Effect of ion exchange rate of Y-type zeolite on selective adsorption of 2,6- and 2,7-dimethylnaphthalene isomers in supercritical carbon dioxide

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Received 9 March 2006; received in revised form 28 June 2006; accepted 20 July 2006
Available online 27 October 2006

Abstract

The selective adsorption amounts of 2,6- and 2,7-dimethylnaphthalene (DMN) isomers dissolved in supercritical carbon dioxide (SC-CO₂) on barium (Ba) ion-exchanged Y-type zeolite were measured by a constant volume method at 308.2 K. The total concentrations of 2,6- and 2,7-DMN in SC-CO₂ were measured with an ultraviolet detector. The concentration ratio of 2,6- and 2,7-DMN in SC-CO₂ was analyzed by gas chromatography. The separation coefficients of 2,6-DMN (2) and 2,7-DMN (3) are defined by

\[ K_{32} = \frac{Q_3}{Q_2} \times \frac{C_2}{C_3} \]

where \( Q_2 \) and \( Q_3 \) (mol/g-zeolite) are the amounts of 2,6- and 2,7-DMN adsorbed on Y-type zeolite and \( C_2 \) and \( C_3 \) (mol/cm³) are the concentrations of 2,6- and 2,7-DMN in SC-CO₂, respectively. The separation coefficients in SC-CO₂ on Ba ion-exchanged Y-type zeolite are much higher than those in liquid octane. The separation coefficients in SC-CO₂ using Ba ion-exchanged Y-type zeolite depend on ion exchange rate and amount of chloride remained on the zeolite. The separation coefficients at high pressure using Ba ion-exchanged Y-type zeolite which is higher ion exchange rate and contains lower chloride in SC-CO₂ system are much higher than those using NaY-type zeolite. Therefore, the use of ion-exchanged zeolite will be useful in applications such as the design of pressure swing adsorption and supercritical chromatography processes.

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Keywords: Y-typed zeolite; Dimethylnaphthalene; Separation coefficient; Ion-exchanged; Supercritical carbon dioxide

1. Introduction

Isomers of dimethylnaphthalenes (DMNs) are produced in large quantities during coal liquefaction, but the selective separation of DMNs isomers is necessary to apply in various chemical industries. The 2,6-DMN isomer is of particular interest as a starting material for the manufacture of polyethylene naphthalate (PEN), a valuable liquid crystal polymer used for high-quality synthetic fibers and functional resins with desirable thermal and mechanical properties. So, it is important to separate 2,6-DMN isomer from other DMN isomers effectively. Kim and Cheon [1] investigated the separation and purification of 2,6-DMN from naphtha cracking raffinates by crystallization. Inui and Pu [2] studied the separation of 2,6-DMN from a mixture of its isomers by solvent extraction using various zeolites. However, conventional methods such as distillation, solvent extraction, and fractional crystallization are difficult in separating the isomers because the individual isomers have similar physical properties and structures.

Supercritical fluids exhibit intermediate physical properties between those of liquids and gases. They have various advantages such as high mass transfer rates between phases, control of solubility by temperature and pressure, and energy saving. Carbon dioxide can be often used as a supercritical fluid because of its low critical temperature of 304.2 K, ease of solvent regeneration, nontoxic, nonflammable, and inexpensive nature. Many researches have been performed using supercritical carbon dioxide (SC-CO₂). Tapia-Corzo et al. [3] studied supercritical adsorption characteristics in naphthalene, benzoic acid, and CO₂...
system to separate binary mixtures of naphthalene and benzoic acid. Goto et al. [4] investigated the fractionation of citrus oil with SC-CO₂ by a pressure swing process.

Meanwhile, it is known that Y-type zeolite, which has a framework of three-dimensional twelve-member oxygen ring, is effective to separate 2,6-DMN from mixtures of its isomers. Iwai et al. [5] and Uchida et al. [6,7] investigated the separation of the mixture of 2,6- and 2,7-DMN dissolved in SC-CO₂ using NaY-type zeolite and showed the possibility of separation of the isomers. Iwai et al. [8] studied the adsorption equilibria of 2,6- and 2,7-DMN mixtures on NaY-type zeolite in SC-CO₂. Rota et al. [9] studied the separation of DMN isomers by solvent extraction using various Y-type zeolites. The interesting results were obtained from potassium ion-exchanged NaY-type zeolite, in the case of 2,6- and 2,7-DMN solution. The separation factor is about four times higher than that of NaY-type zeolite, though the total adsorbed amounts of two cases are almost the same. This shows that it is possible to enhance the separation factor without decreasing the adsorbed amounts of DMN isomers by using potassium ion-exchanged Y-type zeolite instead of NaY-type zeolite.

