. L. King, "Evaluation of Supercritical Fluid Extraction in the Pharmaceutical Industry," *Biotech. Prog.*, **2**(2), 73 (1986).

Lee, K. H., and J. P. Kohn, "Heterogeneous Phase Equilibrium in the Ethane-n-Dodecane System," *J. Chem. Eng. Data*, **14**(3), 292 (1969).

Lee, L., personal communication (1989).

Lee, L. L., and H. D. Cochran, "Solvation Structure and Chemical Potentials in Supercritical Fluid Mixtures Based on Molecular Distribution Functions," AIChE Meeting, Washington, DC (1988).

Legret, D., D. Richon, and H. Renon, "Static Still for Measuring Vapor-Liquid Equilibria up to 50 bar," *Ind. Eng. Chem. Fund.*, **19**, 122 (1980).

Leung, S. S., and R. B. Griffiths, "Thermodynamic Properties near the Liquid-Vapor Critical Line in Mixtures of He^3 and He^4," *Phys. Rev. A*, **8**(5), 2670 (1970).

Levelt Sengers, J. M. H., G. Morrison, G. Nielson, R. F. Chang, and C. M. Everhart, "Thermodynamic Behavior of Supercritical Fluid Mixtures," *Int. J. Thermophys.*, **7**(2), 231 (1986).

Li, Y.-H., K. H. Dillard, and R. L. Robinson, Jr., "Vapor-Liquid Phase Equilibrium for Carbon Dioxide-n-Hexane at 40, 80 and 120 C," *J. Chem. Eng. Data*, **26**, 53 (1981).

Luft, G., and N. S. Subramanian, "Phase Behavior of Mixtures of Ethylene, Methyl Acrylate, and Copolymers under High Pressures," *Ind. Eng. Chem. Res.*, **26**, 750 (1987).

Mackay, M. E., and M. E. Paulaitis, "Solid Solubilities of Heavy Hydrocarbons in Supercritical Solvents," *Ind. Eng. Chem. Fund.* **18**(2), 149 (1979).

Mansoori, G. A., N. F. Carnahan, K. E. Starling, and T. W. Leland, Jr., "Equilibrium Thermodynamic Properties of the Mixture of Hard Spheres," *J. Chem. Phys.*, **54**(4), 1523 (1971).

Mansoori, G. A., and J. F. Ely, "Density Expansion (DEX) Mixing Rules: Thermodynamic Modeling of Supercritical Extraction," *J. Chem. Phys.*, **82**(1), 406 (1985).

Mart, C. J., and K. D. Papadopoulos, "A Modification of the Random-Fluid Approximation for Solid-Supercritical Fluid Equilibria," *Supercritical Fluid Technology*, J. M. L. Penninger et al., eds., Elsevier, New York, 67 (1985).

Mart, C. J., K. D. Papadopoulos, and M. C. Donohue, "Application of Perturbed-Hard-Chain Theory to Solid-Supercritical Fluid Equilibria Modeling," *Ind. Eng. Chem. Proc. Des. Dev.*, **25**(2), 394 (1986).

Mathias, P. M., and T. W. Copeman, "Extension of the Peng-Robinson Equation of State to Complex Mixtures: Evaluation of the Various Forms of the Local Composition Concept," *Fluid Ph. Equil.*, **13**, 91 (1983).

McClellan, A. K., A. G. Bauman, and M. A. McHugh, "Polymer Solution-Supercritical Fluid Phase Behavior," *Supercritical Fluid Technology*, J. M. L. Penninger et al., eds., Elsevier, New York, 161 (1985).

McHugh, M. A., and V. J. Krukonis, *Supercritical Fluid Extraction: Principles and Practice*, Butterworths, Boston (1986).

McHugh, M. A., M. W. Mallett, and J. P. Kohn, "High Pressure Fluid Phase Equilibria of Alcohol-Water-Supercritical Solvent Mixtures," *Chemical Engineering at Supercritical Fluid Conditions,* M. E. Paulaitis et al., eds., Ann Arbor Science, Ann Arbor, MI, 221 (1983).

McKinley, C., J. Brewer, and E. S. J. Wang, "Solid-Vapor Equilibria of the Oxygen-Hydrogen System," *Adv. Cryog. Eng.*, **7,** 114 (1961).

McRae, E. G., "Theory of Solvent Effects on Molecular Electronic Spectra Frequency Shifts," *J. Phys. Chem.*, **61,** 562 (1957).

Meskel-Lesavre, M., D. Richon, and H. Renon, "New Variable Volume Cell for Determining Vapor-Liquid Equilibria and Saturated Liquid Molar Volumes by the Static Method," *Ind. Eng. Chem. Fund.*, **20,** 284 (1981).

