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Separation of Aromatic Compounds Using Retrograde Crystallization in Supercritical Fluid

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We measured the solubilities of pure solids of anthracene, fluorene, acridine, and binary solid mixtures of phenanthrene+anthracene, fluorene+acridine in supercritical CO₂ to determine the appropriate conditions for purification of polycyclic aromatics or heterocyclic compounds using a retrograde crystallization technique. Moreover we attempted to separate specific compounds from these two solid mixtures. As a result, it was found that (1) the crossover region of 2 kinds of solid mixtures in supercritical CO₂ was sufficiently wide to isolate the solid component from the mixture; (2) the Peng–Robinson equation of state gave good predictions for solubilities of pure solids but gave poor predictions for those of the solid mixtures in supercritical CO₂; and (3) phenanthrene, fluorene and acridine of high purity were separated from the solid mixtures, but anthracene was not as its amount predicted from the solubility data was very small.

1. Introduction

In the past decade, much attention has been paid to the use of supercritical fluids as extraction solvents in separation processes¹⁾. The supercritical fluid extraction is especially useful for extracting relatively light hydrocarbons from viscous multicomponent mixtures such as distillation residuum oils and coal tars. However, one of the serious problems for its industrial application is that selectivity of separation is not high. Therefore, it is difficult to purify a specific component from a mixture with similar physical and chemical properties.

Recently several attempts have been made to purify valuable materials using retrograde crystallization from supercritical fluids^{2)~4)}. The technique is based on the following: solubility isotherms at different temperatures intersect at certain pressure called crossover pressure; an increase in temperature causes a decrease in solubility below this pressure, while the opposite effect occurs above the pressure; and a specific component is deposited selectively from the supercritical fluid saturated with many kinds of solutes when each solute has a different crossover

pressure.

The advantage of this purification technique is that it has high separation selectivity. It can avoid thermal decomposition and polymerization of the solutes because it is operated near room temperature, and it does not use toxic solvents. On the other hand, there are such problems as requiring experimental data on phase equilibrium to determine the operating conditions and that the solvent power of the supercritical fluid is not so large for low volatile hydrocarbons.

The objectives of the present work are to determine the crossover pressures of polycyclic aromatics or heterocyclic compounds in supercritical fluids based on the solubility data and to purify the compounds using the retrograde crystallization technique. These compounds are promising as new materials for advanced polymers and fine chemicals. Phenanthrene+anthracene and fluorene+acridine were chosen as solid mixtures to be purified and supercritical CO₂(SC-CO₂) was used as supercritical fluid.

2. Experimental Section

Solubilities of pure solids and solid mixtures in SC-CO₂ were measured with a flow-type apparatus. Details of the apparatus and procedures are available elsewhere⁵⁾.

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Fig. 1 Experimental Apparatus Used for Retrograde Crystallization

A schematic flow diagram of the apparatus used for retrograde crystallization is shown in **Fig. 1**. Liquid CO_2 compressed by a high pressure pump(2) flowed into a preheating coil(5) and became supercritical. The pressure of SC-CO_2 was controlled by a back-pressure regulator(3). SC-CO_2 then entered a saturator(8) placed in the first constant temperature bath(4), and the phase equilibrium between SC-CO_2 and solid mixture was achieved in this vessel. The saturator was a 25-cm long stainless tube, 6-mm inner diameter, and packed with a granulated solid mixture. After flowing past the saturator, SC-CO_2 dissolving the solid mixture entered a crystallizer(11), 8 mm in O.D. $\times$ 6 mm in I.D. $\times$ 200 mm in length, immersed in the second constant temperature bath(10) and the specific component was deposited out of SC-CO_2 due to the decrease in its solubility by temperature change. After passing through the crystallizer, the flow was expanded to atmospheric pressure by a micrometering valve(15). The valve was also used to adjust the flow rate which was measured by a digital mass flowmeter(18). The line between the air bath and the water bath was heated at the same temperature as that of the air bath to avoid solid deposition. SC-CO_2 was forced to flow for more than 12 hours with a flow rate of 10-20 cm^3/min at 273 K and 101.3 kPa.

