J. Chem. Eng. Data **2002,** *47*, 329−332

Solubilities of Pure and Mixed 2-Methylanthracene and 9-Nitroanthracene in Supercritical Carbon Dioxide

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The equilibrium solubilities of two pure solid polycyclic aromatic hydrocarbons (9-nitroanthracene and 2-methylanthracene) and a nearly equimolar 9-nitroanthracene/2-methylanthracene mixture in supercritical CO_2 were measured at temperatures ranging from 318 K to 348 K and pressures from 12.2 MPa to 35.5 MPa. The measured solubilities for pure solid were correlated using a semiempirical model. The calculated results show satisfactory agreement with the experimental data. It was observed that in the ternary system (9-nitroanthracene + 2-methylanthracene + CO_2) the solubility of each substance was increased when compared to the binary systems (pure substance + CO_2).

Introduction

Due to the easy separation of extracts from the solvent after extrication and the avoidance of environmental pollution, the supercritical fluid (SCF) extraction method has been extensively investigated. SCF solvents are an attractive alternative to incompressible organic liquid solvents since they can have liquidlike dissolving power while exhibiting transport properties of a gas. Also, supercritical fluids possess extraordinary properties including high diffusivity, low viscosity, and high compressibility, which make them attractive solvents for many industrial processes.

A factor limiting the application of supercritical fluid extraction (SFE) is the lack of fundamental solubility data needed to design separation units or to develop extraction models. Bartle et al.[1] have gathered data concerning the solubility of slightly volatile compounds in supercritical CO_2.

The majority of experimental studies have dealt with binary systems consisting of a single solute, usually a solid, and a single SCF.[2,3] Solubility data derived from a mixed solute system, in contrast, are meager. The study of mixed solute systems is important because most potential applications of SCF extraction involve the removal of a desired compound from a matrix of components. It was found that the solubility of a component in a mixture was sometimes considerably different from the solubility of a component from a pure solid depending on the type of compounds in the substrate, their volatility, and the density of the supercritical phase.[4−7]

In previous work,[2,8] the solubilities in supercritical CO_2 of polycyclic aromatic hydrocarbons in pure and mixed form were investigated. In this work the solubilities of 9-nitroanthracene and 2-methylanthracene in pure and mixed forms were determined in supercritical CO_2, over wide ranges of temperature and pressure. The solubility data for pure compounds were successfully correlated by using a semiempirical equation.

Experimental Section

HPLC-grade chloroform (Aldrich) were used as received. Carbon dioxide (Sabalan, Tehran, 99.99%) was used for all extraction. Reagent-grade 2-methylanthracene (99%) and 9-nitroanthracene (99.5%) (all from Aldrich) were of the highest purity available and were used as received.

A Suprex (Pittsburgh, PA) MPS/225 system equipped with a modified static system for solubility determination in SFE mode was used. A detailed description of the equipment and operating procedures has been given previously.[9,10] Solubility measurements were accomplished in a pressure range from 12.2 to 35.5 MPa, at temperatures (308, 318, 328, 338, and 348) K for a duration of 45 min. It should be noted that by monitoring the solubility data versus time, 45 min was found to be adequate to ensure the attainment of equilibrium. The equilibrium temperature and pressure were measured to accuracies of ±1 °C and ±0.05 MPa, respectively. The solid solutes (100 mg) were mixed well with a proper amount of glass beads and packed into a 0.5-mL extraction vessel. This procedure prevents channeling, increases the contact surface between the sample and the supercritical fluid, and consequently, reduces the equilibration time. Sintered stainless steel filters (5 μm) were used to prevent any carryover of the solutes. Supercritical CO_2 was pressurized and passed into the extraction vessel. After equilibrium at the desired temperature and pressure was reached, a 145-μL portion of saturated supercritical CO_2 was loaded into an injection loop. Then, the loop was depressurized into the collection vial containing chloroform. Finally, the sample loop was washed with chloroform, which was collected in the collection vial.

The solubilities of 9-nitroanthracene and 2-methylanthracene were calculated by absorbency measurements at λ_{max} of each compound using a model 2100 Shimadzu UV−Vis spectrophotometer with 1-cm pass length quartz cells. Stock solutions of each compound (100 μg mL^{-1}) were prepared by dissolving appropriate amounts of solid sample in chloroform. A set of standard solutions was prepared by appropriate dilution of the stock solutions. The calibration curves obtained (with regression coefficients of about 0.9999) were used to establish the concentration of the PAHs in the collection vial.

