

Monte Carlo simulation of binary mixture adsorption of methane and carbon dioxide in carbon slit pores

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In this article we utilise Grand Canonical Monte Carlo (GCMC) simulation to investigate the adsorption of binary mixture of methane and carbon dioxide in slit-shaped carbon pores, ranging from around 0.75 to 7.5 nm in width, for high pressure up to 300 bar and temperature range of 308 – 348 K, as a preliminary study for the CO₂ sequestration problem that remains a serious challenge to humanity. For the binary adsorption, the selectivity of carbon dioxide relative to methane is lower at higher slit-widths or higher temperatures or lower bulk mole fraction of carbon dioxide. Upon increase of pressure the selectivity initially increases to a maximum value, and subsequently drops before attaining a constant value at pressures higher than 300 bar for any bulk mole fraction of carbon dioxide. While the selectivity increases with temperature in the initial pressure-sensitive region, the constant high-pressure value is temperature independent. Optimum selectivity at any temperature is attained at a pressure of approximately 35 bar at high bulk mole fraction of CO₂, increasing to 90-100 bar at low bulk mole fractions.

1. INTRODUCTION

One of the most important of the current environmental challenges is global warming and climate change, to which the increasing atmospheric concentrations of greenhouse gases is considered a major contributor. Among greenhouse gases (GHG), carbon dioxide is the most important contributor and is responsible for about 64% of the present global warming effects [1]. One of the approaches

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suggested for sequestering CO₂ is by injecting it in coal-bed methane reservoirs (CBMR). In this case, one displaces CH₄ gas in these reservoirs, which can then be utilized as an energy source. The advantage of this approach over other storage/sequestration options is that the value of CH₄ produced helps to alleviate partly or wholly the sequestration costs.

Moreover, ongoing and forthcoming projects on production of coal-bed methane (CBM) and CO₂ storage in CBMR have lead to increasing demand for adsorption data of these two gases and their mixtures on coals under subsurface conditions. Selective adsorption of the main GHG, carbon dioxide, from gaseous mixtures is a promising method to limit its volume released to the atmosphere. Knowledge of the adsorption behaviour of coal-bed gases, mainly under high-pressure sub- and supercritical conditions, is necessary for optimum development of production processes to recover CBM and to sequester CO₂ in coal-beds. Specifically, methane, nitrogen, and CO₂ adsorption measurements are valuable input to CBM production simulations to determine coal-bed storage capacity, economic feasibility, and operating conditions [2].

In preliminary studies, we are examining high-pressure adsorption in carbon above the critical temperature of the adsorbate, which is usually referred to as supercritical gas adsorption. We consider binary adsorption of methane and carbon dioxide in an infinite carbon slit pore by using the Monte Carlo simulation method in the grand canonical ensemble (NVT), abbreviated as GCMC. The calculation is conducted at five different temperatures (308, 318, 328, 338 and 348 K), and pressures up to 300 bar, such conditions that generally apply in practical usage of coal seam reservoirs [3], for several pore widths in the range $H = 0.75\text{-}7.5$ nm, as commonly observed in activated carbon. The GCMC method has been applied successfully to model the adsorption of supercritical gases with a simple molecular structure such as methane, argon, and carbon dioxide [4-11]. The detailed descriptions of this technique will be presented in the next section.

2. THEORETICAL MODELLING

2.1. Grand Canonical Monte Carlo simulation

The Monte Carlo method is originally a mathematical and numerical technique invented to solve complex stochastic problems which are inaccessible to rigorous analytical methods. Here, this technique is carried out in the grand canonical ensemble, including moves for translation or reorientation, creation, and destruction of particles in the simulation box, with successive trials based on a Markov chain. A decision is made according to the Metropolis sampling scheme [12, 13] whether to accept each trial or return to the old configuration

based on a prescribed probability for each trial move. While the number of particles and associated configurational energy are randomly changed to generate a new configuration, micropore volume, temperature and adsorbate chemical potential are fixed, corresponding to the experimental condition in which the adsorbed molecule is in equilibrium with a bulk gas. Therefore, this method is now standard and has been frequently described elsewhere [12, 14]. In our implementation, the fluid-fluid interaction potential is modeled using a Lennard-Jones potential truncated at 1.5 nm. The solid-fluid interaction potential is represented by the Steele 10-4-3 potential [15]. The size of the simulation box, which is always greater than twice the cutoff distance, and the number of configurations to obtain an equilibrium condition are set to $16.5\sigma_{ff}$ and 3×10^6 , respectively. Typical calculations for a single point require between 30 and 40 minutes of CPU time on an Intel Pentium 4.

