COMPUTER SIMULATIONS FOR ADSORPTION OF BENZENE DILUTED IN SUPERCritical CARBON DIOXIDE

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The NVT and $\mu$VT ensemble MC techniques have been used for simulations of adsorptions in a slitpore from a binary mixture of benzene diluted in supercritical CO$_2$. The LJ potential function is used for representing intermolecular interactions between CO$_2$, benzene and surface carbon. A typical curve for adsorption of benzene shows a maximum at a pressure below the critical pressure of CO$_2$ and then decreases with increasing pressure. The magnitude of maximum adsorption increases with increasing interaction energy between benzene and surface carbon. It has been shown that this adsorption behavior is attributable mainly to enhanced solubility in the supercritical CO$_2$ and partly to the competitive adsorption of CO$_2$. The adsorption of carbon dioxide increases linearly with pressure and the slit pore becomes full of CO$_2$ molecules under supercritical fluid conditions. The local density profile of benzene in a pore is scarcely affected by CO$_2$; however, the profile of CO$_2$ is strongly affected by benzene molecules when they occupy the first monolayer near the wall.

Introduction

Supercritical fluids are known to have moderate solvent power and favorable transport properties for heat and mass transfer operations. Recently, combinations of adsorption phenomena with supercritical fluids have been proposed as a new separation technology: for example, caffeine extraction$^9$, debinding of ceramic composites$^{13}$ and purification of 2,6-dimethyl naphthalene from a mixture of naphthalene derivatives$^{15}$. Supercritical fluid regeneration of activated carbon is also an application requiring a knowledge of adsorption equilibria in a supercritical fluid. According to recent experimental data$^{11,14}$, adsorption of benzene or toluene diluted in supercritical carbon dioxide on a commercial activated carbon decreases with increasing pressure. Analysis of these data has been based on single component adsorption so far; the role of a supercritical fluid in pores has not been understood clearly.

Computer simulations, which comprise of Monte Carlo (MC) and molecular dynamics (MD) methods$^3$, have been recognized to be a powerful technique for relating knowledge of intermolecular interactions to macroscopic properties, such as pVT relations, the internal energy and the adsorption isotherm. Computer simulations also provide useful information about microscopic structures of fluids for better understanding of molecular behavior in a pore.

In order to study characteristic features of adsorption from supercritical fluids, we have chosen a system of a binary mixture of benzene diluted in carbon dioxide and a siltlike pore composed of graphite-basal-plane walls. For representing the intermolecular interactions, we use the Lennard-Jones (LJ) potential, which is a simple spherical function. Non-spherical potential models were used for computer simulations of benzene (12-site LJ potential$^{10}$) or CO$_2$ (3-site LJ + Coulomb potential$^{29}$) physisorbed on the basal plane of graphite; the major concern was the orientational structure of monolayers on graphite surfaces. We adopted the LJ potential since our major concern is the study of adsorption characteristics in supercritical fluids, the simulation of which requires knowledge of the vapor-liquid equilibrium in supercritical fluid regions.

In the first section of this paper, we summarize the potential models and simulation methods we have used. The second section describes the simulation results for adsorption isotherms of benzene and carbon dioxide for different sets of potential parameters. In the third section the characteristic features of local densities are shown with emphasis on the difference of potentials interacting between the benzene molecule and carbon atoms on a surface wall. Some concluding remarks for adsorption from supercritical fluids are summarized in the last section.

1. Potential Models and Simulation Method

1.1 Potential models

We consider a binary mixture of components 1 (CO$_2$) and 2 (benzene) interacting with the LJ potential function, $\phi_i(r)$, for a pair of molecules $i$ and $j$ separated by the distance $r$.

$$\phi_i(r) = 4\varepsilon_i \left( \frac{\sigma_i^{12}}{r^6} - \frac{\sigma_i^{12}}{r^6} \right)$$

(1)

The LJ parameters, $\varepsilon_i/k$ and $\sigma_i$, for CO$_2$ are determined from a fit to the critical constants, $T_c$ and $P_c$, by adopting the
Table 1  LJ parameters for like pairs

