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A Recirculating Equilibrium Procedure for Determining Organic Compound Solubility in Supercritical Fluids. Anthracene in Carbon Dioxide

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An instrumental recirculation technique was developed to measure the solubility of organic compounds and thus their potential extractability, in supercritical fluids over the pressure range of 80−500 bar. Anthracene, whose solubility is well defined, was chosen as a model compound to be used in evaluating the recirculation technique. Its solubility in supercritical carbon dioxide was measured at 40, 50, and 60 °C using an off-line spectroscopic technique. The solubility data were found to have good precision and to agree with published results. Anthracene solubility increased with pressure but was more enhanced by higher temperature. An upper crossover pressure of the isotherms due to retrograde vaporization that agreed with theory was found at 142.2 bar.

Introduction

Potential applications of supercritical fluid extraction to replace organic solvent extractions have resulted in a number of laboratory techniques for determining the solubility and extractability of organic compounds in supercritical fluids. These techniques are generally classified as static or dynamic and are described in the literature (McHugh and Krukonis, 1994). The flow through method, a dynamic technique, is probably the most common procedure for determining the solubility of organic compounds in supercritical fluids. However, with the flow through method it is sometimes difficult to determine when equilibrium solubility has been reached or if particulate matter is being carried over in the flowing stream. Consequently, a recirculating system which continuously recirculates the supercritical fluid through the extractor bed should in theory provide a better measure of the true solubility of the compound under study.

The solubility of a solute in a supercritical fluid is of interest because it is probably the most important thermophysical property that must be measured and modeled for an efficient design of any extraction based on a supercritical fluid (Madras et al., 1993). Both temperature and pressure can affect the solubility of a solute in a supercritical fluid (Schmitt and Reid, 1986). In supercritical fluid extraction, solute solubility is a function of the vapor pressure of the solute which in turn is a function of the temperature of the system. Raising the temperature can dramatically increase the vapor pressure of the solute and consequently the extractability of the solute (Miller and Hawthorne, 1994). Thus, in supercritical fluid solubility studies, the solubility should be determined as a function not only of pressure, but also of temperature.

Supercritical fluid extraction is under investigation in this laboratory as a possible replacement for organic solvents in drug residue methods which are currently being used by the Food Safety and Inspection Service (FSIS) of the United States Department of Agriculture (Food Safety and Inspection Service, 1990). One FSIS mission is to detect trace quantities (ppm−ppb) of drug residues in animal products destined for human consumption. Consequently, extractions using supercritical fluids, particularly supercritical carbon dioxide, offer an attractive alternative to conventional liquid extractions because of the decreased need for organic solvents.

In this study the solubility of anthracene in supercritical CO_2 was investigated to evaluate an experimental recirculating fluid technique. The technique, however, is applicable to other organic compounds and supercritical fluids. Anthracene was chosen as a test compound because there are several anthracene solubility studies in the literature with which the data in this study could be compared. Foster et al. (1991) have compiled a comprehensive list of solubility studies in supercritical fluids. Carbon dioxide was chosen as the supercritical fluid as it is generally the first choice as an extraction solvent because of its desirable properties, i.e., low toxicity, low critical temperature and pressure, low expense, and ready availability.

Experimental Section

Materials. Anthracene (99.9%), Gold Label grade, was obtained from Aldrich Chemical Co. (Milwaukee, WI). Carbon dioxide, SFC grade with dip tube, was obtained from Scott Specialty Chemical (Plumsteadville, PA). Methylene chloride, HPLC grade, was obtained from Burdick and Jackson Laboratories (Muskegan, MI). Glass beads (0.25−0.32 mm) were obtained from Thomas Scientific (Swedesboro, NJ).

