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Solubility of Polycyclic Aromatic Hydrocarbons in Supercritical Carbon Dioxide

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The equilibrium solubilities of three solid polycyclic aromatic hydrocarbons (acenaphthene, fluoranthene, and triphenylene) were determined at temperatures ranging from 308 K to 348 K and pressures from 121.6 to 354.6 bar in supercritical CO_2. The data were obtained by using a simple static sampling apparatus which was tested by measuring the solubility of naphthalene in compressed CO_2. The measured solubilities were correlated using a semiempirical model. The calculated results show satisfactory agreement with the experimental data.

Introduction

Supercritical fluid extraction (SFE) has received much attention for the possible application to remove toxic organic mixtures such as polycyclic aromatic hydrocarbons (PAHs) from soils and sludge for either analytical or remediation purposes.

The main benefits of SFE arise from the density dependence of solubility that allows some degree of extraction selectivity, the ease with which the extraction solvent can be removed, the ability to eliminate or minimize the use of organic solvents in sample preparation, and the short extraction time in comparison with that of a traditional extraction system such as Soxhlet. Among supercritical solvents, CO_2 has been the choice for most SFE studies, primarily because of these attractive practical characteristics, relatively low critical temperature and pressure, low toxicity and reactivity, and high purity at low cost.

A major factor limiting the commercial success of SFE is the lack of fundamental solubility data needed to design separation units or to develop extraction models. Solubility data have been tabulated in the literature for a number of different compounds (Bartle et al., 1991; Dohrn and Brunner, 1995). On the other hand, the solubility of some PAHs and polychlorinated biphenyls (PCBs) have been reported in recent years (Iwai et al., 1993; Miller et al., 1996; Yu et al., 1995; Mitra et al., 1988; Kosal and Holder, 1987). We could not find any report for the solubility of acenaphthene, but some results have been reported for the solubility of fluoranthene and triphenylene in the range of various temperatures (35, 45, and 55 °C) and pressures (85−251 bar) (Barna et al., 1995).

We have recently reported the solubility of some 1,4-dihydroxy-9,10-anthraquinone (Fat'hi et al., 1998) and 1,8-dihydroxy-9,10-anthraquinone derivatives (Fat'hi et al., 1999) and dihydroxybenzene isomers (Yamini et al., 1998) and hydroxyxanthone derivatives (Ghiasvand et al., submitted for publication) in supercritical carbon dioxide. This work was undertaken to determine the solubilities of three solid PAH compounds (acenaphthene, fluoranthene, and triphenylene) in supercritical carbon dioxide over a wide range of temperatures and pressures. The measured solubilities were nicely correlated using a semiempirical model proposed by Bartle (Bartle et al., 1991; Safa-Ozcan et al., 1997).

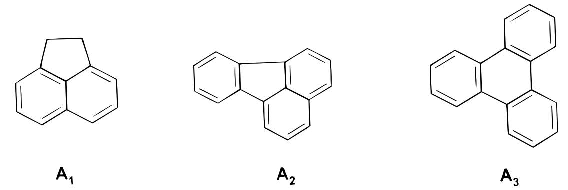

Figure 1. Structures of acenaphthene (A_1), fluoranthene (A_2), and triphenylene (A_3).

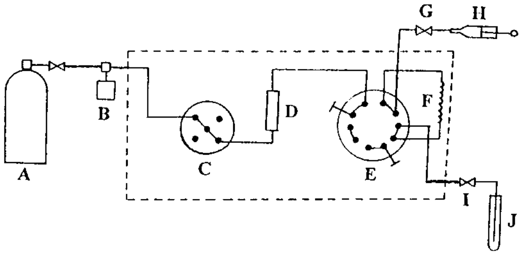

Figure 2. Schematic diagram of experimental apparatus for measuring solubilities: (A) CO_2 gas tank; (B) supercritical fluid pump; (C) 5-port 4-position valve; (D) 1-mL equilibrium cell; (E) 10-port, 2-position valve; (F) injection loop; (G) on/off valve; (H) syringe; (I) microadjust valve; (J) collection vial.

Experimental Section

HPLC-grade chloroform (Aldrich) was used as received. Carbon dioxide (Sabalan, Tehran, 99.99%) was used for all extractions. Reagent-grade acenaphthene (A_1), fluoranthene (A_2) and triphenylene (A_3) (all from Aldrich) were of the highest purity available and were used as received. Structures of the PAHs used are shown in Figure 1.

