148 J. Chem. Eng. Data 1987, 32, 148-150

Solubility of Anthracene and Phenanthrene Mixtures in Supercritical Carbon Dioxide

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Solubility data were obtained for anthracene and mixtures of anthracene with phenanthrene in supercritical CO_2. The equilibrium solubilities were measured at 308 and 318 K isotherms, over a pressure range of 100-275 atm in a semicontinuous flow apparatus. The available experimental data on the solubility of the solids in supercritical CO_2 have been analyzed by using the Peng-Robinson equation of state.

Introduction

Over the past few years, significant interest has been expressed in a separation concept wherein a condensed phase (liquid or solid) is contacted with a supercritical fluid phase. Often-given examples are decaffeination of coffee beans, deasphalting petroleum residue, and extraction of coal. Although considerable work has been done to study the solubility behavior of heavy components in supercritical fluids, much of the published information is concerned with binary systems. Kurnik et al. (*1*) measured solubilities of five different solids including phenanthrene in both supercritical carbon dioxide and ethylene. Johnston et al. (*2*) studied the solubilities of nonpolar solids in supercritical carbon dioxide.

It was found that the solubility of a component in a mixture was sometimes considerably different than 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 (*3*, *4*). Recently, eight ternary mixtures (two solids, one fluid) were studied using supercritical carbon dioxide by Kurnik et al. (*5*). It has been shown that the phenanthrene solubility in the phenanthrene + naphthalene + CO_2 ternary system increases by a maximum of 75% over that when no naphthalene is present. The corresponding increase for naphthalene is 20%.

In this work, equilibrium solubility measurements for anthracene, and mixtures of phenanthrene + anthracene in supercritical CO_2 are reported at 308 and 318 K at pressures between 100 and 275 atm. Although this system was also investigated by Kwiatkowski et al. (*5*), the inconsistency in their binary system solubility data compared to that of other investigators (*1*, *2*) indicates a flaw in their experimental procedure.

Experimental Section

A schematic diagram of the experimental setup used to measure solubilities is shown in Figure 1 and was discussed in detail elsewhere (*6*). Equilibrium was achieved by passing CO_2 through the packed particulate solid in two extraction vessels in series. The fluid mixture exiting the second vessel is depressurized through a heated valve into liquid toluene. The total amount of gas flowing for a given period (1-2 h) was measured with a wet test meter. The solid substances precipitated in the expansion valve were washed out with toluene and the solutions were concentrated by evaporating the solvent. The amount of solute dissolved in toluene was determined by chromatographic analysis using a 5880A HP gas chromatograph with a 60-m capillary column. The maximum variations in the temperature and pressure throughout an experiment were always less than ±0.1 K and ±0.2 atm (at the highest pressure), respectively; at lower pressures, variation was of the order of ±0.1 atm. Temperatures were accurate to 0.1% and pressures to 0.1%. The important physical properties of the two pure solids are listed in Table I and II. These properties are considered the most reliable, although other values for vapor pressures (*10*) and critical properties (*11*) have been reported.

Table I. Physical Properties of Anthracene and Phenanthrene (*8*)

solid	MW	bp, K	mp, K	T_c, K	P_c, atm	w
phenanthrene	178.22	611.55	369.3	882.55	31.30	0.3299
anthracene	178.22	613.4	489.65	869.3	30.83	0.3531

Table II. Vapor Pressure of Anthracene and Phenanthrene at Different Temperatures (*9*)

solid	T, K	P, atm
phenanthrene	303	2.93×10^{-7}
	308	5.41×10^{-7}
	318	1.74×10^{-6}
anthracene	303	1.43×10^{-8}
	308	2.59×10^{-8}
	318	7.99×10^{-8}

Table III. CO_2-Anthracene Data

T = 308 K		T = 318 K	
P, atm	10^5y	P, atm	10^5y
102.9	1.68	102.9	0.89
136.9	5.08	136.9	5.56
170.2	8.01	170.2	8.90
204.0	9.14	204.0	10.1
273.1	9.23	238.9	10.9
		273.1	11.2

Table IV. CO_2-Phenanthrene-Anthracene Data

T, K	P, atm	10^4y_{Phe}	10^5y_{ant}
308	103.1	5.81	3.24
	136.9	9.91	5.99
	171.0	12.90	8.11
	204.2	15.20	9.23
	239.1	16.10	9.60
318	103.1	2.43	1.20
	136.9	9.65	5.78
	171.0	15.60	9.01
	204.2	19.30	11.21
	239.1	22.90	12.28

Results

The measured solubilities of anthracene in supercritical CO_2 are listed in Table III, and the measured solubilities of mixtures of anthracene with phenanthrene are shown in Table IV. In addition to noting the mole fraction of the solutes in the supercritical fluid, the solute-solvent interaction parameters determined from the data and the Peng-Robinson equation of state for the compressed gas model (CGM) are presented in Table V.

