Cosolvent Interactions in Supercritical Fluid Solutions

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The addition of cosolvents to supercritical fluid (SCF) solvents can have large effects on solubilities, giving engineers the ability to tailor loadings and selectivities of solutes for difficult separations. It is necessary to have a better understanding of the special intermolecular interactions that occur in SCF solutions to predict the effects of cosolvents. We use a SCF chromatographic technique to acquire a database of cosolvent effects for a variety of cosolvents and solutes; examination of the cosolvent effects shows evidence of hydrogen bonding, charge transfer complex formation, and dipole-dipole coupling between solute and cosolvent molecules. SCF solvents, carbon dioxide, ethane, and fluoroform, are compared, and then the use of the chromatograph to measure solubilities is discussed.

Introduction

The addition of a small amount of cosolvent can have dramatic effects on supercritical fluid (SCF) phase behavior, especially if specific interactions between the cosolvent and one or more of the solutes exist. For example, the presence of 2% tri-*n*-butyl phosphate in SCF CO_2 increases the solubility of hydroquinone by more than two orders of magnitude relative to the pure fluid (Lemert and Johnston, 1991). This behavior is apparently due to the formation of a charge transfer complex between the solute and cosolvent. By careful selection of a cosolvent, engineers can fine-tune the properties of fluids to perform very precise separations or reactions. In an example of an application, a cosolvent solution has been employed recently to improve the separation of alcohol from nonionic surfactants (Eckert et al., 1992).

The picture that is emerging for supercritical solutions near the critical point is that of a large solute molecule surrounded by smaller solvent molecules at a local density much higher than the bulk (see, for example, Eckert et al., 1986; Kajimoto et al., 1988; Brennecke et al., 1990a; Petsche and Debenedetti, 1989; Cochran and Lee, 1989). This phenomenon has been referred to as "clustering;" we prefer to call it "molecular charisma." In cosolvent solutions, the situation is more complex with differences between the local and bulk compositions in addition to density augmentation (Kim and Johnston, 1987; Brennecke et al., 1990b).

One can envision several mechanisms that could give rise to cosolvent effects. Already mentioned are specific chemical interactions, such as hydrogen bonding or charge transfer complex formation, which can lead to very large cosolvent effects. Addition of a cosolvent can also affect physical interactions in solution, such as dipole-dipole, dipole-induced dipole, or induced dipole-induced dipole interactions between the cosolvent and solute. It is also possible that the cosolvent interacts with the solvent, affecting solvent-solute interactions. Finally, addition of a cosolvent usually increases the density of a SCF solution; since solubility increases exponentially with density, this can have a significant effect on solubilities.

To understand SCF phase equilibria fully, the problems must be approached from several viewpoints. Thermodynamic behavior, which is of most interest to engineers, does not give explicit information about intermolecular interactions; nevertheless, the unique properties of SCF solutions are driven by unusual microscopic behavior. Spectroscopic and computer simulation data give detailed information on the molecular scale, but it is not yet evident how to incorporate this knowledge into predictions of macroscopic behavior. Further work in all of these areas will yield a better understanding of SCF phase behavior.

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Despite the great potential of using cosolvents, there are relatively few data in the literature for solubility of solutes in mixed SCF's (Dobbs et al., 1986; Schmitt and Reid, 1986; Wong and Johnston, 1986; Van Alsten, 1986; Dobbs and Johnston, 1987; Dobbs et al., 1987; Schaeffer et al., 1988; Lemert and Johnston, 1989; Tavana et al., 1989; Cygnarowicz et al., 1990; Hollar and Ehrlich, 1990; Smith and Wormald, 1990; Gurdial and Foster, 1991). One reason is that conventional techniques of measuring solubilities in SCF solutions are time-consuming and require large amounts of pure solute. A chromatographic technique is attractive because data can be obtained rapidly, perhaps five minutes per data point, and very little solute is necessary. Additionally, the solute need not be pure, as impurities are inherently separated by the chromatograph. Previously, supercritical fluid chromatography has been used to measure solubilities of nonpolar solutes in pure supercritical fluids (Smith et al., 1987; Bartle et al., 1990a,b). Also Brown et al. (1987) measured stationary phase Henry's constants for several nonpolar solutes and correlated them with solute properties, making possible the measurement of solubilities from chromatrographic data where no additional solubility data exist.

In prior work, we have described an accurate chromatographic technique to measure cosolvent effects (Ekart et al., 1992). We tested it with nonpolar and polar solutes and obtained results consistent with those obtained by other methods (Figure 1). In addition, it was shown that it is possible to measure solvent effects (comparing two entirely different fluids) with the chromatograph. In this work, we have developed a database of cosolvent effects for several solutes in a variety of cosolvent solutions. The solutes and cosolvents were chosen in an attempt to give insight on different types of molecular-scale interactions in solution.

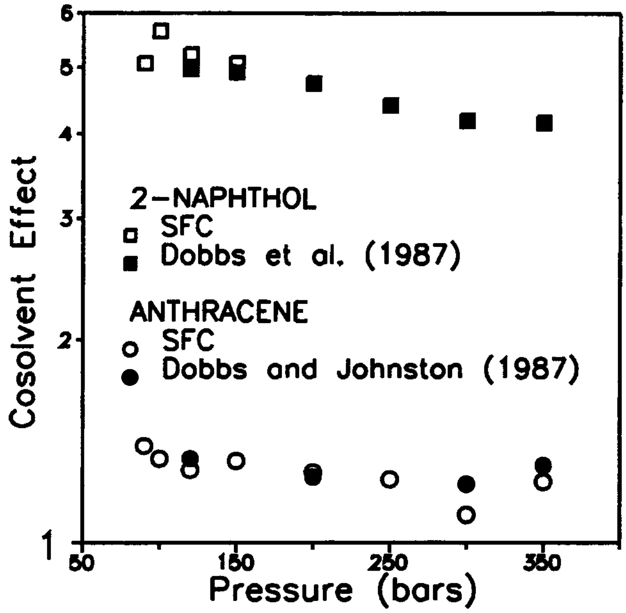


Figure 1. Cosolvent effect for 2-naphthol and anthracene in CO_2 with 3.5 mol percent methanol at 35°C.

Cosolvent effect is ratio of solubility in CO_2/methanol mixture to its solubility in pure CO_2

Theory

The retention time of a solute depends on how it is distributed between the mobile phase (in this case, a SCF) and the stationary phase, and is characterized by k_i, the dimensionless capacity factor:

$$k_i = \frac{t_i - t_o}{t_o} \tag{1}$$

where t_i is the retention time of solute i and t_o is the retention time of a solute that does not interact with the stationary phase. Solutes that spend a higher fraction of time in the mobile phase elute faster than solutes that tend to stay in the stationary phase; the partitioning of solutes between the phases is directly related to thermodynamics. Assuming that equilibrium partitioning of the solute between the mobile and stationary phases is the sole mechanism of solute retention, the capacity factor is related to the equilibrium distribution of the solute between the two phases by:

$$k_i = \frac{x_i}{y_i} \frac{v^F}{v^S} \frac{V^S}{V^F} \tag{2}$$

where x_i and y_i are the mole fractions of component i in the stationary and fluid phases respectively, v^F and v^S are the molar volumes of the fluid and stationary phases, and V^F and V^S are the volumes of the fluid and stationary phases. The validity of this assumption is discussed later.

The fugacity of the solute in the fluid phase, f_i^F, is:

$$f_i^F = y_i \phi_i^\infty P \tag{3}$$

where ϕ_i^∞ is the fugacity coefficient of solute i at infinite dilution, and P is the pressure. Assuming Henry's law is valid in the stationary phase gives:

$$f_i^S = x_i H_i \tag{4}$$

where H_i is the Henry's constant for solute i in a given stationary phase. At equilibrium, the fugacities are equal; substituting Eqs. 3 and 4 into Eq. 2 then gives:

$$\phi_i^\infty = \frac{k_i H_i}{P v^F} \frac{V^F v^S}{V^S} \tag{5}$$

Bartle et al. (1990a,b) assumed that the ratio $V^F v^S / V^S$ depends on the column and should not vary significantly with column conditions. To determine the fugacity of a solute along an isotherm at a series of pressures in the fluid phase then requires knowledge of Henry's constant at that temperature. This leads to the possibility of measuring solubilities of solutes in the chromatograph as follows.