A Suprex (Pittsburgh, PA) MPS/225 system modified for the solubility determination in SFE mode was used. A schematic diagram of the modified static system used is shown in Figure 2. Solubility measurements were accomplished with a 1-mL extraction vessel in the pressure range from 121.6 to 354.6 bar at the temperatures 35, 45, 55, 65, and 75 °C for a duration of 30 min. The solid solutes (200 mg) were mixed with some 1 g of glass beads and packed into the extraction vessel. This procedure prevents channeling, increases the contact surface between the

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Table 1. Solubilities of Acenaphthene (A_1), Fluoranthene (A_2), and Triphenylene (A_3) in Supercritical CO_2

		$10^4 X$		
P/bar	ρ^a/kg·m^{-3}	A_1	A_2	A_3
		t = 35 °C		
121.6	771	20.06	2.36	0.12
152.0	818	21.22	2.84	0.16
182.4	850	23.93	3.28	0.18
212.8	876	26.22	3.63	0.21
243.2	897	26.93	3.99	0.24
273.6	916	27.45	4.23	0.25
304.0	931	28.18	4.65	0.27
334.4	946	31.12	4.68	0.29
354.6	955	31.05	4.97	0.32
		t = 45 °C		
121.6	661	18.33	2.14	0.10
152.0	745	25.60	2.98	0.16
182.4	792	28.77	3.78	0.21
212.8	826	34.24	4.43	0.26
243.2	852	36.57	5.05	0.30
273.6	875	36.61	5.49	0.33
304.0	893	41.93	6.05	0.36
334.4	910	42.86	6.44	0.38
354.6	919	43.90	6.62	0.40
		t = 55 °C		
121.6	516	21.06	1.86	0.06
152.0	657	29.02	3.00	0.15
182.4	726	35.41	4.16	0.23
212.8	771	40.15	5.44	0.31
243.2	804	44.51	6.28	0.37
273.6	831	46.01	7.15	0.43
304.0	853	48.30	7.84	0.46
334.4	872	55.36	8.64	0.53
354.6	884	59.43	9.23	0.55
		t = 65 °C		
121.6	396	13.69	1.04	0.03
152.0	561	30.83	2.63	0.12
182.4	654	47.12	4.33	0.23
212.8	712	59.82	6.15	0.36
243.2	754	71.10	7.35	0.45
273.6	786	81.23	10.13	0.54
304.0	812	86.80	10.21	0.61
334.4	834	91.46	11.26	0.69
354.6	848	94.10	11.78	0.72
		t = 75 °C		
121.6	327	12.77	1.27	0.02
152.0	477	30.29	2.97	0.10
182.4	585	53.81	5.59	0.22
212.8	652	78.18	7.11	0.40
243.2	702	99.05	9.34	0.53
273.6	740	117.81	11.24	0.64
304.0	772	131.12	13.16	0.77
334.4	796	139.47	14.46	0.88
354.6	811	139.95	15.15	0.95

[a] The computer system of the Suprex MPS/225 will show the density calculations of CO_2 directly according to the Pitzer method (Pitzer, 1955; Pitzer et al., 1955).

sample and the supercritical fluid, and, consequently, reduces the equilibration time. Sintered stainless steel filters (5 μm) were used to prevent any carry-over of the solutes. Supercritical CO_2 was pressurized and passed into the vessel D through the five-port, four-position valve C. After equilibrium at the desired temperature and pressure was reached (for about 30 min), a 144 μL portion of the saturated supercritical CO_2 was loaded into injection loop F by means of the 10-port, 2-position valve E. Then the loop was depressurized into the collection vial J containing chloroform by switching the injection valve E. To prevent solvent dispersal, the depressurizing rate of the sample loop was adjusted by the valve I. Finally, the G and I valves were opened completely, and the sample loop was washed with some chloroform, which was collected in the collection vial J. The equilibrium temperature and pressure were measured to accuracies of ±1 °C and ±0.5 bar, respectively.

