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SOLUBILITY OF SOLID CCl_4 IN SUPERCRITICAL CF_4 USING DIRECTLY COUPLED SUPERCRITICAL FLUID EXTRACTION—MASS SPECTROMETRY

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ABSTRACT

A dynamic experimental apparatus developed for supercritical fluid studies was used to determine the solubility of solid CCl_4 in supercritical CF_4. An on-line quadrupole mass spectrometer was utilized for analysis of the effluent. The direct coupling of supercritical extraction with mass spectrometry offers a quantitative method for the direct determination of the solute mole fraction in the supercritical fluid. These data will broaden the data base to support the testing of new theoretical models for predicting supercritical behavior. As the critical point for CF_4 is 227.6 K, these data are among the few supercritical solubility data available at subambient temperature.

INTRODUCTION

Applications of supercritical fluid technology have come to the forefront of technological research including supercritical fluid extraction (SCFE), supercritical fluid chromatography, chemical reactions in supercritical fluids, and polymer fractionation. As a result of high energy costs and the demand for more stringent health and safety standards, SCFE has become increasingly important as an alternative process for conventional separations in commercial processes. Some of the current applications of SCFE are: the decaffination of coffee and tea [1]; the deoiling of potato chips [2]; the recovery of vegetable oils from crushed seeds [3]; and the deasphalting of heavy oils with supercritical propane [4]. Other potential commerical applications for SCFE are: the removal of nicotine from tobacco [5]; the molecular weight fractionation of polymer mixtures [6]; and the removal of organic chemicals from fermentation broths [7]. Perhaps the greatest potential of SCFE lies in the recovery of valuable products produced from bioprocesses.

These products are often present in low concentrations. Product recovery is cost-intensive and technically difficult accounting for as much as 80% of the expense of an antibiotic production operation [8]. For example, many antibiotic or biological compound separations require:

1) 60-100 processing stages using liquid-liquid extraction (LLE)
2) a difficult precipitation or an expensive distillation to recover the antibiotic from the solvent
3) many toxic LLE solvents necessitate extensive and expensive washing procedures for safety before use

SCFE offers considerable flexibility for an effective separation through controlling pressure, temperature, and choice of solvents. Supercritical fluid extraction exploits the pressure-density relationships of the critical region to allow fluids like CF_4 to function as solvents. Figure 1 is a phase diagram of reduced density *vs.* reduced pressure for CO_2 discussed by many authors, *e.g.* Williams [9], Giddings *et al.* [10] and Schneider [11].

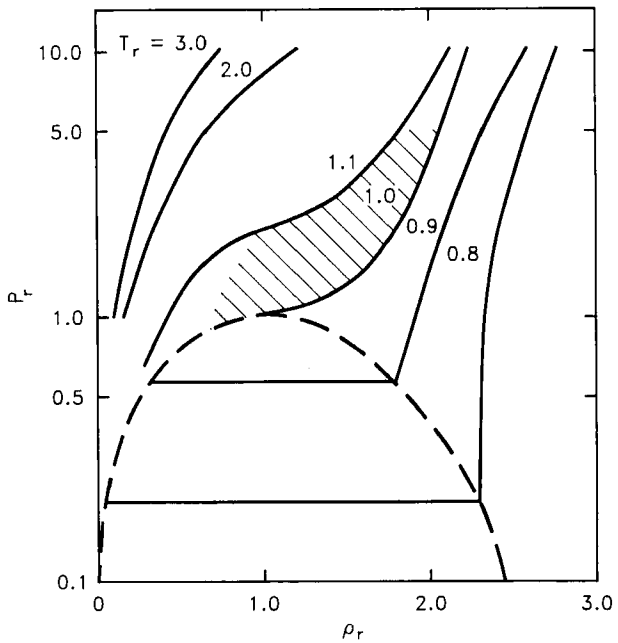

Fig. 1. Phase diagram showing supercritical region.