2.2. Adsorbent model

The microporous surface was approximated by a homogeneous potential function as an assembly of close-packed atoms each of which is characterised by the potential parameters ε and σ . In the slit pore model [16-22] used, the pore comprises two parallel graphitic slabs. The distance between the center of the carbon atoms on each opposing slab is defined as the physical pore width, H_{phys} .

2.3. Potential models

The one-center potential model is used for both methane and carbon dioxide to simplify the simulation process. For carbon dioxide the alternate more representative 3-center model is known to be more accurate at saturation conditions [23], attained at very high pressures of about 3000 bar. However, at low and moderate densities the single-center model is adequate [24].

The intermolecular interaction potential energy between two fluid molecules is assumed to be governed by the 12-6 Lennard-Jones model

$$\phi_{ff} = 4\varepsilon_{ff} \left[\left(\frac{\sigma_{ff}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ff}}{r_{ij}} \right)^6 \right] \quad (1)$$

where r is the separation distance between two fluid atoms. ε_{ff} and σ_{ff} are fitted parameters for the bulk adsorbate well depth and molecular diameter respectively. This potential energy is in a good agreement in the description of noble gases and many spherical molecules (such as methane) in the homogeneous bulk phase.

The wall is modelled as an infinitely thick graphite slab. Two parallel surfaces separated by a distance H between centers of surface carbon atoms constitute a model slit-shaped pore. Assuming the Lennard-Jones pairwise interaction potential, Steele [15] has described the interaction potential for this single graphite slab and a single fluid molecule by

$$\phi_{sf} = A \left[\frac{2}{5} \left(\frac{\sigma_{sf}}{z} \right)^{10} - \left(\frac{\sigma_{sf}}{z} \right)^4 - \frac{\sigma_{sf}^4}{3\Delta(0.61\Delta + z)^3} \right] \quad (2)$$

where A is $2\pi\sigma_{sf}^2\varepsilon_{sf}\rho_s\Delta$, z is the distance of the fluid particle from the graphite surface, σ_{sf} is the effective adsorbate-adsorbent (carbon) intermolecular diameter, Δ is the separation between graphite layers (0.335 nm), ρ_s is the number of carbon atoms per unit volume in graphite (114 nm^{-3}), and ε_{sf} is the parameter for the adsorptive-graphite interaction potential well-depth. The solid-fluid parameters were calculated by combining the graphite parameters with the appropriate fluid parameters using the Lorentz-Berthelot mixing rules [12]:

$$\begin{aligned} \varepsilon_{sf} &= \sqrt{\varepsilon_{ss}\varepsilon_{ff}} \\ \sigma_{sf} &= \frac{\sigma_{ss} + \sigma_{ff}}{2} \end{aligned} \quad (3)$$

The Steele potential describes the interactions between the adsorbate molecule and one side of graphite wall, however, in slit-pore geometry the adsorbate molecule will interact with both pore walls, and hence the wall potential within the pore for the slit system of physical width H is given as

$$\Phi = \phi_{sf}(H - z) + \phi_{sf}(z) \quad (4)$$

This equation ignores the surface corrugation, which is unlikely to significantly affect the results at high enough temperatures [25].

