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Supercritical Fluid Extraction of Trace Organics from Solid Matrices

by

Robert C. Burk

**A Thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of**

Doctor of Philosophy

Department of Chemistry

**Carleton University
Ottawa, Ontario
September 4, 1990
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Robert C. Burk

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the requirements for the degree of
Doctor of Philosophy

Chair, Department of Chemistry

Thesis Supervisor

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Abstract

The use of supercritical fluids for the extraction of trace amounts of organics from solid surfaces was investigated. The variables investigated were time, flowrate, pressure, temperature, type of solid matrix, type of solute, type of fluid, solid particle size and spike level. Single and binary supercritical fluids were used.

Supporting studies of solubilities of solutes in liquids were performed. Enthalpies of solution are reported. Solubilities in pure supercritical CO₂ and in CO₂ modified with small amounts of organic liquids were measured using a simple apparatus. The order of solubilities in modified CO₂ were found to be the same as in the pure liquid modifiers. Enthalpies of solution of several solutes in pure CO₂ are reported.

The adsorption of modifiers onto solid surfaces from the gas phase were measured. Enthalpies of interaction between solid and modifiers were measured. Measurements of adsorption of solutes onto solid surfaces from liquid solutions demonstrated that the surfaces were heterogeneous.

The adsorption of solutes onto solid surfaces from supercritical fluids were studied using a simple supercritical fluid chromatography apparatus, with environmental solids as the stationary phases. The retentions of various solutes were found to be functions of density of the solvent, as well as the type of solvent used. Modifiers tended to reduce retention. The effective heterogeneity of the surface of soil was shown to decrease as the concentration of methanol in the mobile phase was increased. This was attributed to increased adsorption of methanol on the surface. The retention of methanol by the soil was larger than that of the other modifiers used, thus explaining its effectiveness as a modifier.

The order of effectiveness of the modifiers was the same in solubility, adsorption and extraction experiments. This suggests that both surface-modifier and solute-modifier interactions are important. Some evidence suggests that the surface-modifier interactions are the more important ones in extractions.

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Many people have helped with this project in many ways. Most of all, my wife Ewa, and my daughter Ashley have helped by understanding why I had to spend so many evenings and weekends in the laboratory. It is to them that I dedicate this work.

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Publications and Presentations

This work has resulted in one publication so far (see reference 94). Two other publications are planned. Portions of the work have been presented at:

- MOE Technology Transfer Conference, Toronto (1988)
- Analytical Methods Development Seminars, Canada Center for Inland Waters, Burlington (1989)
- Suprex Workshop on Supercritical Fluid Extraction and Chromatography, Ottawa (1990)
- Canadian Chemical Engineering Conference, Halifax (1990)
- International Conference on Solution Chemistry, Ottawa (1990)
- MOE laboratories, Toronto (1989 and 1990)

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1. Introduction

1.1 Extraction of Organics from Solid Matrices by Conventional Means

Some environmental samples (such as polycyclic aromatic hydrocarbons (PAHs) in coke-oven effluents [1]) are rich enough in analytes that the analysis may be done directly, without separation of the analytes from the matrix. However, most samples of interest contain only traces of the desired analytes, at concentrations of $\mu\text{g g}^{-1}$ or lower. For example, benzo(a)pyrene, probably the most studied PAH, is present in cigarette smoke condensate at only 1–2 $\mu\text{g g}^{-1}$ [2]. Pesticides and their metabolites may be present at concentrations of 1 ng g^{-1} or lower. Efficient extraction is thus a necessity in order to effectively remove from the matrix and preconcentrate the analytes sufficiently before the analysis step.

For the purposes of this discussion, we assume that a representative sample of solid material has been taken. The subject of collecting samples has been reviewed by several authors [3,4].

Several methods exist for extracting trace organics from solid matrices. By far the most common are the methods which contact the solid with a liquid solvent. Small quantities of most PAHs, polychlorinated biphenyls (PCBs), insecticides, herbicides, etc are soluble in a wide variety of liquid solvents including cyclohexane, benzene, chloroform, acetone, and alcohols. A relatively simple extraction method is to simply mix the solids with the liquid solvent for several hours, filter off the solids, and then concentrate and analyze the solution. For example, Hagemann et al [5] collected diesel exhaust particulate on a glass filter fiber and extracted the organics in a mixture of 80% dimethyl sulfoxide and 20% cyclohexane for 12 hours.

Probably the most widely used extraction technique is the Soxhlet extraction, in which the solvent is refluxed through a bed of solids. There is essentially no agreement on the protocol for a Soxhlet extraction with respect to which solvent to use, how long to run the extraction, how many solvent cycles, etc. For example, for the extraction of PAHs from carbon black, various workers have suggested 2 hours [6], 12 hours [7], and 20–30 hours [8].

Some of the problems associated with liquid extraction are incomplete extractions, and in the case of very lengthy extractions, analyte decomposition.

Loss of analytes due to evaporation from solution, or adsorption onto glassware may also occur. Incomplete extraction may be minimized by increasing the extraction time, but the extraction step may become too lengthy for routine use. Loss of analytes due to evaporation may be minimized by operating at as low a temperature as possible, but this may slow the extraction process even more.

The potential for decomposition of analytes, and the length of time required for Soxhlet extractions makes the use of alternative extraction procedures attractive. For example, Hagemann et al [5] ultrasonically irradiated their liquid extractions to enhance the rate of desorption. Vacuum sublimation [9] and thermal desorption [10] have been used successfully. However, these methods require the analytes to be sufficiently volatile (a problem for high molecular weight compounds), and to not be thermally sensitive.

Hawthorne [11] summed up the state of conventional extraction technology as follows: "It is ironic that some modern chromatographic techniques have become so highly developed that they can separate, identify and quantitate hundreds of sample components per hour, yet analysts often rely on sample extraction procedures — such as liquid solvent extraction in a Soxhlet apparatus — that were in use when Tswett first reported chromatography in 1906."

1.2 Extraction of Organics from Solid Matrices Using Supercritical Fluids

The use of supercritical fluids to extract compounds from solid matrices has been shown to have a number of advantages over the use of conventional liquid solvents [12]. Probably the most beneficial aspect of supercritical fluid extraction (SFE) is the speed of an extraction. Typical extraction times are 20 to 30 minutes, compared to up to 48 hours for a conventional extraction. The technique is sensitive, since it is possible to extract large samples with small solvent volumes. Large preconcentrations are possible, since the solvent is usually a gas such as carbon dioxide, and is therefore easily removed from the extract. Thus, the use of hazardous solvents is reduced or eliminated. The ability to vary the density of a supercritical solvent allows somewhat selective extractions to be performed, thereby reducing the cleanup steps required after the extraction and before the instrumental analysis. Finally, SFE has been successfully coupled directly to a number of analytical techniques, such as gas chromatography (GC), liquid chromatography (LC), supercritical fluid chromatography (SFC), and Fourier transform infrared spectroscopy (FTIR).

Performing SFE on solid matrices involves three steps. First, the fluid must be compressed to supercritical conditions. Second, the fluid must be contacted with the solid to effect the extraction. Third, the solutes must be recovered from the supercritical fluid. Referring to figure 1.2.1, a plot of solubility versus density, solutes are extracted at high density, where their partition into the fluid phase is favorable. When the solutes have been carried away from the solid matrix, the density is lowered, usually by lowering the pressure, to a point where the solutes become relatively insoluble in the fluid and therefore precipitate out.

Many examples of the use of supercritical fluids for the extraction of trace organics from solids for analytical purposes have been reported in the literature. Some of the more outstanding ones, in terms of extraction methods and results, and equipment design are presented in this section.

1.2.1 Extraction Methods and Results

Schantz and Chesler [13] extracted PAH from an urban particulate sample, and PCB from a sediment using supercritical CO₂. Concentrations ranged

EXTRACTION PROCEDURE

COMPRESS SOLVENT

CONTACT PHASES

EXPAND SOLVENT, RECOVER SOLUTES

Figure 1.2.1

Generalized extraction procedure

from 2 to 8 $\mu\text{g g}^{-1}$. Supercritical carbon dioxide (345 bar, 40°C, 0.93 g mL⁻¹) was passed through the sample for 4 hours. The solutes were recovered by expanding the supercritical fluid through a fused silica capillary tube into a bed of C₁₈ column packing material. The C₁₈ column was then rinsed with dichloromethane to remove the solutes, and the dichloromethane was analyzed by GC or SFC. Recoveries of the PCB from the sediment were in agreement with those from a 16 hour methylene chloride Soxhlet extraction. Recoveries of the PAH from the urban particulate sample were actually greater than the certified values for the material. This publication is typical of many which have appeared since. Supercritical fluid extraction is faster, and sometimes offers more complete recoveries than conventional extraction methods.

Hawthorne and Miller [14] demonstrated several novel aspects of supercritical fluid extraction. They extracted PAH (1.2 to 51 $\mu\text{g g}^{-1}$) from Diesel exhaust particulate using supercritical CO₂ and CO₂ + 5% CH₃OH. Recoveries were quantitative in as little as 30 minutes, and there was no advantage gained from the addition of methanol. Again, the main advantage of the technique was found to be its speed, compared with that of a Soxhlet extraction. The authors also demonstrated the first direct coupling of the extraction cell with a gas chromatograph by inserting the restrictor into the on-column injection port and cryogenically trapping the extract at the head of the column. The potential for doing class selective extractions was demonstrated by extracting a sample of Diesel particulates first at 76 bar pressure, then at 304 bar. The first fraction contained predominantly alkanes, while the second contained predominantly PAH.

Hawthorne and Miller [15] extended their work to include extraction of PAH from other matrices such as urban dust, fly ash, and river sediment. The solvents used were supercritical CO₂, N₂O, ethane, CO₂ + 5% CH₃OH, and N₂O + 5% CH₃OH. The best recoveries from all three matrices were obtained with N₂O + 5% CH₃OH. Ethane and CO₂ gave roughly equal recoveries, a fact which the authors attributed to similar solubilities of PAH in CO₂ and ethane. Furthermore, the extraction efficiencies of high molecular weight PAH were lower than those of the low molecular weight PAH. This was also attributed by the authors to lower solubilities of the former.

Hawthorne and Miller [16] used supercritical N_2O to extract relatively high concentrations ($500 \mu\text{g g}^{-1}$) of PAH from river sediment. Again, the method was coupled SFE-GC, and the sample size was only 10–15 mg. Although recoveries were high, it should be noted that extraction and recovery of $500 \mu\text{g g}^{-1}$ using conventional liquid extraction techniques would not be a problem. Such a small sample size is required since the entire extract is deposited onto the head of the chromatographic column, and the use of a larger sample would result in severe overloading of the column. This may be a problem if a 10 mg sample is not representative of the material being extracted. The authors have defended this [HP Teleconference] by noting that in the cases of fly ash and river sediment, recovery and precision were not improved by the use of a larger sample.

Raymer and Pellizzari [10] used supercritical carbon dioxide to desorb a variety of environmentally significant compounds from *Tenax-GC*, a porous polymer used to adsorb compounds from ambient air. Representative compounds of chlorinated hydrocarbons, chlorinated aromatics, PAH, and organophosphate pesticides at levels of roughly $1 \mu\text{g g}^{-1}$ were extracted using CO_2 . Recoveries were calculated by the use of radiolabelled compounds and scintillation counting of the extracts. The authors found that approximately 14 extraction cell volumes of CO_2 (at 208 bar and 40°C) were required to desorb the compounds. The recoveries were much greater than those obtained using the conventional method, thermal desorption.

Wright et al [17] extracted a range of compounds from various adsorbent and particulate matrices. Matrices used included XAD-2 resin, polyurethane foam (PUF) plugs, and *Sphero carb* (an adsorbent generally reserved for volatile or semi-volatile adsorbates). Once again, the test compounds were PAH species, and were adsorbed onto the solids at a level of $50 \mu\text{g g}^{-1}$. The supercritical solvents used were CO_2 , $i\text{-C}_4\text{H}_{10}$, and $CO_2 + 20\% \text{CH}_3\text{OH}$. The more polar $CO_2 + \text{CH}_3\text{OH}$ mixture gave higher extraction efficiencies for the more polar adsorbates, which was attributed to specific solute-solvent interactions, and to deactivation of specific adsorbent sites. Isobutane was a better extractant for the lower molecular weight, less polar species. Extraction of PAH from *Sphero carb* was poor for both dichloromethane Soxhlet extractions, and supercritical fluid extractions using the

three solvents mentioned previously. Extraction of urban dust suggested that supercritical fluid extractions are more efficient (i.e. give higher recoveries) than conventional Soxhlet extractions, and can be completed in less than one tenth of the time.

Wright et al [18] also demonstrated the coupling of SFE to GC. Again, the extraction cell size was very small (15 μL). The authors demonstrated that PAH adsorbed on glass beads could be fractionated by extracting stepwise at progressively higher pressures in CO_2 , and recording a chromatogram at each pressure. The same procedure was applied to urban dust. The separation obtained was thought to be due to the different solubilities of the various PAH compounds in CO_2 . An effect of the matrix on extraction efficiencies was noted however, since the recoveries from the urban dust were not as complete as those from the glass beads.

Hawthorne and Miller [19] used their coupled SFE-GC technique to extract flavor and fragrance compounds from natural products. The chromatograms showed peak shapes comparable to those from injection of liquid samples. Once again, however, the concentrations of the compounds of interest were relatively high ($\approx 1000 \mu\text{g g}^{-1}$). A major advance was the coupling of the SFE-GC system to a mass spectrometer for the identification of extracted species. A major disadvantage of the coupled technique is that liquid modifiers cannot be used, since the entire sample is focused at the head of the column, and thus there is no way to remove the modifier before the chromatographic analysis.

The extraction of pesticides using supercritical fluids has been reported by several groups [20,21,22]. Engelhardt and Groß [23] extracted the non-polar pesticides Lindane, Aldrin, and p,p'-DDT from soil using CO_2 at 138 bar. Quantitative extraction of the pesticides at $10 \mu\text{g g}^{-1}$ was achieved with no interfering compounds being extracted. The report is also of interest because the SFE cell was coupled directly to an HPLC instrument via a sampling valve.

Schäfer and Baumann [24] extracted several pesticides from glass wool using supercritical CO_2 and water saturated supercritical CO_2 . Non-polar species, such as Linuron, Methoxychlor, and Diclofopmethyl were quantitatively extracted by both solvents. More polar species, such as 2,4-D and Diclofop were less than quantitatively extracted using CO_2 . Somewhat better extractions of these species

were obtained using water saturated CO_2 . The authors attributed this to increased solubility of the polar species in a more polar fluid such as CO_2 + water.

Moderately polar sulfonylurea pesticides were extracted from soil and plant materials by McNally and Wheeler [25], and analyzed using coupled SFE-SFC. A polar cosolvent, methanol, was necessary for quantitative extraction.

Janda et al [26] extracted *s*-triazine herbicides from river sediment using supercritical CO_2 , and methanol modified CO_2 . At concentrations of from 40 to 80 $\mu\text{g g}^{-1}$, recoveries ranged from 42.5% to 96.4%. Poor recoveries of some of the herbicides were attributed to low solubilities in the the supercritical CO_2 . By introducing some liquid methanol into the extraction cell prior to CO_2 extraction, recoveries were increased to from 90.2% to 96.4%. Essentially quantitative recoveries of the herbicides were obtained at concentrations as low as 28 ng g^{-1} using methanol modified CO_2 .

Extraction of more polar species using CO_2 presents more of a problem. Kim et al [27] reported on the extraction of phenol from activated carbon using CO_2 at 100–200 bar. The extraction was incomplete, and some of the phenol could not be removed at all. The proportion of "irreversibly" adsorbed phenol increased as the concentration of phenol on the activated carbon was decreased. This may indicate an inhomogeneous carbon surface, whereby more "active" sites on the surface adsorb the phenol more strongly. A smaller amount of phenol would thus be preferentially adsorbed onto more active sites, making its desorption more difficult.

The authors found that the extraction was enhanced at higher temperatures when operating at 200 bar pressure, but was enhanced at lower temperatures when operating at 100 bar. Since the solubility of phenol in the supercritical CO_2 would be enhanced under these conditions, the authors concluded that solubility of the solute in the extraction fluid is an important parameter in determining the extraction efficiency.

The argument that poor extraction efficiency is due to poor solubility does not make sense for a flow-through extraction system such as that described above. For example, Hawthorne and Miller [15] used approximately 20 mL of supercritical CO_2 to extract a 50 mg sample of fly ash spiked with 2 $\mu\text{g g}^{-1}$ of phenanthrene, pyrene, and perylene. The extraction efficiency of pyrene was about

8%; thus a total of only 8 ng of pyrene was extracted. The average concentration of pyrene in the CO₂ during the course of the extraction was thus $4 \cdot 10^{-14}$ g mL⁻¹. The data of Johnston et al [28] indicate that the solubility of pyrene in carbon dioxide under the same conditions of temperature and pressure is approximately $4 \cdot 10^{-8}$ g mL⁻¹. The pyrene was thus some six orders of magnitude below its saturation level during the extractions. It seems unlikely, therefore, that solubility *per se* was the cause for low extraction efficiencies.

The fly ash and river sediment extracted by Hawthorne and Miller contained equal concentrations of phenanthrene, pyrene, and perylene. Nevertheless, the extraction efficiencies from the river sediment were routinely greater than those from the fly ash. If the extraction efficiencies were determined by solubilities, we would expect the same extraction efficiencies for both matrices (and indeed all other matrices!) under the same extraction conditions. Clearly, solubility is not the only factor in determining extraction efficiencies.

1.2.2 Equipment Design

Proper design of equipment for supercritical fluid extraction is necessary to satisfy the following points:

1. The extraction system must be safe to use. The pressures involved are high (up to 400 bar) and the explosion of an extraction cell would involve the release of a considerable amount of energy.
2. The system must be easy to use. Specifically, it must be possible to do an extraction in a reasonable amount of time, with a minimum of special tools, and with a minimum amount of operator time.
3. The system must be reliable. Pressures and temperatures must be repeatable. The extraction cell must be durable. The pumping system should require a minimum amount of maintenance. The system should have a minimum dead volume to ensure the rapid and complete egress of extracted material from the extraction cell into the collection device.
4. The system should be flexible enough to handle different solid adsorbents and different extractants.

What follows is a brief review of the literature with respect to the equipment used for analytical scale supercritical fluid extraction.

There is a great variety of extraction cell designs. Hawthorne et al used small high pressure tubing fittings [16,19,29,30] for extraction cells. This type of cell generally has a small internal volume (≈ 0.2 mL). The addition of a piece of tubing between two end fittings can increase the volume to whatever volume is required [14,26]. Wright et al [18] fabricated a very small cell (≈ 15 μ L) by using a piece of capillary tubing between the two end fittings. The small volume was justified since the entire extract was being transferred directly onto a GC column for analysis. A 5 mL volume cell was made by Wright et al [17] by boring out a heavy stainless steel cylinder and lining it with a glass test tube. The sealing mechanism was a rather cumbersome lid bolted on over a double O-ring. Much larger cells (up to 100 mL) have been made out of discarded empty HPLC columns [10,13,23,25].

The pumping systems used usually fall into one of two categories: syringe pumps [10,16,18,19,26,29,30] and reciprocating plunger pumps [17,25]. The syringe pumps offer the advantage of rapid and pulse-free pressurization. The reciprocating plunger pumps offer the advantage of economy, being about one fifth the cost of syringe pumps. For an extraction which is not directly coupled to a supercritical analytical device, pulseless operation is not necessary. The major disadvantages of a reciprocating plunger pump are frequent maintenance requirements, and, in the absence of automatic pressure control, the need for constant operator involvement. A third type of fluid delivery system was described by Alexandrou and Pawliszyn [31]. In this system, a high pressure vessel at liquid nitrogen temperature is filled with the fluid to be used. The vessel is then placed in a heater, and the desired pressure is maintained by regulating the temperature of the vessel. This system has the obvious advantage of no moving parts.

For the use of mixed solvent systems, three schemes are in use. The first is the use of a syringe pump, which is filled with the main solvent after adding a measured amount of the modifier to the chamber [30]. The second is the use of two pumps operating in parallel, one pumping the main solvent, and the other pumping the modifier. Finally, the main solvent can be mixed with the modifier in a separate vessel, and the mixture pumped by one pump [17,32].

To maintain the pressure in an extraction system and to allow the recovery of the extract requires a restriction of some sort at the outlet. This may take the form of a short length of fused silica tubing with a small ($\approx 20\ \mu\text{m}$) id [16,18,19,26,29,30,31], a short length of capillary stainless steel tubing used as is [17] or crimped at the outlet with a wire cutter [10], or an HPLC back-pressure regulator [25]. When the extraction cell is coupled directly to a supercritical fluid chromatograph [13], the restrictor at the effluent end of the analytical column serves as the back-pressure device.

Collection of the extracted material can be done by immersing the restrictor in a small volume of a liquid solvent [10,26,29,30,31], by cryogenically trapping it in a large chamber which is subsequently washed out with liquid solvent [17], by trapping it on a solid sorbent [24], or by cryogenically trapping it at the head of a GC column [16,18,19]. See also the discussion of the work of Schantz and Chesler in section 1.2.1.

1.3 Purpose and Plan of Research

The purpose of this research project was to examine the use of supercritical fluids for the extraction of trace organics from solid matrices with the following objectives:

(i) to gather enough empirical extraction data to be able to make some general conclusions regarding such variables as pressure, temperature, time, type of fluid, type of adsorbent, type of adsorbate, adsorbent particle size and adsorbate concentration.

(ii) to examine the role of the modifier and determine the mechanism by which it enhances extraction.

(iii) to determine the reasons for any incomplete extractions.

(iv) to build and test a simple, reliable and inexpensive supercritical fluid extraction apparatus.

(v) to build an apparatus to measure solubilities of solids in supercritical fluids and to use the data to determine whether or not the solubility of the adsorbate in the supercritical fluid influences the efficiency of extraction.

(vi) to build and use a simple supercritical fluid chromatography system to measure the adsorption of various solutes on various adsorbents under supercritical conditions, and to relate the data from this system to the data from extractions.

1.4 Supercritical Fluids

1.4.1 Density

The conditions that define a supercritical fluid are those temperatures and pressures above the critical values T_c and p_c . Referring to the pressure – temperature for carbon dioxide in figure 1.4.1, the critical point is at T_c and p_c . At this point, the density of the fluid is the critical density, ρ_c . Strictly speaking, the supercritical region is above and to the right of the dashed lines in the area labelled "SCF" (supercritical fluid). Many workers define a fluid as being supercritical as long as its temperature is above T_c , no matter what the pressure is. This allows the thermodynamic formalism for gases to be used, and in practice allows continuous variation of the density of the fluid from zero upwards without crossing a phase boundary. If the temperature is near but below T_c , there is still a significant variation of fluid density above the gas–liquid equilibrium line. Thus, for practical purposes, we are not limited to pressures and temperatures above the critical values.

For simplicity, and for comparison of different fluids, the temperature, pressure and density of a system are often stated in terms of their reduced counterparts:

$$T_r = T/T_c \quad (1.4.1.1)$$

$$p_r = p/p_c \quad (1.4.1.2)$$

$$\rho_r = \rho/\rho_c \quad (1.4.1.3)$$

where T_r , p_r and ρ_r are the reduced values of the absolute temperature, pressure and density respectively.

With the above definitions in mind, the region of interest in supercritical fluid extraction is roughly $0.9 < T_r < 1.2$ and $0.9 < p_r < 3$. In the immediate vicinity of the critical point, the density of the fluid can be varied enormously by small changes in the temperature and/or the pressure. An example of this is shown in figure 1.4.2, a plot of reduced density of carbon dioxide versus reduced pressure at various values of reduced temperature. The fluid exists as a single phase to the right

Figure 1.4.1 pVT diagram for carbon dioxide

Figure 1.4.2

Reduced density of carbon dioxide versus reduced pressure

of the curved line passing through the critical point labelled "cp". On the isotherm at $T_r = 1.1$ (a temperature of 61.5°C for CO_2), the density can be varied from 0.10 g mL^{-1} at a pressure of 45 bar to 0.85 g mL^{-1} at a pressure of 300 bar. It is important to note that during such a compression, no phase boundary has been crossed. The fluid has remained as a single phase

The density further away from the critical point is not as strong a function of pressure. For example, consider the isotherm at $T_r = 1.55$ on figure 1.4.2. The density increases from 0.05 g mL^{-1} at 45 bar to only 0.45 g mL^{-1} at 300 bar. Below the critical temperature, the density is relatively high, but still not a strong function of pressure.

1.4.2 Equations of State

The equation of state relating the pressure, volume, and temperature of an ideal gas is

$$p = RT/V \quad (1.4.2.1)$$

where p is the pressure, R is the gas constant, T is the absolute temperature, and V is the molar volume of the gas. Equation 1.4.2.1 is the ideal gas law, and approximates reality only at low density, i.e. at low pressure or high temperature.

The first equation of state which described the critical region of fluids was proposed by van der Waals [33]. This equation expresses the total pressure as the sum of two terms; a repulsion pressure and an attraction pressure:

$$p = p_r + p_a \quad (1.4.2.2)$$

The repulsive forces between gas molecules tend to increase the average intermolecular distance, thus increasing the pressure, and decreasing the effective volume. The molar volume in equation 1.4.2.1 is therefore replaced by $(V - b)$, where b is a constant for a particular gas. The value of b will in general be larger for larger molecules, since they tend to reduce the effective volume by a larger amount than smaller molecules.

The attractive forces tend to reduce the pressure. The number of pairwise interactions is roughly proportional to the square of the concentration, or of the density. The reduction in pressure is therefore a/V^2 , where the value of a is again characteristic of a particular gas. The gas law may now be altered from the ideal form to the van der Waals form:

$$p = \frac{RT}{(V - b)} - \frac{a}{V^2} \quad (1.4.2.3)$$

By realizing that the first and second derivatives of p with respect to V vanish at the critical point, the critical constants are found to be

$$p_c = a/27b^2 \quad (1.4.2.4)$$

$$T_c = 8a/27Rb \quad (1.4.2.5)$$

$$\text{and} \quad V_c = 3b \quad (1.4.2.6)$$

These values for the critical constants suggest that the compression factor for a van der Waals gas at the critical point, z_c , should be:

$$\begin{aligned} z_c &= p_c V_c / RT_c \\ &= 0.375 \end{aligned} \quad (1.4.2.7)$$

The experimental values of z_c vary, and are somewhat less than this value.

Equation 1.4.2.3 can be expressed in terms of the reduced variables p_r , T_r , and V_r :

$$p_r = \frac{8T_r}{(3V_r - 1)} - \frac{3}{V_r^2} \quad (1.4.2.8)$$

where $T_r = t/T_c$, $p_r = p/p_c$, and $V_r = V/V_c$. This allows plots to be made relating p_r with V_r (at selected values of T_r) which are universal i.e. they are valid for any substance. Such a plot is shown in figure 1.4.3.

Note that to obtain figure 1.4.3, equation 1.4.2.8 was first expressed as a

Figure 1.4.3

Universal plot of $1/V_r$ versus p_r at various values of T_r

polynomial in V_r , and the roots were calculated numerically. The root corresponding to the gas phase was used, and figure 1.4.3 presents results above the critical temperature. The figure is plotted as $1/V_r$ versus p_r , since the density is proportional to $1/V_r$, and it is the density that is usually of interest in supercritical fluid extraction.

Many variations of the van der Waals equation have been proposed. One successful equation is that of Peng and Robinson [34]:

$$p = \frac{RT}{(V - b)} - \frac{a(T)}{V(V + b) + b(V - b)} \quad (1.4.2.9)$$

The main features of the equation are that the value of a (the intermolecular attraction constant) is dependent upon temperature and on the acentric factor, a measure of the non-sphericity of the molecule, and that the repulsive pressure term produces more realistic values of the critical compressibility, z_c .

The actual dependence of the factor a upon temperature is:

$$a(T) = a(T_c) \cdot \alpha(T_r, \omega) \quad (1.4.2.10)$$

where:

$$\alpha = (1 + \kappa(1 - \sqrt{T_r}))^2 \quad (1.4.2.11)$$

The constant κ is a characteristic for each substance, and was found by Peng and Robinson to be a function of the acentric factor:

$$\kappa = 0.37464 + 1.54266 \omega - 0.26992 \omega^2 \quad (1.4.2.12)$$

where the acentric factor was defined by Pitzer [35] as

$$\omega \equiv -\log_{10} \left[\frac{p^{sat}}{p_c} \right]_{T_r=0.7} - 1.000 \quad (1.4.2.13)$$

Note that p^{sat} is the saturation vapor pressure of the compound evaluated at a reduced temperature of 0.7. The constant b in equation 1.4.2.9 is assumed to have no temperature dependence.

Applying the Peng–Robinson equation at the critical point, the values of a , b , and z can be found:

$$a(T_c) = 0.45724 R^2 T_c^2 / p_c \quad (1.4.2.14)$$

$$b(T_c) = 0.07780 R T_c / p_c \quad (1.4.2.15)$$

and

$$z_c = 0.307 \quad (1.4.2.16)$$

A comparison of the density versus pressure curves at the critical temperature using the ideal, van der Waals, Peng–Robinson, and experimental values for CO_2 is made in figure 1.4.4. The ideal gas law is apparently of little value above a pressure of a few bar. The accuracy of the van der Waals equation is inadequate at high pressures. The Peng–Robinson equation appears reasonably accurate over a wide range of pressures.

1.4.3 Viscosity

The viscosities of gases below their critical points are essentially independent of pressure. Above the critical pressure, however, viscosity increases with pressure. Figure 1.4.5 shows the variation of viscosity of CO_2 with respect to pressure at various reduced temperatures. Below the critical temperature, the viscosity decreases with increasing temperature, an effect generally associated with liquids, not gases. The viscosities plotted in figure 1.4.5 are nevertheless lower than that of liquid CO_2 . This is true of most supercritical fluids; their viscosities are almost an order of magnitude lower than those of the corresponding liquids, and a few times greater than those of the corresponding gases.

Figure 1.4.4

Comparison of CO₂ density calculated from the ideal gas law (IGL), van der Waals (vdW) and Peng-Robinson (PR) equations of state with the experimental data (EX).

Figure 1.4.5

Viscosity of carbon dioxide versus pressure

1.4.4 Diffusion Coefficients

The diffusion coefficients in supercritical fluids are generally an order of magnitude higher than those in the corresponding liquids, and several orders of magnitude lower than those in the corresponding gases. This is one reason why extractions using supercritical fluids are much faster than those using liquids.

The self-diffusion coefficient of a substance D_{11} is inversely proportional to pressure below the critical pressure, and proportional to the square root of pressure above the critical pressure. The variation of D_{11} of CO_2 with pressure is shown in figure 1.4.6 [36]. The data points are included on the curve to emphasize that no data was collected near the critical point. Other studies [37] indicate anomalous behaviour of the self-diffusion coefficient in this region.

Of more importance to supercritical fluid extraction are the diffusion coefficients of solutes dissolved in the fluid. Several researchers have published such data. Feist and Schneider [38] determined the diffusion coefficients of benzene, phenol, naphthalene and caffeine in supercritical CO_2 . The method used was the measurement of chromatographic peak broadening. In this method, the chromatographic column is an empty capillary tube. With the absence of a stationary phase, the dispersion (broadening) of a sharp pulse of solute introduced into the mobile phase is governed only by convective and diffusive mass transfer of the solute. The diffusion coefficients in CO_2 at 40°C and a density of 0.8 g mL^{-1} are given in table 1.1, along with the diffusion coefficients of the same solutes in liquid benzene at 40°C . Note that the values for phenol, naphthalene and caffeine in benzene were estimated using the empirical correlation of Wilke and Chang [39]. The self diffusion coefficient for benzene is from reference 40.

Table 1.1. Diffusion Coefficients in CO_2 and in Benzene

	$D_{12}(\text{CO}_2)$ cm^2s^{-1}	$D_{12}(\text{C}_6\text{H}_6)$ cm^2s^{-1}
Benzene	$1.45 \cdot 10^{-4}$	$2.85 \cdot 10^{-5}$
Phenol	$1.20 \cdot 10^{-4}$	$2.45 \cdot 10^{-5}$
Naphthalene	$1.10 \cdot 10^{-4}$	$2.03 \cdot 10^{-5}$
Caffeine	$7.76 \cdot 10^{-5}$	$1.74 \cdot 10^{-5}$

Figure 1.4.6

Self diffusion coefficient of carbon dioxide versus density

1.4.5 Surface Tension

The surface tension γ of an interfacial surface may be defined [41] as

$$\gamma = \left[\frac{\partial F}{\partial A} \right]_{T,P,n_i} \quad (1.4.5.1)$$

where F is the total free energy of the interfacial system per unit area, ∂A is the change in interfacial surface area, and the differential is evaluated at constant temperature, pressure, and moles of all components comprising the interface.

In the case of a solid–liquid–gas interface, there will be three interfaces present: solid–liquid, solid–gas, and liquid–gas. The individual ΔA values may be determined by considering figure 1.4.7. The solid S is assumed to be planar and in contact with a liquid L and and gas G . The contact angle between the SL interface and the LG interface is θ . The situation can be represented by a drop of liquid in contact with a plane solid surface. We now let the drop spread outward a small distance so that the line of contact moves from a to b . The LG interface moves essentially parallel to itself and its surface area increases by $bc = ab \cos \theta$ per unit distance along the line. The SL interfacial area is increased by ab , and the SG interfacial area decreased by ab . At equilibrium, the total change in F must vanish. From equation 1.4.5.1 we have

$$\Delta F = \gamma_{sg}\Delta A_{sg} + \gamma_{sl}\Delta A_{sl} + \gamma_{lg}\Delta A_{lg} \quad (1.4.5.2)$$

from which

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta \quad (1.4.5.3)$$

which is known as Young's equation.

In a supercritical fluid, the liquid and gas phases are indistinguishable, and thus $\gamma_{sg} = \gamma_{sl}$. Furthermore, $\gamma_{lg} = 0$, and Young's equation becomes trivial for a supercritical fluid. A more useful construct is the spreading coefficient, S :

$$S = \gamma_{sg} - \gamma_{sl} - \gamma_{lg} \quad (1.4.5.4)$$

Figure 1.4.7

Three phase contact angle diagram

The value of S in a solid–liquid–gas system is greater than zero when the contact angle is greater than zero. If the contact angle is zero, experimental data has shown that S is equal to zero [41]. In a supercritical fluid, the contact angle is zero by definition. The spreading coefficient must also be zero, since $\gamma_{sg} = \gamma_{sl}$, and $\gamma_{lg} = 0$. This implies that there is no resistance to spreading of a supercritical fluid across a solid surface, and that the surface is therefore wetted completely by the fluid.

1.4.6 Thermodynamics of Binary Supercritical Fluids

The discussion on supercritical fluids has thus far only considered one component fluids. Since the use of modifiers is becoming commonplace, a discussion of the thermodynamics of binary supercritical fluids is in order.

During a supercritical extraction, it is desired to have the fluid phase remain as a single phase. This allows variation of the density, hence the solvating power, of the fluid without changing the composition. Therefore, it is important to understand the phase relationships in binary systems as functions of temperature and pressure so that operation in the supercritical region is ensured.

