Clustering in Supercritical Fluid Mixtures

The local compositions of supercritical fluid carbon dioxide and a cosolvent about a solute at infinite dilution have been estimated for the first time using spectroscopic measurements. The solute was phenol blue, the bulk concentrations of the cosolvents *n*-octane, acetone, ethanol, and methanol ranged from 0 to 100 mol %, and the pressure ranged from 80 to 300 bar. In each case, the clusters of solvent about the solute are enriched in cosolvent. Solubility data have been measured for phenol blue in CO_2 with and without the cosolvent acetone, and regressed using an augmented van der Waals-density-dependent local composition model to determine the relevant binary interaction energies. The local compositions calculated from the model agree with those that were esimated spectroscopically. The model was used to predict solubilities of solids in supercritical fluid CO_2 with various cosolvents.

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INTRODUCTION

Supercritical fluid mixtures can be quite complex since the sizes and energies of the solute and solvent are quite different, and the compressibility is large. In the highly compressible near-critical region, the solvent clusters about the solute due to the attractive intermolecular forces. For example, at 308.5 K and 79.8 bar, the partial molar volume of naphthalene in supercritical fluid carbon dioxide at infinite dilution is $-7,800$ cm^3/mol, which corresponds to the condensation of about 80 solvent molecules around a solute molecule (Eckert et al., 1986; Debenedetti, 1987). This large degree of condensation corresponds to macroscopic clusters that extend over many coordination shells. An objective of the present work is to measure the degree of clustering at the microscopic level spectroscopically so as to obtain information that will be used to develop and test phase equilibria models.

The addition of a small amount of liquid cosolvent to a supercritical fluid can increase selectively the solubilities of certain substances (van Alsten and Eckert, 1984; Dobbs, 1986; Schmitt 1984; Walsh et al., 1987) and may have an important impact on the economics of supercritical separation processes. A spectroscopic technique has been developed to estimate local concentrations of the components of a binary solvent about a solute in a compressible supercritical fluid mixture. To our knowledge, local composition data have not been determined previously in supercritical fluid mixtures using either experiment or computer simulation. A dye, phenol blue, was used as a probe to estimate local concentrations by measuring the solvent effect on the absorption wavelength—that is, solvatochromism. A desirable feature of this approach is that the ranges of the attractive intermolecular forces that influence solubilities and solvatochromism are the same. This technique has been used previously to measure the local density of a pure supercritical fluid about phenol blue, for example, ethylene, CF_3Cl, and CF_3H (Kim and Johnston, 1987).

The van der Waals 1 (VDW 1) mixing rule has been used in various cubic and perturbed hard chain equations of state to correlate solid-fluid equilibria data of polar and nonpolar binary systems (Kurnik et al., 1981; Mart et al., 1986). Such data have been predicted for nonpolar systems using no adjustable pair parameters (Wong et al., 1985); however, the predictions are only qualitative for polar systems. The VDW 1 mixing rule is not well suited to describe highly asymmetric mixtures in which the size and energy differences are large.

The density-dependent local composition (DDLC) concept (Mollerup, 1981, 1983; Whiting and Prausnitz, 1982; Mathias and Copeman, 1983; Hu et al., 1983, 1984) shows promise for describing asymmetric mixtures over a wide density range, although several deficiencies have been identified using computer simulation data (Lee et al., 1986; Nakanishi et al., 1982; Nakanishi and Tanaka, 1983; Wong and Johnston, 1984). The density dependence is incorrect in many of these models, for local ordering should decrease as the density is increased, as explained below. In addition, the local composition term often adds a nonrandom contribution that is too large (Mathias and Copeman, 1983). A new density-dependent local composition model has been developed using computer simulation data to attempt to overcome some of these deficiencies (Johnston et al., 1987).

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The spectroscopic local composition data will be used to test this new augmented van der Waals–density-dependent local composition (AVDW-DDLC) model for the solute phenol blue. In order to determine the relevant binary attractive interaction parameters in this model, solubility data have been measured for phenol blue in supercritical fluid carbon dioxide both with and without the cosolvent acetone. Local compositions will be calculated using the model and will be compared with those obtained spectroscopically. After satisfying this test for phenol blue, the model will be used to predict solubilities of other polar and nonpolar solutes in polar and nonpolar mixed supercritical fluid solvents over a wide density range.

Experimental Method

The UV-visible absorption spectra of phenol blue were measured at infinite dilution in CO_2 (Linde, Bone Dry Grade, 99.8%), both with and without a cosolvent, using a stainless steel cell with sapphire windows and a Varian (Cary) 2290 spectrophotometer. The details of the experimental apparatus and procedure were described previously for phenol blue in pure supercritical fluids (Kim and Johnston 1986, 1987). For experiments in CO_2-cosolvent mixtures, a measured weight of CO_2 was condensed into a Ruska high-pressure syringe pump that contained a known weight of a liquid cosolvent. The mixture was equilibrated for at least 16 h. The composition of the cosolvent in the resultant solvent mixture was known to within ±2%. The uncertainties in temperature and pressure were ±0.1°C and ±0.2 bar, respectively. The uncertainty in λ_{max} was ±0.2 nm. The equilibration in temperature and λ_{max} took approximately 15 min for each pressure. This technique could be used for other solutes such as anthracene, although the solvatochromic shifts would be significantly smaller.