Method. Solubility measurements were performed using a sample preparation accessory (SPA) supercritical fluid extraction instrument from LDC Analytical (Riviera Beach, FL). Modifications and operation of the instrument have been previously described (Maxwell et al., 1991). A schematic diagram of the modified SPA system in the recirculating mode is shown in Figure 1. The system plumbing is thermostated within the SPA instrument. The system volume is approximately 17 mL. Recirculation flow through the pump, sample loop, and extractor was 45−55 mL/min, measured at atmospheric pressure. Flow was measured with a liquid (methanol) and also with air. Liquid flow measurement was made with a graduate cylinder and a stopwatch. Air flow measurement was made with a rotameter, Model SHO-Rate, Brooks Instrument Co. (Hatfield, PA). The recirculating pump operation is critical and must be tested daily. Its operation was checked before and

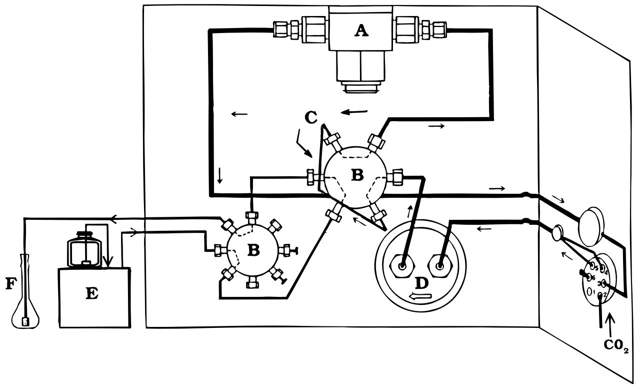

Figure 1. Schematic diagram of modified sample preparation accessory (SPA) in the recirculation mode for off-line solubility measurements: A, extractor; B, injection valves; C, sample loop; D, recirculation pump; E, solvent and HPLC pump; F, sample recovery flask.

after each experiment. After each experiment the instrument was cleaned thoroughly and the recirculating pump tested for flow characteristics, for both liquid and air flow.

In a typical experiment, a 2 mL stainless steel cylindrical extraction cup was filled one-third with glass beads; the cup was fitted with 2 μm frits at the top and bottom and tared prior to mixing in the anthracene (100−200 mg). The cup was reweighed and then placed in the extractor. After reaching a set temperature and pressure, equilibrium solubility was attained by recirculating the supercritical fluid through the extractor for 25 min. This time was determined by experiments up to 1 h to be more than sufficient to reach equilibrium. The dynamic off-line procedure for sample collection (i.e., collection of sample into a container rather than direct injection into another instrument) is reported to be the most common procedure used with supercritical fluids, and for simplicity it was chosen in this work (Scott Monitor, 1992). By means of injection valves, the sample loop (5 mL) was redirected and depressurized into a mobile solvent, methylene chloride, and collected off-line through a diffuser into a 200 mL volumetric flask. The 200 mL flask, covered with plastic netting and a glass wool plug in the mouth, was used to contain the rapid depressurized carbon dioxide from the 5 mL sample loop. The 5 mL sample loop was then washed out three times (15 mL) with the mobile solvent using a minipump (Milton Roy) manufactured by LDC Analytical. The total volume of the collected sample and the washings was transferred from the collection flask and made up to 25 mL in a volumetric flask.

Quantitative analysis by ultraviolet absorption at 358 nm was obtained using a Model DU70 spectrophotometer, Beckman Co. (Fullteron, CA). The best solvent for anthracene was determined prior to establishing the standard calibration curves. These curves were obtained as follows: A stock solution containing 25 mg of anthracene in 25 mL of methylene chloride was prepared. A set of standards was then obtained by serial dilution. The UV curves obtained with the standards were then used to establish the concentration curve for anthracene. The concentration curve had a correlation coefficient of 0.999 and an accuracy of 1 mg L^{-1}. A blank sample for UV analysis at the temperature of interest and 345 bar was obtained prior to each isothermal run to test the cleanliness of the system.

The extractor temperature from the instrument readout was confirmed by attaching a thermocouple, Model HH2a, Omega Engineering (Stamford, CT), directly onto the extractor. This temperature was found to be within ±0.5 °C of the instrument readout. The extractor pressure was measured with a transducer, Model 1203, GP:50 New York Limited (Grand Island, NY), calibrated at the factory. Comparison of the pressure transducer with the SPA instrument pressure readout indicates an accuracy of ±1 bar at 200 bar of pressure and ±4 bar at 500 bar of pressure. Operation of the SPA provides for a range of pressures rather than identical pressures from run to run.