To understand the phase relationships among two or more components in a supercritical fluid, we begin with the phase rule of Gibbs:

$$F = C - P + 2 \quad (1.4.6.1)$$

where F is the number of independent variables required to completely describe the system, C is the number of components, and P is the number of phases. Thus, for a two component one phase system, there can be a maximum of three independent variables. A binary fluid can therefore be described by a three dimensional phase diagram involving pressure, temperature, and the mole fraction of one component. (Alternatively the molar volume could be used in place of one of these variables.) In such a "pTx" diagram, one phase is represented by a volume, equilibrium between two phases by a surface, and equilibrium among three phases by lines, i.e. intersections of two–phase surfaces. Also, the diagrams show equilibrium lines between two phases of a single component (e.g. vapor pressure lines), and critical lines of mixtures.

A pT_x diagram for a class I mixture (the classes are explained below) is shown in figure 1.4.8a. The two solid lines are the vapor pressure lines for the two components, and terminate at their respective critical points. The dotted line joining the two critical points is the locus of critical points of mixtures of the two components. Three isothermal planes are also shown for clarity.

A somewhat simpler method to present some of this information is to plot a projection (usually a pT or px projection) of the three dimensional pT_x diagram on a two dimensional diagram. For example, figure 1.4.8b is a pT projection of the vapor pressure lines and critical locus of figure 1.4.8a. This type of projection is used to classify the various types of binary phase diagrams.

Figure 1.4.8c is a px diagram of the constant temperature planes shown in figure 1.4.8a. Tie-lines relating the coexisting gas and liquid phases run horizontally. The critical locus curve is shown, emphasizing that the critical point of a mixture is not simply a linear function of the composition.

Based on px projections, binary mixtures can be grouped into six classifications [42]:

Class I. The two critical points are joined by a continuous line, and there is complete miscibility of the two liquid phases at all temperatures (figure 1.4.9a). The usual criteria for a binary mixture being a class I type are that the two components are of similar chemical type, and that their critical properties are similar. Some examples are $\text{CO}_2 + \text{O}_2$, $\text{CO}_2 + \text{C}_2\text{H}_6$, and benzene + toluene. The critical locus curve may pass through temperature and pressure maxima greater than the critical point of either component. This implies partial immiscibility of the two components, and since the conditions are supercritical with respect to either component, this must be considered fluid-fluid immiscibility.

Class II. Similar to class I, but there is liquid-liquid immiscibility at low temperatures, and the upper critical solution temperatures (UCSTs) are distinct from the gas-liquid critical line (figure 1.4.9b). Some examples are $\text{CO}_2 + n$ -heptane, n -pentane + nitrobenzene and water + phenol.

Class III. Class III mixtures have a discontinuous critical locus curve, as shown in figure 1.4.9c. There is another critical line joining the critical point of the more volatile component with an upper critical endpoint. Some examples are $\text{CO}_2 +$ large alkanes, and nitrogen + ammonia.

Figure 1.4.8

pTx , px and pT diagrams for a simple binary mixture

Figure 1.4.9

pT projections of the six binary mixture classifications

Class IV. The critical point of the less volatile component is joined by the critical locus curve to the lower critical endpoint of the other component (figure 1.4.9d). A second critical line is similar to that in class III mixtures. There is a region of liquid-liquid immiscibility at low temperatures. Some examples are CO_2 + nitrobenzene and methane + 1-hexene.

Class V. Similar to class IV, but without the liquid-liquid immiscibility region at low temperatures. The liquid-liquid-gas line may be so short that the mixture behaves as a class I mixture. Some examples are ethane + ethanol and ethane + 1-butanol. See figure 1.4.9e.

Class VI. Class VI behaviour results when the triple point temperature of one component is greater than the critical temperature of the other, and the critical curves intersect solid-liquid-gas equilibrium lines at the upper and lower critical endpoints (figure 1.4.9f). This behaviour is found in systems where there is hydrogen bonding between the two components, or in one of the pure components. One of the components is usually water. An example is water + 2-butanone.

1.4.7 Miscibilities of Organic Solvents with Carbon Dioxide

As outlined in section 1.2.2, one of the methods for using a binary mixture of CO_2 and a modifier is to mix the modifier with liquid CO_2 , and pump the mixture. This requires that the modifier be miscible with liquid CO_2 up to at least the desired concentration.

The solubilities of many common organic solvents in liquid CO_2 were published by Francis [43]. Methanol, acetone, and carbon tetrachloride were found to be miscible in all proportions with liquid CO_2 at 25°C . However, data is lacking on other solvents of interest, such as dichloromethane, tetrahydrofuran, hexane, dimethylsulfoxide (DMSO), and N-methyl pyrrolidinone (NMP). Dichloromethane, tetrahydrofuran and DMSO are of interest due to their high solvating powers. NMP is a solvent used in the petroleum industry for de-waxing operations. Hexane is of interest since it has been reported to have a solvating power roughly equal to that of CO_2 .

1.5 Solubilities in Liquids

1.5.1 Intermolecular Forces

The intermolecular forces which ultimately determine solubility and adsorption can be due to a number of phenomena. Coulombic forces between ions are simple in nature, and easily quantified. However, forces between neutral molecules of interest in this work are: (1) forces between two permanent dipolar molecules; (2) forces between a dipole and a quadrupole; (3) forces between permanent and induced dipoles; (4) forces between two non-polar molecules; and (5) repulsive forces.

The interaction energy between two permanent dipoles is

$$\epsilon_{dd} = -\frac{\mu_1\mu_2}{r^3} \left[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2 \cos(\varphi_1 - \varphi_2) \right] \quad (1.5.1.1)$$

where θ and φ are the polar coordinates giving the relative orientations of the dipoles with dipole moments μ_1 and μ_2 a distance r from one another. In the most favorable orientation, where the dipoles point along the line joining them, equation 1.5.1.1 reduces to

$$\epsilon_{dd} = -\frac{2\mu_1\mu_2}{r^3} \quad (1.5.1.2)$$

However, thermal motion of the molecules causes them to be in the best orientation only part of the time. Assuming interaction energies are considerably less than kT , the time averaged potential energy is approximated by

$$\bar{\epsilon}_{dd} = -\frac{2\mu_1^2\mu_2^2}{3r^6kT} \quad (1.5.1.3)$$

Carbon dioxide has a zero dipole moment, but it does have a significant quadrupole moment with which it can interact with dipolar species. The average potential energy between a dipole and a quadrupole can be expressed as

$$\bar{\epsilon}_{dq} = -\frac{\mu_1^2 Q_2^2}{r^8 k T} \quad (1.5.1.4)$$

where Q is the quadrupole moment.

A molecule with a permanent dipole can induce a dipole in another molecule because of the polarizability of the latter. The resulting force is attractive, and the average potential energy is

$$\bar{\epsilon}_{ind} = -\frac{1}{r^6} (\alpha_1 \mu_2^2 + \alpha_2 \mu_1^2) \quad (1.5.1.5)$$

where α_1 and α_2 are the polarizabilities of the two molecules.

Even when neither of the molecules has a permanent dipole, an attractive force between them exists due to dispersion or London forces. The magnitude of the force is

$$\epsilon_{disp} = -\frac{3}{2} \frac{\alpha_1 \alpha_2}{r^6} \cdot \frac{I_1 I_2}{I_1 + I_2} \quad (1.5.1.6)$$

where I_1 and I_2 are the ionization potentials of the two molecules.

In order to compare the magnitudes of the various intermolecular potential energies, dipole moments, polarizabilities and ionization potentials of the molecules are required. These quantities are presented in table 1.5.1. The dipole moments and ionization potentials were calculated (by Dr. Lee Collier of the Chemistry Department of Carleton University) using "AMPAC", a software package which performs LCAO (Linear Combination of Atomic Orbital) calculations. The polarizabilities were calculated using molar refractivities, as described by Atkins [44]. The quadrupole moment of CO_2 was taken as $-4.3 \cdot 10^{-26} \text{ erg} \cdot \text{cm}^{5/2}$ [45].

Table 1.5.2 presents the magnitudes of the four types of attractive potentials discussed above for the interaction of carbon dioxide with several of the solutes of interest in this work. A separation of 1 nm between the CO_2 and the solute was assumed in all cases. The two linear alkanes, *m*-terphenyl and chrysene have essentially zero dipole moment, and thus the dipole-quadrupole and induction potentials are low. Fluoranthene has a dipole moment of 0.56 D, resulting in small dipole-dipole and dipole-quadrupole forces. It is apparent that the dispersion forces

Table 1.5.1 Quantities used in Evaluating Intermolecular Potentials

Compound	Dipole Moment $\text{erg}^5 \text{cm}^{1.5}$	Polarizability cm^3	Ionization Potential eV	Quadrupole Moment $\text{erg}^5 \text{cm}^{2.5}$
CO_2	0	$2.63 \cdot 10^{-24}$	13.8	$4.3 \cdot 10^{-26}$
CH_3OH	$1.7 \cdot 10^{-18}$	$3.23 \cdot 10^{-24}$	10.8	
<i>n</i> -octadecane	$1.8 \cdot 10^{-20}$	$1.99 \cdot 10^{-24}$	10.8	
<i>n</i> -eicosane	$1.0 \cdot 10^{-21}$	$2.22 \cdot 10^{-24}$	7.7	
Fluoranthene	$5.6 \cdot 10^{-19}$	$2.07 \cdot 10^{-24}$	8.7	
<i>m</i> -terphenyl	$4.0 \cdot 10^{-21}$	$2.44 \cdot 10^{-24}$	8.9	
Chrysene	$5.0 \cdot 10^{-21}$	$2.36 \cdot 10^{-24}$	8.4	
2,3,4,5-tcp	$2.5 \cdot 10^{-18}$	$2.15 \cdot 10^{-24}$	10.0	

are the dominant ones between CO_2 and these solutes.

The results for the interaction of methanol with the same solutes are presented in table 1.5.3. The quadrupole moment of methanol was neglected in these calculations. Methanol has a significant dipole moment, and thus the induction forces are significant. Nevertheless, the dispersion forces are the dominant ones between methanol and non-polar solutes. The dipole-dipole potential between methanol and a polar solute such as 2,3,4,5-tetrachlorophenol is very large.

It should be noted that the assumption of molecule-centered point dipoles and polarizabilities is not very good when large molecules are involved. The numbers in tables 1.5.2 and 1.5.3 are therefore semi-quantitative at best.

Table 1.5.2. Potential Energies between CO_2 and Various Solutes

Solute	Dipole- Dipole 10^{-26} J	Dipole- Quadrupole 10^{-26} J	Induction 10^{-26} J	Dispersion 10^{-26} J	Total 10^{-26} J
<i>n</i> -octadecane	0	-.015	-.008	-760	-760
<i>n</i> -eicosane	0	.00004	-.00003	-690	-690
fluoranthene	0	-14.0	-8.2	-690	-712
<i>m</i> -terphenyl	0	-.0007	-.0004	-830	-830
chrysene	0	-.0011	-.0007	-770	-770
2345-tcp	0	-280.	-160.	-790	-1230

Table 1.5.3 Potential Energies Between CH₃OH and Various Solutes

Solute	Dipole-Dipole 10 ⁻²⁶ J	Induction 10 ⁻²⁶ J	Dispersion 10 ⁻²⁶ J	Total 10 ⁻²⁶ J
n-octadecane	-.15	-58	-830	-890
n-eicosane	-.0005	-64	-780	-840
fluoranthene	-.150	-70	-770	-840
m-terphenyl	-.008	-71	-920	-990
chrysene	-.012	-68	-860	-930
2345-tcp	-2900	-260	-866	-4000

A solute molecule can interact with a solid surface in the same ways as it does with another molecule in solution. Thus, surfaces with particularly polar functional groups (silica, for instance) would be expected to interact strongly with polar solutes through dipole-dipole and induction forces. Non-polar surface groups would interact with solutes via dispersion forces. The magnitudes of the interaction potentials will ultimately determine how much of a particular solute can be extracted from a surface using a particular solvent.

The repulsive forces between uncharged molecules take effect only at very small intermolecular distances. It is customary to represent the repulsive potential energy by an inverse power law:

$$\epsilon_r = j/r^n \quad (1.5.1.7)$$

where j is a constant, and n is usually 12. The Lennard-Jones potential reproduces the behaviours of some gases by combining equations 1.5.1.6 and 1.5.1.7 to give:

$$\epsilon = j/r^{12} - k/r^6 \quad (1.5.1.8)$$

1.5.2 Thermodynamics of Dissolution

The thermodynamics of the dissolution process are described as follows. A solid solute is assumed to be in equilibrium with a saturated solution of it:

The equilibrium equation for this process is:

$$K = \frac{a_{\text{soln}}}{a_{\text{solid}}} \quad (1.5.2.2)$$

where a_{soln} and a_{solid} are the activities of the solute in the saturated solution, and in the pure solid respectively, and K is the equilibrium constant. If the pure solid solute has unit activity, and if the solution is sufficiently ideal that mole fraction can be used in place of activity, the free energy of solution is:

$$\Delta G_{\text{soln}}^{\ominus} = -RT \ln(x) \quad (1.5.2.3)$$

where R is the gas constant, T is the absolute temperature, and x is the mole fraction of the solute in solution at saturation. Since $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$, we have:

$$\ln(x) = \frac{-\Delta H_{\text{soln}}^{\ominus}}{RT} + \frac{\Delta S_{\text{soln}}^{\ominus}}{R} \quad (1.5.2.4)$$

where $\Delta H_{\text{soln}}^{\ominus}$ and $\Delta S_{\text{soln}}^{\ominus}$ are the enthalpy and entropy of solution respectively. A plot of $\ln(x)$ versus $1/T$ should thus have a slope of $-\Delta H_{\text{soln}}^{\ominus}/R$, and an intercept of $\Delta S_{\text{soln}}^{\ominus}/R$. Experimentally, the requirement is to measure the mole fraction of a saturated solution as a function of temperature.

1.5.3 Solubility Parameters

A method for predicting solubilities from pure component data was proposed by Hildebrand [46]. A useful parameter for this purpose is the square root of the cohesive energy density:

$$\delta = \left[\frac{-E}{V_m} \right]^{.5} \quad (1.5.3.1)$$

where δ is called the solubility parameter and E is the energy of vaporization of the liquid to the gas at zero pressure. V_m is the molar volume of the liquid, or, in the case of a solid solute, the molar volume of the hypothetical liquid solute supercooled to the temperature of interest. The simplest method of calculating δ is to assume that at low vapor pressure, the gas in equilibrium with the liquid is ideal, and $-E$ may then be replaced by ΔE_v , the energy of vaporization. ΔE_v may in turn be replaced by $\Delta H_v - RT$, where ΔH_v is the molar heat of vaporization. Thus, we have:

$$\delta \approx \left[\frac{\Delta H_v - RT}{V_m} \right]^{.5} \quad (1.5.3.2)$$

Both ΔH_v and V_m are themselves functions of temperature, so the value of δ must be quoted at a specific temperature.

Hildebrand also pointed out that the solubility parameter may be estimated from an empirical correlation with the critical pressure:

$$\delta = 1.25\sqrt{p_c} \quad (1.5.3.3)$$

where p_c is expressed in atmospheres, and δ in $(\text{cal}/\text{cm}^3)^{.5}$.

Some representative values of solubility parameters of liquids are presented in figure 1.6.4 along with those of some supercritical fluids (see page 56).

The solubilities of solids can be predicted using solubility parameters in the following manner. The entropy of mixing of the solid with the solvent is:

$$\Delta S_{\text{mix}} = -R(x_1 \ln(x_1) + x_2 \ln(x_2)) \quad (1.5.3.4)$$

where x_1 and x_2 are the mole fractions of the solvent and solute respectively. The energy of mixing can be found from:

$$\Delta E_{\text{mix}} = V(\delta_1 - \delta_2)^2 \varphi_1 \varphi_2 \quad (1.5.3.5)$$

where φ_1 and φ_2 are the volume fractions of the solvent and solute respectively, and V is the molar volume of the mixture. Combining these two equations, we obtain the Helmholtz free energy of mixing:

$$\Delta A_{\text{mix}} = RT(x_1 \ln(x_1) + x_2 \ln(x_2)) + V(\delta_1 - \delta_2)^2 \varphi_1 \varphi_2 \quad (1.5.3.6)$$

Hildebrand makes the assumption that the partial molal Gibbs energy and the partial molal Helmholtz energy are equivalent, and writes for the partial molal Gibbs energy:

$$\Delta \bar{G}_2 = RT \ln(x_2) + V_2(\delta_1 - \delta_2)^2 \varphi_1^2 \quad (1.5.3.7)$$

where V_2 is the molar volume of the liquid solute supercooled to the temperature of interest, and is assumed to be equal to the molar volume of the pure solid solute.

The enthalpy of fusion of the solute at any temperature may be expressed in terms of the enthalpy of fusion at the melting point, ΔH_m^f , and the difference Δc_p between the heat capacities of the solid and liquid:

$$\Delta H^f = \Delta H_m^f + \int_{T_m}^T \Delta c_p dT \cong \Delta H_m^f - \Delta c_p(T_m - T) \quad (1.5.3.8)$$

and the entropy of fusion is:

$$\Delta S^f = \Delta S_m^f + \int_{T_m}^T \frac{\Delta c_p}{T} dT \cong \frac{\Delta H_m^f}{T_m} - \Delta c_p \ln \left[\frac{T_m}{T} \right] \quad (1.5.3.9)$$

Combining the last two equations, we obtain the Gibbs free energy of fusion:

$$\Delta G^f = \Delta H_m^f \left[1 - \frac{T}{T_m} \right] - \Delta c_p(T_m - T) + T \Delta c_p \ln \left[\frac{T_m}{T} \right] \quad (1.5.3.10)$$

Combining with equation 1.5.1.18, we obtain:

$$\Delta H_m^f \left[1 - \frac{T_m}{T} \right] - \Delta c_p (T_m - T) + T \Delta c_p \ln \left[\frac{T_m}{T} \right] + RT \ln(x_2) + V_2 (\delta_1 - \delta_2)^2 \varphi_1^2 = 0 \quad (1.5.3.11)$$

Converting to base 10 logarithms, we find for x_2 :

$$\log \left[\frac{1}{x_2} \right] = \frac{\Delta H_m^f}{4.575} \cdot \frac{(T_m - T)}{T_m T} - \frac{\Delta c_p}{4.575} \cdot \frac{(T_m - T)}{T} + \frac{\Delta c_p}{1.987} \log \left[\frac{T_m}{T} \right] + \frac{V_2}{4.575 T} (\delta_1 - \delta_2)^2 \varphi_1^2 \quad (1.5.3.12)$$

The terms involving Δc_p are usually unknown, and can be omitted without too much error, yielding:

$$\log \left[\frac{1}{x_2} \right] = \frac{\Delta H_m^f}{4.575} \cdot \frac{(T_m - T)}{T_m T} + \frac{V_2}{4.575 T} (\delta_1 - \delta_2)^2 \varphi_1^2 \quad (1.5.3.13)$$

In dilute solutions, $\varphi_1 \cong 1$, and the equation simplifies further:

$$\log \left[\frac{1}{x_2} \right] = \frac{\Delta H_m^f}{4.575} \cdot \frac{(T_m - T)}{T_m T} + \frac{V_2}{4.575 T} (\delta_1 - \delta_2)^2 \quad (1.5.3.14)$$

which is the desired result, relating the solubility of the solute to the temperature, some constants, and the solubility parameters of the solvent and solute.

In general, equation 1.5.3.14 predicts high solubilities of solutes in solvents with similar solubility parameters. Furthermore, solutes with lower enthalpies of fusion or lower melting temperatures are predicted to be more soluble. The equation must be used with caution, however, since it does not take into account the effects of specific intermolecular forces such as hydrogen bonding between the solute and solvent, and since several assumptions have been made in deriving the equation.

1.6 Solubilities in Supercritical Fluids

An intriguing aspect of the thermodynamics of supercritical fluids is the solubility of solutes. The extraordinary variation of solubility with density near the solvent's critical point first led to the idea that supercritical extraction could be a useful separation technique. For example, figure 1.6.1 is a plot of the solubility of hexamethylbenzene in ethylene at 45°C versus pressure [28]. The solubility is seen to increase from a mole fraction of $0.58 \cdot 10^{-4}$ at 63 bar to $119 \cdot 10^{-4}$ at 483 bar.

There have been several attempts to explain the observed solubilities in supercritical fluids. This section outlines some of the methods used.

1.6.1 Thermodynamic Analysis

1.6.1.1 Ideal Solubilities

According to Dalton's law of partial pressures, we would expect the mole fraction of a solute (subscript 2) in a gas to be simply the ratio of its vapor pressure to the total pressure;

$$y_2^0 = p_2^{\text{sat}}/p \quad (1.6.1.1)$$

where y_2^0 is the mole fraction of the solute in the gas phase, p_2^{sat} is the saturation vapor pressure of the solute, and p is the total pressure. The solubility of a solute at high pressures, however, may be several orders of magnitude greater than that predicted by this simple relation.

1.6.1.2 Enhancement Factors

Solubilities may be stated in terms of the enhancement factor, E ;

$$E = y_2 / y_2^0 \quad (1.6.1.2)$$

where y_2 is the actual solubility under the given conditions.

The solubility of a solid solute in a fluid at high pressure can be calculated provided that we know the fluid phase fugacity coefficient of the solute. To find the

Figure 1.6.1

Solubility of hexamethylbenzene in ethylene at 45° C versus pressure [28]

solubility, we first assume that the solubility of the fluid in the solid is negligible. Thus, the condensed phase is pure, and the only non-ideal behavior is of the fluid phase.

At equilibrium, the fugacity of the solute will be equal in the solid and the fluid phases;

$$f_2^s = f_2^f \quad (1.6.1.3)$$

The fugacity of the solid phase can be found from

$$RT \ln \left[\frac{f_2^s}{p} \right] = \int_0^p \left\{ V_2^f - \frac{RT}{p} \right\} dp \quad (1.6.1.4)$$

where V_2^f is the molar volume of the solute in the fluid phase. The integral can be separated into two integrals, one from zero pressure to the saturation vapor pressure of the pure solid solute, and the other from that point to the system pressure;

$$RT \ln \left[\frac{f_2^s}{p} \right] = \int_0^{p_2^{\text{sat}}} \left\{ V_2^f - \frac{RT}{p} \right\} dp + \int_{p_2^{\text{sat}}}^p \left\{ V_2^s - \frac{RT}{p} \right\} dp \quad (1.6.1.5)$$

where V_2^s is the molar volume of the pure solid solute.

The above equation can be rearranged to give

$$f_2^s = p_2^{\text{sat}} \cdot \phi_2^{\text{sat}} \cdot \exp \int_{p_2^{\text{sat}}}^p \left\{ \frac{V_2^s}{RT} dp \right\} \quad (1.6.1.6)$$

where ϕ_2^{sat} is the fugacity coefficient of the saturated vapor of the solid solute. Thus, ϕ_2^{sat} corrects for the deviations of the saturated vapor of the pure solid solute from ideality. The exponential factor is usually called the Poynting correction, and

accounts for the fact that the saturation vapor pressure of the pure solid solute is itself a function of pressure. If the solid is assumed incompressible, then V_2^s is not a function of pressure, and the Poynting correction is simply

$$\exp \left\{ \frac{V_2^s(p - p_2^{\text{sat}})}{RT} \right\} \quad (1.6.1.7)$$

The fugacity of the solute dissolved in the fluid phase is

$$f_2^f = \phi_2^f \cdot y_2 \cdot p \quad (1.6.1.8)$$

where ϕ_2^f and y_2 are the fluid phase fugacity coefficient and mole fraction of the solute, respectively. Equations 1.6.1.3, 1.6.1.6 and 1.6.1.8 are combined to give

$$y_2 = \frac{p_2^{\text{sat}}}{p} \cdot \left\{ \frac{\phi_2^{\text{sat}}}{\phi_2^f} \cdot \exp \int_{p_2^{\text{sat}}}^p \left[\frac{V_2^s}{RT} dp \right] \right\} \quad (1.6.1.9)$$

Inspection of equations 1.6.1.1 and 1.6.1.2 reveals that the enhancement factor, E , is the quantity in parentheses in equation 1.6.1.9.

If the solid solute is relatively non-volatile, then p_2^{sat} is small, and thus ϕ_2^{sat} is nearly unity. The Poynting correction is usually less than about 3. However, ϕ_2^f can be considerably less than unity, and thus enhancement factors of 10^3 are not uncommon.

To evaluate equation 1.6.1.9 requires, among other things, values for the fugacity coefficient of the solute in the fluid phase. Unlike equation 1.6.1.4, which is only for a pure substance, the fugacity of a substance in a fluid mixture requires information on the volumetric behaviour of a system, i.e. an equation of state. For a pressure explicit equation of state (i.e. pressure as a function of temperature and volume), the fugacity coefficient of the solute in the fluid phase can be found from

$$RT \ln(\phi_2^f) = \int_V^{\infty} \left\{ \left[\frac{\partial p}{\partial n_2} \right]_{T,V,n_1} - \frac{RT}{V} \right\} dV - RT \ln(z) \quad (1.6.1.10)$$

where z is the compressibility factor of the mixture ($z = pV/RT$), and where the partial differentiation of pressure with respect to n_2 must be evaluated from the equation of state.

Using equations 1.6.1.9 and 1.6.1.10, it can be shown that the solubility is expected to go through a minimum, then a maximum as the pressure is increased at constant temperature. At low pressure, the fluid phase is nearly ideal, and the solubility decreases with increasing pressure (equation 1.6.1.1). As the pressure is increased, the fluid becomes less ideal, ϕ_2^f decreases, hence the solubility increases. At high pressure (hence high densities), repulsive forces between the solute and solvent molecules dominate, and the solubility decreases again, resulting in a maximum.

Kurnik et al [47] demonstrated that the solubilities of several low-volatility solids in supercritical CO_2 could be adequately described using equation 1.6.1.10 coupled with the Peng–Robinson equation of state [34]. Fitting of a binary interaction parameter was necessary. Figure 1.6.2 is a plot of the solubility of benzoic acid in carbon dioxide at 45°C versus pressure. The points are experimental data. The solid line is the solubility predicted by the Peng–Robinson equation of state. The dashed line is the solubility predicted by the ideal gas law (without a correction for the compressibility of the solid).

The above treatment is not always successful due to the fact that supercritical solutions are far removed from an ideal reference state, which necessitates an empirical correlation of the interaction coefficients. The attraction constant in the van der Waals equation of state is usually obtained from critical data, but since the critical points of the solute and solvent may be far apart, corresponding states theory does not usually yield an accurate value for that constant. Wong et al [48] calculated the unlike interaction parameter from molecular volumes alone, which can be calculated rigorously from pure component properties. The result was a more accurate prediction of solubility isotherms.

Figure 1.6.2

Solubility of benzoic acid in CO_2 at 45°C . The points are from experiment (ref 47), the solid line is calculated from the Peng-Robinson equation of state and the dashed line is from the ideal gas law.

Ebeling and Franck [49] showed that the virial equation of state can yield the enhancement factor:

$$\ln(E) = (V_2^s - 2B_{12})/V^f \quad (1.6.1.11)$$

where B_{12} is the mixed second virial coefficient and V^f is the molar volume of the supercritical fluid phase.

The above outline and examples indicate that the enhancement factor is easily obtained if volumetric data or a pressure explicit equation of state are available. A volume explicit equation of state, however, can also yield the enhancement factor. For such an equation of state, the fugacity coefficient of the solute in the fluid phase can be found from

$$RT \ln(\phi_2^f) = \int_0^p \left\{ \left[\frac{\partial V}{\partial n_2} \right]_{T,p,n_1} - \frac{RT}{p} \right\} dp \quad (1.6.1.12)$$

The partial differential of volume with respect to the moles of solute is simply the partial molar volume of the solute in the fluid phase, which can be measured by methods not requiring an equation of state. For instance, Eckert et al [50] determined partial molar volumes in supercritical systems based on the variation of density with composition.

The effect of pressure on the fugacity coefficient is thus directly related to the partial molar volume of the solute, $\bar{v}_2$:

$$\left[\frac{\partial(\ln \phi_2^f)}{\partial p} \right]_{T,n_2} = \frac{\bar{v}_2}{RT} - \frac{1}{p} \quad (1.6.1.13)$$

Experimental data show that near the critical point of the solvent, the partial molar volumes of solutes are large and negative. The fugacity coefficient of a solute, and hence its solubility, are thus very sensitive to changes in pressure. This allows for recovery of solutes dissolved in supercritical fluids by simply reducing the pressure of the system.

1.6.2 Solubility Models

1.6.2.1 Expanded Liquid Model

Mackay and Paulaitis [51] determined the solubilities of low-volatility solutes in supercritical fluids by treating the supercritical fluid as an expanded liquid. The fugacity of the solute in the fluid phase is then

$$f_2^f = y_2 \gamma_2 f_2^{ol}(p^0) \cdot \exp \int_{p^0}^p \frac{V_2}{RT} dp \quad (1.6.2.1)$$

where y_2 is the solute mole fraction in the fluid phase, γ_2 is its activity coefficient, and f_2^{ol} is the fugacity of the pure liquid solute evaluated at reference pressure p^0 .

If the reference pressure p^0 is chosen to be the critical pressure, p_c , then the activity coefficient at infinite dilution, γ_2^∞ , and the partial molar volume at infinite dilution, $\bar{v}_2^\infty$, can be used effectively, since the concentration will be low. Thus, we have

$$f_2^f = y_2 \gamma_2^\infty f_2^{ol}(p_c) \cdot \exp \int_{p_c}^p \frac{\bar{v}_2^\infty}{RT} dp \quad (1.6.2.2)$$

The quantity $\bar{v}_2^\infty$ can be evaluated from the desired equation of state using

$$\bar{v}_2^\infty = \lim_{n_2 \rightarrow 0} \left[\frac{\partial V}{\partial n_2} \right]_{T, p, n_1} \quad (1.6.2.3)$$

The fugacity of the pure solid solute is

$$f_2^s = f_2^{os}(p_c) \cdot \exp \int_{p_c}^p \frac{V_2^s}{RT} dp \quad (1.6.2.4)$$

where V_2^s is the molar volume of the pure solid solute, and f_2^{os} is the fugacity of the pure solid solute at the reference pressure. At equilibrium, the fugacities of the solute in the fluid and solid phases must be equal. Thus, from equations 1.6.2.2 and 1.6.2.4, the solute mole fraction in the fluid phase is

$$y_2 = \frac{f_2^{os}(p_c) \exp\left[\frac{V_2^s (p - p_c)}{RT}\right]}{\gamma_2^m f_2^{ol}(p_c) \cdot \exp\left[\int_{p_c}^p \left[\frac{\bar{v}_2^m}{RT} dp\right]}\right]} \quad (1.6.2.5)$$

The ratio of the fugacities of the solute in the solid and liquid forms can be approximated by

$$\ln\left[\frac{f_2^{os}(p_c)}{f_2^{ol}(p_c)}\right] = \left[\frac{\Delta H_2^m}{R}\right] \cdot \left[\frac{1}{T_2^m} - \frac{1}{T}\right] \quad (1.6.2.6)$$

where ΔH_2^m and T_2^m are the enthalpy of fusion and normal melting temperature of the solid respectively. The value of γ_2^m may be found from experimental solubility data.

1.6.2.2 Equilibrium Model

One of the simplest models relating solubility to temperature and pressure was detailed by Chrastil [52]. In this model, k solvent molecules (B) are assumed to be in equilibrium with one solute molecule (A) by forming a solvato complex:

(The symbols A and B are preferred over subscripts 1 and 2 in this case). The equilibrium constant for the reaction can be written as

$$K = \frac{[AB_k]}{[A] [B]^k} \quad (1.6.2.8)$$

which can be rearranged to give

$$\ln(K) + \ln([A]) + k \cdot \ln([B]) = \ln([AB_k]) \quad (1.6.2.9)$$

The equilibrium constant K can be expressed as

$$\ln(K) = \frac{-\Delta H_s}{RT} + q_s \quad (1.6.2.10)$$

where ΔH_s is the enthalpy of solvation of the solute, and q_s is a constant. The vapour concentration of the solute can be found from the Clausius–Clapeyron equation, assuming that the solute is at a temperature well below its critical temperature:

$$\ln([A]) = \frac{-\Delta H_v}{RT} + q_v \quad (1.6.2.11)$$

where ΔH_v is the enthalpy of vapourization of the solute, and q_v is a constant.

Assuming $[A] \ll [AB_k]$, we have

$$\frac{-\Delta H}{RT} + q + k \cdot \ln([B]) = \ln([AB_k]) \quad (1.6.2.12)$$

where ΔH is the total enthalpy of reaction, $\Delta H_s + \Delta H_v$, and $q = q_s + q_v$. Note that we have assumed ΔH_s and ΔH_v to be independent of temperature.

We now note that

$$[AB_k] = \frac{c}{M_A + kM_B} \quad (1.6.2.13)$$

and

$$[B] = \frac{\rho}{M_B} \quad (1.6.2.14)$$

where c is the solute concentration (g L^{-1}), ρ is the density of the fluid (g L^{-1}), and

M_A and M_B are the molecular weights of the solute and solvent, respectively. Thus, from equation 1.6.2.12, we have

$$\frac{-\Delta H}{RT} + q + k \cdot \ln(\rho) - k \cdot \ln(M_B) = \ln(c) - \ln(M_A + kM_B) \quad (1.6.2.15)$$

which can be expressed as

$$c = \rho^k \cdot \exp(a/T + b) \quad (1.6.2.16)$$

where $a = -\Delta H/R$ and $b = \ln(M_A + kM_B) + q - k \cdot \ln(M_B)$. Therefore, a plot of $\ln(c)$ versus $\ln(\rho)$ will have a slope of k and an intercept of $a/T + b$.

The most striking feature of equation 1.6.2.16 is the prediction that solubility should increase with density, a phenomenon seen in practice. Furthermore, the solubility should decrease as the temperature is increased. (An equation of state may be used to predict the variation of density with temperature and pressure.) Chrastil determined the constants of equation 1.6.2.16 for several experimental systems.

Adachi and Lu [53] extended the work of Chrastil by considering the quantity k to be a function of density.

1.6.2.3 Density Dependent Model

Kumar and Johnston [54] modelled the solubility of solids in supercritical fluids using density as the independent variable. The impetus for this work was the fact that the solubilities of solids vary approximately linearly with density (e.g. reference 49). The thermodynamic treatment begins with the usual assumption that at equilibrium, the chemical potentials of the solute (subscript 2) in the solid and fluid phases are equal:

$$\mu_2^s = \mu_2^f \quad (1.6.2.17)$$

In terms of fugacity, we have

$$\mu_2 = RT \ln(f_2) + \lambda_2(T) \quad (1.6.2.18)$$

where λ_2 is a temperature dependent function. The fugacity of the solute, f_2 , may be expressed as

$$f_2 = \rho RT y_2 \psi_2 \quad (1.6.2.19)$$

where ρ is the density of the fluid, y_2 is the solute mole fraction in the fluid, and ψ_2 is the fugacity coefficient of the solute based on the density of the fluid phase. The function ψ_2 can be evaluated from an equation of state [45] using

$$\ln(\psi_2) = - \int_0^p \left[1 - \frac{\bar{v}_2}{RT\kappa_T} \right] d\rho \quad (1.6.2.20)$$

where $\bar{v}_2$ is the partial molar volume of the solute in the fluid phase, and κ_T is the isothermal compressibility of the fluid.

