PURIFICATION OF POLYCYCLIC AROMATIC COMPOUNDS USING RETROGRADE CRYSTALLIZATION IN SUPERCRITICAL CARBON DIOXIDE

TAKESHI SAKO AND MASAHITO SATO
Chemical Systems Division, National Chemical Laboratory for Industry,
Ibaraki 305

SUMIYO YAMANE
Department of Industrial Chemistry, Shibaura Institute of Technology,
Tokyo 108

Key Words: Purification, Retrograde Crystallization, Supercritical Carbon Dioxide, Naphthalene, Phenanthrene

Introduction

In the past decade, much attention has been given to the use of supercritical fluids as extraction solvents in separation processes. Supercritical fluid extraction is especially useful for extracting relatively light hydrocarbons from viscous multicomponent mixtures such as residuum oil of distillation and coal tar. However, a serious problem in its industrial application is that the selectivity of the separation is not high and, therefore, it is difficult to purify a specific component from a mixture with similar physical and chemical properties.

Recently a novel technique was proposed for separation and purification using retrograde crystallization from supercritical fluid, and several attempts have been made to use it for purifying valuable materials such as alkaloids. The technique is based on the following facts: solubility isotherms at different temperatures intersect at a certain pressure called the crossover pressure and an increase in temperature causes a decrease in solubility below this pressure, while the opposite effect occurs above this pressure; and a specific component is deposited selectively from a supercritical fluid saturated with many kinds of solutes when each solute has a different crossover pressure.

The objective of the present work is to construct an apparatus for separation based on the retrograde crystallization phenomena in supercritical fluid and to investigate the feasibility of purifying polycyclic aromatic hydrocarbons, which are very promising as new materials for advanced polymers and fine chemicals. Naphthalene (NA) and phenanthrene (PHT) were chosen as solids to be purified from their mixture and CO₂ was used as the supercritical fluid.

1. Experimental Apparatus and Procedure

Figure 1 shows a schematic flow diagram of the experimental apparatus used for the retrograde crystallization. Liquid CO₂ compressed by a high-pressure pump (2) flowed into a preheating coil (5) and reached supercritical condition. The pressure of the supercritical CO₂ (abbreviated SCCO₂) was controlled by a back-pressure regulator (3) within an accuracy of 0.02 MPa. The SCCO₂ then entered a saturator (7) placed in the first constant-temperature bath (4) and phase equilibrium between the SCCO₂ and solid mixture was achieved in this vessel. The saturator consisted of a 25 cm-long stainless tube of 6-mm inner diameter and was packed with a granulated solid mixture. The temperatures of the saturator and SCCO₂ were controlled within 0.1 K by an air bath. After flowing past the saturator, the

---

* Received August 17, 1990. Correspondence concerning this article should be addressed to T. Sako. S. Yamane is now with Nippon Senso K. K., Kanagawa 210.
SCCO$_2$ in which the solid mixture was dissolved entered a crystallizer (13) immersed in the second constant-temperature bath (10) and a specific component was deposited out of the SCCO$_2$ 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 (16). The valve was also used to adjust the flow rate, which was measured by a digital mass flow meter (19). The line between the air bath and water bath was heated to the same temperature as that of the air bath to avoid depositing the solid, and the line between the water bath and micrometering valve was heated to about 350 K.

At the end of the run, the SCCO$_2$ in the crystallizer was purged by pure CO$_2$ at almost the same pressure as that in the crystallizer, supplied through a valve (8) to minimize contamination during depressurization by deposition of the solid in the SCCO$_2$. The composition of the solid phase in the crystallizer was analysed by HPLC equipped with UV detector. A 15 cm × 6 mm ODS column was used with an eluent containing 70 vol% acetonitrile and 30 vol% water. The purity of CO$_2$ gas was more than 99.9% and that of NA and PHT more than 99 mol%. These were used without further purification.

