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Nonpolar Co-Solvents for Solubility Enhancement in Supercritical Fluid Carbon Dioxide

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A new microsampling experimental technique is described for measuring the solubility of solids in supercritical fluid (SF) CO_2 with liquid co-solvents. Since the polarizability of CO_2 is relatively low, the solubility of hydrocarbons increases significantly with the addition of small amounts of alkane co-solvents. In many cases, the sensitivity of the solubility with respect to pressure actually increases with the addition of the co-solvent. The data are predicted to within an average of 13% by using solubility parameters to calculate the interaction constants in a modified van der Waals equation of state.

Introduction

One of the most attractive features of supercritical fluid solvents is that the isothermal compressibility is several orders of magnitude greater than that of liquids. All of the density-dependent properties such as the solubility parameter, dielectric constant, etc. may be varied markedly by using only modest changes in the temperature and pressure. The ability to adjust the strength of the solvent is the basis of relatively new separations processes such as supercritical fluid (SF) extraction (*1-3*).

While SF carbon dioxide has many desirable properties, its polarizability is less than that of all of the hydrocarbons except methane. Therefore, a pressure of 200 bar is required at 35 °C to attain a solubility parameter of 6.5 $(cal/cm^3)^{1/2}$, a value which is nearly comparable to that of liquid isopentane. At these conditions, the solubility, y_2, of a solid such as phenanthrene in CO_2 is several orders of magnitude below the ideal solubility since the solubility parameters differ by 3-4 $(cal/cm)^{1/2}$. The objective is to enhance considerably the polarizability and therefore the strength of SF solvents by using small amounts of co-solvents, while maintaining the sensitivity of y_2 with respect to temperature and pressure.

Although the concept of adding co-solvents, which have been called modifiers or entrainers, to supercritical fluids is beginning to receive attention (*4-11*), there are few collections of fundamental data in the literature. Kurnik and Reid (*8*) demonstrated that the solubility of a solid in a SF solvent may be enhanced in some instances by the presence of a second solute. Sulfur dioxide has been used as a co-solvent for benzoic acid (*6*, *10*). Van Alsten et al. reported solid–fluid equilibria data for a number of systems (*9*). Dobbs et al. measured and correlated solid–fluid equilibria data for benzoic acid, 2-aminobenzoic acid, phthalic anhydride, and acridine in CO_2 doped with acetone or methanol (*11*). Although most of the systems included complicated molecular interactions, for example, hydrogen bonding, the data were correlated to within an average of 10% by using an adjustable solute–co-solvent interaction constant. The data were predicted only to within about 30%.

Supercritical fluid solutions are far removed from the ideal gas or ideal solution reference states, are highly compressible, and are strongly asymmetric with respect to the size and energy of the components. Because of these complexities, most of the reported models for binary solid–fluid equilibria can be used only for data correlation using adjustable binary interaction parameters (*1-3*). Wong et al. (*12*) developed a model to predict such data for binary nonpolar systems in which the attractive interaction parameters were calculated from molecular volumes. Given the scarcity of solubility data in supercritical fluid solvents, predictive models are quite valuable for engineering practice, especially for multicomponent systems. A major objective of the present study is to predict the effects of co-solvents on the solubility behavior quantitatively without using any adjustable parameters. The attention is focused on systems including nonpolar solutes and co-solvents so that the interaction constants are relatively well-defined. These results will provide an important basis for future attempts to predict the behavior of polar systems.

Experimental Section

The microsampling apparatus shown in Figure 1 combines a solvent delivery system similar to the one of Dobbs et al. (*11*) with a high-pressure sampling valve design used by McHugh and Paulaitis (*13*). In most previous studies (*8*, *11*, *14*), an equilibrated supercritical solution was depressurized continuously across a heated micrometering valve to precipitate 0.05-5 g of solute which was analyzed gravimetrically. In the new microsampling technique, a 0.1-cm^3 sample of an equilibrated supercritical solution was depressurized to precipitate about 10^{-4}-10^{-6} g of solute for analysis using capillary gas chromatography. After performing hundreds of runs with each technique, we conclude that the microsampling technique is far superior to the gravimetric one for numerous reasons listed at the end of this section.