<table>
<thead>
<tr>
<th></th>
<th>$\epsilon/kB$</th>
<th>$\sigma/\text{nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ (1)</td>
<td>225.3</td>
<td>0.3910</td>
</tr>
<tr>
<td>C$_6$H$_5$ (2) [model 1]</td>
<td>416.3</td>
<td>0.5506</td>
</tr>
<tr>
<td>C$_6$H$_6$ (2) [model 2]</td>
<td>468.5</td>
<td>0.5506</td>
</tr>
<tr>
<td>Carbon (s)</td>
<td>28.0</td>
<td>0.340</td>
</tr>
</tbody>
</table>

correlation of Nicolas et al.$^{17}$: $kT/\epsilon = 1.35$ and $p_c\sigma^3/\epsilon = 0.142$. We use two sets of LJ parameters for benzene: (1) the first set is determined from $T_c$ and $p_c$ of benzene in the same way as CO$_2$, and (2) in the second set, the value of $\epsilon/k$ is determined to fit to the vapor pressure of benzene at 313.2 K while the value of $\sigma$ is kept the same as in the first set. The LJ parameters used in the present work are summarized in Table 1, where the parameters for graphic carbon atom are taken from those used in the previous work$^{8,17}$; they were originally suggested by Steele$^{12}$.

Molecules are assumed to be confined in a slit like pore composed of single or double graphite-basal-plane walls$^{8}$ separated by the distance $H = 2$ nm. Potential model 1 adopts the single-plane-wall model (approximated by the 10-4 potential) and potential model 2 uses the double-plane-wall model (approximated by the 10-4-3 potential). The external potential energy for molecule $i$, exerted from a wall plane at perpendicular distance $Z$, $\phi_i(Z)$, is expressed by Eq. (2) for the 10-4 potential and by Eq. (3) for the 10-4-3 potential, respectively.

$$\phi_i(Z) = 4\pi\sigma_i^2\left[\frac{2}{5}\frac{\sigma_i}{Z} - \left(\frac{\sigma_i}{Z}\right)^{10} - \left(\frac{\sigma_i}{Z}\right)^{4}\right]$$  \hspace{1cm} (2)

$$\phi_i(Z) = 4\pi\sigma_i^2\left[\frac{2}{5}\frac{\sigma_i}{Z} - \left(\frac{\sigma_i}{Z}\right)^{10} - \left(\frac{\sigma_i}{Z}\right)^{4} - \frac{\sigma_i^6}{3\Delta[Z+0.61\Delta]}\right]$$  \hspace{1cm} (3)

where $\sigma_i = e_i\sigma_0^2/a_i$ is a constant, $a_i$ the surface area of a graphite basal unit, $a_i/\sigma_0^2 = 0.453$, and $\Delta$ the separation of adjacent basal-planes in the double-plane-wall model, $\Delta = 0.985$. The potential energy $\Phi(Z)$ for molecule $i$ located at distance $Z$ from a wall surface is calculated as

$$\phi_i(Z) = \sum_j \phi_j(r_{ij}) + \phi_i(Z) + \phi_i(H-Z)$$  \hspace{1cm} (4)

where the suffix $j$ runs over different molecules in the pore.

The cross size parameter $\sigma_{ij}$ is presumed to be the arithmetic mean; the cross energy parameter $\epsilon_{ij}$ is represented by the binary parameter $k_{ij}$ which characterizes the deviation from the geometric mean assumption.

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \left[1 - k_{ij}\right]$$  \hspace{1cm} (5)

In potential model 1 all the binary parameters $k_{ij}$ are set at 0.0, while nonzero values for $k_{12}$ and $k_{1s}$ are used in model 2. The value of $k_{1s}$ has been determined$^{18}$ from fitting to the vapor - liquid equilibrium data$^{22}$ for binary mixtures of CO$_2$ and benzene; the value of $k_{1s}$ is determined from a fit to experimental data for adsorption of CO$_2$ on activated carbon M-30$^{9}$. The value of $k_{ss}$ was firstly presumed to be 0.0 (model 2-1) and then changed to 0.15 (model 2-2) in order to investigate the effect of interactions between the benzene molecule and the wall surface.

