Solubility of an Anthracene, Phenanthrene, and Carbazole Mixture in Supercritical Carbon Dioxide

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An experimental flow-type apparatus has been designed to obtain solubility data for an anthracene, phenanthrene, and carbazole mixture in supercritical carbon dioxide. The equilibrium solubilities were measured at 308.2 K, over a pressure range of (111 to 201) bar. The equilibrium cell was tightly packed with a uniform mixture of solute and glass beads with 27 layers of glass wool and sieve trays. In this method, the solvent flow is completely dispersed through solid solute and channeling, formation of dead volume, and caking of the solid during operation of the system are prevented. The measured solubilities for binary and quarternary systems were correlated using the SRK EOS with van der Waals mixing rules, using binary interaction parameters for both cases. The calculated results indicated good agreement with the experimental data. The results of one-step extraction of main components of anthracene oil (phenanthrene, anthracene and carbazole) of Isfahan Coal Tar Refining Co. in supercritical carbon dioxide at 308.2 K and 201 bar are also presented.

Introduction

Supercritical fluid extraction (SCFE) is a new separation technique which has received much interest in the processing of pharmaceutical, natural products, and many other special applications.[1,2] Carbon dioxide is preferred as the supercritical solvent for practical applications since it is inexpensive, nontoxic, inflammable, and environmentally acceptable and has a low critical temperature and a moderate critical pressure. The interest in SCF extraction may be attributed to the unique advantages offered by the process, such as high mass-transfer rates, favorable selectivities, and low operating temperatures. The solubility of a solute in a supercritical fluid is perhaps the most important thermophysical property that must be determined and modeled for an efficient design of any extraction based on supercritical solvents.

The methods used for measuring solubilities of organics in supercritical fluids may be broadly classified into four different categories: dynamic methods, static methods, chromatographic methods, and spectroscopic methods. The advantages and disadvantages of these methods as well as their accuracy and precision have been discussed in details elsewhere.[2,3] The solubility of solids in supercritical fluids is mostly determined by the dynamic or flow methods. Several flow methods have been developed.[4−6] In this work, a special design for the equilibrium cell was developed to determine the solubilities of organic compounds in supercritical fluid.

The available solubility data for the main components of anthracene oil deal with binary or ternary systems,[4,7−10] whereas data for multicomponent systems (quarternary systems) for anthracene oil are scarce. Johnston et al.[7] used the flow technique to determine the solubilities of solid anthracene and phenanthrene in supercritical carbon dioxide at (30, 50, and 70) °C over a range of pressures up to 414.5 bar. Kwiatkowski et al.[4] used the flow technique and limited their study of anthracene, phenanthrene and carbazole in CO_2 at 40 °C and pressures ranging from (100 to 200) bar. Kosal and Holder[8] measured the solubilities of solid anthracene in supercritical carbon dioxide at (35 and 45) °C over a range of pressures up to 273.1 bar. The solubility of anthracene and phenanthrene at temperature 35 °C and pressures up to 350 bar in supercritical carbon dioxide has also been reported by Dobbs.[9,10]

In this work, the solubilities of anthracene, phenanthrene, carbazole, and their mixture have been determined in a flow type apparatus in supercritical carbon dioxide at a temperature of 308.2 K over a pressure range of (101 to 201) bar. The measured solubility data were correlated using the SRK EOS using van der Waals mixing rules.

The solubility of the main components (phenanthrene, anthracene, and carbazole) of anthracene oil of Isfahan Coal Tar Refining Co. in an extraction vessel with 27 sieve trays were measured by one-step extraction in supercritical carbon dioxide at 308.2 K and 201 bar. The results were compared with the solubility of phenanthrene, anthracene, and carbazole obtained from a mixture of the three solids in supercritical carbon dioxide at the same temperature and pressure.

Experimental Section

Materials. The carbon dioxide supplied by Roham Gas Chemical Co., Iran, had a minimum purity of 99.8 mol %. The naphthalene was from Merck with a minimum purity of 99%. The anthracene oil sample was donated by Isfahan Coal Tar Refining Co. The anthracene, phenanthrene, and carbazole were purchased from Merck with a minimum purity of 96, 98, and 98% respectively. The chemicals were additionally purified with supercritical carbon dioxide at 318.2 K and under pressure of 200 bar.