Figure 2 shows the experimental solubility data for anthracene at 308 and 318 K. At each temperature, measurements were made at pressures from 100 to 275 atm. No reliable data were obtained at pressures below 100 atm due to the very low solubility of anthracene at such pressures. In Figure 2, the solid

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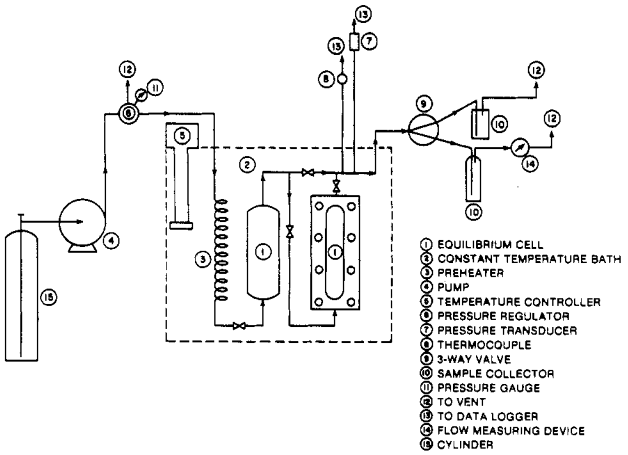

Figure 1. Schematic diagram of the experimental setup.

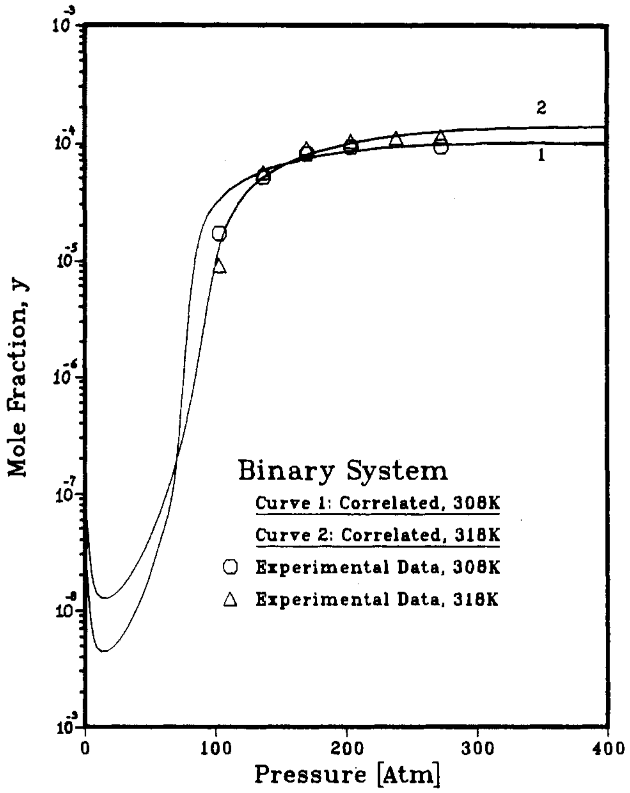

Figure 2. Solubility of anthracene at different temperatures.

Table V. Binary Interaction Parameters Obtained from the Compressed Gas Model Using PR Equation of State

system	T, K	no. of obser	$k_{1,2}$	error[d] in y	source
CO_2–anthracene	303[a]	4	0.062	5.7	*2*
	308	5	0.056	4.3[c]	this work
	318	6	0.055	3.9[c]	this work
CO_2–phenanthrene	303[a]	8	0.069	3.8	*2*
	308	no data	0.068[b]		
	318	5	0.067	6.5	*1*

[a] Liquid–solid isotherms. [b] Value determined with respect to $k_{1,2}$ binary interaction parameters at 303 and 318 K. [c] Without first data point. [d] Error = $(1/N)\ (\sum ((y_{\text{expt}} - y_{\text{pred}})/y_{\text{expt}})^2)^{1/2} \times 100$.

lines represent the correlated solubility when the Peng–Robinson (*7*) equation of state is used.

