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Solubility of Flouranthene, Chrysene, and Triphenylene in Supercritical Carbon Dioxide

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The solubility of polycyclic aromatic hydrocarbons in supercritical carbon dioxide is very low, and very little experimental data exist. A method has been developed for the measurement of such low solubilities, and the solubilities of fluoranthene, chrysene, and triphenylene in a temperature range 308.15 K to 328.15 K and in a pressure range 84 bar to 251 bar have been determined. The solubilities have been fitted to the excess function-equation of state model.

Introduction

Supercritical carbon dioxide is widely used as a solvent in extraction processes involving either liquid−supercritical fluid or solid−supercritical fluid equilibria. The chemical and petrochemical, food, pharmaceutical, and cosmetic industries have mostly benifited from these new extraction technologies. Other applications in environmental protection, materials and analytical chemistry, or reaction chemistry under elevated pressures are possible due to the properties of supercritical solvents.

The solubility of a target compound in the supercritical solvent is a fundamental parameter for a new technology design. Solubility measurements of different compounds have been carried out worldwide. Paulaitis et al. (1983) have carried out a literature survey concerning experimental data for phase equilibria of mixtures containing a supercritical compound. Bartle et al. (1991) have gathered data concerning the solubility of slightly volatile compounds in supercritical CO_2. Recently, Dohrn and Brunner (1995) have collected data concerning experimental methods used to date for measuring phase equilibria at elevated pressures. However, experimental solubilities of very low volatility compounds are scarce because of technical difficulties encountered. Furthermore, the low solubility values of different compounds reported in the literature are subject to considerable errors. Johnston et al. (1982) state the errors increase as the solubility decreases. In the course of our research for the petroleum industry and environment we need a great amount of experimental data in order to improve a group contribution method (Berro et al., 1996) to calculate the solubility of low volatility hydrocarbons in supercritical CO_2. This is why a method for the measurement of low solubilities in supercritical CO_2 has been developed.

The compounds chosen for this study belong to the class of polynuclear aromatic hydrocarbons (fluoranthene, chrysene, and triphenylene). These compounds are solids under the experimental conditions. They have a very low saturated vapor pressure (Table 1), and a very low solubility in supercritical CO_2 can be estimated. Table 1 shows the melting points T_m, the boiling points T_b, the molar volumes of solids V^s, the saturated vapor pressure for different temperatures P^{sat}. The values of P^{sat} are estimated according Hoyer and Peperle (1958).

Table 1. Physical Properties of Fluoranthene, Chrysene, and Triphenylene

solid	T_m/K	T_b/K	V^s/cm^3 mol^{-1}	T/K	P^{sat}/Pa
fluoranthene	381	648	163	308.15	2.57×10^{-3}
				318.15	9.05×10^{-3}
				328.15	2.95×10^{-2}
chrysene	528	721	179	308.15	4.17×10^{-6}
triphenylene	471	711	175	308.15	1.11×10^{-5}
				318.15	4.69×10^{-5}
				328.15	1.83×10^{-4}

Experimental Section

The experimental apparatus shown in Figure 1 consists of a high-pressure system, a sampling system for the liquid phase, and an analytical system. A dynamic method was chosen to saturate the CO_2 with the organic compound.

The high-pressure system consists of a liquid CO_2 reservoir (1), a cryostat (3) to maintain the CO_2 in a liquid state and to cool the pump (4), a back-pressure regulator (5), a pressure gauge (7), and a high-pressure cell (10). The flow is regulated by the valve (13). Sampling of the liquid phase for analysis is carried out using a six-way sampling valve (12) which is rinsed by the liquid solvent from the reservoir (6). The high-pressure cell and the sampling valve are placed in a thermostatic bath (8). The dynamic method and the high-pressure system are similar in principle to the method and the apparatus used by McHugh and Paulaitis (1980) to measure the solubility of naphthalene and biphenyl. The solubilities studied in this work are 10^4 times lower than the solubilities of naphthalene and biphenyl. The measurement of low solubilities was possible thanks to the sampling and analytical systems presented in this work.

The analytical system consists of an HPLC chromatographic column (15), a UV detector (16), and a computer (17, 18) to process data.