3. RESULTS AND DISCUSSION

3.1. Parameter Estimation

Initially bulk isotherms were fitted for both CH_4 and CO_2 to determine suitable L-J parameters using each method. Fitting of bulk fluid data to obtain L-J parameters depends upon the range of adsorbed densities or pressures involved. For this case, it is desired to calculate isotherms by the GCMC method, for adsorption in a slit-pore up to 300 bar, for which the density of the adsorbed phase at that pressure approaches approximately 20 mmol/cm^3 . Therefore it is

necessary to fit the density from bulk simulation to bulk experimental data up to this density. Here we represent the experimental data by using an appropriate equation of state, up to this density (20 mmol/cm³), which is attained at about 1500 bar.

Fluid-fluid interaction, either for carbon dioxide or for methane modelled by the Lennard-Jones equation as discussed earlier. Values of ϵ_{ff} and σ_{ff} for methane and carbon dioxide were obtained by fitting GCMC prediction to the bulk thermodynamic data up to 1500 bar that were estimated from a suitable equation of state at 318.15 K. We used the Bender [26] and Span-Wagner equation of state [27] for single component of methane and carbon dioxide, respectively and both of them are accepted as essentially equivalent to experimental data. The quality of fitting, which can be seen in Figure 1, is much better in the case of methane. From the fluid-fluid interaction parameters, we can determine the solid-fluid interaction parameters by adopting the standard Lorentz-Berthelot mixing rules, the composite parameter σ_{sf} being the arithmetic mean of the gas and carbon values, and the composite parameter ϵ_{sf} being the geometric mean. We use the following parameters for the carbon surface: $\sigma_{ss} = 3.4 \text{ \AA}$, $\epsilon_{ss}/k = 28 \text{ K}$ [15]. All parameters values used in the calculations are listed in Table 1.

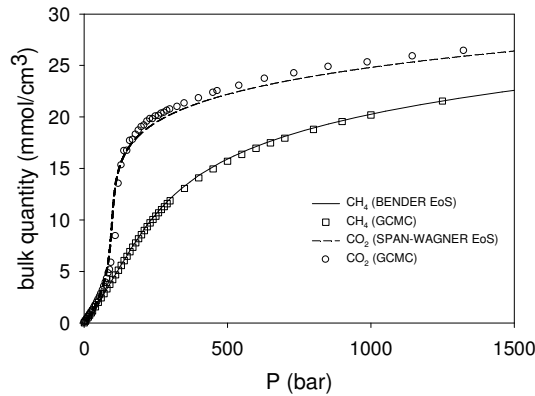


Fig. 1. Bulk isotherm of methane and carbon dioxide at 318.15 K.

Tab. 1. Parameters used for the calculation of model isotherms on graphite at 318.15 K

| Adsorptive | GCMC | | | |
|-----------------|-------------------------|-------------------|-------------------------|-------------------|
| | ϵ_{ff}/k_B (K) | σ_{ff} (Å) | ϵ_{sf}/k_B (K) | σ_{sf} (Å) |
| CH ₄ | 148.0 | 3.751 | 64.3739 | 3.5755 |
| CO ₂ | 242.0 | 3.615 | 82.3165 | 3.5075 |

3.2. Adsorption of CH₄-CO₂ mixtures

3.2.1. *Variation of Selectivity with Pressure.* There is a general expectation that CO₂ is preferentially adsorbed from CH₄/CO₂ mixtures under competitive sorption conditions. When the system consists of adsorbates with different molecular properties, the difference in interaction energies will lead to enhancement of one adsorbate relative to the others (selectivity). The equilibrium selectivity of carbon dioxide with respect to methane is defined as [28]:

$$S_{CO_2/CH_4} = \frac{x_{CO_2}/x_{CH_4}}{y_{CO_2}/y_{CH_4}} \quad (5)$$

representing the ratio of the mole fractions of the two species in the pore relative to the ratio of the mole fractions in the bulk. Values greater than unity imply that carbon dioxide is preferentially adsorbed compared to methane; in contrast, if the selectivity is smaller than unity methane is preferentially adsorbed.

