A New Technique for Measuring Solubilities of Organics in Supercritical Fluids

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A new experimental technique was developed to determine the solubilities of organics in supercritical fluids. Solubilities are determined by determining the weight of organic deposited on activated carbon when a stream of organic and carbon dioxide is passed through the carbon bed. The solubility of naphthalene in carbon dioxide at 308, 318, and 328 K at around 105 bar was determined and was found to be in good agreement with the data reported in the literature. In addition, the method was used to determine the solubilities of hexachlorobenzene and pentachlorophenol in carbon dioxide at 298, 308, and 318 K at 111.5 bar. The solubility data were correlated using a simple model relating the solute solubility and the solvent density.

Introduction

In the past two decades supercritical fluids have been the focus of active research and development programs. The ability of a supercritical fluid (SCF) to separate a multicomponent mixture by capitalizing on *both* the difference in component volatilities as well as the difference in specific interactions between the components and the SCF solvent is unique. Thus, it utilizes the salient features of both distillation and liquid extraction. Since the solvent power of a fluid changes over a wide range in the vicinity of the critical point, there has been increasing interest in supercritical separation processes in the chemical, petrochemical, food, and pharmaceutical industries. These include removal of caffeine from coffee beans and extraction of oils from oil shales. Further, regeneration of carbon (*1–3*) and decontamination of soil (*4*) have been investigated in the laboratory and pilot scale. The solubility of a solute in a supercritical fluid is perhaps the most important thermophysical property that must be determined and modeled for an efficient design of any extraction based on supercritical solvents.

The potential applications of supercritical fluid extraction have resulted in widespread laboratory techniques for the determination of solubilities of the solute in supercritical fluids. The literature available on the solubilities of various organics in different supercritical fluids is given by Foster et al. (*5*). However, data on the solubilities of polychlorinated organics in supercritical fluids are sparse.

The methods used for measuring solubilities of organics in supercritical fluids may be broadly classified into four different categories: dynamic methods, static methods, chromatographic methods, and spectroscopic methods. The advantages and disadvantages of these methods as well as their accuracy and precision have been discussed in detail elsewhere (*6*, *7*).

The method developed in our laboratory is based on loading the solute from a SCF stream onto activated carbon and gravimetrically determining the amount adsorbed. Due to the high adsorption capacity of carbon for organics, a significant amount of organic is adsorbed on carbon (10–30 wt %). Thus, the error in the gravimetric analysis is insignificant. In addition, there is no need to reload the extractor to obtain temperature-dependent data. Thus, rapid and reproducible data can be obtained using the technique. However, this technique is only applicable for measuring single-component solubilities. This apparatus can also be used to determine the adsorption isotherms and desorption profiles of various organics on any solid medium like activated carbon. In this study, solubilities of various solutes in supercritical carbon dioxide have been investigated, but the experimental technique is clearly applicable to any supercritical fluid.

Experimental Section

A schematic diagram of the experimental setup is presented in Figure 1. Two syringe pumps (ISCO 260D and ISCO LC-2600) are initially filled with liquid carbon dioxide and compressed up to 100 bar using nitrogen. Then, the pumps are started and the stream from the first pump, 4, is passed through a preheater in the bath where it is brought to the bath temperature and through a column, 8, which contains the organic solute of interest. Glass wool is inserted at the ends of the column to prevent entrainment of the solute. A pure carbon dioxide stream coming from the second pump, 5, is brought to the bath temperature and mixed with the equilibrated carbon dioxide stream. This technique enables one to achieve different fluid concentrations by adjusting the flow rates of the two pumps. This is particularly convenient for conducting experiments at different inlet concentrations. The mixing of these streams also prevents condensation in the lines. Then, the organic–carbon dioxide mixture is passed through the sample injection valve, 9 (Rheodyne 7010), brought to the conditions of the bath with the aid of a preheater, and passed through the switching valve, 10 (Rheodyne 7000), and the high-pressure UV detector (LDC Analytical, critical extraction monitor). Finally, the organic is stripped from carbon dioxide by adsorption onto activated carbon, and the pure carbon dioxide stream is expanded into the atmosphere with two back-pressure regulators placed in series, 15 and 16 (Tescom Inc. 26-1722-24 and Grove SD91-W). The organic is stripped off by the carbon bed, and thus the back-pressure regulator does not come into contact with the organic. Verification of the flow rate is done by the dry gas meter (DTM 115, Singer), placed after the back-pressure regulators.

The temperature of the bed is controlled to ±0.02 K using an immersion circulator (Haake D1), and the pressure is measured by a factory-calibrated pressure transducer (Hydronics A 006220 TH-1V) accurate to ±0.7 bar. The response from the detector is recorded on disk through a MBC488 Metra-byte board which reads the detector voltage from a digital multimeter (Solartron 7150). The flow rate is monitored by a dry test meter (Singer DTM-115).

