SOLUBILITY AND RESS EXPERIMENTS OF SOLID SOLUTION IN SUPERCRITICAL CARBON DIOXIDE

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An anthracene+phenanthrene mixture forms a solid-solution over the whole composition range. The solubility of anthracene+phenanthrene in supercritical carbon dioxide were measured for the mixture of pure solids and the solid solution at 35°C and between 10.6 and 24.6 MPa. The solubility data of the former were fitted by the Peng-Robinson equation of state (PR EOS), and those of the latter were correlated by the PR EOS and the Wilson equation for a solid phase.

RESS (Rapid expansion from supercritical solution) experiments for pure anthracene, pure phenanthrene and the anthracene+phenanthrene mixtures were performed to study the influence of the operating conditions on the solid formation with emphasis on separation as well as morphology. In the case of RESS for pure compounds, a decrease in the solute concentration brought about an increase in particle size. Operating conditions have scarcely any influence for the mixtures. The particles produced from the CO2 solution containing anthracene and phenanthrene were all homogeneous crystals of the solid solution. It was confirmed on the basis of observations by an optical microphotograph and an X-ray diffractometer. Most of the RESS experiments were carried out at an extraction temperature of 35°C and pressure of 17.0 MPa.

Introduction

Most applications of supercritical fluids have been extractions and separations. Design of these processes requires accurate predictions of the phase behavior, which remains a challenging task (Hutchenson and Foster, 1995).

The solubility of a solid in a supercritical fluid is a sensitive function of both the temperature and pressure of the solution such that even small decreases in pressure produce dramatic changes in the solubility of the dissolved material. The ability of a supercritical fluid (SCF) to separate a multicomponent mixture is based on the difference in volatilities as well as specific interactions between the solute component and the SCF solvent. Thus, it utilizes the salient features of both distillation and extraction processes in the chemical, petrochemical, food, and pharmaceutical industries.

The potential applications of supercritical fluid extraction have resulted in widespread laboratory techniques for the determination of solubilities of the solute in supercritical fluids. Data on the solubilities of mixture solutes in supercritical fluids, however, are sparse (Liu and Nagahama, 1996a). In particular, the solubility data of a solid solution in a SCF, where components are miscible in the solid phase, have never been reported in literatures.

On the other hand, when a supercritical solution containing a solute is rapidly depressurized to near ambient conditions, the solute component becomes essentially insoluble and condenses as a solid in the low pressure gas. Such a rapid expansion of supercritical fluid solutions (RESS) (Matson et al., 1986) exploits this phenomenon. The rapid expansion of high pressure fluids can cause uniform perturbations within the nucleating medium, and thereby produce a narrow size distribution of particles. Recently, RESS has been extensively studied. It can be used to generate ceramic precursors (Matson et al., 1986, 1987a, b; Petersen et al., 1986), polymeric powders and fibers (Matson et al., 1987a; Petersen et al., 1986, 1987; Bush et al., 1991; Lele and Shine, 1992, 1994; Tom et al., 1994; Mawson et al., 1995), and fine powders of pharmaceutical or organic compounds with a narrow size distribution (Larson and King, 1986; Chang and Randolph, 1989; Mohamed et al., 1989a, b; Tom and Debenedetti, 1991; Berends et al., 1993; Reverchon et al., 1993, 1995; Ksibi et al., 1995). Besides, several theoretical studies concerning the dynamics as well as nucleation and growth of crystals for RESS processes have been published (Debenedetti, 1990; Lele and Shine, 1992; Kwaau and Debenedetti, 1993; Debenedetti et al., 1993; Shaub et al., 1995).

The main objectives of this article are to measure the solubility of anthracene+phenanthrene mixture in supercritical CO2 and to study its precipitation behavior by RESS. In this work, solubilities of two kinds of feed mixtures: a mixture of pure solids and a solid solution were first measured to investigate the difference in their solubilities in supercritical CO2.
Next, the feasibility of CO$_2$ as a solvent for producing submicron particles and for the fractional crystallization of organic mixtures was investigated. This work may be the first exploratory study on a binary solid solution with respect to its solubilities in supercritical CO$_2$ and coprecipitation by RESS.