Table 2  External potential and binary parameters

<table>
<thead>
<tr>
<th></th>
<th>$k_{12}$</th>
<th>$k_{1s}$</th>
<th>$k_{ss}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-4 potential</td>
<td>$k_{12}$</td>
<td>$k_{1s}$</td>
<td>$k_{ss}$</td>
</tr>
<tr>
<td>(model 1)</td>
<td>0.1232</td>
<td>0.170</td>
<td></td>
</tr>
<tr>
<td>(model 2)</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10-4-3 potential</td>
<td>$k_{12}$</td>
<td>$k_{1s}$</td>
<td>$k_{ss}$</td>
</tr>
<tr>
<td>(model 1)</td>
<td>0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(model 2)</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1  Potentials of CO$_2$ and benzene in a slitpore vs. distance normal to the wall surface: $H = 2$ nm; (- - -) model 1; (---) model 2-1

The external potential function and the cross parameters used in the two potential models, 1 and 2, are summarized in Table 2. Figure 1 shows the external potentials exerted on one molecule, CO$_2$ and benzene, in a slit pore of width 2 nm. The ordinate is reduced by the LJ energy parameter of CO$_2$. The external potentials for benzene are much deeper than those for CO$_2$; furthermore, the potential curve of benzene for model 2-1 (solid line) is deeper than that for model 1 (dot-solid line), which significantly affects the isotherm curve and the microstructure of fluids in a pore as shown later.

1.2 Simulation methods

The density $\rho$ and the composition $x_i$ of a mixture in a slit pore are calculated by use of the $\muVT$ ensemble MC method, where the transitional probabilities for steps of creation and destruction, $P_{\text{creat}}$ and $P_{\text{destr}}$ are given as follows$^1$:

$$P_{\text{creat}} = \min \left\{ 1, \frac{V^*}{N} \exp \left[ -\frac{\Phi_{i} + \mu_{i}}{kT} \right] \right\}$$  \hspace{1cm} (6)

$$P_{\text{destr}} = \min \left\{ 1, \frac{V}{N} \exp \left[ -\frac{\Phi_{i} - \mu_{i}}{kT} \right] \right\}$$  \hspace{1cm} (7)

where $N$ is the number of molecules, $V^* = (V/\sigma_0^3)$ the dimensionless volume of a pore, $T$ the temperature and $\mu_{i}$ the chemical potential of component $i$. The box volume $V$ was adjusted to contain about 200 - 300 total molecules during a simulation. The frequencies of creation and destruction of molecules are set on equal probability for each component; however, the probability of selecting CO$_2$ and benzene molecules is adjusted so as to obtain almost
the same number of acceptance for the two components during a simulation. One cycle consists of 300 displacements and \( n_{\text{trans}} \) trials for creation or destruction (particle transfer). The number of trials for particle transfer per displacement, \( n_{\text{trans}}/300 \), is within 2 and 150, typically 100. The first 2500 cycles for equilibration were discarded and the last 5000 cycles were used for ensemble averages.

The chemical potentials of each component, \( \mu_i \) and \( \mu_n \), have been determined for a binary fluid mixture of the mole fraction \( y_2 = 0.001 \) by use of Eq. (8)

\[
\mu_i = \mu_i^r + kT \ln \rho^* y_i \quad (i = 1, 2)
\]

where \( \mu_i^r \) is the residual chemical potential of component \( i \) and \( \rho^* (= \sigma_i^3/\rho) \) the dimensionless density. \( \mu_i^r \) was calculated by Widom’s test particle insertion method\(^{11}\), Eq. (9), which was embedded in the \( NVT \) ensemble MC simulation program.

\[
\mu_i^r = -kT \ln \langle \exp(-\Phi_i/kT) \rangle
\]

where the symbol \( \langle \cdots \rangle \) denotes the ensemble average. Since \( y_2 \) is fixed at 0.001 in this work, the \( NVT \) ensemble MC simulations were performed on 256 molecules of pure \( \text{CO}_2 \) by inserting ghost molecules of \( \text{CO}_2 \) and benzene at random positions in a box at every displacement step to yield \( \mu_i^r \) and \( \mu_n^r \). The pressure \( p \) at a specified set of \( T \) and \( \rho \) was also determined in the \( NVT \) ensemble MC calculation.