The solubility, y_i^{sat}, of a pure solute in a fluid at temperature T and pressure P is:

$$y_i^{sat} = \frac{P_i^{vap} \exp\left(\int_{P_i^{vap}}^{P} \frac{v_i}{RT} dP \right)}{\phi_i^{sat} P} \tag{6}$$

where P_i^{vap} is the vapor pressure of the solute at T, v_i is the molar volume of the solute and ϕ_i^{sat} is the fugacity coefficient of the solute at saturation in the SCF. If the solubility of a solute is low (<0.001 mole fraction), the fugacity coefficient at saturation is nearly equal to the fugacity coefficient at infinite dilution; however, for applications, we often choose solvents that give much higher solubilities and the composition dependence of the fugacity coefficient can be important. Further discussion of this topic is presented later. The pressure dependence of the Henry's constant is:

$$H_i = H_i^o \exp\left(\int_{P^o}^{P} \frac{\bar{v}_i^\infty}{RT}\, dP\right) \tag{7}$$

where H_i^o is the Henry's constant at reference pressure P^o and v_i^∞ is the infinite dilution partial molar volume of the solute in the stationary phase. Substituting Eqs. 6 and 7 into Eq. 5 and making the reasonable assumption that the infinite dilution partial molar volume of the solute in the stationary phase is the molar volume gives:

$$y_i^{sat} = \left[\frac{P_i^{vap} V^S}{H_i^o V^F v^S} \exp\left(\frac{v_i(P^o - P_i^{vap})}{RT}\right)\right] \frac{v^F}{k_i} = C_i(T)\,\frac{v^F}{k_i} \tag{8}$$

The expression in brackets, which will be called C, in a given column is a function only of temperature and the solute and does not depend on pressure. To determine C for a solute at any temperature, it is necessary to measure at least one solubility at that temperature with an independent technique; once C is known, the entire solubility isotherm can be measured rapidly with the chromatograph. This is the same result obtained by Bartle et al. (1990a,b).

However, this technique has some limitations. Besides equilibrium partitioning, other mechanisms of solute retention must be considered, including adsorption of the solute at the interface between the mobile and stationary phases and interaction with active sites on the stationary phase support. In addition, the amount of fluid absorbed in the stationary phase can vary. These effects are pressure-dependent, making C vary with pressure, but because they are very difficult to quantify, previous investigators have ignored them when making thermodynamic measurements with chromatography. The size of the uncertainties is unknown and depends on the stationary phase, but Bartle et al. obtained good results. Our measurements of cosolvent effects eliminate the need for such an assumption by using a comparison technique to cancel out the effects of retention mechanisms other than bulk absorption.

In this work, we compare the retention of a solute at the same temperature and pressure in the same column, but with different fluids as the mobile phase. The fluids could be completely different, such as carbon dioxide and ethane, or one could compare a pure fluid with a fluid-cosolvent mixture. Taking the ratio of Eq. 5 for two different mobile phases (denoted by $'$ and $''$) gives:

$$\frac{\phi_i^{\infty\prime}}{\phi_i^{\infty\prime\prime}} = \frac{k_i'}{k_i''}\,\frac{H_i'}{H_i''}\,\frac{v^{F\prime\prime}}{v^{F\prime}}\,\frac{V^{F\prime}\,v^{S\prime}\,V^{S\prime\prime}}{V^{F\prime\prime}\,v^{S\prime\prime}\,V^{S\prime}} \tag{9}$$

Several simplifying assumptions are made: first, because the volume of the mobile phase is much greater than that of the stationary phase in a capillary column, swelling of the stationary phase has negligible effect on V^F; thus it can be considered constant. Second, the ratio v^S/V^S, or the total number of moles in the stationary phase, should not depend greatly on the mobile phase, particularly because we are comparing measurements at the same temperature and pressure.

The third and key assumption is that Henry's constant for a solute is not altered by the changes in composition of the mobile phase. Several researchers have measured significant absorption of solvents and cosolvents into stationary phases (for example, Yonker and Smith, 1989, 1990; Strubinger et al., 1991a,b). It has been proposed that the cosolvent also covers up active sites on the column; this would cause the solute to be retained less thus decreasing the retention time (Levy and Ritchey, 1985). The presence of cosolvent should have some effect on the Henry's constant; however, the magnitude of this effect is unknown and should depend on the stationary phase and the cosolvent. Recent studies have demonstrated that the increase in solvating power of the fluid upon addition of the cosolvent is primarily responsible for the decrease in retention implying that the stationary-phase environment around the solute, thus the Henry's constant, is largely unaffected by the cosolvent (Berger and Deye, 1990; Crow and Foley, 1991). Nevertheless, the assumption of a constant, Henry's constant, should be checked for each column; the best way to do this is to study systems where the fluid-phase thermodynamics are already known.

Previous workers used packed columns to make thermodynamic measurements with SCF chromatography; however, we chose capillary columns for two reasons. First, for the measurements to be meaningful, the pressure drop across the column must be small. In our experiments with capillary columns, we estimated pressure drops ranging from 0.2 bar, at a column pressure of 90 bar, to 0.9 bar when operating at 350 bar; pressure drops in packed columns are usually an order of magnitude larger or more. Second, capillary columns have fewer active sites than packed columns and minimize uncertainties due to adsorption.

After making these assumptions, Eq. 9 becomes:

$$\frac{\phi_i^{\infty\prime}}{\phi_i^{\infty\prime\prime}} = \frac{k_i'}{k_i''}\,\frac{v^{F\prime\prime}}{v^{F\prime}} \tag{10}$$

The ratio of the molar volumes should be near unity and can be estimated from an equation of state, from experimental data, or from the t_0 and flow rate measurements. In this work, we used an equation of state to determine this ratio.

Figure 2 demonstrates the meaning of the ratio of infinite dilution activity coefficients. The fugacity coefficient for a solute is shown as a function of composition up to the solubility limit in two different fluids at the same temperature and pressure. At saturation,

$$\frac{y_i^{sat\prime\prime}}{y_i^{sat\prime}} = \frac{\phi_i^{sat\prime}}{\phi_i^{sat\prime\prime}} \tag{11}$$

If the solubilities of the solute in the SCF's are low (as is the case with the solutes studied here), it is reasonable to assume that the ratio of fugacities at the solubility limits is the same as that at infinite dilution. For example, at saturation the ratio of the fugacity coefficient of benzoic acid in pure CO_2 to its

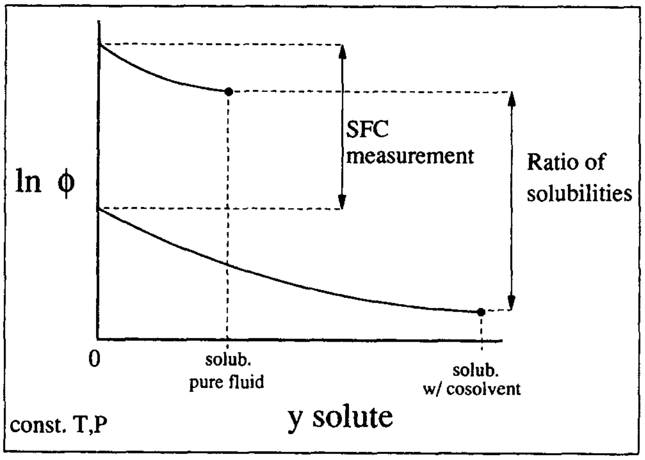


Figure 2. Composition dependence of fugacity coefficient of a solute in pure and mixed fluids.

Top curve is for pure fluid, bottom for mixed.

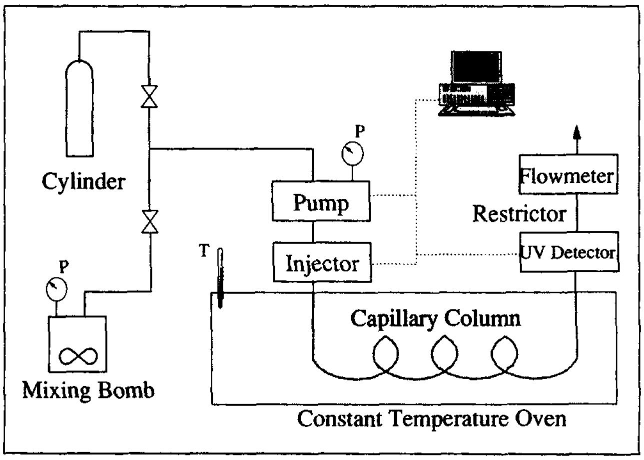


Figure 3. Supercritical fluid chromatograph.

fugacity coefficient in CO_2 with 3.5 mol % methanol is 5.9 at 35°C and 120 bar (Dobbs et al., 1987). The ratio of infinite dilution fugacity coefficients at the same conditions, as estimated by using the Soave-Redlich-Kwong equation of state for composition dependence of the fugacity coefficients, is 5.3, about 10% lower. This represents an extreme example because the solubility of benzoic acid is relatively high (about 0.7 mol % in the CO_2-methanol mixture) and the cosolvent effect is large; generally the difference is much smaller. Because we estimate our experimental error to be 10-15%, we cannot distinguish the difference between infinite dilution and the solubility limit. Thus,

$$\Psi = \frac{y_i^{\text{sat}\,''}}{y_i^{\text{sat}\,'}} \approx \frac{\phi_i^{\infty\,'}}{\phi_i^{\infty\,''}} \tag{12}$$

where Ψ is the cosolvent effect, that is, the relative increase in solubility at some P and T that comes about when the SCF is modified with cosolvent. To obtain the absolute solubility of the solute in the cosolvent solution using this technique, it is necessary to know the solute solubility in the pure SCF.