1. Experimental

1.1 Experimental apparatus and methods

RESS experiment. The apparatus used for RESS experiments is shown schematically in Fig. 1 and the detail was described in our previous paper (Liu and Nagahama, 1996b). This allows the independent control of all process variables: pre- and post-expansion pressure, pre- and post-expansion temperature; and also supercritical solution composition before expansion. The apparatus is divided into extraction, dilution, and precipitation units.

In the extraction unit, a carbon dioxide solvent was supplied from a gas cylinder and liquefied through a cooler, C (Scinics Co., CH-201), then pressurized by a HPLC pump (Jasco, PU-980) at a constant flow rate under the desired pressure. Cell E (stainless steel, 22 cm length, 2.2 cm o.d.) was used. For a pure solid crystallization experiment, the cell E was charged with about 3 g of the pure solute. For crystallization experiments of a mixture of pure solids, cell E was charged with about 5 g of an equal weight of mixture of anthracene and phenanthrene. In the case of precipitation run for a solid solution, the solid mixture of a given composition, which was melted to form a homogeneous liquid, then cooled to crystallize, and granulated, was charged into the cell.

As a dilution unit, a second HPLC pump (Jasco, PU-980) was used to introduce a diluent solvent (CO$_2$) to adjust the pre-expansion composition before entering the crystallizer. In this manner, independent control of the composition of the supercritical solution prior to expansion was obtained.

In the precipitation unit, the supercritical fluid mixture exiting the equilibrium cell or the dilution unit entered a thermostated injection line, and was throttled across a fine-diameter orifice. In this study, a 0.28-mm thick, 35-μm diameter orifice (L/D=8) has been mainly used, along with one of 75 μm diameter. The orifice was observed by a microscope before and after each run to ensure that it was not clogged with fine particles. The expanded fluid is led into a visual observation cell equipped with a see-through glass window and thermostated with a water bath. A sample of the precipitated crystals was then collected for analysis either on a small glass plate or in a small glass bottle (24 mm i.d.×50 mm), which was positioned at the center of the crystallization cell approximately 55 mm from the orifice exit. Two 2-μm frit filters were placed at the entrance of the preheated line and the exit of the precipitation cell to prevent plugging of the expansion nozzle and the metering valve. The crystallization pressure was controlled by a back-pressure regulator (Jasco Co., 880-81).

The running time of an experiment was varied from 25 to 35 minutes, and typical flow rates were between 1.2 and 2 standard liters per minute. At the end of a run, the feed pumps were stopped and the
system pressure was slowly lowered by bypassing with the micrometering valve. 

**Solubility Measurement** Solubility measurements of anthracene+phenanthrene mixture were carried out using the same apparatus as that of RESS experiments, but in this case the precipitation unit was replaced by a micrometering valve of the back-pressure regulator (Jasco Co., 880-81). Besides, in order to prevent valve clogging and solid deposition in the line and the valve of the regulator, a small amount of liquid toluene was added to the extracted supercritical fluid mixture under high pressure by the second HPLC pump (not shown in Fig. 1, see Liu and Nagahama, 1996a). The precipitated solutes via expansion were trapped in a cooled glass bottle charged with toluene. The amounts of anthracene and phenanthrene dissolved in toluene were determined by a gas chromatography analysis.

1.2 **Characterization**

The morphology of precipitated particles was observed with respect to their shape and size by an optical microscope (Olympus BH-2), and about 100 target particles were counted for determination of the particle size distribution. The crystallinities of the collected particles were analyzed through an X-ray diffractometer (MC Science, MXP3). The solid mixtures of anthracene and phenanthrene coprecipitated by RESS were dissolved into toluene and their composition was verified by a gas chromatograph (Simazu, GC-14A) with a capillary column. 2,6-Dimethylnaphthalene was added to the sample as an internal standard substance for GC analysis.

1.3 **Materials**

High purity carbon dioxide (more than 99.95%, Kayama Sanso Co.) was used. Commercially available phenanthrene (+98%) was obtained from Tokyo Kasei Co.. Reagent grade anthracene (+98%), 2,6-dimethylnaphthalene of +99% purity, and toluene of +99.5% purity were supplied from Wako Pure Chemical Industries Co.. All chemicals were used without further purification.