At the end of the run, SC-CO_2 in the crystallizer was purged by pure CO_2 , whose pressure was almost the same as that in the crystallizer, supplied through a valve(22), to minimize contamination by

deposition of solids in SC-CO_2 during depressurization. The composition of the precipitate in the crystallizer was analyzed by using a gas chromatograph.

In both apparatuses for solubility measurement and purification, the temperature was measured with a calibrated platinum resistance thermometer with an accuracy of ± 0.1 K, and the pressure was measured by using a calibrated digital pressure gauge with an accuracy of ± 0.01 MPa. The GC column was a 0.25 mm(dia.) $\times$ 30 m DB-1 column and a FID detector was used. Analytical accuracy of the solutes was within 1.0%.

The purity of CO_2 gas was more than 99.9 vol%; that of phenanthrene, anthracene and acridine more than 98 wt%; and that of fluorene more than 95 wt%. These were used without further purification.

3. Solubilities of Pure Solids and Solid Mixtures in SC-CO_2

Solubilities of pure solids of anthracene, fluorene, acridine, and binary solid mixtures of phenanthrene+anthracene, fluorene+acridine in SC-CO_2 were measured in the temperature range from 308 to 338 K to determine the operating conditions for the retrograde crystallization process. The solubility data of three pure solids are presented in **Tables 1** through **3**. The solubility data of anthracene were compared with those in the literature^{6),7)} to check the reliability of the experimental apparatus and procedure. The

Table 1 Solubility of Anthracene in Supercritical CO₂

Temperature [K]	Pressure [MPa]	Solubility [mole fraction]
308.1	9.90	3.470e-05
308.2	12.26	4.670e-05
308.1	14.02	5.490e-05
308.2	16.87	6.440e-05
308.1	19.81	7.080e-05
308.1	22.95	7.590e-05
308.1	25.60	8.260e-05
308.2	28.24	8.640e-05
337.9	10.20	4.000e-06
337.8	11.67	1.250e-05
338.1	14.32	5.000e-05
338.1	16.08	7.990e-05
337.9	18.24	1.108e-04
337.9	19.81	1.363e-04
338.1	21.77	1.653e-04

Table 2 Solubility of Fluorene in Supercritical CO₂

Temperature [K]	Pressure [MPa]	Solubility [mole fraction]
318.1	12.94	1.646e-03
318.1	14.61	2.031e-03
318.1	16.77	2.481e-03
318.1	18.53	2.642e-03
318.1	20.59	2.885e-03
318.1	22.95	3.078e-03
338.1	13.73	1.219e-03
338.1	14.71	1.720e-03
338.1	15.40	2.071e-03
338.1	16.48	2.644e-03
338.1	17.46	3.017e-03
338.1	19.81	3.859e-03
338.1	21.38	4.423e-03
338.2	24.03	5.257e-03

Table 3 Solubility of Acridine in Supercritical CO₂

Temperature [K]	Pressure [MPa]	Solubility [mole fraction]
318.2	12.94	7.154e-04
318.2	14.71	9.105e-04
318.2	16.77	1.069e-03
318.2	18.63	1.196e-03
318.0	20.69	1.309e-03
318.1	22.75	1.408e-03
338.1	13.93	4.295e-04
338.2	15.30	6.528e-04
338.1	16.77	9.764e-03
338.1	17.75	1.123e-03
338.1	19.32	1.405e-03
338.0	20.59	1.659e-03
338.1	21.77	1.764e-03
338.1	23.63	2.003e-03

results are shown in **Fig. 2**. Our data agreed well with those of literature reported by Johnston *et al.* The solubility isotherms of solid mixtures of phenanthrene+anthracene and fluorene+acridine are shown graphically in **Figs. 3** and **4**. The crossover pressure, in which the isotherms at different temperatures intersect each other, was 16.1 MPa for phenanthrene and 14.6 MPa for anthracene at 308 and 338 K, and 17.2 MPa for fluorene and 19.0 MPa for acridine at 318 and

Fig. 2 Comparison of Experimental Solubilities of Anthracene in SC-CO₂ at 308 K with Those in Literature

---: Solubilities of corresponding pure solids.