Procedure. A schematic flow diagram of the apparatus is presented in Figure 1. Carbon dioxide supplied from a gas cylinder (1) was liquefied through a cooling unit (3). The liquified carbon dioxide was compressed by an air-driven oil-free reciprocating pump (5). The CO_2 then passed through a surge vessel (7) to dampen the fluctuations generated by the operation of the pump, and then to a preheater (14).

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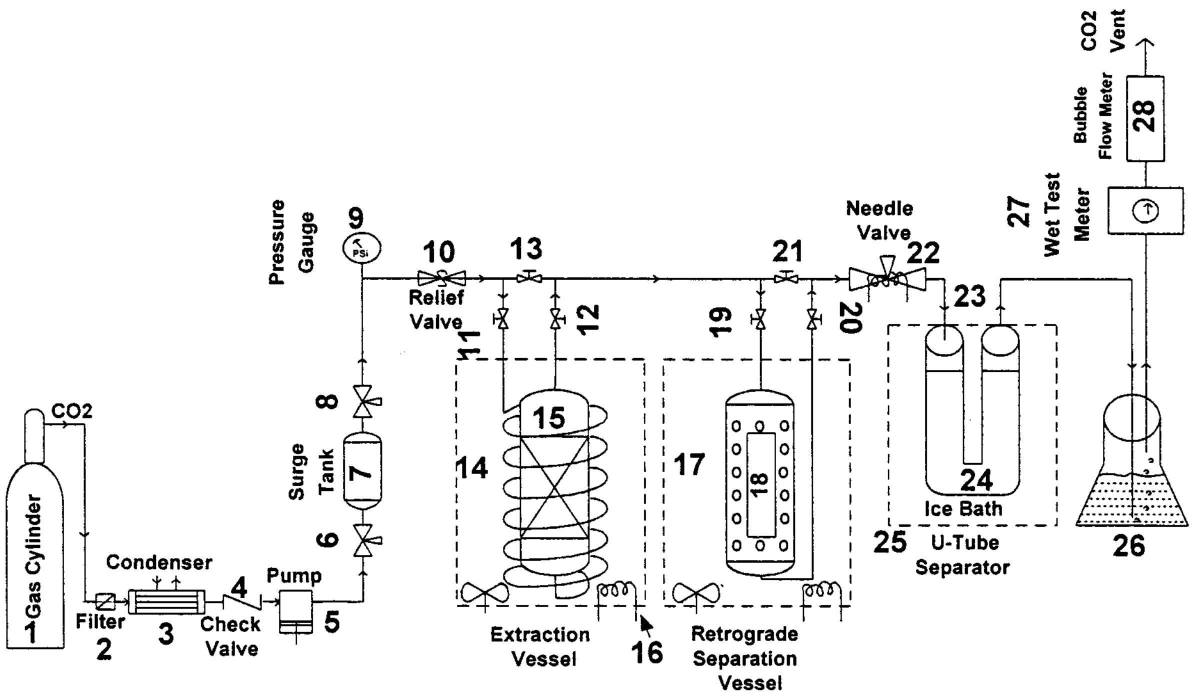

Figure 1. Schematic flow diagram of the apparatus for measuring solute solubility in supercritical fluids: (1) gas cylinder, (2) filter, (3) condenser, (4) check valve, (5) high-pressure pump, (6, 8, 11, 12, 13, 19, 20, 21) stop valves, (7) surge vessel, (9) pressure gauge, (10) relief valve, (14) preheating coil, (15) equilibrium cell, (16, 17) constant-temperature water baths, (18) Jerguson gauge, (22) needle valve, (23) thermostated line, (24) cold trap, (25) ice bath, (26) water saturator, (27) wet test meter, and (28) bubble flow meter.

When carbon dioxide passed through the preheater, it became supercritical. Then supercritical carbon dioxide entered into an equilibrium cell (15). The preheater and equilibrium cell were immersed in a constant temperature water-circulating bath (16). The temperature inside the water bath was regulated within ±0.3 K through the use of a heating element and a proportional type temperature controller using a PTC thermocouple. The equilibrium cell was tightly packed with a uniform mixture of solute and 2 mm glass beads with alternate layers of glass wool and sieve trays to prevent channeling and dead volume. Approximately 16 g of solute was charged into the equilibrium cell before initiating a run. Glass wool and a 50 μM monel stainless steel filter cloth were also plugged at the outlet of the equilibrium cell to prevent entrainment of fine particles during the experiment.