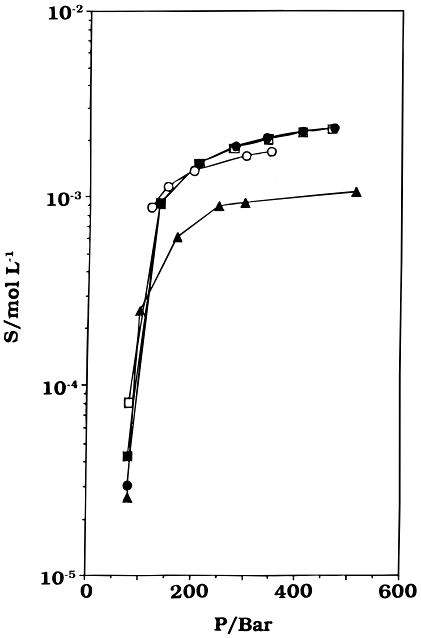

Figure 2. Anthracene solubility in supercritical carbon dioxide at 40 °C: ■, □, ●, this paper; ○ (35 °C), Dobbs and Johnston (dynamic, flow through technique); ▲, Zerda et al. (static, FTIR technique).

Carbon dioxide densities were obtained from tables constructed using the equation of state of Schmidt and Wagner (1985). These densities compared favorably with densities determined experimentally (Langenfeld et al., 1992).

Results and Discussion

The solubility data for anthracene in supercritical CO_2 at 40, 50, and 60 °C in the pressure range 80−500 bar are presented in Figures 2−4. The actual data in triplicate are shown in each figure. To avoid bias, each isothermal curve was obtained on a separate day, i.e., three nonconsecutive days for each temperature or a total of 9 days for the 40, 50 and 60 °C isotherms. As seen in Figures 2−4, the three isothermal curves determined in this study at each temperature overlay each other and indicate good experimental repeatability. Table 1 includes a measure of this precision by the standard deviation and also provides the mole fraction data.

It can also be seen from examination of the figures that the solubility increases with pressure only up to a maximum, after which there is only a slight increase. However, increasing the temperature from 40 to 60 °C raises the solubility substantially. Raising the temperature at high pressures does more to increase the solubility than raising the pressure. Temperature increases the solubility in spite of the fact that, at the same pressure, the supercritical fluid is less dense at the higher temperature. This increased solubility must be due to the increase in vapor pressure of anthracene at the higher temperatures.

Comparing the data in this study with the literature shows that at 40 °C the values are somewhat higher than those of Zerda et al. (1986). The results are more in

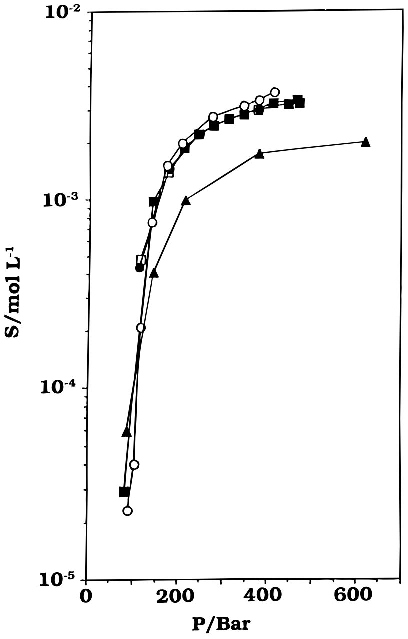

Figure 3. Anthracene solubility in supercritical carbon dioxide at 50 °C: ■, □, ●, this paper; ○, Johnston et al. (dynamic, flow through technique); ▲, Zerda et al. (static, FTIR technique).

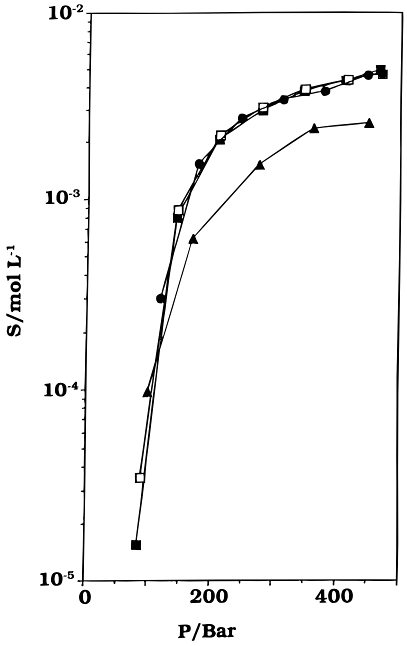

Figure 4. Anthracene solubility in supercritical carbon dioxide at 60 °C: ■, □, ●, this paper; ▲, Zerda et al. (static, FTIR technique).