The variation of selectivity with pressure for various temperatures (at fixed $y_{CO_2} = 0.5$) and various y_{CO_2} (at fixed temperature 318.15 K) at pore width $4\sigma_{CH_4}$ can be seen in Figure 2a and b, respectively. Here y_{CO_2} is the bulk mole fraction of CO₂. Both graphs show that selectivity initially increased with pressure to a maximum value at about 40-50 bar and then reduces with increasing pressure. Initially, as the pressure is increased more CO₂ is adsorbed, in which higher bulk mole fraction of CO₂ gives higher selectivity. Subsequently, CO₂ is saturated in the pore while CH₄ adsorbs further. At high pressure, CO₂ is already adsorbed at close to the maximum density in the pore. However, density of CH₄ keeps increasing with pressure because the critical temperature of CO₂ (304.12 K) is very high compared with the critical temperature of CH₄ (190.56 K). Thus, as we increase the pressure, methane is increasingly compressed more at high pressure. The rise of density of methane in the pore causes the selectivity to decrease and ultimately become nearly independent of pressure.

At a temperature of 318 K, the selectivity value is higher in the smaller pore-sizes, as shown in Figure 2c, as the smaller pore-sizes give stronger solid-fluid potential interaction (c.f. Fig. 3). All three graphs (Fig. 2a-c) show that selectivity is not very sensitive to pressure above 300 bar.

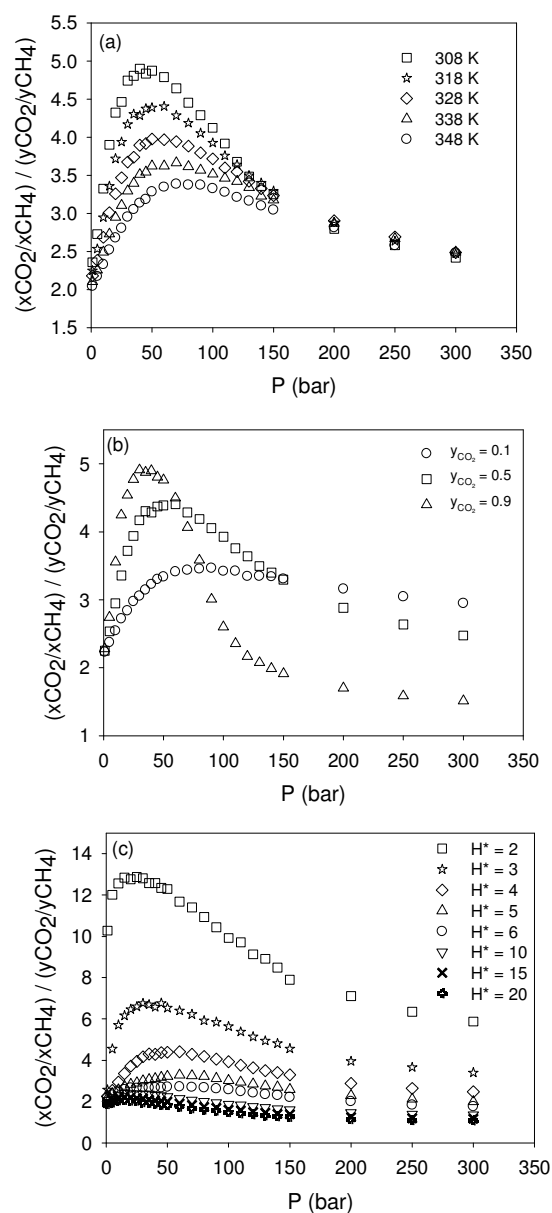


Fig. 2. Selectivity of CO₂ relative to CH₄ versus pressure (a) in pores of reduced slit-width $H^* = 4$ at five different temperatures; (b) in pores of reduced slit-width $H^* = 4$ at 318.15K with different y_{CO_2} ; (c) in pores of various reduced slit-widths at 318 K. For (a) and (c), the gases have equal bulk mole fractions, i.e. y_{CO_2} .

