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Solubilities of Mixed Acenaphthene, Fluoranthene, and Triphenylene in Supercritical Carbon Dioxide and the Separation of Binary Solid Mixtures of Polycyclic Aromatic Hydrocarbons

Yadollah Yamini* and Naader Bahramifar

Department of Chemistry, Tarbiat Modarres University, Tehran, Iran

The equilibrium solubilities of mixtures of acenaphthene, fluoranthene, and triphenylene in supercritical CO_2 were determined at temperatures ranging from 308 K to 338 K and pressures ranging from (121.6 to 354.6) bar. It was observed that in a quaternary system (acenaphthene + fluoranthene + triphenylene + CO_2) the solubility of each substance increased in comparison to each binary system (pure substance + CO_2). Finally the separation of binary solid mixtures of acenaphthene + triphenylene, acenaphthene + fluoranthene, and fluoranthene + triphenylene at 328 K and 121.6 bar was investigated. The results showed that the acenaphthene can be separated from triphenylene and fluoranthene with yields of 99% and 90%, respectively, and fluoranthene was separated from triphenylene with a yield of 89%.

Introduction

In recent years there has been increasing attention paid to the area of supercritical fluid extraction (SFE). This interest has been followed by changes in environmental regulations; conventionally used solvents are being replaced by "cleaner" processes such as those which utilize a supercritical fluid (SF).

Properties of supercritical fluids that are interesting from an extraction viewpoint include the diffusion coefficient, the density, and the viscosity. Faster diffusion leads to more efficient separations than liquids facilitate. The low viscosity and the absence of surface tension in SFs increases the speed of percolation so that the passage of the solvent into the interstices of the matrix is enhanced.

The solvent strength of the SFs is, in general, proportional to the density of the fluid; thus, we have the opportunity to tailor the solvating characteristics of the SFs by controlling the pressure and temperature of the fluid. Among the SFs, carbon dioxide is usually preferred, because it is nontoxic, nonflammable, environmentally acceptable, and relatively inexpensive and its critical point allows for extraction at relatively low temperatures.

Recent studies have demonstrated the use of SFs for extraction of organic contaminants such as polycyclic aromatic hydrocarbons[1−5] and polychlorinated biphenyls from different matrixes.[6,7]

A major factor limiting the commercial success of the SFE is the lack of reliable data for the design of the extraction unit. In recent reviews by Bartle et al.,[8] Dohrn and Brunner,[9] and Foster et al.,[10] a considerable amount of solubility data have been reported. However, much of the available solubility data deals with binary systems, whereas data for multicomponent systems are more scarce. The study of mixed-solute systems is important because most potential applications of SFE involve the removal of a desired compound from a matrix of components. Previous studies involving the extraction of mixtures of solids demonstrate that solute−solute interaction in the SF phase can be significant.[11−18] In most cases, solute−solute interactions lead to an enhancement in the solubilities of components relative to their respective binary systems. However, in some cases, solubility diminution may occur.[19] Thus, there is now a greater need to understand the solubility behavior of such systems.

In previous investigations, we measured the solubilities of some 1,4-dihydroxy-9,10-anthraquinone[20] and 1,8-dihydroxy-9,10-anthraquinone derivatives[21] and dihydroxybenzene isomers[22] and hydroxyxanthone derivatives[23] and polycyclic aromatic hydrocarbons (PAHs)[24] in supercritical carbon dioxide.

This work was undertaken to determine the solubilities of acenaphthene, fluoranthene, and triphenylene in a quaternary system containing all three PAHs in supercritical carbon dioxide, over a wide range of temperatures and pressures. Finally, the possibility of separating the two PAHs from their binary mixtures was considered.