Infinite dilution fugacity coefficients are a more useful measure of solution thermodynamics than solubilities for theoretical techniques of studying solutions such as statistical mechanics or computer simulations. Solute-solute interactions are eliminated at infinite dilution, thus nonidealities under these conditions are due solely to solute-solvent interactions. This approach separates the problem of determining the intermolecular force between two molecules from the problem of adding up all the forces in an ensemble of molecules.

Experimental Studies

A schematic of the experimental apparatus is shown in Figure 3. The supercritical fluid chromatograph used was a Lee Scientific Model 600-D that included a 137-mL syringe pump. Pressure was monitored with a Heise pressure gauge, model 901B, accurate to ±0.035%; temperature was measured with a Hart Scientific model 1006 digital thermometer and controlled to ±0.05°C. Solutes were detected with a Linear high-pressure UV-vis detector (Model 204). The flow rate of the SCF was measured with a soap bubble flowmeter. SB-Octyl-50 capillary columns (50 μm × 10 m, film thickness 0.25 μm; or 100 μm × 10 m, film thickness 0.50 μm) from Lee Scientific were used.

SFE grade CO_2 (99.99%) was obtained from Scott Specialty Gases, CP-grade ethane (99%) from Matheson Gas Products, and fluoroform from Du Pont (98% purity) and were used as received. The cosolvents were obtained from Aldrich Chemical Co. (acetone and chloroform 99.9+%; 2,2,2-trifluoroethanol, 99.5+%; 2-propanol, 99.5%; 1,2-dibromoethane, 1,1,1-trichloroethane, and triethylamine 99+%) and were also used without further purification; dehydrated ethanol (99.95%) was from Quantum Chemical Corporation and stored over molecular sieves. All solutes were obtained from Aldrich Chemical Company and used without further purification since the chromatograph separated out the impurities.

The fluid mixtures were prepared in our labs in a 1-L bomb constructed of 316 stainless steel. A known amount of cosolvent, predetermined to give the desired composition, was loaded into the bomb, which had been previously flushed with SCF solvent to eliminate air. The bomb was pressurized to about 415 bar, and the mixture was then stirred for at least a day by a magnetic stir bar inside the bomb. Using this technique, the bomb contained enough fluid to supply the syringe pump with about 150 mL of the mixture without approaching the two-phase region in the bomb or pump. Special care was taken to avoid the two-phase region in the mixing bomb, syringe pump, and column at all times. Since no VLE data were available for many of the fluid mixtures used, the approximate phase boundaries were determined by visual observation of these mixtures in a Jerguson gauge. Analyses of the mixed fluid were conducted by GC and were accurate to 0.05 mol %.

Experiments were carried out at 50°C and pressures from 80 to 350 bar. The solutes were injected in n-pentane at about 20 μg/mL. The pentane could be detected with the UV detector, apparently because it caused a change in the refractive index of the fluid and the curved walls of the flow cell caused differing amounts of light to be scattered depending on the refractive index of the fluid. It was confirmed that the peak seen with the UV detector coincided with elution of the pentane by connecting a Varex universal detector at the outlet of the UV

Table 1. Supercritical Fluids and Their Properties

Fluid	T_c $(K)^*$	P_c (bar)*	μ $(D)^*$	α (cm$^3 \times 10^{-25}$)
Ethane	305.4	48.8	0	44.7^{**}
Carbon Dioxide	304.1	73.8	0	$26.5^{\dagger}$
Fluoroform	299.3	48.6	1.6	27.4^{**}

* Reid et al. (1987)
** Estimated from Dewar and Stewart (1984)
† Landolt-Börnstein (1951)

Table 2. Cosolvents and Their Properties

Cosolvent	$\pi^{*\ddagger}$	$\alpha^{\ddagger}$	$\beta^{\ddagger}$	μ $(D)^*$	α (cm$^3 \times 10^{-25}$)
Methanol	0.60	0.93	0.62	1.7	$32.3^{\dagger}$
Ethanol	0.54	0.83	0.77	1.7	48.6^{**}
2-Propanol	0.48	0.76	0.95	1.7	64.2^{**}
Acetone	0.71	0.06	0.48	2.9	$63.3^{\dagger}$
Chloroform	0.58	0.44	0.00	1.1	$82.3^{\dagger}$
1,1,1-Trichloroethane	0.49	0.00	0.10	1.7	103.6^{**}
2,2,2-Trifluoroethanol	0.73	1.51	0.00		52.8^{**}
Triethylamine	0.14	0.00	0.71	0.9	134.9^{**}
1,2-Dibromoethane	0.75	0.00	0.00	1.0	106.5^{**}

* Reid et al. (1987)
** Estimated from Dewar and Stewart (1984)
† Landolt-Börnstein (1951)
‡ Kamlet et al. (1983)

detector; both detectors showed the elution of pentane simultaneously; unfortunately the universal detector was not sensitive enough to detect the minute amounts of the solutes. We also determined that the retention of pentane was the same as that of helium under the conditions of our experiments, so it was assumed that pentane was not retained, giving a measurement of t_o. Retention time was not sensitive to the concentration of the solute. All solutes were detected at absorption maxima. The retention times were determined from the maxima in the first derivative of the chromatogram.

Uncertainties in the cosolvent effects are estimated to be 10–15% at most, primarily at lower pressures nearer to the critical point. One possible source of error is estimation of the density ratio used to convert ratios of capacity factors to ratios of infinite dilution fugacity coefficients via Eq. 10. Here, we used the Peng-Robinson equation of state (EOS) with $k_{ij} = 0.1$ to estimate the density ratio; this ratio ranged from very near unity to about 1.15, an effect of up to 15%. The EOS is likely good to within 20% of this effect, meaning an error of 3% in the cosolvent effect at most. Another problem arose with combinations of large cosolvent effects, higher pressures, and relatively volatile solutes. These factors lead to decreased retention times; thus in some cases, the solute eluted very soon after pentane. Because the cosolvent effect is proportional to the difference between these times, the largest uncertainties occurred in these cases.

Results and Discussion

In order to investigate different types of interactions in SCF solutions, several different types of fluids, cosolvents and solutes were studied. The three fluids that were used are shown in Table 1 with their critical properties, dipole moments, and polarizabilities; note that the critical temperatures are similar. Ethane is a nonpolar fluid that has no specific interactions with any of the cosolvents or solutes. Because we were primarily interested in looking at cosolvent-solute interactions, the cosolvent studies were done with ethane mixtures. Carbon dioxide is also nonpolar, but has a large quadrupole moment; in addition, carbon dioxide can participate in acid-base type interactions, as it does when reacting with water to form carbonic acid. For example, Fulton et al. (1991) have found evidence of some type of a weak complex between CO_2 and methanol in a SCF solution. Fluoroform, CHF_3, is polar and is a hydrogen-bond donor.