2. **Solubilities of Anthracene+Phenanthrene Mixture in Supercritical CO₂**

Before measuring the solubilities of anthracene+phenanthrene solid mixture in supercritical carbon dioxide, the solid-liquid equilibrium for this binary system were measured under atmospheric pressure with a differential scanning calorimetry (Seiko Co., DSC-200). As given in Fig. 2, where peak 1 corresponds to the liquid phase and peak 2 to the solid phase, this system is shown to be a perfect solid-solution system over the whole composition range, which agrees with the ICT data (Wasaburn et al., 1928).

For the past decade several solubility data of the mixtures of pure solids have been available. The mixture of anthracene+phenanthrene, however, forms a solid-solution as mentioned above, and we measured solubilities of two kinds of mixtures: a mixture of pure solids and a solid solution of known composition. The solubilities of the simple solid mixture composed of pure solid anthracene and pure solid phenanthrene in supercritical CO₂ were previously measured by Kwiatkowski et al. (1984) at 40°C, and Kosal and Holder (1987) at 35 and 45°C. Up to now, however, solubilities of the solid-solution mixture have been not available.

2.1 **Experimental results**

**Mixture of pure solids** For the experiments of the mixture of pure solids, a mixture containing a weight ratio of 0.3 – 0.7 of pure anthracene to pure phenanthrene solids was charged into the extraction cell. It is because in this case the solubility of each component in the fluid is thermodynamically independent of the mixed solid feed composition. The solubilities of the mixture of pure solids at 35°C are listed in Table 1 along with pressure, density of CO₂ (Angus et al., 1976) and phenanthrene composition on CO₂-free bases. As shown in Fig. 3, these experimental data are in excellent agreement with those of Kosal and Holder (1987).

**Solid solution** On the other hand, the solubility of the solid solution is dependent on its feed composition. In order to investigate the effect of composition of a solid solution on solubility, solubilities of five different composition of mixtures in SC CO₂ were measured at 35°C and 17.0 MPa. The data of the solid solution were shown along with feed composition and phenanthrene composition on CO₂-free bases in Table 2. The solubilities of phenanthrene
Table 1  Experimental solubilities of mixture of
pure phenanthrene and pure anthracene in
supercritical CO₂ at 35°C

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>(y_{ph} \times 10^4)</th>
<th>(y_{an} \times 10^5)</th>
<th>(\rho_1) (g/cm³)</th>
<th>(y_{ph}/(y_{ph}+y_{an}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.62</td>
<td>5.999</td>
<td>3.276</td>
<td>0.7341</td>
<td>0.9482</td>
</tr>
<tr>
<td>13.93</td>
<td>10.56</td>
<td>6.601</td>
<td>0.8010</td>
<td>0.9412</td>
</tr>
<tr>
<td>17.01</td>
<td>13.18</td>
<td>8.530</td>
<td>0.8387</td>
<td>0.9392</td>
</tr>
<tr>
<td>20.62</td>
<td>15.29</td>
<td>9.397</td>
<td>0.8712</td>
<td>0.9421</td>
</tr>
<tr>
<td>24.20</td>
<td>16.65</td>
<td>10.19</td>
<td>0.8966</td>
<td>0.9423</td>
</tr>
</tbody>
</table>

\[z_{ph} = 0.3 - 0.7.\]

Fig. 3  Solubilities of phenanthrene and anthracene in SC CO₂ (feed: mixture of pure solids) at 35°C

Table 2  Experimental solubilities of solid solution
of phenanthrene + anthracene in supercritical CO₂ at 35°C and 17.0 MPa

<table>
<thead>
<tr>
<th>Phenanthrene composition of solid</th>
<th>(y_{ph} \times 10^3)</th>
<th>(y_{an} \times 10^5)</th>
<th>(y_{ph}/(y_{ph}+y_{an}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>solution feed (z_{ph})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.891</td>
<td>1.325</td>
<td>4.201</td>
<td>0.9693</td>
</tr>
<tr>
<td>0.689</td>
<td>1.295</td>
<td>8.589</td>
<td>0.9378</td>
</tr>
<tr>
<td>0.503</td>
<td>1.324</td>
<td>8.512</td>
<td>0.9396</td>
</tr>
<tr>
<td>0.293</td>
<td>1.318</td>
<td>8.907</td>
<td>0.9367</td>
</tr>
<tr>
<td>0.116</td>
<td>1.396</td>
<td>11.58</td>
<td>0.9234</td>
</tr>
</tbody>
</table>