Equation 1.6.1.9 can be simplified to

$$y_2 = \frac{p_2^{\text{sat}}}{p\phi_2^f} \cdot \exp \left\{ \frac{V_2^s p}{RT} \right\} \quad (1.6.2.21)$$

(by assuming that ϕ_2^{sat} is unity, that equation 1.6.1.7 can be used for the Poynting correction, and that $p_2^{\text{sat}} \ll p$). By noting that $\psi_2 = \phi_2^f p / \rho RT$, we have

$$y_2 = \left[\frac{p_2^{\text{sat}}}{\rho RT \psi_2} \right] \cdot \exp \left\{ \frac{V_2^s p}{RT} \right\} \quad (1.6.2.22)$$

An understanding of the dependence of ψ_2 on density allows the prediction of solubility on density. Some experimental results suggest that the quantity $\bar{v}_2/\kappa_{T,1}$ is independent of density, and thus the expression for ψ_2 is

$$\ln(\psi_2) = \left[1 - \frac{\bar{v}_2}{RT\kappa_T} \right]_{\rho_r=1} \ln \rho_r + C_1 \quad (1.6.2.23)$$

where C_1 is an integration constant. Upon substitution of equation 1.6.2.23 into equation 1.6.2.22, we obtain the dependence of the solubility of a solute in a supercritical fluid in the vicinity of the critical point:

$$\ln(y_2) = -C_2 + \ln \left[\frac{p_2^{\text{sat}}}{\rho_c RT} \right] + \frac{pV_2^s}{RT} - \left[\frac{\bar{v}_2}{RT\kappa_T} \right]_{\rho_r=1} \ln(\rho_r) \quad (1.6.2.24)$$

Equation 1.6.2.24 can be simplified by noting that in the critical region, $\bar{v}_2 \gg V_2^s$. The first three terms can thus be combined into one constant yielding

$$\ln(y_2) = C_0 - \left[\frac{\bar{v}_2}{RT\kappa_T} \right]_{\rho_r=1} \ln(\rho_r) \quad (1.6.2.25)$$

If, as other experimental data suggest, the quantity $\bar{v}_2/\rho\kappa_T$ is independent of density, the final result is

$$\ln(y_2) = C_0' - \left[\frac{\bar{v}_2}{RT\kappa_T\rho} \right]_{\rho_r=1} \rho_r \quad (1.6.2.26)$$

Depending on the system, the log of the mole fraction of the solute is predicted to vary linearly with either the density or the log of the density.

Note that the equilibrium model, equation 1.6.2.16, predicts that $\ln y_2$ should vary with $\ln \rho$.

1.6.2.4 Solubility Parameters

The definition of solubility parameters for supercritical fluids is complicated by the fact that the quantity is usually calculated from the enthalpy of vapourization, which is zero in a supercritical fluid. An empirical correlation based on studies of liquid chromatography was proposed by Giddings et al [55]. They proposed that the solubility parameter of supercritical fluids be a product of a "state effect" represented by ρ_{rs}/ρ_{rl} , where ρ_{rs} is the reduced density of the supercritical fluid, and ρ_{rl} is the reduced density of the liquid at its boiling temperature, and a "chemical effect" represented by the square root of the critical pressure. The equation proposed by Giddings et al was

$$\delta = 1.25\sqrt{p_c} \cdot \rho_{rs} / \rho_{rl} \quad (1.6.2.27)$$

Note that this is simply the empirical correlation of Hildebrand (equation 1.5.3.3) with a correction for the density of the fluid. Although equation 1.6.2.27 predicts qualitatively correctly, its quantitative predictions are poor [56].

Allada [57] proposed a modified version of equation 1.5.3.1:

$$\delta = [(E^* - E)/V] \cdot^5 \quad (1.6.2.28)$$

where E^* is the internal energy of the fluid isothermally expanded to near zero pressure where the intermolecular distance is infinite and the intermolecular force is zero, and where E and V are the internal energy and molar volume of the supercritical fluid. Allada modified the above equation to express δ for any fluid in terms of reduced temperature and pressure:

$$\delta_r = \left[\frac{(E^* - E)p_r}{RT_c T_r z} \right] \quad (1.6.2.29)$$

where δ_r is the reduced or generalized solubility parameter $\delta/\sqrt{p_c}$, T_r and p_r are the reduced temperature and pressure respectively and z is the compressibility factor.

The quantities $(E^* - E)/T_c$ and z may be evaluated from an equation of state as follows. If all the nonidealities of the fluid are included in the compressibility factor, we have

$$pV = zRT \quad (1.6.2.30)$$

where z is a function of T_r , p_r , and z_c , the critical compressibility factor. It can be shown [45] that

$$\left[\frac{H^* - H}{T_c} \right]_T = \left[RT_r^2 \int_0^{p_r} \left[\frac{\partial z}{\partial T_r} \right]_{p_r} \frac{dp_r}{p_r} \right]_T \quad (1.6.2.31)$$

and that

$$\frac{E^* - E}{T_c} = \frac{H^* - H}{T_c} - (1 - z)RT_r \quad (1.6.2.32)$$

Figure 1.6.3 (reproduced from reference 57) is a plot of the reduced solubility parameter δ_r versus the reduced pressure at various reduced temperatures. The lines were calculated using equations 1.6.2.29 to 1.6.2.32. For a given temperature, the solubility parameter rises with increasing pressure. To illustrate the sensitivity of the solubility parameter to pressure, table 1.6.1 presents the calculated solubility parameter of CO_2 versus pressure at a temperature of 40.5°C (a temperature used for extraction throughout this work). It is apparent from table 1.6.1 that the solubility parameter of CO_2 can be markedly increased simply by increasing the pressure. To compare the solubility parameters of several supercritical solvents and liquids, figure 1.6.4 was reproduced from reference 58.

Figure 1.6.3

Reduced solubility parameter versus reduced pressure at various reduced temperatures

Figure 1.6.4

Scale of Hildebrand solubility parameters for liquids and supercritical fluids

Table 1.6.1. Solubility Parameter of CO₂ versus Pressure at 40.5° C

Pressure, bar	δ , (cal mL ⁻¹) ^{1/2}
80	2.6
100	4.6
150	6.0
200	6.5
300	7.0

1.6.3 Effects of Modifiers on Solubilities

Compared to the amount of data available on unmodified supercritical fluids, relatively little has been published on the effects of added modifiers on the solubilities of solids. Peter et al [as quoted in reference 59] were apparently the first to use a small amount of a miscible organic compound to increase the solubility of a solute in a supercritical fluid. The modifiers commonly used are liquids such as methanol, acetone, hexane, carbon tetrachloride, dichloromethane, benzene and water.

Although modifiers are usually liquids with volatilities between those of the supercritical solvent and the solute to be extracted, solids may also be interpreted as being modifiers. For instance, Kurnik and Reid [60] found that the solubility of phenanthrene in CO₂ was increased significantly when naphthalene was present, and vice-versa.

Brunner [61] measured the solubilities of hexadecanol and octadecane in supercritical CO₂ and in supercritical CO₂ modified with small amounts of one of n-hexane, cyclohexane, methylene chloride, benzene, methylacetate, acetone or methanol. At low temperatures (less than 80° C), the solubility of both compounds increased markedly with increasing modifier concentration. Brunner concluded that chemical similarity of the solute to the solvent was the most important factor in determining solubility. This observation is in agreement with the overused adage that "like dissolves like".

Sunol et al [62] attempted to simplify the choice of modifier for an extraction by considering the effects of solute-solvent interactions, specifically hydrogen bonding, on the solubilities of solutes. The assumption was that the solute-solvent interactions were the dominant ones in an extraction. This may not be the case for the extraction of solutes from solid matrices where the solute-matrix interactions are very strong.

Schmitt and Reid [59] measured the solubilities of phenanthrene and benzoic acid in supercritical CO_2 modified with benzene, acetone, methylene chloride or cyclohexane. The solubilities of both solutes increased with increasing modifier concentration, but the choice of modifier made little difference to the observed solubilities at a relatively high pressure (202 bar). At lower pressures, where the solubility is a much stronger function of pressure, one would expect the differences in solubilities to be more pronounced.

Walsh et al [63] proposed that the effect of the modifier was due to a chemical association between the solute and the modifier. Infrared absorption measurements in systems of the solutes in liquid modifiers were used to support this hypothesis. The authors suggested that such measurements could be used to predict the effect a particular modifier could have on the solubilities in a particular system.

The use of spectroscopic measurements to infer the local composition of a modified supercritical fluid about a solute molecule has been reported [64]. Such measurements indicated that the region around a solute molecule may be significantly enriched with respect to the modifier compared to the bulk fluid phase. For example, in a mixture of CO_2 + .051 mole fraction 2-propanol, the composition of the 2-propanol about the solute (2-nitroanisole) was calculated to be as high as 0.2 mole fraction. These results support the idea that there are specific modifier-solute interactions which lead to higher solubilities in modified fluids. In this particular case, the interactions are undoubtedly hydrogen bonding between 2-propanol and 2-nitroanisole.

Since the specific solute-solvent interactions vary from one solute to another, the selectivity (the ratio of the solubilities of two different solutes) can also be markedly influenced by the choice of entrainer. For example, the separation factor of hexadecanol to octadecane in pure nitrous oxide at 120 bar and 70°C is 2.0 [61]. With the addition of 1.5 wt% hexane, the factor drops to 1.7. With the addition of

1.5 wt% acetone instead, the factor increases to 3.0.

1.6.4 Published Experimental Methods and Results

The usual method for measuring solubilities of solids in supercritical fluids is to pass the fluid through a thermostatted bed of the solid sufficiently long to ensure saturation, and then to collect and analyze a portion of the saturated solution. McHugh and Paulaitis [65] used two equilibrating cells in series, each with a volume of 32 mL, and packed with a mixture of solute and glass beads. The fluid was passed through the beds of solute and through a sampling valve. A sample was trapped in a sample loop on the valve, then washed out with liquid solvent and analyzed by gas chromatography.

Kosal and Holder [66] had a similar setup to the one described above, except that the saturated solution was expanded through a heated valve into liquid toluene to trap the solids.

Brandani et al [67] measured the solubilities of several solids in supercritical CO₂ by measuring the loss in weight of a small sample of the solid suspended for a time in the stirred fluid.

Schafer and Baumann [68] used an extraction apparatus with the extraction cell loaded with the solute to be tested. The outlet of the apparatus was connected through a sampling valve to an HPLC for analysis. The solubilities of six pesticides in CO₂ at 200 bar and 40° C are shown in table 1.6.2.

Table 1.6.2 Solubilities of Some Pesticides in CO₂ at 200 bar and 40° C [68]

Compound	Solubility (g L ⁻¹)
Linuron	4.3±0.2
Methoxychlor	3.8±0.1
Dichlofopmethyl	8.5±0.4
Dichlofop	0.34±0.07
2,4-D	0.43±0.06
3,4-Dichloroaniline	11.6±0.5

Two interesting points are evident from the data in table 1.6.2. First, the solubilities of the acids dichlofop and 2,4-D are much lower than the non-acidic pesticides. Second, methylation of dichlofop increases the solubility by a factor of 25.

Schaeffer et al [69] measured the solubility of monocrotaline in CO_2 + ethanol mixtures at 274 bar and 45.0°C. The solubility (expressed as mole fraction) increased from $0.323 \cdot 10^{-4}$ in pure CO_2 to $1.49 \cdot 10^{-4}$ in CO_2 + 5% ethanol to $2.16 \cdot 10^{-4}$ in CO_2 + 10% ethanol. The CO_2 and ethanol were delivered to the system by separate metering pumps.

Ohgaki et al [70] measured the solubilities of indole and its derivatives in supercritical CO_2 , C_2H_4 , C_2H_6 and CHF_3 . The method used a static equilibration cell coupled with SFC for analysis. The solubilities of all the compounds tested were highest in CHF_3 , which the authors attributed to the dipole of CHF_3 .

Saraf and Kiran [71] measured the solubilities of polystyrenes of various molecular weights in supercritical *n*-butane and *n*-pentane. The work was of interest because the concentrations were determined using an on-line optical absorbance measurement scheme.

Ebeling and Franck [49] determined the solubility of caffeine in supercritical CO_2 spectroscopically. The solubility at constant density was shown to decrease with increasing temperature. At a CO_2 density of 0.55 g mL^{-1} , the enthalpy of solution was determined to be roughly 70 kJ mol^{-1} .

1.7 Adsorption

1.7.1 Adsorption of Gases

Evaluation of the adsorption of gases on a solid surface requires a functional form of the relationship between the gas pressure and the extent of adsorption. The derivation given below is essentially that of Langmuir [72].

The surface is assumed to consist of a number S of identical adsorption sites of which S_1 are occupied and S_0 ($=S-S_1$) are unoccupied. The rate of desorption from the surface is proportional to S_1 , or equal to k_1S_1 , and the rate of adsorption proportional to the unoccupied surface S_0 and the gas pressure, or equal to k_2pS_0 . At equilibrium, the rates will be equal:

$$k_1S_1 = k_2pS_0 = k_2p(S - S_1) \quad (1.7.1.1)$$

Since S_1/S equals θ , the fraction of surface covered, the above equation may be written in the form

$$\theta = \frac{bp}{1 + bp} \quad (1.7.1.2)$$

where $b = k_2/k_1$. The quantity θ may be replaced by n/n^w , where n is the number of moles adsorbed per gram of adsorbent, and n^w is the same quantity at monolayer coverage of the surface:

$$n = \frac{n^w bp}{1 + bp} \quad (1.7.1.3)$$

The above equation can be put in a linear form:

$$\frac{p}{n} = \frac{1}{bn^w} + \frac{p}{n^w} \quad (1.7.1.4)$$

and thus a plot of p/n versus p should have a slope of $1/n^w$ and an intercept of $1/bn^w$.

The isosteric (i.e. equal surface coverage) enthalpy of adsorption may be determined as follows. The chemical potential of the adsorbate may be defined as

$$\mu_a = \left[\frac{\partial U_a}{\partial n_a} \right]_{s,v,n_g} \quad (1.7.1.5)$$

where U_a is the internal energy and n_a is the amount of the adsorbate, and the conditions are those of constant entropy, volume, and amount of adsorbent n_s . When the adsorbate is in equilibrium with the gas, we have

$$\mu_a = \mu_g \quad (1.7.1.6)$$

and

$$d\mu_a = d\mu_g \quad (1.7.1.7)$$

where μ_g is the chemical potential of the gas. If the gas is assumed ideal, $d\mu_g$ is given by

$$d\mu_g = -S_g dT + V_g dp + \left[\frac{\partial G_g}{\partial n_g} \right]_{T,p} dn_g \quad (1.7.1.8)$$

For the adsorbate, the expression is

$$d\mu_a = -S_a dT + V_a dp + \left[\frac{\partial G_a}{\partial n_a} \right]_{T,p} dn_a \quad (1.7.1.9)$$

At constant n_a and n_g , the above three equations give

$$(S_g - S_a) dT = (V_g - V_a) dp \quad (1.7.1.10)$$

or

$$\left[\frac{\partial p}{\partial T} \right]_{n_a} = \frac{(S_g - S_a)}{(V_g - V_a)} \quad (1.7.1.11)$$

Since $V_g \gg V_a$, and assuming $V_g = RT/p$, we have

$$\left[\frac{\partial \ln(p)}{\partial T} \right]_{n_a} = (S_g - S_a)/RT \quad (1.7.1.12)$$

or

$$\left[\frac{\partial \ln(p)}{\partial T} \right]_{n_a} = -\Delta S_a/RT \quad (1.7.1.13)$$

where ΔS_a is the isosteric entropy change of adsorption. Since at equilibrium

$$\Delta H_a = T\Delta S_a \quad (1.7.1.14)$$

where ΔH_a is the isosteric enthalpy of adsorption, we have

$$\left[\frac{\partial \ln(p)}{\partial T} \right]_{n_a} = -\frac{\Delta H_a}{RT^2} \quad (1.7.1.15)$$

When integrated, this expression allows the calculation of ΔH_a from adsorption isotherms obtained at two or more temperatures. If isotherms are available for only two temperatures, ΔH_a can be found from

$$\Delta H_a = -\frac{RT_1T_2}{T_2 - T_1} \cdot (\ln(p_2) - \ln(p_1))_{n_a} \quad (1.7.1.16)$$

where p_1 and p_2 are the equilibrium pressures at temperatures T_1 and T_2 respectively, when the amount adsorbed is n_a .

The enthalpy of adsorption must be calculated under isosteric conditions because of the effects both of energetic heterogeneity of the adsorbent surface and of the interaction of adsorbed molecules in the adsorbed layer. For the purposes of comparison of different systems, the calculation is often made at $n_a = .5n^w$, where n^w is calculated as described above.

1.7.2 Adsorption from Liquids

The formulation for the adsorption of a solute from a solution assumes the equilibrium process is:

where the subscript 'a' refers to an adsorbed species and 's' refers to a species in solution.

Thus, at equilibrium, we have

$$\mu_2^s = \mu_2^a \text{ and } \mu_1^s = \mu_1^a \quad (1.7.2.2)$$

where, to be consistent, we are using the subscripts 1 and 2 for the solvent and solute, respectively. The chemical potentials in equation 1.7.2.2 are related to the activities of the species by the following equations:

$$\mu_1^a = \mu_1^{a^\ominus} + RT \ln(a_1^a) \quad (1.7.2.3)$$

$$\mu_1^s = \mu_1^{s^\ominus} + RT \ln(a_1^s) \quad (1.7.2.4)$$

$$\mu_2^a = \mu_2^{a^\ominus} + RT \ln(a_2^a) \quad (1.7.2.5)$$

$$\mu_2^s = \mu_2^{s^\ominus} + RT \ln(a_2^s) \quad (1.7.2.6)$$

where 'a' is activity, and the superscript $^\ominus$ refers to the standard state for the particular phase. For the solution phase, the standard state of the solvent would be the pure solvent at 25°C, and that of the solute would be the hypothetical ideal solute at unit concentration in the solvent. For the adsorbed phase, the standard state would be the (hypothetical) fully covered surface.

Assuming the surface phase to behave ideally, we may use the solvent and solute surface mole fractions, x_1^a and x_2^a , in place of the surface activities. Similarly, concentrations in solution, c_1 and c_2 , may be used in place of the solution phase activities.

The equilibrium constant for the equilibrium written in equation 1.7.2.1 is

$$K = \frac{x_2^a c_1}{x_1^a c_2} \quad (1.7.2.7)$$

If we restrict ourselves to dilute solutions (usually the case for analytical extractions), then c_1 is essentially constant. Setting $b=K/c_1$, and noting that $x_1^a + x_2^a = 1$, equation 1.7.2.7 becomes

$$x_2^a = \frac{bc_2}{(1 + bc_2)} \quad (1.7.2.8)$$

If n^w is the total number of moles of adsorption sites per gram of adsorbent, then the number of moles of solute adsorbed is

$$n_2^a = x_2^a n^w \quad (1.7.2.9)$$

Thus, equation 1.7.2.8 can be written

$$n_2^a = \frac{n^w bc_2}{(1 + bc_2)} \quad (1.7.2.10)$$

The two constants in the above equation can be evaluated by casting the equation in the form:

$$\frac{c_2}{n_2^a} = \frac{1}{n^w b} + \frac{c_2}{n^w} \quad (1.7.2.11)$$

Thus, a plot of c_2/n_2^a versus c_2 will give a straight line of slope $1/n^w$, and an intercept of $1/n^w b$.

The equilibrium constant in equation 1.7.2.7 can also be written as

$$\begin{aligned} K &= \exp(-\Delta G^\ominus/RT) \\ &= \exp(\Delta S^\ominus/R) \cdot \exp(-\Delta H^\ominus/RT) \end{aligned} \quad (1.7.2.12)$$

where $\Delta G^\ominus$, $\Delta S^\ominus$ and $\Delta H^\ominus$ are the net free energy, entropy, and enthalpy changes of the reaction as written (equation 1.7.2.1). This allows calculation of the values of $\Delta S^\ominus$ and $\Delta H^\ominus$ by plotting $\ln(K)$ versus $1/T$. Recalling that $b=K/c_1$, it is apparent that the value of $\Delta H^\ominus$ can be gained from a plot of $\ln(b)$ versus $1/T$.

There is generally an inverse relationship between the extent of adsorption on a specific matrix, and the solubility of the solute in the solvent used [72]. In other words, a very soluble solute will not adsorb extensively, because its chemical potential in the solution will be lower relative to that in a "poor" solvent. Thus a "good" solvent affects $\Delta S^\ominus$ and $\Delta H^\ominus$ in such a way that K is reduced, and the desorption of the solute from the adsorbent is favored.

For extractions, therefore, it would make sense to use a solvent in which the solutes of interest are quite soluble. (This is true even though the resultant solution from an extraction might be several orders of magnitude below saturation in the solutes.) The extent to which variation of the solvent affects the desorption of the solute will, however, also depend on the relative magnitude of the solute-adsorbent interactions.

1.7.3 Adsorption from Supercritical Fluids

1.7.3.1 Supercritical Fluid Chromatography

Supercritical fluid chromatography (SFC) is a variation of gas-liquid chromatography in which the mobile phase is a supercritical fluid (SF), usually carbon dioxide. The advantage of SFC over GC and HPLC is the ability to vary the density, hence the solvating power, of the mobile phase. This allows for some very fine separations. A further advantage stems from the high solubilities of some high molecular weight compounds in SCFs relative to those in a gas. This allows separations to be carried out which could normally only be done using the lower resolution technique of HPLC, or the less common technique of high temperature GC. SFC can be carried out at low temperatures ($\approx 50^\circ\text{C}$), which allows the separation of thermally sensitive compounds.

1.7.3.2 Variation of Partition Ratio with Solvent Density

Yonker et al [73] have summarized the retention mechanism formalism for SFC utilizing a liquid stationary phase. The object in the following derivation is to find the relationship among retention, solubility, pressure and temperature for a given solute, supercritical mobile phase and liquid stationary phase.

As in gas-liquid chromatography, solute retention is determined by a capacity factor, k' :

$$k' = (c^s / c^m) \cdot (V_t^s / V_t^m) \quad (1.7.3.1)$$

where c^s and c^m are the solute concentration in the stationary and mobile phases, and V_t^s and V_t^m are the total volumes of the pure stationary and mobile phases, respectively.

Since a concentration c can be expressed as

$$c = x / V_m \quad (1.7.3.2)$$

where x is the mole fraction of solute in a phase of molar volume V_m , it follows that:

$$k' = (x^s / x^m) \cdot (V_m^m / V_m^s) \cdot (V_t^s / V_t^m) \quad (1.7.3.3)$$

Taking the log of both sides, we have

$$\ln(k') = \ln(x^s / x^m) + \ln(V_m^m V_t^s / (V_m^s V_t^m)) \quad (1.7.3.4)$$

When equilibrium is established, the solute chemical potentials in the stationary and mobile phases will be equal. Assuming ideal behaviour, i.e. using mole fractions in place of activities:

$$\mu^s = \mu^m = \mu^{s^\ominus} + RT \ln(x^s) = \mu^{m^\ominus} + RT \ln(x^m) \quad (1.7.3.5)$$

where $^\ominus$ denotes the standard state of the solute in the particular phase. Equation 1.7.3.5 can be rearranged and substituted into equation 1.7.3.4 to give

$$\ln(k') = (\mu^{m^\ominus} - \mu^{s^\ominus}) / RT + \ln(V_m^m V_t^s / (V_m^s V_t^m)) \quad (1.7.3.6)$$

The only pressure dependent part of the second term of the right hand side of equation 1.7.3.6 is V_m^m , the molar volume of the mobile phase. Differentiation of equation 1.7.3.6 with respect to pressure at constant temperature therefore yields:

$$\left[\frac{\partial \ln(k')}{\partial p} \right]_T = \frac{1}{RT} \left\{ \left[\frac{\partial \mu^m}{\partial p} \right]_T - \left[\frac{\partial \mu^s}{\partial p} \right]_T \right\} + \left[\frac{\partial \ln(V_m^m)}{\partial p} \right]_T \quad (1.7.3.7)$$

The first two terms on the right hand side of equation 1.7.3.7 can be recognized as the partial molar volumes of the solute in the standard state in the mobile and stationary phases, $V_m^\ominus$ and $V_s^\ominus$, and the last term is the isothermal compressibility of the mobile phase fluid, κ . Equation 1.7.3.7 therefore reduces to:

$$\left[\frac{\partial \ln(k')}{\partial p} \right]_T = \frac{1}{RT} [V_m^\ominus - V_s^\ominus] - \kappa \quad (1.7.3.8)$$

The term $V_m^\ominus$ can be evaluated from solubility data, since it has been shown by Gitterman and Procaccia [74] that the variation of solubility with pressure is related to $V_m^\ominus$:

$$\left[\frac{\partial \ln(x^m)}{\partial p} \right]_T = \frac{1}{RT} [V_2^s - V_m^\ominus] \quad (1.7.3.9)$$

where x^m is the mole fraction of the solute in the mobile phase (i.e. its solubility), and V_2^s is the molar volume of the pure solid solute. Solving equation 1.7.3.9 for $V_m^\ominus$, substituting into equation 1.7.3.8 and rearranging gives:

$$\left[\frac{\partial \ln(k')}{\partial p} \right]_T = [V_2^s - V_s^\ominus] / RT - \left[\frac{\partial \ln(x^m)}{\partial p} \right]_T - \kappa \quad (1.7.3.10)$$

which is the desired result, relating retention to solubility.

The first term on the right hand side of equation 1.7.3.10 is a constant. The second is the variation of solubility of the solute in the mobile phase with pressure, which can be calculated from an appropriate equation of state. The isothermal

compressibility κ can also be found from an equation of state. Inspection of equation 1.7.3.10 reveals that the retention in SFC should decrease as the pressure is increased.

Note also in equation 1.7.3.10, that it is the solubility of the solute in the mobile phase that is important. No account is taken of variation of any properties of the stationary phase with pressure.

1.7.3.3 Effects of Modifiers

Modifiers are liquid solvents added to the primary mobile phase in SFC to decrease the retention and increase the selectivity. The modifiers are thought to function by occupying active sites on the stationary phase, thereby preventing the solute from being strongly adsorbed and thus decreasing its retention. The modifier also may increase the solubility of the solute in the mobile phase, which would favor partitioning of the solute into the mobile phase.

In general, more polar modifiers are adsorbed more strongly on the stationary phase, and thus very polar modifiers such as methanol are commonly used. For example, Crowther and Henion [75] used methanol to modify the CO_2 mobile phase in packed column SFC analysis of polar drug compounds. The capacity factor for codeine decreased from 14 at a methanol concentration of 2% to less than unity at 16%. Mourier et al [76] demonstrated that the capacity factor of a phosphine oxide on a packed octadecyl bonded silica column decreased with the use of more polar modifiers. Specifically, the effectiveness of the modifiers increased in the order 2-propanol < ethanol < methanol < water, which is the same order as the polarities of the modifiers. Janicot et al [77] found that the capacity factors for opium alkaloids on a bare silica stationary phase were decreased by adding an amine modifier to the mobile phase. However, on an aminopropyl silica stationary phase, the capacity factors went through a minimum or even increased monotonically with respect to increasing modifier concentration.

Yonker and Smith [78] concluded that for less "active" columns, the major changes due to modifiers were due to the altered solvating power of the mobile phase. Wright and Smith [79] concluded that for capillary columns, the major effect was one of altering the solvating power of the mobile phase, whereas for

packed columns, the major effect was one of stationary phase modification. Levy and Ritchie [80] showed that the mechanism which predominates depends on the stationary phase used.

Lochmüller and Mink [81] measured the adsorption of methanol and 1-hexanol on silica from supercritical carbon dioxide. The maximum stationary phase concentration of methanol was found to be greater than that of 1-hexanol. The authors concluded that the decrease in retention of several solutes in the presence of the modifiers was due to adsorption of the modifiers, with the concomitant desorption of the solutes.

1.7.3.4 Surface Heterogeneity

Supercritical fluid chromatography sometimes suffers from heterogeneity of the stationary phase. The results are poor peak shapes (usually severe tailing) and longer retention times. This is usually attributed to adsorption of the solute on "active sites", which are believed to be sites on the bare support not covered by the stationary phase. In SFC with a bare support material, the retention mechanism will exclusively be one of adsorption. Since an extraction is the desorption of the analyte from a solid surface, the same principles apply in extraction as in SFC with a stationary phase that has not been fully deactivated.

Schoenmakers et al [82] described a method for determining the heterogeneity of a stationary phase in SFC. For the distribution of the solute between the adsorption sites and the mobile phase, the solute is assumed to obey a Langmuir – type distribution isotherm (as discussed in sections 1.7.1 and 1.7.2):

$$c^s = \frac{ac^m}{bc^m + 1} \quad (1.7.3.11)$$

where c^s and c^m are the solute concentrations on the stationary phase and in the mobile phase respectively, and a and b are coefficients that depend on the solute and stationary phase. The authors point out that different values of a and b may also be found for different mobile phases or different pressures and temperatures. The distribution coefficient for the process can be written

$$K_{ads} = \frac{c^s}{\bar{c}^m} \quad (1.7.3.12)$$

combining the last two equations, we have

$$K_{ads} = \frac{a}{bc^m + 1} \quad (1.7.3.13)$$

For the distribution of the solute between the chemically bonded phase and the mobile phase, a linear distribution is assumed, i.e. the equilibrium constant for the process is assumed to be independent of concentration. The effective equilibrium constant is the sum of the two:

$$K = K_{ads} + K_{cbp} \quad (1.7.3.14)$$

where K_{ads} is for the adsorption process, and K_{cbp} is for the equilibrium involving the chemically bonded phase.

The dimensionless capacity factor k' can be calculated from

$$k' = K_{ads} \cdot \frac{A^s}{V_t^m} + K_{cbp} \cdot \frac{A^s}{V_t^m} \quad (1.7.3.15)$$

where A^s is the surface area of the stationary phase, and V_t^m is the total volume of the mobile phase.

Equation 1.7.3.15 can be combined with equation 1.7.3.13 to give

$$k' = \frac{aA^s}{V_t^m(bc^m + 1)} + \frac{K_{cbp}A^s}{V_t^m} \quad (1.7.3.16)$$

where c^m has been replaced by $\bar{c}^m$, the average value of c^m along the length of the chromatographic column. The actual concentration in the mobile phase will vary with the position along the column, and along the profile of the peak, but $\bar{c}^m$ is assumed to be proportional to the amount of solute injected:

$$\bar{c}^m = \beta(Q) \cdot Q \quad (1.7.3.17)$$

where Q is the mass of solute injected, and $\beta(Q)$ is a function of Q . The authors assume that $\beta(Q)$ does not vary with Q . Equation 1.7.3.16 can then be written as

$$k' = \frac{a'}{(b'Q + 1)} + d' \quad (1.7.3.18)$$

where $a' = aA^s/V_t^m$ (1.7.3.19)

$$b' = \beta b \quad (1.7.3.20)$$

and

$$d' = K_{cbp}A^s/V_t^m \quad (1.7.3.21)$$

In analogy with the development of the Langmuir equation for gas adsorption (see section 1.7.1), the total number of accessible adsorption sites is simply a/b . From this fact, and using equations 1.7.3.19 and 1.7.3.20, we have:

$$a/b = (a'/b')(V_t^m\beta/A^s) \quad (1.7.3.22)$$

Also from the development of the Langmuir equation, the parameter b is a measure of the energy of interaction of the solute with the adsorption sites. Since the parameter β is not known, we cannot obtain values for a/b and b . However, using equation 1.7.3.22, we may use the values of a'/b' and b' as measures of the relative numbers of sites, and the relative energy of interaction, respectively. To determine the constants a' and b' for a particular system experimentally, the requirement is to measure the capacity factor k' as a function of the amount injected, Q , and then fit equation 1.7.3.18 to the data. In a system consisting only of adsorption sites (and no chemically bonded phase), the d' term in equation 1.7.3.18 is zero.

2. Equipment and Methods

2.1 Extraction

2.1.1 Sample Preparation

Solid samples were prepared for extraction experiments by spiking them with known amounts of organic compounds. Several solid matrices were chosen for study. Silica (SiO_2) was chosen as a reference material because it was expected that extractions from this material would be relatively easy. A sample of dried soil was chosen as a more realistic matrix. Graphite was chosen because of its large surface area, and the knowledge that extraction from it can be very difficult, as pointed out by Jacob and Grimmer [83]. However, extraction from graphite proved so difficult that no data for it is presented. Other matrices such as XAD-2 resin (a non-polar co-polymer of styrene and divinylbenzene), Florisil (a magnesium silicate) and aluminum metal were also used.

Solid samples were dry sieved into size fractions using wire screens. The desired size fraction was then washed at least five times with clean dichloromethane in a 250 mL beaker. The solid was then covered with dichloromethane, and aliquots of stock solutions of the desired organic compounds were added to the dichloromethane with stirring. The stirring was continued intermittently until most of the solvent had evaporated, and the solid was allowed to dry completely overnight. The solid thus prepared was tumbled for several minutes to ensure complete mixing, and then transferred to glass vials with aluminum foil lined caps. The samples were stored in the dark to minimize photodegradation of light sensitive compounds as recommended by Griest and Caton [84].

Any solutes remaining in the beaker were washed out with a small quantity of dichloromethane and analyzed by gas chromatography. The actual spike level of the solids were calculated by subtracting this quantity from the total quantity added during the spiking. The amount remaining in the beaker was generally less than one percent of the amount added during the spiking (except for the aluminum metal), reflecting the fact that the solid matrices adsorbed the solutes very effectively.

Spiking levels ranged from 10 ng g⁻¹ to 50 µg g⁻¹, depending on the compounds used and the information sought. Rather than present a comprehensive list of matrices and spike levels here, this data is presented along with the extraction recoveries in the results and discussion section.

2.1.2 Supercritical Fluid Extractions

2.1.2.1 Solvent Preparation

For extractions using only carbon dioxide, the CO₂ cylinder was connected directly to the pump inlet. Other solvents such as N₂O, SF₆, and CHF₃ were received as liquids, but could not be used directly from their cylinders. N₂O could not be purchased with a dip tube in the cylinder, and thus had to be transferred by distillation into a reservoir which could be connected to the system in such a way as to supply liquid to the pumphead. The SF₆ and CHF₃ did not have sufficient purity to be used as-received. They were therefore also distilled into auxiliary reservoirs.

The reservoir used for these operations is diagrammed in figure 2.1.1. Originally designed to be used as a large extraction cell, the reservoir had a volume of 150 mL, and was equipped with a 1/4" ball valve at one end. To distill a solvent, the reservoir was first cooled in an ice bath, and connected to the gas cylinder. The valve was opened for a few minutes, then closed. The amount of solvent transferred was measured by weighing the tared reservoir.

Binary solvents were prepared in a similar manner, except that the liquid modifier was pipetted into the reservoir before filling with the main solvent (usually CO₂). These mixtures were inverted several times, and allowed to stand overnight before using to ensure complete mixing. The liquid phase was withdrawn from the reservoir by connecting the bottom valve to the pump inlet.