agreement with those calculated from Dobbs and Johnston (1987) even though their results were obtained at 35 °C. At 50 °C we obtained maximum solubilities 39% higher than those of Zerda, but in good agreement with the results of Johnston et al. (1982). At 60 °C our results were 42% higher than those of Zerda. But, for all of these determinations, the absolute differences are relatively small considering the different techniques used to determine solubility. For example, at 60 °C and 450 bar our study shows the solubility to be 4.55×10^{-3} mol L^{-1} (0.811 g L^{-1}) whereas it is 2.54×10^{-3} mol L^{-1} (0.453 g L^{-1}) in the work of Zerda.

Table 1. Solubility, *S*, of Anthracene in Supercritical Carbon Dioxide at 40, 50, and 60 °C

P/bar	$\rho(CO_2)$/(mol L^{-1})	S^a/(mol L^{-1})	*y*
		t = 40 °C	
80.0	6.30	$5.11(2.60) \times 10^{-5}$	8.09×10^{-6}
135	17.15	$9.14(0.09) \times 10^{-4}$	5.33×10^{-5}
210	19.30	$1.50(0.00) \times 10^{-3}$	7.77×10^{-5}
280	20.45	$1.81(0.02) \times 10^{-3}$	8.85×10^{-5}
340	21.15	$2.03(0.03) \times 10^{-3}$	9.60×10^{-5}
410	21.85	$2.21(0.02) \times 10^{-3}$	1.01×10^{-4}
470	22.35	$2.31(0.01) \times 10^{-3}$	1.03×10^{-4}
		t = 50 °C	
83.4	5.45	$2.90(-) \times 10^{-5}$	5.32×10^{-6}
115	12.50	$4.71(0.29) \times 10^{-4}$	3.77×10^{-5}
175	17.05	$1.42(0.03) \times 10^{-3}$	8.33×10^{-5}
245	18.85	$2.22(0.04) \times 10^{-3}$	1.18×10^{-4}
310	19.95	$2.64(0.01) \times 10^{-3}$	1.22×10^{-4}
380	20.80	$2.97(0.04) \times 10^{-3}$	1.43×10^{-4}
445	21.45	$3.20(0.08) \times 10^{-3}$	1.49×10^{-4}
470	21.65	$3.25(0.08) \times 10^{-3}$	1.50×10^{-4}
		t = 60 °C	
83.4	4.70	$1.55(-) \times 10^{-5}$	3.29×10^{-6}
88.3	5.20	$3.53(-) \times 10^{-5}$	6.78×10^{-6}
145	13.30	$8.42(0.38) \times 10^{-4}$	6.33×10^{-5}
210	16.80	$2.20(0.12) \times 10^{-3}$	1.31×10^{-4}
280	18.55	$3.03(0.05) \times 10^{-3}$	1.63×10^{-4}
345	19.55	$3.73(0.16) \times 10^{-3}$	1.91×10^{-4}
415	20.45	$4.20(0.22) \times 10^{-3}$	2.05×10^{-4}
470	20.95	$4.76(0.14) \times 10^{-3}$	2.27×10^{-4}

[a] The standard deviation is given in parentheses.

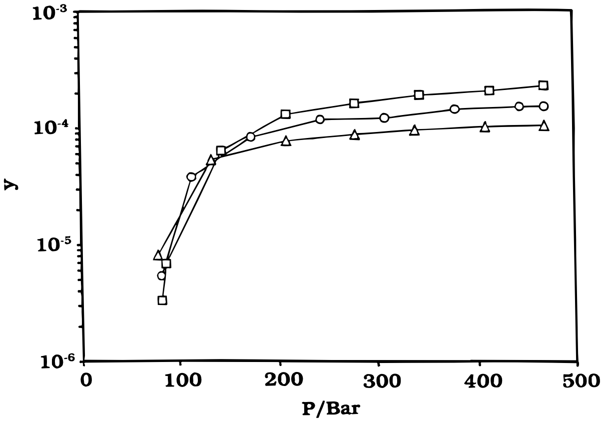

Figure 5. Crossover curves for the isotherms: △, 40; ○, 50; □, 60 °C.