In the \( \muVT \) ensemble MC simulations at high pressures, benzene molecules happen to disappear from a simulation box of a slit pore. In this case, \( \mu_i^r \) (pore) has been calculated through Eq. (9) embedded in the \( \muVT \) ensemble MC simulation program. The mole fraction of benzene in the slit pore \( x_2 \) is then calculated as

\[
x_2 = \frac{1}{\rho^* \text{pore}} \exp \left( \frac{\mu_2 \text{ [fluid]} - \mu_2 \text{ [pore]}}{kT} \right)
\]

The pair potential in a fluid phase is cut off at a distance of \( \min(3.5\sigma_{22}, L_2/2) \), where \( L_2 \) is the length of a simulation box. The long range correction is applied to the fluid region, but not to the pore region where the cut-off radius is essentially \( 3.5\sigma_{22} \).

2. Results for Adsorption Isotherms

2.1 Chemical potentials

The residual chemical potentials of \( \text{CO}_2 \) and benzene are calculated at 313.2 K by varying the density of pure \( \text{CO}_2 \) in the \( NVT \) ensemble MC simulations. Figure 2 shows the chemical potentials of each component for a mixture of dilute benzene (\( y_2 = 0.001 \)) in fluid \( \text{CO}_2 \) against the dimensionless pressure \( p^* (= \rho \sigma_2^3/\varepsilon_2) \). The chemical potential of \( \text{CO}_2 \) increases monotonically with increasing pressure, while those of benzene for the two potential models show a maximum point at a pressure approximately 0.06 in \( p^* \), which is below the reduced critical pressure \( p^*_c (= 0.142) \) for \( \text{CO}_2 \). The chemical potentials then decrease with increasing pressure. At low pressures, the partial pressure of benzene increases with an increase in pressure, which results in an increase of the chemical potential of benzene. The decrease in chemical potential with increasing pressure in a high-pressure region is because the benzene molecule attracts \( \text{CO}_2 \) molecules through attractive intermolecular interactions, thus forming clusters around the benzene molecule\(^{4, 5, 10}\). We may refer to the decrease as enhanced solubility in supercritical \( \text{CO}_2 \); this behavior will be common for any attractive solutes in a supercritical fluid.
Table 3 Results of pressure and chemical potentials for a binary mixture of \( y_2 = 0.001 \) for CO\(_2\)(1) + C\(_6\)H\(_6\)(2) at 313.2 K and the equilibrium density and composition in a double-plane-wall slit pore of width 2 nm (potential model 2-1)

<table>
<thead>
<tr>
<th>( \rho^* )</th>
<th>( p^* )</th>
<th>( \mu_{1}^* )</th>
<th>( \mu_{2}^* )</th>
<th>( \rho^*_2 )</th>
<th>( x_1 )</th>
<th>( U_{p}^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.00139(1)</td>
<td>-6.915(-)</td>
<td>-13.831(-)</td>
<td>0.137(2)</td>
<td>0.077(6)</td>
<td>-20.32(12)</td>
</tr>
<tr>
<td>0.005</td>
<td>0.00685(1)</td>
<td>-5.329(-)</td>
<td>-12.284(-)</td>
<td>0.247(2)</td>
<td>0.099(10)</td>
<td>-20.70(25)</td>
</tr>
<tr>
<td>0.010</td>
<td>0.0135(-)</td>
<td>-4.664(-)</td>
<td>-11.669(-)</td>
<td>0.259(1)</td>
<td>0.135(10)</td>
<td>-20.27(23)</td>
</tr>
<tr>
<td>0.050</td>
<td>0.05982(2)</td>
<td>-3.279(1)</td>
<td>-10.666(1)</td>
<td>0.311(3)</td>
<td>0.365(18)</td>
<td>-16.79(29)</td>
</tr>
</tbody>
</table>