Solubility vs. pressure isotherms were obtained for phenol blue in pure CO_2 and CO_2-acetone mixtures using a microsampling flow apparatus (Dobbs et al., 1986). Approximately 100 μL of a flowing equilibrated solution at a known temperature, pressure, and density was sampled using a six-port valve and expanded to atmospheric pressure. The solute was recovered using a liquid solvent and an internal standard was added. A gas chromatograph (Hewlett Packard 5890A) equipped with a nonpolar capillary column (SGE BP-5) and flame ionization detector was used for analysis. The solubility was determined from the total number of moles in the sampling loop and the number of moles of solute. The experimental uncertainty in the solubility was 5%.

Estimation of Local Compositions from Spectroscopic Measurements

The measured maximum absorption wavelengths for phenol blue in carbon dioxide are listed in Table 1. Since the excited state is more polar than the ground state, it is stabilized to a greater degree as the solvent strength; for example, the polarity or the cohesive energy density is increased. As a result, the transition energy, $E_T = hc/\lambda_{max}$, decreases or the maximum wavelength increases (red shift) as the pressure is increased. The relationship between E_T and the solvent strength is well established in the literature for solvent effects on solubility phenomena, reaction rate constants, equibrium constants, retention indices in chromatography, and other properties (Reichardt, 1979).

Table1. Wavelength of Absorption Maximum (λ_{max}) of Phenol Blue in Carbon Dioxide

Temp. °C	Press. bar	λ_{max} nm	Temp. °C	Press. bar	λ_{max} nm
5	39.7*	533.7	31	75.0	527.3
8	42.8*	536.7		85.0	529.7
10	45.0*	536.1		100.0	530.8
13	48.4*	535.2		150.0	532.8
15	50.9	534.6		200.0	534.2
	70.0	536.3		300.0	536.4
	300.0	540.9	35	75.0	518.7
18	54.7	533.9		80.0	523.0
	70.0	535.2		85.0	526.9
	300.0	540.4		100.0	529.4
20	57.3	533.4		200.0	533.4
	70.0	534.6		300.0	535.8
	300.0	540.0	40	80.0	518.0
23	61.6	532.7		85.0	520.3
	70.0	533.5		100.0	526.2
	300.0	539.3		150.0	530.0
25	64.3	532.1		200.0	531.7
	70.0	532.4		300.0	534.5
	300.0	538.5	45	85.0	516.0
				90.0	517.8
				100.0	523.0
				150.0	528.7
				200.0	530.6
				300.0	533.4

*Saturation curve

The wavelength vs. pressure isotherms follow trends that are observed for density vs. pressure isotherms. For example, at temperatures below the critical temperature, $T_c = 31°C$, the wavelength varies only a modest amount with respect to pressure since the liquid is relatively incompressible. The wavelength varies more strongly with respect to pressure in the near-critical region where the fluid is more compressible.

The maximum absorption wavelengths for phenol blue in CO_2-cosolvent mixtures are listed in Table 2 as a function of pressure and cosolvent concentration. All of the data were obtained in the one-phase region. At 35°C, the maximum pressure in the vapor-liquid two-phase region is below 80 bar for each of the solvent binaries, according to the literature (Takishima et al., 1986; Semenova et al. 1979, King et al. 1983). For each of the solvent-cosolvent pairs, the pressure exceeds the critical pressure of the mixture. In many of the cases, the temperature is below the critical temperature of the mixture. At pressures well above the critical pressure, the density does not change significantly when the temperature is raised from just below to just above the mixture critical temperature, so that the distinction between the terms supercritical and liquid is not important. In a region where both the pressure and temperature are near the mixture critical point, the fluid is highly compressible and so λ_{max} is highly variable.

A wide range of types of cosolvents was investigated: an aprotic dipolar liquid, acetone; two protic liquids, methanol and ethanol; and a relatively polarizable nonpolar liquid, octane. Figure 1 shows the transition energy of phenol blue vs. pressure for a range of cosolvent concentrations from 0 to 100%, for acetone in carbon dioxide. At a given cosolvent concentration, the E_T and λ_{max} are more sensitive functions of pressure at lower pressures where the fluid is more compressible. For a given pressure, the compressibility of the solvent decreases as the concen-

Table 2. Wavelength of Absorption Maximum (λ_{max}) of Phenol Blue in CO_2-Cosolvent Mixtures at 35°C

System	% Cosolvent Conc.	λ_{max}, nm, at Pressure, bar 80	85	100	200	300
CO_2-acetone	1.0	527.8	529.7	531.5	535.3	537.8
	2.0	531.9	532.4	533.6	537.2	539.1
	3.5	533.7	534.1	535.2	538.7	541.3
	5.25	536.7	537.2	538.0	540.1	543.2
	20	553.3	553.6	553.9	555.8	557.3
	30	560.2	560.4	560.7	562.2	563.3
	50	568.6	568.7	569.0	570.4	571.5
	80	575.9	576.0	576.1	577.1	578.0
	100	580.2	580.3	580.4	581.2	581.8
CO_2-methanol	1.0	527.3	529.4	531.5	535.4	537.5
	2.0	532.7	533.5	535.5	539.2	541.3
	3.5	538.8	539.5	540.0	543.0	545.4
	5.25	543.5	544.1	544.6	546.9	549.1
	100	605.4	605.4	605.5	606.4	607.4
CO_2-ethanol	1.0	528.4	530.0	531.2	535.0	537.2
	2.0	531.8	532.5	533.9	537.2	539.2
	3.5	536.3	537.2	538.4	541.0	542.9
	5.25	541.2	541.7	542.3	544.7	546.5
	100	603.1	603.2	603.3	604.2	605.1
CO_2–*n*-octane	1.0	527.0	528.5	530.1	534.2	536.3
	2.0	529.7	530.6	531.4	535.0	537.0
	3.5	531.5	532.3	532.9	535.7	537.7
	5.25	533.6	534.0	534.4	536.9	538.8
	100	547.1	547.1	547.2	548.0	548.7

tration of the cosolvent increases; for example, it is relatively small for pure liquid acetone. As a result, the solvent strength or E_T in the fluid mixture becomes less sensitive with respect to pressure as the acetone concentration increases, even though the overall solvent strength (red shift) increases.