The solvent solution was prepared by adding a measured weight of liquid co-solvent to a known volume of pure CO_2 at about 2000 psia. Liquid carbon dioxide was compressed by an air-driven oil-free reciprocating compressor, Haskell AG-152, to fill the 906 ± 5 cm^3 solvent reservoir. The pressure and temperature were recorded to determine the density. A measured weight of co-solvent was added with a high-pressure liquid metering pump, Milton Roy 396-31, so that the composition of the solution was known to within ±2%. The composition was monitored during each run by using a densitometer, which is described below. After the solvent mixture was prepared, the storage reservoir was heated to approximately 70 °C to generate a sufficient source pressure. The pressure was controlled from 0 to 35.0 MPa with a Tescom pressure regulator, No. 26-1021, with 70 durometer buna-N O-rings. The digital pressure gauge, Heise 710A, was factory calibrated to ±0.1% as traced to an NBS standard. Pressure fluctuations were on the order of ±0.1 MPa.

The temperature of the solvent was equilibrated in a $^1/_8$-in.-o.d. × 0.085-in.-i.d., 5-m-long 316 SS heat exchanger in a water bath shown by the dashed line. The water bath was controlled to better than ±0.1 °C by an Omega Model 6000 temperature controller with a platinum resistance thermometer. The density of the solvent was measured to $\pm 1.0 \times 10^{-4}$ g/cm^3 by using a Mettler Paar DMA-512 vibrating tube densitometer placed immediately in front of the first saturator. Each 316 SS saturator (0.79-cm i.d. by 15-cm long) was packed with equal volumes of reagent grade sand, MCB-SX76, and solid solute in order to disperse the solvent flow and to minimize the pressure drop through the saturators to less than 1 bar. Glass wool was

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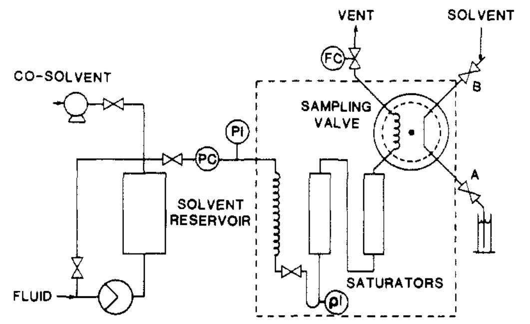

Figure 1. Microsampling apparatus for solid-fluid equilibria.

Table I. Comparison of Methods for the Measurement of the Solubility of Solids in Supercritical CO_2 at 35 °C

P, bar	ρ, mol/L	10^3y	10^3y^c
Hexamethylbenzene–CO_2			
150	18.54	1.66[a]	1.70
200	19.67	1.76[a]	1.78
300	21.11	1.92[a]	
350	21.62	1.99[a]	1.91
Naphthalene–CO_2			
122	17.61	12.5[b]	12.9
193	19.50	16.3[b]	16.9
243	20.62	17.7[b]	17.1

[a] Flow gravimetric technique (*11*). [b] Static gravimetric technique (*16*). [c] Microsampling technique, this work.

inserted at the top of each saturator to prevent entrainment of the solid. The effluent of the second saturator was in equilibrium as the solubility varied less than ±2% for flow rates varying from 0.03 to 0.30 standard L/min. The equilibrated solution was sampled by using a calibrated 0.1085 ± 0.0005 cm^3 sampling loop inserted in a Valco C6U-HC high-pressure chromatographic switching valve. A modified Autoclave 39VRM-4812 micrometering valve, which was heated to approximately 30 °C above the melting point of the solute, was used to control the flow rate although accurate control was unnecessary.

With the switching valve in the sampling mode shown in Figure 1, two residence volumes of the saturators were displaced through the sample loop. The total number of grams of solution in the loop was calculated from the volume of the loop and the density of the mixture. The density of the mixture was essentially the same as the density of the solvent (less than 1.5% relative difference) for solid solubilities below 1 mol % (*15*). The sample valve was switched to expand the equilibrated sample between valves A and B. Valve A was opened slowly and the effluent mixture was bubbled through a liquid solvent, e.g., acetone. Valve B was opened and about 5–10 cm^3 of a liquid solvent was injected through the system to recover the solute. Typically, the amount of solute collected was on the order of 10^{-4}–10^{-6} g. An internal standard was added to the extract which was analyzed with a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a 10 m × 0.53 mm poly(dimethylsiloxane) bonded phase capillary column (Alltech NON-PAKD), and a Hewlett-Packard 3392 integrator.