Mollerup, J., "A Note on Excess Gibbs Energy Models, Equations of State and the Local Composition Concept," *Fluid. Ph. Equil.*, **7,** 121 (1981).

Monge, A., and J. M. Prausnitz, "An Experimental Method for Measuring Solubilities of Heavy Fossil-Fuel Fractions in Compressed Gases to 100 Bar and 300°C," *Chemical Engineering at Supercritical Fluid Conditions,* M. E. Paulaitis et al., eds., Ann Arbor Science, Ann Arbor, MI, 159 (1983).

Morris, W. O., P. Vimalchand, and M. D. Donohue, "The Perturbed-Soft-Chain Theory: An Equation of State Based on the Lennard-Jones Potential," *Fluid Ph. Equil.*, **32,** 103 (1987).

Morrison, G., J. M. H. Levelt Sengers, R. F. Chang, and J. J. Christensen, "Thermodynamic Anomalies in Supercritical Fluid Mixtures," *Supercritical Fluid Technology,* J. M. L. Penninger et al., eds., Elsevier, New York, 25 (1985).

Nagarajan, N., and R. L. Robinson, Jr., "Equilibrium Phase Compositions, Phase Densities, and Interfacial Tensions for CO_2 + Hydrocarbon Systems: 2. CO_2 + *n*-Decane," *J. Chem. Eng. Data,* **31,** 168 (1986).

———, "Equilibrium Phase Compositions, Phase Densities, and Interfacial Tensions for CO_2 + Hydrocarbon Systems: 3. CO_2 + Cyclohexane; 4. CO_2 + Benzene," *J. Chem. Eng. Data,* **32,** 369 (1987).

Najour, G. C., and A. D. King, Jr., "Solubility of Anthracene in Compressed Methane, Ethylene, Ethane, and Carbon Dioxide: The Correlation of Anthracene-Gas Second Cross Virial Coefficients Using Pseudocritical Parameters," *J. Chem. Phys.*, **52**(10), 5206 (1970).

Nielson, G. C., and J. M. H. Levelt Sengers, "Decorated Lattice Gas Model for Supercritical Solubility," *J. Phys. Chem.*, **91**(15), 4078 (1987).

Nitsche, K. S., and P. Suppan, "Solvatochromic Shifts and Polarity of Solvent Mixtures," *Chimia,* **36,** 346 (1982).

Nouacer, M., and K. S. Shing, "Grand Canonical Monte Carlo Simulation for Solubility Calculation in Supercritical Extraction," *Molecular Simulation,* **2,** 55 (1989).

Panagiotopoulos, A. Z., U. W. Suter, and R. C. Reid, "Phase Diagrams of Nonideal Fluid Mixtures from Monte Carlo Simulation," *Ind. Eng. Chem. Fund.*, **25,** 525 (1986).

Pang, T.-H., and E. McLaughlin, "Supercritical Extraction of Aromatic Hydrocarbon Solids and Tar Sand Bitumens," *Ind. Eng. Chem. Proc. Des. Dev.*, **24**(4), 1027 (1985).

Park, S. J., T. Y. Kwak, and G. A. Mansoori, "Statistical Mechanical Description of Supercritical Fluid Extraction and Retrograde Condensation," *Int. J. Thermophy.*, **8**(4), 449 (1987).

Paulaitis, M. E., J. R. DiAndreth, and R. G. Kander, "An Experimental Study of Phase Equilibria for Isopropanol-Water-CO_2 Mixtures Related to Supercritical-Fluid Extraction of Organic Compounds from Aqueous Solutions," *Supercritical Fluid Technology,* J. M. L. Penninger et al., eds., Elsevier, New York, 149 (1985).

Paulaitis, M. E., K. P. Johnston, and C. A. Eckert, "Measurement of Partial Molar Volumes at Infinite Dilution in a Supercritical-Fluid Solvent Near Its Critical Point," *J. Phys. Chem.*, **85**(12), 1770 (1981).

Paulaitis, M. E., R. G. Kander, and J. R. DiAndreth, "Phase Equilibria Related to Supercritical-Fluid Solvent Extractions," *Ber. Bunsenges. Phys. Chem.*, **88,** 869 (1984).

Paulaitis, M. E., V. J. Krukonis, R. T. Kurnik, and R. C. Reid, "Supercritical Fluid Extraction," *Rev. Chem. Engr.*, **1**(2), 179 (1982).

Peaden, P. A., and M. L. Lee, "Supercritical Fluid Chromatography: Methods and Principles," *J. Liq. Chromat.*, **5**(Suppl. 2), 179 (1982).