Experimental Section

HPLC-grade chloroform, methanol, and water (all from Aldrich) were used as received. Carbon dioxide (99.99%; Sabalan, Tehran, Iran) was used for all extractions. Reagent-grade acenaphthene (99%, A_1), fluoranthene (98%, A_2), and triphenylene (98%, A_3) (all from Aldrich) 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 is given elsewhere.[20,22] The solid solutes (100 mg) were mixed with proper amounts of glass beads and packed into the 1-mL extraction vessel. This procedure prevents channeling, increases the contact surface between the sample and the SF, and, consequently, reduces the equilibration time. Sintered stainless steel filters (5 μm) were used to prevent any carryover of the solutes. Solubility measurements were accomplished in the pressure range from 121.6 bar to 354.6 bar at temperatures (308, 318, 328, and 338) K for a duration of 30 min. It should be noted that by monitoring of the solubility data versus time 30 min was found adequate to ensure the

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* To whom correspondence should be addressed. E-mail: yyamini@net1cs.modares.ac.ir.

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attainment of equilibrium. The equilibrium temperature and pressure were measured to accuracies of ±1 K and ± 0.5 bar, respectively.

Analysis of Mixtures. The solid substances precipitated in the injection loop were washed out with chloroform and collected in the collection vial. Then 20 μL of the resulting solution was injected onto a Philips model PU 4110M (Cambridge, U.K.) liquid chromatograph equipped with a 4.6 × 250 mm Zorbax octadecyl-bonded silica column (Rockland Technology, Rockville, MD). A Philips model PU 4110 variable UV detector with a 9-μL cell volume set at 254 nm was used for detection. The column was operated in reversed-phase mode using a mobile phase of water and methanol (10:90 vol %). Calibration standards were injected so as to generate an area−concentration calibration curve. The relative standard deviation of peak areas for each component based on three replicate injections was less than 1%. The calibration curves obtained (with regression coefficients of better than 0.999) were used to establish the concentration of the PAHs in the collection vial. The mole fractions of the solutes were generally reproducible within ±3%.

Table 1. Solubilities of Acenaphthene (1) + Fluoranthene (2) + Triphenylene (3) in Supercritical CO_2 (Quaternary System)

	acenaphthene		fluoranthene		triphenylene	
P/bar	10^4x_1	SE (%)[a]	10^4x_2	SE (%)	10^4x_3	SE (%)
			$T = 308$ K			
121.6	23.95	19.39	3.16	34.07	0.15	21.35
152.0	26.22	23.56	3.68	29.66	0.18	16.04
182.4	29.84	24.72	4.38	33.82	0.24	31.98
212.8	30.79	17.45	4.95	36.58	0.25	18.89
243.2	32.83	21.89	5.36	34.26	0.28	17.00
273.6	35.17	28.14	5.82	37.51	0.34	32.31
304.0	37.04	31.43	6.36	36.84	0.38	42.18
334.4	39.02	25.39	6.63	41.55	0.41	41.01
354.6	39.91	28.52	6.74	35.53	0.43	33.89
average		24.50		35.54		28.29
			$T = 318$ K			
121.6	25.07	36.76	2.84	32.61	0.13	30.40
152.0	31.26	22.13	4.23	42.01	0.21	34.23
182.4	38.11	32.46	5.32	40.51	0.27	28.68
212.8	42.90	25.30	6.37	43.81	0.39	51.60
243.2	46.14	26.17	7.29	44.32	0.45	49.65
273.6	47.81	30.58	7.76	41.31	0.49	50.39
304.0	52.84	26.04	9.12	50.84	0.51	42.91
334.4	54.60	27.41	9.48	47.26	0.58	52.40
354.6	57.02	29.89	10.16	53.43	0.63	56.42
average		28.53		44.01		44.08
			$T = 328$ K			
121.6	24.45	16.07	1.60	−13.74	0.04	−36.05
152.0	36.08	24.33	3.01	0.38	0.23	59.93
182.4	50.81	43.49	5.05	21.63	0.54	136.34
212.8	61.80	53.92	6.66	22.53	0.74	141.17
243.2	70.69	58.81	8.50	35.27	1.02	173.63
273.6	80.42	74.76	10.10	41.40	1.17	174.94
304.0	76.67	58.73	10.96	39.78	1.16	152.58
334.4	85.67	54.76	12.14	40.43	1.16	119.85
354.6	88.80	49.43	12.99	40.73	1.24	124.30
average		48.26		34.54		135.35
			$T = 338$ K			
121.6	14.92	9.00	0.52	−49.36		
152.0	34.40	11.57	2.08	−21.10	0.02	−81.04
182.4	47.69	1.22	6.93	60.15	0.25	9.82
212.8	62.97	5.27	9.95	61.90	0.39	10.36
243.2	71.43	0.47	9.66	31.36	0.34	−24.87
273.6	83.43	2.71	10.68	5.46	0.27	−50.78
304.0	98.98	14.03	13.34	30.59	0.84	36.25
334.4	51.72	−43.45	15.23	35.25	0.96	39.29
354.6	47.37	−49.66	15.73	33.55	1.21	66.43
average		−5.43		36.89		0.68