Fig. 4  Solubilities of solid solution in SC CO₂ at 35°C and 17.0 MPa: (a) dependence of solubilities on feed concentration (b) solid-fluid phase equilibrium relationship

and anthracene vs. the phenanthrene composition of
the solid solution are shown in Fig. 4(a), and the
relationship between solid composition of feed and
fluid composition of CO₂-rich phase on CO₂ free basis
is plotted in Fig. 4(b).

A moderate effect of the solid-solution feed
composition on solubilities in supercritical CO₂ was
observed. From the thermodynamical point of view,
this is because the number of Gibbs degrees of freedom
for the solid solution system is larger by one than that
of the mixture of two pure solids. For ternary systems
composed of one solid solution phase of two
components and one fluid phase, the number of degree
becomes three. So the solubility of the solid solution
in CO₂ depends on the composition of the solid phase
even when fixing the process variables such as pressure
and temperature. On the contrary the solubility of
the mixture of two pure solids is independent of its
composition under constant temperature and pressure
because the number of degree is two.

Those results listed in Tables 1 and 2 represent
the average of three separate experimental measure-
ments. The maximum deviation among the three
measurements was within ±5%.

2.2 Modeling of solubilities
Mixture of pure solid  The experimental solubility
data of the mixture of pure solids (Table 1) were
modeled in a usual way using the Peng-Robinson
equation of state (PR EOS, Peng and Robinson, 1976) with the van der Waals mixing rules. For the ternary system, the three binary interaction parameters were determined by minimizing the following objective function (OF). The OF is given by

$$OF = \sum_{i}^{N} \left[ \frac{|y_{i,3}^{exp} - y_{i,3}^{cal}|}{y_{i,3}^{exp}} \right] + \sum_{i}^{N} \left[ \frac{|y_{i,2}^{exp} - y_{i,2}^{cal}|}{y_{i,2}^{exp}} \right]$$

where $N$ is the number of experimental points, subscripts 1, 2 and 3 stand for CO$_2$, phenanthrene and anthracene. The three interaction parameters so determined are $k_{12}=0.056$, $k_{13}=0.069$ and $k_{23}=0.05$. A comparison between the experimental solubility data and predicted results for the solid mixture is also shown in Fig. 3. The correlated average deviations are 1.2% for phenanthrene and 3.6% for anthracene. The required properties for CO$_2$, anthracene and phenanthrene are the same as those given in the literature (Kosal and Holder, 1987).

Solid solution To correlate the solid solution-supercritical fluid equilibrium the solid phase was assumed to be represented by an activity coefficient like a liquid solution composed of phenanthrene and anthracene. For both components i in a solid solution phase, the fugacity is given by

$$f_i = P_i^{\mu i}/Z_i^{\mu i}[exp[\gamma_i(P - P_i^{\mu i})/RT]]$$

where $P_i^{\mu i}$ is the sublimation pressure, $\gamma_i$ the activity coefficient, $Z_i^{\mu i}$ the composition of component i in the solid solution, $v_i$ the molar volume, and $P$ and $T$ represent the system pressure and temperature, respectively. For the fluid phase, the fugacity of the component i is

$$f_i = y_i\phi_i/P$$

where $y_i$ is the mole fraction of component i in the fluid phase, $\phi_i$ the fugacity coefficient in this phase.