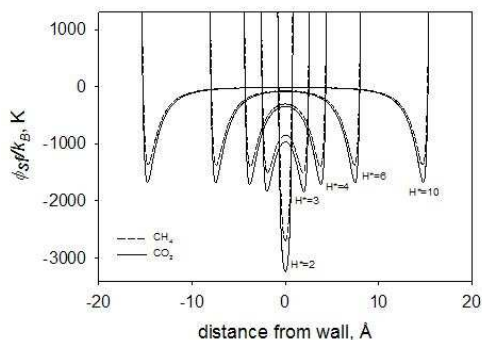


Fig. 3. Solid-fluid interaction potential for methane and carbon dioxide in pores of reduced slit-width $H^* = 2 - 10$, at temperature 318.15 K.

3.2.2. Optimum Pressure. From Figure 2, we obtain an optimum pressure, which gives maximum selectivity, for certain conditions (particular temperature, bulk mole fraction of CO_2 , and pore size). These results are depicted in Figure 4a and 4b, showing the variation of optimum pressure with temperature and pore size for three different bulk mole fraction of CO_2 , respectively. It is seen that in order to obtain maximum selectivity it is necessary to increase the pressure for lower CO_2 in the bulk; i.e. optimum pressure for lower y_{CO_2} is always higher than higher y_{CO_2} in the bulk for all temperatures in the range studied. We also observed that the optimum pressure increases linearly with increase in temperature. In the real CBM reservoir condition, the bulk composition varies during production and cannot be specified uniquely. Therefore, it is necessary to determine pressure and temperature conditions which can give maximum selectivity over a range of bulk compositions. As in Figure 4a, in Figure 4b we find that the optimum pressure for lower y_{CO_2} is always higher than that at higher y_{CO_2} in the bulk for all range of pore size, except for $y_{\text{CO}_2} = 1$ at the range of H^* equal to 6-10. However, in the region of y_{CO_2} lying between 0.5 and 0.9 the optimum pressure changes only slightly, and a value of about 35 bar maybe a reasonable compromise given that micropores in carbons are typically 1 nm or smaller in width.

3.2.3. Selectivity versus bulk mole fraction of CO_2 . Figure 5a shows the selectivity CO_2/CH_4 as a function of y_{CO_2} at five bulk pressures in the range of 1 – 200 bar. At 1 bar, the selectivity is nearly constant with bulk mole fraction of carbon dioxide, while at 10 and 50 bar the selectivity increases monotonically. At a pressure of 50 bar and $y_{\text{CO}_2} = 0.8$, the selectivity becomes constant after an initial increase; however at the higher pressures of 100 and 200 bar, it decreases after reaching a maximum. This is due to the relative saturation of the pores with CO_2 at lower y_{CO_2} when the bulk pressure is higher.

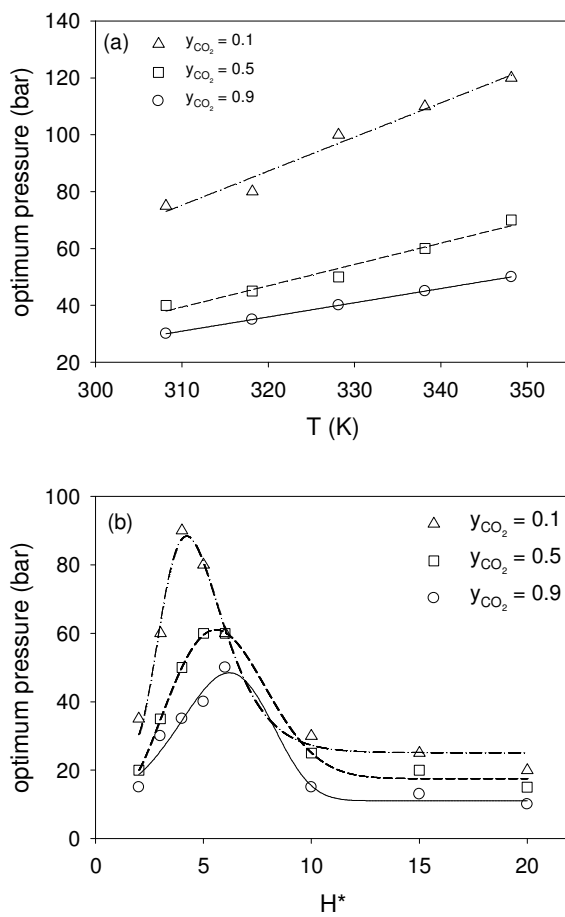


Fig. 4. Variation of optimum pressure for maximum selectivity at three different bulk mole fraction of CO₂: (a) with temperature, at $H^* = 4$; (b) with pore size, at 318 K. The lines are drawn to guide the eye.