Ternary experiments were carried out with an equimolal mixture of anthracene and phenanthrene. For a solid mixture, the fugacity of each heavy component in the gas and solid phases is equal to the pure solid fugacity at the same temperature and pressure and is independent of the solid mixture composition; i.e., a 60:40 mixture would give the same results. The eutectic melting temperature for this mixture is calculated to be 364 K, which is well above the temperatures used in these experiments. Although the CO_2 can cause the melting point to drop slightly, it is highly improbable that the 46 K depression required to melt this mixture at 318 K could be achieved. In addition, the solid remaining after the extraction

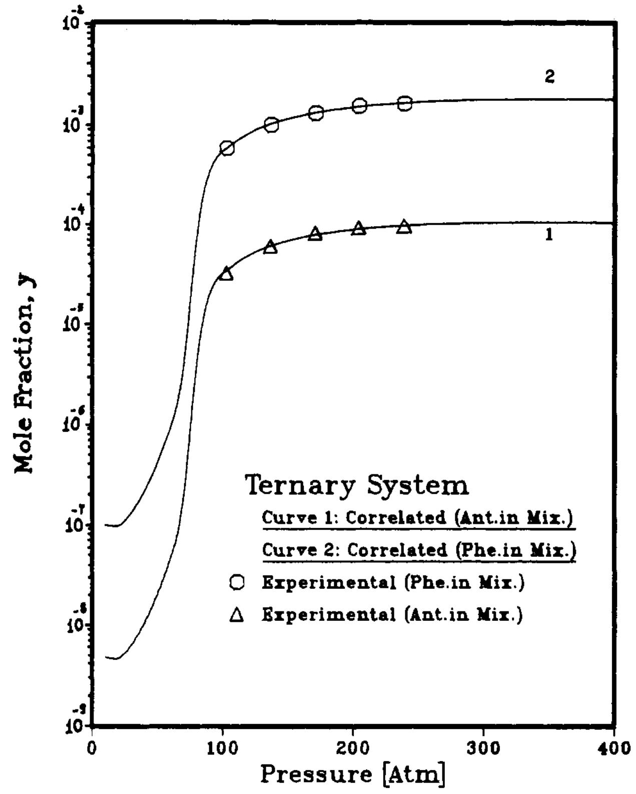

Figure 3. Solubility of anthracene and phenanthrene at 308 K.

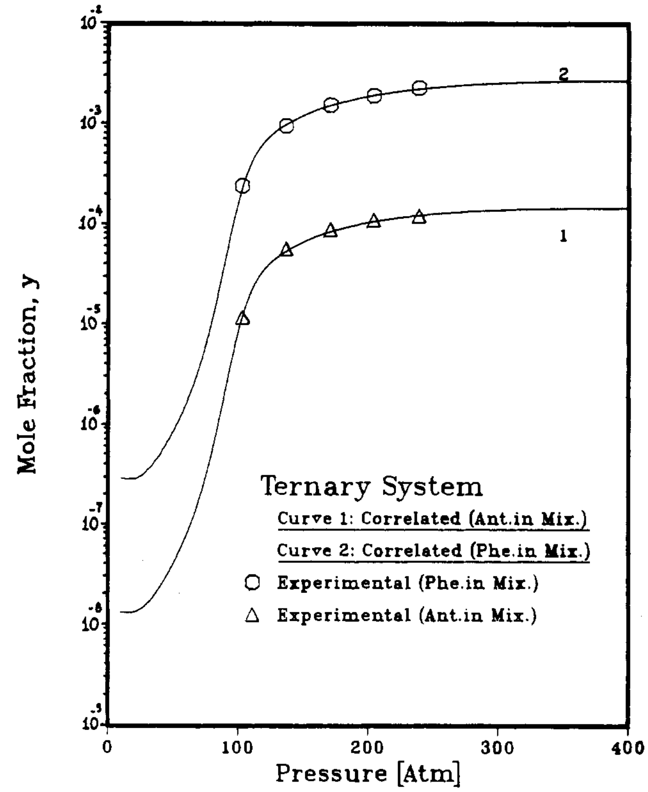

Figure 4. Solubility of anthracene and phenanthrene at 318 K.