2.1.2.2 Pressurization

Pressurization of the solvent was accomplished using the system diagrammed in figure 2.1.2. Liquid solvents were introduced to the pump inlet in the manner described in the previous section. The pump used was a Milton-Roy "Minipump", model 92014903, with two pumpheads driven by a single motor. Each pumphead

Figure 2.1.1

Diagram of solvent mixing reservoir. Dimensions are in mm.
Material of construction is 316 stainless steel.

Figure 2.1.2 Diagram of extraction system

had a rated capacity of 460 mL h^{-1} . One pumphead was used for extractions, and the second served as a backup, or was used for other concurrent experiments. The pumpheads were cooled by circulating a 5°C solution of ethylene glycol through a heat exchanger mounted on the back of the pumpheads. This was necessary to prevent vaporization of the solvent in the pumphead.

The outlet of the pump was connected to a pulse dampener. This device consisted of a flattened and coiled piece of $1/8"$ of stainless steel tubing approximately 2 m long. Pressurization upon each forward stroke of the pump piston caused the pulse dampener to uncoil slightly, absorbing some of the pulsations. This was particularly necessary at high flowrates, where the pump stroke was quite long. However, with the flowrates typically used (150 mL min^{-1} measured as gas), pulsation was usually less than ± 1 bar. At low pressure or at low flowrate, pulsation of the pressure could not be observed.

The outlet of the pulse dampener was connected to the pressure gauge (Span Instruments, 0–6000 psig (0–415 bar)). The flow-through construction of the gauge ensured that the entire volume of the gauge was swept with solvent. This allowed for easy cleaning of the gauge by simply passing CO_2 through it. Although the gauge was calibrated in 100 psi increments, it was easily read to 20 psi (1.3 bar). The gauge was calibrated by measuring the vapor pressure of carbon dioxide as a function of temperature from 5°C to 30°C and comparing to published values [85].

The outlet of the gauge was connected to a six port HPLC valve (Valco C6W). As shown in figure 2.1.2, the valve was configured to allow solvent through the extraction cell in one position, and to vent the cell in the other position. The extraction cell was positioned below the valve in a thermostatted water bath. The outlet of the cell was routed back through the valve and into the depressurization device.

2.1.2.3 Extraction Cells

The requirements of an extraction cell are that the matrix must be prevented from escaping, and that there is adequate contact between the fluid and the solid. Since supercritical fluids have zero spreading pressure (see section 1.4.5), the

contact between the solid and fluid is very good. Thus, the extraction cell need only ensure that there are no dead volumes, where the solid is in contact with fluid that is not moving.

Several extraction cells were assembled and used. Since the requirements are for a fairly small sample (≈ 1 g), high pressure fittings themselves can be used as extraction cells. The first extraction cell evaluated was a 1/4" NPT union as described by Hawthorne and Miller [30]. This cell had an internal volume of approximately 0.2 mL, and was thus suitable only for very small samples.

A second small volume cell (≈ 0.2 mL) which proved very reliable was an HPLC in-line filter. The cell was suitable for any solid material which could be loaded through the small hole in the filter element. This restricted its use to samples which are free-flowing, such as sand.

A larger volume cell (≈ 1 mL) was constructed from a short length of 1/4" od stainless steel tubing and a 1/4" – 1/16" reducing union at either end. A 1/4" diameter 5 μm pore size stainless steel frit was inserted into each end fitting to prevent the sample from escaping. Figure 2.1.3 is a diagram of the above three extraction cells.

A commercially available 5 mL extraction cell (Suprex EX-60005) was used for many extractions. This cell had the definite advantage of replaceable seals.

2.1.2.4 Depressurization and Solute Recovery

Depressurization of the effluent from the extraction cell was accomplished using fused silica capillary tubing as a restrictor (Polymicro Technologies, Phoenix, Arizona). The restrictor was fitted into the system using a reducing graphite ferrule in a 1/16" *Swagelok* union. The outer diameter of the restrictor was 150 μm . To achieve the required pressures and flowrates, restrictors of different inner diameters and lengths were used. Figure 2.1.4 shows flowrate versus pressure curves for several of the restrictors used. For a typical extraction, the flowrate at 311 bar was 150 mL min^{-1} (measured as CO_2 gas) using a 20 μm i.d., 20 cm long restrictor.

Another type of restrictor used was a piece of 1/16" o.d. stainless steel tubing crimped at the outlet with a pair of pliers. Although simple to construct, it was difficult to reproduce the desired flowrate using the device.

Figure 2.1.3

Diagrams of extraction cells used. As described by Hawthorne and Miller [30] (A), an HPLC in-line filter (B) and made from tubing fittings (C)

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Figure 2.1.4

Flowrate of CO₂ versus pressure for various restrictors. The restrictor size (μm id × cm length) is indicated for each curve.

Recovery of the solutes was accomplished by immersing the outlet end of the restrictor in a small volume of dichloromethane or methanol in a 5 mL *Reactivial*. The restrictor was inserted through a rubber septum which rested on the top of the vial. This prevented the restrictor from flying out of the vial, and reduced the loss of solvent due to evaporation.

2.1.2.5 Extraction Procedure

The sample to be extracted was weighed into the tared extraction cell. The solvent inlet and outlet lines were connected, and the cell was immersed in a thermostatted water bath. The end of the fused silica restrictor was placed in the *Reactivial* containing 3 mL dichloromethane. After allowing the cell to thermally equilibrate for at least 15 minutes, the pump was started, and the system was pressurized up to the six port valve. The valve was then opened, and the cell was allowed to pressurize to the desired operating pressure. A timer was started when the operating pressure was reached.

When it was desired to follow the extraction as a function of time, the *Reactivials* were changed at prescribed time intervals. Usually, six time intervals were used, namely 0-1, 1-2, 2-4, 4-8, 8-16, and 16-32 minutes. Alternatively, the total extractable under certain conditions could be determined by extracting into one *Reactivial* for, say, 20 minutes, and then into a second for another 20 minutes.

2.2 Miscibilities of Organic Liquids with Carbon Dioxide

The miscibilities of several organic liquids were tested using the device diagrammed in figure 2.2.1. The device consisted of a heavy walled quartz glass tube (8 mm o.d., 1 mm i.d., 12 cm long) blown shut at one end, and fitted with a 5/16"-1/4" reducing *Swagelock* union. The 5/16" end of the union was fitted with teflon ferrules. A small piece of iron wire was dropped in to act as a stir bar. The device was clamped into a retort stand in such a way as to prevent the fitting from being pushed off by the gas pressure.

Figure 2.2.1

Diagram of miscibility testing apparatus

The liquid solvent to be tested was placed into the bottom of the tube to a depth of approximately 2 cm using a fine glass syringe. The tube was then connected to a cylinder of carbon dioxide, and the fitting and about 10 cm of tubing leading to the cylinder were cooled with ice. The CO₂ valve was opened and the tube was allowed to almost fill with liquid CO₂. The tube then contained about 20% organic solvent and 80% CO₂. Usually, a phase boundary between the organic liquid and the CO₂ was clearly visible.

The stir bar was moved by sliding two magnets up and down the sides of the tube. If the phase boundary disappeared, the system was judged "miscible". Although a "miscible" organic liquid and carbon dioxide may not have been miscible in all proportions, 20% modifier was thought to be the largest concentration of modifier that would be needed. This simple test was therefore sufficient to determine whether a particular organic liquid solvent could be mixed with carbon dioxide before pumping.

2.3 Solubilities

2.3.1 Solubilities in Liquids

The solubilities of several solid solutes in several liquid solvents were measured as follows. A small amount of the solute (≈ 0.5 g) was placed in a 19 x 48 mm glass vial and covered with solvent. The vial was placed in a thermostatted water bath and swirled several times over a period of at least one hour, then the solid was allowed to settle. Samples of the saturated solutions were diluted in dichloromethane, methylated with diazomethane where necessary, and analyzed by GC.

2.3.2 Solubilities in Supercritical Fluids

The solubilities of several compounds in supercritical fluids were measured using a flow apparatus. This apparatus (see figure 2.3.1) maintained the compound to be dissolved at a constant temperature. The supercritical fluid was forced through the bed of compound, then expanded through a stainless steel restrictor at approximately 300°C. This high temperature ensured that the solute vaporized

Figure 2.3.1

Diagram of apparatus for measuring solubilities in supercritical fluids

rapidly, and did not plug the restrictor. After expansion, the CO_2 + solute gas stream was cooled to 0°C in a glass trap to collect the solute and the CO_2 was vented through a bubble flowmeter. The glass trap was dismantled, cooled, and washed out with dichloromethane. The washings were diluted, methylated when appropriate, and analyzed by GC.

2.3.2.1 Vapor Pressure Measurements

Vapor pressure measurements were made using the same apparatus as for the supercritical solubility measurements, except that the restrictor was replaced with an open (unrestricted) tube. The measurements were made in a manner similar to the solubility experiments, except that the gas used was either nitrogen or helium at atmospheric pressure. (The pressure was measured by inserting a pressure gauge at the inlet of the $1/4$ " tube.) The gas flowrate was set to approximately 75 mL min^{-1} , and the sample was collected for approximately one hour.

2.3.2.2 Isothermal Solubility Measurements

Solubilities under isothermal conditions were measured over a range of pressures, usually 77 to 311 bar. The pressure was increased from one solubility measurement to the next, since decreasing the pressure sometimes caused the solute to precipitate out and block the restrictor. The restrictor was removed and cleaned in an appropriate solvent after each isotherm was completed.

2.3.2.3 Isochoric Solubility Measurements

Solubilities in CO_2 under isochoric conditions were measured over a range of temperatures, usually 10 to 70°C . The density was made constant by also varying the pressure accordingly. The equation of state used to determine the density of CO_2 was that of Huang et al [86].

The enthalpy of solution was calculated by plotting the logarithm of the solubility versus $1/T$, as described in section 1.5.2. The solubility measurements below 40°C were erratic for some compounds, presumably due to slow dissolution kinetics. Thus, only the values above 40°C were used for these compounds.

2.4 Adsorption

2.4.1 Adsorption from Liquids

An adsorption experiment measured the adsorption of 2,3,4,5 tetrachlorophenol on sand from hexanes solution as a function of concentration. A 0.1 mL volume of a solution of 2,3,4,5 tetrachlorophenol in hexanes (15 mg mL^{-1}) was diluted in 50 mL hexanes in a 50 mL Erlenmeyer flask. The solution was analyzed by GC. Washed sand was added (29.9 g +60 mesh), and the mixture was allowed to equilibrate overnight. The solution was analyzed again; then the hexane was decanted and replaced with fresh hexane. The solution was stirred for thirty minutes, analyzed, and the procedure of replacing the hexane, equilibrating, and analyzing was repeated five times. Finally, the hexane was replaced with acetone to desorb all remaining 2,3,4,5 tetrachlorophenol in order to calculate a mass balance. Hexane was chosen for this experiment because it reportedly has similar solvating properties to those of carbon dioxide [58].

To demonstrate that the solvent used affects the distribution of solute between the matrix and solution, the adsorption of hexachlorobenzene onto charcoal from several different solvents was studied. The solvents used were the same as those used to measure solubilities. The experimental procedure was as follows: A 0.6 mL volume of a solution of hexachlorobenzene (0.15 mg mL^{-1}) was pipetted into a 50 mL volumetric flask. The flask was made up to the mark with the appropriate solvent. A 0.1 mL sample of the solution was diluted to 1.00 mL, and analyzed by GC. Roughly 30 mg of charcoal (Darco G-60, Anachemia, used as received), was weighed into the flask, a stir bar was dropped in, and the solution was stirred on a magnetic stirrer for one hour. The stirrer was stopped, the charcoal was allowed to settle (this took up to 30 minutes, depending on the density of the solvent) and a sample was withdrawn and analyzed as before.

2.4.2 Adsorption from Supercritical Fluids

An experiment to measure the distribution of 2,3,4,5-tetrachlorophenol between sand and CO_2 as a function of solvent density was carried out using the device diagrammed in figure 2.4.1. The device is a high pressure chamber with an

Figure 2.4.1

Diagram of static SF adsorption apparatus

internal volume of approximately 15 mL, equipped with a pressure gauge, inlet and outlet shutoff valves, and a fused silica restrictor at the outlet.

A weighed amount of sand (6.19 g +60 mesh) was placed into the chamber. A 230 μL volume of a 0.15 mg mL^{-1} solution of 2,3,4,5 tetrachlorophenol in hexanes was introduced into the chamber and the solvent was allowed to evaporate. The chamber was sealed and pressurized to the desired operating pressure with carbon dioxide and allowed to equilibrate with periodic mixing over a period of at least two hours. The bottom valve was opened and a sample was withdrawn through the restrictor into 3 mL of acetone over a period of a few minutes. The flowrate of carbon dioxide was measured. The sample was evaporated to near dryness, methylated with diazomethane, made up to 1 mL in acetone, and analyzed by GC.

The retention volumes of various compounds in various solvents using various stationary phases were measured using the apparatus diagrammed in figure 2.4.2. The apparatus consisted of a pumping system, followed by a six-port two-position valve, followed by a column containing the desired stationary phase.

Detection at supercritical pressure was accomplished using a UV-VIS single beam spectrophotometer (Milton Roy Critical Extraction Monitor). The optimum detection wavelength for each compound was determined by measuring a UV-VIS spectrum of the compound using a Lambda-4B spectrophotometer. The six-port valve was configured to allow filling of a 10 μL sample loop in one position, and injection of the sample onto the column in the other position.

The experiments were carried out as follows. The sample loop was filled with a hexane solution of the desired solute. The system was pumped up to operating pressure using the desired solvent. The sample was rapidly injected onto the column by turning the valve, and the integrator was started. The flowrate was measured using a bubble flowmeter. The retention time of the peak was measured using an integrating recorder (Spectra-Physics 4270). Although the peaks were skewed to longer times, the position of the peak maximum was taken as the elution time.

Retention volumes were calculated using:

$$V_r = t_r \cdot f \cdot \frac{\rho_g}{\rho_{sf}} \quad (2.4.2.1)$$

Figure 2.4.2

Diagram of SFC apparatus

where t_r is the retention time of the peak, f and ρ_g are the flowrate and density of carbon dioxide gas respectively, measured at room temperature and atmospheric pressure, and ρ_{sf} is the density of the supercritical fluid carbon dioxide. A retention volume was thus the volume of *supercritical fluid* required to elute the compound. Capacity factors could then be calculated using:

$$k' = \frac{V_r - V_o}{V_o} \quad (2.4.2.2)$$

where V_o is the retention volume of an unretained solute. This approach allows the direct comparison of different stationary phases since the effects of dead volumes in the system as well as the void volume in the stationary phase are taken care of by normalizing by the solvent retention volume.

2.4.3 Adsorption of Gases

Adsorption of modifiers on solids from the gas phase were studied using a vacuum circuit as diagrammed in figure 2.4.3. The system employed a constant volume manometer for pressure measurement, and a five-bulb gas burette for volume adjustment.

The dead volume bounded by position 1 on the gas burette, the manometer, valve #5, and valve #4 was calculated by measuring pressure as a function of position on the gas burette. If the dead volume is V_d and the burette is adjusted to add a volume V_b , we have:

$$P(V_d + V_b) = nRT \quad (2.4.3.1)$$

where P is the system pressure, n is the number of moles of gas in the system, and T is the absolute temperature. A plot of $1/P$ versus V_b will thus have a constant slope of $1/(nRT)$, and an intercept on the x-axis of $-V_d$. The measurement was repeated with valve #4 open to determine the volume of the sample bulb.

A measurement of gas adsorption was made as follows. The solid sample was weighed into the sample bulb. The sample was degassed by heating under vacuum for 15 minutes. The sample bulb was thermostatted by placing a beaker of water of

Figure 2.4.3

Diagram of apparatus for measuring gas adsorption

the correct temperature around it. Valve #4 was closed, isolating the sample. The solvent to be used was frozen in liquid nitrogen, and the system was evacuated. The solvent was thawed, and valve #5 was rotated to admit solvent gas into the system to the desired pressure. The gas burette was set to position 6, and the pressure was measured. Valve #4 was opened, and the pressure was measured after stabilizing. Stabilization took from 5 to 20 minutes. The gas burette was adjusted to each of the other five positions, and a pressure was taken at each.

The total amount of gas adsorbed at each pressure was calculated from:

$$\Sigma (\Delta n_x) = \frac{p_x V_x}{RT} + \Delta n_{x-1} \quad (2.4.3.2)$$

where p_x is the equilibrium pressure and V_x is the total system volume (corrected for the sample volume).

Plots were made of $p_x/\Sigma (\Delta n)_x$ versus p_x . The number of moles adsorbed at monolayer coverage (n^m) was calculated from the slope and the value of k from the intercept, as outlined in the introduction.

2.4.4 Surface Area Measurements

Surface areas of adsorbents were measured using an automatic single point nitrogen adsorption instrument (Micromeritics model 2200). Weighed samples were degassed under nitrogen for several hours at 300° C, except for XAD-2 resin, which was degassed at room temperature. Samples were then equilibrated at liquid nitrogen temperature for several minutes, and nitrogen gas was admitted until the pressure stabilized. The amount of gas adsorbed was converted by the instrument into an equivalent surface area of the sample, and displayed in units of m². Specific surface areas were calculated by dividing this result by the mass of sample.

2.5 Analyses

2.5.1 Preparation of Diazomethane

Diazomethane was prepared using two different methods. The first method was suitable for producing a large quantity at one time. The procedure was as follows. A mixture of 5 g KOH, 8 mL distilled water and 25 mL ethanol were placed into a 250 mL round bottom flask. The flask was immersed in a water bath, then 22.5 g Diazald was dissolved in 200 mL ether and put in a dropping flask above the KOH/ethanol solution. The Diazald solution was introduced dropwise into the other solution as the diazomethane was co-distilled at roughly 50°C with the ether into an ice-bath cooled 500 mL round bottom flask. The product was stored in a freezer.

Since the diazomethane was not stable for more than a few weeks, a second quicker method was used to produce only as much diazomethane as was required for a day or two. This procedure for this method was as follows. A mixture of 6 mL aqueous 50% KOH and 20 mL diethyl ether were placed in a 50 mL erlenmeyer flask, and 2 g of nitrosomethylurea was added. The ether layer immediately turned yellow, indicating the production of diazomethane. The ether layer was withdrawn into a small container and stored in the freezer.

The nitrosomethylurea was prepared as follows [87]. Approximately 148 g of a 32.5 % aqueous solution of methylamine was placed in a 1000 mL round bottom flask and neutralized with concentrated HCl (approximately 155 mL HCl was required). Water was added to bring the total weight to 500 g, then 300 g urea was added, and the solution was boiled gently under reflux for 2.75 h, then vigorously for another 0.25 h. The reaction was thus:

The solution was cooled to room temperature and 110 g sodium nitrite was dissolved in it. A mixture of 600 g ice and 100 g concentrated sulfuric acid was cooled in a 3 L beaker surrounded by an ice bath. The cold methylurea-nitrite solution was added over a period of about one hour with mechanical stirring. The reaction was thus:

The precipitate formed was filtered off, washed twice with cold water, sucked as dry as possible on the filter, and stored in a freezer.

2.5.2 Extract Preparation and Derivatization

Extracts were left standing for at least thirty minutes with the caps on loosely to allow dissolved carbon dioxide to evolve. Failure to do this resulted in "bumping" of the solvent during evaporation, with loss of part of the extract. An extract was evaporated by connecting the 5 mL *Reactivial* to a water aspirator, and immersing most of the vial in room temperature water. The water was necessary to prevent excessive cooling of the extract, which would otherwise slow the evaporation significantly. For FID analysis, the extract was evaporated to approximately 0.1 mL. The exact volume was determined by weighing the tared *Reactivial*.

For ECD analysis, the extract at approximately 0.1 mL was methylated by adding approximately 0.1 mL of an ethereal solution of diazomethane. This solution was allowed to stand for at least 15 minutes to ensure complete methylation. The solvent was then evaporated to near dryness, and approximately 1 mL solvent (methanol or dichloromethane) was added. The exact volume was determined by weighing, as above.

2.5.3 Gas Chromatography

Extracts were analyzed using a Varian 3400 gas chromatograph equipped with a flame ionization detector (FID) and an electron capture detector (ECD). The column used was a 0.25 mm diameter, 22 m long DB-5 (methyl polysiloxane, 5% phenyl) capillary column with a 0.25 μm film thickness. Sample introduction was via a split/splitless injector operated in the splitless mode. The effluent end of the column was connected to the FID or ECD as required.

The conditions used during FID runs were as follows:

injector temperature:	350° C
detector temperature:	300° C
column temperature program:	80° C for 2 min 25° C min ⁻¹ to 300° C 300° C for 2 min

The conditions used during the ECD runs were as follows:

injector temperature:	300° C
detector temperature:	300° C
column temperature program:	80° C for 2 min 15° C min ⁻¹ to 300° C 300° C for 2 min

The carrier gas used was chromatographic grade helium at a flow rate of approximately 4 mL min⁻¹. The air and hydrogen (zero grade) flowrates were 300 mL min⁻¹ and 30 mL min⁻¹ respectively. Makeup gas (zero grade nitrogen) was supplied to the FID and ECD at 30 mL min⁻¹ each. All gases were supplied by Air Products Ltd.

For most runs, a 2.6 µL sample was injected at a rate of approximately 0.1 µL s⁻¹. Integration was performed by the "IBDH" data handling system of the Varian 3400. Quantitation was based on peak area.

Calibration of the GC was performed using standards dissolved in dichloromethane or hexanes. These standards were made by diluting the same stock solutions used to spike the solid matrices. Generally, one standard served to calibrate both the FID and ECD for extractions of a specific matrix. The concentration of the calibration standard was such that the peak areas from a calibration run were approximately the same as for a typical analysis run. Response factors were calculated by averaging at least three calibration runs. Figures 2.5.1 and 2.5.2 are chromatograms of FID and ECD calibration runs, respectively. Baseline separation of all peaks was obtained.

Figure 2.5.1

Gas chromatogram of hydrocarbon standard. The indicated peaks are: phenanthrene (1), *n*-octadecane (2), *n*-eicosane (3) fluoranthene (4), *m*-terphenyl (5) and chrysene (6).

Figure 2.5.2

Gas chromatogram of chlorinated compound standard (methylated). The indicated peaks are:

2,3,4,5-tetrachlorophenol (1), pentachlorobenzene (2), 2,4-D (3), hexachlorobenzene (4), γ -BHC (5), Silvex (6), PCB-33 (7), α -Chlordane (8), PCB-77 (9), PCB-153 (10), Mirex (11)

3. Results and Discussion

3.1 Solubilities

3.1.1 Solubilities in Liquids

The solubilities of some representative solutes in eight liquid solvents were measured at temperatures from 0°C to 30°C. The results are presented in tables 3.1.1 to 3.1.4. The solubilities are expressed in mole fractions of the solutes to be consistent with the units used in determination of solubilities in supercritical fluids.

Most of the numbers in tables 3.1.1 to 3.1.4 represent the average of several determinations. In many cases, the solubility of the solute was so high that the solution solidified. No data is presented for these systems. The system NMP + PCB-77 showed evidence of reaction between the solute and solvent. (The solution was observed to change color over a period of time.) No data is reported for this system either.

For some systems, the solubility did not vary with temperature. However, in these same systems, there was much scatter in the data. It is possible that the true solubility was not being measured, but that there were small particles of the solid suspended in the solvent. The scatter is reflected in large uncertainties in the calculated enthalpies of solution (see table 3.1.5).

Dimethylsulfoxide has a freezing temperature of 18.5°C [85], and thus little data was collected for solubilities in this solvent at 10.5°C or 0.0°C. Only pentachlorobenzene and hexachlorobenzene caused sufficient freezing point depression that their solubilities could be measured at 10.5°C.

The solubilities have been quoted to 2 significant figures. The estimated uncertainties are $\pm 10\%$.

Some interesting observations can be made from inspection of the solubility data. First, tetrahydrofuran (THF) and N-methyl pyrrolidinone (NMP) are the best solvents overall. NMP is a particularly good solvent for non-polar species such as the four PAH compounds. THF is a good solvent for these species, as well as the polar species 2,3,4,5 tetrachlorophenol (2,3,4,5-tcp) and 2,4-dichlorophenoxyacetic acid (2,4-D). Second, methanol is the worst solvent overall for the compounds

Table 3.1.1. Solubilities at 30.1° C (mole fraction solute):

	MeOH	Acetone	DMSO	C ₆	DCM	NMP	CCl ₄	THF
<i>n</i> -octadecane	9.0 · 10 ⁻⁴	3.0 · 10 ⁻²	4.3 · 10 ⁻⁴		3.0 · 10 ⁻³			
<i>n</i> -eicosane	2.2 · 10 ⁻⁴	1.0 · 10 ⁻²	1.2 · 10 ⁻⁴		8.2 · 10 ⁻⁴			
<i>m</i> -terphenyl	8.8 · 10 ⁻⁴	3.6 · 10 ⁻²	4.7 · 10 ⁻²	2.1 · 10 ⁻²	1.0 · 10 ⁻¹	8.4 · 10 ⁻²	9.5 · 10 ⁻²	
fluoranthene	2.9 · 10 ⁻⁴	3.8 · 10 ⁻²	7.0 · 10 ⁻²	1.6 · 10 ⁻²	1.3 · 10 ⁻¹	8.3 · 10 ⁻²	1.2 · 10 ⁻¹	
chrysene	2.5 · 10 ⁻⁵	8.7 · 10 ⁻⁴	2.1 · 10 ⁻³	2.1 · 10 ⁻⁴	8.7 · 10 ⁻³	1.4 · 10 ⁻³	7.4 · 10 ⁻³	
perylene	3.8 · 10 ⁻⁶	2.9 · 10 ⁻⁴	1.2 · 10 ⁻³	7.5 · 10 ⁻⁵	3.3 · 10 ⁻³		2.9 · 10 ⁻³	
penclb	3.9 · 10 ⁻³	3.7 · 10 ⁻²	6.7 · 10 ⁻³	9.1 · 10 ⁻²	1.8 · 10 ⁻¹	4.5 · 10 ⁻²		
hexclb	9.0 · 10 ⁻⁵	1.0 · 10 ⁻³	3.9 · 10 ⁻⁴	2.9 · 10 ⁻³	7.4 · 10 ⁻⁴	6.0 · 10 ⁻⁴	1.2 · 10 ⁻²	6.9 · 10 ⁻³
2,3,4,5-tcp	3.4 · 10 ⁻¹	5.4 · 10 ⁻¹		1.4 · 10 ⁻²	9.2 · 10 ⁻²	5.0 · 10 ⁻²	5.1 · 10 ⁻²	3.8 · 10 ⁻¹
2,4-D	1.3 · 10 ⁻¹	1.8 · 10 ⁻¹		3.8 · 10 ⁻³	1.5 · 10 ⁻²		3.1 · 10 ⁻³	3.0 · 10 ⁻¹
PCB-77	1.6 · 10 ⁻⁴	3.2 · 10 ⁻³		6.5 · 10 ⁻³	5.8 · 10 ⁻³			

Table 3.1.2. Solubilities at 20.2° C (mole fraction solute):

	MeOH	Acetone	DMSO	C ₆	DCM	NMP	CCl ₄	THF
<i>n</i> -octadecane	5.0 · 10 ⁻⁴	1.0 · 10 ⁻²	1.0 · 10 ⁻⁴		7.9 · 10 ⁻⁴			
<i>n</i> -eicosane	1.0 · 10 ⁻⁴	2.8 · 10 ⁻³	3.3 · 10 ⁻⁵	8.8 · 10 ⁻²	8.3 · 10 ⁻⁴			
<i>m</i> -terphenyl	7.4 · 10 ⁻⁴	4.4 · 10 ⁻²	2.2 · 10 ⁻²	1.4 · 10 ⁻²	8.9 · 10 ⁻²	8.3 · 10 ⁻²	9.6 · 10 ⁻²	
fluoranthene	3.2 · 10 ⁻⁴	5.4 · 10 ⁻²	5.7 · 10 ⁻²	1.2 · 10 ⁻²	9.1 · 10 ⁻²	1.2 · 10 ⁻¹	5.5 · 10 ⁻²	1.1 · 10 ⁻¹
chrysene	2.1 · 10 ⁻⁵	8.8 · 10 ⁻⁴	1.4 · 10 ⁻³	1.4 · 10 ⁻⁴	8.1 · 10 ⁻³	1.3 · 10 ⁻³	5.8 · 10 ⁻³	
perylene	8.0 · 10 ⁻⁶	2.9 · 10 ⁻⁴	8.0 · 10 ⁻⁴	5.5 · 10 ⁻⁵	1.7 · 10 ⁻³	3.8 · 10 ⁻³		2.2 · 10 ⁻³
penclb	3.0 · 10 ⁻³	3.0 · 10 ⁻²	5.5 · 10 ⁻³	6.6 · 10 ⁻²	1.6 · 10 ⁻¹	4.9 · 10 ⁻²		
hexclb	8.5 · 10 ⁻⁵	9.3 · 10 ⁻⁴	2.2 · 10 ⁻⁴	3.6 · 10 ⁻³	5.4 · 10 ⁻⁴	5.7 · 10 ⁻⁴	9.9 · 10 ⁻³	5.0 · 10 ⁻³
2,3,4,5-tcp	3.8 · 10 ⁻¹	5.6 · 10 ⁻¹		9.8 · 10 ⁻³	7.6 · 10 ⁻²	4.6 · 10 ⁻²	2.5 · 10 ⁻²	3.5 · 10 ⁻¹
2,4-D	1.2 · 10 ⁻¹	1.6 · 10 ⁻¹		3.6 · 10 ⁻³	1.7 · 10 ⁻²		6.7 · 10 ⁻³	2.4 · 10 ⁻¹
PCB-77	8.4 · 10 ⁻⁵	2.0 · 10 ⁻³		5.4 · 10 ⁻³	8.1 · 10 ⁻³			

Notes: MeOH is methanol
DMSO is dimethylsulfoxide
C₆ is a mixture of C₆H₁₄ isomers
DCM is dichloromethane
NMP is N-methyl pyrrolidinone
THF is tetrahydrofuran
penclb is pentachlorobenzene
hexclb is hexachlorobenzene
2,3,4,5-tcp is 2,3,4,5 tetrachlorophenol
2,4-D is 2,4 dichlorophenoxyacetic acid
PCB-77 is 3,3',4,4' tetrachlorobiphenyl

Table 3.1.3. Solubilities at 10.5° C (mole fraction solute):

	MeOH	Acetone	DMSO	C ₆	DCM	NMP	CCl ₄	THF
<i>n</i> -octadecane	1.8 · 10 ⁻⁴	3.1 · 10 ⁻³		8.8 · 10 ⁻²	2.9 · 10 ⁻²	9.8 · 10 ⁻⁴		
<i>n</i> -eicosane	3.7 · 10 ⁻⁵	7.8 · 10 ⁻⁴		3.9 · 10 ⁻²	1.8 · 10 ⁻²	8.2 · 10 ⁻⁴		3.5 · 10 ⁻²
<i>m</i> -terphenyl	7.2 · 10 ⁻⁴	3.7 · 10 ⁻²		9.2 · 10 ⁻³	5.2 · 10 ⁻²	9.3 · 10 ⁻²	8.6 · 10 ⁻²	9.6 · 10 ⁻²
fluoranthene	2.4 · 10 ⁻⁴	4.7 · 10 ⁻²		7.6 · 10 ⁻³	7.7 · 10 ⁻²	1.2 · 10 ⁻¹	5.2 · 10 ⁻²	1.0 · 10 ⁻¹
chrysene	3.2 · 10 ⁻⁵	7.7 · 10 ⁻⁴		1.2 · 10 ⁻⁴		8.4 · 10 ⁻³	1.5 · 10 ⁻³	4.5 · 10 ⁻³
perylene	8.0 · 10 ⁻⁶	2.6 · 10 ⁻⁴		3.5 · 10 ⁻⁵	6.3 · 10 ⁻⁴	2.0 · 10 ⁻³		2.4 · 10 ⁻³
penclb	2.9 · 10 ⁻³	1.7 · 10 ⁻²	3.8 · 10 ⁻³	5.3 · 10 ⁻²	9.0 · 10 ⁻²	2.2 · 10 ⁻²		
hexclb	5.8 · 10 ⁻⁵	4.8 · 10 ⁻⁴	1.6 · 10 ⁻⁴	1.5 · 10 ⁻³	3.6 · 10 ⁻⁴	3.1 · 10 ⁻⁴	6.3 · 10 ⁻³	3.8 · 10 ⁻³
2,3,4,5-tcp	3.9 · 10 ⁻¹	5.3 · 10 ⁻¹		7.0 · 10 ⁻³	5.8 · 10 ⁻²	2.8 · 10 ⁻²	2.7 · 10 ⁻²	7.8 · 10 ⁻¹
2,4-D	1.2 · 10 ⁻¹	1.4 · 10 ⁻¹		3.5 · 10 ⁻³	1.3 · 10 ⁻¹		2.6 · 10 ⁻³	2.9 · 10 ⁻¹
PCB-77	1.2 · 10 ⁻⁴	8.8 · 10 ⁻⁴			3.7 · 10 ⁻³	5.1 · 10 ⁻³	4.3 · 10 ⁻³	

Table 3.1.4. Solubilities at 0.0° C (mole fraction solute):

	MeOH	Acetone	DMSO	C ₆	DCM	NMP	CCl ₄	THF
<i>n</i> -octadecane	7.0 · 10 ⁻⁵	7.4 · 10 ⁻⁴		6.6 · 10 ⁻²	1.4 · 10 ⁻²	3.0 · 10 ⁻⁴	3.4 · 10 ⁻²	2.7 · 10 ⁻²
<i>n</i> -eicosane	2.9 · 10 ⁻⁵	2.2 · 10 ⁻⁴		3.8 · 10 ⁻²	3.8 · 10 ⁻³	7.2 · 10 ⁻⁴	3.3 · 10 ⁻²	1.4 · 10 ⁻²
<i>m</i> -terphenyl	5.2 · 10 ⁻⁴	1.9 · 10 ⁻²		8.4 · 10 ⁻³	4.6 · 10 ⁻²	7.9 · 10 ⁻²	4.9 · 10 ⁻²	6.5 · 10 ⁻²
fluoranthene	3.7 · 10 ⁻⁴	3.1 · 10 ⁻²		7.3 · 10 ⁻³	6.6 · 10 ⁻²	1.0 · 10 ⁻¹	2.0 · 10 ⁻²	7.2 · 10 ⁻²
chrysene	2.0 · 10 ⁻⁵	5.1 · 10 ⁻⁴		9.3 · 10 ⁻⁵		5.7 · 10 ⁻³	8.1 · 10 ⁻⁴	3.4 · 10 ⁻³
perylene	1.9 · 10 ⁻⁵	1.5 · 10 ⁻⁴		4.5 · 10 ⁻⁵	7.8 · 10 ⁻⁴	1.4 · 10 ⁻³		1.3 · 10 ⁻³
penclb	3.2 · 10 ⁻³	9.9 · 10 ⁻³		3.1 · 10 ⁻²	5.4 · 10 ⁻²	1.5 · 10 ⁻²		
hexclb	1.0 · 10 ⁻⁴	2.6 · 10 ⁻⁴		3.1 · 10 ⁻³	1.2 · 10 ⁻⁴	2.7 · 10 ⁻⁴	6.7 · 10 ⁻³	3.4 · 10 ⁻³
2,3,4,5-tcp				6.6 · 10 ⁻³		2.1 · 10 ⁻²		4.2 · 10 ⁻¹
2,4-D	4.4 · 10 ⁻¹	2.8 · 10 ⁻¹		4.7 · 10 ⁻³	1.7 · 10 ⁻²		2.8 · 10 ⁻³	6.5 · 10 ⁻¹
PCB-77	6.2 · 10 ⁻⁵	1.3 · 10 ⁻³			2.2 · 10 ⁻³			

Notes: MeOH is methanol
DMSO is dimethylsulfoxide
C₆ is a mixture of C₆H₁₄ isomers
DCM is dichloromethane
NMP is N-methyl pyrrolidinone
THF is tetrahydrofuran
penclb is pentachlorobenzene
hexclb is hexachlorobenzene
2,3,4,5-tcp is 2,3,4,5 tetrachlorophenol
2,4-D is 2,4 dichlorophenoxyacetic acid
PCB-77 is 3,3',4,4' tetrachlorobiphenyl

tested. Exceptions were the two polar species mentioned above, which were fairly soluble in methanol. Third, hexanes is also a poor solvent, except for the two linear alkanes. Fourth, acetone and dichloromethane (DCM) were roughly similar in solvating power. DCM was a better solvent for the non-polar species, while acetone was better for the polar compounds. Fifth, dimethylsulfoxide (DMSO) and carbon tetrachloride did not show high solubilities for any of the compounds tested, except that pentachlorobenzene was very soluble in CCl_4 .