The shaded area is the critical region where the densities are acceptable for SCFE. This region lies just above the critical temperature (T_r = 1.0 isotherm) and below moderate temperatures (T_r = 1.1 isotherm). Here in this flat region small changes in pressure result in large changes of volume or density. This increase to liquid-like density allows a supercritical fluid to be an effective solvent. SCFE thus offers these advantages over

conventional solvents:

1) combines gas like transport properties with liquid like solvent powers;
2) offers moderate operating temperature;
3) utilizes non-toxic gases as solvents;
4) dissolves non-volatiles; and
5) provides for efficient product recovery [6].

From Table 1 [12] one can compare the physicochemical properties of supercritical fluid phases to those of gases and liquids. The enhanced solvent power of up to ten orders of magnitude in supercritical fluids is quite similar to that of liquids. The density of the supercritical fluid phase is much closer to that of a liquid; however, the binary diffusion coefficients and viscosities resemble those of compressed gases. Most of these phenomena are favorable for SCFE with respect to mass transfer.

Table 1. Properties of Gas, Supercritical, and Liquid Phases

Properties	Gas (1atm)	SCF Phase	Liquid
density (g/cm^3)	10^{-3}	0.3	1.0
diffusivity (cm^2/s)	10^{-1}	10^{-3} to 10^{-4}	$<10^{-5}$
viscosity (g/cm·s)	10^{-4}	10^{-3} to 10^{-4}	10^{-2}

EXPERIMENTAL

Many extraction devices are described in literature. They are classified as either dynamic (flow type) or static apparatuses [6]. In this experiment we were interested only in the equilibrium composition of the solute rich supercritical gas phase. Thus a flow type apparatus was chosen because:

1) off-the-shelf equipment may be used;
2) a straight forward sampling procedure may be used; and
3) reasonably large amounts of solubility data can be obtained rapidly and reproducibly [6].

Most extraction devices are provided with a trap allowing quantitative recovery of solute during a measured extraction time. The usual methods for determining solubility are to weigh trapped material [13- 17] or to dissolve and analyze the trapped material [18]. More elegant methods of on-line analysis exist. Direct coupling of SCFE to gas chromatography [19] and to HPLC [20] have been described. This study presents another alternative of on-line analysis — mass spectrometry different than that discussed in SCF-MS interface [21]. In addition this study is among the few supercritical solubility studies at subambient temperature.

Materials — Tetrafluoromethane, CF_4, was obtained from Air Products and Chemicals, Inc. in standard cylinders with stated purity of 99.9%; the CF_4 was used without further processing. Tetrachloromethane, CCl_4, was obtained from Fisher Scientific as Certified A. C. S. grade. The CCl_4 was frozen with liquid nitrogen, crushed, and loaded as a solid into the cold equilibrium cell which was then closed and maintained near liquid nitrogen temperature until installation in the apparatus. Handling of CCl_4 from the bottle to the closed equilibrium cell was performed in a dry-box to prevent contamination by moisture.