Foster et al. (1991) noted that when at least three isotherms of supercritical fluid solubility versus pressure data are plotted, a crossover pressure in the curves is obtained due to the existence of retrograde vaporization, i.e., a decrease in solute solubility with an isobaric increase in temperature. This indicates that the data are reliable. An upper crossover pressure is shown in Figure 5 at 142.2 bar. This value, 142.2 bar, was obtained by plotting the mole fraction data and magnifying the crossover area to obtain the intersection. This gave a value close to Foster's calculated value. Using a semiempirical model, Foster calculated that the upper crossover pressure for anthracene should be 139.7 or 140.7 bar with an absolute deviation of 6.2−6.9% from the experimental value for nonpolar compounds like anthracene. The upper crossover pressure presented in this paper has an absolute deviation of 1.4% from the average of Foster's calculated values.

In conclusion, the results indicate that the recirculating equilibrium technique was capable of accurately determining the solubility of organics in supercritical fluids. This instrumental technique will be used in the future to determine the solubility of veterinary drugs with the prospect of predicating their extractability from animal tissue with supercritical CO_2.

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Nomenclature

P = pressure
S = solubility
t = temperature
y = mole fraction
ρ = molar density

Literature Cited

Dobbs, J. M.; Johnston, K. P. Selectivities in Pure and Mixed Supercritical Fluid Solvents. *J. Chem. Eng. Data*, **1987**, *26*, 1476–1482.

Food Safety and Inspection Service, Compound Evaluation and Analytical Capability National Residue Program, U.S. Department of Agriculture, 1990.

Foster, N. R.; Gurdial, G. S.; Yun, J. S. L.; Liong, K. K.; Tilly, K. D.; Ting, S. S. T.; Singh, H.; Lee, J. H. Significance of the Crossover Pressure in Solid-Supercritical Fluid Phase Equilibria. *Ind. Eng. Chem. Res.* **1991**, *30*, 1955–1964.

Johnston, K. P.; Ziger, D. H., Eckert, C. A. Solubilities of Hydrocarbon Solids in Supercritical Fluids. The Augmented van der Waals Treatment. *Ind. Eng. Chem. Fundam.* **1982**, *21*, 191–197.

Langenfeld, J. J.; Hawthorne, S. B.; Miller, D. J. Method for Determining the Density of Pure and Modified Supercritical Fluids. *Anal. Chem.* **1992**, *64*, 2263–2266.

Madras, G.; Erkey, C.; Akgerman, A. A New Technique for Measuring Solubilities of Organics in Supercritical Fluids. *J. Chem. Eng. Data* **1993**, *38*, 422–423.

Maxwell, R. J.; Hampson, J. W.; Cygnarowicz-Provost, M. Solute Recovery from Equilibrium Solubility Determinations Using a Modified Supercritical Fluid Extractor. *LC–GC* **1991**, *9*, 788–794.

McHugh, M.; Krukonis, V. *Supercritical Fluid Extraction*, 2nd ed.; Butterworth-Heinemann: Stoneham, MA, 1994; p 85.

Miller, D. J.; Hawthorne, S. B. *Proceedings, the Fifth International Symposium on Supercritical Chromatography and Extraction*; Baltimore, MD, Supercritical Conferences: Cincinnati, OH, 1994; p A-2.

Schmidt, R.; Wagner, W. A New Form of the Equation of State for Pure Substances and Its Application to Oxygen. *Fluid Phase Equilib.* **1985**, *19*, 175–200.

Schmitt, W. J.; Reid, R. C. Solubility of Monofunctional Organic Solids in Chemically Diverse Supercritical Fluids. *J. Chem. Eng. Data* **1986**, *31*, 204–212.

The Scott Monitor. *Collection Efficiency of Various Solid-Phase Traps for Off-Line Supercritical Fluid Extraction*; Scott Specialty Gases, Inc.: Plumsteadville, PA, 1992; Vol. 4, p 1.

Zerda, T. W.; Wiegand, B.; Jonas, J. FTIR Measurements of Solubilities of Anthracene in Supercritical CO_2. *J. Chem. Eng. Data* **1986**, *31*, 274–277.

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