The addition of a small amount of a cosolvent to carbon dioxide at 35°C and 120 bar can increase the solubility of certain solids to a greater degree than a pressure increase of several hundred bar (Dobbs et al., 1986, 1987). For example, the addition of 3.5 mol% methanol at these conditions increases the solubility of benzoic acid by a factor of 6, whereas an increase in the pressure of 200 bar increases it by only a factor of 1.5. The primary reason for the large effect of the methanol is that the benzoic acid-methanol interaction constant is about two times that for benzoic acid and CO_2, as will be discussed in a later section. The solvatochromic data for the phenol blue-acetone-carbon dioxide system and the solubility data for the benzoic acid-methanol-CO_2 system exhibit the same type of behavior as shown in Figure 1. At 80 bar and 35°C, the addition of 5.25% acetone decreases the transition energy (increases λ_{max}) to a greater degree than an increase in the pressure to 300 bar. The similarities in the two types of data suggest that solvatochromic data may be used qualitatively to estimate the effects of cosolvents on solubilities. Such a correlation could be developed given additional solvatochromic data for a variety of solutes to interpret the effects of dispersion, induction, dipole-dipole, and specific forces.

The transition energy of phenol blue is plotted with respect to cosolvent concentration for several isobars in Figure 2. The solvatochromic red shift exceeds the value that would be predicted from linear behavior; that is, the concavity is positive. This means that the cosolvent is attracted preferentially to the polar solute, since it causes a solvatochromic shift that is greater than expected from its bulk concentration. The excess red shift is larger at 80 bar, where the fluid is more compressible, than at 300 bar. In a highly compressible fluid, it is known from high-temperature perturbation theory that the attractive forces move solvent molecules into energetically favorable locations (Alder et al., 1972). This effect is much smaller in an incompressible liquid.

Nitsche and Suppan (1982) explained the nonlinearities in solvatochromic shift data for mixed liquid solvents in terms of dielectric enrichment. A model was developed to calculate the local polarity by considering a balance between electrostatic stabilization energy and the entropy of unmixing of a solvent shell. In this work, a new model is formulated to estimate local compositions from solvatochromic data.

The residual transition of a dye in a pure solvent i, ΔE_{Ti}, is defined by

$$\Delta E_{Ti} = E_{Ti} - E_T^{\text{ideal gas}} \tag{1}$$

at constant temperature and pressure.

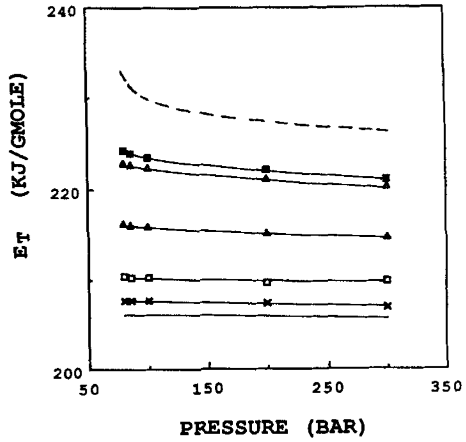

Figure 1. E_T **of phenol blue vs. pressure as a function of cosolvent concentration in CO_2-acetone mixtures.**

--- pure CO_2; ■ 3.5%; △ 5.25%; ▲ 20%; □ 50%; X 80%; — 100%

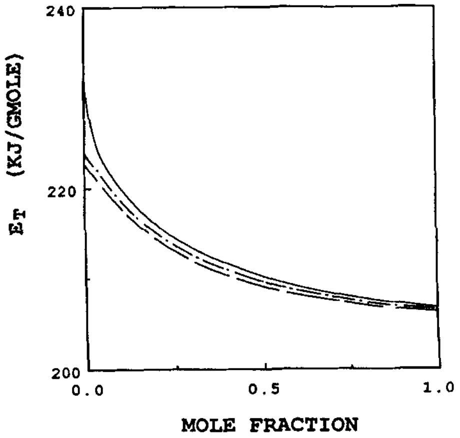

Figure 2. Nonlinearity of E_T of phenol blue with respect to composition of cosolvent in CO_2-acetone mixtures.