The numbers in parentheses are the standard deviations in units of the last decimal digit of the corresponding quantity. The symbol (-) indicates that the standard deviation is smaller than the last digit. \( p^* = p \sigma_1^2 / \varepsilon_{11}, \mu^* = \mu / kT - 31 n (\varepsilon_1 / \sigma_{11}), \rho^*_2 = \sigma_1^2 \rho_2, U_{p}^* = U / N \varepsilon_{11} \)

2.2 Adsorption isotherm for model 1

Figure 3 shows the true adsorptions of CO\(_2\) and benzene from a mixture of dilute benzene (\( y_2 = 0.001 \)) in CO\(_2\) into the single-plane-wall slit pore of width 2 nm for potential model 1; the ordinate is the dimensionless true adsorption, \( \sigma_1^2 \Gamma_{1,i}^* \), and the abscissa the dimensionless pressure. The true adsorption for component \( i \) is defined as

\[
\Gamma_{1,i} = \frac{\langle N_{i,1} \rangle}{2A} = \rho_0 x_i H / 2
\]

where the suffix \( p \) denotes the pore phase. The true adsorption of CO\(_2\), \( \Gamma_{1,1} \), increases monotonically with an increase in pressure while that of benzene \( \Gamma_{1,2} \) shows a maximum at about 0.05 in \( p^* \). This adsorption behavior is understandable given curves of the chemical potentials of CO\(_2\) and benzene shown in Fig. 2.

Snapshots in the slit pore at the end of the MC simulations are shown in the lower portion of Fig. 3 for three points, \( a, b, \) and \( c \) marked on the points of the true adsorptions of benzene. The molecules in Fig. 3a are drawn in slightly smaller size than others since the size of pore boxes is adjusted to be the same. From these snapshots, we can get an idea for relative compositions of CO\(_2\) and benzene molecules in a pore. It is interesting to see that at supercritical conditions, the slit pore is almost filled with CO\(_2\) molecules. Benzene molecules are excluded from the pore mainly because of the decrease of the chemical potential of benzene and partly because of the competitive adsorption of CO\(_2\); the latter will be illustrated later.

During the simulations at two points, \( b \) and \( c \) in Fig. 3, benzene molecules disappear occasionally from the box; therefore, the adsorptions are calculated from Eq. (10) for the two cases.

2.3 Adsorption isotherms for model 2

Figure 4 shows the true adsorptions of CO\(_2\) and benzene in the double-plane-wall slit pore for potential model 2-1, where \( \varepsilon_{2,k} / k \) is determined to fit the vapor pressure of benzene and \( k_{2,k} \) is presumed to be 0. The simulation results in this case are displayed in Table 3 along with the estimated errors shown in parentheses, which are the standard deviation of the block averages obtained by dividing each simulation run into 10 blocks. Compared to model 1, the maximum adsorption of benzene has increased up to almost saturation and the corresponding pressure has decreased far below the critical pressure. Then, with an increase in pressure, the adsorption of benzene decreases and that of CO\(_2\) increases. Comparing Fig. 4 with Fig. 3, we may conclude that there are two causes for the decrease in benzene adsorption: the first is the enhanced solubility in supercritical CO\(_2\) and the second is the competitive adsorption of CO\(_2\), which is promoted by an increase in the chemical potential of CO\(_2\).

The lower part of Fig. 4 shows snapshots of the three states, \( a, b, \) and \( c \). At low pressures, benzene molecules almost fill the pore, but as the pressure increases, CO\(_2\) molecules seem to wash out the benzene molecules.