[a] SE: solubility enhancement.

Results and Discussion

The reliability of the apparatus was preliminary checked by measuring the solubility of naphthalene in supercritical CO_2 at 308 K, as was described before.[20,22] The solubilities of the PAHs in a quaternary system (three PAHs plus CO_2) at the temperatures (308, 318, 328, and 338) K and in the pressure range from (121.6 to 354.6) bar were then determined. The resulting solubilities in terms of equilibrium mole fraction x of solute in supercritical CO_2 are summarized in Table 1. Each reported solubility is the average value of three replicate samples. The tabulated results also show the corresponding solubility enhancements relative to the binary solubility data.[24] Solubility enhancement is defined as the percent relative deviation of the quaternary solubility from the binary solubility of a component at the same temperature and pressure. The quaternary solubility data were measured at the same pressures and temperatures as those used for the binary solubility data so that direct comparisons between the data sets could be made, eliminating the need to interpolate. At each temperature, the binary and quaternary 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 acenaphthene, fluoranthene, and triphenylene in the quaternary system were found to be enhanced by up to 48.3, 44.0, and 135.35, respectively. Similar results were reported for other ternary or quaternary systems.[11,12,15]

From the data given in Table 1, it is readily seen that as a binary system the solubility of PAHs increases with increasing pressure at constant temperature. The influence of pressure on the solubilities is more pronounced at higher temperatures. This is in contrast to conventional wisdom stating that the SF density must increase in order to increase the solubility and extraction efficiency.[25,26] The crossover pressure of acenaphthene is located at about 120 bar, and those of fluoranthene and triphenylene are located at about 150 bar.

Mixture Separation. The data obtained for binary systems of PAHs in our previous study[24] allow some comments to be made regarding the use of SFs to separate solid mixtures. The selectivity of the SF is defined as

$$S = x_1/x_2 \tag{1}$$

where x_1 and x_2 are the mole fractions of more and less soluble components in SF, respectively. Figure 1 shows the predicted selectivity of SF as a function of pressure for acenaphthene + triphenylene, acenaphthene + fluoranthene, and fluoranthene + triphenylene mixtures at different temperatures based on binary solubility data.[24] At low pressures, the selectivity is simply the ratio of the pure-solid vapor pressure. At higher pressure, the selectivity decreases sharply and levels off at a constant value for high pressures. On the other hand, the selectivity increases at higher temperatures. In this work we try to reach the optimum condition for extraction and separation of different PAHs. According to Figure 1, at low pressure, 120 bar, and 338 K or higher temperatures, the best selectivity was observed. On the other hand, because of the low solubility of various species, the efficiency of extraction is too low. Thus, for one-step separation of equimolar solid mixtures of acenaphthene + triphenylene, acenaphthene + fluoranthene, and fluoranthene + triphenylene, supercritical CO_2

Table 2. Mole Fraction, Selectivity, and Purity of PAHs in a Ternary System at 328 K and 120 bar

binary solid mixture	x_1	x_2	x_3	S_1[a]	S_2[b]	purity[c]/%
acenaphthene + triphenylene	2.55×10^{-3}		1.73×10^{-5}	147.40	351.00	99
acenaphthene + fluoranthene	2.55×10^{-3}	2.27×10^{-4}		11.23	11.32	90
fluoranthene + triphenylene		2.14×10^{-4}	2.14×10^{-5}	10.00	31.00	89

[a] Selectivity (x_1/x_2) based on ternary solubility data. [b] Selectivity based on binary solubility data. [c] Purity of the more soluble analyt.