Analysis of Mixture. The solubilities of mixtures of PAHs were measured with the same apparatus and procedure used for binary systems. The composition of final solution was determined by a absorbency measurement at

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10.1021/je0101911 CCC: $22.00

Table 1. Solubilities of 9-Nitroanthracene and 2-Methylanthracene in Supercritical CO_2 for Binary and Ternary Systems

P	ρ	9-nitroanthracene			2-methylanthracene		
(MPa)	(kg·m^{-3})	$10^4 X$	$10^4 X$ [a]	S.E.[b] (%)	$10^4 X$	$10^4 X$ [a]	S.E.[b] (%)
			$T = 308$ K				
12.2	771	0.35	0.46	31.88	0.97	1.10	13.94
15.2	818	0.46	0.56	22.97	1.16	1.37	18.46
18.2	850	0.51	0.64	25.06	1.46	1.57	7.31
21.3	876	0.53	0.74	40.59	1.68	1.89	12.17
24.3	897	0.53	0.93	76.25	1.85	2.07	11.61
27.4	916	0.58	0.89	54.35	2.01	2.42	20.48
30.4	931	0.60	0.92	52.56	2.17	2.66	22.46
33.4	946	0.62	0.96	55.06	2.33	3.18	36.46
35.5	955	0.62	1.15	84.52	2.40	3.57	48.53
average				49.25			21.27
			$T = 318$ K				
12.2	661	0.30	0.55	84.62	0.74	1.01	35.66
15.2	745	0.45	0.68	49.82	1.20	1.33	11.23
18.2	792	0.63	0.91	45.52	1.61	1.88	16.93
21.3	826	0.70	0.98	39.46	1.92	2.14	11.50
24.3	852	0.80	1.16	44.53	2.27	2.62	15.20
27.4	875	0.88	1.23	40.39	2.55	3.32	30.04
30.4	893	0.92	1.31	41.82	2.79	3.77	35.16
33.4	910	0.99	1.39	41.12	3.04	4.38	44.28
35.5	919	1.00	1.47	46.62	3.16	5.38	70.07
average				48.21			30.01
			$T = 328$ K				
12.2	516	0.33	0.24	−26.94	0.60	0.54	−10.38
15.2	657	0.52	0.73	40.20	1.09	1.31	20.44
18.2	726	0.75	1.05	40.28	1.63	2.00	22.97
21.3	771	0.96	1.24	29.04	2.18	2.53	16.09
24.3	804	1.10	1.66	50.56	2.70	3.48	28.68
27.4	831	1.22	2.11	73.33	3.12	4.19	34.36
30.4	853	1.40	2.06	46.98	3.54	4.50	27.02
33.4	872	1.45	2.74	88.95	3.85	5.83	51.30
35.5	884	1.49	2.44	63.51	4.10	6.40	56.28
average				45.11			27.44
			$T = 338$ K				
12.2	396	0.40	0.31	−21.71	0.42	0.34	−19.06
15.2	561	0.54	0.85	56.52	0.89	1.17	31.95
18.2	654	0.92	1.47	60.00	1.57	2.14	36.31
21.3	712	1.22	2.08	70.08	2.35	3.21	36.72
24.3	754	1.48	2.63	77.29	2.98	4.48	50.22
27.4	786	1.70	3.09	81.33	3.63	5.33	46.86
30.4	812	2.00	3.62	80.74	4.29	6.46	50.49
33.4	834	2.08	4.15	99.23	4.81	7.60	58.09
35.5	848	2.22	4.39	97.88	5.15	8.17	58.74
average				66.82			39.92
			$T = 348$ K				
12.2	327	0.28	0.18	−35.00	0.24	0.18	−24.44
15.2	477	0.52	0.73	39.95	0.65	0.76	16.34
18.2	585	0.97	1.62	67.41	1.34	1.92	42.86
21.3	652	1.48	2.49	68.04	2.29	3.28	43.04
24.3	702	1.92	3.29	71.39	3.17	4.69	48.03
27.4	740	2.35	4.06	72.79	4.14	6.01	45.23
30.4	772	2.68	4.79	78.67	5.00	7.51	50.34
33.4	796	3.04	5.08	67.26	5.84	8.63	47.75
35.5	811	3.20	5.36	67.54	6.41	10.57	64.86
average				55.34			37.12

[a] Average solubility for ternary system. [b] Solubility enhancement.

two wavelengths of 381 and 400 nm. At a wavelength of 400 nm, the molar absorptivity of 9-nitroanthracene is zero and only 2-methylanthracene shows an absorbance. On the other hand, the absorbance at 381 nm is related to 9-nitroanthracene and 2-methylanthracene.

Results and Discussion

Table 1 presents the solubilities of 9-nitroanthracene and 2-methylanthracene in binary and ternary systems at temperatures (308, 318, 328, 338, and 348) K over a pressure range from (12.2 to 35.5) MPa. The resulting solubilities are reported in terms of equilibrium mole fraction, X, of the solute in supercritical carbon dioxide. Each reported data point is the average of at least three replicate samples. The mole fractions of the solutes were reproducible within ±3%.