Table 2 shows various cosolvents studied along with their Kamlet-Taft solvatochromic parameters (Kamlet and Taft, 1976; Taft and Kamlet, 1976; Kamlet et al., 1977, 1983), dipole moments, and polarizabilities. The Kamlet-Taft format is useful for rating solvent strength by using linear solvation energy relationships to relate quantities such as reaction rates, UV absorption maxima, or chromatographic retention times to chemical characteristics of the solvent. A measurable quantity, XYZ, is related to the parameters by:

$$XYZ = XYZ_o + a\alpha + b\beta + s\pi^* \tag{13}$$

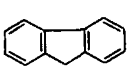
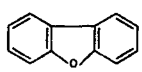
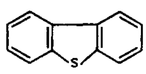
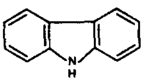
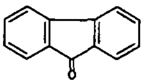
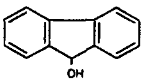
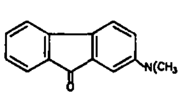
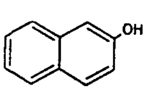
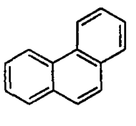
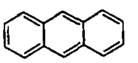
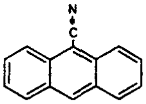
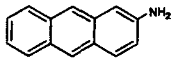
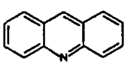
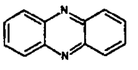
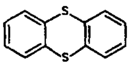
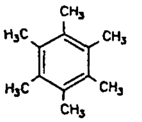
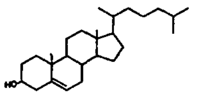
where XYZ_o is an intercept, and a, b, and s are solute-specific constants. The parameter α indicates the ability of the solvent to donate hydrogen bonds, β denotes the ability to accept hydrogen bonds, and π^* is a measure of solvent polarity/polarizability. It is important to remember that α and β are only indications of hydrogen-bonding ability and no more.

The cosolvents used included commonly used alcohols and acetone. In addition, chloroform and 2,2,2-trifluoroethanol (222-TFE) were examined because of their ability to donate protons but not accept them. 1,1,1-trichloroethane (111-TCE) is similar to chloroform, but is not a hydrogen-bond donor. Conversely, triethylamine (TEA) will not donate protons but is an excellent acceptor; it also is a Lewis base that can take part in charge-transfer complexes. Finally, 1,2-dibromoethane (12-DBE) was chosen because it neither accepts nor donates protons, but it has a large π^* indicative of high polarity/polarizability. This choice of cosolvents allows us to study various effects independently, including hydrogen bonding, in SCF solutions.

Various solutes were chosen (Table 3). These include nonpolar compounds such as anthracene and phenanthrene, alcohols like 9-hydroxyfluorene and the phenolic 2-naphthol, and amines such as carbazole with a pyrollic nitrogen and acridine with a pyridinic nitrogen. To study the effect of specific constituents, we looked at series of compounds such as fluorene, fluorenone, dibenzofuran, dibenzothiophene, carbazole, and 9-hydroxyfluorene. In addition, we looked at environmentally important sulfur compounds, like thianthrene and dibenzothiophene. Because we were using a UV detector, all of the solutes were UV-active; however, if a more versatile detector were used, such as FTIR or a mass spectrometer, virtually any compound could be studied.

In the following discussion, we examine the results obtained for cosolvent effects, including the different cosolvents and the effect of composition of the cosolvent. Next, we discuss the solvent effect, and finally consider using supercritical fluid chromatography as a tool to measure absolute solubilities.

Table 3. Solute Structures and Properties

Solute	P^{vap} (Pa)	v^{mol} (cm^3/mol)[h]	Δh^{sub} (kJ/mol)[i]	μ (D)[j]	Solub. Ref.
Fluorene 	1.23[a]	139	87.3	~0.2	k
Dibenzofuran 	3.20[b]	155	79.1	0.8	b,l
Dibenzothiophene 	0.36[b]	168	91.2	0.8	l
Carbazole 	0.010[c]	152	96.5	2.1	m
Fluorenone 	0.27[b]	160	92.2	3.3	b
9-Hydroxyfluorene 				1.9	
2-Dimethylaminofluorenone 					
2-Naphthol 	0.38[d]	118	94.3	1.5	n
Phenanthrene 	0.35[e]	168	87.5	0	k
Anthracene 	0.019[b]	143	102.6	0	*k*
9-Cyanoanthracene 					
2-Aminoanthracene 					
Acridine 	0.11[f]	178	90.8	2.0	n
Phenazine 	0.067[f]	164	90.4	0	o
Thianthrene 	0.012[c]	197	99.2	1.5	l
Hexamethylbenzene 	2.37[g]	153	84.4	~0	k
Cholesterol 				2.0	p

[a] Osborn and Douslin (1975)
[b] Hansen (1985)
[c] Alferi (1989)
[d] Colomina et al. (1974)
[e] Kudchadker et al. (1979)
[f] deKruif (1975)
[g] Ambrose et al. (1976)
[h] Weast (1978)
[i] Calculated from vapor pressure data
[j] McClellan (1963)
[k] Johnston et al. (1982)
[l] Hess (1987)
[m] Pouillot (1991)
[n] Schmitt and Reid (1986)
[o] Van Alsten (1986)
[p] Yun et al. (1991)

Cosolvent effect

Table 4 shows the cosolvent effects, Ψ, that were measured at 50°C in ethane at pressures from 80 to 200 bar. Note that Ψ usually decreases with pressure. This may occur because a portion of Ψ is due to the increased density of the fluid mixture relative to the pure SCF at the same pressure. As pressure increases, the relative increase in density decreases; hence, this portion of Ψ becomes smaller.

On the other hand, for some combinations of cosolvent and solute, Ψ increases with pressure, particularly when there seems to be strong, specific interactions, for example, 2-naphthol with the cosolvents ethanol, isopropanol, or acetone. This may be due to proximity to an upper critical endpoint (UCEP); like the more familiar lower critical endpoint, in the region of the UCEP small variations in pressure or temperature can have large effects on solubility. The melting point of 2-naphthol is

Table 4 Cosolvent Effects in Ethane at 50°C

	Cosolvent and Composition (mol%)											
Pres. (bar)	0.79% Ethanol	1.60% Ethanol	2.79% Ethanol	4.83% Ethanol	9.52% Ethanol	3.56% Isoprop.	3.76% Acetone	2.86% C′form	3.48% 111-TC	1.03% 222-TFE	2.37% TEA	2.51% 12-DBE
Anthracene												
80			1.40			1.48	1.66				2.26	
100	1.04	1.24	1.27	1.36	1.78	1.30	1.45	1.54	1.58	1.19	1.77	1.31
120	1.13		1.19	1.28	1.74	1.25	1.36	1.49	1.42	1.12	1.55	1.21
150	1.03	1.01	1.17			1.20	1.30	1.35	1.36	1.13	1.50	1.19
200		1.00	1.11			1.18	1.22		1.23	1.08	1.38	1.08
9-Cyanoanthracene												
80						1.67	1.87				2.50	
100	1.12	1.25	1.35	1.79	2.57	1.37	1.55	1.65	1.49	1.58	1.80	1.27
120	1.10	1.26	1.32	1.66	2.44	1.32	1.53	1.57	1.47	1.58	1.62	1.23
150	1.09	1.18	1.31			1.30	1.47	1.45	1.42	1.58	1.55	1.19
200	1.08	1.27	1.29			1.27	1.51	1.44	1.30	1.62	1.49	1.16
Fluorene												
80			1.34			1.38	1.54	1.78			2.12	
100	1.09	1.18	1.24	1.30		1.24	1.38	1.49	1.46	1.18	1.68	1.21
120	1.09	1.22		1.23		1.17	1.35	1.32	1.36	1.13	1.54	1.14
150	1.04	1.06				1.16	1.32	1.28	1.24	1.05	1.45	1.14
200	1.06	1.10	1.13			1.13	1.44	1.27	1.28	1.12	1.50	1.12
9-Fluorenone												
80			*1.45*			*1.49*	*1.66*	*2.00*			*2.19*	
100	*1.09*	*1.21*	*1.32*	*1.58*	*2.12*	*1.34*	*1.45*	*1.70*	*1.52*	*1.62*	*1.68*	*1.19*
120	*1.07*		*1.31*	*1.56*	*2.54*	*1.32*	*1.44*	*1.63*	*1.40*	*1.62*	*1.56*	*1.16*
150	*1.10*	*1.19*	*1.24*			*1.29*	*1.39*	*1.46*	*1.31*	*1.69*	*1.50*	*1.15*
200	*1.15*		*1.22*			*1.29*	*1.44*	*1.42*	*1.25*	*1.64*	*1.45*	*1.12*
9-Hydroxyfluorene												
80			2.13			2.18	1.82	1.89			2.41	
100	1.14	1.58	2.07	2.87	3.79	2.04	1.64	1.34	1.51	1.85	1.96	1.16
120	1.28	1.87	2.18	2.96		2.09	1.64	1.44	1.36	1.91	1.94	1.15
150	1.31	2.06	2.36			2.56	1.61	1.40	1.26	1.90	1.86	1.17
200	1.33		2.77			2.55	1.67	1.34	1.30	2.02		1.12
2-Naphthol												
80			3.07			3.17	2.93	1.91			2.87	
100	1.82	2.72	4.63	5.48	10.97	4.19	3.47	2.15	2.11	2.33	3.13	1.65
120	2.02	3.13	4.40	5.74		4.26	3.31	1.82	1.87		2.86	1.49
150	1.79	3.13	5.23			5.05	3.85	2.00	1.97	2.49		1.66
200	2.34	3.04	5.66			5.27	4.15	2.16	1.94	2.60		1.64
Carbazole												
80			2.04			2.05	2.16	1.91			2.09	
100	1.18	1.56	2.10	2.99	6.07	2.15	2.18	1.68	1.72	1.45	1.87	1.31
120	1.24	1.56	2.15	2.93	5.83	2.03	2.14	1.58	1.59	1.45	1.74	1.27
150	1.16	1.74	2.24			2.14	2.18	1.51	1.52	1.48	1.66	1.29
200	1.12	1.70	2.27			2.19	2.27	1.53	1.53	1.47	1.71	1.26
Dibenzothiophene												
80			1.40			1.43	1.58	1.96				
100	1.09	1.19	1.24	1.39	1.84	1.26	1.39	1.49	1.62	1.13	1.67	1.24
120	1.10	1.26	1.20	1.31	1.73	1.25	1.35	1.40	1.52	1.14	1.55	1.21
150	1.09	1.21	1.15			1.17	1.29	1.35	1.43	1.11	1.48	1.15
200	1.06		1.13			1.17	1.29	1.33	1.40	1.10	1.44	1.12
Acridine												
80			1.61			1.63	1.74	2.24				
100		1.19	1.48	1.87	2.60	1.48	1.57	1.92	1.51	2.23	1.83	1.23
120		1.26	1.47	1.77	2.75	1.46	1.51	1.74	1.38	2.22	1.73	1.20
150		1.21	1.48			1.41	1.51	1.69	1.32	2.30	1.74	1.20
200		1.33	1.51			1.46	1.48	1.68	1.26	2.48	1.64	1.14
Phenazine												
80			1.51			1.53	1.66	2.04				
100			1.36			1.36	1.48	1.64	1.51	1.85	1.54	1.20
120			1.31			1.34	1.46	1.54	1.39	1.85	1.40	1.18
150			1.27			1.33	1.47	1.51	1.32	1.90	1.38	1.13
200			1.35			1.29	1.41	1.65	1.24	2.00	1.20	1.14