Fig. 3 Solubility Isotherms of Mixture of Phenanthrene+Anthracene in SC-CO₂ at 308 and 338 K

338 K. The temperature dependence of solubility reversed at the crossover pressure. The increase in temperature led to the increase in solubility above the crossover pressure, while the same condition of temperature led to the decrease below the crossover pressure. **Figure 3** also shows a comparison of the solubilities of pure solids with those of solid mixture of phenanthrene+anthracene at 308 and 338 K. The solubility of more soluble component (phenanthrene) in the solid mixture was almost the same as that of the corresponding pure solid,

Fig. 4 Solubility Isotherms of Mixture of Fluorene+Acridine in SC-CO₂ at 318 and 338 K

while the solubility of less soluble component (anthracene) in the mixture was smaller than that of the pure solid. The solubility change for the more soluble component was common but, for the less soluble one, it was not common as in usual cases.

Solid solubility y_i in a supercritical fluid is given by

$$y_i = \frac{p_i^{\text{sat}}}{p} \frac{1}{\phi_i^{\text{v}}} \exp \left[\frac{v_i^{\text{s}}(p - p_i^{\text{sat}})}{RT} \right] \quad (1)$$

where p_i^{sat} is the vapor pressure of a solid, v_i^{s} is the molar volume of the solid, and ϕ_i^{v} is the fugacity coefficient of the solid in the supercritical fluid. The ϕ_i^{v} was calculated from the Peng-Robinson (PR) equation of state⁸⁾:

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (2)$$

The parameters of a mixture, a and b , were determined by

$$a = \sum_i \sum_j y_i y_j (1 - k_{ij}) (a_i a_j)^{0.5} \quad (3)$$

$$b = \sum_i \sum_j y_i y_j (1 - l_{ij}) \left[\frac{b_i + b_j}{2} \right] \quad (4)$$

where the parameters of a pure component, a_i and b_i , were calculated from the critical properties and acentric factor of the component, and the binary interaction parameters, k_{ij} and l_{ij} , were determined from the best fit to the solubility data of the pure solid in the supercritical fluid. p_i^{sat} was calculated from the Antoine equation:

$$\log p_i^{\text{sat}} = A - \frac{B}{T + C} \quad (5)$$

Most of the required properties and Antoine constants of the pure solids are available in the literature⁹⁻¹¹⁾ and some critical properties have been estimated by Lydersen method¹²⁾. The

Table 4 Physicochemical Properties of Pure Components

Component	T_c [K]	p_c [MPa]	ω [-]	v^{s} (298 K) [cm ³ /mol]	$\log p^{\text{sat}}$ [bar] = $A - B/(T[K] + C)$		
					A	B	C
CO ₂	304.2	7.37	0.225	—	—	—	—
Phenanthrene	873	2.89 ^{a)}	0.431	167.6	9.6310	4873.4	0
Anthracene	869.3	2.89 ^{a)}	0.426	142.6	7.1464	4397.6	0
Fluorene	820.8 ^{a)}	2.99 ^{a)}	0.428	138.2	9.2046	4561.8	0
Acridine	883.2 ^{a)}	3.19 ^{a)}	0.498	178.3	8.7208	4740.1	0

a) T_c , p_c were estimated by Lydersen method¹²⁾.