Many authors have hypothesized that high solubilities in the extracting fluid are required for high recoveries in a supercritical fluid extraction. If solubilities in liquids correlate with solubilities in a supercritical fluid modified with those same liquids, then it would make sense to use as modifiers those fluids which exhibit the highest solubilities of the compounds being extracted. Many authors have also found, however, that methanol is one of the most effective modifiers for supercritical fluid extractions. Thus, either solubilities in supercritical fluids do not correlate with those in the pure liquid modifiers, or solubility in the modified supercritical fluid is not a factor in determining recoveries in an extraction.

As described in section 1.5.3, solubilities can be predicted using Hildebrand's solubility parameters. The measured solubilities of fluoranthene at 20.2°C are compared to those predicted by equation 1.5.3.14 in figure 3.1.1. The predicted values are within a factor of two of the measured values, except for DMSO and methanol, which are better solvents for fluoranthene than Hildebrand's theory would predict. This is likely due to the small dipole moment of fluoranthene (0.6 Debye), which would interact with those of methanol or DMSO.

A similar plot for 2,3,4,5-tetrachlorophenol is shown in figure 3.1.2. The agreement between measured and predicted values is not as good as for fluoranthene. The solubilities of 2,3,4,5-tetrachlorophenol in polar solvents such as methanol, acetone and THF are much greater than Hildebrand's theory predicts, likely due to hydrogen bonding between the solute and these solvents.

The values of the solubility parameters for the solvents used in figures 3.1.1 and 3.1.2 were given in figure 1.6.4. By the use of equation 1.5.3.2, the value calculated for fluoranthene was 8.8 and that for 2,3,4,5-tetrachlorophenol was 8.4.

The enthalpies of solution for solutes in liquids solvents were calculated from plots of $\log(\text{solubility})$ versus $1/T$. These plots are shown in figures 3.1.3 to 3.1.13.

Figure 3.1.1

Measured solubility versus predicted solubility of fluoranthene at 20.2° C. The solvents are: 1-methanol; 2-acetone; 3-DMSO; 4-hexanes; 5-DCM; 7-CCl₄; 8-THF

Figure 3.1.2

Measured solubility versus predicted solubility of 2,3,4,5-tetrachlorophenol at 20.2°C. The solvents are: 1-methanol; 2-acetone; 4-hexanes; 5-DCM; 7-CCl₄; 8-THF

Figure 3.1.3.

$\log(\text{solubility})$ of *n*-octadecane in liquid solvents versus $1/T$.
The solvents are: 1-methanol; 2-acetone; 6-NMP

Figure 3.1.4.

$\log(\text{solubility})$ of *n*-eicosane in liquid solvents versus $1/T$. The solvents are: 1-methanol; 2-acetone; 4-hexanes; 6-NMP

Figure 3.1.5.

$\log(\text{solubility})$ of *m*-terphenyl in liquid solvents versus $1/T$.
 The solvents are: 1-methanol; 2-acetone; 4-hexanes; 6-NMP;
 7- CCl_4 ; 8-THF

Figure 3.1.6.

log(solubility) of fluoranthene in liquid solvents versus $1/T$.
 The solvents are: 1—methanol; 2—acetone; 4—hexanes; 5—DCM;
 6—NMP; 7—CCl₄

Figure 3.1.7.

$\log(\text{solubility})$ of chrysene in liquid solvents versus $1/T$. The solvents are: 1-methanol; 2-acetone; 4-hexanes; 6-NMP; 7- CCl_4 ; 8-THF

Figure 3.1.8.

$\log(\text{solubility})$ of perylene in liquid solvents versus $1/T$. The solvents are: 2-acetone; 4-hexanes; 5-DCM; 6-NMP; 8-THF

Figure 3.1.9.

$\log(\text{solubility})$ of pentachlorobenzene in liquid solvents versus $1/T$. The solvents are: 1-methanol; 2-acetone; 3-DMSO; 4-hexanes; 5-DCM; 6-NMP

Figure 3.1.10.

$\log(\text{solubility})$ of hexachlorobenzene in liquid solvents versus $1/T$. The solvents are: 1-methanol; 2-acetone; 3-DMSO; 4-hexanes; 5-DCM; 6-NMP; 7-CCl₄; 8-THF

Figure 3.1.11.

$\log(\text{solubility})$ of 2,3,4,5-tetrachlorophenol in liquid solvents versus $1/T$. The solvents are: 1-methanol; 2-acetone; 4-hexanes; 5-DCM; 6-NMP

Figure 3.1.12.

$\log(\text{solubility})$ of 2,4-dichlorophenoxyacetic acid in liquid solvents versus $1/T$. The solvents are: 1-methanol; 2-acetone; 4-hexanes; 5-DCM; 7- CCl_4 ; 8-THF

Figure 3.1.13.

$\log(\text{solubility})$ of PCB-77 in liquid solvents versus $1/T$. The solvents are: 1-methanol; 2-acetone; 5-DCM

For some systems, the solubility was very high (greater than 0.1 mole fraction solute). The meaning of the plot in such a system is questionable. In some cases (methanol + 2,3,4,5-tcp for instance), the solubility actually decreased with increasing temperature.

Table 3.1.5 presents the enthalpies of solution of the solutes in liquid solvents. The data show some expected trends. First, the enthalpy of solution is less endothermic for systems in which the solute and solvent are both polar (e.g. pentachlorobenzene + methanol). This implies an especially favorable solute-solvent interaction, since the solution process is normally endothermic. Similarly, the interactions are not as favorable for unlike solute - solvent pairs such as octadecane + methanol, leading to more endothermic enthalpies of solution.

The solubilities of the solutes in liquid solvents at the standard reference temperature of 25° C are listed in appendix 1. These values were calculated from the regression lines shown on figures 3.1.3 to 3.1.13. Along with the enthalpies of solution, they allow calculation of a solubility at any temperature from 0 to 30° C.

Table 3.1.5. Enthalpies of solution in liquid solvents (kJ mol⁻¹):

	MeOH	Acetone	DMSO	C ₆	DCM	NMP	CCl ₄	THF
Octadecane	60±4	84±1				46±14		
Eicosane	49±9	86±3		27±17		3±2		
m-terphenyl	11±2	14±9		22±5		5±2	12±6	8±5
fluoranthene	-3±6	5±8		19±5	11±1	5±2	30±8	11±4
chrysene	2±8	12±4		18±3		9±4	11±7	18±2
perylene		14±5		13±8	24±24	21±7		17±6
pencb	4±4	31±4	20±3	24±3	29±5	28±8		
hexcb	-1±9	33±6	34±5	4±14	41±8	21±5	16±5	16±3
2,3,4,5-tcp	-4±2	1±2		17±4	17±1	21±4		
2,4-D	3±3	10±1		-5±5			8±15	
PCB-77	17±9	22±7			25±3			

3.1.2 Solubilities in Supercritical Fluids

Two methods were employed to test the apparatus described in section 2.3.2. First, the solubility of anthracene in CO_2 was measured as a function of pressure at 35°C and compared to the data of Kosal et al [66]. As shown in Figure 3.1.14, the agreement is good, especially at higher pressures. The disparity at lower pressures is due to the sensitivity of the density to pressure changes in this region. Also plotted in figure 3.1.14 is the solubility of anthracene in CO_2 as predicted by the Peng–Robinson equation of state [34]. A binary interaction parameter of 0.056 was used, as suggested by Kosal et al.

As a second check on the system, the vapor pressure of fluoranthene was measured as a function of temperature at atmospheric pressure, and compared to the data of Sonnefeld et al [88]. In Figure 3.1.18 (page 123), the lower solid line represents the vapor pressure measured by Sonnefeld et al, and the three points on the line are data measured with the apparatus described in section 2.3.2. The agreement is again good indicating that the apparatus can be used for measurement of both low and high solubilities.

It was found that the flowrate of gas through the device had to be above 20 mL min^{-1} (measured as gas at atmospheric pressure), or the restrictor would often become blocked. Furthermore, if the flowrate was above approximately 150 mL min^{-1} , the measured solubilities were low, probably due to insufficient contact time between the fluid and the solute. Thus, the flowrate was typically maintained at between 30 and 120 mL min^{-1} to avoid these problems.

3.1.2.1 Vapor Pressure Measurements

The vapor pressures of several compounds were measured as described in the methods and equipment section. Table 3.1.6 presents the vapor pressure data. Due to the extremely small amount of solute collected (even after a one-hour collection period), the estimated uncertainty of the values in table 3.1.6 is $\pm 10\%$.

As mentioned above, the measured vapor pressures of fluoranthene can be compared to those from reference 88 in figure 3.1.18 (page 123). The agreement is excellent, in view of the simplicity of the apparatus used in this work.

Figure 3.1.14.

Solubility of anthracene in CO₂ at 35° C versus pressure from this work (□), Kosal et al (○) [66] and predicted by the Peng-Robinson equation of state with $k_{ij} = 0.056$ (△)

Table 3.1.6 Measured vapor pressures at 1 bar total pressure

Compound	Temperature °C	Vapor Pressure bar
Fluoranthene	50.0	$1.9 \cdot 10^{-7}$
	60.0	$7.4 \cdot 10^{-7}$
	70.0	$1.1 \cdot 10^{-6}$
<i>m</i> -terphenyl	40.5	$1.8 \cdot 10^{-8}$
2,3,4,5-tcp	50.0	$1.1 \cdot 10^{-5}$
Hexachlorobenzene	50.0	$2.4 \cdot 10^{-7}$

The vapor pressure of *m*-terphenyl, which is one order of magnitude lower than that of fluoranthene, was also measured. The vapor pressures of the more volatile compounds 2,3,4,5-tetrachlorophenol and hexachlorobenzene were easily measured since so much material was available in the gas phase.

3.1.2.2 Isothermal Solubility Measurements

Measurements of solubilities under isothermal conditions were made in ascending steps of pressure, since decreasing the pressure often led to plugging of the restrictor due to precipitation of solute.

The solubility of anthracene in carbon dioxide as a function of pressure at 35°C was shown in figure 3.1.14. The solubilities of anthracene and three other PAH compounds in CO₂ at 35°C are shown in figure 3.1.15 as functions of density. The solubilities of *m*-terphenyl, fluoranthene, and chrysene are seen to increase approximately linearly with density. The order of solubilities in CO₂ (*m*-terphenyl > fluoranthene >> chrysene) is the same as the order in liquid hexanes, a solvent that is often stated to be comparable to CO₂ in solvating strength.

The solubility of fluoranthene in CO₂ was measured as a function of density at three temperatures. The results are plotted in figure 3.1.16. At each temperature, the solubility increases approximately linearly with increasing density until levelling off above a density of 0.85 to 0.90 g mL⁻¹. At a constant density, the solubility is seen to increase with increasing temperature, as seen in most of the solute-solvent combinations in figures 3.1.3 to 3.1.13.

Figure 3.1.15

Solubilities of anthracene ($\square$), fluoranthene ($\triangle$), *m*-terphenyl ($\circ$) and chrysene ($\hexagon$) in CO_2 versus density at 35°C

Figure 3.1.16

Solubility of fluoranthene in CO₂ versus density at 25°C (□), 35°C (Δ) and 45°C (O)

3.1.2.3 Isochoric Solubility Measurements

The solubility of several compounds (namely fluoranthene, chrysene, hexachlorobenzene, 2,3,4,5-tetrachlorophenol and 2,4-dichlorophenoxyacetic acid) in CO_2 were measured at a constant density of 0.80 g mL^{-1} as a function of temperature from 20°C to 70°C . The data are presented in figure 3.1.17 as plots of $\log(\text{solubility})$ versus $1/T$. Thermodynamic quantities were calculated from regressions of the lines shown in figure 3.1.17. The enthalpies, entropies, and free energies of solution at 25°C are presented in table 3.1.7. The available enthalpies of sublimation are also given.

Since CO_2 is non-polar, it is not surprising that the enthalpies of solution for the non-polar species listed in table 3.1.7 are not very endothermic. The values for the polar species (a phenol and a phenoxy acid) are more endothermic, indicating less favorable interactions between them and CO_2 .

Table 3.1.7. Enthalpies, Entropies and Free Energies of Solution in CO_2 at $\rho=0.80 \text{ g mL}^{-1}$

Compound	$\Delta H_{\text{soln}}^\ominus$ kJ mol^{-1}	$\Delta S_{\text{soln}}^\ominus$ $\text{J K}^{-1} \text{mol}^{-1}$	$\Delta G_{\text{soln},298}^\ominus$ kJ mol^{-1}	$\Delta H_{\text{subl}}^\ominus$ kJ mol^{-1}
Hexachlorobenzene	22 ± 6	-18	27	$92.9 [85]$
Chrysene	36 ± 11	13	32	
Fluoranthene	37 ± 6	55	21	$85 [88]$
2,3,4,5-tcp	81 ± 7	200	22	
2,4-D	86 ± 7	180	33	

The solubility of fluoranthene in CO_2 was measured at densities of 0.50 , 0.60 , 0.70 , and 0.80 g mL^{-1} and as a function of temperature. The results are plotted in figure 3.1.18 as $\log(\text{solubility})$ versus $1/T$. Also plotted in the figure is the vapor pressure of fluoranthene. The heat of solution of fluoranthene in CO_2 varied from a high of $83 \pm 2 \text{ kJ mol}^{-1}$ at a CO_2 density of 0.5 g mL^{-1} to a low of $37 \pm 6 \text{ kJ mol}^{-1}$ at 0.8 g mL^{-1} . This seems reasonable, since the limiting heat of solution ought to be the

Figure 3.1.17

$\log(\text{Solubility})$ of 2,3,4,5-tetrachlorophenol (1), fluoranthene (2), 2,4-dichlorophenoxyacetic acid (3), hexachlorobenzene (4) and chrysene (5) in CO_2 versus $1/T$ at 0.80 g mL^{-1}

Figure 3.1.18

log(solubility) of fluoranthene in CO₂ versus $1/T$ at densities of 0.50, 0.60, 0.70, and 0.80 g mL⁻¹. The line labelled 'vp' is the vapor pressure of fluoranthene at 1 bar total pressure [88]. The points on the vp line are from this work

heat of sublimation ($85 \pm 1 \text{ kJ mol}^{-1}$ [88]). As the density of CO_2 is increased, the amount of solvation of the fluoranthene is increased, hence the process of solution is more exothermic.

The entropy of solution of fluoranthene in CO_2 was also calculated from the plots in figure 3.1.18. As expected, the entropy change of the solution process decreased as the CO_2 density was increased. This reflects the greater degree of ordering of a more highly solvated fluoranthene molecule at higher solvent densities. The enthalpies, entropies and free energies of solution of fluoranthene in carbon dioxide as functions of density are listed in table 3.1.8.

The equilibrium model of solubilities in supercritical fluids (see section 1.6.2.2) can be used to estimate the degree of solvation of fluoranthene by CO_2 . Using equation 1.6.2.16, a plot of $\ln(c)$ versus $\ln(\rho)$ should have a slope of k , the number of CO_2 molecules associated with each fluoranthene. At 40°C , the value of k calculated was 6 ± 1 at 0.55 g mL^{-1} , and 14 ± 1 at 0.65 g mL^{-1} . This indicates that the

Table 3.1.8. Enthalpies, Entropies and Free Energies of Solution of Fluoranthene in CO_2

CO_2 density g mL^{-1}	$\Delta H_{\text{soln}}^\ominus$ kJ mol^{-1}	$\Delta S_{\text{soln}}^\ominus$ $\text{J K}^{-1} \text{mol}^{-1}$	$\Delta G_{\text{soln},298}^\ominus$ kJ mol^{-1}
0.5	83 ± 2	170	33
0.6	81 ± 3	170	31
0.7	53 ± 2	100	24
0.8	37 ± 6	55	21

number of CO_2 molecules associated with each fluoranthene molecule increases with density, as expected

Using the calculated values of k , we can estimate the average enthalpy of a fluoranthene- CO_2 interaction. Interpolating values from table 3.1.8, the difference in $\Delta H_{\text{soln}}^\ominus$ between 0.55 and 0.65 g mL^{-1} is $-15 \pm 1 \text{ kJ mol}^{-1}$. This difference must be due to the difference in the number of CO_2 molecules associated with the

fluoranthene molecule at the two densities. Thus, the enthalpy per CO_2 molecule is $-15 \pm 1 \text{ kJ mol}^{-1} / ((14 \pm 1) - (6 \pm 1)) = -1.9 \pm 0.4 \text{ kJ mol}^{-1}$. It is interesting to compare this number with the total of the interaction potentials calculated in section 1.5.1. The sum of dipole-quadrupole, induction, and dispersion potentials calculated for CO_2 + fluoranthene (see table 1.5.2) was $-38.4 \cdot 10^{-22} \text{ J molecule}^{-1}$, or -2.3 kJ mol^{-1} (assuming an intermolecular distance of $2.8 \cdot 10^{-10} \text{ m}$). The agreement between the experimental and theoretical values is excellent, but perhaps fortuitous, in light of the number of simplifying assumptions made in the theory.

3.1.2.4 Solubilities in Binary Supercritical Fluids

Since modifiers are known to have positive effects on extraction recoveries, it seemed reasonable to measure solubilities in modified CO_2 (and later attempt to correlate these with results from adsorption and extraction experiments). The solubilities of fluoranthene and 2,3,4,5-tetrachlorophenol were measured in CO_2 modified with organic liquids. The apparatus used was the same as for the measurements of solubilities in pure CO_2 , except that a pre-mixed solution of CO_2 + modifier was pumped from the 150 mL reservoir described in the equipment and methods section.

Figure 3.1.19 is a plot of $\log(\text{solubility})$ at $22.0 \pm 0.1^\circ \text{C}$ versus density for fluoranthene in CO_2 , CO_2 + hexanes, CO_2 + methanol and CO_2 + acetone. The mole fraction of the modifier in each case was 0.032 ± 0.001 . At low density, the solubility increases in the order: $\text{CO}_2 < \text{CO}_2 + \text{methanol} < \text{CO}_2 + \text{hexanes} < \text{CO}_2 + \text{acetone}$. This order is the same as for the pure liquid solvents. At a density of 0.87 g mL^{-1} (a density used in the adsorption and extraction experiments), the solubility of fluoranthene in CO_2 + hexanes is about the same as in CO_2 + acetone.

The data for 2,3,4,5-tetrachlorophenol are plotted in figure 3.1.20. The solvents used were CO_2 , CO_2 + hexanes and CO_2 + methanol. Once again, the order of solubilities in the modified CO_2 is the same as in the pure liquid modifiers. In this case, the order of the solubilities is $\text{CO}_2 + \text{methanol} > \text{CO}_2 + \text{hexanes} > \text{CO}_2$. The high solubility of 2,3,4,5-tetrachlorophenol in CO_2 + methanol is expected based on the tendency of the solute and modifier to hydrogen bond.

Figure 3.1.19

$\log(\text{solubility})$ of fluoranthene at 22.0°C in CO₂ (○), CO₂ + methanol (△), CO₂ + hexanes (□) and CO₂ + acetone (⬡) versus density. The mole fraction of each modifier was 0.032.

Figure 3.1.20

$\log(\text{solubility})$ of 2,3,4,5-tetrachlorophenol at 22.0°C in CO₂ (○), CO₂ + methanol (○) and CO₂ + hexanes (□). The mole fraction of each modifier was 0.032.

The solubility of 2,3,4,5 tetrachlorophenol in CO_2 + methanol was measured as a function of density at two methanol concentrations. The results are plotted in figure 3.1.21. As expected, the solubility increases as the mole fraction of methanol is increased. This effect was described by Walsh and Donohue [89], who predicted that solubility will be higher in a system where there is more hydrogen bonding of the solute with the modifier.

Many of the adsorption experiments (described in section 3.2.2) were performed with a modifier concentration of 0.52 ± 0.01 mole percent. The solubility of 2,3,4,5-tetrachlorophenol was measured in mixtures of CO_2 + modifier at this same concentration. The conditions used were $22.0 \pm 0.1^\circ\text{C}$ and a density of 0.87 g mL^{-1} . The results are shown in table 3.1.9.

The solubility of 2,3,4,5-tetrachlorophenol is not affected greatly by the addition of 0.52 mole percent modifier, with the exception of methanol, which increased the solubility over that of the un-modified CO_2 by a factor of roughly two.

Table 3.1.9 Solubility of 2,3,4,5-tetrachlorophenol in CO_2 + 0.52 $\pm$ 0.01 Mole Percent Modifier at $22.0 \pm 0.1^\circ\text{C}$ and 0.87 g mL^{-1}

Modifier	Solubility (mole fraction)
Methanol	$2.7 \cdot 10^{-3}$
Acetone	$1.3 \cdot 10^{-3}$
Hexanes	$1.3 \cdot 10^{-3}$
DCM	$1.6 \cdot 10^{-3}$
CCl_4	$1.5 \cdot 10^{-3}$
THF	$1.4 \cdot 10^{-3}$
No Modifier	$1.4 \cdot 10^{-3}$

Figure 3.1.21

$\log(\text{solubility})$ of 2,3,4,5-tetrachlorophenol at 22.0°C in CO₂ (○), CO₂ + 1.59 mole % methanol (□) and CO₂ + 3.21 mole % methanol (○)

3.1.2.5 Miscibilities of Organic Liquids with Carbon Dioxide

Several organic liquids were tested for miscibility with carbon dioxide to ensure that they could be pre-mixed with the carbon dioxide prior to pumping. The liquids were judged "miscible" if they were soluble at least to the extent of 20% by volume in liquid CO₂ at room temperature. Table 3.1.9 lists the results of these experiments. Since N-methyl pyrrolidinone was not miscible with CO₂, it was not used as a modifier in any subsequent experiments. Although DMSO was miscible with CO₂, it was very difficult to clean it out of the solvent mixing reservoir, and frequently it appeared to have separated from the CO₂ during an extraction. Thus, DMSO was not used in subsequent experiments either.

Table 3.1.9 Miscibilities of Modifiers with Liquid Carbon Dioxide at Room Temperature

Modifier	Miscibility
Tetrahydrofuran	Miscible
Dimethylsulfoxide	Miscible
Dichloromethane	Miscible
Hexanes	Miscible
N-methyl pyrrolidinone	Not Miscible

Note: "miscible" means the modifier was soluble to the extent of at least 20% by volume with the CO₂

3.2 Adsorption Measurements

3.2.1 Adsorption of Gases

This section presents the results of all experiments involving the adsorption of gases (at low or atmospheric pressure) onto solid surfaces. Section 3.2.1.1 deals with the measurements of specific surface areas of the solids used. The adsorptions of potential SFE modifiers from the gas phase onto soil, as well as the measurement of enthalpies of interaction of these modifiers with soil and charcoal, are discussed in section 3.2.1.2.

3.2.1.1 Measurement of Specific Surface Areas

Specific surface areas of several adsorbents were measured as described in section 2.4.4. The results are presented in table 3.2.1. The uncertainties quoted on the measurements represent the range of two determinations.

Table 3.2.1 Measured specific surface areas

Adsorbent	Specific Surface Area ($\text{m}^2 \text{g}^{-1}$)
Sand	0
Soil	5.8 ± 1
Florisil	78 ± 5
XAD-2 resin	329 ± 3
Charcoal	386 ± 10

The surface area of sand was too low to be measured by the apparatus. Assuming spherical, non-porous particles of pure quartz (density = 2.65 g mL^{-1}) of average diameter 0.188 mm (60–120 mesh size), the surface area of the sand was calculated to be $0.12 \text{ m}^2 \text{g}^{-1}$.

The larger surface area of soil implies that the soil is a porous material, since the particle size of the soil was approximately the same as that of the sand.

The measured surface area of the XAD-2 resin was $329 \text{ m}^2 \text{ g}^{-1}$. This compares well with the manufacturer's stated surface area of $330 \text{ m}^2 \text{ g}^{-1}$, and indicates that the instrument was functioning properly.

The charcoal had a very large surface area. This may partially account for the difficulty in extracting adsorbates from charcoal and other carbonaceous materials [83].

3.2.1.2 Adsorption of Modifiers from the Gas Phase

Adsorptions of modifiers from the gas phase were performed as outlined in section 2.4.3. The modifiers used were methanol, acetone, hexanes, dichloromethane, carbon tetrachloride and tetrahydrofuran.

The dead volume of the system was calculated from the plots in figure 3.2.1 with the aid of equation 2.4.3.1. The upper line in figure 3.2.1 is for the dead volume calculation including the sample bulb, while the lower line is without the sample bulb. The dead volumes calculated were 22.04 mL with the sample bulb connected, and 7.51 mL without.

The adsorption experiments using sand as the adsorbate were unsuccessful because the amount of adsorption was too small to be measured. This is likely because of the very low specific surface area of the sand.

Plots of $p_x/\Sigma(\Delta n)_x$ versus p_x at $22.0 \pm 0.1^\circ \text{C}$ for the six modifiers are shown in figures 3.2.2 to 3.2.7. The constants b and n^0 in equation 1.7.1.4 were evaluated from the slopes and intercepts of these plots, and are presented in table 3.2.2. The regressions were performed on the data at low pressure, since at higher pressure the values of $p_x/\Sigma(\Delta n)_x$ become independent of pressure due to multilayer adsorption. Only small amounts of carbon tetrachloride were adsorbed, and thus the uncertainties on the results for this modifier are large.

Also presented in table 3.2.2 are the apparent specific surface areas of the soil, which were calculated as follows. The effective volume of a modifier molecule in the liquid phase was calculated from:

$$V_{\text{eff}} = \frac{M}{L \rho_1} \quad (3.2.1.1)$$

Figure 3.2.1

$1/p$ versus V plots for dead volume calculations with (Δ) and without (O) the sample bulb connected

Figure 3.2.2

 $p_x/\Sigma(\Delta n)_x$ versus p_x for the adsorption of methanol on soil

Figure 3.2.3

 $p_x/\Sigma(\Delta n)_x$ versus p_x for the adsorption of acetone on soil

Figure 3.2.4

 $p_x/\Sigma(\Delta n)_x$ versus p_x for the adsorption of hexanes on soil

Figure 3.2.5

$p_x/\Sigma(\Delta n)_x$ versus p_x for the adsorption of dichloromethane on soil

Figure 3.2.6

$p_x/\Sigma(\Delta n)_x$ versus p_x for the adsorption of carbon tetrachloride on soil

Figure 3.2.7

$p_x/\Sigma(\Delta n)_x$ versus p_x for the adsorption of tetrahydrofuran on soil

where M is the molecular weight of the modifier, ρ_l is the density of the liquid modifier, and L is Avogadro's number. Assuming the molecules are spherical, the effective area of an adsorbed molecule will be A_{eff} :

$$A_{\text{eff}} = 4.84 V_{\text{eff}}^{2/3} \quad (3.2.1.2)$$

The calculated specific surface area of the soil is thus

$$\text{SSA} = A_{\text{eff}} L n^0 \quad (3.2.1.3)$$

Table 3.2.2 Values of b and n^0 and calculated specific surface areas for adsorptions from the gas phase of modifiers on soil at 22.0° C

Modifier	b bar ⁻¹	n^0 mole g ⁻¹	SSA m ² g ⁻¹
Methanol	1200±100	$(7.0 \pm 2) \cdot 10^{-5}$	34±1
Acetone	1000±100	$(4.2 \pm 1) \cdot 10^{-5}$	30±1
Hexanes	190±20	$(4.9 \pm 4) \cdot 10^{-5}$	50±4
DCM	3900±1200	$(3.3 \pm 1) \cdot 10^{-5}$	21±1
CCl ₄	250±100	$(2.5 \pm 1) \cdot 10^{-5}$	21±9
THF	2700±200	$(2.7 \pm 1) \cdot 10^{-5}$	20±1

The assumptions made in the above calculations of specific surface areas were numerous: the molecules were assumed spherical, their effective surface areas were assumed to be calculable from the liquid phase densities, and all the assumptions of the Langmuir equation were employed (see section 1.7.1). Nevertheless, the calculated specific surface areas are within an order of magnitude of the value measured by nitrogen adsorption (see table 3.2.1). Perhaps more importantly, the calculated values are very close to one another. The exception was the value for hexanes. This is because the amount of hexanes adsorbed was very low, which makes the uncertainty on the value very high. The uncertainties on the values in table 3.2.2 were derived from the standard errors on the slopes and intercepts of the

plots in figures 3.2.2 to 3.2.7. Inspection of figures 3.2.4 and 3.2.6 shows that the choices of points for the regression on the initial slope for hexanes and carbon tetrachloride were subject to large uncertainties.

The values of b in table 3.2.2 vary greatly from one solvent to another. Recalling that b is essentially the equilibrium constant for the adsorption of the gas on the solid (see equation 1.7.1.2, page 61), we see that hexane and carbon tetrachloride are not extensively adsorbed. Methanol and acetone are adsorbed to a larger extent, while dichloromethane and tetrahydrofuran are adsorbed even more extensively.

Attempts were made to calculate the isosteric enthalpies of adsorption of the six modifiers on soil by measuring the adsorption isotherms at two temperatures, 0°C and 22.0°C. The results were erratic, however, since the difference in the amount of gas adsorbed at these two temperatures was very small. Only the isotherms for methanol were sufficiently different at 0°C and 22.0°C to allow calculation of ΔH_a at $n^w = 0.5$. The value calculated was -21 kJ mol^{-1} .

The enthalpies of adsorption of the modifiers on soil (and on charcoal) were therefore measured using a different method. Table 3.2.3 presents the results as the amount of heat released when the degassed solid at $22.0 \pm 0.1^\circ\text{C}$ was suddenly exposed to the solvent at approximately 0.13 bar pressure. Note that these values are not ΔH_a , the isosteric enthalpy of adsorption. The pressure was sufficient to cause the adsorption of more than a monolayer of gas (see below for evidence of this), hence the calculated enthalpies of interaction are closer to enthalpies of immersion. The values are quoted in units of Joules per gram of solid, rather than Joules per mole of adsorbed gas, since the amount of gas adsorbed under these conditions is unknown.

If the above experiment did indeed result in monolayer formation, then the heat released per mole of methanol would have been twice the isosteric enthalpy of adsorption, or 42 kJ mol^{-1} . The amount of methanol adsorbed at monolayer coverage of the soil surface was $7.0 \cdot 10^{-5} \text{ mol g}^{-1}$ (see table 3.2.2). The actual amount of heat released was thus $42 \text{ J g}^{-1} / 7.0 \cdot 10^{-5} \text{ mole g}^{-1} = 600 \text{ kJ mol}^{-1}$. This is clearly more than would be released upon adsorption of a mole of methanol. Thus, the ΔH values in table 3.2.3 must represent the heat released when several layers are adsorbed.

Table 3.2.3. Enthalpies of interaction of soil and charcoal with modifiers

Modifier	$\Delta H, \text{J g}^{-1}$ (soil)	$\Delta H, \text{J g}^{-1}$ (charcoal)
Methanol	-42±5	-17
Acetone	-37±3	-7
THF	-27±3	-9
Hexanes	-12±2	-23
DCM	-2.9±0.4	-34
CCl ₄	-2.1±0.5	-3

Notes: The results for soil are the averages of at least five measurements.
The results for charcoal are single measurements.

It is apparent that for soil, the largest amounts of heat are evolved for the adsorptions of the polar modifiers methanol, acetone, and THF. This seems reasonable, since the soil is predominantly silica, and the silicon – oxygen bonds are themselves polar. The adsorptions of the less polar modifiers hexanes, dichloromethane and CCl₄ do not cause the evolution of as much heat.

For charcoal, adsorptions of methanol, hexanes and DCM release the most amount of heat. The non-polar surface of charcoal would be expected to interact favorably with non-polar modifiers through dispersion type forces.

3.2.2 Adsorption from Liquids

The experiments involving adsorption of solutes onto solid surfaces from liquid solutions are presented in this section. In section 3.2.2.1, the results of varying the concentration of the solute are shown. The effects of using different solvents are discussed in section 3.2.2.2. The adsorption equilibrium position was determined as a function of temperature, and the results are presented in section 3.2.2.3.

3.2.2.1 Effect of Concentration of Solute

Figure 3.2.8 is a plot of c/N versus c for the adsorption of 2,3,4,5 tetrachlorophenol on sand from hexanes solution. If the surface were homogeneous,

Figure 3.2.8

c/N versus c for the adsorption of 2,3,4,5-tetrachlorophenol on sand from hexanes solution

the plot would be linear and have a non-zero intercept as discussed in section 1.7. The non-linearity in figure 3.2.8 is a clear indication of a heterogeneous surface. As the total amount of solute present decreases, it is preferentially adsorbed onto the surface of the solid. This is also reflected in the calculated distribution coefficients:

$$K = \frac{a_{\text{surf}}}{a_{\text{soln}}}$$

where a_{surf} is the activity of the solute on the surface of the solid, and a_{soln} is the activity of the solute in the solution. If, as in the discussion on solubilities, we use concentration instead of activity, we can calculate a distribution coefficient at each stage of the 2,3,4,5 tetrachlorophenol / sand / hexane experiment. The units of K will thus be (g solute/g sand)/(g solute/mL solution) = mL g⁻¹. As shown in table 3.2.4, the distribution coefficient increases as the total amount of solute decreases.