Peng, D.-Y., and D. B. Robinson, "A New Two-Constant Equation of State," *Ind. Eng. Chem. Fund.*, **15**(1), 59 (1976).

Penninger, J. M. L., "Extraction of Oil from Wyoming Coal with Aqueous Solvents at Elevated Pressure," *Supercritical Fluid Technology,* J. M. L. Penninger et al., eds., Elsevier, New York, 309 (1985).

Peschel, W., and H. Wenzel, "Equation-of-State Predictions of Phase Equilibria at Elevated Pressures in Mixtures Containing Methanol," *Ber. Bunsenges. Phys. Chem.*, **88,** 807 (1984).

Prausnitz, J. M., R. N. Lichtenthaler, and E. Gomes de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria,* Prentice-Hall, Englewood Cliffs, NJ (1986).

Radosz, M., "Vapor-Liquid Equilibrium for 2-Propanol and Carbon Dioxide," *J. Chem. Eng. Data,* **31,** 43 (1986).

Rainwater, J. C., and M. R. Moldover, "Thermodynamic Models for Fluid Mixtures Near Critical Conditions," *Chemical Engineering at Supercritical Fluid Conditions,* M. E. Paulaitis et al., eds., Ann Arbor Science, Ann Arbor, MI, 199 (1983).

Reamer, H. H., and B. H. Sage, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behavior of the Ethane-*n*-Decane System," *J. Chem. Eng. Data,* **7**(2), 161 (1962).

———, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behavior of the *n*-Decane-CO_2 System," *J. Chem. Eng. Data,* **8**(4), 508 (1963).

———, "Phase Equilibria in Hydrocarbon Systems. Phase Behavior in the *n*-Butane-*n*-Decane System," *J. Chem. Eng. Data,* **9**(1), 24 (1964).

Rodrigues, A. B. J., D. S. McCaffrey, Jr., and J. P. Kohn, "Heterogeneous Phase and Volumetric Equilibrium in the Ethane-*n*-Octane System," *J. Chem. Eng. Data,* **13**(2), 164 (1968).

Reichenberg, D., "The Viscosities of Gases at High Pressures," *NPL Rep. Chem. 38,* National Physical Laboratory, Teddington, England (Aug., 1975).

Rizvi, S. S. H., A. L. Benado, J. A. Zollweg, and J. A. Daniels, "Supercritical Fluids Extraction: Fundamental Principles and Modeling Methods," *Food Technol.*, **40**(6), 55 (1986).

Rössling, G. L., and E. U. Franck, "Solubility of Anthracene in Dense Gases and Liquids to 200°C and 2000 Bar," *Ber. Bunsenges. Phys. Chem.*, **87,** 882 (1983).

Ross, D. S., G. P. Hum, T.-C. Min, T. K. Green, and R. Mansani, "Isotope Effects in Supercritical Water: Kinetic Studies of Coal Liquefaction," *Supercritical Fluids,* T. G. Squires and M. E. Paulaitis, eds., ACS, Washington, DC, 242 (1987).

Rozen, A. M., "The Unusual Properties of Solutions in the Vicinity of the Critical Point of the Solvent," *Russ. J. Phys. Chem.*, **50**(6), 837 (1976).

Saad, H., and E. Gulari, "Diffusion of Liquid Hydrocarbons in Supercritical CO_2 by Photon Correlation Spectroscopy," *Ber. Bunsenges. Phys. Chem.*, **88,** 834 (1984a).

———, "Diffusion of Carbon Dioxide in Heptane," *J. Phys. Chem.*, **88,** 136 (1984b).

Scarrah, W. P., "Liquefaction of Lignite Using Low Cost Supercritical Solvents," *Chemical Engineering at Supercritical Fluid Conditions,* M. E. Paulaitis et al., eds., Ann Arbor Science, Ann Arbor, MI, 395 (1983).

Schantz, M. M., and S. N. Chesler, "Supercritical Fluid Extraction Procedure for the Removal of Trace Organic Species from Solid Samples," *J. Chromat.*, **363,** 397 (1986).

Schmitt, W. J., and R. C. Reid, "Solubility of Monofunctional Organic Solids in Chemically Diverse Supercritical Fluids," *J. Chem. Eng. Data,* **31,** 204 (1986).

Sebastian, R. M., J. J. Simnick, H.-M. Lin, and K.-C. Chao, "Vapor-Liquid Equilibrium in Binary Mixtures of Carbon Dioxide + *n*-Decane and Carbon Dioxide + *n*-Hexadecane," *J. Chem. Eng. Data,* **25,** 138 (1980).