(Continued on next page)

Table 4 Cosolvent Effects in Ethane at 50°C (continued)

	Cosolvent and Composition (mol%)											
Pres. (bar)	0.79% Ethanol	1.60% Ethanol	2.79% Ethanol	4.83% Ethanol	9.52% Ethanol	3.56% Isoprop.	3.76% Acetone	2.86% C'form	3.48% 111-TC	1.03% 222-TFE	2.37% TEA	2.51% 12-DBE
Hexamethylbenzene												
80						1.29	1.50					
100			1.22			1.13	1.42			1.12		
120			1.23			1.18	1.27			1.17		
150			1.21			1.10	1.31			1.17		
200			1.07			1.09	1.22			1.18		
Phenanthrene												
80			1.36			1.43	1.61	1.90				
100			1.24			1.28	1.41	1.53	1.53	1.17	1.53	1.29
120			1.18			1.19	1.34	1.38	1.39	1.12	1.40	1.19
150			1.16			1.19	1.32	1.30	1.28	1.14	1.37	1.16
200			1.12			1.16	1.32	1.22	1.27	1.10	1.04	1.21
Dibenzofuran												
80			1.30			1.35	1.52	1.71				
100			1.19			1.25	1.37	1.44	1.45	1.15	1.49	1.19
120			1.15			1.18	1.31	1.31	1.30	1.10	1.28	1.13
150			1.12			1.12	1.28	1.24	1.26	1.09	1.27	1.11
200			1.10			1.13	1.34	1.17	1.25	1.09	1.13	1.11
2-Dimethylamino-9-fluorenone												
80			1.84			1.89	2.03	2.63				
100			1.58			1.63	1.70	1.99	1.75	2.20	1.82	1.38
120			1.61			1.61	1.68	1.92	1.64	2.27	1.70	1.40
150			1.53			1.55	1.67	1.79	1.56	2.23	1.60	1.31
200			1.55			1.52	1.64	1.74	1.51	2.32	1.54	1.36
Thianthrene												
80			1.42			1.50	1.66	2.02				
100			1.27			1.31	1.44	1.57	1.62	1.17	1.59	
120			1.24			1.26	1.40	1.44	1.47	1.17	1.43	1.25
150			1.18			1.21	1.34	1.38	1.36	1.13	1.44	1.19
200			1.16			1.17	1.39	1.34	1.33	1.12		1.16
Cholesterol												
80						1.69	1.39					
100			1.81			1.86	1.46			1.62		
120			2.27			2.22	1.72			1.98		
150			2.52			2.40	1.73			2.22		
200			2.66			2.57	2.20			2.48		
2-Aminoanthracene												
80						1.95	2.08	2.37				
100			1.76			1.69	1.80	1.83	1.68	1.56	1.91	1.34
120			1.77			1.70	1.81	1.79	1.55	1.61	1.90	1.31
150			1.67			1.54	1.65	1.60	1.35	1.48	1.66	1.21
200			1.62			1.51	1.63	1.47	1.26	1.36	1.59	1.15

normally 122.5°C; however, in the presence of a SCF this can be lowered significantly. In the presence of pure CO_2, 2-naphthol's melting point is lowered to 107°C at 210 bar; with CO_2 and 4% methanol, the melting point is lowered to 63°C at 204 bar, and 43°C at 107 bar (Lemert and Johnston, 1989). In both cases, the UCEP was over 200 bar. It seems reasonable to assume similar melting depression for 2-naphthol in some of the ethane-cosolvent mixtures; thus we were probably approaching a UCEP at 50°C and 200 bar.

To compare the data better, we attempted to remove the portion of Ψ due to the density increase that occurs upon addition of cosolvent. The density dependence was estimated from the solubility isotherms in pure ethane. Also, we facilitated quantitative comparison by assuming that Ψ was related linearly to the mole fraction of cosolvent; in each case, we then calculated Ψ for 3 mol % cosolvent at 150 bar (Table 5). Because of the approximations involved in removing the density and composition dependence of Ψ, there may be some uncertainty in comparing Ψ for a solute across different cosolvents; however, there is no problem looking at several solutes in the same cosolvent mixture.

First, we compare the solutes fluorene and fluorenone. The major differences are for the cosolvents chloroform, 222-TFE, and TEA. Fluorenone is a proton acceptor, although the conjugation in the five-membered ring weakens the basicity relative to other carbonyl compounds. In contrast, fluorene is incapable of forming strong H-bonds. 222-TFE is a very potent proton donator; thus the apparent strong specific interaction between 222-TFE and fluorenone (Figure 4a) is not surprising. Chloroform is a lesser, but still good, donor, again making possible a specific interaction (Figure 4b). Note the nearly identical Ψ for fluorene and fluorenone in 111-TCE; 111-TCE

Table 5 Normalized Cosolvent Effects

Solute	Ethanol	Isoprop.	Acetone	C′form	111-TCE	222-TFE	TEA	12-DBE
Fluorene	0.99	1.00	1.17	1.20	1.18	1.16	1.21	0.88
Dibenzofuran	0.97	1.00	1.14	1.15	1.16	1.12	1.31	0.87
Dibenzothiophene	0.98	1.02	1.13	1.24	1.29	1.16	1.38	0.88
Carbazole	1.91	1.72	1.76	1.42	1.38	2.14	1.60	1.01
Fluorenone	1.07	1.10	1.21	1.39	1.19	2.64	1.48	0.87
9-Hydroxyfluorene	2.05	1.90	1.36	1.24	1.19	3.46	2.28	0.89
2-Dimethylaminofluorene	1.29	1.25	1.35	1.63	1.37	4.28	1.80	1.01
2-Naphthol	4.59	3.82	2.90	1.91	1.72	5.06	3.16	1.41
Phenanthrene	0.98	1.01	1.14	1.20	1.19	1.17	1.35	0.91
Anthracene	0.97	1.02	1.12	1.27	1.19	1.14	1.39	0.86
9-Cyanoanthracene	1.08	1.08	1.25	1.34	1.23	2.46	1.67	0.88
2-Aminoanthracene	1.39	1.25	1.37	1.45	1.22	2.07		0.87
Acridine	1.26	1.20	1.27	1.58	1.19	4.56	1.70	0.91
Phenazine	1.11	1.11	1.22	1.43	1.19	3.39	1.43	0.88
Thianthrene	0.99	1.02	1.16	1.26	1.24	1.20	1.46	0.90
Hexamethylbenzene	1.02	0.98	1.13			1.33		
Cholesterol	1.90	1.79	1.43			4.08		

is similar to chloroform except that it does not donate protons. This is further evidence of a specific H-bonding-type interaction between fluorenone and chloroform.

