Solubilities of 2-Nitroanisole and 3-Phenyl-1-propanol in Supercritical Carbon Dioxide

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A method has been developed to measure solubilities in supercritical carbon dioxide. The solubilities of 2-nitroanisole and 3-phenyl-1-propanol have been determined in the temperature range 313 K to 333 K and in the pressure range 8.0 MPa to 20.0 MPa. These solubilities have been fitted using the model proposed by Chrastil.

Introduction

Since the early 1980s, supercritical carbon dioxide has been widely used as a solvent (extraction, chemical and biochemical reactions, nucleation, recrystallization, impregnation). Supercritical fluids have received considerable attention due to their potential applications in the special chemical, food-processing, pharmaceutical, and petroleum industries. Carbon dioxide is usually used as a supercritical solvent because it is nontoxic and inexpensive and has a low critical temperature and a moderate critical pressure. For the design of chemical processes, solubility or phase equilibria data are most important. However, the solubility data in supercritical fluids are limited, and the thermodynamic analysis of solubility behavior has not yet been fully developed. Different experimental methods for determining the solubilities of solid and liquid components in supercritical fluids have been described in the literature (McHugh and Krukonis, 1986; Brunner, 1994).

The experimental techniques are either static or dynamic. Static methods comprise all methods where both the solute and solvent are loaded into some type of cell and equilibrium is established by waiting until equilibrium conditions have been reached. In a dynamic method, the liquid phase remains in an equilibrium cell, while the supercritical carbon dioxide flows through the equilibrium cell. Therefore, there is no way of knowing the solubility of the supercritical carbon dioxide in the liquid phase. This method can be used for determining solubilities in the supercritical phase and has been traditionally used with solid solutes. With a liquid solute, entrainment of the liquid phase in the supercritical phase is possible and the dynamic method yields higher values of solubility.

This work describes an experimental technique for the rapid and accurate determination of the solubilities of heavy liquids (hydrocarbons) in supercritical carbon dioxide, using a packed column coupled to a UV detector. The method developed is based on loading the solute onto activated carbon and gravimetrically determining the amount desorbed. The regeneration of activated carbon by desorption with supercritical carbon dioxide was first proposed by Model et al. (1979). Since then, the desorption of a variety of adsorbates has been studied (Tan and Liou, 1988; Recasens et al., 1989; Srinivasan et al., 1990; Madras et al., 1993). The desorbed solute is collected in a trap, and the cumulative concentration is measured periodically. The solubility is determined to be the ratio of the amount of solute desorbed and the amount of supercritical fluid passed through the column filled with the activated carbon.

In this work the solubilities of 2-nitroanisole and 3-phenyl-1-propanol in supercritical carbon dioxide were measured in the temperature range 313 to 333 K and for pressures between 8.0 and 20.0 MPa. These compounds have been chosen because they have also been selected to obtain diffusion coefficients and to compare the influence of molecular size and shape (Suárez et al., 1993; Suárez et al., 1998). The resultant solubility data were correlated using the model proposed by Chrastil (1982).

Experimental Section

The experimental apparatus used is a commercially available supercritical fluid chromatograph (SFC), Hewlett-Packard model G1205A. This HP SFC system consists of a pumping module, a column oven, a manual injection system, a multiple-wavelength UV detector (MWD), a modifier pump, a mass flow sensor, an HP Vectra PC, and an HP printer.

The oven module can accommodate fused silica capillary and standard HPLC columns. The oven has a temperature range from −80 to +450 °C. The HP SFC can use different detectors: a flame ionization detector (FID) and a multiple-wavelength UV detector (MWD). The chromatograph uses an electrothermally cooled reciprocating pump to supply supercritical fluids to the system. Electrothermal cooling allows clean, self-contained, quiet, and reliable operation. The pump has feedback control, which compensates for fluid compressibility, minimizes pressure ripple, and provides more reproducible results. The variable restrictor is a programmable, backpressure control device located inside the pump module. Specifically, the variable restrictor consists of a pressure transducer and a nozzle. The pressure transducer sends electronic signals to the a nozzle, which opens and closes accordingly, releasing the mobile phase to control pressure. The maximum operating pressure is 400 bar. The SFC ChemStation consists of a PC and the HP SFC software. The SFC ChemStation enables instrument control and data handling on a Microsoft Windows-based platform. The mass flow sensor is a device located inside the pumping module.