Table 5 Binary Interaction Parameters and Correlated Results with Peng-Robinson Equation of State

System	T [K]	k_{ij}	l_{ij}	Error [%] ^{a)}
CO ₂ +Phenanthrene ⁵⁾	308.3	0.1104	-0.00415	8.5
	337.9	0.1093	-0.01162	3.3
CO ₂ +Anthracene	308.1	0.1659	0.0803	4.7
	338.0	0.1122	0.00248	7.1
CO ₂ +Fluorene	318.1	0.0639	-0.0646	1.6
	338.1	0.0425	-0.1034	2.7
CO ₂ +Acridine	318.2	0.00323	-0.2457	2.4
	338.1	0.00080	-0.2486	2.2

a) Error (%) = $\frac{1}{n} \sum_{i=1}^n \frac{|y_i^{\text{exp}} - y_i^{\text{cal}}|}{y_i^{\text{exp}}} \times 100$.

Fig. 5 Calculated Solubilities of Acridine in SC-CO₂ with PR Equation

Fig. 6 Calculated Solubilities of Mixture of Fluorene+Acridine in SC-CO₂ with PR Equation ($k_{23}=l_{23}=0$)

values are summarized in Table 4.

The regressed binary interaction parameters and correlated deviations for CO₂+pure solid systems are given in Table 5. Calculated results of the CO₂+acridine system are given in Fig. 5. The PR equation correlated the solubilities of the pure solids satisfactorily. Figure 6 shows the solubility of the solid mixture of fluorene+acridine predicted by the PR equation, where the binary interaction parameters between the two solids were assumed to be zero to the first approximation. The predicted results were in fairly good agreement with the experimental results at 318 K but not

$$k_{12}=0.0425, l_{12}=-0.1034, k_{13}=0.00080, l_{13}=-0.2486.$$

Fig. 7 Influence of k_{23} and l_{23} on Calculated Solubilities for CO₂(1)+Fluorene(2)+Acridine(3) System at 338 K

at 338 K. Figure 7 shows the influence of k_{23} and l_{23} on the calculated result of the solid solubility for the CO₂+fluorene+acridine system at 338 K, where subscripts 2 and 3 mean the 2 kinds of solids in SC-CO₂. Increase in k_{23} at constant l_{23} caused a decrease in the solubility of both solids, and increase in l_{23} at constant k_{23} gave the opposite effect on the solid solubility. Judging from Fig. 7, the PR equation could not satisfactorily predict the solubility of solid mixtures especially in the region where solubility changed with pressure steeply. As a result, the crossover pressure of the solid mixtures had to be determined experimentally.

4. Purification of Binary Solid Mixtures

As shown in Figs. 3 and 4, the crossover region between the crossover pressures of both solid components was from 14.6 to 16.1 MPa for CO₂+phenanthrene+anthracene system and from 17.2 to 19.0 MPa for CO₂+fluorene+acridine system. Purification of phenanthrene and anthracene in the mixture was performed at 15.0 and 15.7 MPa in the crossover region. Under these pressure conditions, lowering the temperature from 338 to 308 K should cause deposition of pure anthracene from SC-CO₂ containing both phenanthrene and

PHT: Phenanthrene, ANT: Anthracene.

Fig. 8 Comparison of Recovery of Phenanthrene and Anthracene from Their Mixture Using Retrograde Crystallization with That Using Conventional Supercritical Fluid Extraction

FL: Fluorene, ACR: Acridine.

Fig. 9 Comparison of Recovery of Fluorene and Acridine from Their Mixture Using Retrograde Crystallization with That Using Conventional Supercritical Fluid Extraction

anthracene, while raising the temperature should cause deposition of pure phenanthrene owing to the retrograde crystallization phenomenon, which is the reverse solubility behavior of solubility *versus* temperature. On the other hand, purification of the solid mixture of fluorene+acridine was carried out by increasing the temperature from 318 to 338 K at 17.5 MPa to precipitate pure acridine and by decreasing it from 338 to 318 K at 18.3 MPa to precipitate pure fluorene. Theoretically, this method has infinite selectivity in a single stage for purification of a solid mixture containing two components.