The solubilities measured with the new microsampling technique agreed with literature values to within ±4% for naphthalene (*16*) and hexamethylbenzene (*11*) in CO_2 at 35 °C and 120–350 bar as shown in Table I. The typical experimental reproducibility was about 4%. The major source of error may be attributed to the chromatographic analysis, which is widely known to be accurate to within only a few percent for polynuclear aromatic hydrocarbons.

All of the experimental data points represent solid–fluid equilibria, without a liquid phase present, as verified by using a 2-mm-i.d. glass tube described elsewhere (*11*).

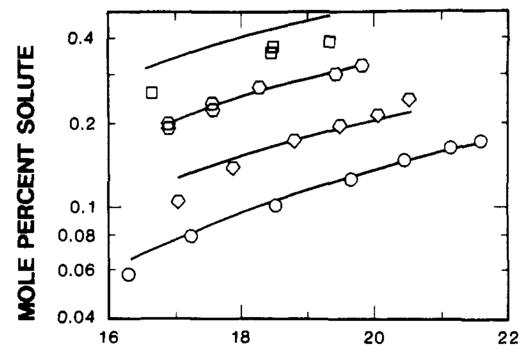

Figure 2. Solubility of phenanthrene in carbon dioxide with 3.5 mol % co-solvent at 35 °C (○, pure CO_2; ⬡, pentane + CO_2; ◇, octane + CO_2; □, undecane + CO_2; —, predicted by using eq 6 and 7).

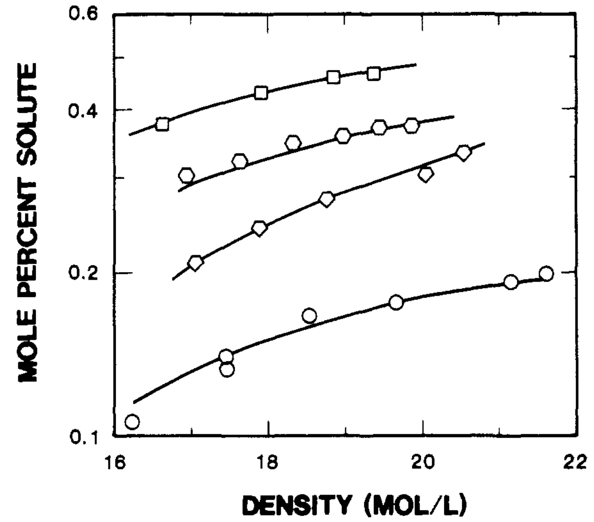

Figure 3. Solubility of hexamethylbenzene in carbon dioxide with 3.5 mol % co-solvent at 35 °C (○, pure CO_2; ⬡, pentane + CO_2; ◇, octane + CO_2; □, undecane + CO_2; —, correlated by using HSVDW EOS).

The microsampling technique offers several important advantages over the gravimetric technique: (1) Multicomponent solvent and solute systems can be analyzed directly. In the gravimetric technique, the sample must be dried to remove the co-solvent. (2) Thermally labile compounds are not denatured nor decomposed during depressurization at ambient temperatures. (3) The run time is reduced significantly because of the smaller sample size. (4) A major source of error in the gravimetric technique is due to precipitation of solute upstream of the trap which plugs up the system. The high temperature of the micrometering valve does not always alleviate this problem, particularly at lower pressures where the solubility decreases with temperature. This problem is eliminated in the new technique. (5) Accurate flow rate measurement and control are unnecessary since the solubility is not calculated from an integrated flow rate. (6) Only a few milligrams of valuable compounds are required for analysis. (7) The new technique is safer since the glass traps used in the gravimetric technique which can explode have been removed, and since exposure to toxic solid particles has been reduced if not eliminated.