The carbon dioxide supplied by Air Liquide had a minimum purity of 99.998%. The 2-nitroanisole and 3-phenyl-1-propanol with minimum purities of 98% were obtained from Merck (synthesis grade). The activated carbon was

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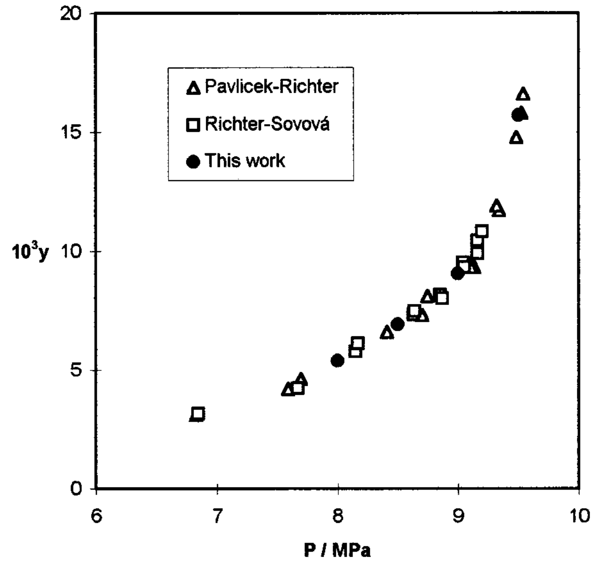

Figure 1. Solubilities of α-pinene in supercritical carbon dioxide at 323 K versus pressure.

also obtained from Merck (charcoal activated granular about 1.5 mm in diameter, extra pure).

An equilibrium cell (25 cm in length with a 1 cm internal diameter stainless steel pipe, with reducer adapter couplings at each end) of 20 mL volume is filled with the activated carbon. Glass wool is inserted at the end of the cell to prevent entrainment of the solute. For each experimental run, the cell was loaded with a sufficient amount of substance, about 25 g of activated carbon. Due to the high adsorption capacity, a significant amount of solute is adsorbed on the carbon (6−8 g). Solutes were adsorbed on the activated carbon by mixing these compounds with the adsorbent and waiting for the complete disappearance of the liquid phase. Following thermal equilibrium in the oven, the cell was slowly pressurized by pumping in carbon dioxide. The system was allowed to equilibrate for about 2−3 h. The mass flow rate of CO_2 was adjusted to 0.10 g·min^{-1}. In this range, tests demonstrated that measured solubilities were not affected by the contact time between carbon dioxide and the solute. The CO_2 delivered during the experiments was also measured with a bubble flow meter.

After leaving the extractor, the supercritical carbon dioxide stream was passed through a high-pressure cell of a variable-wavelength UV detector. The progress of the extraction process was monitored by the UV detector, since the absorbance reading is analogous to the amount of solute in the supercritical phase. When this absorbance reading becomes constant with time, the equilibrium between the solute and the supercritical fluid has been reached. The absorbance was monitored at three wavelengths (235, 280, and 305 nm).

Supercritical fluid saturated with the liquid component was depressurized through the variable restrictor, and the solute was collected in two traps containing activated carbon. These traps were placed in an analytical balance. The amount of solute in the traps was weighed with an accuracy of ±0.1 mg. The determination of solubility was based on the mass of solute trapped and the corresponding mass of carbon dioxide. The typical mass of solute collected in each experiment was >100 mg.

Results and Discussion

A certain number of assays were performed in order to verify that the technique guaranteed adequate precision.

Table 1. Solubilities of 2-Nitroanisole in Supercritical Carbon Dioxide

T = 313 K			T = 323 K			T = 333 K		
P/MPa	10^3y^a	S/g·L^{-1}	P/MPa	10^3y	S/g·L^{-1}	P/MPa	10^3y	S/g·L^{-1}
8.0	1.23	1.31	8.0	0.58	0.47	8.0	0.32	0.22
10.0	3.70	8.17	10.0	1.39	2.05	10.0	0.62	0.66
12.5	4.62	11.88	12.5	2.50	5.42	12.5	1.25	2.14
15.0	5.17	14.15	15.0	2.95	7.24	15.0	1.71	3.63
17.5	5.53	15.80	17.5	3.33	8.76	17.5	2.03	4.81
20.0	5.81	17.12	20.0	3.56	9.78	20.0	2.27	5.75

[a] Mole fraction of solute.

Table 2. Solubilities of 3-Phenyl-1-propanol in Supercritical Carbon Dioxide

T = 313 K			T = 323 K			T = 333 K		
P/MPa	10^3y	S/g·L^{-1}	P/MPa	10^3y	S/g·L^{-1}	P/MPa	10^3y	S/g·L^{-1}
8.0	0.55	0.58	8.0	0.22	0.18	8.0	0.11	0.07
10.0	3.65	8.08	10.0	0.99	1.46	10.0	0.33	0.35
12.5	5.39	13.87	12.5	2.74	5.93	12.5	1.14	1.95
15.0	6.24	17.12	15.0	3.60	8.85	15.0	1.96	4.16
17.5	7.16	20.49	17.5	4.36	11.47	17.5	2.60	6.17
20.0	7.52	22.20	20.0	4.94	13.60	20.0	3.12	7.92

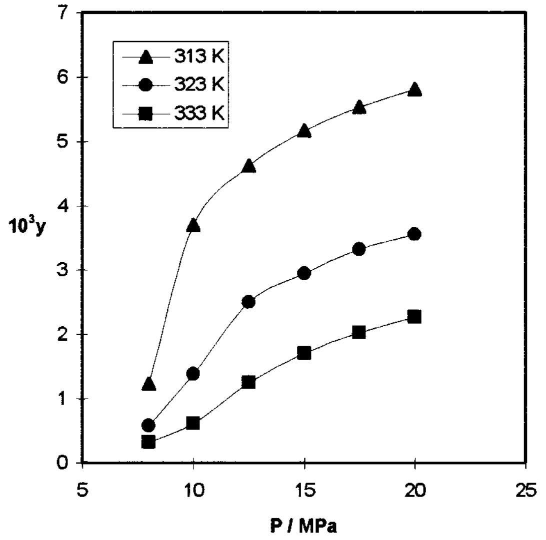

Figure 2. Solubilities of 2-nitroanisole in supercritical carbon dioxide versus pressure.