— 80 bar; —·— 200 bar; --- 300 bar

It is assumed that each dye-solvent pair interaction causes a fixed solvatochromic shift equal to $\Delta E_{Ti}/z_{i2}$ where z_{i2} is the coordination number for a pure solvent i about the dye, component 2. Since the dye is at infinite dilution, it is assumed that dye-dye interactions are negligible. The interactions between the primary solvent and cosolvent are neglected since this is a second-order effect compared with the solvent-solute and cosolvent-solute interactions. As a result, the residual transition energy for the mixture may be written as a sum of the contributions from the primary solvent (1) and the cosolvent (3) (Nitsche and Suppan, 1982; Kolling and Goodnight, 1973). For a given component of the solvent, i, the residual transition energy is a product of two factors: the transition energy for a solute-solvent pair interaction, $\Delta E_{Ti}/z_{i2}$, and the number of i molecules about the dye $x_{i2}z_m$, where x_{i2} is the local mole fraction of i about the solute in the first coordination shell and z_m is the coordination number for the solvent mixture about the dye. The sum of the contributions for each component of the solvent gives

$$\Delta E_{Tm} = x_{12}z_m(\Delta E_{T1}/z_{12}) + x_{32}z_m(\Delta E_{T3}/z_{32}) \qquad (2)$$

where the local compositions x_{12} and x_{32} sum to unity since the dye is at infinite dilution. This equation will be used to estimate the local compositions after developing a technique to determine the ratios z_m/z_{12} and z_m/z_{32}.

The coordination number of a pure solvent, i, around a dye molecule, 2, at infinite dilution is

$$z_{i2} = \rho_i \int g_{i2}(r) 4\pi r^2\, dr \qquad (3)$$

where $g_{i2}(r)$ is the radial distribution function. For the mixed solvent, the coordination number is given by

$$z_m = x_1\rho_m \int g_{12}^m(r) 4\pi r^2\, dr + x_3\rho_m \int g_{32}^m(r) 4\pi r^2\, dr. \qquad (4)$$

It is necessary to make an approximation for the radial distribution functions in a ternary mixture in order to calculate a coordination number z_m. It is assumed that $g_{12}^m(r)$ and $g_{32}^m(r)$ may be approximated by the respective radial distribution functions for the binary systems, $g_{12}(r)$ and $g_{32}(r)$, at the same reduced number density. Combination of Eqs. 3 and 4 gives

$$z_m = x_1\rho_m(z_{12}/\rho_1)_r + x_3\rho_m(z_{32}/\rho_3)_r \qquad (5)$$

where the subscript r means that the quantities in brackets must be evaluated at the same reduced number density as that in the mixed solvent system.

The coordination number of a pure solvent i about a dye, z_{i2}, may be related to a reference value z_{i2}^o at the reference pressure by the relationship

$$\Delta E_{Ti}/z_{i2} = \Delta E_{Ti}^o/z_{i2}^o. \qquad (6)$$

Using Eqs. 5 and 6, ratios of coordination numbers can be written as

$$z_m/z_{12} = A_1 + B_{13}(z_{32}^o/z_{12}^o) \qquad (7)$$

and

$$z_m/z_{32} = A_3 + B_{31}(z_{12}^o/z_{32}^o) \qquad (8)$$

where

$$A_i = (x_i\rho_m/\Delta E_{Ti})(\Delta E_{Ti}/\rho_i)_r \qquad (9)$$

and

$$B_{ij} = (x_j\rho_m/\Delta E_{Ti})(\Delta E_{Ti}^o/\Delta E_{Tj}^o)(\Delta E_{Tj}/\rho_j)_r. \qquad (10)$$

The coefficients A_i and B_{ij} are obtained directly from the data while the ratio of coordination numbers at the reference, for example, z_{32}^o/z_{12}^o, may be obtained theoretically. The reference state is chosen at a high pressure, 300 bar, where the fluid is relatively incompressible. At this condition, ratios of reference coordination numbers may be approximated by ratios of coordination numbers for rigid spheres of different size using an equation developed by Deiters (1982). Even if the absolute value of each reference coordination number, z_{32}^o or z_{12}^o, is not calculated exactly, the ratio of reference coordination numbers may be calculated with reasonable accuracy. The ratio of reference coordination numbers is

$$\frac{z_{32}^o}{z_{12}^o} = \frac{2 + 10 \exp\left[(7/9)(R_{23}^{0.828} - R_{32}^{0.828})\right]}{2 + 10 \exp\left[(7/9)(R_{21}^{0.828} - R_{12}^{0.828})\right]} \qquad (11)$$

where R_{ji} is the ratio of diameters i and j, that is, σ_i/σ_j.

The local compositions are estimated using the experimental transition energies for the pure solvents, E_{T1} and E_{T3}, and the mixed solvent, E_{Tm}, in Eqs. 2, 7, and 8. Table 3 shows the local compositions for a series of cosolvents at various concentrations and pressure. In all cases, the local compositions exceed the bulk concentrations since the cosolvent interacts more strongly with the solute than does carbon dioxide. The local compositions decrease toward the bulk values as the pressure increases, since the isothermal compressibility decreases. The effect of the attractive forces on the structure of the fluid decreases as the isothermal compressibility decreases since the molecules be-

Table 3. Local Compositions of Cosolvent about Phenol Blue from Spectroscopic Data at 35°C