Results and Discussion

The solubility vs. density isotherms are shown in Figures 2 and 3 for hexamethylbenzene and phenanthrene, respectively. The data are represented straightforwardly on this type of plot, whereas a solubility vs. pressure plot is quite complex due to the effect of pressure on density (*14*). The entire set of solu-

Table II. Solubility of Solids in CO_2 and in CO_2 Doped with Co-Solvents at 35 °C

P, bar	ρ, mol/L	10^3y
Hexamethylbenzene–n-Pentane (3.5 mol %)–CO_2		
350	20.54	3.08
300	20.08	3.04
200	18.84	2.74
150	17.88	2.47
120	17.06	2.36
100	16.23	2.06
Hexamethylbenzene–n-Octane (3.5 mol %)–CO_2		
350	19.85	3.70
300	19.45	3.71
250	18.99	3.61
200	18.30	3.50
150	17.60	3.27
120	16.92	3.00
Hexamethylbenzene–n-Undecane (3.5 mol %)–CO_2		
350	19.29	4.73
300	18.90	4.60
200	17.94	4.25
120	16.68	3.85
Phenanthrene–CO_2		
350	21.62	1.71
300	21.11	1.62
250	20.47	1.46
200	19.67	1.25
150	18.54	1.01
120	17.46	0.787
100	16.24	0.571
Phenanthrene–n-Pentane (3.5 mol %)–CO_2		
350	20.54	2.43
300	20.08	2.14
250	19.53	1.97
200	18.84	1.73
150	17.89	1.39
120	17.06	1.06
Phenanthrene–n-Octane (3.5 mol %)–CO_2		
350	19.85	3.22
300	19.45	3.00
200	18.30	2.70
150	17.60	2.26
150	17.60	2.36
120	16.92	2.00
120	16.92	1.94
Phenanthrene–n-Octane (5.25 mol %)–CO_2		
350	19.07	4.58
250	18.28	4.07
200	17.85	3.54
150	17.09	2.98
120	16.55	2.52
Phenanthrene–n-Octane (7 mol %)–CO_2		
350	18.44	5.36
250	17.69	5.14
200	17.24	4.71
200	17.24	4.57
150	16.64	4.06
120	16.18	3.84
Phenanthrene–n-Undecane (3.5 mol %)–CO_2		
350	19.29	3.78
250	18.47	3.62
250	18.47	3.57
120	16.68	2.56

bility, pressure, and density data are listed in Table II. The listed compositions of the co-solvent refer to a solute-free basis.

Table III. Co-Solvent-Induced Solubility Enhancements of Solids in Carbon Dioxide at 35 °C and at a Density of 18.54 g mol/L

solid	co-solvent	y_3	y_2(ternary)/ y_2(binary)
hexamethylbenzene	n-pentane	3.5	1.6
	n-octane	3.5	2.1
	n-undecane	3.5	2.6
phenanthrene	n-pentane	3.5	1.6
	n-octane	3.5	2.8
	n-octane	5.25	4.2
	n-octane	7.0	5.4
	n-undecane	3.5	3.6

The shape of each ternary isotherm (solute + CO_2 + co-solvent) is similar to the binary one (solute + CO_2) such that the ratio of y_2 in the ternary system to y_2 in the binary system is relatively independent of density. This type of co-solvent-induced solubility enhancement, which can be considered qualitatively as an upward translation of a binary isotherm, has also been observed for polar systems (*11*). Table III lists the co-solvent-induced solubility enhancements for the three nonpolar co-solvents and two solutes at 35 °C and at a reference density of 18.54 mol/L (15.0 MPa for pure CO_2). The enhancement increases with the chain length or the polarizability (see Table IV) of the n-alkane co-solvent. Therefore, the increase in the attractive forces with chain length more than compensates for the increase in the repulsive forces which is related to the van der Waals volume. For these three n-alkanes, a plot of the co-solvent-induced solubility enhancement vs. the co-solvent solubility parameter is linear, although more data would be needed to validate such a correlation. The fact that these properties are related is realistic since the solubility parameter is the square root of a cohesive energy per unit volume, and thus includes effects of attractive as well as repulsive forces.

The solubilities of the solids are increased more by the presence of several mole co-solvent than by changes in the pressure of several hundred bar. For example, the co-solvent-induced solubility enhancement of phenanthrene is 1.6 for 3.5 mol % pentane and 3.6 for 3.5 mol % undecane (see Table III). Again, these values are relatively invariant with respect to pressure. In comparison, an increase in the pressure from 150 to 350 bar raises the solubility by a factor of only 1.7 in pure CO_2.