The cell (10) with a volume of 10 mL is filled with the solid. After purging at low pressure with gaseous CO_2, the apparatus is set to operating conditions. The temperature is regulated with a precision of ±0.1 K. The cell is pressurized with the pump (4). Pressure is regulated by a back-pressure regulator (5) and measured by the pressure gauge (7) with an accuracy of 1 bar. The supercritical CO_2 solubilizes the product in the cell (10) and at a low flow rate (about 1 g/min), sweeps through the sampling loop mounted on the sampling valve (12). The solubilized product is collected in the flask (14) containing a solvent,

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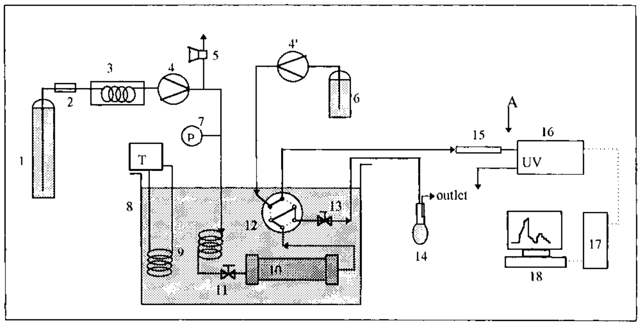

Figure 1. Experimental apparatus: (1) bottle of liquid CO_2; (2) filter; (3) cryostat; (4 and 4′) pumps; (5) back-pressure regulator; (6) solvent reservoir; (7) pressure gauge; (8) thermostatic bath; (9) heating coil; (10) cell; (11) valve; (12) sampling valve; (13) restriction valve; (14) collection flask; (15) HPLC column; (16) UV detector; (17) analog−digital converter; (18) computer.

Table 2. Mole Fraction Solubility y of Phenanthrene in Supercritical CO_2

T/K = 318.15		T/K = 328.15	
P/bar	y	P/bar	y
101	3.54×10^{-4}	102	1.76×10^{-4}
127	1.01×10^{-3}	125	6.43×10^{-4}
151	1.28×10^{-3}	145	1.09×10^{-3}
175	1.54×10^{-3}		

and the CO_2 is evacuated into the atmosphere. The sampling loop has a volume of 20 μL. The sampling valve (12) enables the sampling loop to be positioned either in the "load" position (the supercritical CO_2 circuit) or in the "inject" position (the solvent rinsing liquid circuit). The rinsing solvent is pumped from the reservoir (6) by the pump (4′) and transports the contents (CO_2 + product) of the sampling loop to the analytical system.

In the HPLC column, separation of the CO_2 + product mixture is carried out by retention of the organic compound. The chromatograms obtained are processed by computer. For a given compound, the choice of wavelength of the UV detector and calibration of the analytical system are determined according to the extent of solubility. If the solubilities are too high and tend to saturate the analytical system, the system is decoupled at position A. In this case the liquid is collected in flasks at the output of the column (15). An appropriate dilution is thus obtained. Preliminary solubility trials are necessary in order to determine which configuration and analytical parameters are adapted to a certain product.

The purity of all the compounds studied is 98% (supplied by Aldrich). The CO_2 used had a level of impurity lower than 16 ppm (supplied by Alphagaz, l'Air Liquide).

A certain number of trials were carried out in order to verify that the technique ensured adequate precision. As a reference the solubility measurements of phenanthrene reported by Kurnik et al. (1981) were used. The solubility values of phenanthrene are close to the range of solubilities in our studies. The results obtained for two temperatures are presented in Table 2. Other measurements were made after modifying the CO_2 flow rate or the quantity or position of the solid in the cell in order to ensure that thermodynamic equilibrium was attained. The experimental solubilities of phenanthrene were in agreement with those of Kurnik et al. (1981). Figure 2 shows the enhancement factor $E = yP/P^{sat}$ versus fluid density ρ at 318.15 K and 328.15 K. It is well-known that the variation of ln(E) with the fluid density has a linear shape. The experimental data obtained in this work are on the same line as the data taken from the literature.