Table 3.2.4. Distribution coefficients for 2,3,4,5 tetrachlorophenol on sand from hexane

Hexane Replacement Number	Solution Concentration g mL ⁻¹	Distribution Coefficient mL g ⁻¹
0	1.22 · 10 ⁻⁷	1.47
1	5.43 · 10 ⁻⁸	2.22
2	2.74 · 10 ⁻⁸	3.52
3	1.50 · 10 ⁻⁸	5.45
4	5.69 · 10 ⁻⁹	13.4
5	5.43 · 10 ⁻⁹	13.0

The 2,3,4,5 tetrachlorophenol remaining on the sand surface was removed with acetone. A calculation showed the overall mass balance to be 94.1 %, which is excellent in view of the number of the times the solution was changed.

The heterogeneity of the surface is of great importance when extracting very small amounts of compounds from the surface. Thermodynamically, only the most energetically favorable surface sites should be occupied. The smaller is the amount

of adsorbate, the higher will be the average interaction energy between it and the surface. The practical consequence of this is that the adsorbate will be more difficult to desorb. From the viewpoint of the analytical chemist, the recovery of the adsorbate in an extraction will be more difficult at low surface concentration.

3.2.2.2 Effect of Solvent

To demonstrate that the solvent has an effect on adsorption from solution, the amount of hexachlorobenzene adsorbed onto charcoal from different solvents at $22.0^{\circ} \pm 0.1^{\circ}\text{C}$ was calculated via the experiment described in section 2.4.1. The results are presented in table 3.2.5 along with the solubilities at 22.0°C (from section 3.1.1) and the measured enthalpies of interaction of the solvents with the charcoal from table 3.2.3. There is no obvious correlation between the amount adsorbed and either the enthalpy of interaction of the modifier with the charcoal or the solubility of hexachlorobenzene in the liquid solvents. Similarly, the enthalpy of solution (from table 3.1.5) shows no correlation with the amount adsorbed.

Table 3.2.5. Hexachlorobenzene adsorbed onto activated charcoal from various liquid solvents at 22.0°C

Solvent	Hexachlorobenzene Adsorbed, $\text{mg (g charcoal)}^{-1}$	ΔH , J g^{-1}	Solubility, mole frac.
dichloromethane	0.17	34	$5.5 \cdot 10^{-4}$
tetrahydrofuran	0.32	9	$5.4 \cdot 10^{-3}$
hexanes	0.71	23	$2.7 \cdot 10^{-3}$
acetone	0.74	7	$8.1 \cdot 10^{-4}$
carbon tetrachloride	0.94	3	$9.9 \cdot 10^{-3}$
dimethyl sulfoxide	0.99		$2.6 \cdot 10^{-4}$
methanol	2.40	17	$8.2 \cdot 10^{-5}$

notes: The total available hexachlorobenzene was $2.90 \text{ mg (g charcoal)}^{-1}$

This indicates that in this system, neither the the solvent-solute interactions nor the solvent-surface interactions alone determine the equilibrium amount of adsorbed solute.

3.2.2.3 Effect of Temperature

The temperature used affects the adsorptions of both the solvent and the solute. The measured enthalpy of adsorption is thus the difference between those of the solute and solvent. Adsorption isotherms of hexachlorobenzene on charcoal from methanol, acetone, and hexanes solutions were measured at several temperatures from -20°C to 40°C . For acetone and hexanes, the isotherms did not vary with temperature. This indicates that the enthalpy (and entropy) of adsorption for the solute are approximately the same as they are for either of these two solvents.

The isotherms for the adsorption of hexachlorobenzene on charcoal from methanol are shown in figure 3.2.9. At higher temperatures, less hexachlorobenzene is adsorbed. Table 3.2.6 presents the calculated values of n^0 and b at the four temperatures used.

Table 3.2.6 Values of b and n^0 for the adsorption of hexachlorobenzene on charcoal from methanol solution

Temperature C	b L mol^{-1}	n^0 mol g^{-1}
-20.0	$(1.8 \pm .6) \cdot 10^6$	$(3.3 \pm .2) \cdot 10^{-5}$
0.0	$(1.4 \pm .5) \cdot 10^6$	$(2.9 \pm .3) \cdot 10^{-5}$
20.0	$(1.2 \pm .4) \cdot 10^6$	$(2.7 \pm .2) \cdot 10^{-5}$
40.0	$(1.1 \pm .4) \cdot 10^6$	$(2.3 \pm .1) \cdot 10^{-5}$

The values of b in table 3.2.6 can be used to calculate the enthalpy change for the adsorption process. Recalling again that b is the equilibrium constant for the process (see section 1.7.2), figure 3.2.10 is a plot of $\ln(b)$ versus $1/T$. The enthalpy change calculated from the slope of this plot is $-5.4 \pm .6 \text{ kJ mol}^{-1}$. The fact that this quantity is negative indicates that the enthalpy of adsorption of methanol on charcoal is less exothermic than that of hexachlorobenzene. In other words, as the temperature is increased, the adsorption of hexachlorobenzene decreases, with the concomitant increase of the adsorption of methanol, according to equation 1.7.2.1.

Figure 3.2.9

c/N versus c for the adsorption of hexachlorobenzene on charcoal from methanol solution at -20.0°C (○), 0.0°C (□), 20.0°C (○) and 40.0°C (△).

Figure 3.2.10

$\ln(b)$ versus $1/T$ for the adsorption of hexachlorobenzene on charcoal from methanol solution

3.2.3 Adsorption from Supercritical Fluids

The adsorption of 2,3,4,5-tetrachlorophenol on sand from CO₂ was measured as a function of density using the static equilibrium device diagrammed in figure 2.4.1 (page 87). The device was rather clumsy to use, requiring disassembly to replace the sand and clean the inside walls after each adsorption measurement.

Figure 3.2.11 shows the fraction of 2,3,4,5-tetrachlorophenol remaining in solution after equilibrating with a sample of sand for several hours as a function of density at 22±1°C. It is apparent that at higher density, the amount of solute in solution increases, hence the amount adsorbed must be decreasing. The solute was not simply precipitating as a solid on the sand or the walls of the device at low density, since the total concentration of solute was maintained well below its saturation limit in CO₂ (see section 3.1.2).

The positive slope in figure 3.2.11 must be due to the increase of adsorption of CO₂ on the surface of the sand as the density is increased. According to equation 1.7.2.1, this would tend to decrease the amount of solute adsorbed, hence increase its concentration in the solution.

Due to the cumbersome procedures required to use the static equilibrium device, the device outlined in section 2.4.2 (see figure 2.4.2) was used for all subsequent experiments on adsorption from supercritical fluids. This device was found to be simple to use, and experiments could be done quickly and much more precisely. Although not used to separate compounds, the device was essentially a supercritical fluid chromatograph (SFC).

The stationary phases used in the SFC experiments were chosen from the adsorbents used in the adsorption experiments (section 3.2.1 and 3.2.2) and the extraction experiments (section 3.3). Since there appears to be no data in the literature regarding the use of packed columns using stationary phases of soil, silica sand or Florisil, some experimentation was necessary to find the best column dimensions.

For the experiments using silica as the stationary phase, a 1/4" od × 15 cm long tube packed with 3.82 g 60–120 mesh silica sand was found to give reasonable retention times. Smaller columns packed with silica gave sharper peaks, but the

Figure 3.2.11

Fraction of 2,3,4,5-tetrachlorophenol remaining in CO₂ solution in equilibrium with sand as a function of the density of the solution

retention times were too low to be useful. For the experiments using soil as the stationary phase, a smaller column was necessary since soil was so much more retentive than silica sand. Thus, a 1/8" od $\times$ 15 cm long tube packed with 0.299 g 60–120 mesh soil was used. The last column prepared was 1/8" od $\times$ 15 cm long packed with 60–100 mesh Florisil.

The value of V_o , the retention volume of an unretained solute, was calculated for each column by injecting hexanes. The values of V_o were $1.43 \pm .01$ mL for the silica column, $0.49 \pm .01$ mL for the soil column and $1.43 \pm .01$ mL for the Florisil column. Column data are summarized in table 3.2.7.

Table 3.2.7 Data on SFC columns used

Column Packing	Length (cm)	Internal diameter (mm)	Mass of Packing (g)	Packing Mesh Size	V_o (mL)
Silica	15	5.0	3.82	60–120	$1.43 \pm .01$
Soil	15	2.0	0.299	60–120	$0.49 \pm .01$
Florisil	15	2.0	0.156	60–100	$1.43 \pm .01$

The absorption spectra of several compounds of interest were measured on a Perkin–Elmer Lambda 4B double beam UV–VIS spectrophotometer in dichloromethane using dichloromethane as reference. The wavelengths of maximum absorption for the solutes used are listed in table 3.2.8. The wavelength setting of the detector used for the SFC experiments was previously calibrated [90].

The linearity of the detector was tested by injecting various masses of 2,3,4,5–tetrachlorophenol (dissolved in hexanes) and recording the resultant peak area. Figure 3.2.12 is a plot of mass injected versus peak area. The plot is linear up to at least 35 μ g solute, which was the maximum amount of solute used for any subsequent SFC experiment. Injection of pure hexanes produced a negative peak, and the 2,3,4,5–tetrachlorophenol was not well resolved from the hexanes under the conditions used ($22.0 \pm .1^\circ\text{C}$, $0.87 \pm .01$ g mL $^{-1}$ CO $_2$). Thus, the intercept on the area axis in figure 3.2.12 is negative.

Figure 3.2.12

Mass of 2,3,4,5-tetrachlorophenol injected versus peak area. The conditions were $22.0 \pm 0.1^\circ \text{C}$ and $0.87 \pm 0.01 \text{ g mL}^{-1}$ with a CO_2 mobile phase using the silica column

Table 3.2.8 Wavelengths of maximum absorption of solutes

Compound	Wavelength, nm
Fluoranthene	359.6
Chrysene	268.8
2,4-D	233.0
Hexachlorobenzene	233.6
2,3,4,5-tcp	230.8

3.2.3.1 Effect of Density

As described in the introduction, retention is expected to decrease as the density of the mobile phase is increased. The experiment described at the beginning of this section showed that the adsorption equilibrium is shifted towards desorption of the solute as the density is increased. To test this further, the retentions of three solutes on the silica column were measured as a function of density at $22.0 \pm 1^\circ \text{C}$. The results are plotted in figure 3.2.13 as the capacity factor versus density. For all three compounds, the capacity factor decreased as the density was increased, as expected.

Fluoranthene was not retained strongly on this column at any density from 0.8 to 0.98 g mL^{-1} . The polar compound 2,3,4,5-tetrachlorophenol was retained more strongly, especially at low density, and 2,4-D was strongly retained even at high density. The order of the retentions of these three compounds may be due to their relative dipole moments, but may also be due to their tendencies to hydrogen bond with the silica surface. Fluoranthene would not hydrogen bond, whereas the tetrachlorophenol would, and the 2,4-D (a carboxylic acid) would do so even more.

Figure 3.2.13

Capacity factor versus density for fluoranthene (Δ), 2,4-D ($\circ$) and 2,3,4,5-tetrachlorophenol ($\square$) with a CO_2 mobile phase at $22.0 \pm 0.1^\circ\text{C}$ using the silica column

3.2.3.2 Effect of Concentration of Solute

Most analytical chromatography is carried out in a regime where the equilibrium between the solute in the mobile and stationary phases is invariant with the concentration of the solute. From the point of view of the analytical chemist, this means that the retention time of a compound in a chromatographic separation will not change with the amount of the compound injected onto the column. If the retention of a compound is found to vary with concentration, it may be an indication of adsorption of the compound on bare sites of the stationary phase support material or on some other part of the chromatographic system. In the present system, the entire stationary phase is bare (i.e. uncoated), and so the primary retention mechanism is one of adsorption. Thus, the retention of any compound is expected to vary considerably with its concentration.

Figure 3.2.14 is a plot of the capacity factor of 2,3,4,5-tetrachlorophenol versus the mass injected on the silica column at $22.0 \pm 1^\circ\text{C}$ and $0.87 \pm 0.01 \text{ g mL}^{-1}$ in CO_2 . Upon increasing the mass of solute injected from $4 \mu\text{g}$ to $26 \mu\text{g}$, the capacity factor drops by roughly a factor of two. According to equation 1.7.3.18 (page 72), the capacity factor is expected to decrease as the mass of solute injected is increased.

This has serious consequences for the analytical chemist wishing to extract an adsorbate from an adsorbent, since at sufficiently low concentrations of adsorbate, the retention will be very large. This was also noted for the liquid system discussed in section 3.2.2.1.

3.2.3.3 Effects of Modifiers

The solvent is expected to have a large effect in adsorption SFC, since the retention mechanism is one of competition for surface sites by the solute and solvent. One method to change the activity of the solvent on the solid surface is to change the density of the fluid, as described in section 3.2.3.1. Another method is to change the solvent itself, from CO_2 to some other supercritical fluid. Yet another method is the use of small amounts of modifiers dissolved in the CO_2 .

The retention of 2,3,4,5-tetrachlorophenol at $22.0 \pm 1^\circ\text{C}$ on the silica column was measured as a function of density in CO_2 , CO_2 + hexanes and CO_2 + methanol. The concentration of the modifier was 3.2 mole percent in each case. A constant

Figure 3.2.14

Capacity factor versus mass of 2,3,4,5-tetrachlorophenol injected onto the silica column at $22.0 \pm 0.1^\circ \text{C}$ and $0.87 \pm 0.01 \text{ g mL}^{-1}$ with CO_2 as the mobile phase

amount of 13.4 μg of solute was injected. Referring to figure 3.2.15, the capacity factor drops dramatically upon addition of hexanes to the CO_2 . Addition of methanol results in an even larger effect.

At higher densities, the curves in figure 3.2.15 converge towards one another. This could be due to one of two reasons. First, as the density is increased, the carbon dioxide alone becomes a more effective eluent, as shown in figure 3.2.14. Thus, in mixtures of CO_2 +modifier at high densities, elution of the solute may be due as much to the CO_2 as to the modifier. Second, the fugacities of the modifiers used are not equal, even though the mole fraction of modifier was constant at 0.032. This point is expanded upon in the following paragraphs.

Inspection of the extraction reaction (equation 1.7.2.1) shows that two equilibria are present. First, the solute in the fluid phase is in equilibrium with the adsorbed solute. Equilibrium implies that the fugacities of the solute in the two phases are equal. Similarly, the solvent fugacities in the adsorbed and fluid phases must be equal to each other. Since the solvents considered here are binary mixtures, the equivalence of fugacities in the adsorbed and fluid phases applies, separately, to both the CO_2 and the modifier. The important point is that by calculating the fugacity of the modifier in the fluid phase, we have also calculated the fugacity of the adsorbed modifier.

The fugacities of the modifiers can be calculated using equation 1.6.2.10 (page 49) in conjunction with an equation of state. The Peng–Robinson equation was used, with the required binary interaction parameters from reference 91. Figure 3.2.16 shows the predicted fugacities of 3.2 mole percent hexane and methanol in CO_2 at 22.0°C as a function of density. It is apparent that as the density is increased, the fugacity of hexane increases rapidly, while that of methanol is almost constant.

The relationship between the fugacity of an adsorbate and its molar surface area has been treated by Van Ness [92]. The adsorbed phase can be described using a two dimensional equation of state. The two dimensional analog of the three dimensional ideal gas equation of state is $\pi a_m = R T$ where π is the spreading

Figure 3.2.15

Capacity factor of 2,3,4,5-tetrachlorophenol on the silica column at 22.0±.1°C versus density using CO₂, CO₂ + hexanes and CO₂ + methanol

Figure 3.2.16

Fugacities of 3.2 mole percent hexane (O) and methanol (Δ) in carbon dioxide at 22.0°C versus density. The Peng–Robinson equation of state was used.

pressure and a_m is the molar surface area.

Van Ness has shown that π is simply the fugacity of the adsorbate. Thus, the molar surface area of the adsorbate is inversely proportional to the fugacity of the adsorbate. A smaller molar surface area can be interpreted as more complete coverage of the surface.

Thus, according to the above arguments and the data presented in figure 3.2.16, the molar volume of adsorbed hexane decreases as the fluid density is increased, while that of methanol remains almost constant. The result should be that at high density, the coverage of the surface by hexane is as large as that by methanol, and the two modifiers should be equally effective in reducing the retention of a solute.

In order to determine the effects different modifiers have on retention on the soil column, some standard conditions were chosen as the basis for comparison. The solute used was 2,3,4,5-tetrachlorophenol, since its retention on soil was found to be strong without the use of modifiers. A constant amount of 13.4 μg was injected. The conditions chosen were $22.0 \pm 0.1^\circ\text{C}$ and a solvent density of $0.87 \pm 0.01 \text{ g mL}^{-1}$ with mobile phases consisting of $\text{CO}_2 + 0.52 \pm 0.01$ mole percent modifier.

The pressures required to achieve a constant density of $0.87 \pm 0.01 \text{ g mL}^{-1}$ were calculated using the Peng–Robinson equation of state and are presented in table 3.2.9.

Table 3.2.9 Pressures required to achieve $0.87 \pm 0.01 \text{ g mL}^{-1}$ in binary systems of $\text{CO}_2 + 0.52 \pm 0.01$ mole percent modifier

Modifier	Pressure, bar
Methanol	132.0
Acetone	133.0
Hexanes	136.9
Dichloromethane	132.0
Carbon Tetrachloride	125.8
Tetrahydrofuran	131.6

The pressures required do not vary greatly from one modifier to another, because the mole percent of modifier is so low. The system was operated at as close to these pressures as possible, since it was already known that variations in the density would cause the retention to change.

The capacity factor of 2,3,4,5-tetrachlorophenol on soil was measured five or more times in each of the binary solvent systems, and the results are presented in table 3.2.10. Some results for retention on Florisil are also presented.

Table 3.2.10 Capacity factors for 2,3,4,5-tetrachlorophenol on soil and on Florisil in $\text{CO}_2 + 0.52 \pm 0.01$ mole percent modifier systems

Modifier	Capacity Factor on Soil	Capacity Factor on Florisil
Methanol	1.7 ± 1	3.0 ± 1
Dichloromethane	2.4 ± 1	
Hexanes	2.6 ± 1	17 ± 1
Carbon Tetrachloride	3.4 ± 2	
Tetrahydrofuran	4.6 ± 2	
Acetone	6 ± 1	8.5 ± 5
No Modifier	∞	∞

Carbon dioxide alone could not elute the solute from the soil column. It is easily shown that this is not due to a lack of solubility of 2,3,4,5-tetrachlorophenol in pure CO_2 . The amount of the solute injected was $5.8 \cdot 10^{-8}$ moles ($13.4 \mu\text{g}$). The amount of CO_2 at 22.0°C and 0.87 g mL^{-1} required to solubilize this amount of solute can be calculated from the data in table 3.1.9 as $4.2 \cdot 10^{-5}$ moles. The actual amount of CO_2 passed through the soil column was approximately $1.3 \cdot 10^{-1}$ moles, or some 3,000 times the amount required to solubilize the solute. Thus, the retention of 2,3,4,5-tetrachlorophenol on the soil must be due to strong solute-surface interactions.

Of the six modifiers used, methanol had the greatest effect on the retention of 2,3,4,5-tetrachlorophenol by soil. Referring again to table 3.1.9, the solubility of this solute is greater in CO_2 + methanol than in any of the other CO_2 + modifier combinations. However, if the solubility in the solvent was the factor controlling the retention, then the order of solubilities in table 3.1.9 would be the reverse of the order of capacity factors in table 3.2.10. This is not the case, and once again it appears that retention is not related only to solubility in the fluid phase.

Methanol was also the best modifier for elution of 2,3,4,5-tetrachlorophenol from Florisil. The order of effectiveness of acetone and hexanes was reversed, however, indicating specific modifier-surface interactions influence the retention.

Assuming the modifiers function by adsorbing onto the soil, it was hoped that gas phase adsorption data would correlate with adsorption from supercritical CO_2 , hence also to the observed capacity factors. The enthalpies of interaction of the gaseous modifiers with soil were presented in table 3.2.3. There is essentially no correlation between those values and the measured capacity factors. There is also no correlation between the capacity factors and the calculated equilibrium constants for the adsorptions of the modifiers on soil from the gas phase (i.e. the b values in table 3.2.2). Thus, gas phase adsorption data can not be used to explain adsorption of the modifiers from supercritical CO_2 .

As described for the 2,3,4,5-tetrachlorophenol/silica system, the fugacities of four of the the six modifiers in CO_2 were calculated and are presented in table 3.2.11. Binary interaction parameters necessary for the calculations were not available for the other two modifiers.

Table 3.2.11 Fugacities of 0.52 mole percent modifiers in CO_2 at 22.0°C and 0.87 g mL^{-1}

Modifier	Fugacity
Methanol	.00524
Acetone	0.0351
Hexane	0.0159
Carbon Tetrachloride	0.0225

The fugacities of the modifiers vary considerably, even though their concentrations in the CO₂ were identical. As mentioned above, however, the relationship between the fugacity of an adsorbed modifier and its surface coverage is unknown. Hence, nothing definite can be deduced from the solution phase modifier fugacities.

3.2.3.4 Effect of Modifier Concentration

The concentration of modifier is expected to have an effect on the capacity factor. Figure 3.2.17 is a plot of the capacity factor of 2,3,4,5-tetrachlorophenol on soil at 22.0±1°C and 132±1 bar in four different concentrations of methanol in CO₂ versus the mass of solute injected. The capacity factors are seen to decrease with increasing amounts of injected solute, as shown previously. However, the higher is the mole fraction of methanol, the lower is the capacity factor, and the smaller is the dependence of the capacity factor on mass injected. At 3.2 mole percent methanol, the capacity factor ceases to be a function of the amount injected, and there is essentially no retention.

The interpretation is that as the concentration of methanol is increased, the adsorption of methanol onto the surface of the soil increases. This decreases the number of sites available for adsorption of the solute. Hence the retention of the solute is decreased.

The effect of increasing the methanol concentration can be quantitatively treated by the method of Schoenmakers et al (see section 1.7.3.4). The linear form of equation 1.7.3.18, ignoring the d' term for a chemically bonded stationary phase, is

$$k'Q = -k'/b' + a'/b' \quad (3.2.1.5)$$

where Q is the mass of injected solute, and k' is the capacity factor. As discussed in section 1.7.3.4, b' is a measure of the relative energy of adsorption of the solute, and a'/b' is a measure of the relative number of adsorption sites on the surface. Figure 3.2.18 is a plot of $k'Q$ versus k' for the four methanol concentrations used. The values of b' and a'/b' and the regression coefficients calculated from the regressions of the lines are presented in table 3.2.12.

Figure 3.2.17

Capacity factor of 2,3,4,5-tetrachlorophenol on the soil column versus mass injected at four different concentrations of methanol in CO_2

Figure 3.2.18

$k'Q$ versus k' for 2,3,4,5-tetrachlorophenol on the soil column at $22.0 \pm 0.1^\circ \text{C}$ and $0.87 \pm 0.01 \text{ g mL}^{-1}$ in CO_2 with methanol mole fractions of 0.0053 (○), 0.0088 (○), 0.0167 (△) and 0.0320 (□)

Table 3.2.12 Calculated values of b' and a'/b' for the adsorption of 2,3,4,5-tetrachlorophenol on soil at various methanol concentrations

Methanol Mole Fraction	b'	a'/b'
0.0053	0.093	39±8
0.0088	0.070	31±5
0.0167	0.045	20±2
0.0320	0	

The retention of the 2,3,4,5-tetrachlorophenol was invariant with the mass injected when the methanol mole fraction was 0.032, as mentioned above. Thus, the plot of $k'Q$ versus k' was vertical at this concentration, implying that the value of b' was zero. However, since the capacity factor at this concentration was not zero, there is no intercept on the plot from which to calculate a'/b' .

Some generalizations can be made about the calculated values of b' and a'/b' . As the concentration of methanol was increased, the value of a'/b' decreased. This implies fewer adsorption sites are available for the solute at higher methanol concentration, and is due simply to more extensive adsorption of methanol on the soil. A linear extrapolation of a plot of a'/b' versus the mole fraction of methanol (for which there is no theoretical basis) predicts that a'/b' will become zero at 0.029 mole fraction methanol.

The calculated values of b' indicate that the energy of interaction of the 2,3,4,5-tetrachlorophenol decreases as the mole fraction of methanol is increased. This is again due to increased coverage of the surface by the methanol. With no methanol present, the most energetically favorable sites (often termed the most 'active' sites) for adsorption are occupied by CO_2 . The solute competes successfully for these sites, and is therefore retained on the soil. As the methanol concentration is increased, sites of progressively lower 'activity' are occupied by the methanol. The value of the solute-surface interaction energy, as reflected by the value of b' , decreases, and retention of the solute decreases accordingly.

An alternative explanation is that at high concentrations, adsorption of the methanol produces, in effect, a stationary phase in which the solute is somewhat

soluble. Thus, the chromatography changes from an adsorption mechanism at low methanol concentration to a partition mechanism at high methanol concentration. This would also explain the non-zero capacity factor observed at a methanol concentration of 0.0320 mole fraction, since a finite solubility of a solute in a stationary phase implies at least some retention. Furthermore, it was shown in section 3.2.1.2 that methanol adsorbed from the gas phase likely results in far more than a monolayer coverage of the surface. If the same is true for adsorption of methanol from supercritical CO_2 , then formation of a methanol stationary phase is plausible.

3.2.3.5 Retention of Modifiers

If it is true that lower retention of a solute in the presence of a modifier is due to increased adsorption of the modifier on the solid surface, then a modifier which is more effective at lowering retention should itself be retained to a greater extent than a less effective modifier. This was tested by measuring the retentions of the pure liquid modifiers on the soil column with pure CO_2 as the mobile phase at $22.0 \pm 1^\circ \text{C}$ and $0.87 \pm 0.01 \text{ g mL}^{-1}$. The detector was operated at 190 nm, which is below the UV cutoff wavelength for all of the modifiers used. The amount of modifier injected was calculated based on equal surface coverage using effective surface areas of the modifier molecules calculated from equations 3.2.1.1 and 3.2.1.2. Table 3.2.13 presents the amounts injected and the capacity factors of the six modifiers.

Table 3.2.13 Injection volumes and capacity factors on soil for modifiers at $22.0 \pm 1^\circ \text{C}$ and $0.87 \pm 0.01 \text{ g mL}^{-1}$ with CO_2 as the mobile phase

Modifier	Volume Injected (μL)	Capacity Factor, k'
Hexanes	2.6	0.0
Dichloromethane	2.0	0.0
Carbon Tetrachloride	2.3	0.0
Tetrahydrofuran	2.2	4.4
Acetone	2.1	4.9
Methanol	1.7	15.8

Methanol is retained to a much larger extent on the soil than are the other modifiers. This is consistent with the fact that it is the most effective modifier for elution of the 2,3,4,5-tetrachlorophenol. Carbon tetrachloride and dichloromethane are not retained at all by the soil, and yet they are still very effective modifiers (see table 3.2.10). This may be due in part to the high solubility of the 2,3,4,5-tetrachlorophenol in solutions of CO_2 with these modifiers (see table 3.1.9).

Tetrahydrofuran and acetone are retained to some extent by the soil, but are rather poor modifiers. The elution profiles of these two modifiers may provide some insight as to why they are poor modifiers. Figure 3.2.19 shows the peaks resulting from the injection of the pure modifiers, normalized to equal area. (The data for hexanes was omitted from the figure, since the peak area was very small and the peak shape was thus difficult to determine.) The peak shapes for carbon tetrachloride, dichloromethane and the later eluting methanol were fairly sharp. However, the peak shapes for acetone and THF were broad, indicating that the injected volumes of these modifiers were smeared out along the length of the column. This may be an indication of why these two modifiers are not as effective as their retention times would suggest.

Hexanes appears to be an excellent modifier in this system, but is not retained by the soil. Furthermore, the 2,3,4,5-tetrachlorophenol is less soluble in CO_2 + hexanes than in the other CO_2 + modifier systems.

Thus, with the exception of CO_2 + hexanes, the retention of a solute depends on the modification of the surface by the solvent, and possibly on the solute-modifier interactions as well.

Figure 3.2.19

Elution profiles of modifiers on the soil column normalized to equal area plotted versus the capacity factor, k' . The peaks are CCl_4 (1), DCM (2), Acetone (3), THF (4) and methanol (5)

3.3 Extractions

Results from supercritical fluid extractions are presented in this section. The variables investigated included time, flowrate, pressure, temperature, type of solid matrix, type of solute, type of fluid, solid particle size and spike level. The dependent variable was, in all cases, the recovery of the solute, expressed in percent of the spike level.

3.3.1 Time Dependence

The time dependence of the extraction yield is of interest, since one of the advantages of using supercritical fluids as extraction media over liquid solvents is the decrease in extraction times required to achieve high recoveries. However, very little has been published on rates of extraction using supercritical solvents.

The time dependence of extractions were followed using the procedure described in section 2.1.2.5. Many of the extractions noted in the following sections were followed as functions of time, and thus no results specifically related to the time dependence of extractions are presented in this section.

3.3.2 Flowrate Dependence

The flowrate of the extraction fluid could be expected to have an effect on the rate of recovery of solutes during an extraction for one of three reasons. First, the dead volume of the cell and fittings may simply retard the egress of the extracted solutes from the extraction cell. This effect would be common to all solutes during an extraction. Second, if the flowrate is sufficiently low, the fluid may become saturated in one or more solutes, and thus the rate of recovery of such a solute would be directly proportional to the flowrate. Third, the diffusion of solutes from the surface of the solid into the bulk fluid may depend upon the concentration of the solute in the fluid, which in turn will depend upon the flowrate.

Extractions were performed with different volumetric flowrates of supercritical fluid through the extraction cell. The extractions were performed in CO₂ at 63.5 bar and 40.5°C, where the density was only 0.16 g mL⁻¹. These conditions were necessary in order to easily see the difference that flowrate makes. The initial concentrations of *n*-octadecane and *m*-terphenyl on the sand were 0.45 µg g⁻¹. The sample size was 0.7 g in each case.

Figure 3.3.1 shows the percent of *m*-terphenyl extracted from sand as a function of time at four different flowrates. The amount extracted per unit time increased as the flowrate was increased from 0.30 to 2.02 mL min⁻¹ CO₂ (measured as a supercritical fluid at 0.16 g mL⁻¹). Figure 3.3.2 shows the same results when plotted as percent extracted versus total volume of supercritical CO₂ passed through the cell. The similarity of the curves in figure 3.3.2 suggests that the flowrate *per se* is not an important variable. What matters is the total amount of fluid passed through the bed of solids.

If the extraction rate of *m*-terphenyl from sand is being limited by the solubility of the former in the CO₂, we may calculate the actual solubility using simple arguments. The *m*-terphenyl was extracted from the sand at a rate of roughly 13.5% per 120 minute period at a flowrate of 2.02 mL CO₂ per minute. The total *m*-terphenyl extracted was thus

$$\frac{(0.135 \times 0.7 \text{ g} \times 0.45 \text{ } \mu\text{g g}^{-1})}{(120 \text{ min} \times 2.02 \text{ mL min}^{-1})} = 1.75 \cdot 10^{-4} \text{ } \mu\text{g (mL CO}_2\text{)}^{-1}$$

Converting this result to mole fraction, we find that the average mole fraction of *m*-terphenyl in the CO₂ during the extraction was $2.1 \cdot 10^{-10}$. Since the pressure was 63.5 bar, the partial pressure of the *m*-terphenyl was $63.5 \text{ bar} \times 2.1 \cdot 10^{-10} = 1.3 \cdot 10^{-8} \text{ bar}$.

The vapor pressure of *m*-terphenyl at 40.5°C and 1 bar total pressure is $1.8 \cdot 10^{-8}$ (see table 3.1.6). Applying the Poynting correction for vapor pressure at elevated pressure (equation 1.5.2.7), we find that the vapor pressure of *m*-terphenyl at 63.5 bar and 40.5°C should be $3.2 \cdot 10^{-8} \text{ bar}$.

The solubility of *m*-terphenyl in CO₂ at 0.16 g mL⁻¹ would not be much greater than its vapor pressure. Inspection of figure 1.6.2, for instance, reveals that the solubility of phenanthrene in CO₂ at 65 bar and 45°C is only a few times higher than its vapor pressure. Thus, we can estimate that the saturation partial pressure of *m*-terphenyl in CO₂ at 0.16 g mL⁻¹ and 40.5°C would be roughly $10 \cdot 10^{-8} \text{ bar}$.

Figure 3.3.1

Recovery of *m*-terphenyl from sand versus time at CO₂ flowrates of 2.02 (○), 1.39 (△), 1.00 (□) and 0.30 mL min⁻¹ (⬡)

Figure 3.3.2

Recovery of *m*-terphenyl from sand versus total volume of CO₂ at flowrates of 2.02 (○), 1.39 (△), 1.00 (□) and 0.30 mL min⁻¹ (◇)

The transfer of a molecule from the adsorbed phase to the bulk fluid phase is thought to occur via an interfacial region [93]. The solute thus diffuses through the interfacial region under the influence of a concentration gradient. It is conceivable that the side of the interfacial region in contact with the solid surface could become saturated with the solute. Thus, in the case of the extraction of *m*-terphenyl, the rate of recovery may be limited by the solubility in the interfacial region, even though the bulk fluid is not saturated.

The flow pattern of the solvent through the extraction cell could cause portions of the solutes to be carried from the cell very slowly. An effect of flowrate on the apparent rate of extraction could also arise from a significant dead volume in the apparatus, which would show up as a delay in the first appearance of extracted solutes. If these effects were serious, they could become the rate limiting factors. However, the effect would be of the same magnitude for all solutes. Figure 3.3.3 shows the percent of *n*-octadecane extracted from sand as a function of time at the same four flowrates as in figure 3.3.1. The extraction is roughly 75% complete after 120 minutes, no matter what flowrate is used. This should be compared to the extraction of *m*-terphenyl, where the greatest extraction after 120 minutes was only 13.5%. Furthermore, there was no observable delay in the first appearance of either solute. Thus, the differences in extraction rate cannot be attributed to the extraction apparatus.

When the data in figure 3.3.3 are plotted versus the total volume of CO₂ (figure 3.3.4), it is apparent that at lower flowrates, less fluid is required to extract a certain amount of *n*-octadecane. This is because at lower flowrates, the fluid is in contact with the solid for a longer time, and more of the solute desorbs into a given volume of the fluid. Thus, diffusion of the solute from the surface to the bulk fluid is most likely the rate limiting step for extraction of this solute.

Arguments similar to those used for the *m*-terphenyl may be used to show that the recovery rate of *n*-octadecane was not limited by its solubility in the CO₂. The average partial pressure of *n*-octadecane in the CO₂ during the initial stages of the extractions was $4.4 \cdot 10^{-9}$ bar. The vapor pressure of *n*-octadecane at 63.5 bar and 40.5°C is $4.3 \cdot 10^{-5}$ bar. Thus, the rate of recovery of *n*-octadecane was limited by something other than its solubility, possibly the diffusion of the compound through the interfacial region.

Figure 3.3.3

Recovery of *n*-octadecane from sand versus time at using CO₂ at flowrates of 2.02 (Δ), 1.39 (○), 1.00 (○) and 0.30 mL min⁻¹ (□)

Figure 3.3.4

Recovery of *n*-octadecane from sand versus total volume of CO₂ at flowrates of 2.02 (○), 1.39 (□), 1.00 (△) and 0.30 mL min⁻¹ (○)

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)

For most analytical extractions, solubility will not be the parameter limiting the rate of recovery. This is because extractions are generally performed at higher solvent density where solubilities are higher. Furthermore, the concentrations of adsorbates used in the above experiments were rather high. Lower concentrations would make it less likely that the interfacial region would become saturated.