The equilibrium cell is made of SS 316 along with 27 sieve trays. Sieve trays are made of SS 316 with an outside diameter of 1 cm and each plate having nearly 50 holes. Perforations are 0.3 mm diameter on triangular pitch. Only, for observation of phase behavior the Jerguson gauge (18) with a sight glass is used along with the equilibrium cell. The equilibrium pressure was measured by a Bourdon gauge (9) with a division of 2 bar in the range of (0 to 250) bar.

The system pressure was maintained constant to within ±1% of the desired value throughout the experiment. After the cell was held at pressure for 1 h, the carbon dioxide saturated with solute was allowed to flow through a heated needle valve (22), where the mixture was expanded to atmospheric pressure. The solid solute, which precipitated as a result of the loss in the solvating power of the carbon dioxide, was collected in a cold trap (24). The cold trap was attached directly to the needle valve with a high-pressure connection (23) and was submerged in an ice bath (25). The temperature of the needle valve wrapped with heating tape was measured by a K-type thermocouple thermometer and adjusted using a proportional type temperature controller to a temperature about (30 to 50) °C above the corresponding melting point of the solute with an accuracy of ±1 °C, to prevent clogging of the valve with the precipitated solute. Typically, the amount of solute collected was of the order of (0.01 to 0.27) g. The solute was collected in a U-tube cold trap, which was partly packed with 0.5 μM filter SS plate, and six layers of fine Whatman filter papers in order to catch the small particles of solute in the expanded gas stream. The solute collected in the cold trap was weighed by an analytical balance with an accuracy of 10^{-4} g (Mettler AC100). The gas liberated from the trap was allowed to flow through a water saturator (26) and wet test meter (27) having an accuracy of 28.32 cm^3 to measure the total volume of solvent used in each run. Solubilities were determined from the mass of the solute and the volume of carbon dioxide. In the case of measuring solubilities of mixed solids, the solutes collected in the cold trap were analyzed with a HPLC chromatograph (Shimadzu Co., model LC-6A) equipped with an UV detector. An ODS column (Shimadzu Shim-Pack CLC-ODS) was used with a mobile phase containing 80 vol. % methanol and 20 vol. % water at a 1 mL/min. flow rate. The solid solubilities were calculated from the peak area of UV analysis. The reproducibility of peak areas was typically better than 99%. Solvent flow rates used in this study for the main components of anthracene oil range from (0.0038 to 0.008) standard m^3/h. Within this range, the flow rate has a negligible effect on the experimental results.

Results and Discussion

The reliability of the apparatus was preliminarily tested by measuring the solubilities of naphthalene in supercritical carbon dioxide at 308.2 K over a pressure range of (98 to 200) bar. The data are listed in Table 1. The reported mole fractions represent an average value of two independent measurements. The measurements were carried out for several flow rates of carbon dioxide (0.012 to 0.042 standard m^3/h) at the same temperature and pressure. The

Table 1. Experimental Mole Fractions of Naphthalene (2) in Supercritical Carbon Dioxide (1) at 308.2 K

P/bar	10^2y_2
98	0.9301
107	1.041
133	1.398
169	1.671
200	1.754

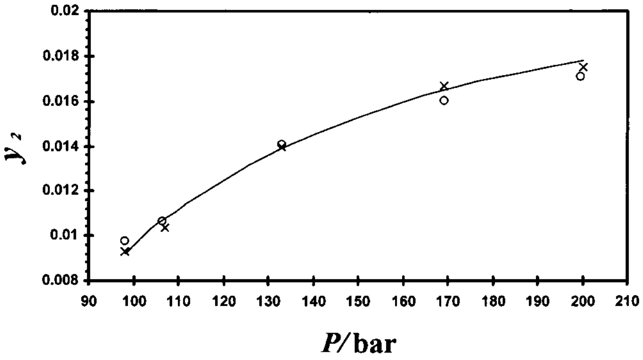

Figure 2. Solubility of naphthalene (2) in supercritical carbon dioxide (1) at 308.2 K: (×) this work; (○) McHugh & Paulaitis;[12] (−) correlated by using the SRK EOS.