2. Results and Discussion

The solubilities of NA and PHT for the CO$_2$-NA-PHT system were measured at 308.2 and 328.2 K in order to determine the operating condition for the retrograde crystallization process. Details of the apparatus used are available elsewhere. The solubility isotherms of both components are given graphically in Fig. 2. The crossover pressure in which the isotherms at the different temperatures (308.2 and 328.2 K) intersect each other, was 12 MPa for NA and 23 MPa for PHT. As is evident in Fig. 2, the temperature dependence of the solubility was reversed at the crossover point; that is, an increase in temperature led to an increase in solubility above the crossover pressure, while the same effect led to a decrease in solubility below the crossover pressure. The crossover region between the crossover pressures of the two components was from 12 to 23 MPa for the CO$_2$-NA-PHT system. Therefore, the purification of each component in the mixture of NA and PHT was made at 14 MPa in the crossover region. Under this pressure condition, raising the temperature from 308.2 to 328.2 K should cause the deposition of pure PHT from SCCO$_2$ containing both NA and PHT, while lowering the temperature from 328.2 to 308.2 K should cause the deposition of pure NA, owing to the inverse solubility-versus-temperature behavior called the retrograde crystallization phenomenon. This method has theoretically infinite selectivity in a single stage for purification of the mixture. On the other hand, a single-stage supercritical fluid extraction gives a solid product containing only 15 wt% PHT at 308.2 K or 4 wt% PHT at 328.2 K.

Table 1 gives the solubilities of NA and PHT in SCCO$_2$ at 14 MPa and the two temperatures (308.2 and 328.2 K) employed in this retrograde crystallization process. Table 2 presents the experimental results for the purification of PHT and NA using this process. The highest recovery was 97.1 wt% for PHT and 96.5 wt% for NA from a binary solid mixture composed of 50 wt% NA and 50 wt% PHT. The best value of the purity enhancement factor was 33.5 for PHT and 27.6 for NA, where the purity enhancement factor was defined as the ratio of the mass of the objective compound/the mass of the other compound in the precipitate to that in the feed. It should theoretically be possible to obtain the pure component PHT or NA under this experimental condition, but a small amount of impurity contaminated the product during the depressurization at the end of the experiment due to insufficient replacement of the SCCO$_2$ containing both solutes by pure CO$_2$.

Conclusions

The separation of each component in a mixture composed of naphthalene and phenanthrene was examined by using retrograde crystallization from supercritical CO$_2$. The crossover region at 308.2 and 328.2 K for the CO$_2$-naphthalene-phenanthrene system was between 12 and 23 MPa. Therefore, pure phenanthrene was deposited at 14 MPa by increasing the temperature from 308.2 to 328.2 K, while pure naphthalene was deposited at the same pressure by
Table 2. Recovery of phenanthrene and naphthalene from mixture composed of 50 wt% phenanthrene and 50 wt% naphthalene

<table>
<thead>
<tr>
<th>$p$ [MPa]</th>
<th>$T_1^1$ [K]</th>
<th>$T_2^2$ [K]</th>
<th>Composition of precipitate</th>
<th>Purity enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) purification of phenanthrene</td>
<td>14.2</td>
<td>308.2</td>
<td>328.2</td>
<td>97.1</td>
</tr>
<tr>
<td>(2) purification of naphthalene</td>
<td>13.9</td>
<td>328.2</td>
<td>308.2</td>
<td>3.5</td>
</tr>
</tbody>
</table>

*1: Temperature in saturator  *2: Temperature in crystallizer

decreasing the temperature from 328.2 to 308.2 K. As a result, we could obtain 97.1 wt% phenanthrene and 96.5 wt% naphthalene, respectively, from a mixture containing equal mass of the two components.

Acknowledgement

The authors wish to thank Professor I. Yamada of Nagoya Institute of Technology for his helpful advice and Mr. T. Taguchi for his assistance in the experimental work.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td>naphthalene</td>
</tr>
<tr>
<td>$p$</td>
<td>pressure</td>
</tr>
<tr>
<td>PHT</td>
<td>phenanthrene</td>
</tr>
<tr>
<td>SCCO$_2$</td>
<td>supercritical CO$_2$</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$T_1$</td>
<td>temperature in saturator</td>
</tr>
</tbody>
</table>

$T_2$ = temperature in crystallizer [K]

$y$ = mole fraction of solute in supercritical fluid phase [—]

Literature Cited