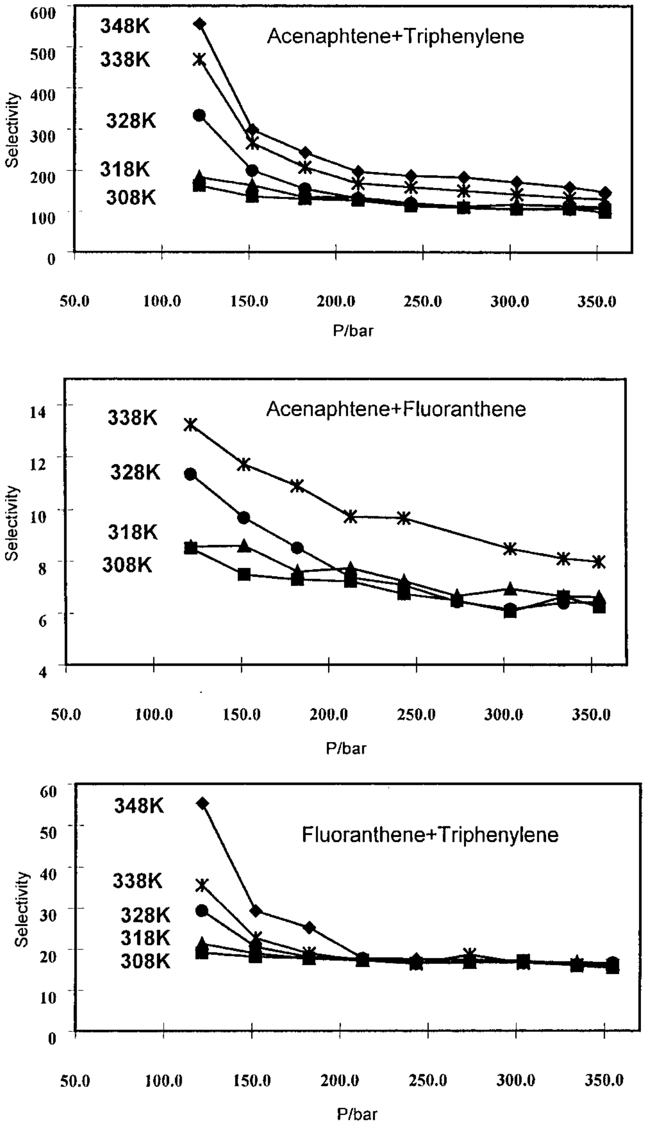

Figure 1. Plots of predicted selectivity versus pressure based on the binary system data (plotted based on results obtained in ref 24).

at 328 K and 120 bar was used (Table 2). Under these conditions, separation of acenaphthene from acenaphthene + triphenylene and acenaphthene + fluoranthene mixtures and fluoranthene from a fluoranthene + triphenylene mixture with purities of 99, 90, and 89%, respectively, are feasible. It is obvious that these purities are less than those predicted from the binary data. If the extracted-solute mixture is precipitated in a different extractor and again put into contact with fresh supercritical CO_2 under the same conditions, no further separation results. This is, in effect, an azeotropic situation. Table 2 indicates that the selectivity of supercritical CO_2 in ternary systems decreases in comparison to that predicted from the binary data. For example, the selectivity of supercritical CO_2 based on binary solubility data for an acenaphthene + triphenylene system ($S = x_{\text{acenaphthene in binary system}}/x_{\text{triphenylene in binary system}}$) is 351. On the other hand, the selectivity of supercritical CO_2 for that mixture based on ternary solubility is reduced to 147.

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