(a) With sieve trays (b) without sieve trays

Figure 3. Demonstration of solid form of phenanthrene in the equilibrium cell at 200 bar and 308.2 K in supercritical fluid of carbon dioxide (a) with and (b) without using sieve trays.

solubilities obtained were independent of the carbon dioxide flow rate. The results were compared with those of McHugh and Paulaitis[11,12] as shown in Figure 2. Our results indicate good agreement with those of McHugh and Paulaitis (to within ±5 mol %).

Figure 3 show the effect of using sieve trays on reducing caking of solid form of phenanthrene with flowing supercritical fluid of carbon dioxide in the equilibrium cell at 308.2 K and 200 bar. According to this figure (Figure 3a), the special design prevents channeling, formation of dead volume, and caking of the solid during the operation of system due to dispersion of solvent flow. Figure 3b shows caking formation of phenanthrene around the glass beads due to insufficient dispersion of solvent flow. McHugh and Paulaitis,[12] Gurdial and Foster,[13] Dobbs et al.,[9,14] Yun et al.,[15] Kosal and Holder,[8] and Chen and Tsai[16] had used two or more vessels in series to make sure of reaching equilibrium. However, by using sieve trays, we only need one vessel with a lower volume to get equilibrium. This subject is very important especially in a commercial scale as it can prevent formation of dead volume.

Table 2. Experimental Solubilities of the Main Components of Anthracene Oil in Supercritical Carbon Dioxide at 308.2 K in Binary System

anthracene		phenanthrene		carbazole	
P/bar	10^5y_2	P/bar	10^5y_2	P/bar	10^5y_2
102	1.31	101	55.55	103	1.43
121	3.77	121	73.42	121	1.62
141	5.35	141	93.74	161	1.79
161	7.21	161	110.74	181	2.29
181	8.38	181	124.41	201	2.76

Table 3. Experimental Solubilities of the Main Components of Anthracene Oil (Anthracene (2), Phenanthrene (3), and Carbazole (4)) in Supercritical Carbon Dioxide (1) at 308.2 K in the Quarternary System

pressure P/bar	anthracene 10^5y_2	phenanthrene 10^5y_3	carbazole 10^5y_4
111	3.553	77.57	1.222
131	6.534	88.28	2.102
161	7.495	116.74	2.308
181	11.09	119.61	2.825
201	11.65	143.77	2.852

The solubilities of pure and mixed solid (40 mass % phenanthrene, 40 mass % anthracene, and 20 mass % carbazole) of the main components of anthracene oil in supercritical carbon dioxide at a temperature of 308.2 K and pressures up to 201 bar are listed in Tables 2 and 3. Each reported solubility is the average of two replicate samples. The sample compositions of the solute were generally reproducible to within 5% in the mole fraction solubilities of the solute y_2 in carbon dioxide.

The calculated results for the solubilities of phenanthrene in carbon dioxide at 308.2 K and pressures up to 181 bar using the SRK EOS with van der Waals mixing rules gave good agreement with the experimental data, as shown in Figure 4. It can be seen that the solubilities of phenanthrene in supercritical carbon dioxide increase with pressure. In Figure 4, we include the solubility data of phenanthrene in carbon dioxide of Dobbs et al.[10] and Bartle et al.[17] at 308.2 K for comparison. Our results agree with them to within ±3.5 mol %.

The solubility of phenanthrene in the presence of anthracene and carbazole (a quarternary system) is approximately the same as its solubility in a binary system within the range of experimental precision (±5 mol %), whereas the solubility of anthracene and carbazole in a quarternary system are higher than in a binary system due to interactions with phenanthrene. For example in the pressure range of 161 to 181 bar, phenanthrene raises anthracene's solubility at most up to 32.3% and carbazole's solubility by a maximum of 28.9%, but not vice versa.

The results of extracting main components of anthracene oil of Isfahan and mixed solid composed of 40 mass % phenanthrene, 40 mass % anthracene, and 20 mass % carbazole along with yield and purity enhancement factors at 308.2 K and 201 bar are presented in Table 4.