3.3.3 Pressure Dependence

Extraction from Silica

The pressure dependence of extraction recoveries has been demonstrated several times in the literature [14,18,29]. Generally, the extraction recoveries increase with increasing pressure. The effect is usually attributed to greater solubility of the solutes at higher pressure (hence higher density) of the fluid. However, few publications have shown how the pressure influences the rate of extraction, nor has it been demonstrated that solubility is indeed the factor limiting the recoveries.

A sample of silica sand was spiked with the following five compounds, each at approximately $10 \mu\text{g g}^{-1}$: *n*-eicosane, fluoranthene, *m*-terphenyl, chrysene and perylene. Extractions were performed using CO_2 at 20.6°C and three different pressures: 138, 207 and 310 bar. The results are plotted in figures 3.3.5 to 3.3.9 as percent recovered from a 1 g sample versus time.

Referring to figure 3.3.5, the recovery of *n*-eicosane at 138 bar was 64% after 10 minutes, and increased to only 68% after 30 minutes. When the operating pressure was 207 bar, the recovery levelled off at 83%, and at 310 bar, the final recovery was 110%. This confirms what many investigators have noted — that higher pressures give higher recoveries. This pressure effect was common to all five solutes used.

If we assume that an equilibrium such as that postulated in equation 1.7.2.1 is in effect, and that the solvent is a supercritical fluid, then equation 1.7.2.6 may be used to provide the functional form of the relationship between the amount of solute adsorbed at a given pressure and the amount of solute in solution. However, the value of a_1 (the solvent activity in the fluid phase) in equation 1.7.2.2 will no longer be a constant, but rather a function of pressure. Recalling that $K=b \cdot a_1$, where K is

Figure 3.3.5

Recovery of *n*-eicosane from sand versus time at 138 bar (Δ), 207 bar ($\square$) and 310 bar ($\circ$)

Figure 3.3.6

Recovery of fluoranthene from sand versus time at 138 bar (Δ), 207 bar ($\square$) and 310 bar ($\circ$)

Figure 3.3.7

Recovery of *m*-terphenyl from sand versus time at 138 bar (Δ), 207 bar ($\square$) and 310 bar ($\circ$)

Figure 3.3.8

Recovery of chrysene from sand versus time at 138 bar ($\triangle$), 207 bar ($\square$) and 310 bar ($\circ$)

Figure 3.3.9

Recovery of perylene from sand versus time at 138 bar (Δ), 207 bar ($\square$) and 310 bar ($\circ$)

the equilibrium constant, and b is a constant, it is apparent that K will also be a function of pressure. Specifically, increasing the pressure will decrease the value of a_1 (more correctly, the fugacity of the fluid will decrease), thereby decreasing the value of K . According to equation 1.7.2.2, this will shift the equilibrium in a direction such that desorption of the solute is increased. From a phenomenological point of view, increasing the pressure favors the adsorption of the solvent, hence the desorption of the solute.

Even though the position of the equilibrium may be such that very little solute is in solution, and most of the solute is adsorbed, we would nevertheless expect to eventually desorb all of the solute from the surface of the solid in a flow-through extraction system such as the one used in these studies. Although the recoveries do not completely level off with time, the difference between the initial and final rates of extraction is striking, and suggests that something is limiting the recoveries at a given pressure.

Heterogeneity of the Surface

A possible explanation (which was proposed in a recent publication [94]) is that a solute is adsorbed onto the surface with a range of interaction energies. The dispersion of energies could be due to heterogeneity of the surface, and possibly a range of orientations of the solute to the surface. Solutes are also known to diffuse across surfaces [95] to more energetically favorable sites, and thus we can not assume that all adsorbed molecules of a solute have the same energy of adsorption.

The heterogeneity of the solute–solid interaction is reflected in the variation of the value of b (equation 1.7.2.11) with surface coverage. Specifically, the value of b becomes larger at smaller surface coverages, when the solute molecules on the surface interact with the most energetically favorable sites on the surface. Thus, Langmuir plots for a heterogeneous surface do not become linear at low surface coverages, but remain convex to the concentration axis.

This was demonstrated for the adsorption of 2,3,4,5-tetrachlorophenol on sand from liquid hexane in section 3.2.3.1. More importantly, this was demonstrated for the 2,3,4,5-tetrachlorophenol / soil / CO₂ + methanol system in section 3.2.3.5. There it was shown that increasing the methanol concentration decreased the value of *b*. The interpretation was that at high surface coverages of methanol, the surface was less heterogeneous, i.e. it had a smaller range of energies of interaction with the solute. Hence, the dependence of retention on solute mass decreased with increasing methanol concentrations, and was essentially zero at a sufficiently high concentration of methanol.

Given that the surface is indeed heterogeneous, the use of a low density extracting fluid will result in the desorption of only those solute molecules that are adsorbed with low energies. Thus, the plots in figures 3.3.5 to 3.3.9 level off due to the inability of the extracting fluid to compete successfully with solutes adsorbed with energies greater than some threshold values. Desorption of the remaining solute would require the use of a different fluid, or operation at higher density.

The initial rate of extraction was also observed to increase with increasing pressure. Note that this was not due to higher flowrates, since the flowrate was maintained at 150 mL min⁻¹ (measured as CO₂ gas at atmospheric pressure). Since the CO₂ density is higher at higher pressure, the volumetric flowrate of supercritical CO₂ was actually lower at higher pressure.

Selective Extraction

Under certain conditions it is possible to extract some species from the surface, and leave others behind. This "selective" extraction was demonstrated, for instance, by Hawthorne [14], who found that alkanes could be selectively extracted from diesel exhaust particulates, leaving behind the majority of adsorbed PAH, simply by operating at lower pressure.

Selective extraction was also demonstrated in this work by extracting the sand noted above in CO₂ at 40.5±.1°C at various pressures from 61 to 132 bar. This gave CO₂ densities from 0.15 to 0.75 g mL⁻¹. The extractions were carried out for twenty minutes, then for a further twenty minutes to verify completeness of extraction.

The extraction of perylene was negligible at low densities (below roughly 0.5 g mL^{-1}). However, measurable quantities of the other five solutes were extracted. The selectivity was defined as the ratio of the total percent recovery of one compound divided by that of the other.

Figures 3.3.10 to 3.3.13 are plots of the log of the selectivity versus density for four pairs of solutes. Referring to figure 3.3.10, the selectivity of *n*-eicosane / fluoranthene is low at high density, and rises to approximately 55 at 0.2 g mL^{-1} . In other words, 100 times more *n*-octadecane than fluoranthene is extracted at low density.

The selectivity of fluoranthene / chrysene (figure 3.3.11) reaches a maximum of approximately 25 at approximately 0.28 g mL^{-1} . The selectivity is not as high in this system presumably due to the similarity of fluoranthene and chrysene, compared to that of *n*-octadecane and fluoranthene.

The selectivity of fluoranthene / *m*-terphenyl (figure 3.3.12) is less than unity over the entire density range used (i.e. less fluoranthene than *m*-terphenyl is recovered). It should be noted that fluoranthene actually has a higher vapor pressure than *m*-terphenyl, and would thus be expected to have a higher solubility. The reversal of the selectivity likely implies that fluoranthene is more strongly adsorbed on the silica sand, perhaps due to its slight dipole moment (see table 1.5.1 for dipole moments of the solutes).

The selectivity of *n*-octadecane / *n*-eicosane (figure 3.3.13) reaches a maximum of approximately 2 at 0.2 g mL^{-1} . This selectivity is substantial when one considers the chemical similarity of the two compounds.

It can be demonstrated that the above noted selectivities were not due simply to differences in the vapor pressures of the compounds. The vapor pressures of the five solutes were calculated as functions of pressure using the Poynting relation (equation 1.6.1.7). Vapor pressure data at 40°C for fluoranthene and *m*-terphenyl were taken from this work (section 3.1.2.1). The values for *n*-octadecane and *n*-eicosane were from reference 85, and the value for chrysene was estimated from references 88 and 96 by interpolation of a plot of the log of vapor pressure versus molecular weight for several PAH species.

Figure 3.3.10

log of selectivity for *n*-eicosane / fluoranthene versus density

Figure 3.3.11

log of selectivity for fluoranthene / chrysene versus density

Figure 3.3.12

log of selectivity for fluoranthene / m-terphenyl versus density

Figure 3.3.13

log of selectivity for n -octadecane / n -eicosane versus density

Comparisons were made of the relative vapor pressures of the two components in each of the pairs mentioned above. The ratio of vapor pressures for each pair was calculated as a function of fluid phase density, assuming the fluid to be CO₂. The results are plotted in figure 3.3.14 as the log of the ratio versus density for each pair.

Referring to figure 3.3.14, the ratio of the vapor pressure of one solute to another does not change appreciably with density. Thus, the trends in selectivities with respect to density were not due to changes in the relative vapor pressures of the two components. Furthermore, for some systems the component with the lower vapor pressure had a higher recovery. For instance, the recovery of *n*-eicosane is higher than that of fluoranthene (figure 3.3.10), but the vapor pressure of *n*-eicosane is actually the same as, or a little lower than that of fluoranthene (lower line in figure 3.3.14). The same is true for the fluoranthene / *m*-terphenyl pair. The vapor pressure of *n*-octadecane is roughly 20 times that of *n*-eicosane, and yet the greatest selectivity obtained for the pair was approximately 2 (see figure 3.3.13).

The selectivities observed must therefore be due to interactions among the solvent, solutes, and the solid surface.

3.3.4 Temperature Dependence

In order to study the effect of temperature on the extraction recoveries, it must be realized that the density of the fluid is a function of temperature as well as pressure. Since, as demonstrated in the previous section, the extraction rate and recovery are affected by the density, the effect of temperature can be found only if the extractions are performed at constant density. Thus, the assumption is made that the pressure *per se* is not an important variable. The extractions described below were performed using CO₂ at a density of 0.77 g mL⁻¹. The conditions which gave this density were:

91 bar	28.1° C,
146 bar	40.5° C,
and 180 bar	48.1° C

The flowrate of CO₂ was maintained at a constant value of 0.20 mL min⁻¹ (measured as supercritical fluid). Thus, the only variable in the experiments was the temperature.

Figure 3.3.14

$\log(\text{ratio of vapor pressures})$ at 40° C versus CO_2 density for $n\text{-C}_{20}$ / fluoranthene (Δ), fluoranthene / chrysene ($\square$), fluoranthene / *m*-terphenyl ($\circ$) and $n\text{-C}_{18}$ / $n\text{-C}_{20}$ ($\circ$)

The first matrix examined was aluminum metal dust. This matrix was chosen because it was expected to have relatively low interaction energies with organic compounds. This would allow examination of the extraction essentially free of interference from the matrix. The extraction rate and recoveries should thus be the highest attainable from any matrix. The aluminum was a rather poor adsorbent – it was possible to adsorb only roughly $5 \mu\text{g g}^{-1}$ of the five compounds listed in the previous section.

The rates of recovery of *n*-eicosane, fluoranthene, and *m*-terphenyl were so high that it was not possible to see the effect of temperature on them. However, the less volatile and less soluble chrysene and perylene were extracted slowly enough that their rates of recovery could be measured as functions of temperature. The extraction recovery versus volume of CO_2 is plotted in figures 3.3.15 and 3.3.16 for chrysene and perylene, respectively. For both of these solutes, the rate of recovery increased as the temperature was increased.

From an Arrhenius plot, it is possible to calculate an experimental activation enthalpy for the extractions. The rates of recovery were calculated over the first few minutes of the extractions, where recovery versus time plots were fairly linear. For chrysene, the experimental activation enthalpy was 17.0 kJ mol^{-1} , and for perylene, 19.5 kJ mol^{-1} . These relatively low values suggest a weak interaction of the solutes with the surface of the aluminum metal, as expected.

If the interaction of a solute with a surface is very small, we would expect the experimental activation enthalpy of desorption into a solvent to be equivalent to the enthalpy of solution of the pure solid solute in the same solvent. The enthalpies of solution of these two compounds were not measured in CO_2 ; however, hexane is often stated to be roughly equivalent to CO_2 in solvating power. The enthalpies of solution of chrysene and perylene in hexane were found to be $18 \pm 3 \text{ kJ mol}^{-1}$ and $13 \pm 8 \text{ kJ mol}^{-1}$, respectively (see section 3.1.1.1). The similarities of these values to the experimental enthalpies of activation for the extraction process suggest that the solutes are not strongly bound to the surface of aluminum metal. The extraction of the compounds from the surface of aluminum is therefore equivalent to the dissolution of the pure compounds.

Figure 3.3.15

Recovery of chrysene from aluminum versus volume of CO₂ at 28.1°C (△), 40.5°C (□) and 48.1°C (○)

Figure 3.3.16

Recovery of perylene from aluminum versus volume of CO₂ at 28.1°C (Δ), 40.5°C (□) and 48.1°C (○)

The temperature did not affect the total recoveries of chrysene and perylene from aluminum either. If the solutes were interacting strongly with the surface, we might expect the temperature to affect the solvating power of the solvent, hence its ability to desorb all of the solute molecules. The same arguments as for the pressure dependence of the total recovery would apply. The fact that the total recovery is not influenced by the temperature in this case is further evidence that the interaction between these solutes and aluminum is very weak.

With Florisil as the solid adsorbent, it was found that the temperature dependence of the extractions was also very small. The rates of recovery and the final recoveries were not affected by varying the temperature from 28.1 to 48.1°C under constant density and flowrate conditions.

Silica sand was spiked with approximately 250 ng g⁻¹ of each of *n*-C₁₈, *n*-C₂₀, fluoranthene, *m*-terphenyl and chrysene, as well as 27 ng g⁻¹ of PCB-33 and 72 ng g⁻¹ of 2,3,4,5-tetrachlorophenol. Samples of this sand were extracted at different temperatures, while keeping the density of the CO₂ constant at 0.80±0.01 g mL⁻¹ by setting the pressure appropriately. The extractions were followed as functions of time, but the objective was to measure the final recoveries as functions of the temperature.

The recovery of *n*-octadecane (plotted versus time in figure 3.3.17) was not affected by the temperature. Both the initial rate of extraction and the final recovery were essentially the same at temperatures from 25.3°C to 69.5°C. This was the case for all of the compounds on the sand, and indicates that neither the temperature nor the pressure affect the recovery, insofar as the density is kept constant.

3.3.5 Matrix Dependence

Four different matrices (sand, soil, XAD-2 resin and Florisil; see section 2.1.1) were spiked with 50 to 100 ng g⁻¹ of each of the following compounds: pentachlorobenzene, hexachlorobenzene, γ -BHC (hexachlorocyclohexane), 2,4-D (2,4-dichlorophenoxyacetic acid), 2,4,5-T (2,4,5 trichlorophenoxyacetic acid), Silvex (2-(2,4,5- trichlorophenoxy) propionic acid), α -Chlordane (1,2,4,5,6,7,8,8-octachloro- 2,3,3a,4,7,7a-hexahydro-4,7-methanoindene), Mirex (dodecachloro-

Figure 3.3.17

Recovery of *n*-octadecane from sand versus time using CO₂ at 0.80 g mL⁻¹. The temperatures used were 23.5°C (□), 40.8°C (○), 46.2°C (●), 51.3°C (△) and 69.5°C (○)

octahydro-1,3,4-methano-2H-cyclobuta[*cd*]pentalene), PCB-33, PCB-153, 2,4-dinitrotoluene, 2,4-dinitrophenol and paranitrophenol. Note that a given compound was spiked at exactly the same level in each matrix. This allowed a direct comparison of the effect of the matrix on extraction recoveries.

Samples of each matrix were extracted in pure CO₂ at 311 bar and 40.5°C for thirty minutes. Additional extractions from 30 to 60 minutes confirmed that the extractions were complete after 30 minutes. Table 3.3.1 presents the recoveries after 30 minutes of each of the solutes from each of the four matrices. The recoveries are the averages from at least three extractions.

Table 3.3.1 Recoveries (%) of compounds at 50–100 ng g⁻¹ from various matrices using CO₂ at 311 bar and 40.5°C.

Compound	Sand	Soil	XAD	Florisil
Pentachlorobenzene	20 ± 10	17 ± 16	5 ± 2	6.2 ± .9
2,4-D	50 ± 30	5 ± 3	3.0 ± .3	5 ± 2
Hexachlorobenzene	50 ± 20	37 ± 30	4 ± 4	10.8 ± .8
γ-BHC	10 ± 3			1.8 ± .4
Silvex	90 ± 20	100 ± 20	60 ± 20	70 ± 4
2,4,5-T	20 ± 5	11 ± 6		16 ± 3
PCB-33	3.8 ± 0.8	36 ± 12	8 ± 4	26 ± 3
α-Chlordane	80 ± 20	83 ± 25	30 ± 10	100 ± 10
PCB-153	50 ± 20	53 ± 16	17 ± 8	60 ± 10
Mirex	5 ± 2	6 ± 3	2 ± 1	9 ± 1
2,4-Dinitrotoluene	30 ± 20	50 ± 20		15 ± 6
2,4-Dinitrophenol	40 ± 20	60 ± 20	30 ± 10	18 ± 4
Paranitrophenol	20 ± 10	6 ± 2	8 ± 4	5 ± 2

Note: blank entries are due to contamination of the extracts

Inspection of the data in table 3.3.1 shows that there is a strong effect of the matrix on the recoveries. In general, the poorest recoveries were those from the XAD-2 resin. The recoveries from sand and soil were similar, although the recovery of polar species such as 2,4-D were somewhat lower from soil than from sand. This trend was noticed in the SFC experiments (see figure 3.2.13 for instance), where the

polar species eluted later on soil than on sand. The recoveries from Florisil were intermediate between those from XAD-2 and those from sand and soil.

The fact that the matrix influences the recoveries at all indicates that the matrix-solute and/or the matrix-solvent interactions are important, and that the solute-solvent interactions are not the only factors.

3.3.6 Particle Size Dependence

There is no reason to believe that particle size *per se* would have any effect on recoveries. However, it was thought that upon grinding the matrix to obtain smaller size particles before spiking, some new sites might be exposed which would retain solutes more strongly, and thus the recoveries would be decreased.

The effect of particle size was determined by spiking silica of three different particle sizes with *n*-C₁₈, *n*-C₂₀, fluoranthene, *m*-terphenyl and chrysene, and extracting each sample under identical conditions (310 bar, 40.5°C in CO₂). Figure 3.3.18 shows the recovery of fluoranthene versus time from each of these silica samples. There is apparently no effect of particle size on either the rate of recovery or the final recovery of fluoranthene. (The same was observed for the other solutes.) Thus, it appears that grinding the silica did not change the surface sufficiently to cause stronger retention of the solutes.

3.3.7 Spike Level Dependence

There was some concern that due to the heterogeneity of some of the adsorbents used, smaller amounts of adsorbates would be more strongly adsorbed. This was tested by spiking adsorbents with a range of concentrations of adsorbates, and extracting each under identical conditions.

Five samples of silica were spiked with *n*-octadecane, *n*-eicosane, fluoranthene, *m*-terphenyl and chrysene each at 0.01, 0.03, 0.05, 0.1, or 1.0 µg g⁻¹. Extractions were carried out in CO₂ at 145 bar and 40.5°C for 20 minutes. The results are plotted in figure 3.3.19 as the recovery versus spike level for each compound. Contamination in the extracts of the samples spiked at 0.01 µg g⁻¹ made the results at this level for fluoranthene, *m*-terphenyl and chrysene unusable. Nevertheless, it is clear from examination of figure 3.3.19 that the spike level has little influence on the recovery of any of these compounds from silica.

Figure 3.3.18

Recovery of fluoranthene from silica versus time. The silica particle sizes were .063-.125 mm (Δ), .125-.18 mm ($\bullet$) and >.5 mm ($\square$)

Figure 3.3.19

Recovery of *n*-octadecane, *n*-eicosane, fluoranthene, *m*-terphenyl and chrysene from silica versus spike level using CO_2 at 145 bar and 40.5°C

A more retentive and heterogeneous matrix (soil) was therefore spiked with several compounds at three spike levels. The compounds used were the same as those listed in section 3.3.5, except that PCB-77 was substituted for paranitrophenol. The low, medium and high spike levels were 25, 50 and 250 ng g⁻¹ for the chlorinated species, and 50, 100 and 500 ng g⁻¹ for the 2,4-dinitrotoluene and 2,4-dinitrophenol. Table 3.3.2 presents the results in terms of the % recovery for each of the species at each of the spike levels. Each recovery is the average of three determinations.

There is an obvious correlation between the spike level and the recoveries of all of the compounds. (The reason for the low result for the high spike level of 2,4,5-T is unknown.) In all cases, the recoveries decreased as the spike level was decreased. Poor recoveries at low spike levels can only be attributed to poor extractions, since it was also shown that quantitative recoveries of these adsorbates are possible from adsorbents which do not interact strongly with them. In other words, in these experiments, low recoveries were not due to a systematic loss of solutes after extraction.

Table 3.3.2. Recovery (%) from soil of compounds at different spike levels

Compound	Low Spike	Medium Spike	High Spike
Pentachlorobenzene	ND	ND	.46 ± .05
Hexachlorobenzene	2.5 ± 0.7	6 ± 2	27 ± 5
γ-BHC	ND	ND	3 ± 1
2,4-D	2.8 ± 0.8	3 ± 1	10 ± 3
2,4,5-T	20 ± 6	40 ± 5	5 ± 2
Silvex	3.8 ± 0.5	6 ± 1	15 ± 2
α-Chlordane	9.8 ± 0.8	18 ± 2	42 ± 3
Mirex	0.7 ± 0.4	2 ± 1	7 ± 2
PCB-33	1.8 ± 0.3	3 ± 1	25 ± 3
PCB-77	1.2 ± 0.6	1.9 ± 0.7	12 ± 2
PCB-153	6 ± 2	14 ± 4	38 ± 6
2,4-Dinitrotoluene	0.9 ± 0.4	2.1 ± 0.5	17 ± 3
2,4-Dinitrophenol	1.9 ± 0.9	2.5 ± 0.7	14 ± 2

Note: ND means not detected

This implies that the less adsorbate there is on a surface, the more strongly it interacts with that surface. This is another way of saying that the surface is heterogeneous, and the arguments are similar to those for the pressure dependence of the recoveries. This also implies that lower levels of adsorbed species require stronger solvents to extract them quantitatively. Increasing the strength of the solvent may involve increasing the density of the solvent (CO_2 in this case), switching to another supercritical fluid (e.g. N_2O) or adding a modifier such as methanol to the CO_2 .

3.3.8 Supercritical Fluid Dependence

This section presents the results of using supercritical fluids other than pure CO_2 to extract organics from solid surfaces. Some extractions were performed using supercritical N_2O , SF_6 , and CHF_3 . Many extractions were performed using CO_2 modified with small amounts of methanol, hexane, dichloromethane, carbon tetrachloride, acetone or tetrahydrofuran.

3.3.8.1 Single Fluids

Samples of sand spiked with approximately 400 ng g^{-1} of each of *n*-octadecane, *n*-eicosane, fluoranthene, *m*-terphenyl, chrysene and perylene were extracted with CO_2 , N_2O , CHF_3 and SF_6 . The extractions were performed at a reduced pressure of 0.86 and a reduced temperature of 1.03 in order that a direct comparison could be made of the effectiveness of each solvent. The flowrate was maintained at $25 \pm 2 \text{ mL min}^{-1}$ (measured as gas at atmospheric pressure). The extractions were slow enough under these conditions that they could be easily followed over time. The actual pressures and temperatures used are given in table 3.3.3.

Figure 3.3.20 shows the % recovery of *n*-octadecane from silica as a function of time for the four solvents. The best solvent, in terms of the rate of extraction, was N_2O . CO_2 and CHF_3 appeared to have roughly similar extraction powers, while SF_6 was rather poor. The results for *n*-eicosane (figure 3.3.21) were similar, except that CO_2 and CHF_3 were not much better than SF_6 .

Table 3.3.3 Temperatures and pressures required for $T_r=1.03$ and $p_r=0.86$

Solvent	Pressure bar	Temperature °C
CO ₂	63.5	40.2
N ₂ O	62.6	45.7
CHF ₃	41.6	34.9
SF ₆	32.3	55.1

For fluoranthene (figure 3.3.22), SF₆ and CHF₃ appear to be the best solvents. For *m*-terphenyl (figure 3.3.23), CHF₃ was again the best solvent, followed by N₂O, CO₂ and then SF₆. The recoveries of chrysene and perylene were erratic and less than 1%

Since CO₂ is not a dipolar molecule, it does not interact strongly with either the solutes or the adsorbent surface. This explains its rather poor overall performance in these extractions. N₂O has a small dipole (0.17 Debye), which may account for its ability to extract the linear alkanes. CHF₃ has a somewhat larger dipole (1.65 Debye) which may account for its ability to extract fluoranthene, which is itself a polar molecule (0.6 Debye). SF₆ has no permanent dipole, but because of the large size of the molecule, it is very polarizable. SF₆ is known to solubilize large molecules such as polymers. This may account for its ability to extract the large molecule perylene in these experiments more effectively than the other three solvents.

3.3.8.2 Binary Fluids

Since modifiers generally increase the recoveries (relative to those in pure CO₂), it was necessary to use an adsorbent with relatively low concentrations of adsorbates. Otherwise, all extractions would be almost quantitative, and the differences between modifiers would not be obvious. Thus, a sample of silica was spiked with five hydrocarbons each at a level of approximately 300 ng g⁻¹, as well as two chlorinated compounds at approximately 50 ng g⁻¹.

Figure 3.3.20

Recovery of *n*-octadecane from silica versus time using N_2O (○), CHF_3 (□), CO_2 (△) and SF_6 (○)

Figure 3.3.21

Recovery of *n*-eicosane from silica versus time using N_2O ($\circ$), CHF_3 ($\square$), CO_2 ($\triangle$) and SF_6 ($\hexagon$)

Figure 3.3.22

Recovery of fluoranthene from silica versus time using N₂O (○), CHF₃ (□), CO₂ (△) and SF₆ (○)

Figure 3.3.23

Recovery of *m*-terphenyl from silica versus time using N_2O (○), CHF_3 (□), CO_2 (△) and SF_6 (○)

The mixtures of CO_2 with the modifiers were made as described in section 2.1.2.1. The modifiers used were methanol, acetone, hexanes (a mixture of hexane isomers), carbon tetrachloride, dichloromethane and tetrahydrofuran. The modifier concentration was 6.5 mole percent in each case.

Conditions for Comparison of Modifiers

The question arises as to whether the different binary fluids should be compared at equal densities, pressures, or reduced conditions. Operation at constant pressure is the simplest method from a practical viewpoint, since densities do not have to be calculated. Operation at constant reduced conditions requires knowledge of the critical points of the mixtures. Comparison of systems at constant density is the most often used approach. However, a case is made here for operation at constant pressure, because of both practical considerations, and the fact, demonstrated below, that this leads to approximately equivalent densities anyway.

When the supercritical fluid is a binary mixture, and when the modifier is believed to be the more important component in terms of increasing recovery (or reducing retention in the case of the SFC experiments), then attention should be paid not to the mass density of the mixture, but to the particle density of the modifier. Thus, the distinction between mass and particle density is made in the following discussion.

To achieve a constant mass density of 0.87 g mL^{-1} at 40.5°C in $\text{CO}_2 + 6.5$ mole % modifier, the required pressures were calculated using the Peng–Robinson equation of state. (The binary interaction parameters for THF and DCM were not available, and so arbitrary values of 0.10 were used in both cases. The densities calculated using an equation of state do not depend heavily on the value of the parameter, and so the use of this arbitrary value will not affect the results discussed below. Note that this was not the case for the calculation of fugacities in section 3.2, which depend heavily on the value of the parameter.) The particle densities were also calculated, and both are presented in table 3.3.4. Note that the particle density is that of the solvent (CO_2) and the modifier combined. The particle densities of the modifiers would be the values in table 3.3.4 multiplied by 0.065.

Table 3.3.4 Pressure and particle density at a mass density of 0.87 g mL^{-1} for mixtures of CO_2 + 6.5 mole % modifier

Modifier	Pressure bar	Particle Density mol mL^{-1}
Methanol	229	0.020
Acetone	243	0.019
Hexane	294	0.019
DCM	195	0.019
CCl_4	137	0.017
THF	248	0.019

It is apparent that at constant mass density, the particle densities are not equal, but are similar. The low value for CCl_4 arises from its high molecular weight.

Table 3.3.5 presents the densities of the same CO_2 + modifier systems at 40.5°C and a constant pressure of 125 bar. The mass densities are quite different from one another. The particle densities are also different from one another, but the differences are no greater than when the mass densities are the same (table 3.3.4).

Thus, there is no advantage to operating at either constant mass density or constant pressure. The particle densities of the different modifier systems are roughly the same as one another whether the mass density of the pressure is held constant. The extractions described in this section were therefore carried out at a constant pressure of 125 bar and a temperature of 40.5°C .

Table 3.3.5. Mass density and particle density at 125 bar and 40.5°C for mixtures of CO_2 + 6.5 mole % modifier

Modifier	Mass Density g mL^{-1}	Particle Density mol mL^{-1}
Methanol	0.74	0.017
Acetone	0.73	0.016
Hexane	0.70	0.015
DCM	0.77	0.016
CCl_4	0.85	0.017
THF	0.73	0.016

Extractions from Silica

Table 3.3.6 lists the recoveries of the eight compounds from silica for pure CO₂ and the six binary fluids. In most cases, recoveries using modified CO₂ were greater than those using pure CO₂. Exceptions were the extractions of 2,3,4,5-tetrachlorophenol, where pure CO₂ was better than CO₂ + CCl₄, and the extractions of PCB-33, where CO₂ was better than all modified systems except for CO₂ + methanol.

Table 3.3.6 Recoveries (%) from silica using CO₂ and modified CO₂

Compound	CO ₂	CO ₂ + Methanol	CO ₂ + Hexanes	CO ₂ + Acetone	CO ₂ + CCl ₄	CO ₂ + DCM	CO ₂ + THF
<i>n</i> -C ₁₈	53	138	120	113	105	108	87
<i>n</i> -C ₂₀	58	147	105	89	83	90	70
Fluoranthene	50	107	87	82	70	69	69
<i>m</i> -terphenyl	71	93	82	79	71	72	58
Chrysene	2	16	5	10	7	15	22
2,3,4,5-tcp	21	79	65	40	10	65	92
PCB-33	48	90	36	22	5	37	28

Notes: *n*-C₁₈ and *n*-C₂₀ are *n*-octadecane and *n*-eicosane, respectively
 2,3,4,5-tcp is 2,3,4,5 tetrachlorophenol
 all recoveries are the averages of at least three determinations
 standard deviations were typically ±15%

Some general conclusions can be drawn from the data in table 3.3.6. For instance, CO₂ + methanol was the best solvent system used. The recoveries using CO₂ + methanol were the highest in all cases except for the extractions of chrysene and 2,3,4,5 tetrachlorophenol by CO₂ + THF. This is consistent with the results of the SFC experiments, where methanol was found to be a very effective modifier using soil (which was predominantly silica) as the stationary phase.

The fact that THF was a better modifier for the extraction of 2,3,4,5-tetrachlorophenol from sand and not as good in the SFC experiments involving soil may be due to differences in the solids (even though both are

predominantly silica) or to the different modifier mole fractions used (.065 in the former, and 0.0052 in the latter). The fugacity of THF may be greater than those of most of the other modifiers at a mole fraction of 0.065, but lower at a mole fraction of 0.0052. Unfortunately, the binary interaction parameter required for the evaluation of the fugacity of THF in CO_2 solutions is unavailable.

The extraction of 2,3,4,5-tetrachlorophenol from silica deserves more attention, since the capacity factors for this system were measured using the same CO_2 + modifier combinations (see section 3.2.3.4), albeit using soil instead of sand, and a lower modifier concentration. The order of effectiveness of the modifiers in the two types of experiments are listed in table 3.3.7, along with the order of the solubility of 2,3,4,5-tetrachlorophenol in CO_2 + 0.52 mole percent modifier (from table 3.1.9).

Table 3.3.7 Order of effectiveness of modifiers in SFC and extraction experiments for 2,3,4,5-tetrachlorophenol/ CO_2 +modifier, and order of solubilities of 2,3,4,5-tetrachlorophenol in CO_2 +0.52 mole percent modifier

Modifier	Order of Effectiveness in SFC experiments	Order of Effectiveness in extraction experiments	Order of Solubility (see table 3.1.9)
Methanol	1	2	1
Dichloromethane	2	3	2
Hexanes	3	4	7
CCl_4	4	7	3
THF	5	1	4
Acetone	6	5	6
No Modifier	7	6	5

Note: '1' denotes the most effective or soluble, '7' the least.

Except for THF, there is a remarkable similarity in the order of effectiveness of the six modifiers in the two types of experiments. This indicates that the SFC type experiments can successfully be used to determine the best solvent(s) for an analytical extraction.

Except for hexanes, there is also a remarkable similarity between the order of effectiveness of the modifiers and the solubility of the 2,3,4,5-tetrachlorophenol in CO₂ modified with 0.52 mole percent of the modifiers. It was pointed out in section 1.7.2 that there is usually a direct relationship between the desorption of a solute and its solubility in the solvent.

The retentions of methanol, THF and acetone were found to be significant (section 3.2.3.5). Thus, it appears that for these three modifiers, the reduction in capacity factor (and the increase in extraction recoveries) over those in pure CO₂ is due to a combination of high solubility in the solvent, and adsorption of the modifier.

Concentration Dependence

The concentration of the modifier is expected to have an effect on the extraction recoveries. The reasons are analogous to those discussed in section 3.2.3.4. Briefly, increasing the fluid phase concentration of the modifier will increase the adsorbed phase concentration of the modifier, thereby desorbing more solute. Since methanol was found to be an effective modifier, it was used to determine the effect of modifier concentration on recoveries.

Silica sand was spiked with approximately 250 ng g⁻¹ of each of *n*-C₁₈, *n*-C₂₀, fluoranthene, *m*-terphenyl and chrysene, as well as 27 ng g⁻¹ of PCB-33 and 72 ng g⁻¹ of 2,3,4,5-tetrachlorophenol. Samples of this sand were extracted using solutions of methanol in CO₂ at 132 bar and 40.5°C (density = 0.87±.01 g mL⁻¹) for twenty minutes, then for a further twenty minutes to test for completeness of extraction. In all cases, the first twenty minutes was sufficient to ensure complete extraction of all that could be extracted under these conditions. Fluids from zero to 0.065 mole fraction in methanol were used. At least three extractions were performed at each methanol concentration.

Figures 3.3.24 to 3.3.30 are plots of average recovery versus mole percent methanol for each of the solutes. In all cases, there was a general trend of increasing recovery with increasing methanol concentration, as expected. This is in agreement with the SFC experiments, where for example it was found that the retention of 2,3,4,5-tetrachlorophenol on soil decreased as the mole fraction of methanol in the CO₂ was increased.