In this study, in order to investigate the selective separation of 2,6- and 2,7-DMN isomers dissolved in SC-CO₂ with Ba ion-exchanged Y-type zeolite, the adsorption amounts of 2,6- and 2,7-DMN isomers were measured at 308.2 K and 9.0–19.8 MPa by an isochoric method with an ultraviolet detector. The experimental conditions were chosen such that the temperature was slightly higher than the critical temperature of CO₂ (304.2 K) and the pressures were under the limitation of the apparatus and were enough to investigate the pressure dependency of the selective separations. Also, the separation coefficients of 2,6- and 2,7-DMN isomers dissolved in liquid octane using Ba ion-exchanged Y-type zeolite were measured for comparison. Ba ion which has large ionic radius and high atomic weight was selected to study how properties of adsorbed amounts of DMN isomers by using potassium ion-exchanged Y-type zeolite instead of NaY-type zeolite.

In this study, in order to investigate the selective separation of 2,6- and 2,7-DMN isomers dissolved in SC-CO₂ with Ba ion-exchanged Y-type zeolite, the adsorption amounts of 2,6- and 2,7-DMN isomers were measured at 308.2 K and 9.0–19.8 MPa by an isochoric method with an ultraviolet detector. The experimental conditions were chosen such that the temperature was slightly higher than the critical temperature of CO₂ (304.2 K) and the pressures were under the limitation of the apparatus and were enough to investigate the pressure dependency of the selective separations. Also, the separation coefficients of 2,6- and 2,7-DMN isomers dissolved in liquid octane using Ba ion-exchanged Y-type zeolite were measured for comparison. Ba ion which has large ionic radius and high atomic weight was selected to study how properties of exchanged ion affect the selective separation of 2,6- and 2,7-DMN isomers. The selective separation of 2,6- and 2,7-DMN isomers was focused in this study. The adsorbed amounts of pure DMN were not measured.

2. Experimental

2.1. Materials

High-purity CO₂ (more than 99.9%, Sumitomo Seika Co.) was used. Reagent-grade 2,6- and 2,7-DMN were supplied by Wako Pure Chemical Industries, Ltd. Gas chromatographic analysis indicated that their purities were more than 99.0 and 98.0%, respectively. The structures of 2,6- and 2,7-DMN are shown in Fig. 1. Reagent-grade octane, ethanol, acetone, and barium chloride (BaCl₂) were supplied by Wako Pure Chemical Industries, Ltd. The purities of octane, ethanol, acetone, and barium chloride were more than 98.0%, 99.5%, 99.5%, and 95.0%, respectively. NaY-type zeolite pellets (Tosoh Co. HSZ series 320NAD; SiO₂/Al₂O₃ = 5.6; pore volume, 0.35–0.5 cm³/g; specific surface area, 600 m²/g; pore size, 0.8 nm) was used. The specific volume of NaY-type zeolite was 1.137 cm³/g, which was measured with vernier calipers and total mass of 20 zeolite pieces.

2.2. Ba ion exchange

Ba ion-exchanged Y-type zeolite was prepared as follows: 10 g of NaY-type zeolite was immersed in 40 ml of 1.0 M barium chloride aqueous solution and stirred at room temperature for 2 h. The zeolite was filtered from the solution. The zeolite was washed with deionized water (18.2 MΩ/cm) and dried in an oven at 393 K for 72 h. The conversion of Ba ion-exchange to Na ion was obtained from energy dispersive spectroscopy (EDX, Horiba EX-200) analysis equipped with a field emission scanning electron microscopy (FE-SEM, Hitachi S-4300).

