Separation of Caffeine from Supercritical Carbon Dioxide with a Zeolite Membrane

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Caffeine was separated from supercritical carbon dioxide with a zeolite membrane that had been tested for pervaporation. The pore size of the NaY zeolite membrane was evaluated to be of subnanometer scale from the result of a Dubinin–Astakhov analysis. The rejection of caffeine was 0.98 by the zeolite membrane which would make it applicable for SCCO$_2$ membrane separation.

Key words: supercritical carbon dioxide; membrane separation; zeolite membrane; Dubinin–Astakhov analysis; caffeine

Supercritical carbon dioxide (SCCO$_2$) can be used as a ‘clean’ solvent to substitute organic solvents: carbon dioxide is nontoxic for human beings with excellent properties of low viscosity and high diffusivity, and it has been used for decaffeination and for the extraction of flavors. However, there is the disadvantage that a large amount of SCCO$_2$ is required due to the low solubility of the solute. Therefore, a hybrid process consisting of an SCCO$_2$ extraction or reaction process and membrane separation would be more useful for future clean applications. Fujii et al. have prepared a thin porous silica membrane by the sol-gel method and investigated the effect of solute adsorption properties on the permeation behavior. They have reported that the rejection of caffeine contained in SCCO$_2$ was 0.65. However, these rejection results are not satisfactory for practical use, although the permeability for SCCO$_2$ was better than that reported for a multilayer composite nanofilter by Sarrade et al. Zeolites are crystalline microporous solids containing cavities and channels of the subnanometer scale. A thin layer of zeolite has recently been prepared on the surface of a tubular alumina membrane by hydrothermal synthesis. It was tested in various membrane processes because of its combination of high thermal and pressure resistance with such important characteristics of zeolite crystals as adsorption, catalysis, and molecular sieving. In the pervaporation of water/alcohol mixtures, a zeolite membrane has been reported to preferentially permeate water with high flux. In this present work, we characterize the microporous structure of an asymmetric membrane with a thin layer of zeolite, and report its testing it to separate caffeine from SCCO$_2$ with reference to lauric acid.

Caffeine (MW 194.2) was purchased from Kanto Kagaku (Tokyo, Japan) and lauric acid (MW 200.3) was obtained from Sigma Chemical Co. (St. Louis, MO, U.S.A.). The NaY zeolite membrane was presented by Mitsui Engineering & Shipbuilding Co. (Tokyo, Japan).

The N$_2$ and CO$_2$ adsorption isotherms were measured with an accelerated surface area and porosimeter instrument (Shimadzu ASAP 2000) in order to evaluate the microporous structure of the membrane. Beforehand, the surface of the sample was exposed to a high vacuum at 100°C for 1 day to remove any adsorbed species.

The equipment used for the separation experiments was the same as that reported previously. The zeolite membrane was set in a high-pressure module. Liquid CO$_2$ was fed from a siphon-type cylinder to an HPLC pump and then pressurized. The solute was contacted with SCCO$_2$ in a high-pressure cell for dissolution, and the resulting solution was supplied to the membrane module which was maintained at 40°C in a water bath. The operating pressure and the transmembrane pressure were automatically controlled with backpressure regulators at the ports on the permeation and retention sides of the membrane. The gas flow rate was measured with a wet gas flow meter. The SCCO$_2$ solution was then depressurized to atmospheric pressure at the outlet of the backpressure regulator, and the solute was separated from CO$_2$ and collected in a test tube. The collected solute was dissolved in ethanol, and its concentration was measured with a Hitachi U-2000 spectrophotometer. The permeability constant for SCCO$_2$ (Pc) and the rejection (R) were respectively calculated by Eqs. (1) and (2).

$$P_c = J / AP$$
$$R = 1 - (C_o/C_i)$$

where $J$ is the permeation flux of SCCO$_2$, $AP$ is the transmembrane pressure, and $C_o$ and $C_i$ are the solute concentrations in the permeate and in the feed, respectively. The concentrations in the feed of caffeine and lauric acid were $5.6 \times 10^{-4}$ and 0.18%, respectively, while the operating and transmembrane pressures were 20 and 1.0 MPa, respectively.

The mixing ($k_a$) and desorption ($k_d$) rate constants were evaluated from a residual concentration function by using the same procedure as that reported previously. The $k_a$ and $k_d$ values can be obtained by fitting the double-exponential function:

$$C = A \exp(-k_{dl}) + B \exp(-k_{dl})$$

to the time-dependent residual concentration curve $C$.