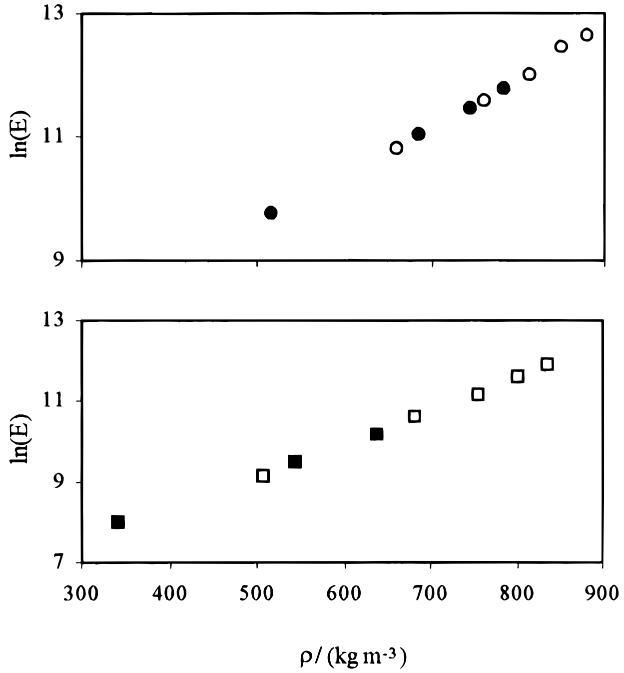

Figure 2. Enhancement factor ln(E) of phenanthrene as a function of fluid density ρ: (●) 318.15 K, this work; (○) 318.15 K, Kurnik et al. (1981); (■) 328.15 K, this work; (□) 328.15 K, Kurnik et al. (1981).

Table 3. Mole Fraction Solubility y of Fluoranthene in Supercritical CO_2

T/K = 308.15		T/K = 318.15		T/K = 328.15	
P/bar	y	P/bar	y	P/bar	y
89	1.13×10^{-4}	86	9.13×10^{-6}	100	1.66×10^{-5}
98	1.83×10^{-4}	90	1.38×10^{-5}	121	9.85×10^{-5}
109	2.41×10^{-4}	100	5.92×10^{-5}	140	2.58×10^{-4}
121	3.10×10^{-4}	110	1.43×10^{-4}	159	5.08×10^{-4}
135	3.43×10^{-4}	120	2.35×10^{-4}	180	6.09×10^{-4}
150	3.88×10^{-4}	136	3.59×10^{-4}	209	9.30×10^{-4}
160	4.16×10^{-4}	153	4.33×10^{-4}		
173	4.48×10^{-4}	176	5.24×10^{-4}		
175	4.55×10^{-4}	198	6.03×10^{-4}		
198	4.91×10^{-4}	249	7.79×10^{-4}		
200	5.17×10^{-4}				
247	5.72×10^{-4}				

Table 4. Mole Fraction Solubility y of Chrysene in Supercritical CO_2

T/K = 308.15			
P/bar	y	P/bar	y
84	7.29×10^{-7}	160	5.70×10^{-6}
96	2.03×10^{-6}	182	6.63×10^{-6}
100	2.44×10^{-6}	199	7.35×10^{-6}
111	3.24×10^{-6}	221	7.82×10^{-6}
125	4.00×10^{-6}	251	8.84×10^{-6}
140	4.93×10^{-6}		

The solubility values obtained for fluoranthene, chrysene, and triphenylene in supercritical CO_2 are presented in Tables 3−5. A minimum of three repetitions were carried out for each experimental point, and each solubility value fell in the interval $\bar{y} \pm 5\%$.

Tables 3−5 show that the solubilities of the three compounds are very low, on the order of 10^{-4} for fluoranthene, 10^{-5} for triphenylene, and 10^{-6} for chrysene. The best parameter for comparison of the solvent power of supercritical CO_2 is the enhancement factor. The values of E at 308.15 K for the three compounds are shown in Figure 3. The enhancement factor is 10 times greater for chrysene and triphenylene than for fluoranthene. Chry-

Table 5. Mole Fraction Solubility *y* of Triphenylene in Supercritical CO_2

T/K = 308.15		*T*/K = 318.15		*T*/K = 328.15	
P/bar	*y*	*P*/bar	*y*	*P*/bar	*y*
85	3.14×10^{-6}	96	1.01×10^{-6}	107	1.15×10^{-6}
91	5.50×10^{-6}	105	3.98×10^{-6}	117	3.05×10^{-6}
103	8.38×10^{-6}	116	7.86×10^{-6}	133	7.89×10^{-6}
116	1.11×10^{-5}	119	9.18×10^{-6}	155	1.52×10^{-5}
132	1.37×10^{-5}	135	1.29×10^{-5}	177	2.35×10^{-5}
149	1.57×10^{-5}	152	1.76×10^{-5}	197	3.18×10^{-5}
168	1.85×10^{-5}	172	2.33×10^{-5}	222	3.74×10^{-5}
192	2.05×10^{-5}	192	2.59×10^{-5}	251	4.22×10^{-5}
221	2.27×10^{-5}	223	3.01×10^{-5}		
247	2.45×10^{-5}	252	3.28×10^{-5}		