Bulk Conc. %	Press. bar	x_{32} Acetone %	x_{32} Methanol %	x_{32} Ethanol %	x_{32} n-Octane %
1.0	80	7.5	6.8	6.9	7.1
	85	4.2	3.7	3.8	3.2
	100	3.1	3.0	2.3	2.1
	200	2.5	2.6	1.8	1.5
	300	2.4	2.1	1.6	1.1
2.0	80	13.9	15.1	11.4	12.0
	85	8.2	9.6	7.0	7.4
	100	6.2	8.6	5.6	5.0
	200	5.0	7.3	4.3	3.0
	300	4.1	6.5	3.7	2.5
3.5	80	16.8	24.2	17.2	15.9
	85	11.1	18.2	12.9	11.7
	100	9.0	15.0	11.1	8.7
	200	7.1	12.0	8.3	4.6
	300	6.9	11.2	7.5	4.5
5.25	80	21.5	30.8	23.5	20.7
	85	16.1	24.8	18.8	16.4
	100	13.4	21.3	16.2	12.4
	200	10.1	16.8	12.4	7.3
	300	9.6	15.7	11.3	7.1

come less mobile, a phenomenon that has been observed in computer simulation data (Lee et al., 1986) and may be explained using high-temperature expansion perturbation theory (Weeks et al., 1971). The decay in the local composition behavior with pressure is larger for *n*-octane than for the polar cosolvents. This suggests the possibility that preferential solvation due to hydrogen bonding is less dependent on the compressibility than that due to nonpolar forces.

At bulk concentrations of 3.5 and 5.25%, the local compositions are greater for methanol and ethanol, which form hydrogen bonds with phenol blue (Figueras, 1971), than for acetone. The opposite behavior takes place at a bulk concentration of 1.0%. In order to understand this result, it would be useful in the future to measure the isothermal compressibility of the mixed solvent. At 80 bar and a bulk concentration of 1.0%, the local composition of octane exceeds that of the alcohols, while at 300 bar the value for methanol is at least twice that of octane at each value of x_3. The local compositions are slightly higher for methanol than for ethanol, perhaps since it is more acidic. The values are about as large for *n*-octane as for acetone at the lower pressures, because of its relatively large polarizability.

In order to examine the composition dependence of the local compositions, it is convenient to use the normalized function $X_Q = (x_{32}/x_{12})(x_1/x_3)$, which equals unity when the local and bulk concentrations are the same. This function is plotted vs. the solvent density in Figure 3 for acetone at various bulk concentrations. These data show clearly that the amount of local ordering increases as the cosolvent concentration decreases, which is the same type of result obtained by the computer simulation data for square-well molecules (Lee et al., 1986). It is not possible to compare the magnitude of X_Q in the present study with the square-well data since the concentration ranges are so different. The difference in the local ordering for the various bulk concentrations decreases as the compressibility decreases, that is, as the density increases. The local compositions, which will be calculated below using a DDLC model, follow each of these trends.

Comparison of Local Compositions from Solubility Data and from Spectroscopic Measurements

The spectroscopic local composition data will be used to test the new augmented van der Waals–density-dependent local composition (AVDW-DDLC) model (Johnston et al., 1987). The key advancement in the model is that the total and reference pair attraction energies in the short-range and long-range terms are treated in such a way that the local composition effects on the free energy are not overpredicted as in many previous models.

Solubilities of phenol blue were measured in pure CO_2 and in CO_2-acetone mixtures, Table 4, to determine the unlike pair attraction constants in the model. The objective is not to perform solvatochromic studies for each solute of interest but to obtain accurate solvatochromic data and solubility data for one solute to test the model. Solvatochromic shifts are much larger for phenol blue than for the other solutes in this study.

The solubility of a solid in a supercritical fluid mixture is given by

$$y_2 = P_2^{sat} \exp\,[v_2^s(P - P_2^{sat})/RT]/(\phi_2 P) \tag{12}$$

where P_2^{sat} and v_2^s are the vapor pressure and the molar volume of a solid, respectively. The fugacity coefficient, ϕ_i, is obtained from the thermodynamic expression

$$RT \ln\,(\phi_i z) = (\mu_i^{\text{rep}} - \mu_i^{i.g.}) + \mu_i^{s.r.} + \mu_i^{l.r.} \tag{13}$$

The DDLC model has been used successfully to calculate local compositions and excess Helmholtz free energies of equisized Lennard-Jones mixtures and solubility data for binary solid-supercritical fluid systems (Johnston et al., 1987). The short-range contribution of the Helmholtz free energy is treated as a correction with respect to a long-range contribution and is given by

$$\Delta a^{s.r.}/RT = \left(\frac{2}{3} \cdot \pi\rho\sigma^3/\alpha\right) \sum_i \sum_j (L_{ji}^3 - 1)x_i \ln \cdot \left\{\sum_j x_j \exp\,[\alpha\beta(\epsilon_{ji} - \epsilon_{ji}^o)]\right\} \tag{14}$$

where $\beta = 1/kT$, $L_{ji} = r_{ji}^*/\sigma_{ji}$, r_{ji}^* is the radius of the first coordination shell, and, ϵ_{ji}^o is a reference energy given by

$$\epsilon_{ji}^o = \alpha\epsilon_{ii} + (1 - \alpha)(\epsilon_{ii}\epsilon_{jj})^{1/2} \tag{15}$$

The local composition of a cosolvent 3, about a solute, 2, is

$$x_{32} = \frac{x_3 \exp\,[\alpha\beta(\epsilon_{32} - \epsilon_{32}^o)]}{x_1 \exp\,[\alpha\beta(\epsilon_{12} - \epsilon_{12}^o)] + x_2 \exp\,[\alpha\beta(\epsilon_{22} - \epsilon_{22}^o)] + x_3 \exp\,[\alpha\beta(\epsilon_{32} - \epsilon_{32}^o)]}. \tag{16}$$

Because of the form of the reference energy, the local compositions approach the bulk values and thus the short-range term becomes small as the unlike pair energy, ϵ_{ji}, approaches the geometric mean of the like pair energies. The form of the expression for the "degree of randomness factor"

$$\alpha = 1 - (\rho\sigma^3)/\sqrt{2} \tag{17}$$

forces the local compositions to become closer to the bulk values as the density increases, which is consistent with the square-well computer simulation data of Lee et al. (1986) and the spectroscopic data in Table 3. Many of the earlier DDLC models cited in the Introduction predict incorrectly the opposite density dependence for the local compositions.