Approximately 19 g of anthracene oil was charged into the equilibrium cell. The composition of Isfahan anthracene oil is also listed in Table 4. It was analyzed by the Isfahan Coal Tar Refining laboratory with a Variance (Star 3400 CX) gas chromatography with a flame ionization detector. Chromatography columns 30 m in length whose outside diameter is 0.32 mm were filled with 5% phenylpolysilphenylene siloxane. The results showed that (31.95, 6.69, and 1.35) mass % purity of phenanthrene, anthracene, and carbazole were obtained from the extraction of anthracene oil in supercritical carbon dioxide, respectively. The equilibrium solubility, yield, and purity enhancement factors for anthracene and carbazole material in anthracene oil are higher than that in the mixed solid as a quarternary system due to solute−solute interaction. Anthracene's solubility is increased 133.8 mass % and carbazole's

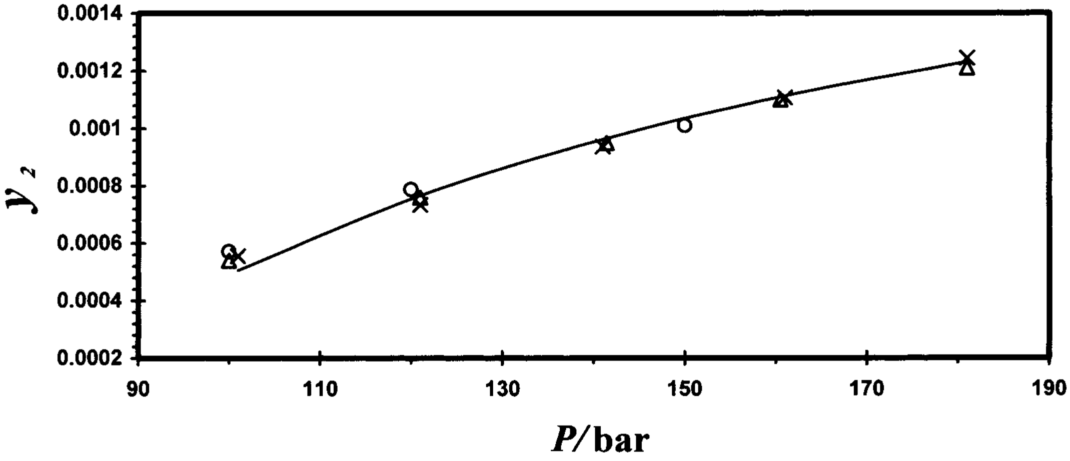

Figure 4. Solubility of phenanthrene in supercritical carbon dioxide at 308.2 K: (×) this work; (○) Dobbs et al.;[10] (△) Bartle et al.;[17] (−) correlated by using the SRK EOS.

Table 4. Equilibrium Solubilities, Yield, Purity Enhancement Factors for Phenanthrene, Anthracene, and Carbazole Material Extracted from Anthracene Oil of Isfahan Coal Tar Refining Company and Mixed Solid in Supercritical Carbon Dioxide at 308.2 K and 201 bar

		anthracene oil of Isfahan coal tar refining			mixed solid		
component	feed mass/%[a]	solubility[b] 10^3 mass fraction	yield[c]	purity enhancement factor[d]	solubility 10^3 mass fraction	yield	purity enhancement factor
phenanthrene	34.46	5.24	0.35	0.89	5.79	0.64	15.05
anthracene	33.8	1.098	0.075	0.14	0.469	0.052	0.12
carbazole	13.89	0.2216	0.037	0.089	0.1078	0.024	0.069

[a] Anthracene oil compounds are phenanthrene (34.46 mass %), anthracene (33.8 mass %), carbazole (13.89 mass %), dibenzofuran (2.03 mass %), fluorene (8.97 mass %), acenaphthene (2.2 mass %), and fluoranthene(4.63 mass%). [b] Solubility = ratio of the mass of the objective compound/total mass (solutes + solvent). [c] Yield = (mass of component in extract/mass of component in feed) × 100. [d] Purity enhancement factor = ratio of (the mass of the objective compound/the mass of the other compound in the precipitate) to that in the feed.

solubility is increased by 105.5 mass % due to solute−solute interaction while phenanthrene's solubility was decreased 9.5 mass %, which can be an indication for the complexity of factors influencing the solubility of solids in supercritical carbon dioxide.