Table 1 shows barium ion-exchange rate calculated from EDX analysis. All the samples are measured above five times and the concentrations were averaged. Then, the ion exchange rate (A) is calculated by the following equation:

\[
A = \frac{2 \times N_{\text{Ba}} - N_{\text{Cl}}}{2 \times N_{\text{Ba}} - N_{\text{Cl}} + N_{\text{Na}}} \times 100,
\]

where \(2\) is the valence of exchanged barium ion, \(N_{\text{Ba}}, N_{\text{Cl}}\), and \(N_{\text{Na}}\) are the amounts (mol/g) of exchanged barium ion, chloride ion, and sodium ion on the zeolite, respectively. The ion exchange rate was calculated under the assumption that chloride ion remained in salt state, that is, BaCl₂ on the surface of Ba ion-exchanged Y-type zeolite. Table 1 shows that the three samples have different Ba ion exchange rates.
2.3. Apparatus and procedure for supercritical adsorption

Fig. 2 shows the schematic diagram of the apparatus adopted in this work. The volumes of a loading cell (9) and an adsorption cell (10) with connection tubes were 58.1 and 180 cm³, respectively. The adsorption cell was packed with Ba ion-exchanged Y-type zeolite pellets (about 68 g). The loading cell was packed with the mixtures of 2,6- and 2,7-DMN. The ratio of the mixtures was 1:1. Then, the adsorption cell and the loading cell were immersed into a water bath (17) at an experimental temperature. Next, CO₂ was introduced into the loading cell. After the system became a steady state, pressure in the loading cell was measured by a digital quartz precision pressure gauge (16, Paroscientific, Inc., MODEL46 K, ± 0.0041 MPa). CO₂ was introduced into the system at 9.0 MPa and zero point adjustment of the ultraviolet detector was performed. Then, valves V6 and V8 were closed and the pressure in the loading cell was reduced to atmospheric pressure by opening valves V10 and V11. Then, CO₂ was introduced again into the loading cell at 9.0 MPa. Valves V6 and V8 were opened and the SC-CO₂ containing 2,6- and 2,7-DMN was well mixed in the circulation part by using the magnetic pump (11) and 2,6- and 2,7-DMN were adsorbed on Ba ion-exchanged Y-type zeolite. After the ultraviolet detector became a constant value, the total concentrations of 2,6- and 2,7-DMN in the gas phase were calculated using a calibration curve. Then, valves V12 and V13 were closed, and valve V10 was opened to introduce a small sample of the gas phase into a sample tube. The volume of the sample tube was 5.2 cm³. Valve V10 was closed and valves V13, V12 and V11 were opened. 2,6- and 2,7-DMN in the sample tube were trapped in a cooled trap (13). The trapped 2,6- and 2,7-DMN were dissolved in acetone, and the concentration ratio of 2,6- and 2,7-DMN was analyzed by a gas chromatograph (Shimadzu Co., GC14-B). The adsorption amounts of 2,6- and 2,7-DMN, \( Q_i \) (mol/g), were calculated by

\[
Q_i = \frac{N_i - C_i(V_L + V_A - V_Z)}{W_Z},
\]

where \( C_i \) is the concentration (mol/cm³) of DMN in gas phase, \( N_i \) the amounts (mol) of DMN loaded, \( W_Z \) the amount (g) of zeolite, and \( V_L \), \( V_A \), and \( V_Z \) the volumes (cm³) of the loading cell, the adsorption cell, and the zeolite, respectively. Furthermore, in order to measure the adsorption amounts at higher pressures, CO₂ was added in the system.

2.4. Apparatus and procedure for liquid phase adsorption

The adsorption amounts of 2,6- and 2,7-DMN in liquid octane were measured for comparison. Liquid octane (50 cm³) was put in a flask. After 2,6- and 2,7-DMN weighed were dissolved in octane, 1.0 g of Ba ion-exchanged Y-type zeolite was added. The flask was set in an air bath (TAITEC Co., BR-30LF) and shaken for 48 h at 308.2 K and atmospheric pressure. The concentrations of 2,6- and 2,7-DMN in octane were analyzed by the gas chromatograph.
chromatograph. The adsorption amounts of 2,6- and 2,7-DMN were calculated from the mass balance.