At 350 bar, the solubility of hexamethylbenzene in pure CO_2 is 2×10^{-4}. By adding only 3.5 mol % pentane as a co-solvent, it is possible to achieve the same solubility at a greatly reduced pressure of 100 bar. The magnitude of this pressure reduction could have profound effects on the economics of a supercritical process. The use of co-solvents could have marked effects on the yield as well as on the pressure reduction. At 120 bar, the solubility of phenanthrene in a ternary system with 7.0 mol % octane is over 2 times greater than in pure CO_2 even at 350 bar. At 350 bar and 35 °C, the addition of 7.0 mol % octane raises the solubility of phenanthrene in CO_2 by a factor of 3.1. This increase, which will be shown to be the result of the solute–co-solvent attractive forces, is striking as the density of the binary solvent is 15% less than that of pure CO_2.

Many investigators have suggested that the solvent strength of supercritical fluids should approach that of liquids since the densities are similar. This is clearly an oversimplification. Even when the densities are the same, the polarizability or the solubility parameter of CO_2 is lower than that of most hydrocarbons. As a result, at a given pressure, octane increases the solvent strength even though it lowers the molar density of the solution.

For these nonpolar systems, the co-solvent-induced solubility enhancements are significant yet not that specific with respect to the solute, a result which is typical for dispersion forces. The co-solvent pentane produces the same enhancement for phenanthrene and hexamethylbenzene, although n-octane and n-undecane produce a slightly greater one for phenanthrene. In contrast, Dobbs et al. (*1*) demonstrated both experimentally and theoretically that polar co-solvents interact specifically with certain polar solutes in SF CO_2. For example, the addition of

Table IV. Physical Properties of Solutes and Co-Solvents

	α, 10^{25} cm^3	v^L, cm^3/(g mol)	P^{sat}(35 °C), Pa	b, cm^3/(g mol)	δ, (cal/cm^3)$^{1/2}$
solutes					
hexamethylbenzene	208	175	0.5	95.0	8.3
phenanthrene	247	162	0.065	102.1	9.8
co-solvents					
n-pentane	100	115.2		58.0	7.0
n-octane	154	163.5		89.0	7.6
n-undecane	208	211.2		119.4	7.9

Table V. Comparison of Predicted and Experimentally Regressed Values of the Solute–Co-Solvent Attraction Energy

solute	co-solvent	y_3	a_{12}, 10^{-7} bar cm^6	a_{23}/a_{12}	Δu_{23}^{exptl}, kJ/(g mol)	Δu_{23}^{calcd}, kJ/(g mol)	y_2,[a] % AAD	y_2,[b] % AAD
hexamethylbenzene	*n*-pentane	3.5	1.66	3.23	37.9	33.3	3.8	31.8
	n-octane	3.5	1.66	4.57	44.9	43.1	1.8	15.3
	n-undecane	3.5	1.66	5.85	50.6	50.8	1.0	1.7
phenanthrene	*n*-pentane	3.5	1.83	3.05	40.8	39.2	8.9	12.1
	n-octane	3.5	1.83	4.56	51.2	50.7	2.7	3.9
	n-octane	5.25	1.83	4.62	51.8	50.7	8.6	9.8
	n-octane	7.0	1.83	4.61	51.7	50.7	4.7	11.7
	n-undecane	3.5	1.83	5.84	57.3	59.9	3.8	18.8
							av 4.4	13.1

[a] % AAD in y_2, using the regressed a_{23} shown in the table (correlated). [b] % AAD in y_2, using Δu_{23}^{calcd} to obtain a_{23} (predicted).

3.5 mol % methanol increased the solubility of 2-aminobenzoic acid in CO_2 at 35 °C and 20.5 mol/L by a factor of 6 while it had no effect on the solubility of hexamethylbenzene. The former was explained by specific acid–base interactions while the latter by the fact that the polarizability of methanol is not much greater than that of CO_2. Extremely large co-solvent-induced solubility enhancements greater than 5 were observed only in systems with strong acid–base interactions when 3.5 mol % co-solvent was used.

The above examples illustrate that a polar co-solvent may increase markedly the solubility of a polar solute, but may not affect that of a nonpolar solute. In contrast, a nonpolar co-solvent such as octane has about the same effect on polar and nonpolar solutes if the molecular weights or polarizabilities are similar. For example, at 35 °C and 20.5 g mol/L, the co-solvent-induced solubility enhancements of benzoic acid, hexamethylbenzene, and phenanthrene differed by only 20%. These conclusions have important implications for supercritical fluid separations. Although nonpolar co-solvents may be used to increase the yield, it appears that polar co-solvents are required to achieve large changes in the selectivity for a series of solutes of similar molecular weight. These observations for solid–fluid equilibria are consistent with those for solid–liquid and liquid–liquid equilibria which suggests that many existing engineering models could be extended to supercritical fluid systems.