There is a lesser cosolvent effect for fluorenone relative to fluorene for the alcohols ethanol and isopropanol. We believe this may be due to self-association of the alcohols in solution, diminishing their ability to interact specifically with fluorenone. Recent FTIR investigators of methanol in supercritical ethane and CO_2 indicate self-association (Fulton et al., 1991).

H-bonding interactions between fluorenone and TEA are not possible; TEA, however, is capable of forming charge-transfer complexes with electron deficient pi-systems. Because the carbonyl group associated with fluorenone removes electron density from the pi-system, it would be expected that fluorenone would be more likely to interact with TEA via a charge-transfer mechanism (Figure 4c) compared with the more electron rich fluorene.

Next, we compare the solutes fluorene, dibenzofuran, dibenzothiophene, and carbazole. This series represents a general structure with minor perturbations (Figure 5a). For fluorene, dibenzofuran, and dibenzothiophene, the Ψ's are identical within experimental error for all cosolvents. This should be expected because these compounds do not readily participate in H-bonding. One might expect dibenzofuran to be somewhat basic, but because of the aromaticity, it is a very poor base (for example, tetrahydrofuran is a weak base, but furan is much weaker still). The N-H bond of carbazole, on the other hand, gives a proton capable of interacting with lone pairs of electrons on the oxygen atoms of ethanol (Figure 5b), isopropanol, acetone, and 222-TFE; thus, Ψ is larger for carbazole in these cosolvents relative to fluorene.

Next, one may compare anthracene and 9-cyanoanthracene (9-ACN). As with fluorenone, 222-TFE is capable of forming strong hydrogen bonds with 9-ACN, and TEA can interact with the electron-deficient aromatic ring of the 9-ACN via a charge transfer mechanism (Figures 6a and 6b). There also

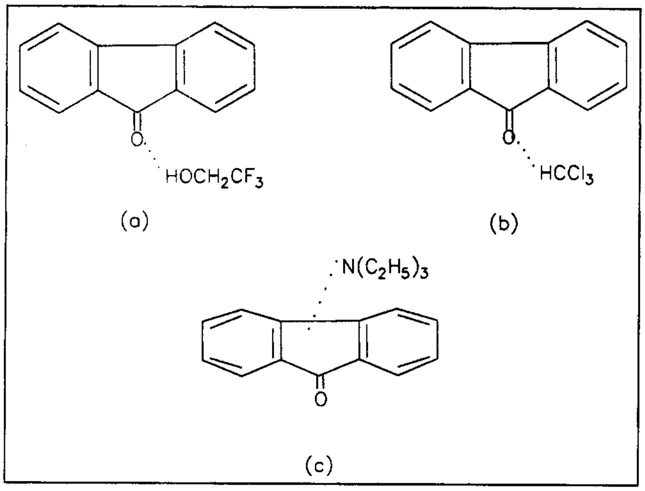


Figure 4. Specific interactions of fluorenone. Hydrogen bonding with 222-TFE (a) and chloroform (b); charge transfer with TEA (c).

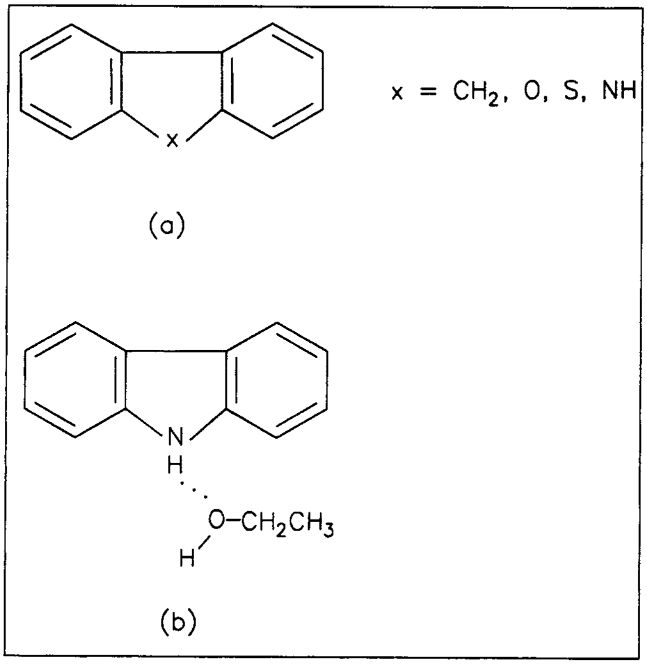


Figure 5. General structure of fluorene, dibenzofuran, dibenzothiophene, and carbazole (a) and hydrogen bond between carbazole and ethanol (b).

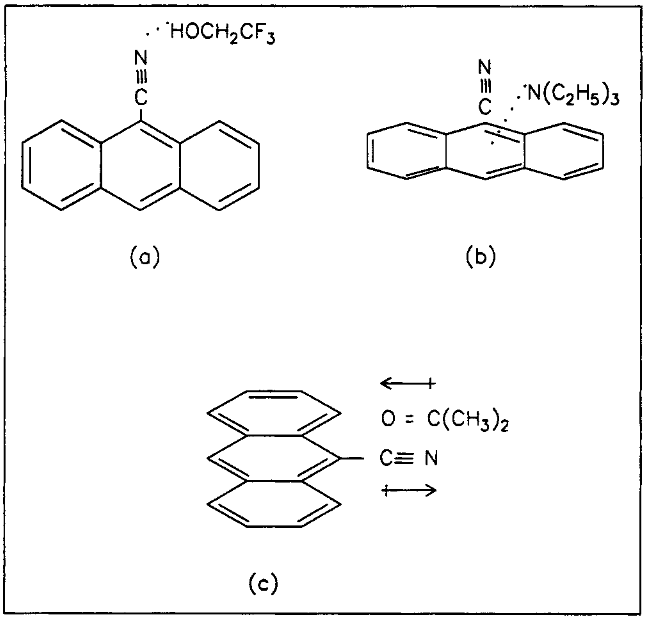


Figure 6. Specific interactions with 9-ACN. Hydrogen bond with 222-TFE (a), charge transfer with TEA (b), and dipole alignment with acetone (c).

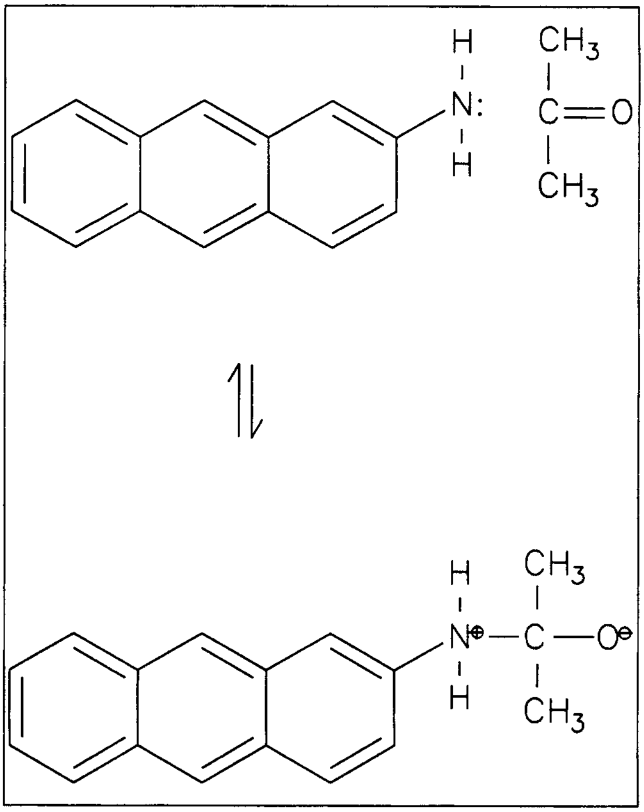


Figure 7. Reaction between 2-AA and acetone to form azahemiacetal intermediate.

appears to be a small increase in Ψ for 9-ACN in acetone. This may be due to an alignment of the dipoles of the planar 9-ACN and acetone (Figure 6c); similar alignment has been observed in X-ray diffraction studies of polyacrylonitrile (Bohn et al., 1961).