Once a steady voltage is reached in the detector, the organic–carbon dioxide solution is diverted into the bed loaded with activated carbon using a switching valve. The effluent concentration is monitored on-line using a UV detector, and

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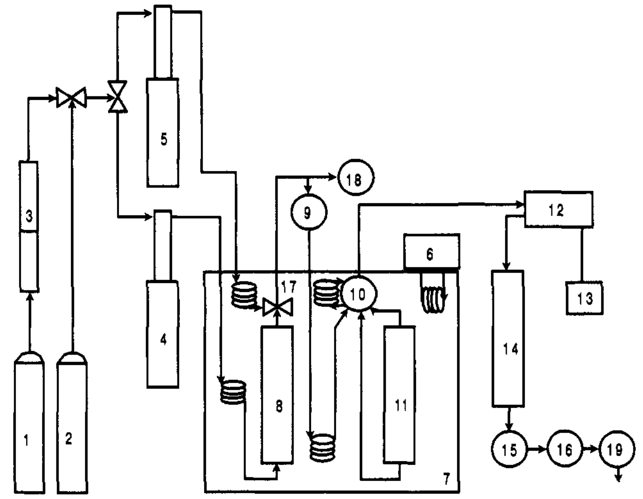

Figure 1. Schematic diagram of the experimental setup: (1) nitrogen cylinder, (2) carbon dioxide cylinder, (3) piston cylinder, (4) syringe pump, (5) syringe pump, (6) immersion circulator, (7) water bath, (8) saturator, (9) sampling valve, (10) six-port switch valve, (11) adsorbent bed, (12) UV detector, (13) data acquisition, (14) activated carbon trap, (15, 16) back-pressure regulators, (17) three-way valve, (18) pressure transducer, (19) dry gas meter.

after a while the solute breaks through the column, enabling determination of the breakthrough time (time required for the saturation of the solid with the solute). The column is then isolated, emptied, and filled with a known amount of fresh treated activated carbon. In order to determine the amount of organic deposited accurately, the amount deposited is maximized by conducting the experiment for 70–80% of the breakthrough time. Then, the amount of solute deposited on the carbon is determined gravimetrically after expansion. The amount of solvent passed through the column is determined by the flow rate measured by the dry gas meter and verified by the total flow rate of the pumps. The solubility of the solute is thus determined by the ratio of the amount of solute deposited and the amount of saturated solution passed through the column. In all the flow methods, it is important to ensure that the solute and the solvent attain equilibrium when the SCF solvent floods the column containing the solute. The same solubility was obtained when the experiment was repeated at three different flow rates, indicating solute–solvent equilibrium. In addition, to verify that the solubilities were independent of the inlet concentration, solubilities were measured at three different inlet concentrations. The solubilities obtained were within the experimental error of 4–5%. This experimental setup has also been used to determine the adsorption isotherms of naphthalene, phenanthrene, hexachlorobenzene, and pentachlorophenol on soil and carbon (*3*, *4*).

Results and Discussion

The solubilities of naphthalene at 308, 318, and 328 K were determined using the above technique. These data compared with the data obtained by Tsekhanskaya (*8*) within 1–2% are shown in Table I. The solubilities of hexachlorobenzene and pentachlorophenol in carbon dioxide at 298, 308, and 318 K and 111.5 bar were determined and are presented in Table II.

Solubilities of various solutes in supercritical carbon dioxide can be modeled by the following equation (*8*):

$$\log(m) = A + B\rho$$

where m is the solubility of the solute in supercritical carbon dioxide (kg/m^3) and ρ is the density of the supercritical carbon dioxide (kg/m^3). A plot of log(m) and ρ yielded a straight line, as shown in Figure 2. The constants A and B were calculated from the regressed line and are presented in Table III.

Table I. Solubilities, *S*, of Naphthalene in Carbon Dioxide

solute	t/K	P/bar	S^a/(mmol/mol)	S^b/(mmol/mol)
naphthalene	308	108.5	11.7	11.7
	318	106.5	11.3	11.2
	328	108.5	6.1	6.2

[a] Experimental data from Tsekhanskaya (*8*). [b] Experimental data obtained in this study.

Table II. Solubilities, *S*, of Hexachlorobenzene and Pentachlorophenol in Carbon Dioxide at 111.5 bar

solute	t/K	S/(mmol/L)	solute	t/K	S/(mmol/L)
hexachlorobenzene	298	0.695	pentachlorophenol	298	2.95
	308	0.685		308	2.71
	313	0.576		318	2.24
	318	0.509			

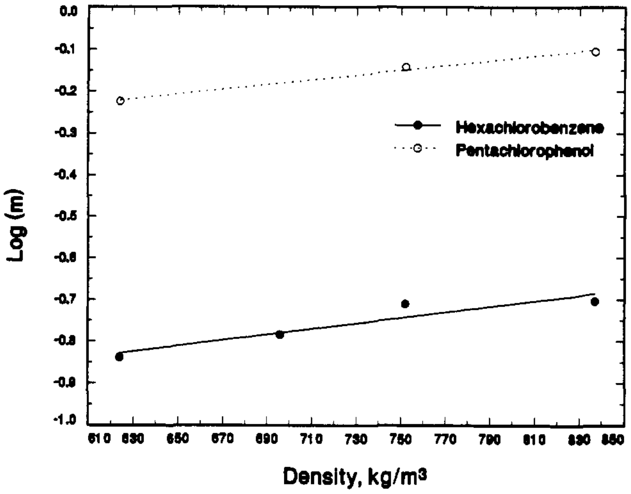

Figure 2. Variation of solute solubility with density.

Table III. Constants *A* and *B* for Hexachlorobenzene and Pentachlorophenol

solute	A	$B \times 10^4$
hexachlorobenzene	−1.249	6.73
pentachlorophenol	−0.576	5.68

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