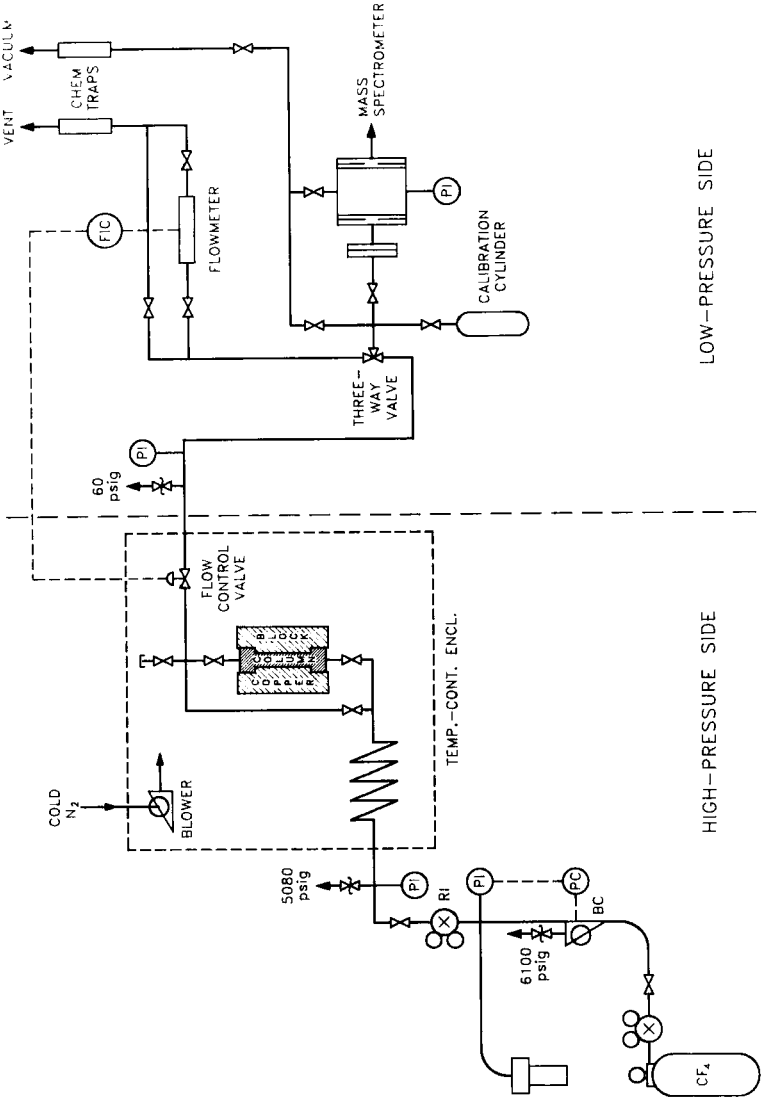

Fig. 2. DIRECT-COUPLED, HIGH-PRESSURE-FLOW MASS SPECTROMETER APPARATUS

Pressurizing system and extraction column — The apparatus used in this study was a single pass flow system shown schematically in Figure 2. CF_4 from a standard cylinder is compressed with a Sprague air-driven booster compressor and held in a 300 cm^3 Autoclave Engineers, Inc. vessel. CF_4 flows from this supply via a high pressure regulator, R1, to equipment within a temperature-controlled enclosure.

The maximum extraction pressure is limited to 415 bar by the booster compressor, BC, and the extraction temperature can be varied from ambient temperature to about 210 K. Normal operating conditions were between 15 and 315 bar and 250.2 K (m.p. of CCl_4) to 226.7 K (critical temperature of CF_4).

The temperature-controlled enclosure is an insulated, doubled-walled box cooled by vaporized liquid nitrogen. A small internal blower circulates the cold nitrogen within the enclosure. A Foxboro control unit regulates the amount of cold nitrogen entering the enclosure from an input provided by a thermocouple suspended in the air bath.

The CF_4 equilibrated to the enclosure temperature by passing through 20 feet of coiled tubing prior to entering the column. The CF_4 then passes through the column at a flow rate slow enough to ensure equilibrium (approximately 1 cm/min at moderate pressures (135 bar). The column is a stainless steel tube (19 cm long, 0.84 cm ID) containing a packed bed of solid CCl_4. At each end and every 3.75 cm a glass wool pad was placed to prevent entrainment and channeling.

A split, cylindrical copper block of 12 cm OD is placed around the column to ensure temperature uniformity. Column temperature is monitored by two chromel/gold (0.07 wt% iron) thermocouples inserted in the ends of the block. These thermocouples were accurate to ±0.1 K. They were calibrated repeatedly at the normal boiling point of nitrogen and the melting point of ice.

Expansion and analysis — The solute-rich CF_4 is expanded to atmospheric pressure across a flow control valve, FCV. Heat is applied to the valve to prevent clogging of the valve by frozen CCl_4 or solute precipitation. The flow rate is observed on a Hastings flow meter, FM, which controls the FCV. Typical flow rates were between 0.03 to 0.06 standard liters per minute to ensure column equilibrium (see Figure 3).

The analysis principle is simple. When the equilibrium of supercritical CF_4- CCl_4 is reached, the effluent is diverted to the mass spectrometer. In order to ensure that CCl_4 did not condense in the low pressure tubing, heating tape was wrapped around the tubing to maintain a temperature above the boiling point of CCl_4, 349.7 K. The effluent was admitted through a double orifice assembly (see Figure 4) reducing the pressure to approximately 3 Torr. This was to ensure laminar flow, hence representative sampling, prior to entering the HVC of the quadrupole mass spectrometer. A UTI Model 100C quadrupole mass spectrometer was utilized in this experiment with the following optimized instrument settings: emission current- 2.20 ma, focus voltage- 20 v, ion energy- 15 v, electron energy- 70 v, and emission current (Total Pressure mode)- 0.41 ma.