Figure 3.3.24

Recovery of *n*-octadecane from silica versus mole percent methanol

Figure 3.3.25

Recovery of *n*-eicosane from silica versus mole percent methanol

Figure 3.3.26

Recovery of fluoranthene from silica versus mole percent methanol

Figure 3.3.27

Recovery of *m*-terphenyl from silica versus mole percent methanol

Figure 3.3.28

Recovery of chrysene from silica versus mole percent methanol

Figure 3.3.29

Recovery of PCB-33 from silica versus mole percent methanol

Figure 3.3.30

Recovery of 2,3,4,5-tetrachlorophenol from silica versus mole percent methanol

For the particular case of 2,3,4,5-tetrachlorophenol, the recovery increased from 20% with no methanol present to almost 80% with 6.5 mole percent methanol present. In the SFC experiments, the retention was reduced to essentially zero using a methanol mole fraction of only 3.2 percent. However, the concentration of solute was much smaller in the extraction experiments, and thus it is expected that a larger methanol concentration would be required in that case due to the heterogeneity of the surface, as discussed in section 3.2.3.4.

The solubility of 2,3,4,5-tetrachlorophenol is greater in methanol-modified CO_2 than in pure CO_2 (section 3.1). However, it can be shown that the solubility is not a factor in determining the extraction recovery in this system. The solubility of 2,3,4,5-tetrachlorophenol in CO_2 and methanol modified CO_2 as a function of density was presented in figure 3.1.26. At a density of 0.87 g mL^{-1} , the solubility in $\text{CO}_2 + 1.59$ mole percent methanol was the same as it was in pure CO_2 at approximately 0.93 g mL^{-1} . The extraction recovery of the solute using pure CO_2 at 0.93 g mL^{-1} (determined in separate experiments) was $20 \pm 2\%$, while in $\text{CO}_2 + 1.59$ mole percent methanol, the recovery was approximately 44% (see figure 3.3.30). Thus, even though the solubility was the same in the two fluids, the methanol modified CO_2 was a superior extracting fluid. This is attributed to the adsorption of methanol on the surface, with the concomitant desorption of the solute.

4. Conclusions

Equipment

A simple system for extracting trace organics from solid matrices has been demonstrated. The system was inexpensive to build due to the use of off-the-shelf fittings. The use of a commercially available extraction cell was a definite advantage over the use of extraction cells made from tubing fittings. The use of silica capillary tubing was a convenient method for depressurizing and recovering the extract.

A device for measuring the solubilities of solids in supercritical fluids was demonstrated. The device was constructed from tubing and tubing fittings. Using the device, it was possible to measure the vapor pressures of low-volatility PAH at atmospheric pressure, and well as solubilities in single and binary supercritical fluids at high density.

A simple supercritical fluid chromatograph was constructed. The device employed matrices such as soil, silica sand, and Florisil as the stationary phases so that the interaction of these materials with solutes dissolved in supercritical fluids could be studied.

Solubilities in liquids

The solubilities of several solids in several liquid solvents were measured (section 3.1.1). Of the solvents used, tetrahydrofuran and N-methyl pyrrolidinone were found to be the best solvents. Methanol was the worst overall solvent, except for the more polar solutes.

The Hildebrand solubility parameter was found to be a poor measure of solubility in these systems, especially when the solute and solvent are polar.

Enthalpies of solution were found to be less endothermic when both the solvent and solute were polar, implying favorable solute-solvent interactions. Unlike solute-solvent pairs generally showed more endothermic enthalpies of solution.

Solubilities in Supercritical Fluids

The device used to measure solubilities in supercritical fluids was shown to give reliable results at low and high density by comparison of results from this work to published values (section 3.1.2).

Vapor pressures of two PAHs, 2,3,4,5-tetrachlorophenol and hexachlorobenzene were measured. It was possible to measure vapor pressures as low as $1.8 \cdot 10^{-8}$ bar (section 3.1.2.1).

The solubilities of several PAH were measured in CO_2 as a function of density (section 3.1.2.2). The order of solubilities of *m*-terphenyl, fluoranthene and chrysene was the same in CO_2 as in liquid hexane.

The solubility of fluoranthene was shown to increase with increasing density at constant temperature, and to increase with increasing temperature at constant density.

The solubility of fluoranthene in CO_2 was measured as a function of temperature at several densities (section 3.1.2.3). The calculated enthalpy of solution decreased as the density increased, suggesting more favorable solvation at higher density. The limiting enthalpy of solution at low density was the enthalpy of sublimation at atmospheric pressure. Assuming the number of CO_2 molecules solvating a fluoranthene molecule varies with the density, the enthalpy of interaction between fluoranthene and a single CO_2 molecule was estimated to be $-1.9 \pm 0.4 \text{ kJ mol}^{-1}$.

The isochoric solubilities of several compounds in CO_2 were measured as functions of temperature. Polar species had large endothermic enthalpies of solution, and large positive entropies of solution.

The solubilities of fluoranthene in binary supercritical fluids were found to be in the same order as those in the pure liquid modifiers. This was also true for 2,3,4,5-tetrachlorophenol (section 3.1.2.4).

Several potential modifiers were tested for miscibility with liquid CO_2 (section 3.1.2.5). The only one found to be immiscible with CO_2 was N-methyl pyrrolidinone.

Adsorption of Gases

Adsorption of modifiers from the gas phase onto soil were measured (section 3.2.1.2). Dichloromethane and tetrahydrofuran were extensively adsorbed at a given pressure. Very little carbon tetrachloride and hexane were adsorbed. Surface areas calculated from these measurements agreed with one another, but were higher than those measured by nitrogen adsorption (section 3.2.1.1).

Enthalpies of adsorption of modifiers onto soil and charcoal were measured (section 3.2.1.2). Polar modifiers such as methanol and acetone had large enthalpies of adsorption on the polar surface of the soil. Less polar modifiers such as hexanes had large enthalpies of adsorption on the nonpolar surface of the charcoal.

Adsorption from Liquids

The surface of silica was shown to be heterogeneous in section 3.2.2.1. The distribution coefficient of 2,3,4,5-tetrachlorophenol between sand and hexane was shown to vary with the concentration of the solute.

A strong effect of solvent on adsorption was shown for the system hexachlorobenzene/charcoal/solvent. Neither solute-surface nor solute-solvent interactions alone could account for the effect.

The adsorption of hexachlorobenzene on charcoal was found to decrease as the temperature was increased (section 3.2.2.3). The enthalpy of adsorption of hexachlorobenzene from methanol was found to be -5.4 ± 0.6 kJ mol⁻¹. This value is the difference in the enthalpies of adsorption of the hexachlorobenzene and the methanol.

Adsorption from Supercritical Fluids

The adsorption of 2,3,4,5-tetrachlorophenol on sand from CO₂ was measured using a static equilibrium device, and was found to decrease as the density of the CO₂ was increased (section 3.2.3). This was due to increased solvation of the solute, and increased adsorption of the CO₂ on the solid surface.

The SFC system was used to show that retention of solutes on a bare stationary phase decreases as the density of the fluid is increased (section 3.2.3.1). Polar solutes were retained more than non-polar solutes, due to the polarity of the stationary phase used (silica).

It was shown that the retention of a solute increases as the amount of solute injected decreases. This indicates that the extraction of solutes from adsorbents would become more difficult at lower solute concentrations. Thus, operation at higher densities, or the use of modifiers are necessary to extract very small amounts of adsorbed solutes.

The capacity factor of 2,3,4,5-tetrachlorophenol on silica was shown (section 3.2.3.3) to decrease upon the addition of hexane or methanol to the CO_2 . Methanol was the more effective modifier. At sufficiently high density, the two modifiers become equally effective. This may be due to the CO_2 being a more effective eluent at high density, or to the fact that the fugacity of hexane rises with increasing density, while that of methanol remains essentially constant.

The abilities of six modifiers to decrease the retention of 2,3,4,5-tetrachlorophenol on soil were compared at equal mole fractions in CO_2 , and at equal density. The effectiveness decreased in the order methanol > dichloromethane > hexanes > carbon tetrachloride > tetrahydrofuran > acetone > no modifier. On Florisil, the order of the modifiers used was methanol > acetone > hexanes. This indicates that the effect of the modifier is not simply one of solubility enhancement, but involves the interactions of the modifier with the surface.

The surface of the soil was shown to be heterogeneous by measuring the retention of 2,3,4,5-tetrachlorophenol on soil as a function of density at different methanol concentrations in CO_2 (section 3.2.3.4). As the methanol concentration was increased, the number of bare adsorption sites was shown to decrease, and the energy of interaction between the solute and the surface decreased also. This is attributed to increased adsorption of methanol at higher methanol concentrations.

The retentions of the modifiers themselves were measured on the soil column (section 3.2.3.5). Methanol was retained the most, followed by acetone, then tetrahydrofuran. Hexanes, dichloromethane and carbon tetrachloride were not retained at all. Thus, the reason for the effectiveness of methanol as a modifier appears to be its adsorption on the surface, with the concomitant desorption of the solute.

Extractions

It was demonstrated that the solubility of a solute, if sufficiently low, might slow the desorption of it from a surface into a supercritical fluid (section 3.3.2). The solubility can not, however, limit the eventual extraction of the solute in a flow-through system such as that used in this work. Very soluble solutes may be extracted using less fluid simply by reducing the volumetric flowrate of fluid.

The rates of extraction of several solutes were shown to increase with increasing pressure (section 3.3.3). The recoveries of the solutes were also greater at high pressure. It was postulated that this is due to the heterogeneity of the surface. Thus, different solute molecules are adsorbed with different energies, and only a higher density (pressure) fluid is capable of competing with these molecules for sites on the surface.

Selective extraction of alkanes and PAHs were demonstrated. It was shown that the selectivities were not due to vapor pressure differences.

Temperature was shown to have a negligible effect on extraction rates and recoveries, as long as the density is kept constant (section 3.3.4). It was possible to measure the activation enthalpy for the desorption of chrysene and perylene from the surface of aluminum. The values found were close to the experimental (section 3.1.1) enthalpies of solution in liquid hexane, suggesting very weak interactions of the solutes with the aluminum.

The matrix was found to have an effect on extraction recoveries using CO₂ (section 3.3.5). Recoveries from sand and soil were similar, presumably due to the fact that both were predominantly silica. Recoveries from Florisil were lower, and lower still from XAD-2 resin. This is further evidence that solute-surface or solvent-surface interactions are just as important as solute-solvent interactions in an extraction.

Particle size was found to have no effect on recoveries (section 3.3.6).

The spike level was found to have no effect on the recoveries from silica sand, but a large effect on recoveries from soil. This is attributed to greater surface heterogeneity of the latter (section 3.3.7).

The recovery of several species from sand using different supercritical fluids (section 3.3.8.1) showed that the best fluid to use depends on the solute in question. Nitrous oxide was the best solvent for extraction of the alkanes. The polar molecule fluoranthene was extracted best by SF₆ and CHF₃, possibly due to the polarizability of the former and polarity of the latter.

Extractions using binary supercritical fluids (section 3.3.8.2) showed that methanol was the best modifier of those used. This agrees well with the observations

that methanol is extensively adsorbed from supercritical CO_2 onto the surface of silica. With respect to the system 2,3,4,5-tetrachlorophenol/silica/ CO_2 +modifier, the order of effectiveness of the modifiers in the extraction experiments was essentially the same as in the SFC experiments. The order of solubilities of the solute in the CO_2 +modifier systems was also essentially the same. Thus, both modifier-surface and modifier-solute interactions determine the recovery in an extraction.

The extraction recoveries were observed to increase with increasing methanol concentration in CO_2 . For the case of 2,3,4,5-tetrachlorophenol, it was established that the extraction recovery was greater using CO_2 +methanol than using CO_2 of a greater density, even though the solubility of the solute was the same in the two systems. This indicates that the adsorption of the modifier was more important than the solubility of the solute.

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Appendix 1. Solubilities at 298.15 K

	MeOH	Acetone	DMSO	Hexanes	DCM	NMP	CCl ₄	THF
<i>n</i> -octadecane	$6.4 \cdot 10^{-4}$	$1.7 \cdot 10^{-2}$				$1.8 \cdot 10^{-3}$		
<i>n</i> -eicosane	$1.4 \cdot 10^{-4}$	$5.2 \cdot 10^{-2}$		$8.9 \cdot 10^{-2}$		$8.2 \cdot 10^{-4}$		
<i>m</i> -terphenyl	$8.3 \cdot 10^{-4}$	$4.0 \cdot 10^{-2}$		$1.7 \cdot 10^{-2}$		$9.7 \cdot 10^{-2}$	$8.6 \cdot 10^{-2}$	$9.4 \cdot 10^{-2}$
fluoranthene	$2.8 \cdot 10^{-4}$	$4.5 \cdot 10^{-2}$		$1.3 \cdot 10^{-2}$	$9.7 \cdot 10^{-2}$	$1.2 \cdot 10^{-1}$	$7.2 \cdot 10^{-2}$	$1.2 \cdot 10^{-1}$
chrysene	$2.5 \cdot 10^{-5}$	$8.8 \cdot 10^{-4}$		$1.8 \cdot 10^{-4}$		$8.7 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	$6.5 \cdot 10^{-3}$
perylene		$3.0 \cdot 10^{-4}$		$6.0 \cdot 10^{-5}$	$1.6 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$		$2.7 \cdot 10^{-3}$
penCB	$3.4 \cdot 10^{-3}$	$3.3 \cdot 10^{-2}$	$5.97 \cdot 10^{-3}$	$7.9 \cdot 10^{-2}$	$1.7 \cdot 10^{-1}$	$4.4 \cdot 10^{-2}$		
hexCB	$8.1 \cdot 10^{-5}$	$9.3 \cdot 10^{-4}$	$2.98 \cdot 10^{-4}$	$2.8 \cdot 10^{-3}$	$6.5 \cdot 10^{-4}$	$5.6 \cdot 10^{-4}$	$1.1 \cdot 10^{-2}$	$5.8 \cdot 10^{-3}$
2,3,4,5 tcp				$1.1 \cdot 10^{-2}$	$8.3 \cdot 10^{-2}$	$4.7 \cdot 10^{-2}$		
2,4 D				$3.6 \cdot 10^{-3}$	$6.0 \cdot 10^{-3}$		$4.0 \cdot 10^{-3}$	
PCB-77	$1.3 \cdot 10^{-4}$	$2.3 \cdot 10^{-3}$						

Appendix 2.

Fortran Program for Calculating the Density of a Binary Supercritical Fluid

```

1.000      IMPLICIT REAL (A-Z)
2.000      R=83.1439
3.000      PC1=73.9
4.000      TC1=309.56
5.000      W1=.16
6.000      MW1=44.
7.000      1 PRINT*, 'ENTER PC2, BAR:.'
7.500      READ*, PC2
8.000      PRINT*, 'ENTER TC2, k:.'
8.500      READ*, TC2
9.000      PRINT*, 'ENTER W2:.'
9.500      READ*, W2
10.000     PRINT*, 'ENTER MW2:.'
10.500     READ*, MW2
12.000     PRINT*, 'ENTER X2'
13.000     READ*, X2
13.100     PRINT*, 'ENTER DELIJ:.'
13.200     READ*, DELIJ
14.000     X1=1.-X2
15.000     AVGMW=X1*MW1+X2*MW2
16.000     TLOW=319.0
17.000     THIGH=319.0
18.000     TINC=1.
19.000     PRINT*, 'PC1=', PC1, 'TC1=', TC1, 'W1=', W1
20.000     PRINT*, 'PC2=', PC2, 'TC2=', TC2, 'W2=', W2
21.000     PRINT*, 'DELIJ=', DELIJ
22.000     PRINT*, 'X1=', X1
23.000     ATC1=0.45724*R*R*TC1*TC1/PC1
24.000     ATC2=0.45724*R*R*TC2*TC2/PC2
25.000     K1=0.37464+1.54226*W1-0.26992*W1*W1
26.000     K2=0.37464+1.54226*W1-0.26992*W2*W2
27.000     BT1=0.0778*R*TC1/PC1
28.000     BT2=0.0778*R*TC2/PC2
29.000     B=X1*BT1+X2*BT2
30.000     DO 10 T=TLOW, THIGH, TINC
31.000     PRINT*, 'T=', T
32.000     PRINT*, ' '
33.000     AL1=(1+K1*(1-(T/TC1)**0.5))**2
34.000     AL2=(1+K2*(1-(T/TC2)**0.5))**2
35.000     AT1=ATC1*AL1
36.000     AT2=ATC2*AL2
37.000     A12=(AT1*AT2)**0.5*(1-DELIJ)
38.000     A=X1*X1*AT1+2*X1*X2*A12+X2*X2*AT2
39.000     DO 5 D1=.5, 1.1, .01
40.000     V=AVGMW/D1

```

```
41.000      D=D1
42.000      P=(R*T)/(V-B)-A/(V*(V+B)+B*(V-B))
43.000      IF(P.GT.400.OR.P.LE.0.0) GO TO 5
43.500      PSIG=P*14.504
44.000      PRINT*,P,PSIG,D
45.000  5    CONTINUE
46.000      PRINT*,', '
47.000      PRINT*,', '
48.000  10   CONTINUE
48.500      GO TO 1
49.000      END
```

Appendix 3.

Fortran for Calculating Solubilities in Supercritical Fluids

```

1.000      IMPLICIT REAL*8(A-Z)
2.000      INTEGER IFAIL1
3.000      COMMON P,V,X1,A1,A2,A12,B1,B2,T,R,PSAT1,V1
4.000      EXTERNAL F
5.000      R=83.1439
6.000 *    TLOW=308.15
7.000 *    THIGH=308.15
8.000 *    TINC=10.
8.100      PRINT*, 'ENTER T, K:'
8.200      READ*, TLOW
8.300      THIGH=TLOW
8.400      TINC=10
9.000 *    TC1=910
10.000 *   PC1=26.1
11.000 *   W1=.561
12.000 *   MW1=202.26
13.000 *   D1=1.252
14.000 *   V1=MW1/D1
15.000 *   TC2=304.2
16.000 *   PC2=73.8
17.000 *   MW2=44.01
18.000 *   W2=.225
19.000      TC1=748.4
20.000      PC1=40.5
21.000      W1=.302
22.000      MW1=128.19
23.000      D1=1.0253
24.000      V1=MW1/D1
25.000      TC2=282.4
26.000      PC2=50.4
27.000      MW2=28.05
28.000      W2=.085
29.000      PRINT*, 'ENTER DELIJ:'
29.500      READ*, DELIJ
30.000      K1=.37464+1.54226*W1-.26992*W1*W1
31.000      K2=.37464+1.54226*W2-.26992*W2*W2
32.000      B1=.0778*R*TC1/PC1
33.000      B2=.0778*R*TC2/PC2
34.000      WRITE(6,11) TC1,TC2
35.000      WRITE(6,12) PC1,PC2
36.000      WRITE(6,13) W1,W2
37.000      WRITE(6,14) D1
38.000      WRITE(6,15) V1
39.000      WRITE(6,17) DELIJ
40.000  11  FORMAT(' TC1 = ',F6.2,1X,'K',10X,'TC2 = ',F6.2,1X,'K')
41.000  12  FORMAT(' PC1 = ',F6.2,1X,'BAR',8X,'PC2 = ',F6.2,1X,'BAR')

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42.000 13      FORMAT(' W1 = ',F6.3,12X,'W2 = ',F6.3)
43.000 14      FORMAT(' D1 = ',F6.3,1X,'G/CC')
44.000 15      FORMAT(' V1 = ',F6.1,1X,'CC/MOLE')
45.000 17      FORMAT(' DELIJ = ',F6.3)
46.000          PRINT*,''
47.000          DO 800 T=TLOW,THIGH,TINC
48.000          AL1=(1+K1*(1-(T/TC1)**.5))**2
49.000          AL2=(1+K2*(1-(T/TC2)**.5))**2
50.000          A1=.45724*R*R*TC1*TC1/PC1*AL1
51.000          A2=.45724*R*R*TC2*TC2/PC2*AL2
52.000          A12=(1.-DELIJ)*(A1*A2)**.5
53.000          PRINT*,''
54.000          WRITE(6,18) T-273.15
55.000 18      FORMAT(' T = ',F6.2,1X,'DEG C')
56.000          PRINT*, 'ENTER PSAT1:'
57.000          READ*,PSAT1
58.000          WRITE(6,16) PSAT1
59.000 16      FORMAT(' PSAT1 = ',E9.3,1X,'BAR')
60.000          PRINT*,''
61.000          PRINT*, 'PRESSURE VOLUME DENSITY Y1
LOG(Y1)'
62.000          PRINT*,''
63.000 *** USE PSAT1 AS AN APPROXIMATION AT LOW PRESSURE
64.000          LASTLX1=DLOG10(PSAT1)
65.000          DO 750 SET=1,2
66.000          IF(SET.EQ.2.) GO TO 32
67.000          IF(SET.EQ.3.) GO TO 33
68.000          PA=4.
69.000          PB=120.
70.000          PINC=4.
71.000          GO TO 34
72.000 32      PA=130.
73.000          PB=300.
74.000          PINC=10.
75.000          GO TO 34
76.000 33      PA=80
77.000          PB=300.
78.000          PINC=20.
79.000 34      DO 700 P=PA,PB,PINC
80.000          LX1=LASTLX1
81.000          EPS=1.E-10
82.000          ETA=0.
83.000          AP=LX1-1.
84.000          BP=LX1+4.
85.000          IF(BP.GT.-0.5) BP=-0.5
86.000          IFAIL1=0
87.000          CALL C05ADF(AP,BP,EPS,ETA,F,LX1,IFAIL1)
88.000          DENS=(X1*MW1+(1-X1)*MW2)/V
89.000          WRITE(6,600) P,V,DENS,X1,DLOG10(X1)

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90.000 600      FORMAT(F8.1,5X,F6.0,5X,F9.3,5X,E9.3,5X,F7.2)
91.000          LASTLX1=DLOG10(X1)
98.000 700      CONTINUE
99.000 750      CONTINUE
100.000 800     CONTINUE
101.000         END
102.000         FUNCTION F(LX1)
103.000         IMPLICIT REAL*8(A-Z)
104.000         COMMON P,V,X1,A1,A2,A12,B1,B2,T,R,PSAT1,V1
105.000         DIMENSION COEFF(4),ZRE(4),ZIM(4)
106.000         INTEGER I,N,IFAIL2
107.000         X1=10.**LX1
108.000         X2=1.-X1
109.000         A=X1*X1*A1*2*X1*X2*A12+X2*X2*A2
110.000         B=X1*B1+X2*B2
111.000         AA=A*P/(R*R*T*T)
112.000         BB=B*P/(R*T)
113.000         COEFF(1)=1
114.000         COEFF(2)=BB-1
115.000         COEFF(3)=AA-3*BB*BB-2*BB
116.000         COEFF(4)=-AA*BB+BB**2+BB**3
117.000         N=4
118.000         TOL=X02AAF(0.0)
119.000         IFAIL2=0
120.000         CALL C02AEF(COEFF,N,ZRE,ZIM,TOL,IFAIL2)
121.000         Z=-9.99E99
122.000         DO 10 I=1,3
123.000         IF(ZIM(I).NE.0.) GO TO 10
124.000         IF(ZRE(I).LT.0.) GO TO 10
125.000         IF(ZRE(I).GT.Z) Z=ZRE(I)
126.000 10      CONTINUE
127.000         V=Z*R*T/P
128.000         F1=B1/B*(Z-1.)-DLOG(Z-BB)
129.000         1-AA/(2.828*BB)*(2*(X1*A1+X2*A12)/A-B1/B)
130.000         1*DLOG((Z+2.414*BB)/(Z-0.414*BB))
131.000         F=PSAT1/(P*DEXP(F1))*DEXP(V1*P/(R*T))-X1
132.000         RETURN
133.000         END

```

Appendix 4. Glossary of Units Used in This Work

Variable	Units Used
Temperature	°C
Pressure	bar (note that 1 bar=0.1 MPa=0.987 atm=14.5 lb in ⁻²)
Volume	mL
Density	g mL ⁻¹
Composition	mole fraction
	mg mL ⁻¹
	µg g ⁻¹
	ng g ⁻¹
Flowrate	mL min ⁻¹
Extraction Recovery	%
Enthalpy	kJ mol ⁻¹
Entropy	J K ⁻¹ mol ⁻¹
Free Energy	kJ mol ⁻¹
Dipole Moment	Debye
Gas Constant	83.1439 bar cm ³ K ⁻¹ mol ⁻¹

Appendix 5. Glossary of Terms Used in This Work

Term	Meaning	Section First Used
a	Molar area of adsorbent	1.6.3
a	Constant in van der Waals equation	1.4.2
a	Constant in Chrastil equation	1.6.2
a_{soln}	Activity of component in solution	1.5.2
a_{solid}	Activity of adsorbed component	1.5.2
a	Initial position of interface	1.4.5
a	Coefficient in SFC adsorption equations	1.7.3.4
a'	Coefficient in SFC adsorption equations	1.7.3.4
A	Interfacial surface area	1.4.5
A_s	Total surface area of stationary phase	1.7.3.4
ΔA_{sg}	Change in solid-gas interfacial area	1.4.5
ΔA_{sl}	Change in solid-liquid interfacial area	1.4.5
ΔA_{lg}	Change in solid-gas interfacial area	1.4.5
ΔA^{mix}	Helmholtz free energy of mixing	1.5.3
b	Initial position of interface	1.4.5
b	Constant in van der Waals equation	1.4.2
b	Constant in Chrastil equation	1.6.2
b	Coefficient in SFC adsorption equations	1.7.3.4
b	Constant in Langmuir equation	1.7.1
b'	Coefficient in SFC adsorption equations	1.7.3.4
B_{12}	Second mixed virial coefficient	1.6.1
c	Concentration	1.6.2
c^{m}	Concentration in stationary phase	1.7.3.2
$\overline{c}_{\text{m}}$	Average concentration in stationary phase	1.7.3.4
Δc_{p}	Difference between liquid and solid heat capacities	1.5.3
c^{s}	Concentration in mobile phase	1.7.3.2
C	Number of components in a system	1.4.6
d'	Coefficient in SFC adsorption equations	1.7.3.4

Term	Meaning	Section First Used
D_{11}	Self diffusion coefficient	1.4.4
D_{12}	Diffusion coefficient of solute	1.4.4
E	Enhancement factor	1.6.1
E	Internal energy of supercritical fluid	1.6.2.4
E^*	Internal energy of expanded fluid	1.6.2.4
ΔE^{mix}	Energy of mixing	1.5.3
ECD	Electron capture detector	2.5.3
f	Gas flowrate	2.4.2
f_2	Fugacity of solute	1.6.2
f_2^s	Fugacity of solute in solid phase	1.6.1
f_2^f	Fugacity of solute in fluid phase	1.6.1
f_2^{ol}	Fugacity of pure liquid solute at p_0	1.6.2
f_2^{os}	Fugacity of pure solid solute at reference pressure	1.6.2
F	Interfacial force per unit surface area	1.4.5
F	Number of degrees of freedom	1.4.5
ΔF	Change in interfacial force per unit area	1.4.5
FID	Flame ionization detector	2.5.3
$\overline{G}_2$	Partial molal Gibbs free energy	1.5.3
ΔG^f	Gibbs free energy of fusion	1.5.3
$\Delta G_{\text{soln}}^\ominus$	Free energy of solution	1.5.2
GC	Gas Chromatography	2.3.1
H	Enthalpy of supercritical fluid	1.6.2.4
H^*	Enthalpy of expanded fluid	1.6.2.4
ΔH_a	Isosteric enthalpy of adsorption	1.7.1
ΔH^f	Enthalpy of fusion	1.5.3
ΔH_m^f	Enthalpy of fusion at the melting temperature	1.5.3
$\Delta H_{\text{soln}}^\ominus$	Enthalpy of solution	1.5.2
ΔH_v	Enthalpy of vaporization	1.5.2
HPLC	High Pressure Liquid Chromatography	2.1.3.3

Term	Meaning	Section First Used
I_1	Ionization potential	1.5.1
k	Boltzmann constant	
k	Constant in Chrastil equation (number of solvent molecules)	1.6.2
k_1	Desorption rate constant	1.7.1
k_2	Adsorption rate constant	1.7.1
k'	Capacity factor	1.7.3.2
K	Equilibrium constant	1.7.2
K_{ads}	Adsorption equilibrium constant	1.7.3.4
K_{cbp}	Chemically bonded phase equilibrium const	1.7.3.4
LC	Liquid chromatography	
LG	Liquid-Gas	1.4.5
M	Molecular weight	1.6.2
n	Moles adsorbed per gram adsorbent	1.7.1
n_i	Moles of species i	
n^0	Moles adsorbed at monolayer coverage	1.7.1
p	Pressure	
p_a	Attraction pressure in van der Waals equation	1.4.2
p_c	Critical pressure	1.4.1
p_o	Reference pressure	1.6.2
p_r	Reduced pressure	1.4.1
p_r	Repulsion pressure in van der Waals equation	1.4.2
p_{sat}	Saturation vapor pressure	1.4.2
p_{2}^{sat}	Saturation vapor pressure of pure solute	1.6.1
P	Number of phases in system	1.4.6
PAH	Polycyclic aromatic hydrocarbon	
PCB	Polychlorinated biphenyl	
q_s	Constant in Chrastil equation	1.6.2
q_v	Constant in Chrastil equation	1.6.2
Q	Quadrupole moment	1.5.1

Term	Meaning	Section First Used
Q	Mass of solute injected	1.7.3.4
r	Intermolecular distance	1.5.1
R	Gas constant	
ΔS_a	Isosteric entropy of adsorption	1.6.3
ΔS^f	Entropy of fusion	1.5.3
$\Delta S_{soln}^\ominus$	Entropy of solution	1.5.2
S	Spreading coefficient	1.4.5
S	Number of surface sites	1.6.3
S_0	Number of unoccupied surface sites	1.7.1
S_1	Number of occupied sites	1.7.1
S_a	Molar entropy of adsorbate	1.7.1
S_g	Molar entropy of gas	1.7.1
SFC	Supercritical Fluid Chromatography	
SFE	Supercritical Fluid Extraction	
SL	Solid-Liquid	1.4.5
SG	Solid-Gas	1.4.5
t_r	Retention time	2.4.2
T	Temperature	
T_c	Critical temperature	1.4.1
T_m	Melting temperature	1.5.3
T_r	Reduced temperature	1.4.1
U_a	Internal energy of adsorbate	1.7.1
UCST	Upper critical solution temperature	1.4.6
$\bar{v}_2$	Partial molar volume of solute in fluid	1.6.2.3
$\bar{v}_2^\infty$	Partial molar volume of solute in fluid at infinite dilution	1.6.2.1
V	Volume	
V_a	Molar volume of adsorbate	1.7.1
V_c	Critical volume	1.4.2
V^f	Molar volume of supercritical phase	1.6.1

Term	Meaning	Section First Used
V_g	Molar volume of gas	1.6.3
V_m	Molar volume	1.5.2
V_m^m	Molar volume of mobile phase	1.7.3.2
$V_s^\ominus$	Partial molar volume in mobile phase	1.7.3.2
V_m^s	Molar volume of stationary phase	1.7.3.2
$V_s^\ominus$	Partial molar volume of solute in stationary phase	1.7.3.2
V_0	Retention volume of unretained solute	2.4.2
V_2^f	Molar volume of solute in fluid phase	1.6.1
V_2^s	Molar volume of pure solid solute	1.6.1
V_t^m	Total volume of mobile phase	1.7.3.2
V_r	Retention Volume	2.4.2
V_r	Reduced volume	
V_t^s	Total volume of stationary phase	1.7.3.2
x	Mole fraction	
x_i	Mole fraction of species i	1.6.3
x^m	Mole fraction in mobile phase	1.7.3.2
x^s	Mole fraction in stationary phase	1.7.3.2
y_2	Mole fraction of solute in fluid phase	1.6.1
y_2^0	Ideal mole fraction of solute in gas	1.6.1
z	Compressibility factor	
z_c	Compressibility factor at the critical point	1.4.2
α_1	Polarizability	1.5.1
β	Function of Q , the mass injected	1.7.3.4
δ	Hildebrand solubility parameter	1.5.2
ϵ_{dd}	Dipole-dipole interaction energy	1.5.1
ϵ_{disp}	Dispersion force interaction energy	
ϵ_{dq}	Dipole-quadrupole interaction energy	1.5.1
ϵ_{ind}	Dipole induced interaction energy	1.5.1
ϵ_r	Repulsive potential energy	1.5.1

Term	Meaning	Section First Used
γ	Surface tension	1.4.5
γ_{lg}	Liquid-gas interfacial tension	1.4.5
γ_{sg}	Solid-gas interfacial tension	1.4.5
γ_{sl}	Solid-liquid interfacial tension	1.4.5
γ_2	Solute activity coefficient	1.6.2
γ_2^{∞}	Solute activity coefficient at infinite dilution	1.6.2
κ	Constant in Peng-Robinson Equation of state	1.4.2
κ_T	Isothermal compressibility of fluid phase	1.6.2
μ_2^f	Chemical potential of solute in fluid phase	1.6.2
μ_2^s	Chemical potential of solid solute	1.6.2
μ_a	Chemical potential of adsorbate	1.7.1
μ_g	Chemical potential of gas	1.7.1
μ^m	Chemical potential in mobile phase	1.7.3.2
$\mu^{m\ominus}$	μ^m at standard state conditions	1.7.3.2
μ^s	Chemical potential in stationary phase	1.7.3.2
$\mu^{s\ominus}$	μ^s at standard state conditions	1.7.3.2
μ_1	Dipole component of component 1	1.5.1
ω	Acentric factor	1.4.2
π	Spreading pressure	1.6.3
ρ_c	Critical density	1.4.1
ρ_g	Density of gas	2.4.2
ρ_r	Reduced density	1.4.1
ρ_{rl}	Reduced density of liquid at its boiling temperature	1.6.2.4
ρ_{rs}	Reduced density of supercritical fluid	1.6.2.4
ρ_{sf}	Density of supercritical fluid	2.4.2
φ_1	Polar coordinate	1.5.1
φ_1	Volume fraction of component 1	1.5.3
ϕ_2^{sat}	Fugacity coefficient of saturated solute gas	1.6.1
ϕ_2^f	Fugacity coefficient of solute in fluid	1.6.1

Term	Meaning	Section First Used
θ	Contact angle	1.4.5
θ	Fraction of surface covered	1.7.1
θ	Polar coordinate	1.5.1
Ψ_2	Fugacity of solute	1.6.2

Appendix 6. Structures of Solutes Used in This Work

n-octadecane *n*-eicosane fluoranthene *m*-terphenyl chrysene perylene

2,3,4,5-tetrachlorophenol pentachlorobenzene hexachlorobenzene γ -BHC (Lindane)

1,2,4,5,6,7,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene
(Chlordane)

2,4-dichlorophenoxyacetic acid (2,4-D)

2,4,5-trichlorophenoxyacetic acid (2,4,5-T)

2-(2,4,5-trichlorophenoxy)propionic acid (2,4,5-TP, Silvex)

dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta[cd]pentalene (Mirex)

PCB-33

PCB-77

PCB-153

2,4-dinitrophenol

2,4-dinitrotoluene

END

28.02.92

FIN