The solubilities of a solid solution in a supercritical fluid can be derived from the condition of equal fugacities in both phases.

$$y_i = \frac{P_i^{\mu i}/Z_i^{\mu i}[exp[\gamma_i(P - P_i^{\mu i})/RT]]}{P\phi_i}$$

In this work the Wilson equation (Wilson, 1964) was adopted to calculate the activity coefficient $\gamma_i$, and $\phi_i$ is calculated by the PR EOS. For the solid solution system, three binary interaction parameters of the PR EOS ($k_{ij}$) and two parameters of the Wilson equation ($A_{ij}$) were determined by minimizing the value of OF as mentioned previously in Eq. (1). The obtained values are $k_{12}=0.058$, $k_{13}=0.034$ and $k_{23}=0.05$ for the PR EOS, $A_{32}=0.99$ and $A_{32}=0.25$ for the Wilson equation, respectively. The average deviations for $y_2$ and $y_3$ are 29.9% for phenanthrene and 10.8% for anthracene. The correlated results are illustrated along with the experimental results in Fig. 4(a) and (b). As shown in Fig. 4(a), larger deviations for phenanthrene appear in the low phenanthrene composition range, but the agreement for anthracene is acceptably good.

3. RESS Experimental Results

Here, we discuss the precipitation of pure anthracene, pure phenanthrene, and two kinds of the anthracene+phenanthrene mixture from a CO$_2$ rich phase by RESS. All of these experiments were conducted under an extraction temperature of 35°C and an extraction pressure of 17.0 MPa, as well as an expansion chamber pressure of one atmosphere. Particle shape and size analysis was done by hand from optical photographs. Most runs were repeated at least twice or three times.

3.1 Pure anthracene

Solute concentration in the fluid phase is an important variable for controlling morphology (Mohamed et al., 1989a; Reverchon et al., 1993; Liu and Nagahama, 1996b). Until now, the precipitation of pure anthracene by RESS has not been reported in the literature. In order to investigate the effect of solute concentration on the particle sizes and morphology, we conducted several experiments under various concentrations by keeping other process variables constant. Figure 5 shows optical microphotographs of pure anthracene particles produced from the extracted (saturated) solution (Fig. 5(a)) and the diluted one (Fig. 5(b)). The latter's concentration may be about one-third of that of the former. As can be seen in Fig. 5, a profound change in morphology from 20 μm hexagonal particles to 45 μm dendritic particles takes place with an increase in the dilution. This trend of increase in particle size with decreasing the solute concentration is similar to the results reported by Mohamed et al. (1989a), Reverchon et al. (1993), and Liu and Nagahama (1996b). Mohamed et al. (1989b) explained their observation that decreasing particle size with increasing solute concentration was due to the result of higher nucleation rates, which in turn yield smaller growth rates. Therefore, a decrease in solute concentration results in an increase in particle size.

3.2 Pure phenanthrene

In our previous study (Liu and Nagahama, 1996b), we investigated the morphology of pure phenanthrene crystals produced by RESS and reported the shape of the crystal was needle-like. In this work, RESS experiments of pure phenanthrene were also performed under different pre-expansion concentrations. Figure 6 shows the morphology of pure phenanthrene precipitated by the expansion of
extracted (saturated) solution (Fig. 6(a) and the diluted one (Fig. 6(b)), respectively. Increasing the dilution ratio, the size of the needle particles grew larger as shown in Fig. 6. This observation corresponds to that of pure anthracene.

3.3 Mixture of anthracene+phenanthrene

Fractional crystallization of the eutectic organic mixture (naphthalene+phenanthrene) by RESS have been investigated by us (Liu and Nagahama, 1996b), and discussed using the enrichment factor $\beta$, as defined below:

$$\beta = \frac{x_{ph}/x_{an}}{y_{ph}/y_{an}}$$ \hspace{1cm} (5)$$

where $x_{ph}$ and $x_{an}$ are the mole fractions of phenanthrene and anthracene in precipitated solids, $y_{ph}$ and $y_{an}$ are the mole fractions of phenanthrene and anthracene in supercritical CO$_2$ under extracted conditions, where the values of $y$ were determined from experimental solubility data mentioned above. If $\beta$ is larger than unity, it means enrichment of phenanthrene is carried out by controlling RESS conditions.

Two series of RESS experiments for the anthracene+phenanthrene mixtures were performed: one was a precipitation experiment employing the feed of the mixture of pure solids and the other was that employing the feed of the solid solution. The former was conducted to vary pre-expansion (nozzle) and post-expansion (crystallization cell) temperatures. The latter was made by changing feed compositions of a solid-solution mixture. Results are given in Table 3 for the case of the mixture of pure solids and in Table 4 for the case of the solid-solution mixture, where $x_{ph}$ is a feed composition of the solute solution.