A modified version of the AVDW model that includes a term in $1/T$ and $1/T^2$ (Johnston and Eckert, 1982) was chosen to represent the long-range attractive free energy

$$\Delta a^{l.r.}/RT = \beta \sum_{m=1}^{6} A_{1m}(1.35b\rho)^m\epsilon + \beta^2 R_k \sum_{m=1}^{9} A_{2m}(1.35b\rho)^m\epsilon^2 \tag{18}$$

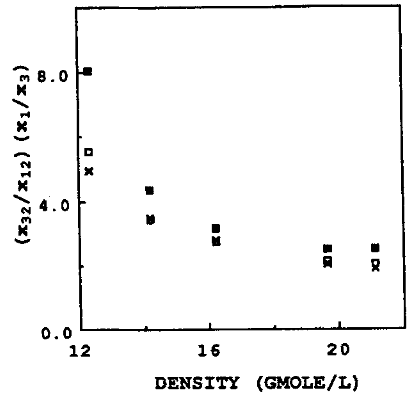

Figure 3. Density dependence of spectroscopic local compositions as a function of bulk composition of cosolvent.
■ 1%; □ 3.5%; X 5.25%

where

$$R_k = k_T/k_{T,max.} \tag{19}$$

The parameter $k_{T,max}$ is the maximum value of the isothermal compressibility at a given temperature. The short-range and long-range contributions to the chemical potential are obtained by differentiation of the free energies and have been reported (Johnson et al., 1987).

The phenol blue solubility data were regressed using the AVDW-DDLC model to obtain the unlike pair interaction energies, ϵ_{12} and ϵ_{23}. The CO_2-acetone interaction constant, ϵ_{13}, which plays an important but secondary role compared to ϵ_{12} and ϵ_{23}, was assumed to equal ϵ_{13}^0 to avoid adding an extra parameter to the model. The constant ϵ_{13} appears only in the short-range term. The local compositions were calculated using Eq. 16 along with these regressed ϵ_{ij}'s. Table 5 compares the local compositions estimated from the spectroscopic data with those calculated using the AVDW-DDLC model along with the regressed ϵ_{ij}'s. The values are similar and also have similar composition and density dependencies. This suggests that the AVDW-DDLC model has a reasonable reference state and can be used to calculate meaningful values of the short-range contribution to the chemical potential. It will be used to predict solubilities of other solids in mixed supercritical fluid solvents in the next section.

Table 4. Solubilities of Phenol Blue in Pure CO_2 and CO_2-Acetone Mixtures at 35°C

System	Press. bar	Solvent Density gmol/L	Solubility y_2 $\times 10^5$
CO_2	100.8	16.31	1.31
	121.0	17.55	1.72
	150.5	18.63	2.43
	199.6	19.77	3.24
	300.2	21.27	4.27
CO_2-acetone 3.5 mol %	100.8	17.36	3.25
	120.1	18.10	4.46
	150.7	18.91	4.46
	200.0	19.82	6.60
	298.2	21.07	8.80
CO_2-acetone 5.25 mol %	100.6	17.66	6.46
	120.9	18.28	8.02
	151.2	18.96	10.2
	200.2	19.82	11.1
	299.9	20.98	14.6

Table 5. Local Compositions of Cosolvent about Phenol Blue at 35°C: Spectroscopic Data Compared with Solubility Data with AVDW-DDLC Model

Cosolvent Conc.	Press. bar	Local Composition, x_{32}	
		Spectroscopic Data	Solubility Data
3.5 mol %	100	0.090	0.074
	120	—	0.073
	150	—	0.071
	200	0.071	0.069
	300	0.069	0.066
5.25 mol %	100	0.134	0.107
	120	—	0.105
	150	—	0.103
	200	0.102	0.100
	300	0.096	0.097

*$\epsilon_{12}/k = 450\ K$, $\epsilon_{23}/k = 744$ K, $\epsilon_{22}/k = 654\ K$

Prediction of Solubilities of Solids in Mixed Supercritical Solvents

Dobbs et al. (1986, 1987) predicted solubility isotherms in ternary mixtures using component solubility parameters and the hard sphere van der Waals (HSVDW) equation of state with VDW 1 mixing rules. Since solubilities were underpredicted for systems with polar solutes and cosolvents, it was suggested that a mixing rule which includes the preferential solvation by the cosolvent should lead to improvement. The new AVDW-DDLC model shows promise for accomplishing this goal since the calculated local compositions are consistent with those obtained from spectroscopic data.

The unlike pair potential parameters for a solute-solvent pair, ϵ_{12}, were correlated from binary solubility data using Eqs. 14, 15, and 18. An alternative approach, which would be only modestly less accurate, would be to determine ϵ_{12} from the molecular volumes of the components using the correlation of Wong et al. (1985). The pure component energies, ϵ_{ii}'s, were calculated from critical properties as discussed elsewhere (Kim, 1986). The universal constant $L_{ji} = 1.69$ was determined previously for binary systems (Johnston et al., 1987). The solubility data for ternary systems, which include a cosolvent, were predicted without using an adjustable ϵ_{32}. The parameter ϵ_{32} was calculated in terms of physical properties of the pure constituents, that is, the component solubility parameters, using the approach of Dobbs et al. (1986).