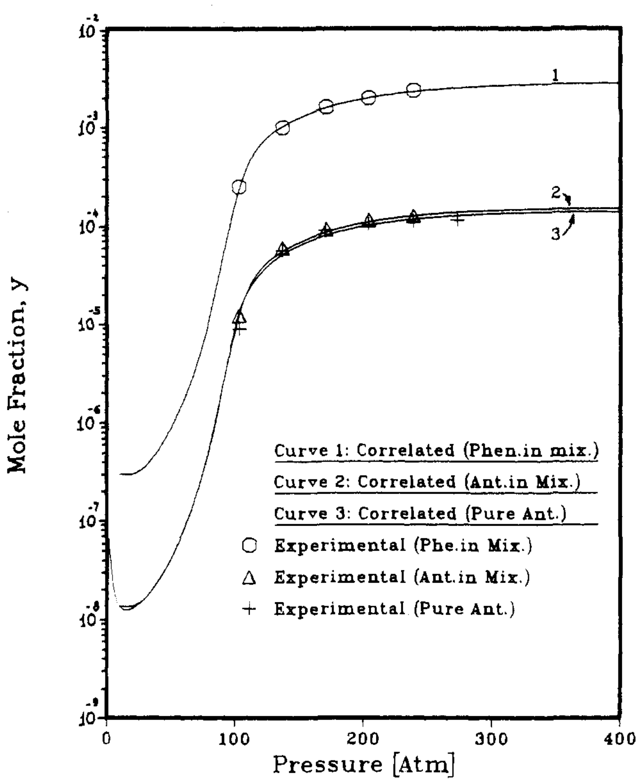

Figure 5. Solubility of anthracene and phenanthrene at 318 K.

was visually examined and it was observed that it had not melted. Figures 3 and 4 compare the experimental solubility values of the solid mixture at 308 and 318 K isotherms and those correlated by the CGM treating the solids as eutectic mixture with pure phenanthrene and anthracene phases. The 318 K data for the anthracene + phenanthrene + CO_2 system are plotted in Figure 5. The binary solubility data of anthracene are also shown.

In applying an equation of state to a gas or fluid solution, a binary interaction parameter represents the interaction between two species. Thus, for a ternary system containing two solids and a supercritical fluid, it is necessary to specify three interaction parameters. Two can be obtained from the solubility data for the individual solids in the supercritical fluid. The third is presumably characteristic of the interaction between the solid components which are dissolved in the supercritical fluid. In this study, in order to find the third interaction parameter for the phenanthrene + anthracene + CO_2 ternary system, ternary solubility data were regressed by using binary interaction parameters (Table V), and the results are given in Table VI. As can be seen from Table VI, the binary interaction parameters between the two solids do not affect the correlated solubility values due to the fact that the solubilities of these compounds in the supercritical carbon dioxide are low. Experimental results at 103 atm and 308 or 318 K show that the anthracene solubility in the ternary system is considerably higher than the solubility obtained when no phenanthrene is present. At higher pressures, however, the anthracene solubility in the ternary system is very close, though somewhat lower (average 6%) than the solubility in the binary system. As shown in Figure 5, the model predicts a slight increase in solubility in the ternary system. The small variations in the experimental results from the binary to ternary systems are possibly due to the experimental error.

Table VI. Binary Interaction Parameter between Solute-Solute for the Anthracene-Phenanthrene-CO_2 Ternary System

T, K	$k_{2,3}$	error in y_{Phe}	error in y_{Ant}	total error
308	−0.100	0.78	1.42	2.20
308	−0.038	0.76	1.33	2.09 (min)
308	0.000	0.75	1.38	2.13
308	0.100	0.72	1.81	2.53
318	−0.100	0.85	2.66	3.51
318	−0.091	0.84	2.66	3.50 (min)
318	0.000	0.84	2.82	3.66
318	0.100	0.85	3.26	4.11

If the binary solubility data of phenanthrene at 318 K (*1*) is compared with the present work (Figure 4), one can see that the correlated solubilities of phenanthrene in the ternary and in the binary systems are quite close to each other. The 308 and 318 K data for the phenanthrene + anthracene + CO_2 system are plotted in Figures 3 and 4, respectively. From these two figures, it is clear that the data are fairly well described by the theoretical model with no ternary interaction parameter.

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Received for review August 7, 1985. Revised August 5, 1986. Accepted December 1, 1986.