Seckner, A. J., A. K. McClellan, and M. A. McHugh, "High-Pressure Solution Behavior of the Polystyrene-Toluene-Ethane System," *AIChE J.*, **34**(1), 9 (1988).

Šerbanović, S. P., and B. D. Djordjević, "Influence of the Optimized Temperature-Dependent Interaction Parameter on Vapor-Liquid Equilibrium Binary Predictions of Supercritical Methane with Some Alkanes by Means of the Soave Equation of State," *Ind. Eng. Chem. Res.*, **26**(3), 618 (1987).

Shing, K. S., and S. T. Chung, "Computer Simulation Methods for the Calculation of Solubility in Supercritical Extraction Systems," *J. Phys. Chem.*, **91,** 1674 (1987).

Sigman, M. E., S. M. Lindley, and J. E. Leffler, "Supercritical Carbon Dioxide: Behavior of π^* and β Solvatochromic Indicators in Media of Different Densities," *J. Amer. Chem. Soc.*, **107,** 1471 (1985).

Smith, R. D., S. L. Frye, C. R. Yonker, and R. W. Gale, "Solvent Properties of Supercritical Xe and SF_6," *J. Phys. Chem.*, **91**, 3059 (1987).

Stahl, E., and E. Willing, "Extraktion von Naturstoffen mit Uberkritischen und Verflussigten Gasen," *Mikrochim Acta*, 465 (1980).

Stephan, K., and K. Lucas, *Viscosity of Dense Fluids*, Plenum Press, New York, 75 (1979).

Swaid, I., and G. M. Schneider, "Determination of Binary Diffusion Coefficients of the Benzene and Some Alkylbenzenes in Supercritical CO_2 between 308 and 328 K in the Pressure Range 80 to 160 bar with Supercritical Fluid Chromatography (SFC)," *Ber. Bunsenges. Phys. Chem.*, **83**, 969 (1979).

Tan, C.-S., and J.-Y. Weng, "Solubility Measurements of Naphthol Isomers in Supercritical CO_2 by a Recycle Technique," *Fluid Ph. Equil.*, **34**, 37 (1987).

Teja, A. S., and R. L. Smith, "The Correlation and Prediction of Critical States of Mixtures Using a Corresponding States Principle," *Chemical Engineering at Supercritical Fluid Conditions*, M. E. Paulaitis et al., eds., Ann Arbor Science, Ann Arbor, MI, 341 (1983).

Tiffin, D. L., A. L. DeVera, K. D. Luks, and J. P. Kohn, "Phase-Equilibria Behavior of the Binary Systems Carbon Dioxide-*n*-Butylbenzene and Carbon Dioxide-*trans*-Decalin," *J. Chem. Eng. Data*, **23**(1), 45 (1978).

Trappeniers, N. J., J. A. Schouten, and C. A. Ten Seldam, "Gas-Gas Equilibrium and the Two-Component Lattice-Gas Model," *Chem. Phys. Lett.*, **5**(9), 541 (1970).

Triday, J., and J. M. Smith, "Dynamic Behavior of Supercritical Extraction of Kerogen from Shale," *AIChE J.*, **34**(4), 658 (1988).

Tsang, C. Y., and W. B. Streett, "Vapor-Liquid Equilibrium in the System Carbon Dioxide/Dimethyl Ether," *J. Chem. Eng. Data*, **26**, 155 (1981).

Tsekhanskaya, Y. V., "Diffusion in the System *p*-Nitrophenol-Water in the Critical Region," *Russ. J. Phys. Chem.*, **42**, 532 (1968).

———, "Diffusion of Naphthalene in Carbon Dioxide Near the Liquid-Gas Critical Point," *Russ. J. Phys. Chem.*, **45**, 744 (1971).

Tsekhanskaya, Y. V., N. G. Roginskaya, and E. V. Mushkina, "Volume Changes in Naphthalene Solutions in Compressed Carbon Dioxide," *Russ. J. Phys. Chem.*, **40**(9), 1152 (1966).

Van Alsten, J. G., "Structural and Functional Effects in Solutions with Pure and Entrainer-Doped Supercritical Solvents," PhD Thesis, Univ. of Illinois, Urbana (1986).

Van Alsten, J. G., P. C. Hansen, and C. A. Eckert, "Supercritical Enhancement Factors for Nonpolar and Polar Systems," AIChE Meeting, San Francisco (1984).

Van Leer, R. A., and M. E. Paulaitis, "Solubilities of Phenol and Chlorinated Phenols in Supercritical Carbon Dioxide," *J. Chem. Eng. Data*, **25**(3), 257 (1980).