3. Results and discussion

The separation coefficient \( K_{32} \) of 2,6-DMN (2) and 2,7-DMN (3) is defined by the following equation:

\[
K_{32} = \frac{Q_3}{Q_2} = \frac{C_3}{C_2},
\]

The experimental results of the adsorption characteristics of 2,6- and 2,7-DMN mixture on Ba ion-exchanged Y-type zeolite are listed in Tables 2 and 3 and shown in Fig. 3. The separation coefficients in SC-CO\(_2\) are higher than those in octane. The adsorption of 2,6-DMN decreased considerably with the total pressure whereas that of 2,7-DMN only slightly decreased with the total pressure. The tendency is consistent with that using NaY-type zeolite [8]. The tendency can be explained with the polarities of 2,6-DMN, 2,7-DMN, and CO\(_2\). Usually, polar compounds strongly adsorb on zeolite. The dipole moments of 2,6-DMN and 2,7-DMN are \( 0.472 \times 10^{-30} \) and \( 1.37 \times 10^{-30} \) Cm, respectively [10]. The polarity of 2,7-DMN is higher than that of 2,6-DMN. The interaction between 2,7-DMN and the zeolite is stronger than that between 2,6-DMN and the zeolite. The dipole moment of CO\(_2\) is zero, however, CO\(_2\) has a quadrupole. The amount of CO\(_2\) adsorbed on the zeolite increased with increasing the pressure of CO\(_2\) [8]. As increasing the pressure of CO\(_2\), a competitive adsorption occurs. The amount of 2,6-DMN adsorbed on the zeolite is much influenced with the adsorption of CO\(_2\), because the interaction between 2,6-DMN and the zeolite is weaker than that between 2,7-DMN and the zeolite. So, the adsorption of 2,6-DMN decreased considerably with the total pressure whereas that of 2,7-DMN only slightly decreased with the total pressure. However, the present experimental results show other characteristics as compared with those using NaY-zeolite.

### Table 2
Adsorption amounts of 2,6-DMN (2) and 2,7-DMN (3) mixture dissolved in supercritical carbon dioxide on barium ion-exchanged Y-type zeolite at 308.2 K

| Sample | \( P \) (MPa) | \( C_2 \times 10^6 \) (mol/cm\(^3\)) | \( C_3 \times 10^6 \) (mol/cm\(^3\)) | \( P_2 \) (kPa) | \( P_3 \) (kPa) | \( Q_2 \times 10^5 \) (mol/g-zeolite) | \( Q_3 \times 10^5 \) (mol/g-zeolite) | \( K_{32} \) (dimensionless) |
|--------|---------------|-------------------------------|-------------------------------|---------------|---------------|-------------------------------|-------------------------------|-----------------|
| A      | 9.0           | 1.61                          | 0.754                         | 0.958         | 0.451         | 0.94                          | 1.26                          | 2.8             |
| B      | 9.0           | 2.80                          | 0.528                         | 0.788         | 0.241         | 0.34                          | 0.60                          | 5.7             |
| C      | 9.0           | 1.80                          | 0.319                         | 1.08          | 0.191         | 1.11                          | 1.56                          | 7.9             |
| A      | 12.0          | 2.69                          | 0.503                         | 1.82          | 0.340         | 0.54                          | 1.35                          | 13.4            |
| B      | 12.0          | 3.84                          | 0.410                         | 1.30          | 0.276         | 0.17                          | 0.60                          | 16.6            |
| C      | 12.0          | 2.67                          | 0.457                         | 1.80          | 0.309         | 0.84                          | 1.52                          | 10.5            |
| A      | 14.8          | 3.09                          | 0.513                         | 2.48          | 0.411         | 0.37                          | 1.34                          | 22.0            |
| B      | 14.8          | 4.05                          | 0.571                         | 1.59          | 0.422         | 0.13                          | 0.56                          | 16.0            |
| C      | 14.8          | 2.94                          | 0.506                         | 2.35          | 0.405         | 0.75                          | 1.50                          | 11.7            |
| A      | 19.8          | 3.66                          | 0.666                         | 3.61          | 0.671         | 0.13                          | 1.28                          | 52.2            |
| B      | 19.8          | 4.48                          | 0.772                         | 2.21          | 0.646         | 0.06                          | 0.53                          | 31.0            |
| C      | 19.8          | 3.38                          | 0.569                         | 3.41          | 0.573         | 0.59                          | 1.48                          | 14.8            |