A major goal of this work is to predict the experimental ternary data by using physical properties of the pure components without any adjustable parameters. The solubility of a solid (2) in a supercritical fluid (1) is (*17*)

$$y_2 = \frac{P_2^{sat} \exp\left(\dfrac{v_2(P - P_2^{sat})}{RT}\right)}{\phi_2 P} \qquad (1)$$

where the key variable ϕ_2 is given by

$$RT \ln \phi_2 = \int_v^\infty [(\partial P/\partial n_2)_{T,V,n_1,n_3} - RT/v]\, dv - RT \ln z \qquad (2)$$

The hard-sphere van der Waals (HSVDW) equation of state was used in this study in eq 2. The same approach could also be used for the Peng–Robinson or other suitable equations of state. The HSVDW equation of state consists of an accurate expression for the hard-sphere mixture (*18*) plus the standard van der Waals attractive term. Substitution of the HSVDW equation of state including the van der Waals one-fluid theory (VDW1) mixing rule

$$a = \sum_i \sum_j y_i y_j a_{ij} \qquad (3)$$

into eq 2 yields

$$\ln (\phi_2 z) = \frac{\partial}{\partial n_2}\left(\frac{A - A^\circ}{RT}\right)_{T,V,n_1,n_3}^{\text{hard sphere}} - 2(y_1 a_{12} + y_2 a_{22} + y_3 a_{23})\rho/RT \qquad (4)$$

The key parameters in this expression are the binary interactions constants a_{12} and a_{23}.

Since the density is not predicted accurately by modified van der Waals nor by other cubic equations of state, especially for mixtures, the experimental values of the density were used in this study. The size parameter, b_1, was regressed from experimental *PVT* data for CO_2 (*19*), and calculated on the basis of structural models for the co-solvents (*20*) and for the solutes (*12*). For hexamethylbenzene, the a_{12} was optimized from the binary data by using a procedure described elsewhere (*11*). The a_{12} for phenanthrene was predicted by using eq 26 and 28 of ref *12*. The physical properties of the solutes and co-solvents used in the model were obtained from ref *11* except for the data for undecane which were obtained elsewhere (*20–22*, see Table IV).

The results were somewhat inaccurate for hexamethylbenzene, such that it was necessary to adjust the b_2 downward about 11%. This was not a serious concern as the emphasis of this work is on predicting ternary systems from binary data. Wong et al. (*12*) developed a model to predict solid–fluid equilibria for numerous binary nonpolar systems using no adjustable parameters and no critical properties. The hexamethylbenzene system was the most difficult one to predict in that study perhaps because of the basicity of the π-electrons surrounded by six electron-releasing methyl groups.

In the ternary systems, there is only one additional interaction parameter, a_{23}, compared with the binary case. Initially, the a_{23} was correlated by using the ternary data to minimize the average absolute deviation (AAD) defined by

$$\text{AAD} = (1/N)\sum_{i=1}^{N} |(y_{2i}^{calcd} - y_{2i}^{exptl})/y_{2i}^{exptl}| \qquad (5)$$

The results are shown for hexamethylbenzene in Figure 2 and for both solutes in Table V. The average of the AAD's for all of the ternary systems was 4.4% which is within the experimental uncertainty.

The ratio of the regressed solute-co-solvent vs. CO_2 interaction parameters, a_{23}/a_{12}, was approximately the same for the two nonpolar solutes. This follows from the experimental observation that the co-solvent-induced solubility enhancements were similar for the two solutes, although not identical, perhaps because of the difference in their sizes.

A physical description of co-solvent-induced solubility enhancement can be stated concisely by using van der Waals theory (see eq 4). The substitution of an octane for a CO_2 molecule in the solvent shell about the solute lowers ln ϕ_2 or the chemical potential of the solute, μ_2, since a_{23} is larger than a_{12}. This increase in the attractive forces more than compensates for the increase in μ_2 due to the repulsive forces. This behavior was observed for all of the data in Table V. Furthermore, the solubility increases for the series of co-solvents, *n*-pentane, *n*-octane, and *n*-undecane as does a_{23}.