Correlation

The following fundamental equation is used to calculate the solubilities of high-boiling compounds in supercritical fluid:

$$y_i = (p_i^{\text{sat}}/p)(1/\varphi_i^{\text{scf}}) \exp\left[\frac{v_i^{\text{s}}}{RT}(p - p_i^{\text{sat}})\right] \tag{1}$$

where y_i denotes the gas-phase mole fraction of component i, p is the equilibrium pressure, T is the equilibrium temperature, R is the universal gas constant, and p_i^{sat} and v_i^{s} are the saturation vapor pressure and solid-state molar volume of solute, respectively. The value of p_i^{sat} and v_i^{s} can be obtained from the properties of the pure component. The nonideal behavior of the fluid system is characterized by the fugacity coefficient, φ_i^{scf} in eq 1 which is evaluated by using the SRK EOS and thermodynamic relationships. The accuracy of solubility calculation depends on the proper mixing rules to evaluate the fugacity coefficients and the equation of state.

To evaluate φ_i^{scf}, the following cubic equation of state was adopted:

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)} \tag{2}$$

where $a(T)$ and b are pure component parameters that can be correlated as follows:

$$a(T) = a(T_c)(1 + K(1 - (T/T_c)^{0.5})^2 \tag{3}$$

$$b = 0.08664RT_c/P_c \tag{4}$$

$$a(T_c) = 0.42748R^2T_c^2/\text{P}_c \tag{5}$$

and K is expressed in terms of the acentric (ω) factor as

$$K = 0.48508 + 1.55171\omega - 0.15613\omega^2 \tag{6}$$

Equation 6 has been developed by Graboski and Dauber,[18] using experimental vapor pressure data for paraffins up to n-decane, and also ethylene, propylene, cyclopentane, and toluene. This expression yields accurate vapor pressure for heavy hydrocarbons as well as for certain polar compounds, mentioned in the literature by Graboski and Dauber and by Radosz et al.[19]

For the extension of the EOS to mixtures, the van der Waals mixing and combining rules are adopted.

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} y_i y_j a_{ij}, \quad a_{ij} = (1 - K_{ij})(a_i a_j)^{1/2} \tag{7}$$

$$b = \sum_{i=1}^{n}\sum_{j=1}^{n} y_i y_j b_{ij}, \quad b_{ij} = (1 - L_{ij})(b_i^{1/3} + b_j^{1/3})^3/8 \tag{8}$$

where K_{ij} and L_{ij} are adjustable interaction parameters fitted by using the experimental data. In this work, the mentioned parameters have been evaluated with the