To understand the contribution of the competitive adsorption of CO\(_2\) to the decrease in benzene adsorption, we calculated adsorptions of pure benzene (CO\(_2\)-free), by specifying the chemical potential of pure benzene to the same value of benzene (\( y_2 = 0.001 \)) in CO\(_2\). Figure 5 shows the comparison of adsorptions of benzene coexisting with CO\(_2\) (\( \bullet \)) and without CO\(_2\) (\( \bigcirc \)), the corresponding
Fig. 5 Effect of competitive adsorption of CO₂ for adsorption of benzene in a slitspace ($H = 2$ nm) at 313.2 K: (●) adsorption of benzene from a CO₂ mixture ($y_2 = 0.001$); (○) adsorption of pure benzene (no CO₂) having the same fugacity in a CO₂ mixture at each pressure.

Fig. 6 The effect of $k_{23}$ on the true adsorption of benzene in a slitpore of $H = 2$ nm from a fluid mixture of $y_2 = 0.001$ at 313.2 K (potential model 2). The ratio of adsorptions of benzene obtained in the two simulations (●/○) is 3.5 for the lower pressure and 5.5 for the higher. This ratio is a measure of the contribution of the competitive adsorption of CO₂. It is noteworthy here that these calculations required large number of trials for creation/destruction steps due to the high density of benzene in the pore.

Figure 6 compares the simulated adsorptions of benzene for different values of $k_{23}$, to show the effect of interactions between adsorbate molecules and surface carbon. When the interaction potential decreases by 15%, the adsorption of adsorbate decreases as a whole as shown in the figure. Potential model 1 (Fig. 3) is considered to be an extreme case in that the interaction between an adsorbate molecule and the surface carbon becomes much weaker than in model 2. The potential depth for interactions of adsorbate (2) - surface (s) carbon, $\phi_{2s}(Z)$, is the most sensitive factor for the adsorption from the supercritical fluid since the adsorption equilibrium is essentially determined by the Boltzmann factor, $\exp(-\Phi/kT)$.

3. Local Density Profile

In order to obtain more information about the microstructure of molecules in a pore, we define the local density function $\zeta_i(Z)$ for component $i$ by Eq. (12)\textsuperscript{77}:

$$\zeta_i(Z) = \rho_i(Z)/x_i\rho_p$$

where $\rho_i(Z)$ is the local density of component $i$. If the local density profile is uniform in the pore, the value for $\zeta_i(Z)$ becomes unity in the whole region.

Figure 7 shows the local density functions for two components at three points a, b, and c shown in Fig. 3. They are for potential model 1 characterized by CO₂ molecules filling the slit pore. The solid lines represent benzene and the broken lines CO₂. In a low density region shown in Fig. 7a, the solid and broken lines have two peaks near the wall, which means that adsorptions occur in the first monolayer near the wall. In the middle density region shown in Fig. 7b, the broken line (CO₂) has two additional peaks in the inner region of the pore while small shoulders are seen for the benzene curve. Only a broken line is shown in Fig. 7c because we could not get a meaningful curve for benzene due to a lack of sufficient sample points for benzene mole-
Fig. 8 The local density function \( \zeta_{\text{CO}_2}(Z) \) for CO\(_2\) (1) + benzene (2) mixtures in a pore: potential model 2-1; \( H = 2 \) nm, 313.2 K; (\( \longrightarrow \)) benzene; (\( \cdots \)) CO\(_2\).

cules existing in the pore. However, we can expect that in the region of supercritical CO\(_2\), the curve of the local density function of benzene will resemble the solid line shown in Fig. 7b.

Figure 8 shows the local density functions for model 2-1, which has been characterized by benzene molecules filling the pore at low pressures. Figure 8a shows that benzene molecules occupy the first monolayer near the wall as is shown by the solid line, while the broken line for CO\(_2\) shows a swell in the middle region of the pore. In Fig. 8b the solid curve shows that benzene molecules fill over the pore, which affects the local density profile of CO\(_2\), to avoid the benzene-rich regions in the pore. The change in CO\(_2\) curve-shape is understandable because CO\(_2\) molecules have to find their locations in the middle region of the pore due to a large difference in adsorption energy. At higher pressure shown in Fig. 8c, however, the CO\(_2\) curve resembles that of Fig. 7c for potential model 1 because the pore is again filled almost entirely with CO\(_2\) molecules.