The final objective is to predict the solubility data by calculating the co-solvent-solute interaction constant, a_{23}. We choose to apply a novel approach, developed recently by Dobbs et al. (*11*), which combines physical property information for a liquid phase with an equation of state. It is particularly appropriate for the supercritical fluid state, in which multibody interactions are important as in liquids, yet the compressibility is large. The solubility parameters of the components are used to calculate the attraction constant a_{23}, which is used in the equation of state. This approach avoids critical properties, which are often unavailable. It is more applicable than Regular Solution Theory, which was not intended for compressible solutions, yet it takes advantage of huge data bases for solubility parameters of polynuclear aromatic hydrocarbons, solvents, polymers, etc. (*22*). This approach is quite general as it can be used for polar systems (*11*) by including orientation, and acid-base component solubility parameters which have received much attention in the literature for paints, solvents, chromatography, and polymers (*22*).

The pair configurational internal energy may be expressed in terms of solubility parameters

$$\Delta u_{ij} = \delta_i \delta_j (v_i v_j)^{1/2} \tag{6}$$

such that

$$a_{ij} = \Delta u_{ij} (v_i v_j)^{1/2} \tag{7}$$

(see ref *11* for details). In Table V, the $\Delta u_{ij}^{\text{calcd}}$ was obtained by using eq 6, while $\Delta u_{ij}^{\text{exptl}}$ was obtained by using the regressed parameter, a_{23}^{exptl}, in eq 7. A comparison of a_{23}^{calcd} and a_{23}^{exptl} would be just as meaningful; however, the units of Δu_{23} are more convenient. The typical difference between the regressed (experimental) and calculated Δu_{23}'s is 1-2 kJ/g mol, such that the average of the AAD's for the predicted solubilities is only 13.1%. As stated above, the a_{12} was calculated for phenanthrene, while it was regressed from binary data for hexamethylbenzene. Consequently, the solubility of phenanthrene is predicted with no binary parameters. For hexamethylbenzene, the solubility is predicted for the ternary system, which includes co-solvent, using only the solute-CO_2 parameter, a_{12}. The predicted solubilities for phenanthrene are shown in Figure 2, for co-solvent concentrations of 3.5 mol %. The disagreement is greatest for undecane; further data would be useful as a function of carbon number for long-chain co-solvents.

Predictions are shown in Figure 4 for the solubility of phenanthrene in CO_2 at 35 °C for three different co-solvent concentrations. For these three isotherms, the average of the AAD's in y_2 is 8% which is only twice the experimental uncertainty. The ability to predict the solubility behavior as a function of the co-solvent concentration is a major strength of the model as it is time consuming to change the co-solvent concentration in the laboratory.

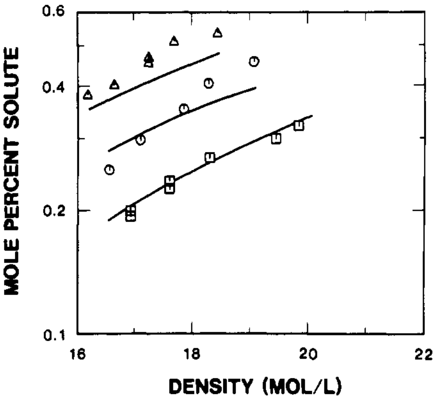

Figure 4. Solubility of phenanthrene in carbon dioxide with *n*-octane co-solvent at 35 °C (□, 3.5 mol % octane in CO_2; ○, 5.25 mol % octane in CO_2; △, 7.0 mol % octane in CO_2; —, predicted by using eq 6 and 7).

Table VI. Effects of Chain Length and Branching of Alkane Co-Solvents on the Solubility of Phenanthrene in CO_2 at 35 °C and 350 bar

co-solvent[a]	predicted solubility, mol %
pure CO_2	0.171
propane	0.152
butane	0.171
2-methylpropane	0.172
pentane	0.194 (0.243)
2-methylbutane	0.184
neopentane	0.169
hexane	0.221
heptane	0.256
2,2,3-trimethylbutane	0.194
octane	0.297 (0.322)
isooctane	0.217
nonane	0.334
decane	0.386
undecane	0.461 (0.378)
dodecane	0.529

[a] 3.5 mol % solute-free basis.