When employing the mixture of pure phenanthrene and pure anthracene, the increase of the
post-expansion temperature increases the enrichment factor slightly. However, the maximum enrichment factor was only 1.24 when the post-expansion temperature was 60°C. Comparing to the previous study for the naphthalene and phenanthrene mixture (Liu and Nagahama, 1996b), the enrichment factor is very small. This may be due to the difference of degree of supersaturation and second to the difference of physical properties of solid phase: an anthracene-phenanthrene mixture forms a solid solution and a naphthalene-phenanthrene mixture is a eutectic system. In addition, the change of pre-expansion temperature has no effect on fractional separation. This result qualitatively agrees with our previous study (Liu and Nagahama, 1996b). The morphology of precipitated particle by RESS employing the mixture of pure solids as a feed was presented in Fig. 7(a).

For the solid solution of phenanthrene and anthracene, as shown in Table 4, the compositions of precipitated crystals are almost equal to the pre-expansion composition ($\beta$s are close to 1). For all runs, the expansion chamber temperature was 25°C. Figure 7(b) shows the micrograph of particles precipitated through the expansion of a solid solution feed.

As shown in Fig. 7, the particles collected from the RESS of the solid solution were almost the same as those from the RESS of the mixture of pure solids with regard to the size and shape. The average particle sizes were 3.5 $\mu$m for the case of the mixture of pure solids, and 3.8 $\mu$m for the case of the solid solution. Regardless of state of feed mixture, once it dissolved in SC CO$_2$ the properties of this supercritical solution are always identical.

Comparing to the morphologies of particles of pure anthracene (Fig. 5(a)), pure phenanthrene (Fig. 5(b))

### Table 4 RESS experiments of solid solution using SC CO$_2$

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Composition of feed $x_{ph}$</th>
<th>Composition of crystals $X_{ph}$</th>
<th>Pre-expansion composition $y_{ph}/(y_{ph} + y_{um})$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>0.8906</td>
<td>0.9655</td>
<td>0.9693</td>
<td>0.886</td>
</tr>
<tr>
<td>K2</td>
<td>0.6685</td>
<td>0.9388</td>
<td>0.9378</td>
<td>1.02</td>
</tr>
<tr>
<td>K3</td>
<td>0.5035</td>
<td>0.9390</td>
<td>0.9396</td>
<td>0.990</td>
</tr>
<tr>
<td>K4</td>
<td>0.2931</td>
<td>0.9397</td>
<td>0.9367</td>
<td>1.05</td>
</tr>
<tr>
<td>K5</td>
<td>0.1160</td>
<td>0.9269</td>
<td>0.9234</td>
<td>1.05</td>
</tr>
</tbody>
</table>

$P_{ex}$=17.0 MPa, $T_{ex}=35^\circ$C, $T_{pre}=135^\circ$C, $T_{post}=25^\circ$C.

### Table 3 RESS experiments of mixture of pure solids using SC CO$_2$

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$T_{pre}$ ($^\circ$C)</th>
<th>$T_{post}$ ($^\circ$C)</th>
<th>Composition of crystals ($x_{ph}$)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increasing expansion chamber temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-1</td>
<td>135</td>
<td>25</td>
<td>0.9436</td>
<td>1.08</td>
</tr>
<tr>
<td>M-2</td>
<td>135</td>
<td>35</td>
<td>0.9450</td>
<td>1.11</td>
</tr>
<tr>
<td>M-3</td>
<td>135</td>
<td>45</td>
<td>0.9455</td>
<td>1.12</td>
</tr>
<tr>
<td>M-4</td>
<td>135</td>
<td>60</td>
<td>0.9503</td>
<td>1.24</td>
</tr>
<tr>
<td>Decreasing pre-expansion temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-1</td>
<td>135</td>
<td>35</td>
<td>0.9450</td>
<td>1.11</td>
</tr>
<tr>
<td>M-5</td>
<td>100</td>
<td>35</td>
<td>0.9449</td>
<td>1.11</td>
</tr>
<tr>
<td>M-6</td>
<td>70</td>
<td>35</td>
<td>0.9452</td>
<td>1.12</td>
</tr>
</tbody>
</table>