Binary Solubilities. From the data given in Table 1, it can be readily seen that, at constant temperature, the solubility of two PAHs increases with increasing pressure. The influence of pressure on the solubilities is more pronounced at higher temperature. This is in contrast to conventional wisdom that the supercritical fluid density must always increase to increase the solubility and extraction.[11,12] By observing the effect of the temperature on the solubilities, we find the crossover region exists at about 15.0 MPa for 2-methylanthracene and at abut 18.0 MPa for 9-nitroanthracene. It is worthy to point out that the crossover point is difficult to see from Table 1, but easy to see from Figure 3. Beyond the crossover point, solubilities increase with an increase of both the pressure and the temperature, while below the crossover point, solubilities increase with an increase of pressure but decrease with an increase of temperature.

Below the crossover point, the volatility of the solute increases with temperature, which is favorable to increasing the solubility, but the density of the fluid decreases with temperature, which is not favorable to increasing the solubility. As seen in Table 1, the density of CO_2 at 348 K is much lower than that at 308 K at the lower pressures. Thus, the density effect is dominant, and the solubility decreases with temperature. At higher pressures, the density of CO_2 is not as sensitive to the pressure as that at lower pressures, and the volatility affect becomes dominant and the solubility increases with temperature.

The results obtained in this study indicate that the solubility of 9-nitroanthracene (mp = 418 K) is higher than 2-methylanthracene (mp = 478 K). The solubilities parallel the order of the relative melting point. Similar results have been reported in the literature.[2,3,13]

The experimental solubility data for the PAHs in a binary system were correlated using the following equation:[1,11]

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

where

$$A = a + b/T \qquad (2)$$

and

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

The parameters of the above equations have been previously discussed.[1,2,11]

In the first step, $\ln(XP/P_{\mathrm{ref}})$ values were plotted against density (Figure 1), and the values were fitted with a straight line by least-squares regression to estimate the C and A parameters. According to eq 1, the plots are expected to be straight lines of similar slopes (correlation coefficients, r^2, of the lines lie between 0.9991 and 0.9998). However, as seen from Figure 1, 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).

When the C was held 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 vs $1/T$ for each compound resulted in a straight line (Figure 2), from which the intercept and slope (a and b) were obtained. The resulting a and b values for compounds are also included in Table 2. Finally, the values of a, b, and c were used to predict solubility from eq 3. Figure 3 compares the calculated isotherms with the experimental data. As seen, the agreement is satisfactory.

The parameter b is approximately related to the enthalpy of sublimation of the solid solutes, $\Delta_{\mathrm{sub}}H$ by[11]

$$\Delta_{\mathrm{sub}}H = -Rb \qquad (4)$$

where R is the gas constant. The validity of eq 4 relies on the assumption that the enhancement factor $\ln(XP/P_v)$, 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 $\Delta_{\mathrm{sub}}H$ values are also included in Table 2.

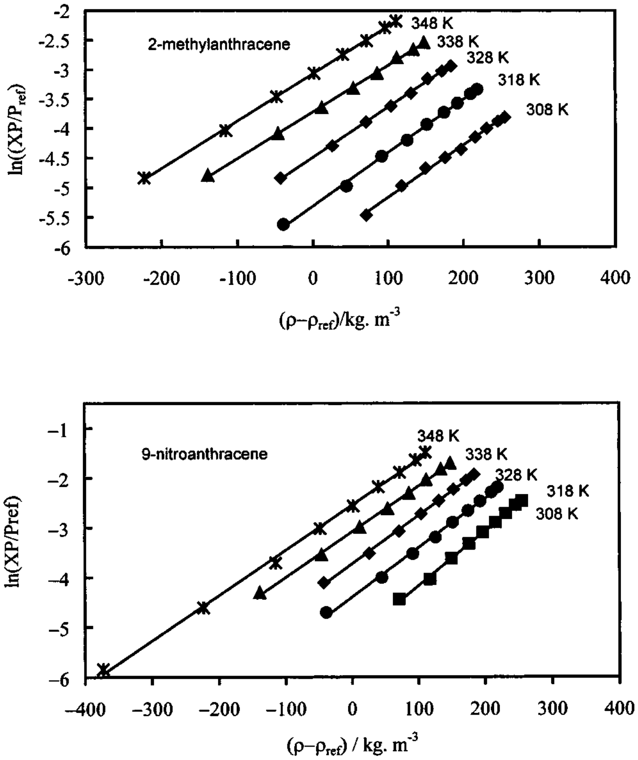

Figure 1. Plots of $\ln(XP/P_{\mathrm{ref}})$ versus $(\rho - \rho_{\mathrm{ref}})$ for 9-nitroanthracene and 2-methylanthracene at various temperatures.