The solute-co-solvent parameter, a_{23}, was regressed for each co-solvent concentration in Figure 4 to determine if there was a composition dependence. The regressed a_{23}'s or likewise Δu_{23}'s varied a negligible amount over the range of co-solvent concentrations shown.

Table VI lists predicted values of the solubility of phenanthrene for a series of straight and branched-chain alkane co-solvents, where CO_2 is the primary solvent. In each case, the co-solvent concentration is 3.5 mol % on a solute-free basis. The calculational procedure is the same as above; the a_{23} is calculated by using eq 6 and 7. At 350 bar and 35 °C, it is assumed that the excess volume is zero for each of the nonpolar solvent mixtures. For pentane, octane, and undecane, the experimental density was within 0.5% of the density which was calculated on the basis of this assumption. The solubility parameters (*22*), molar volumes (*22*), and van der Waals volumes (*20*) of the co-solvents were obtained from the literature. Based on the experimental values which are shown in parentheses for pentane, octane, and undecane, it appears that the predictions are within about 20%. The solubility increases with chain length for the straight-chain co-solvents, while it decreases as the degree of branching increases. These results are expected as the same trends are observed for the polarizability and the solubility parameter of the alkanes.

The results in Table V are reasonably accurate despite the use of the VDW1 mixing rule, eq 3, which assumes that the attractive forces do not influence the structure of the fluid. The second VDW1 mixing rule for the size of a hypothetical component, b, was not used, as the repulsive contribution was calculated by using an accurate expression for the hard-sphere mixture. The use of the second VDW1 mixing rule gives poor results for Henry's constants of Lennard-Jones mixtures of molecules of different size (*23*). Although the results in Table V do not prove that the attractive forces do not influence the fluid structure, they do indicate that the data can be predicted without including this effect. For polar systems the solubility data were underpredicted when the VDW1 attractive mixing rule (11) is used, since specific interactions increase preferentially the concentration of co-solvent in the solvent shell about the solute. For nonpolar systems, the co-solvent–solute interactions do not appear to be strong enough to lead to a significant excess concentration of co-solvent near the solute.

Conclusions

The new microsampling experimental technique is a significant improvement over those which use gravimetric analysis, since multicomponent systems can be analyzed directly, and the equilibrated solution is sampled isobarically and isothermally. The ratio of the solubility in the ternary vs. the binary case, or the co-solvent-induced solubility enhancement, is relatively constant over a wide range of pressure or density. In most cases, the solubility increases more by the addition of 3.5 mol % co-solvent than by changes in the pressure of hundreds of bar, even though the solvent density decreases in the former while it increases in the latter.

The solubility increases with the size of the co-solvent as the additional attraction predominates over the repulsion. The solubility data can be predicted quantitatively by using widely available solubility parameters to calculate the a_{23} in a modified van der Waals equation of state. The model treats successfully the effects of pressure, co-solvent chain length, and co-solvent composition. At a concentration of 3.5 mol %, alkane co-solvents increase the solubilities significantly; yet the increase is of similar magnitude for hexamethylbenzene, phenanthrene, and benzoic acid. Although polar co-solvents are attracted preferentially relative to CO_2 to polar solutes, this behavior appears to be minor if not negligible for nonpolar solutes and co-solvents.

The use of small amounts of properly selected nonpolar or polar co-solvents could impact the economics of supercritical fluid processes significantly due to an increased yield and/or reduced pressures.

Glossary

a	van der Waals attractive interaction constant
A	Helmholtz free energy
Δu_{ij}	pair configurational energy of an i–j pair
v_2	molar volume of solute
y_2	mole fraction solute

Subscripts

1	CO_2
2	solute
3	co-solvent

Greek Letters

ϕ	fugacity coefficient
δ	solubility parameter

Registry No. CO_2, 124-38-9; phenanthrene, 85-01-8; hexamethylbenzene, 87-85-4; octane, 111-65-9; undecane, 1120-21-4; pentane, 109-66-0; propane, 74-98-6; butane, 106-97-8; 2-methylpropane, 75-28-5; 2-methylbutane, 78-78-4; neopentane, 463-82-1; hexane, 110-54-3; heptane, 142-82-5; 2,2,3-trimethylbutane, 464-06-2; isooctane, 540-84-1; nonane, 111-84-2; decane, 124-18-5; dodecane, 112-40-3.

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