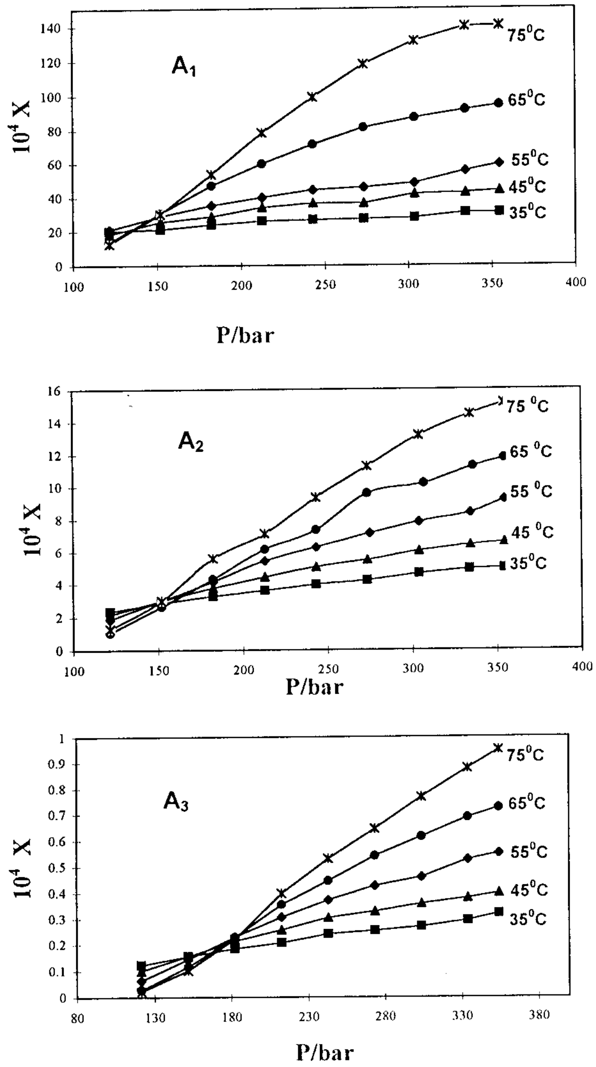

Figure 3. Experimental mole fraction (X) solubilities for acenaphthene (A_1); fluoranthene (A_2), and triphenylene (A_3) in supercritical carbon dioxide.

The solubilities were calculated by absorbance measurements at λ_{max} of each compound using a model 2100 Shimadzu UV−vis spectrophotometer. The stock solutions of the compounds A_1, A_2, and A_3 (100 μg·mL^{-1}) were prepared by dissolving appropriate amounts of the solid samples in chloroform. A set of standard solutions were then prepared by appropriate dilution of the stock solutions. The calibration curves obtained (with regression coefficients about 0.9999) were used to establish the concentration of the PAHs in the collection vial. The mole fractions of the solutes were generally reproducible within ±2%.

Results and Discussion

The reliability of the apparatus was preliminarily checked by measuring the solubility of naphthalene in supercritical CO_2 at 35 °C. This has already been described (Fat'hi et al., 1998; Yamini et al., 1998). The solubilities of the PAHs at the temperatures 35, 45, 55, 65, and 75 °C and in the pressure range from 121.6 to 354.6 bar were then determined. The resulting solubilities in terms of equilibrium mole fractions of solute in supercritical CO_2 are summarized in Table 1. Those data are also shown graphically

