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Supercritical Extraction of Phenanthrene in the Crossover Region

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An experimental flow-type apparatus has been tested for the separation of phenanthrene from a mixture of solids (phenanthrene, anthracene, and carbazole) and also from anthracene oil of the Isfahan Coal Tar Refining Company based on retrograde crystallization phenomena in supercritical carbon dioxide. The results show that by exploiting the crossover effect it is possible to obtain (82 and 24) mass % of phenanthrene from the solid mixture and anthracene oil, respectively, with a single temperature cycle.

Introduction

Supercritical fluid extraction (SCFE) is a new separation technique that has received much interest in the processing of pharmaceuticals, natural products, and many other special applications.[1,2] Carbon dioxide has several desirable properties that make it attractive for separation process (e.g., it is inexpensive, nontoxic, inflammable, environmentally acceptable, and has a low critical temperature and a moderate critical pressure).

Crossover regions in supercritical fluids and their potential use for separations were discussed by Chimowitz and Pennisi.[3] Also, several attempts have been made to use this method to purify valuable materials.[4−7] The crossover pressure can be defined as the point where the slope of the plot of solubility versus temperature changes sign.[6] For two solids with different crossover pressures, a crossover region exists between the crossover pressures. In this region, the solubility of one solute increases with an isobaric increase in temperature, whereas that of the other decreases. Therefore, it is possible to use this phenomenon to extract solvents in separation processes.

In this work, the previously constructed apparatus in ref 7 was modified by using a new vessel as a retrograde condenser instead of sight glass to investigate the feasibility of separating phenanthrene from solid mixtures (phenanthrene, anthracene, and carbazole) and also from anthracene oil of the Isfahan Coal Tar Refining Company by using retrograde crystallization in supercritical carbon dioxide.

Experimental Section

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

Procedure. A flow-type apparatus was used for solubility studies and retrograde crystallization. A detailed description of the equipment and sampling procedure for the solubility studies was reported previously.[8] Solubilities were determined from the weight of the solute and the volume of carbon dioxide. Carbon dioxide supplied from a gas cylinder was liquefied through a cooling unit. Liquid carbon dioxide was compressed by a high-pressure air-driven oil-free reciprocating pump allowing flow into a surge vessel to dampen the fluctuations generated by the operation of the pump, and then it went to a preheating coil and reached the supercritical condition. Then supercritical carbon dioxide entered into the first equilibrium cell.

The preheater and equilibrium cell were immersed in a constant-temperature water-circulating bath. 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 pressure was measured by a Bourdon gauge with a division of 2 bar in the range of 0−250 bar. The system pressure was constant to within ±1% of the desired value throughout the experiment. After flowing past the equilibrium cell, the carbon dioxide saturated with solute was allowed to flow through a crystallizer immersed in the second constant-temperature bath, and a specific component was deposited out of the supercritical carbon dioxide because of the decrease in its solubility induced by a temperature change. The crystallizer was packed with 2-mm glass beads, glass wool, and a 0.5-μm quartz filter. The level of water was kept up to the top of the crystallizer so that the inlet line could be kept colder to avoid plugging. After passing through the crystallizer, the flow was expanded to atmospheric pressure by using a heated needle valve. The solid solute, which precipitated as a result of the loss in solvating power of the carbon dioxide, was collected in a cold trap. The cold trap was attached directly to the needle valve with a high-pressure connection and was submerged in an ice bath. 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 30−50 °C above the corresponding melting point of the solute with an accuracy of ±1 °C to prevent the valve from clogging with the precipitated solute. The solute collected in the cold trap was weighed on an analytical balance with an accuracy of 10^{-4}g (Mettler AC100). The gas liberated from the trap was allowed to flow through a

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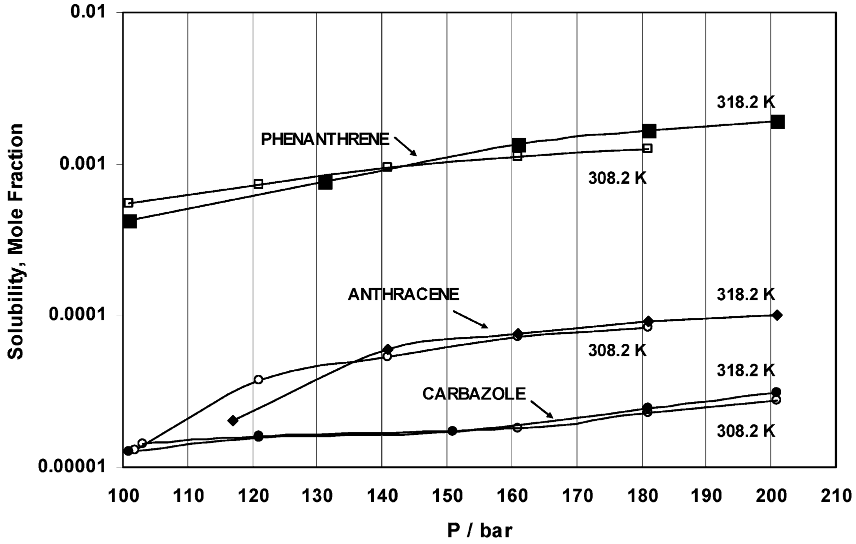

