

A Static Method Coupled with Gravimetric Analysis for the Determination of Solubilities of Solids in Supercritical Carbon Dioxide

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A static method coupled with gravimetric analysis was developed to measure the solubility of solids in supercritical carbon dioxide. To test the validity and accuracy of this method, the solubilities of naphthalene and phenanthrene were determined. Excellent agreement was obtained between the data in the literature and the data obtained using this method.

Introduction

One of the more important parameters that determines the technical and/or economical viability of supercritical carbon dioxide- (scCO_2 -) based processes is the solubility of solute in scCO_2 . During the past 2 decades, a variety of methods have been developed to measure the solubility of solutes in scCO_2 . These may be classified as dynamic or static methods.¹ In the dynamic methods, the solute is loaded into a high-pressure extraction vessel that is continuously swept with scCO_2 , and the solubility is calculated from an analysis of the solute concentration in the effluent stream. The static methods may be divided into two categories on the basis of the type of vessel used. A variable-volume view cell enables one to determine the solubility by visual inspection of a cloud point. The use of a fixed-volume cell requires an analysis of the fluid phase to determine the solubility. Alternatively, one can couple a fixed volume cell with a suitable high-pressure spectroscopic method that directly measures the solute concentrations in the fluid phase.² However, high-pressure absorption spectroscopy requires special equipment that is usually very expensive. In this communication, we report a simple static method using a fixed-volume vessel combined with gravimetric analysis for determining the solubility of solids in scCO_2 .

Experimental Section

A schematic diagram of the experimental setup for the solubility measurements is given in Figure 1. The high-pressure vessel was custom manufactured (3-Moran Tool and Die, Bolton, CT) and is fitted with a sapphire window (Sapphire Engineering, Inc.), PEEK o-rings (Valco Instruments, Inc.), T-type thermocouple assembly (5-Omega Engineering, DP41-TC-MDSS), pressure transducer (6-Omega Engineering, PX01K1-5KGV), vent line (7), and rupture disk assembly (Autoclave Engineers). The temperature is controlled by circulating water using a circulating heater (8-Haake FJ) through a copper coil wrapped around the vessel. The vessel rests on a magnetic stir plate (4), and CO_2 is introduced into the pressure vessel using a syringe pump (2-ISCO, 260D).

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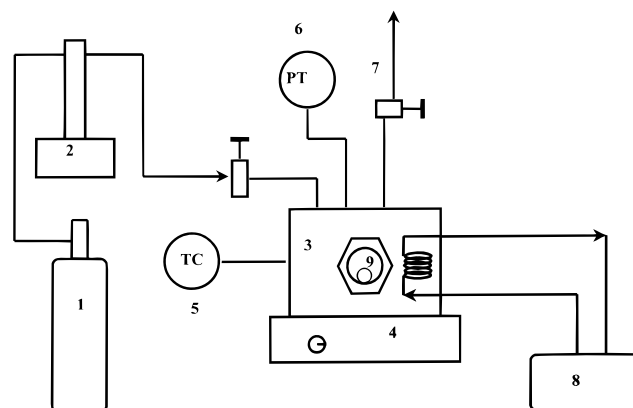


Figure 1. Schematic diagram of the experimental setup.

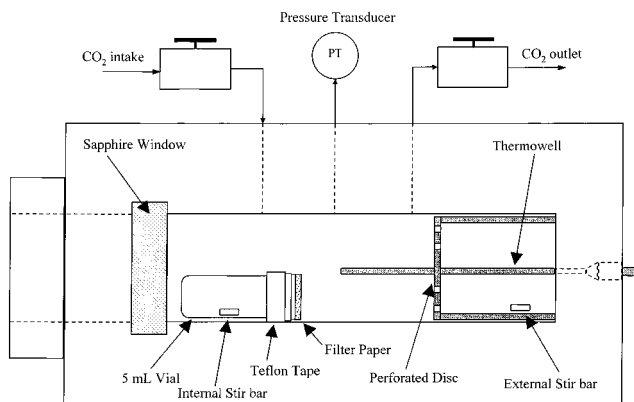
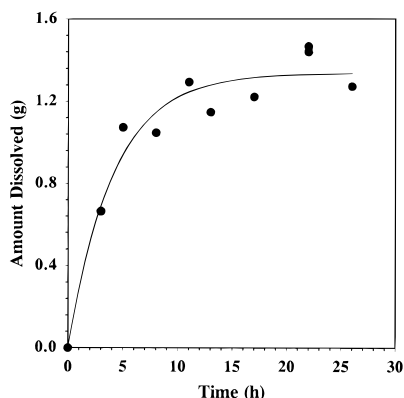


Figure 2. Schematic diagram of the pressure vessel.