Figure 5b depicts the variation of selectivity of CO₂ over CH₄ with bulk mole fraction of CO₂ for various H^* , at 318 K and pressure 100 bar. Each of the pore sizes gives a similar trend, with the selectivity increasing with bulk mole fraction of CO₂ up to y_{CO_2} equal to about 0.3-0.4, and then decreasing. As in Figure 5a, the selectivity decrease after the maximum occurs, as the CO₂ density in the pore reaches saturation. As expected this occurs at lower y_{CO_2} at smaller pore sizes.

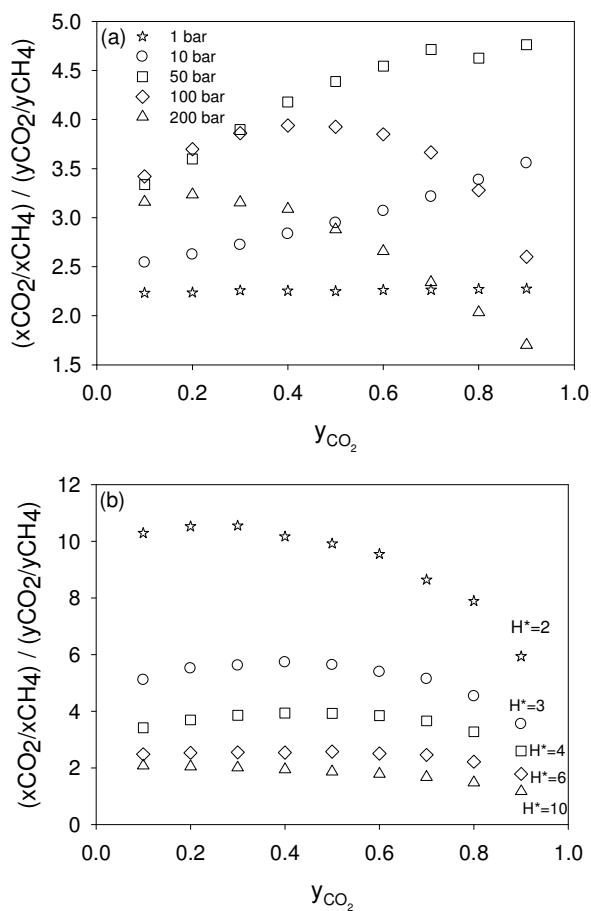


Fig. 5. Selectivity of CO₂ over CH₄ as a function of bulk mole fraction of CO₂ (a) at 318 K, and five different pressures for $H^*=4$, and (b) at 318 K and 100 bar for several different reduced slit-widths (H^*).

3.2.4. Adsorbed density versus bulk mole fraction of CO₂. Simulated adsorption isotherms at 318 K and 100 bar, for several different pore sizes, for methane, carbon dioxide, and total mixture are shown in Figure 6a-c respectively. At small CO₂ in the bulk, either methane or carbon dioxide is adsorbed more in smaller pore since it has stronger interaction, except for $H^* = 2$ in the case of methane. At this pore size, CO₂ is more easily adsorbed as it has stronger attraction with the wall and its molecular size is smaller than methane.