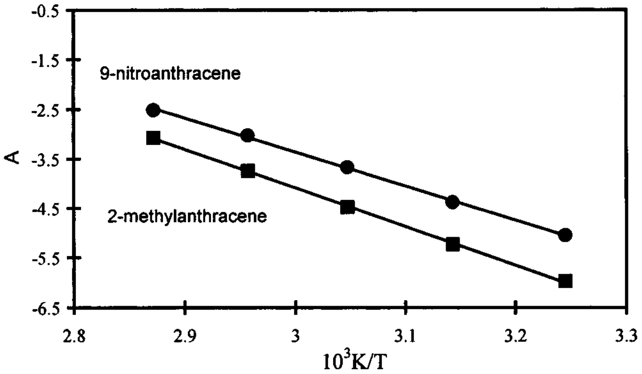

Figure 2. Plots of A versus $1/T$ for 9-nitroanthracene and 2-methylanthracene.

Table 2. Solubility Constants a, b, and c and the Estimated $\Delta_{\mathrm{sub}}H$ Values Obtained from the Data Correlation Procedure

compound	a	b (K)	C ($m^3 \cdot kg^{-1}$)	$\Delta_{\mathrm{sub}}H$ ($kJ \cdot mol^{-1}$)
2-methylanthracene	19.376	−7820.1	0.0084	65
9-nitroanthracene	17.344	−6901.6	0.0098	57

Ternary Solubility. The solubility data for a 50:50 wt % mixture of 2-methylanthracene and 9-nitroanthracene in supercritical CO_2 at different conditions are presented in Table 1. The tabulated results also show the corresponding solubility enhancement relative to the binary solubility data. Solubility enhancement is defined as the percentage relative deviation of the ternary solubility from the binary solubility of the component at the same pressure and temperature.[5] The ternary solubility data were measured at the same pressure and temperature used for the binary solubility data so that a direct comparison between the data

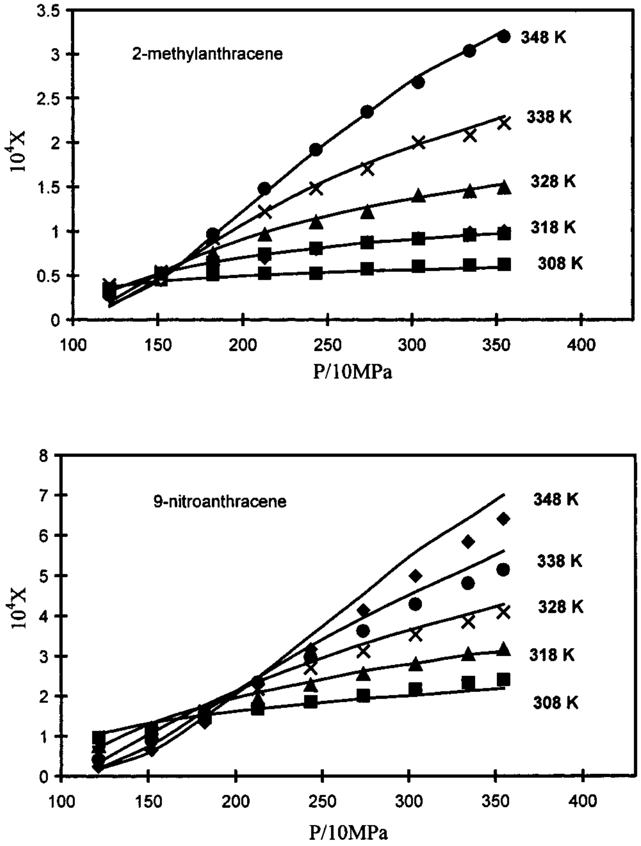

Figure 3. Comparison of experimental (point) and calculated (line) solubilities at various temperatures for 9-nitroanthracene and 2-methylanthracene.

sets were possible, thus eliminating the need to interpolate. At each temperature, the binary and ternary solubilities of a component were determined at nine different pressures and an average value for the solubility enhancement was calculated from the nine individual values.

The solubilities of 2-methylanthracene and 9-nitroanthracene in a ternary system were found to be enhanced by up to 66.82 and 39.92%, respectively. Similar results were reported for other ternary or quaternary systems.[5,6,8] Solubility enhancement in a mixed solute system usually follows a pattern described by Dobbs and Johnston.[7] They proposed that the solubility of a solid in a ternary system will increase, relative to its binary system, in proportion to the solubility of other solids in the ternary system. This implies that each of the solutes in the supercritical phase behaves like a modifier (or cosolvent). The entrainer effect is commonly encountered in systems that display solid−fluid equilibria.[7]

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Received for review July 10, 2001. Accepted January 2, 2002.

JE0101911