Typical MS operational settings were Faraday Cup mode at 10^{-12} amps full scale and a MS pressure of 1.4×10^{-6} Torr. Data were recorded on a strip chart recorder.

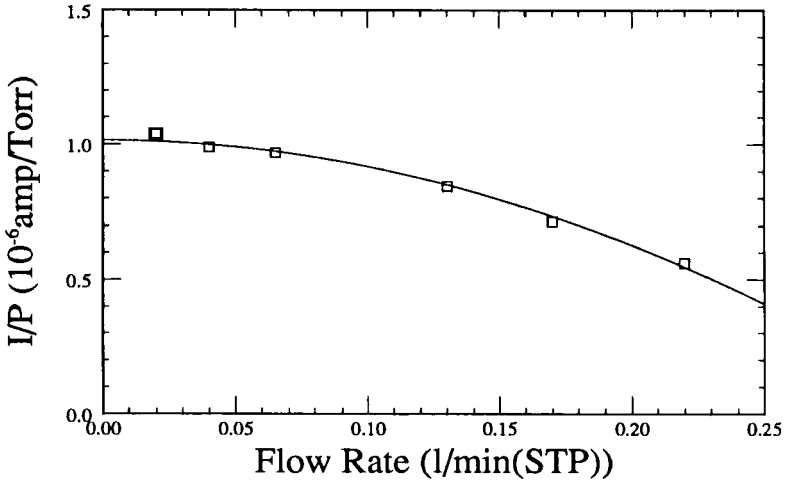

Fig. 3. To ensure maximum mass transfer conditions, the optimum flow rate was determined. Equilibrium is achieved at ≤ 0.06 SLPM.

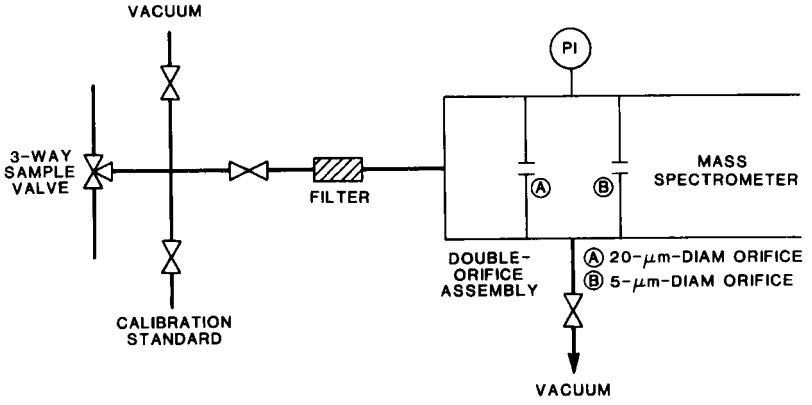

Fig. 4. Double orifice sample inlet to MS.

CALIBRATION AND INTERPRETATION

A 303.4 ml cylinder was evacuated and flushed three times with CF_4. The cylinder was then charged to 2.6±0.1 psig. Using a gas chromatograph syringe a precise amount of CCl_4 (5–20μl) was injected. After heating to ensure no CCl_4 was in a liquid phase and thermal mixing for ≥ 24 h, the cylinder was opened to the evacuated low pressure side of the apparatus. MS data were taken directly. The 1.40×10^{-12} amp point was repeated and found to be within 1.0%.