Characterization of the microporous structure of the zeolite membrane. Figure 1 shows the N$_2$ adsorption isotherms for a silica membrane and the zeolite membrane measured at $-196$°C. An isotherm like that shown in Fig. 1 is given by a microporous solid; the uptake is governed by the accessible micropore volume rather than by the surface area under low-pressure conditions. Nitrogen was strongly adsorbed to the zeolite membrane under conditions of quite low relative pressure due to micropore filling. The N$_2$ adsorption isotherm for the zeolite membrane is steeper at relative pressures below 0.01 than that for the silica membrane, whose average pore size was 3.3 nm, and it thus seemed that the pore size of the zeolite membrane was smaller than 3.3 nm.

In order to assess the microporous structure of the zeolite membrane, the Dubinin–Astakhov (DA) equation was applied to the CO$_2$ adsorption isotherm measured at 0°C. The DA equation has been proposed for the characterization of an adsorbent on the grounds of a general distribution function of micropore diameter and is in the form of

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Abbreviation: PEG200, polyethylene glycol (MW 200).
Membrane Separation of Caffeine from Supercritical CO₂

Table I. Results of the Dubinin–Astakhov Analysis on the Zeolite Membrane

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total micropore volume</td>
<td>6.69 × 10⁻³ cm³/g STP</td>
</tr>
<tr>
<td>Characteristic energy</td>
<td>12.0 kJ/mol</td>
</tr>
<tr>
<td>Micropore surface area</td>
<td>21.9 m²/g</td>
</tr>
<tr>
<td>Modal equivalent pore diameter</td>
<td>1.10 nm</td>
</tr>
</tbody>
</table>

Table II. Separation Capability from Supercritical Carbon Dioxide of the Zeolite Membrane

<table>
<thead>
<tr>
<th>Solute</th>
<th>Membrane</th>
<th>R</th>
<th>Pe [mol/m²·s·Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caffeine</td>
<td>Zeolite</td>
<td>0.98</td>
<td>1.1 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>Silica</td>
<td>0.65</td>
<td>2.3 × 10⁻⁸</td>
</tr>
<tr>
<td>Lauric acid</td>
<td>Zeolite</td>
<td>0.88</td>
<td>9.0 × 10⁻⁹</td>
</tr>
</tbody>
</table>

R, rejection; Pe, permeability constant.
* Reference 1.

\[
\ln A = \ln A_0 - \left(\frac{RT \ln(P_0/P)}{E}\right)^n
\]

where \( A \) is the volume of micropores filled, \( A_0 \) is the total volume of micropores, \( E \) is the characteristic energy of adsorption, \( P/P_0 \) is the relative pressure, \( R \) is the gas constant, and \( T \) is the absolute temperature. This equation is one of the most popular isotherm equations in adsorption theory, and has been widely used to describe the experimental data for adsorption of gases and vapors to microporous materials.\(^{1-9}\) Figure 2 shows the plot of \( \ln(A) \) vs. transformed pressure \( \ln(P_0/P) \) at \( n = 1.92 \). The log of the volume adsorbed was a linear function of the transformed pressure, and the DA equation could be applied to obtain the parameters that characterize the microporous structure. Table I shows the results of the DA analysis obtained from the CO₂ adsorption isotherm. The zeolite membrane was asymmetric, so the micropore diameter of the skin layer for separation was evaluated to be smaller than 1.10 nm. Although the effective pore diameter of the zeolite membrane for separation couldn’t be exactly determined, its microporous structure could be characterized with the DA equation.

Separation of caffeine from supercritical carbon dioxide with the zeolite membrane. Table II shows the experimental results for membrane separation of the solute from SCCO₂. The rejection of caffeine by the zeolite membrane was 0.98, being higher than that for the silica membrane, although the permeability constants of SCCO₂ for both membranes were similar. The zeolite membrane also effectively separated lauric acid whose molecular weight was nearly equal to that of caffeine. These results indicate that the zeolite membrane could provide good separation performance by the molecular-sieving effect of pores or channels of a subnanometer scale.

Figure 3 shows the effect of supplying caffeine on the CO₂ flux through the zeolite membrane and the silica membrane. At zero time, the solute was supplied. The flux for pure SCCO₂ through the silica membrane was higher than that through the zeolite membrane due to the difference in pore size. The CO₂ flux through the silica membrane then decreased rapidly for 10 min after the supply of the solute had been started, probably because of the adsorption layer formed in the pores. On the other hand, the CO₂ flux through the zeolite membrane did not decrease. The desorption rate constant \( k_{des} \) for caffeine was 0.28 [min⁻¹] from the zeolite membrane in this work, this value being 10 times more than that.
from the silica membrane. These results suggest that caffeine was little adsorbed to the zeolite crystals and that the zeolite membrane would not be easily fouled with the solute in SCCO₂.

We have shown in this work that a zeolite membrane developed for pervaporation was also useful in the membrane separation of an SCCO₂ solution. If the pore size of the zeolite membrane can be well controlled at the subnanometer scale, it may be possible to develop membrane processes for separating solutes from SCCO₂ with high rejection and high permeation.

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References