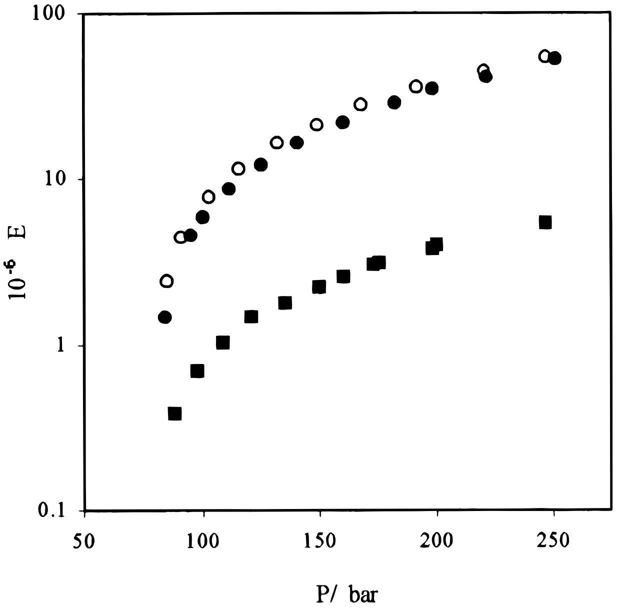

Figure 3. Enhancement factor *E* at 308.15 K as a function of pressure: (●) chrysene; (○) triphenylene; (■) fluoranthene.

sene and triphenylene are isomeric compounds with very similar boiling points and sublimation pressures. The graph shows that the affinity of CO_2 for these two compounds is practically the same. The difference in solubility of the two isomers, for a given pressure and temperature, arises from the difference in the saturated vapor pressures.

Modeling of Solubility

The solubility of a solid compound in a supercritical fluid was calculated by the compressed gas method:

$$y_1 = \frac{P_1^{\mathrm{sat}} \exp[v_1^{\mathrm{s}}(P - P_1^{\mathrm{sat}})/(RT)]}{\phi_1 P}$$

where the index 1 denotes the solute (hydrocarbon) in the fluid phase which is composed of CO_2 and hydrocarbon. The saturated vapor pressure and the molar volume of the solid are given in Table 1 for the three compounds. The fugacity coefficient ϕ_1 was calculated using the excess function-equation of state model described previously (Péneloux et al., 1989; Barna et al., 1994; Berro et al., 1996). This model accommodates the equations of state given for each constituent of the mixture with an adequate excess function. The only parameter necessary to calculate the coefficients is the boiling point of the hydrocarbon. Other parameters such as the covolume *b* or the temperature function *a*(*T*) in the equation of state of the hydrocarbon are calculated by the group contribution method of Coniglio et al. (1993). The binary interaction parameter E_{12} was adjusted to the experimental solubility data for each temperature. The interaction parameter and the mean relative deviation $\delta_r(x)$ between experimental and calculated solublities are shown in Table 6.

The calculated solubilities and the experimental values are presented in Figures 4–6. Good agreement was obtained even for low solubility values.

Table 6. Interaction Parameter and Mean Relative Deviation for Calculated Solubilities

solid	*T*/K	E_{12}/J cm^{-3}	$100\delta_r(y)^a$
fluoranthene	308.15	940.4	7.7
	318.15	904.6	27.0
	328.15	863.9	15.0
chrysene	308.15	888.8	7.2
triphenylene	308.15	777.2	10.8
	318.15	749.8	18.7
	328.15	744.0	18.4

[a] $\delta_r(y) = N\Sigma|x_{\mathrm{exp}} - x_{\mathrm{cal}}|/x_{\mathrm{exp}}$; *N* is the number of data points.

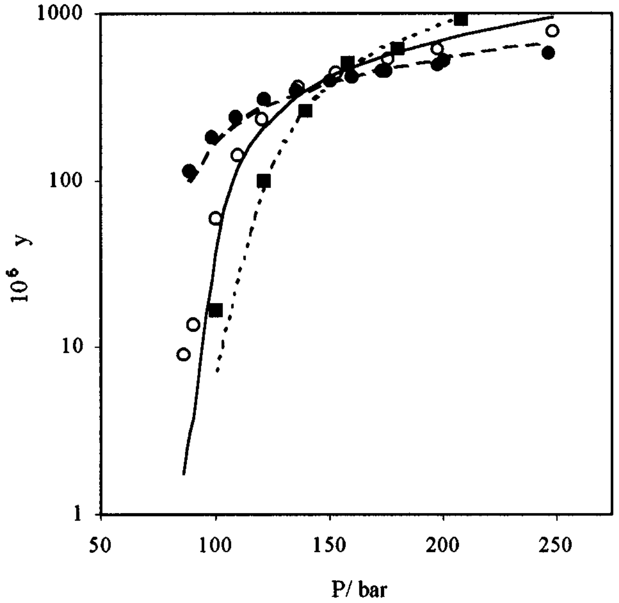

Figure 4. Mole fraction solubility y of fluoranthene in supercritical CO_2: (●) 308.15 K exp; (- - -) 308.15 K cal; (○) 318.15 K exp; (—) 318.15 K cal; (■) 328.15 K exp; (···) 328.15 K cal.