If the detector signal is linear, the solubility x is given by the relation $x = (I/P)\times(C/(I/P))$ where I/P is the ion current normalized by the MS pressure and $C/(I/P)$ is a constant. Figure 5 is the calibration curve for the system at 1.38×10^{-6} Torr. Although it is essentially linear in the region where $x > 0.005$, an excellent fit is provided by the cubic polynomial equation (1).

$$x = a_0 + a_1(I/P) + a_2(I/P)^2 + a_3(I/P)^3 \quad (1)$$

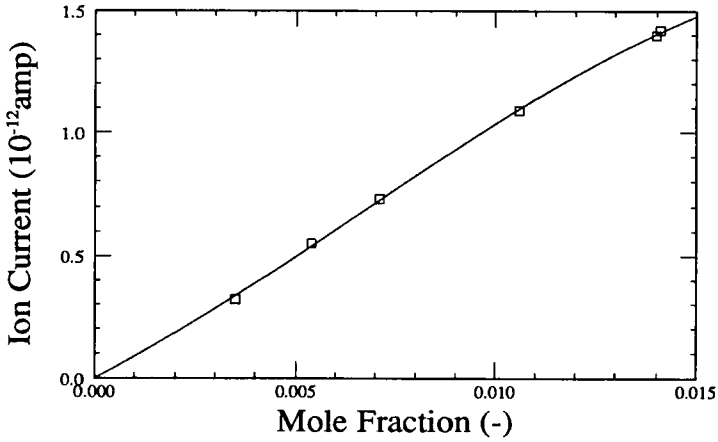

Fig. 5. Mass spectrometer calibration curve.

At $\leq10^{-5}$ Torr the MS was expected to be linear with respect to pressure; however, it was found to be nonlinear such that a 3-fold increase in pressure resulted in a 5-fold increase in ion current. The pressure calibration shown in Figure 6 was used to correct ion current at any pressure to the pressure of the calibration curve in order to calculate the mole fraction, x.

The CCl_4—CF_4 system proved very easy to interpret. [22] Figure 7 is the mass spectrum of CCl_4 overlayed on that of CF_4. The distinct triplet at AMU's 117, 119, and 121 provided the fingerprint for determining the mole fraction of the solute. Of the three peaks the 117 AMU was the largest from the splitting pattern of the MS and calculations are based on its amplitude.

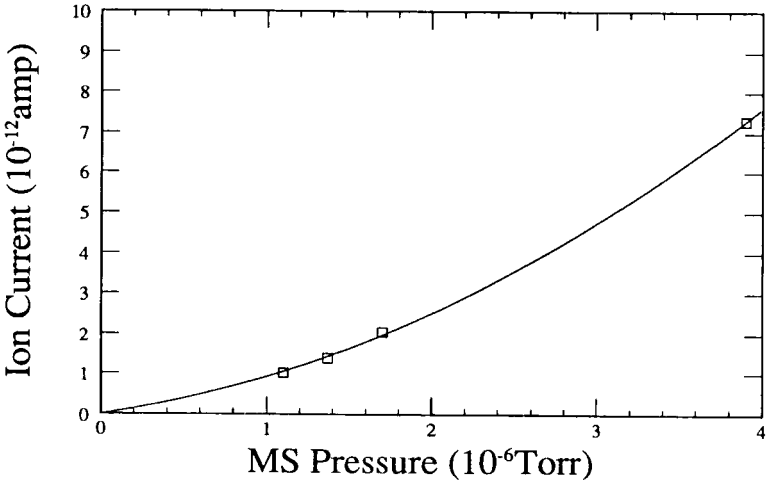

Fig. 6. Pressure correction for MS.

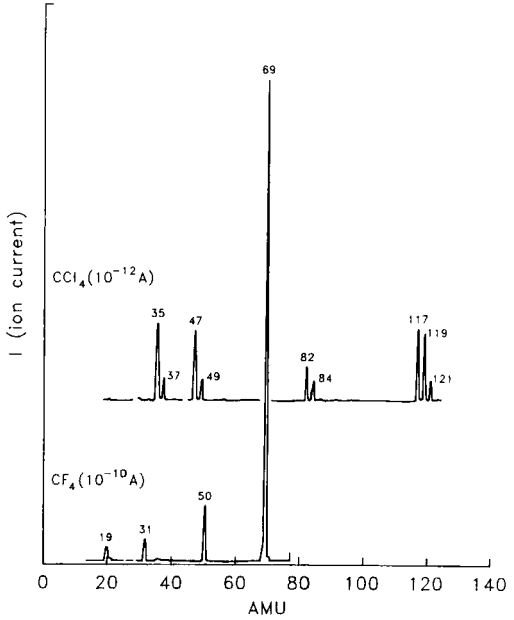

Fig. 7. Mass spectra of CCl_4 and CF_4

RESULTS AND DISCUSSION

The apparatus was used to measure carbon tetrachloride solubility in supercritical CF_4 at four different temperatures. For the two isotherms displayed (244 and 249 K) the 138 bar points were repeated three times and found to be with in ±1.0% of each other. Two other isotherms (239 and 234 K) were not reproducible and thus are not presented. It is believed that a third (liquid) phase was being formed at the lower temperatures, complicating the operation and the interpretation of results.