As expected, Ψ for 2-aminoanthracene (relative to anthracene) is largest for the protic cosolvents ethanol, isopropanol, chloroform, and 222-TFE. In addition, there seems to be an enhancement with the cosolvent acetone. Amines are known to react with carbonyls to form imines; it is conceivable that 2-aminoanthracene and acetone interact to form the azahemiacetal intermediate (Figure 7).

The solute acridine has been much studied in SCF's, but there is some disagreement on its solubilities (Schmitt and Reid, 1986; Van Alsten, 1986; Dobbs et al., 1987). Perhaps one reason for this is that acridine must be handled carefully since in the presence of air it readily forms acridine-*N*-oxide. One advantage of the chromatographic technique is that impurities, such as the oxide, are separated away from the solute of interest and do not affect the measurement. Phenazine, despite having two pyridinic type nitrogens, is not as basic as acridine because each nitrogen decreases the electron density around the other. In addition, acridine has a dipole moment of 2.1 D, but phenazine has no dipole moment due to its symmetry. One would then expect to see larger Ψ's for acridine than phenazine, and indeed this is the case. Relative to anthracene, acridine exhibits large Ψ for the protic cosolvents 222-TFE, chloroform, isopropanol, and ethanol, and also for TEA, perhaps due again to a charge transfer type interaction.

Of all the solutes, 2-naphthol displays the largest Ψ's in every cosolvent studied. The phenolic hydroxy group is a superb H-bond donor; thus the large cosolvent effects for the H-bond acceptors acetone, TEA, and the alcohols are expected. However, large enhancements are also seen for 111-TCE and 12-DBE which do not participate in H-bonding. 2-Naphthol has the least hydrocarbon nature of the solutes studied, with fewer carbons and a hydrophilic substituent. Apparently, the enhancement in the polarity and polarizability of the fluid upon addition of these cosolvents is responsible for 2-naphthol's behavior. The same is true to a lesser extent for carbazole and 2-dimethylaminofluorenone, solutes that are also less hydrocarbon-like in nature relative to the rest of the solutes. Other than these solutes, there is very little difference in Ψ in the cosolvents 111-TCE and 12-DBE, the only cosolvents studied not capable of forming strong hydrogen bonds.

Effect of cosolvent composition

We studied the effect of the concentration of the cosolvent on Ψ for ethanol from 0.8 to 9.5 mol % in ethane. Spectroscopic studies have indicated that the local composition of a cosolvent around a solute molecule may be much greater than the bulk composition, particularly near the critical point (for example, Kim and Johnston, 1987; Brennecke et al., 1990b); how this manifests itself on a macroscopic scale requires more study, however.

Figures 8, 9 and 10 show Ψ for anthracene, 2-naphthol, and carbazole, respectively, as a function of ethanol composition at 50°C. Also shown is an approximation of the portion of the cosolvent effect due to the increase in the bulk density of the fluid as cosolvent concentration increases. Note that the cosolvent effect for anthracene can be completely explained

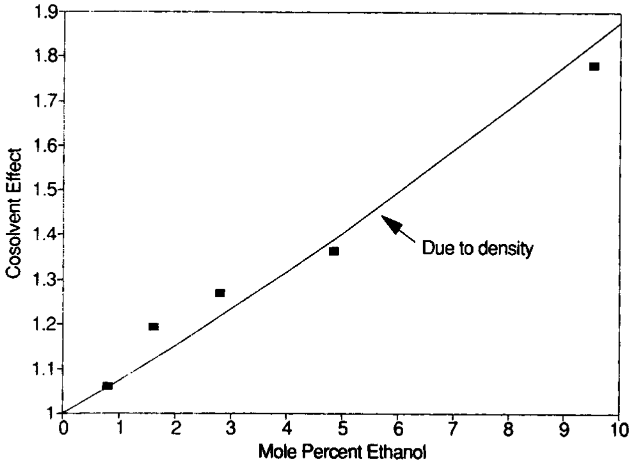


Figure 8. Cosolvent effect for anthracene in ethane/ ethanol mixtures at 50°C.

by the increase in the bulk density of the fluid mixtures. Conversely, only a small portion of Ψ for carbazole and 2-naphthol is due to the density enhancement. One explanation would be that there is some sort of specific interaction between these solutes and ethanol. Alternatively, an increase in the local dielectric environment may be partially responsible. The cosolvent effect appears to be fairly linear with respect to the mole fraction of ethanol.

Solvent effect

We compared the behavior of solutes in nonpolar ethane with CO_2, which has a large quadrupole moment and may be capable of weak specific interactions, and fluoroform, which is polar and is a hydrogen bond donor.

Results showing the solvent effect in CO_2 relative to ethane are shown in Table 6. Figure 11 depicts typical results, the solvent effect for 2-naphthol and anthracene as a function of pressure. The solvent effect for anthracene is roughly an order of magnitude larger than that of 2-naphthol. Not surprisingly, nonpolar anthracene is more soluble in the hydrocarbon ethane than CO_2; however, for polar 2-naphthol, CO_2 is a better solvent, perhaps indicating a weak specific interaction between CO_2 and 2-naphthol. This demonstrates how large changes in selectivity can be realized even by use of different pure supercritical fluids. In general, we observed the same trend as Schmitt and Reid (1986); ethane was a better solvent for the nonpolar aromatic hydrocarbons and CO_2 solvated the polar compounds better.

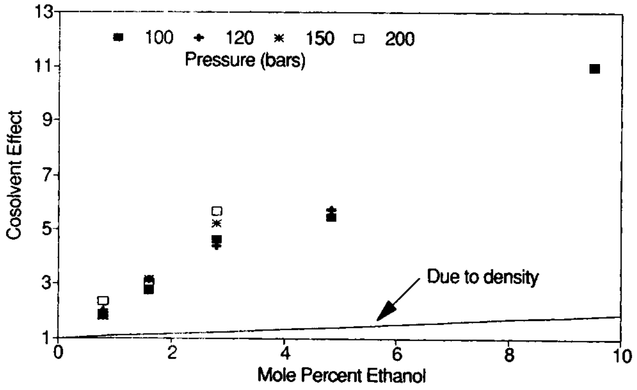


Figure 9. Cosolvent effect for carbazole in ethane/ ethanol mixtures at 50°C.

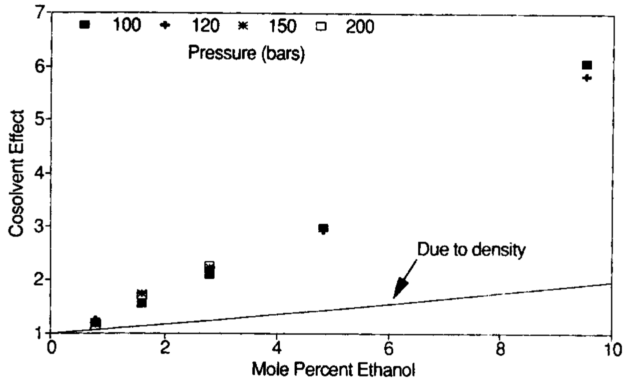


Figure 10. Cosolvent effect for 2-naphthol in ethane/ ethanol mixtures at 50°C.

Also note that the solvent effect decreases with increasing pressure. This occurs because the critical pressure of carbon dioxide (73.8 bar) is larger than the critical pressure of ethane (48.8 bar). Since solubility increases more rapidly closer to the critical point, at the pressures we studied the rate of increase of solubility for ethane with pressure is smaller than that for CO_2, causing the decrease in solvent effect. For 2-naphthol, the solvent effect goes from greater than unity to less than one. This indicates that the solubility isotherms for 2-naphthol in CO_2 and ethane cross.