Figures 8 and 9 present the experimental results for purification of the solid mixtures of phenanthrene+anthracene and fluorene+acridine using this process. Phenanthrene was deposited and its purity was more than 99.9 wt% but none was

deposited for anthracene from the 50 wt%-50 wt% mixture. This was because the deposit of anthracene was very small, less than 0.04 mg/gCO₂, and it was difficult to entrap it in the crystallizer. The maximum purity of fluorene was 90.9 wt% and that of acridine 92.0 wt%. The contamination of the deposits was caused by the insufficient replacement of SC-CO₂ dissolving both solutes by pure CO₂. The impurities precipitated during depressurization at the end of the experiment. On the other hand, a single-stage conventional supercritical fluid extraction gave much less selectivity for separation of solid mixtures. Compositions of the extracts predicted from the solubility data are also given in these figures.

Amounts of the precipitates per gram of CO₂ are given in the parentheses in Figs. 8 and 9. The

recovery, which was defined by the ratio of the actual amount of the precipitate to the expected amount of the precipitate from solubility data, was 50-75% for each experiment except for anthracene.

5. Conclusions

Solubilities of pure solids of anthracene, fluorene, acridine, and solid mixtures of phenanthrene+anthracene, fluorene+acridine in supercritical CO₂ were measured in the temperature range from 308 to 338 K. Their solubility data showed that the crossover region for both mixtures was sufficiently wide to isolate each component from the mixtures by using the retrograde crystallization technique. Experimental data were correlated by the Peng–Robinson equation of state with 2-parameter mixing rules. This equation correlated the solubility of the pure solids well. However it gave poor prediction for the solid mixtures in supercritical CO₂.

Separation of each component in the mixtures of phenanthrene+anthracene and fluorene+acridine was examined by using retrograde crystallization from supercritical CO₂. As a result, the solids of high purity could be obtained from the mixtures except for anthracene.

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Nomenclatures

A, B, C	: Antoine constants	[—]
a	: energy parameter of equation of state	[MPa cm ⁶ mol ⁻²]
b	: size parameter of equation of state	[cm ³ mol ⁻¹]
k, l	: binary interaction parameters	[—]

n	: number of data points	[—]
p	: system pressure	[MPa]
p_c	: critical pressure	[MPa]
p^{sat}	: vapor pressure	[MPa]
R	: gas constant	[MPa cm ³ mol ⁻¹ K ⁻¹]
T	: system temperature	[K]
T_c	: critical temperature	[K]
v	: molar volume	[cm ³ mol ⁻¹]
v^S	: solid molar volume	[cm ³ mol ⁻¹]
y	: mole fraction of solid in supercritical fluid phase	[—]
ϕ^v	: fugacity coefficient of solid in supercritical fluid phase	[—]
ω	: acentric factor	[—]
<Subscripts>		
i, j	: components i and j	
1	: supercritical CO ₂	
2, 3	: solids	

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要 旨

超臨界流体中での逆行析出現象を用いる芳香族化合物の分離

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逆行析出分離法による多環芳香族および複素環式化合物の精製に必要な基礎データを得るために, 超臨界 CO₂ 中の純アントラセン, 純フルオレン, 純アクリジン, フェナントレン+アントラセン混合物, フルオレン+アクリジン混合物の溶解度を測定した。さらに, 上記の 2 種類の混合物から各成分を単離することを試みた。その結果, (1) 超臨界 CO₂ 中において 2 種類の混合物の交差圧力領域は十分広いので, 混合物中の各成

分を単離できること, (2) Peng-Robinson 状態方程式は超臨界 CO₂ 中の純固体の溶解度を良好に表すことができるが, 固体混合物の場合には推算誤差が大きくなること, (3) フェナントレン, フルオレンおよびアクリジンは混合物中から高純度で単離できるが, アントラセンは溶解度データから予想されるように析出量が非常に少ないために, 分析可能な量を捕集することが困難であることが明らかになった。

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Keywords

Separation, Retrograde crystallization, Solubility, Supercritical carbon dioxide, Aromatics