The total configuration internal energy, ΔU_{ij}^T, is a sum of component configurational internal energies that arise from the various molecular interactions such as dispersion, orientation (dipole-dipole), induction, and acid-base interactions

$$\Delta U_{32}^T = \Delta U_{32}^D + \Delta U_{32}^o + \Delta U_{32}^I + \Delta U_{32}^{AB} \tag{20}$$

The component configurational internal energies can be calculated using widely available component solubility parameters. The dispersion and orientation configurational internal energies are calculated according to the literature (Barton, 1983). The induction configurational internal energy may be calculated using a combination of the dispersion and the induction solubility parameters (Barton, 1983; Karger et al., 1976)

$$\Delta U_{32}^{I} = C^{I}(\delta_2^I \delta_3^D + \delta_2^D \delta_3^I)(v_2 v_3)^{1/2} \tag{21}$$

where δ_i^I is an induction solubility parameter for component i and the empirical constant C^I equals 0.6 (Wong, 1986). The hydrogen bonding configurational internal energy is

$$\Delta U_{32}^{AB} = C^{AB}(\delta_2^A \delta_3^B + \delta_2^B \delta_3^A)(v_2 v_3)^{1/2} - RT \tag{22}$$

where δ_i^A and δ_i^B are acid and base solubility parameters of component i, respectively. The empirical constant C^{AB}, which equals 1.8, was determined by Karger et al. (1976) using spectroscopic data for n-alcohols. The component solubility parameters in Eqs. 21 and 22 can be calculated using a group contribution method (Barton, 1983) and have been reported for the systems of interest (Dobbs et al., 1986, 1987).

The reference energy for the solute-cosolvent pair, ϵ_{32}^{o}, was calculated using Eq. 15, which has already been shown to be successful for treating binary solid-fluid equilibria data as well as computer simulation data, as explained above. Table 6 lists the solute-CO_2 energy parameters, ϵ_{12}, that were correlated from the binary solubility data. The solute-cosolvent energy parameters, ϵ_{32}'s, were regressed from the data and correlated linearly with the physical property ΔU_{32}^{T} by the universal relationship (Figure 4 and Table 6):

$$\epsilon_{32}/k = 11.19 \Delta U_{32}^{T} + 320.3 \tag{23}$$

The solubilities of five solutes in various CO_2-solvent mixtures were predicted using Eqs. 14, 18, and 23; Table 6. Since the pair energy parameter for the cosolvent-solute (3-2) pair is much larger than that for the CO_2-solute (1-2) pair, the cosolvent is attracted preferentially to the solute. The results are superior to those of the HSVDW model (Dobbs et al., 1987) since the AVDW-DDLC model includes the effect of preferential solvation by the cosolvent. In addition, the attractive contribution of the AVDW equation of state is superior to that of the HSVDW equation of state in the highly compressible near-critical region (Johnston et al., 1982), although most of these data are at pressures that are above this region.

Table 6. Predictions of HSVDW and AVDW-DDLC Models (Dobbs et al., 1987)

Solute	Cosolvent	ϵ_{12}/k K	ϵ_{32}^{pred}/k K	y_2^{HSVDW} % AAD	y_2^{DDLC} % AAD
Acridine	Acetone	466.7	782.4	23.8	7.2
	Methanol	—	821.6	50.0	13.0
Benzoic acid	Acetone	477.5	850.7	7.0	12.9
	Methanol	—	976.0	32.0	11.4
Phthalic anhydride	Acetone	465.5	774.6	28.2	8.0
Hexamethyl benzene	Acetone	431.8	661.6	26.4	10.4
	Methanol	—	584.4	29.9	9.3
Phenanthrene	n-Pentane	453.5	758.9	12.1	23.5
	n-Octane	—	887.6	3.9	6.8
	n-Undecane	—	990.6	18.8	12.0

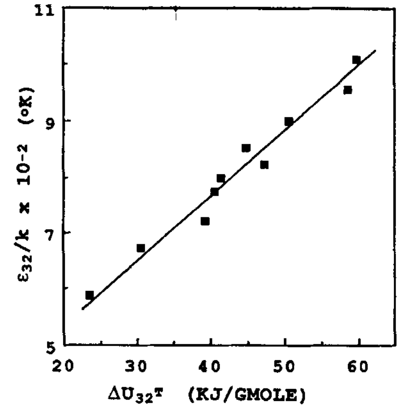

Figure 4. Linear relationship between solute-cosolvent unlike pair potential energy and total configurational internal energy at 308°K.

Figure 5 shows the predicted solubilities of acridine in a mixture of CO_2 with 3.5 mol % acetone for both the AVDW-DDLC and HSVDW models. The HSVDW model underpredicts the solubilities with an AAD of 23.8% since it does not include the additional attractive forces that are due to the enrichment in the concentration of the cosolvent near the solute. This underprediction is corrected to a significant degree by the AVDW-DDLC model due to the inclusion of the short-range contribution.

The two models are compared for the acridine-CO_2-methanol system in Figure 6. In this system, the improvement is even more significant since methanol, which is acidic, is enriched about acridine even more strongly than is acetone. The % Average Absolute Deviation (AAD) was improved from 28 to 8 for the phthalic anhydride-CO_2-acetone system. The enrichment of cosolvent about the solute in this system would be expected to be large because of the large dipole moment of phthalic anhydride, 5.2 D.