The solvent effects for solutes in fluoroform relative to ethane are shown in Table 7. In this case, because the critical pressures of ethane and fluoroform are nearly identical (48.8 and 48.6 bar, respectively), the solvent effect was not a strong function of pressure. For most of the solutes studied, ethane was a better solvent than fluoroform. Fluoroform is a polar molecule with highly electronegative fluorine atoms which may create repulsive interactions with the electronegative aromatic rings. Also, liquid hydrocarbons and perfluorocarbons are generally

Table 6. Solvent Effect for CO_2 Relative to Ethane, 50°C

Solute	Pressure (bar) 120	150	200
Fluorene	0.28	0.42	0.50
Dibenzofuran	0.34	0.51	0.58
Dibenzothiophene	0.25	0.36	0.53
Carbazole	0.46	0.72	0.93
Fluorenone	0.44	0.71	0.87
9-Hydroxyfluorene	0.55	0.93	1.13
2-Dimethylamino-9-Fluorenone	0.39	0.68	0.80
2-Naphthol	1.09	1.98	2.48
Phenanthrene	0.23	0.35	0.41
Anthracene	0.23	0.35	0.40
9-Cyanoanthracene	0.34	0.58	0.74
Acridine	0.33	0.53	0.60
Phenazine	0.37	0.60	0.74
Thianthrene	0.20	0.32	0.38
Hexamethylbenzene	0.24	0.33	0.36

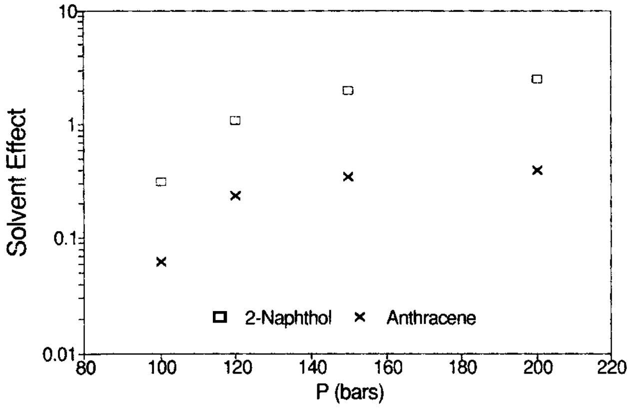


Figure 11. Solvent effect for 2-naphthol and anthracene in CO_2 relative to ethane at 50°C.

immiscible. Considering that the solutes studied are largely aromatic and hydrocarbon in nature, it is not surprising that the solutes are not well solvated relative to ethane. Notice that there is a dichotomy between the solutes with functional groups and those without. Clearly the functional groups have attractive interactions with fluoroform. These may be dipole-dipole interactions, or there may be a certain amount of hydrogen bonding between protic fluoroform and the basic solutes fluorenone, 9-ACN, and 9-hydroxyfluorene.

Solubility

As described by Eq. 8, the pressure dependent retention data can be used to determine a solubility isotherm with one adjustable parameter, C. As with the cosolvent and solvent effects above, the thermodynamics of the stationary phase can be assumed to be unaffected by the mobile phase, thus C is not solvent dependent.

Figure 12 shows the solubility of anthracene in three fluids as a function of density at 50°C. Along with the data obtained in this study are the data of Johnston et al. (1982) in ethane and CO_2 and data at 55°C in fluoroform from Schmitt and Reid (1986). The constant C was obtained by fitting the chromatographic data in ethane to the solubilities of anthracene in ethane, then the solubilities of anthracene in CO_2 and fluoroform were measured by using the same value of C and the chromatographic data for these fluids. There is excellent agreement between the chromatographic measurements and literature values. The pressure dependence of the solubility is accurately measured by the chromatograph.

Table 7. Solvent Effect for Fluoroform Relative to Ethane, 50°C

Solute	Pressure (bar) 120	150	200
Fluorene	0.39	0.39	0.37
Dibenzothiophene	0.24	0.24	0.21
Carbazole	0.80	0.80	0.81
Fluorenone	1.23	1.37	1.53
9-Hydroxyfluorene	0.73	0.80	0.84
2-Naphthol	1.12	1.16	1.19
Anthracene	0.29	0.27	0.25
9-Cyanoanthracene	0.82	0.85	0.85
Acridine	0.59	0.57	0.50

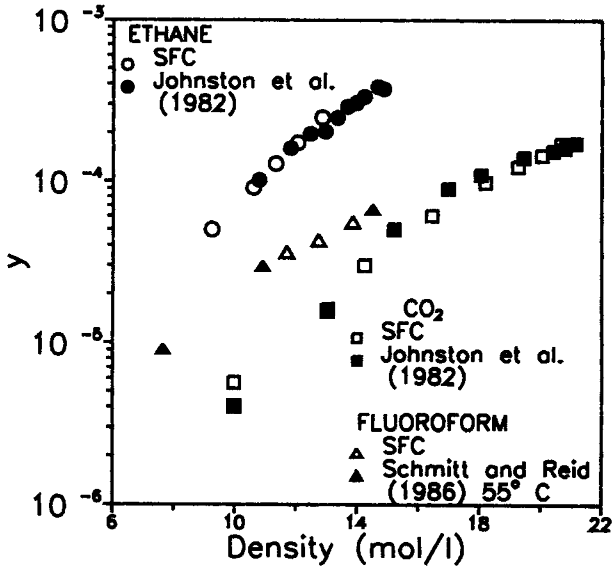


Figure 12. Solubility of anthracene in SCF's at 50°C; comparison between chromatographic measurements and literature.

This demonstrates the ability of the chromatograph to measure solubilities rapidly in a variety of fluids once C is known. Unfortunately, this requires independent measurements of solubility, unless C can be predicted. Brown et al. (1987) found a linear correlation between the log of the stationary phase Henry's constants for nonpolar, aromatic compounds with the product of the enthalpy of sublimation and the Peng-Robinson b parameter.

Examination of Eq. 8 shows that Henry's constant is the product of P_i^{vap}/C_i with a negligible exponential term and volume terms that are not solute dependent. In addition, equation of state volume parameters such as b should be roughly proportional to molar volume; thus, following the approach of Brown et al., we plotted P_i^{vap}/C_i vs. the product of the heat of sublimation and the molar volume for several solutes (Figure 13). The C_i's were determined by fitting the chromatographic data in ethane with the solubility data indicated in Table 3. There appears to be a reasonable correlation for this wide

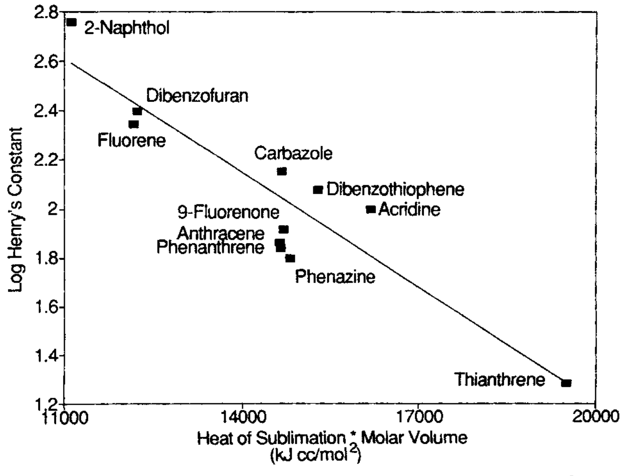


Figure 13. Correlation of C with solute properties.

variety of nonpolar and polar solutes. The scatter is within error due to the combination of the uncertainties in the vapor pressures, solubilities, and chromatographic retentions. This demonstrates that SCF chromatography can be used to measure solubilities even in the absence of independent data. The results may not be terribly accurate, but for many engineering applications, a reasonable estimate is all that is necessary. This technique complements traditional methods of solubility measurement, which are probably more accurate, but are more time-consuming and require large amounts of pure solute.

Conclusions

In summary, we used supercritical fluid chromatography to measure cosolvent effects for several solutes in diverse SCF solutions. Additionally, the solvents carbon dioxide, ethane, and fluoroform were compared. The results were qualitatively consistent with the expected intermolecular interactions, and provided us with new information on how these molecular level interactions contribute to the macroscopic cosolvent effect. Future studies will further delineate the effects of various chemical and physical interactions on solution behavior.

These studies, when complemented with spectroscopic investigations and computer simulations, will provide a more complete understanding of supercritical fluid solutions at all levels. Armed with this knowledge, researchers may finally achieve the goal of developing an accurate, predictive model of supercritical-phase behavior.

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Notation

a, b, s = solute-specific constants in linear solvation energy relationship
C = constant for solute in given chromatograph column
f = fugacity of solute
H = Henry's constant
k = capacity factor
P = total pressure
P^{vap} = vapor pressure
R = ideal gas constant
t_i = retention time of solute i
t_0 = retention time of unretained solute
T = temperature
v = molar volume
V = total volume
x = mole fraction of solute in stationary phase
XYZ = observable quantity correlated by linear solvation energy relationship
y = mole fraction of solute in supercritical fluid

Greek letters

α = Kamlet-Taft hydrogen-bond donor strength
β = Kamlet-Taft hydrogen-bond acceptor strength
π^* = Kamlet-Taft polarity/polarizability
ϕ = fugacity coefficient
Ψ = cosolvent effect

Superscripts and subscripts

o = reference state
∞ = property at infinite dilution
F = fluid phase
i = solute i
S = stationary phase
sat = property at saturation

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