Figures 8 and 9 represent two different ways of displaying supercritical solubility data. The enhancement factor, E, is the extent to which pressure enhances the solubility of a solid in the gas compared to the solubility calculated from the ideal gas expression $x_{ideal} = p^{sat}/P$. The enhancement factor ($E = x_{obs}P/p^{sat}$) was calculated using equilibrium vapor pressure for solid CCl_4 from the *International Critical Tables* [23].

The shape of the curves is common. However, as density and pressure approach zero, ln$E$ should also approach zero. The difference between this ideal and the actual experimental results can be attributed to the error in the nonlinearity of ion current *vs.* x at low mole fractions.

Coupled SCFE-MS provides a new approach to the extraction and analysis of SCFE. Though this technique was applied to a simple binary mixture it can be applied to multicomponent mixtures as well. If each compound has a characteristic AMU ion fragment, both inorganic and organic compounds can be studied by direct coupling which yields easy to interpretate spectra and quantitative measurement of the analyzed species. The apparatus also provided a means for conducting low temperature extractions.

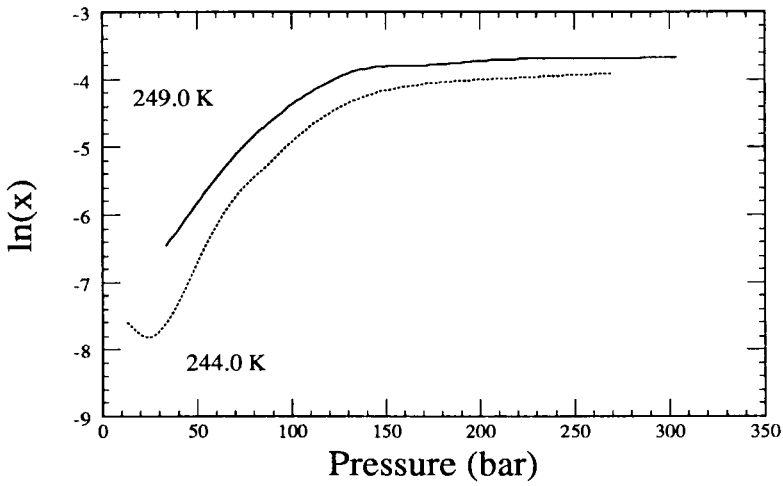

Fig. 8. Solubility *vs.* pressure at 244 and 249 K

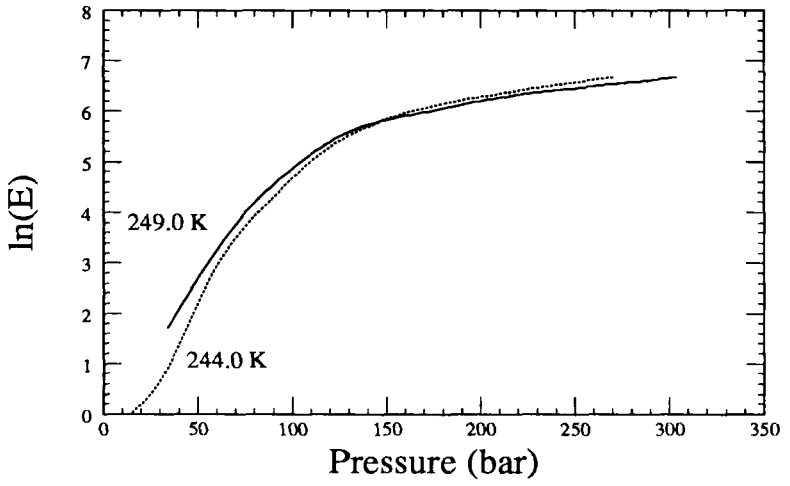

Fig. 9. Enhancement factor *vs.* density at 244 and 249 K

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REFERENCES

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

2. Wolkomir, R.,"Supercritical Potatoe Chips Breakthrough," *Omni*, **6**, 28 (1984).

3. Stahl, E., E. Schutz, and H.K. Mangold, "Extraction of Seed Oils with Liquid and Supercritical Carbon Dioxide," *J. Agric. Food Chem.*, **28**, 1153 (1980).