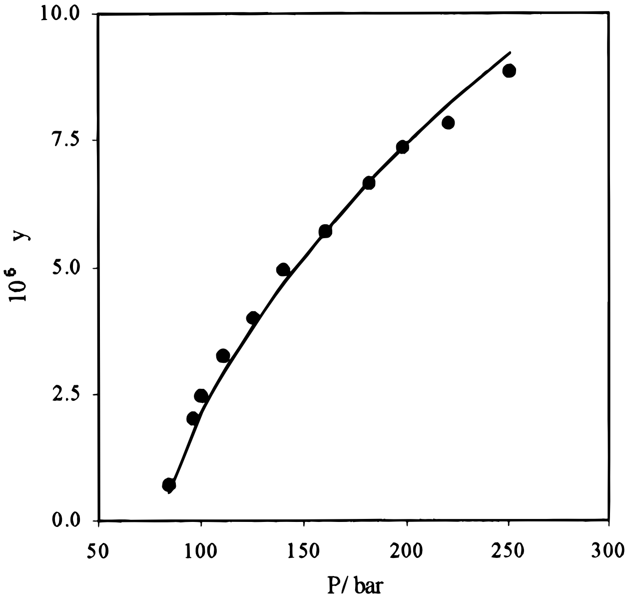

Figure 5. Mole fraction solubility *y* of chrysene in supercritical CO_2: (●) 308.15 K exp; (—) 308.15 K cal.

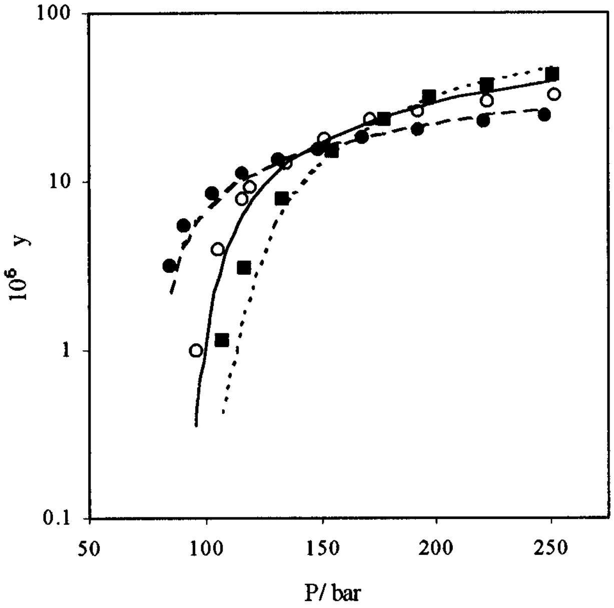

Figure 6. Mole fraction solubility *y* of triphenylene in supercritical CO_2: (●) 308.15 K exp; (- - -) 308.15 K cal; (○) 318.15 K exp; (—) 318.15 K cal; (■) 328.15 K exp; (···) 328.15 K cal.

As Figures 4 and 6 show, the fluoranthene and the triphenylene have a solubility crossover point at about 150 bar. When the temperature increases, the solubility increases for pressures above this value and the solubility decreases for pressures below the crossover point.

This behavior may be explained by the influence of density and temperature on the dissolution process. A raise in temperature causes an increase of the saturated vapor pressure of the solid compound, and then the solubility increases. At the same time the density of the fluid and the solvent power diminish. For pressures below the crossover point the density effect on the dissolution process is dominant, while for high pressures the fluid is less compressible and the effect of the saturated vapor pressure prevails.

Conclusions

We have described an apparatus to measure low solubilities of solid compounds in supercritical fluids. Solubilities of three polycyclic aromatic hydrocarbons, fluoranthene, chrysene, and triphenylene, were determined at temperatures from 308.15 K to 328.15 K and pressures from 84 bar to 251 bar. Their mole fraction solubilities in supercritical CO_2 are very low, on the order of 10^{-4} for fluoranthene, 10^{-5} for triphenylene and 10^{-6} for chrysene. The solubility enhancement factor in supercritical CO_2 is on the order of 10^6 for fluoranthene and 10 times greater for the other two hydrocarbons.

The solubilities were fitted to the excess function-equation of state model by adjusting an interaction parameter to the experimental data. Agreement between the experimental values and calculated values was good.

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