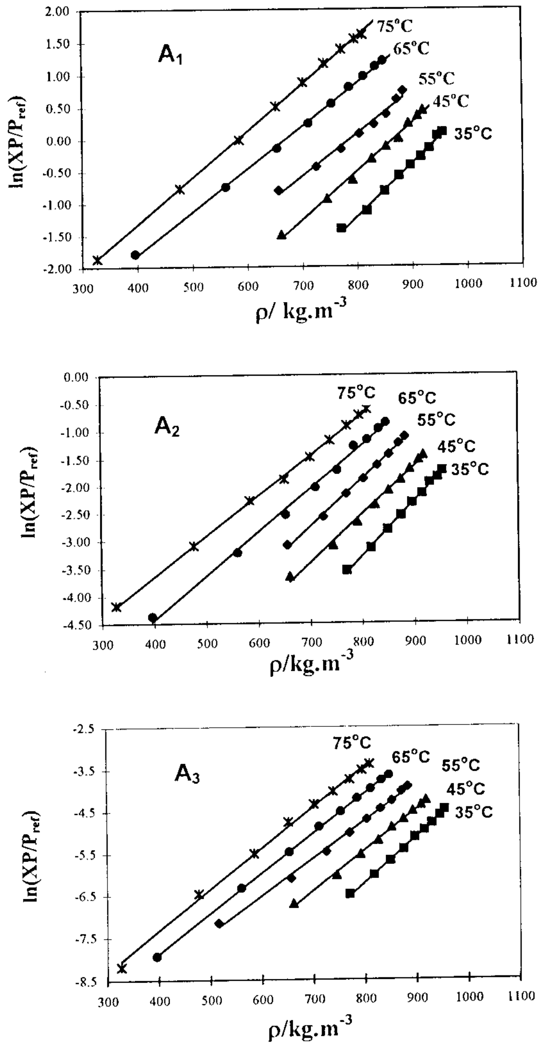

Figure 4. Plots of $\ln(XP/P_{\text{ref}})$ versus ρ for A_1, A_2, and A_3 at various temperatures.

in Figure 3. Each solubility is from the average of three replicate experiments. The relative standard deviations of the measurement (%RSD = [standard deviation of three replicate solubility measurements/average solubility] × 100) are <2%.

From the data given in Table 1, the results of triphenylene solubilities are consistent with those of Barna et al. (1996), but our solubility data for fluoranthene are clearly different from those of Barna et al. (1996).

From the data given in Table 1, it is readily seen that, at constant temperature, the solubilities of all three compounds increase with increasing pressure. The influence of pressure on the solubilities is more pronounced at higher temperatures. This is in contrast to conventional wisdom stating that the supercritical fluid density must increase in order to increase the solubility and extraction efficiency (Miller et al., 1996; Mitra and Wilson, 1991).

By observing the effect of the temperature on the solubilities, we find that the crossover region exists at pressures above 150 bar. For acenaphthene and fluoranthene, the crossover region is located at about 150, and for triphenylene, it is at about 180 bar. Beyond the crossover point, solubilities increase with increases of both the pressure and the temperature, while, below the crossover point, solubilities increase with the increase of pressure but decrease with the increase of temperature. The different effects of temperature on the solubilities are due to the influences of temperature on the vapor pressure, the density, and the molecular interaction of the supercritical fluid phase.

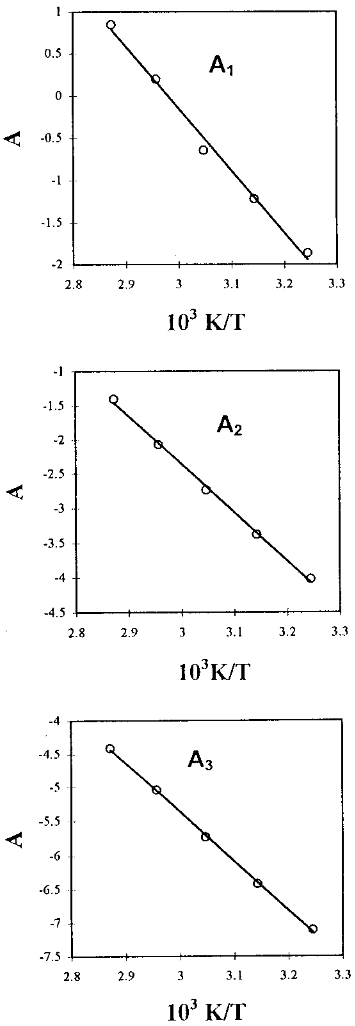

Figure 5. Plots of A versus $1/T$ for A_1, A_2, and A_3.

Table 2. Solubility Constants *a*, *b*, and *C* and the Estimated $\Delta_{\text{vap}}H$ Values Obtained from the Data Correlation Procedure

PAH	a	b/K	C/m^3·kg^{-1}	$\Delta_{\text{vap}}H$/kJ·mol^{-1}
acenaphthene	21.85	−7334	0.01	61
fluoranthene	18.69	−7014	0.01	58
triphenylene	16.41	−7257	0.01	60

The experimental solubility data for the PAHs were correlated using the following equation (Bartle et al., 1991; Miller et al., 1996):

$$\ln(XP/P_{\text{ref}}) = A + C(\rho - \rho_{\text{ref}}) \tag{1}$$

where X is the mole fraction solubility, P is the pressure, P_{ref} is a standard pressure of 1 bar, ρ is the density (taken as the density of pure CO_2), ρ_{ref} is a reference density, for which a value of 700 kg·m^{-3} was used, and A and C are constant values. The reason for using ρ_{ref} is to make the constant A much less sensitive to experimental errors in the solubility data and avoid the large variations caused by extrapolation to zero density. The value of C, which results physically from solvation of the solute by the supercritical fluid, is assumed to remain constant over the entire temperature range studied. The value of A, which arises from the vapor pressure (fugacity) of the solute, is