Van Wasen, U., and G. M. Schneider, "Partial Molar Volumes of Naphthalene and Fluorene at Infinite Dilution in Carbon Dioxide Near its Critical Point," *J. Phys. Chem.*, **84**, 229 (1980).

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

Vasilakos, N. P., J. M. Dobbs, and A. S. Parisi, "Solvent Effects in Supercritical Extraction of Coal," *Ind. Eng. Chem. Proc. Des. Dev.*, **24**, 121 (1985).

Vezzetti, D. J., "Solubility of Solids in Supercritical Gases," *J. Chem. Phys.*, **77**(3), 1512 (1982).

———, "Solubility of Solids in Supercritical Gases: II. Extension to Molecules of Differing Sizes," *J. Chem. Phys.*, **80**(2), 868 (1984).

Vidal, J., "Phase Equilibria and Density Calculations for Mixtures in the Critical Range with Simple Equations of State," *Ber. Bunsenges, Phys. Chem.*, **88**, 784 (1984).

Vimalchand, P., and M. D. Donohue, "Thermodynamics of Quadrupolar Molecules: The Perturbed-Anisotropic-Chain Theory," *Ind. Eng. Chem. Fund.*, **24**, 246 (1985).

Vogelsang, R., and C. Hoheisel, "Structure and Dynamics of a Supercritical Fluid in Comparison with a Liquid: A Computer Simulation Study," *Mole. Phys.*, **53**(6), 1355 (1984).

Walsh, J. M., G. D. Ikonomou, and M. D. Donohue, "Supercritical Phase Behavior: The Entrainer Effect," *Fluid. Ph. Equil.*, **33**, 295 (1987).

Wheeler, J. C., "Behavior of a Solute near the Critical Point of an Almost Pure Solvent," *Ber. Bunsen-Gessellschaft*, **76**(3/4), 308 (1972).

Whiting, W. B., and J. M. Prausnitz, "Equations of State for Strongly Nonideal Fluid Mixtures: Application of Local Compositions Toward Density-Dependent Mixing Rules," *Fluid Ph. Equil.*, **9**, 119 (1982).

Wilhelm, A., and K. Hedden, "Supercritical Fluid Extraction of Coal: Development of a 'Second Generation' Process Concept," *Supercritical Fluid Technology*, J. M. L. Penninger et al., eds., Elsevier, New York, 357 (1985).

Williams, D. F., "Extraction with Supercritical Gases," *Chem. Eng. Sci.*, **36**, 1769 (1981).

Wise, W. S., "Solvent Extraction of Coal," *Chem. Ind.*, London, 950 (1970).

Won, K. W., "Phase Equilibria of High-Boiling Organic Solutes In Compressed Supercritical Fluids. Equation of State with New Mixing Rule," *Chemical Engineering at Supercritical Fluid Conditions*, M. E. Paulaitis et al., eds., Ann Arbor Science, Ann Arbor, MI, 323 (1983).

Wong, J. M., and K. P. Johnston, "Solubilization of Biomolecules in Carbon Dioxide Based Supercritical Fluids," *Biotech. Prog.*, **2**(1), 29 (1986).

Wormald, C. J., and J. M. Eyears, "Excess Enthalpies and Excess Volumes of $[xCO_2 + (1-x)N_2O]$ in the Liquid and Supercritical Regions," *J. Chem. Soc., Farad. Trans. 1*, **84**(9), 3097 (1988).

Wu, P. C., and P. Ehrlich, "Volumetric Properties of Supercritical Ethane-*n*-Heptane Mixtures: Molar Volumes and Partial Molar Volumes," *AIChE J.*, **19**(3), 533 (May, 1973).

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 (1988a).

———, "Solvatochromic Behavior of Binary Supercritical Fluids: The Carbon Dioxide/2-Propanol System," *J. Phys. Chem.*, **92**, 2374 (1988b).

Yonker, C. R., S. L. Frye, D. R. Kalkwarf, and R. D. Smith, "Characterization of Supercritical Fluid Solvents Using Solvatochromic Shifts," *J. Phys. Chem.*, **90**, 3022 (1986).

Ziger, D. H., and C. A Eckert, "Correlation and Prediction of Solid-Supercritical Fluid Phase Equilibria," *Ind. Eng. Chem. Proc. Des. Dev.*, **22**, 582 (1983).

Zosel, K., "Separation with Supercritical Gases: Practical Applications," *Angew. Chem. Int. Ed., Engl.*, **17**, 702 (1978).

Zosel, K., U. S. Patent 3969196, Studiengesellschaft Kohle (1963).

Manuscript received Mar. 10, 1989, and revision received June 8, 1989.

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