As a reference, the solubility measurements of α-pinene reported by Pavlícek and Richter (1993) and Richter and Sovová (1993) were used. The solubility data for liquid α-pinene in supercritical carbon dioxide at 323 K were measured by a static method (Pavlícek and Richter, 1993) and a dynamic method (Richter and Sovová, 1993). The solubility values of α-pinene were in agreement with the solubilities obtained in these works, as illustrated in Figure 1. The experimental data obtained in this work are on the same line as the data taken from the literature. Three measurements were made for each set of conditions and for several flow rates of carbon dioxide (0.10 to 0.30 g·min^{-1}). The solubilities obtained were independent of the flow rate of carbon dioxide. The reproducibility of the solubilities was within ±1%.

The solubilities of 2-nitroanisole and 3-phenyl-1-propanol in supercritical carbon dioxide were determined at 313, 323, and 333 K from 8.0 MPa to 20.0 MPa. The solubilities in the pressure range above 20.0 MPa could not be measured because equilibrium between the solute and the supercritical fluid was not possible. The experimental results are listed in Tables 1 and 2 in terms of the mole fraction of solute and the concentration of the solute in the CO_2 in

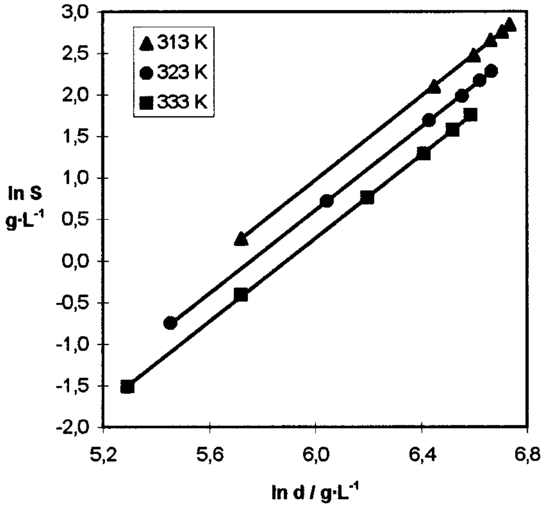

Figure 3. Solubilities of 2-nitroanisole in supercritical carbon dioxide (Experimental data are plotted in a ln−ln form).

grams per liter. Solubilities of 2-nitroanisole in supercritical carbon dioxide are also presented in Figure 2. The reported values are the average of at least two measurements with a deviation of < ±5%. Reproduction of the data points was more difficult at higher pressures and 313 K due to the high solubilities encountered. It can be seen that the solubilities of the solutes in supercritical carbon dioxide increase with pressure. The increase in density is the main cause of solubility enhancement. Comparing the 2-nitroanisole and 3-phenyl-1-propanol solubilities measured confirms that 2-nitroanisole is less soluble in supercritical carbon dioxide. Also, several measurements were carried out for two flow rates of carbon dioxide (0.10 or 0.20 $g \cdot min^{-1}$). The flow rate was satisfactory in order to ensure that solubility equilibrium was achieved in the supercritical carbon dioxide at the exit of the equilibrium cell. It was noticed that the solubilities for the two compounds showed a similar density dependence. The results exhibit trends that are typical of the solubility of nonvolatile organic molecules in supercritical carbon dioxide.

The solubility data were correlated using the model proposed by Chrastil (1982). This model is based on the assumption that the molecules of a solute associate with the molecules of a gas for the formation of a solvato complex, which is in equilibrium with the gas.

$$S = d^{k} \exp(a/T + b) \qquad (1)$$

where S is the concentration of a solute in a gas in grams per liter, d is the density of a gas in grams per liter, k is an association number, and a and b are constants. According to the Chrastil equation, the natural logarithm versus natural logarithm relationship between solubility and density should be linear. The association number k is the slope of the linear correlation and represents the average number of solvent molecules in the solvato complex. The constant a depends on the heat of solvation, and b depends on the molecular weights and melting points of the solute and solvent. A plot of the solubility of 2-nitroanisole in supercritical carbon dioxide as a function of density is shown in Figure 3. For both systems (2-nitroanisole and 3-phenyl-1-propanol) the isotherms are almost parallel and exhibit a linear relationship between ln solubility and ln density. The slopes of the isotherms are greater for 3-phenyl-1-propanol. The coefficients a, b, and k calculated using the Chrastil equation are given in Table 3. These values were obtained by least-squares analysis.

Table 3. Solubility Constants in Supercritical Carbon Dioxide

	k	a/K	b
2-nitroanisole	2.510	2998.5	−23.731
3-phenyl-1-propanol	3.600	3810.7	−33.190

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