The AVDW-DDLC model did not give an improvement for the phenanthrene-pentane-CO_2 system. A partial explanation of this may be made using the spectroscopic local composition data for the phenol blue–n-octane–CO_2 system. For a bulk cosolvent concentration of 3.5 mol %, the local compositions were much

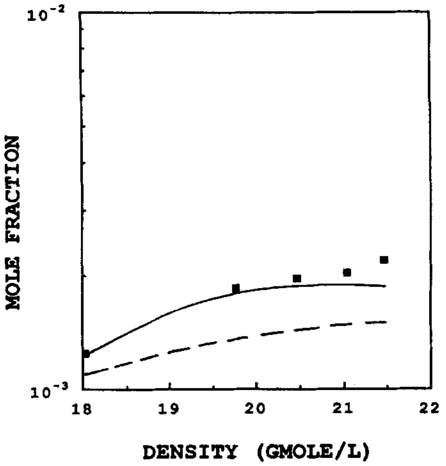

Figure 5. Prediction of solubilities of acridine in CO_2-acetone (3.5 mol %) mixtures.

■ experimental data at 35°C; — AVDW-DDLC model; --- HSVDW model

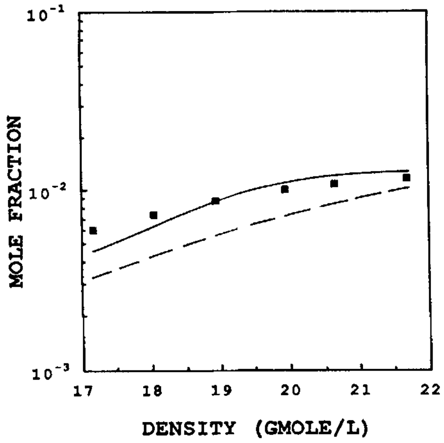

Figure 6. Prediction of solubilities of acridine in CO_2-methanol (3.5 mol %) mixtures.

■ experimental data at 35°C; — AVDW-DDLC model; --- HSVDW model

larger for the polar cosolvents than for *n*-octane at pressures above 85 bar. Therefore, the short-range term is relatively small for the phenanthrene-pentane system. The error in the predicted solubilities is due to the inaccuracies in ΔU_{32}^{T} or the correlation in Eq. 23, which is used for the long-range term. The AVDW-DDLC model gave improved results for solubilities of phenanthrene in a solvent consisting of CO_2 and undecane.

Conclusions

While partial molar volume data may be used to estimate the size of clusters over many coordination shells, solvatochromic measurements may be used to estimate concentrations in the local solute environment. The values of local compositions of solvent components about a solute, which were estimated from solvatochromic data, follow trends that are to be expected based on high-temperature expansion perturbation theory. The enrichment of cosolvent about the solute decreases as the isothermal compressibility decreases in all cases, but to a greater degree for *n*-octane than for the polar liquids. In all cases, the degree of local ordering as described by X_Q increases as the bulk cosolvent concentration decreases, which is consistent with results from computer simulation for square-well molecules. The values of the local compositions that are calculated with the DDLC model of Johnston et al. (1987) are physically realistic as they agree with the values that were estimated spectroscopically.

The addition of a small amount of certain cosolvents increases solubilities of certain solids in CO_2 significantly because:

1. It interacts more strongly with the solute than does CO_2
2. This strong interaction increases its concentration in the local solute environment

The AVDW-DDLC model can be used to predict the effect of cosolvents on solubilities more accurately than previous models since it includes the second effect as well as the first. Future work is needed to include the effects of the size differences of the components on the local compositions, and to obtain computer simulation data to compare with the solvatochromic data and the DDLC model. In addition, it would be useful to test these types of models for higher cosolvent concentrations, and liquid-fluid phase equilibria.

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Notation

a = Helmholtz free energy
A_{1m}, A_{2m} = Alder's constants
b = molecular volume, cm^3/mol
E_{Ti} = molar transition energy of dye in a pure solution *i*, kJ/mol
$E_T^{\text{ideal gas}}$ = molar transition energy of dye in vapor phase, kJ/mol
ΔE_{Ti} = molar residual transition energy, Eq. 1
ΔE_{Tm} = molar residual transition energy in ternary mixture, kJ/mol
$g_{ij}(r)$ = radial distribution function
h = Planck's constant
k = Boltzmann's constant
k_T = isothermal compressibility, $-(1/v)\partial v/\partial P$
ΔU_{ij} = configurational internal energy
v_2^s = molar volume of solid
x_{ji} = local composition of component *j* around a central *i* molecule
x_i = bulk composition of component *i*
y_i = solubility of component *i*
z_{ij} = coordination number of *i* around *j*

Greek letters

β = reduced temperature, $1/kT$
δ_i = solubility parameter of *i*
ϵ = energy parameter
λ = wavelength, nm
ρ = bulk density
ρ_m = bulk density of mixture
σ = size parameter
ϕ_i = fugacity coefficient of *i*th component in solution

Subscripts

1 = solvent
2 = solute
3 = cosolvent
i,j = component designation
r = reduced value

Superscripts

AB = acid-base
D = dispersion
I = induction
i.g. = ideal gas
l.r. = long-range force
o = reference state or orientation
rep = repulsive force
s = solid
sat = saturation
s.r. = short-range force
T = total value

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