Figure 1. Solubility isotherms of the main components of anthracene oil as a binary system (phenanthrene + CO_2, anthracene + CO_2, and carbazole + CO_2) in supercritical carbon dioxide at (308.2 and 318.2) K: ■, phenanthrene; ◆, anthracene; ●, carbazole.

Table 1. Experimental Solubilities of the Main Components of Anthracene Oil in Supercritical Carbon Dioxide at 45 °C in a Binary System

anthracene		phenanthrene		carbazole	
P/bar	10^5Y_2	P/bar	10^5Y_2	P/bar	10^5Y_2
117	2.05	101	42.485	101	1.26
141	5.99	131	77.330	121	1.56
161	7.51	161	134.31	151	1.74
181	9.22	181	167.31	181	2.45
201	10.18	201	194.25	201	3.07

water saturator and wet test meter having an accuracy of 28.32 cm^3 to measure the total volume of solvent used in each run.

The experiment began by heating the two water baths up to the desired temperature. Valve 11 was opened, and the extractor was pressurized. Then it was closed, and valves 13 and 19 were opened to pressurize the crystallizer up to the same pressure as that of the extractor. After the crystallizer reached the desired operating pressure, valves 20 and 22 were opened. The outlet flow rate of carbon dioxide was normally adjusted to be approximately 0.003 standard m^3/h by using a needle valve. After stabilizing the flow, valve 13 was closed, and valves 11 and 12 were opened. Then, the experiment was continued until 0.0057 m^3 of gas volume passed through the system. At the end of the run, the crystallizer was depressurized. The material in the crystallizer and cold trap was removed, and any residual materials were washed with acetone, which was then evaporated.

The composition of the solid phase in the crystallizer and cold trap for the retrograde crystallization process and solubility studies of mixed solids was analyzed with an HPLC chromatograph (Shimadzu Co., model LC-6A) equipped with a UV detector. An ODS column (Shimadzu Shim-Pack CLC-ODS) was used with a mobile phase containing 80% (v/v) methanol and 20% (v/v) water at a 1 mL/min flow rate. To measure the solubilities of mixed solids, we calculated the solid solubilities from the peak area of UV analysis.

Results and Discussion

Table 2. Experimental Solubilities of the Main Components of Anthracene Oil (Anthracene (2), Phenanthrene (3), and Carbazole (4)) in Supercritical Carbon Dioxide (1) at 45 °C in a Quaternary System

	anthracene	phenanthrene	carbazole
P/bar	10^5Y_2	10^5Y_3	10^5Y_4
111	1.539	71.95	1.161
131	4.882	76.31	1.287
161	14.25	130.7	2.826
181	14.79	163.3	3.904
201	15.90	202.5	5.316

The solubilities of the main components of anthracene oil (phenanthrene + CO_2, anthracene + CO_2, and carbazole + CO_2) as a binary system in supercritical carbon dioxide at 318.2 K are listed in Table 1. Figure 1 shows these data and the experimental solubility data of the main components of anthracene oil at 308.2 K8 graphically displayed with the familiar cross overpressure for phenanthrene, anthracene, and carbazole (the pressure around which the various isotherms converge) occurring at approximately 144, 137, and 152 bar, respectively.

The solubilities of the mixed solid of phenanthrene, anthracene, and carbazole, which are the main components of anthracene oil, were measured in supercritical carbon dioxide at (308.2[8] and 318.2) K over a pressure range of (111 to 201) bar to determine the operating conditions for the retrograde crystallization process. The solubility isotherms of three components are given graphically in Figure 2.

The solubility versus pressure at 318.2 K for phenanthrene + anthracene + carbazole + CO_2 as a quarternary system are also given in Table 2.