### Table 3
Adsorption amounts of 2,6-DMN (2) and 2,7-DMN (3) mixture dissolved in liquid octane on barium ion-exchanged Y-type zeolite at 308.2 K and atmospheric pressure

| Sample | \( W_6 \) (g) | \( N_2 \times 10^4 \) (mol) | \( N_3 \times 10^4 \) (mol) | \( C_2 \times 10^6 \) (mol/cm\(^3\)) | \( C_3 \times 10^6 \) (mol/cm\(^3\)) | \( Q_2 \times 10^4 \) (mol/g-zeolite) | \( Q_3 \times 10^4 \) (mol/g-zeolite) | \( K_{32} \) (dimensionless) |
|--------|---------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-----------------|
| A      | 1.003         | 4.80                          | 4.81                          | 8.82                          | 6.31                          | 0.39                          | 1.65                          | 5.9             |
|        | 1.018         | 6.41                          | 6.46                          | 11.96                         | 8.84                          | 0.42                          | 2.01                          | 6.4             |
| B      | 1.012         | 4.90                          | 4.89                          | 9.04                          | 6.38                          | 0.38                          | 1.67                          | 6.3             |
|        | 1.012         | 6.21                          | 6.23                          | 10.95                         | 8.09                          | 0.73                          | 2.16                          | 4.0             |
| C      | 1.011         | 4.69                          | 4.71                          | 7.80                          | 4.81                          | 0.79                          | 2.28                          | 4.8             |
|        | 1.018         | 6.25                          | 6.24                          | 9.66                          | 6.54                          | 1.40                          | 2.92                          | 3.1             |
First, the separation coefficients in octane using Ba ion-exchanged Y-type zeolite are a little higher than those using NaY-type zeolite [8]. This demonstrates Ba ion exchange in NaY-type zeolite is effective in terms of separation coefficients. Second, the deviation of separation coefficients in SC-CO₂ system is larger than that in the case of NaY-type zeolite. The reason would be due to the difference of the barium ion exchange rate among the three samples. Last but not least, all of the separation coefficients regardless of such deviation are higher than those using NaY-type zeolite. This indicates that cation exchange in NaY-type zeolite is able to enhance the separation coefficients of 2,6- and 2,7-DMN in SC-CO₂ system. Considering the ion exchange rate and the separation coefficients in Fig. 3, it can be said that the separation coefficients of 2,6- and 2,7-DMN depend upon the ion exchange rate and the amounts of chloride remained on the zeolite. When Ba ion exchange rate is higher (sample A), the separation coefficients at high pressure are much larger than those of the other samples. Then, as sample A compared with sample C, the amounts of chloride decrease the separation coefficients. Therefore, it is important to remove or reduce the amounts of chloride remained on ion-exchanged zeolite.

Figs. 4 and 5 show that the adsorption amounts of 2,6- and 2,7-DMN on Ba ion-exchanged zeolite are lower than those on NaY-type zeolite in both two solvents. This indicates that barium ion exchange in NaY-type zeolite hinders DMN adsorption on the zeolite, but because the concentration in solvent phase is changed at the same time, the separation coefficients of 2,6- and 2,7-DMN on Ba ion-exchanged zeolite increase.

4. Conclusion

The selective adsorption equilibria of CO₂ and 2,6- and 2,7-DMN isomers dissolved in SC-CO₂ on Ba ion-exchanged Y-type zeolites were measured at 308.2 K. The separation coefficients in SC-CO₂ are much higher than those in liquid octane. From the point of the separation coefficient, SC-CO₂ is more effective to separate 2,6-DMN and 2,7-DMN than liquid octane. In the case of octane, the separation coefficients on Ba ion-exchanged zeolite are a little higher than those on NaY-type zeolite. Meanwhile, the experimental results show that the separation coefficients on Ba ion-exchanged Y-type zeolite depend on the ion exchange rate and the amount of chloride remained on the zeolite. The separation coefficients at high pressure in SC-CO₂ using Ba ion-exchanged
Y-type zeolite with higher ion exchange rate and lower concentration of chloride are much higher than those using NaY-type zeolite. These results demonstrate that Ba ion-exchanged Y-type zeolite is able to enhance the separation coefficients of 2,6- and 2,7-DMN in SC-CO₂ system. The use of ion-exchanged zeolite will be useful in applications such as the design of pressure swing adsorption and supercritical chromatography processes. The authors are currently researching how other cation-exchanged Y-type zeolites such as potassium, calcium, and magnesium affect the separation coefficients of 2,6-DMN and 2,7-DMN.

Acknowledgements

The authors gratefully acknowledge the financial support provided by a Grant-in-Aid for the 21st century center of excellent (COE) program, “Functional Innovation of Molecular Informatics” from the Ministry of Education, Science, Sports and Culture of Japan.

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