4. Zhuze, T. P., "Compressed Hydrocarbon Gases as a Solvent," *Petroleum*, **23**, 289 (1960).

5. Hubert, P. and O. G. Vitzthum, "Fluid Extraction of Hops, Spices and Tobacco with Supercritical Gases," *Ang. Chem. Int. Ed.*, **17**, 710 (1978).

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

7. Willson, R. C., and C. L. Cooney, "Use of Supercritical and Near Critical Solvents for Recovery of Fermentation Products," Chicago ACS Meeting September 1985.

8. Bienkowski, P. R., D. D. Lee, and C. H. Byers, "Evaluation of Separation and

Purification in the Antibiotic Industry," *Applied Biochem. & Biotechnol.*, **18**, 262 (1988).

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

10. Giddings, J. C., M. N. Myers, and J. W. King, "Dense Gas Chromatography at Pressures up to 2000 Atmospheres," *J. Chrom. Sci.*, **7**, 67 (1968).

11. Schneider, G. M., "Physicochemical Principles of Extraction with Supercritical Gases," *Agnew. Chem. Int. Ed. Engl.*, **17**, 716 (1978).

12. Schneider, G. M., "Extraction of Fluid Mixtures at High Pressures — Basis of Supercritical Fluid Technology," *Proc. of the Int. Symp. on Supercritical Fluids*, **1**, 1 (1988).

13. McHugh, M. A. and M. E. Paulaitis, "Solid Solubilities of Naphthalene and Biphenyl in Supercritical Carbon Dioxide," *J. Chem. Eng. Data*, **25**, 326 (1980).

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

15. Adachi, Y. and C. Y. Benjamin, "Supercritical Fluid Extraction with Carbon Dioxide and Ethylene," *Fl. Ph. Equilib.*, **14**, 147 (1983).

16. Moradinia, I. and A. S. Teja, "Solubilities of *n*-Octacosane, *n*-Triacontane, and *n*-Dotriacontane in Supercritical Ethane," *Fl. Ph. Equilib.*, **28**, 199 (1986).

17. Mitra, S., J. W. Chen, and D. S. Viswanath, "Solubility and Partial Molar Volumes of Heavy Hydrocarbons in Supercritical CO_2," *J. Chem. Eng. Data*, **33**, 35 (1988).

18. Schneiderman, M. A., A. K. Shara, and D. C. Locke, "Determination of Anthraquinone in Paper and Wood Using Supercritical Fluid Extraction and High-Performance Liquid Chromatography with Electrochemical Detection," *J. Chrom.*, **409**, 343 (1987).

19. Hawthorne, S. B., and D. J. Miller, "Directly Coupled Supercritical Fluid Extraction-Gas Chromatographic Analysis of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls from Environmental Solids," *J. Chrom.*, **403**, 63 (1987).

20. Billoni, N., J. Jose, and J. C. Merlin, "Solubility of Heavy Components in Supercritical CO_2 Using Directly Coupled Supercritical Fluid Extraction-High Performance Liquid Chromatography," *Proc. Int. Symp. on Supercritical Fluids*, **2**, 373 (1988).

21. Smith, D. S., H. T. Kalinoski, and H. R. Udseth, "Fundamentals and Practice of Supercritical Fluid Chromatography-Mass Spectrometry," *Mass Spectrometry Reviews*, **6**, 445 (1987).

22. Cornu, A., and R. Massot, *Compilation of Mass Spectral Data*, Vol. 1, Heyden and Son, Inc. (1975).

23. *International Critical Tables of Numerical Data, Physics, Chemistry, and Technology*, Vol. 3, 215, McGraw-Hill Book Co. (1933).