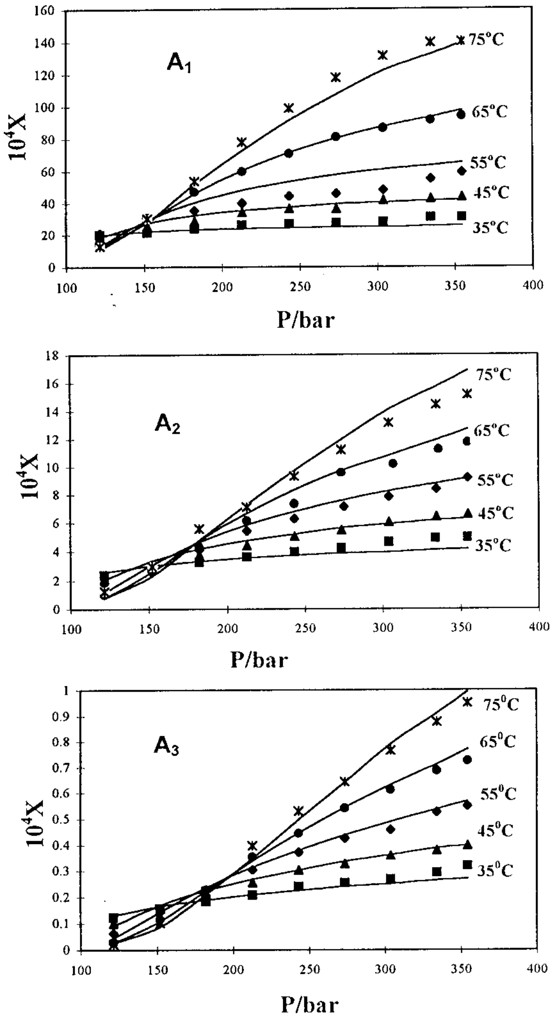

Figure 6. Comparison of experimental (points) and calculated (lines) solubilities at various temperatures for A_1, A_2, and A_3.

assumed to obey the equation

$$A = a + b/T \tag{2}$$

where T is absolute temperature and a and b are constants. Substitution of eq 2 into eq 1 will result in

$$\ln(XP/P_{\text{ref}}) = a + b/T + C(\rho - \rho_{\text{ref}}) \tag{3}$$

In the first step, the $\ln(XP/P_{\text{ref}})$ values were plotted against density (Figure 4), and the resulting plots were fitted to a straight line by least squares regression to estimate C and A values. According to eq 2, the plots are expected to be reasonably straight lines of similar slopes. However, as is seen from Figure 4, the slopes show a small increase at lower temperatures. Such deviations can be improved by removing the experimental points at lower pressures from the corresponding graphs. The values of C, obtained from the slopes of the corresponding plots, were then averaged for each compound (Table 2).

By holding C at its average value, the experimental solubility data were then used to evaluate the A values at various temperatures for each PAH. The plots of A versus $1/T$ for each compound resulted in a straight line (Figure 5), from which the intercept and slope (a and b) were obtained. The resulting a and b values for three compounds are also included in Table 2.

Finally, the values of a, b, and C were used to predict solubilities from eq 3. Figure 6 compares the calculated isotherms with the experimental data. The agreement is satisfactory, and the poor consistency is limited to data points obtained at the high-pressure limits of the isotherms, which are close to the melting points of the PAHs. Similar results have been observed for anthracene and pyrene (Miller et al., 1996) and xanthene derivatives (Ghiasvand et al.).

The parameter b is approximately related to the enthalpy of vaporization of the solid solutes $\Delta_{\text{vap}}H$ (Miller et al., 1996) by

$$\Delta_{\text{vap}}H = -Rb \tag{4}$$

where R is the gas constant. The validity of eq 4 relies on the assumption that the enhancement factor $\ln(XP/P_{\text{v}})$, where P_{v} is the vapor pressure of the solute, is independent of temperature; this was found to be nearly true in practice. The estimated $\Delta_{\text{vap}}H$ values are also included in Table 2.

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