Concluding Remarks

The NVT and \( \mu \)VT ensemble MC techniques have been used for simulations of adsorptions in a slit pore from a binary mixture of benzene diluted in supercritical CO\(_2\) as a model system for studying characteristic features of adsorptions of favorable adsorbates dissolved in supercritical fluids. The LJ potential function has been used for representing intermolecular interactions between CO\(_2\), benzene and surface carbon. Simulated adsorptions of benzene show a maximum at \( p < p_c \) CO\(_2\) and then decrease with increasing pressure, while adsorptions of CO\(_2\) increase with increasing pressure. The magnitude and shape of a curve for the adsorption isotherm of benzene against pressure differ significantly with the interaction between the benzene molecule and the surface carbon; the stronger the interaction, the larger the magnitude and the smaller the pressure corresponding to the maximum adsorption.

It has been shown that enhanced solubility in supercritical CO\(_2\) is the major reason for the decrease in benzene adsorption at high pressures and that the competitive adsorption of CO\(_2\) is the second reason. If an adsorbate molecule has much stronger interaction with surface atoms than the benzene molecule, there would be a possibility that the adsorbed molecule could not detach from the surface, even when the system pressure increased.

The local density function \( \zeta(Z) \) is a normalized function to represent the local density profile of each component in a pore. Since benzene molecules interact with the surface carbon more strongly than CO\(_2\) molecules, \( \zeta_{\text{benzene}}(Z) \) gets affected only a little by CO\(_2\) molecules coexisting in the pore. On the other hand, \( \zeta_{\text{CO}_2}(Z) \) is strongly affected by benzene molecules when they occupy the first monolayer near the wall.

Acknowledgment

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Nomenclature

- \( A \) = surface area \( [\text{m}^2] \)
- \( A_0 \) = energy parameter for pair of fluid-solid interaction \( [\text{J}] \)
- \( a_s \) = surface area of a graphite basal unit \( [\text{m}^2] \)
- \( H \) = slitwidth \( [\text{m}] \)
- \( k \) = Boltzmann constant \( [\text{J} \cdot \text{K}^{-1}] \)
- \( k_{ij} \) = binary energy parameter for pairs of \( i \) and \( j \) \( [-] \)
- \( N \) = number of molecules \( [-] \)
- \( p \) = pressure \( [\text{Pa}] \)
- \( r \) = intermolecular distance \( [\text{m}] \)
- \( T \) = temperature \( [\text{K}] \)
- \( U \) = internal energy \( [\text{J}] \)
- \( V \) = volume \( [\text{m}^3] \)
- \( x \) = mole fraction in a pore \( [-] \)
- \( y \) = mole fraction in a fluid phase \( [-] \)
- \( Z \) = distance perpendicular to the surface \( [\text{m}] \)
- \( \Gamma_0 \) = true adsorption per unit area of surface \( [\text{mol} \cdot \text{m}^{-2}] \)
- \( \Delta \) = spacing of the graphite basal planes \( [\text{m}] \)
- \( \varepsilon \) = LJ energy parameter \( [\text{J}] \)
- \( \Lambda \) = thermal de Broglie wave number \( [\text{m}] \)
- \( \zeta \) = local density function \( [-] \)
- \( \mu \) = chemical potential \( [\text{J}] \)
- \( \rho \) = number density \( [\text{m}^{-3}] \)
- \( \sigma \) = LJ size parameter \( [\text{m}] \)
- \( \Phi \) = potential energy exerted on a molecule \( [\text{J}] \)
- \( \phi \) = pair potential energy \( [\text{J}] \)

<Subscripts>

- \( 1 \) = carbon dioxide
- \( 2 \) = benzene
- \( f \) = fluid phase
- \( i \) = component or molecule \( i \)
- \( ij \) = pair of molecules \( i \) and \( j \)
is = molecule i and solid surface
p = pore phase
s = surface
trans = particle transfer through a simulation box

<Superscripts>
* = refers to a dimensionless quantity
r = residual quantity

Literature Cited