$P_{ex}$=17.0 MPa, $T_{ex}=308.2^\circ$C, $x_{ph}=0.5$ - 0.7.
6(a)) and their mixture (Fig. 7), which were produced by RESS under saturated conditions, the morphology of the mixture particles have definitely changed. That is, they were smaller particles of diameters ranging from 1 to 8 μm (mean value 3.7 μm) than the particles of pure compounds. Moreover, the shapes were obviously different with those of the two pure compounds. As can be seen in Fig. 7, the particles of the mixture are composed of homogeneous crystals and not of two kinds of pure solids. These results form a striking contrast to the case of a eutectic organic mixture (Liu and Nagahama, 1996b). It may be attributed mainly to the solid solution characteristic of the mixture of interest, and such a big change of size as well as morphology may strongly suggest that the mixture particles would be solid-solution crystals.

3.4 The X-ray diffraction patterns analysis

Figure 8 shows X-ray diffraction (XRD) patterns of the powder for pure anthracene, pure phenanthrene, and a mixture obtained by RESS (about 0.94 mole fraction of phenanthrene). The lattice parameters a, b and c of each sample were determined and compared to the standard JCPDS Powder Diffraction files (ASTM cards) except the mixture sample.

The results of two pure solids (Fig. 8(a) and (b)) were almost identical with those of ASTM cards. The XRD pattern for the mixture (Fig. 8(c)) shows that it still had crystal structure and definitely different patterns for both pure solids. This indicates that the mixture is not a simple eutectic mixture. However, it was very difficult to see if the mixture might form a solid solution. It may be due to the fact that XRD analysis of organic crystals produced from a mixture is not easy because of the weak bonding energy between the organic molecules. As a result we could not proceed further with XRD analysis of the mixture crystals.

Conclusion

Solubilities of anthracene+phenanthrene mixtures in supercritical CO₂ were measured. Two kinds of mixtures (the mixtures of pure solids and solid solution) have been used as feeds for the measurements and their solubilities have been determined using a modified flow method. The PR EOS was able to correlate successfully the solubilities of the mixture of pure solids in SC CO₂. For the solid solution, the solubilities showed a moderate dependence on its composition, and were correlated using the PR EOS for fluid phase and the Wilson equation for solid phase. Such behavior and correlation may be the first such finding to be reported over.

RESS experiments of pure anthracene, pure phenanthrene, and two kinds of this mixtures have been performed. For the pure solids, the increase in particle size occurred with decrease of the concentration. For the mixture solid obtained by RESS the morphology and the XRD patterns are definitely different from those for the pure solids. It may support that the mixture crystals must be a solid solution. The results for the mixture may provide the RESS with a new technique for producing micro-size particles of a solid solution.

Acknowledgment

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Nomenclature

\[ f \] = fugacity [MPa]
\[ k \] = adjustable interaction parameter between i and j in PR EOS
\[ N \] = number of experimental points
\[ P \] = pressure [MPa]
\[ R \] = universal gas constant [J/(mol·K)]
\[ T \] = temperature [K]
\[ ν \] = molar volume [m³/mol]
\[ x \] = mole fraction in precipitated solids
\[ y \] = mole fraction of solute in supercritical CO₂
\[ z \] = mole fraction in feed mixture
\[ β \] = enrichment factor
\[ γ \] = activity coefficient
\[ ρ \] = density [g/cm³]
\[ φ \] = fugacity coefficient
\[ λ \] = adjustable interaction parameter between i and j in Wilson equation

<Superscript>
\[ \text{cal} \] = calculation
\[ \text{exp} \] = experiment
\[ \text{f} \] = fluid phase
\[ s \] = solid phase
\[ sul \] = sublimation

<Subscript>
1 = carbon dioxide
2 = phenanthrene
3 = anthracene
an = anthracene
EX = extraction
i = component i
j = component j
ph = phenanthrene
pre = pre-expansion
post = expansion chamber

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