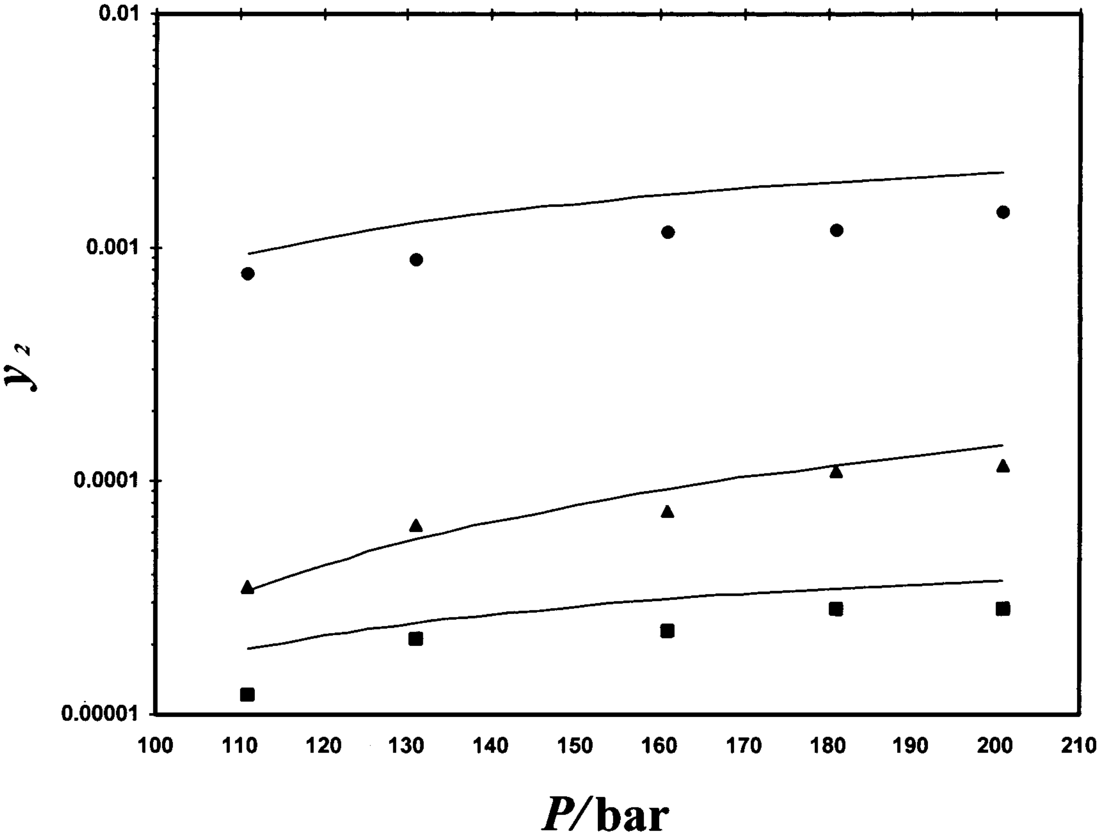

Figure 5. Solubility of the (●) phenanthrene, (▲) anthracene, and (■) carbazole mixture in supercritical carbon dioxide at 308.2 K and modeling results using (−) the SRK EOS with van der Waals mixing rules.

Table 5. Values of Interaction Parameters at 308.2 K and Deviations

system	K_{12}	L_{12}	AADY^a/%
CO_2 (1) + phenanthrene (2)	0.250	−0.343	3.45
CO_2 (1) + anthracene (2)	0.073	0.130	13.62
CO_2 (1) + carbazole (2)	0.433	0.012	9.35

[a] AADY = $1/n \sum_{i=1}^{n} |y_i^{\text{exptl}} - y_i^{\text{calcd}}|/y_i^{\text{exptl}} \times 100$; n = number ofdata points.

method of Marquart optimization with the help of partial derivatives by a computer program. The following objective function (obf) was minimized in order to evaluate the model parameters.

$$\text{obf} = \sum_{i=1}^{\text{NDP}} (y_i^{\text{calcd}} - y_i^{\text{exptl}})^2/(n+1)^{1/2} \tag{9}$$

where n is the number of data points.

The optimum solute−solute interaction parameters between anthracene, phenanthrene, and carbazole with carbon dioxide are calculated from the experimental solubility data of the binary systems shown in Table 2, and these factors are then used for modeling the experimental data of quarternary system. The optimized interaction parameters are listed in Table 5. The calculated results for the solubilities of anthracene, phenanthrene, and carbazole as a quarternary system in carbon dioxide by using the SRK EOS with van der Waals mixing rules indicated good agreement with the experimental data, as shown in Figure 5. It can be seen that the solubilities of the main components of anthracene oil in supercritical carbon dioxide increase with pressure. The average absolute deviation in calculated mole fractions of the quarternary system for phenanthrene, anthracene, and carbazole were 44.33%, 13.84%, and 49.43% respectively. To give better representation for the experimental data, the solute−solute interaction parameters can be considered.

Conclusion

The developed method allows the determination of solubilities of pure solids and their mixtures in supercritical fluids with an accuracy of about 5%. The constructed apparatus is simple. The special design of the equilibrium cell equilibrium is reached, and this prevents channeling, formation of dead volume, and caking of solid during the operation of the system.

The experimental solubility data of the phenanthrene, anthracene, and carbazole mixture have been presented for a supercritical fluid of carbon dioxide at 308.2 K and pressures up to 201 bar. The solubility data of the main components of anthracene oil of Isfahan Coal Tar Refinery Co. have been also presented at 308.2 K and 201 bar. The solubility of anthracene and carbazole in the main components of anthracene oil (multicomponent mixture) increases relative to that in a quaternary system and more so in binary system at constant pressure and temperature due to solute−solute interaction. The solubility data of binary and quarternary system are predicted quantitively by using the SRK EOS with van der Waals mixing rules. The model treats successfully the effect of pressure.

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Received for review March 20, 2001. Accepted January 14, 2002. The authors are grateful to the Sharif University of Technology, Isfahan Coal Tar Refining Company, Industrial Development and Renovation Organization of Iran and Khod-payesh Industrial Research Center for supporting this research.

JE010093F