A detailed schematic diagram of the internal configuration of the pressure vessel is given in Figure 2. For each experiment, an excess amount of solute and a small magnetic stir bar was placed in a 5-mL glass vial that was then capped with coarse filter paper (Whatman) attached to the vial with Teflon tape. A larger magnetic stir bar was placed inside the pressure vessel and a perforated stainless steel disk was then slid through the thermowell. The sample vial was then weighed and placed inside the pressure vessel. The perforated disk isolates the external stir bar from the stir bar in the sample vial and prevents the two stir bars from becoming coupled, which stops both from stirring. The per-

Table 1. Experimental Solubility Data and Comparison to Literature Values

solute	<i>T</i> (K)	<i>P</i> (atm)	run no.	weight difference (g)	solubility (mole fraction)	literature solubility (mole fraction)
naphthalene	308	130	1	1.294	0.013 4	
			2	1.146	0.011 7	
			3	1.222	0.012 5	
			4	1.467	0.015 0	
			5	1.441	0.014 7	
			6	1.272	0.013 0	
					0.013 4 ± 0.001 3	0.013 2 ⁴
phenanthrene	318	163	1	0.139	0.001 49	
			2	0.150	0.001 60	
			3	0.145	0.001 55	
					0.001 55 ± 0.000 05	0.001 40 ⁵ 0.001 38 ± 0.000 12 ⁶ 0.001 52 ± 0.000 25 ⁷

**Figure 3.** Approach to equilibrium for the naphthalene–scCO₂ system at 35 °C and 130 atm.

forations on the disk enable sufficient convection for mixing both sides of the pressure vessel.

The vessel was sealed, connected to the circulating bath, and heated to the desired temperature. Once the test temperature was reached, stirring was initiated and the vessel was slowly filled with CO₂ until the desired pressure was achieved. After sufficient time was allowed for equilibration of the scCO₂/solute solution, the vessel was depressurized and opened. The vial was removed, wiped with a clean tissue, and reweighed. The solubility of the solute is then given by

$$\text{solubility (wt/vol)} = \frac{\text{initial measured mass of solute in the vial} - \text{final measured mass of solute in the vial}}{\text{volume of vessel} - \text{volume of vial}}$$

The equation incorporates a correction factor which accounts for precipitation of the solute in the fluid phase in the vial. The volume of the vessel in the equation is the volume accessible to the fluid phase which was determined as 47 mL.

Results and Discussion

To test the validity and accuracy of this method, a series of experiments were performed with naphthalene and phenanthrene; solubility data of both these compounds in scCO₂ can be found in the literature. The first set of experiments was conducted to determine the time necessary for achieving equilibrium. The mass of solute lost from the vial is plotted against time in Figure 3 for naphthalene in scCO₂ at 35 °C and 130 atm. The fluid phase became saturated with naphthalene after about 10 h. The average solubility value calculated using the

data obtained after 11 h is given in Table 1. In the calculation, the density of pure scCO₂ was calculated using a 52-parameter equation of state given by IUPAC.³ Excellent agreement was obtained between the results of the experiments run here and the literature value⁴ for the solubility of naphthalene in scCO₂. Similar experiments were carried out for phenanthrene. The average solubility calculated from three experiments conducted for 22 h is also given in Table 1. Again, the agreement between these experiments and data in the literature^{5–7} is very good.

Conclusions

A static method coupled with gravimetric analysis was developed for measuring the solubility of solids in scCO₂. The appealing feature of the technique is its simplicity; it requires no specialized equipment other than a suitable pressure cell. Although a vessel with a sapphire window was utilized for these experiments, visualization of the internal volume of the vessel is not necessary. The technique can, in principle, be easily extended to measurement of solubilities of mixtures of solids in scCO₂ if the composition of the remaining mixture in the vial can be determined by a suitable chemical analysis such as GC, HPLC, or infrared or UV–vis spectroscopy. Preliminary mass-transfer calculations of the technique indicate that the major resistance to mass transfer was the filter paper. The time necessary for achieving equilibrium can probably be reduced by using a thinner membrane to cap the sample vial.

The major disadvantage of the method is that it is probably not suitable for solutes with very low solubility in scCO₂. The limitation is the ability to accurately measure very small changes of the mass of the solute in the sample vial. The solubility limit above which this technique can be used is around 1×10^{-4} wt fraction.

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