The crossover pressures for phenanthrene, anthracene, and carbazole, in which the isotherm solubility curves at temperatures of (308.2 and 318.2) K intersect each other, were approximately (148, 140, and 155) bar, respectively. The crossover regions between the crossover pressures of phenanthrene + anthracene + carbon dioxide and phenanthrene + carbazole + carbon dioxide in a quaternary system were approximately from (148 to 140) bar and (148 to 155) bar, respectively. These results show that the crossover region for phenanthrene, anthracene, and carbazole in a quaternary system is changed slightly with respect to that of the binary system because of solute−solute interaction. Therefore, the purification of phenanthrene in the mixture solid was made at 145 bar in the crossover region. Under this condition, raising the temperature from (308.2 to 318.2) K should cause a deposition

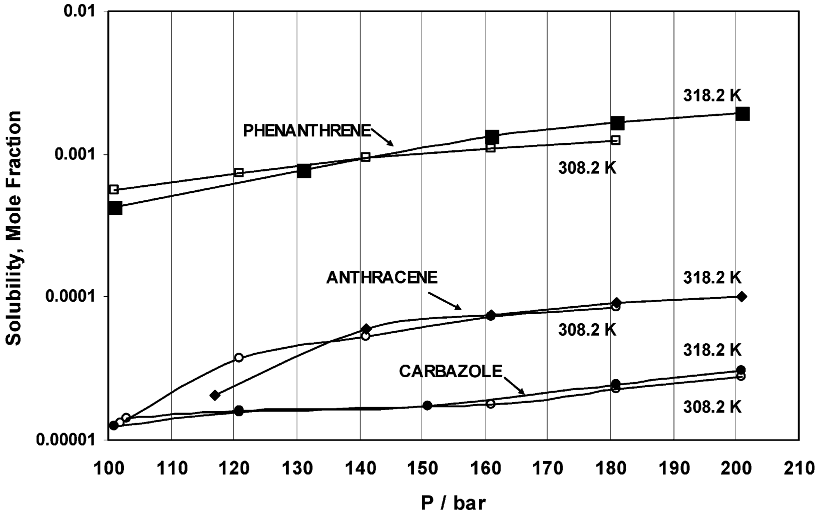

Figure 2. Solubility isotherms of the main components of anthracene oil as a quarternary system (phenanthrene + anthracene + carbazole + CO_2) in supercritical carbon dioxide at (308.2 and 318.2) K: ■, phenanthrene; ◆, anthracene; ●, carbazole.

Table 3. Results for the Retrograde Crystallization Process for the Solid Mixture of 40 Mass % Phenanthrene, 40 Mass % Anthracene, and 20 Mass % Carbazole in Supercritical Carbon Dioxide Using Temperature Cycling from 35 °C to 45 °C

system pressure *P*/bar	crystallizer mass (g)	crystallizer mass fraction phenanthrene	anthracene	carbazole	CO_2 flow rate at standard conditions ($m^3\ h^{-1}$)
145	0.00126	82.72	11.29	5.99	0.0035
145	0.00149	81.38	13.51	5.11	0.0026

Table 4. Results for the Retrograde Crystallization Process for the Solid Mixture of Anthracene Oil from the Isfahan Coal Tar Refining Company (34.46 Mass % Phenanthrene, 33.8 Mass % Anthracene, and 13.89 Mass % Carbazole) in Supercritical Carbon Dioxide Using Temperature Cycling from 35 °C to 45 °C

system pressure *P*/bar	crystallizer mass (g)	crystallizer mass fraction phenanthrene	anthracene	carbazole	CO_2 flow rate at standard conditions ($m^3\ h^{-1}$)
145	.0251	24.9	2.7	2.1	0.0033
145	.0248	23.44	2.54	2.1	0.0033

of phenanthrene from supercritical fluid containing phenanthrene, anthracene and carbazole.

Tables 3 and 4 present the results of the retrograde crystallization experiments for a quaternary system (phenanthrene, anthracene, and carbazole) and anthracene oil of the Isfahan Coal Tar Refining Company.

The results from Tables 3 and 4 show the average mass fraction purities of phenanthrene in the crystallizer material for the solid mixture and anthracene oil to be approximately 82% and 24%, respectively, with a single temperature cycle. The data indicate that it is difficult to obtain a high purity when the retrograde is narrow. The average mass percent purity of phenanthrene extracted from a multicomponent system (anthracene oil) is decreased by a factor of 3.4 compared to that in a quaternary system. The reason for this is obvious. Anthracene oil is a mixture of many components, each of which has a crossover point. Therefore, more components are deposited from anthracene oil when the temperature is changed from (308.2 to 318.2) K.

Conclusions

The separation of phenanthrene from a solid mixture (phenanthrene, anthracene, and carbazole) and also anthracene oil of the Isfahan Coal Tar Refining Company was examined by using retrograde crystallization from supercritical carbon dioxide. The results show that the average mass percent purity of phenanthrene separated from anthracene oil (multicomponent mixture) decreases relative to that in a quaternary system at constant pressure and different temperature because of more crossover pressures.

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