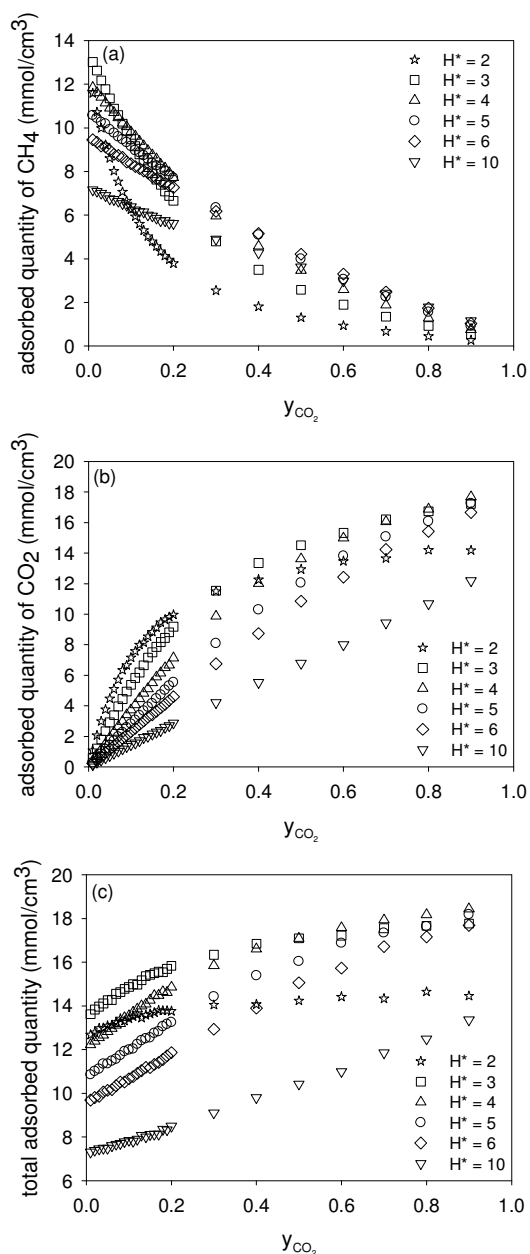


Fig. 6. Adsorbed density of (a) methane, (b) carbon dioxide, and (c) total mixture at temperature 318 K, and pressure 100 bar for several reduced slit-widths.

When y_{CO_2} in the bulk is increased, the carbon dioxide displaces methane, and this effect is stronger in the smallest pore sizes because of the greater strength CO_2 -carbon interaction in these pores. This is evident in Figure 6a, where the curves for the lower pore sizes show steeper declines in CH_4 adsorption. At the smallest pore size of $H^* = 2$ saturation is achieved at relatively low y_{CO_2} , and as Figure 6c shows, the binary adsorption is unchanged beyond about $y_{CO_2} = 0.2$.

4. CONCLUSIONS

Binary adsorption equilibrium of methane and carbon dioxide in carbon slit-pores with different pore sizes for various temperatures and pressures has been studied by using GCMC simulation.

Separation factors obtained are discussed as functions of the pressure, temperature, pore size and the bulk mole fraction of carbon dioxide. Adsorption of carbon dioxide is preferred to methane from binary mixtures under studied conditions. While the pressure is increased, the selectivity of carbon dioxide with respect to methane in the binary mixture initially increases to a maximum value and then decreases before becoming constant (i.e. independent of pressure). This optimum pressure is about 40 bar at 328 K, and only weakly dependent on temperature. All selectivity results demonstrate that many factors can affect adsorptive separation for a gas mixture; therefore, optimization of the conditions is needed in practical CO_2 sequestration.

As small pore size has strong interaction potential energy between the adsorbate and the pore wall, higher selectivity is observed here. Varying the pressure will give different selectivity, while there is a much weaker selectivity variation with temperature. While we increase the mole fraction of CO_2 in the bulk, the selectivity goes through a maximum.

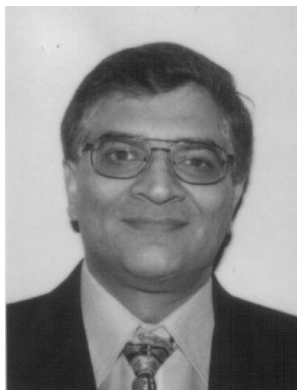
This present simulation knowledge on separation of carbon dioxide from binary mixture of carbon dioxide and methane may constitute a good starting point for further research on carbon dioxide sequestration. Especially, promising is to treat other binary systems such as carbon dioxide – nitrogen or nitrogen – methane or even ternary mixtures.

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