Molecular Simulations of CO2/CH4, CO2/N2 and N2/CH4 Binary Mixed Hydrates

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Abstract—Grand canonical Monte Carlo simulations were performed to study the occupancy of structure I multicomponent gas hydrates by CO2/CH4, CO2/N2, and N2/CH4 binary gas mixtures with various compositions at a temperature of 270 K and pressures up to 70 atm. The presence of nitrogen in the gas mixture allows for an increase of both the hydrate framework selectivity to CO2 and the amount of carbon dioxide encapsulated in hydrate cages, as compared to the CO2/CH4 hydrate. Despite the selectivity to CH4 molecules demonstrated by N2/CH4 hydrate, nitrogen can compete with methane if the gas mixture contains at least 70% of N2.

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INTRODUCTION

Gas hydrates are crystalline solids comprised of gas molecules enclosed in cavities of water lattice. Methane hydrate is the most abundant gas hydrate occurring in nature [1]. Methane is known to form sI hydrates with a unit cell comprised of 46 water and 8 gas molecules located in 6 large (512) and 2 small (512) cavities [2, 3].

Permanent CO2 storage in hydrates has been recognized as a potentially attractive carbon capture technology [4]. Among other possible methods of large-scale production of CO2 hydrate, injection of carbon dioxide into natural methane hydrate deposits is considered. The injection process leads to the replacement of methane in clathrate cavities by carbon dioxide, thereby increasing the efficiency of methane recovery and resulting in the formation of stable CO2 hydrates [5, 6]. However, injection of pure CO2 is likely to be unfeasible, since it requires preliminary separation of carbon dioxide from other components of flue gas, as well as its subsequent compression. It is possible to overcome this drawback by replacing pure carbon dioxide by its mixture with nitrogen [7], which is the predominant component of flue gas. Furthermore, experimental studies have shown that the use of CO2/N2 mixtures leads to more efficient CH4 recovery, as compared to pure CO2 injection [7–9]. These findings have been recently verified by testing on the industrial scale [10].

The mechanism of methane replacement in hydrates by carbon dioxide and nitrogen largely relies upon competition of the gas molecules for occupancy of clathrate cages of different types. As indicated by experimental data for pure and mixed hydrates, methane molecules are capable of occupying both small (512) and large cages (51262), though large cages typically have somewhat higher occupancies, especially at higher temperatures [11]. Carbon dioxide molecules are significantly larger than that of methane, which makes them relatively unsuitable guests for occupying small cages. Earlier studies have suggested that small cavities in pure CO2 sI hydrates are not occupied [11, 12], but more recent experiments reported filling of up to 70% of small cages by carbon dioxide [13, 14]. Nitrogen molecules are the smallest of all three gases, which makes them potential competitors for the filling of small cages.

Experimental studies of mixed hydrates composition and distribution of gas molecules over cages of different types are mainly focused on the properties of CO2/CH4 and, to a smaller degree, CO2/N2 hydrates, while other mixtures are quite rare. In CO2/CH4 hydrates methane loses the competition for large cages to carbon dioxide, as shown by the decrease of large vs. small cage occupancy ratio for CH4 upon mixed hydrate formation [6]. According to Raman spectra measurements [15], in CO2/N2 hydrates nitrogen molecules can be found in both small and large cavities regardless of the gas mixture composition. Carbon dioxide predominantly occupies large cages, and the amount of CO2 in these cavities increases with carbon dioxide content in the gas mixture. NMR studies frequently have problems detecting signals from CO2 in small cages, which also suggests that carbon dioxide tends to occupy large cages [16, 17]. In ternary
CH$_4$/CO$_2$/N$_2$ hydrates nitrogen prevails over the two other gases in the competition for the filling small cages, while CO$_2$ does the same for large cages [18]. Methane occupancy in small cages was shown to be higher than in the large ones [19].

A molecular-level insight into the mechanism of competitive cage occupancy in gas hydrate can be obtained from molecular simulation studies. However, despite the successful application of molecular dynamics and Monte Carlo simulation techniques to one-component hydrates, including those of CH$_4$, CO$_2$, and N$_2$, there is only a very limited number of simulation studies considering the properties of mixed hydrates [20–22]. A comparison of molecular dynamics simulation data for one-component CH$_4$ and CO$_2$ hydrates and CH$_4$/CO$_2$ mixed hydrate suggests that the latter species may be more stable than either of the one-component gas hydrates [23]. Estimates of free energies of methane replacement by CO$_2$ and N$_2$ molecules obtained from molecular dynamics simulations show that only the replacement of methane by carbon dioxide in large cages of sI hydrates has a negative free energy [24]. Therefore, in agreement with experimental studies [6], a complete replacement of methane in its hydrates by other gases is impossible, since some CH$_4$ molecules are likely to remain in small cages. A molecular dynamics simulation study of the replacement of methane in sI hydrate by carbon dioxide reported the formation of amorphous CO$_2$ hydrate on the surface of CH$_4$ hydrate, which proceeded along with the decomposition of the latter [25]. A Monte Carlo simulation study for one-component and mixed hydrates of methane and carbon dioxide was reported [26]. According to simulation data, small cages are preferably occupied by CH$_4$; large cages do not show any preference for either of the gases, except for high pressures (100 bar or more), for which preferential occupancy by CH$_4$ molecules was observed. Finally, the energy barriers of gas diffusion through rings of water between the cages of sI hydrate were calculated [27]. Simulation data suggest that nitrogen has more possibilities than CO$_2$ to diffuse into the large cages, which are already occupied by methane, though this effect is relatively weak.

In the present study, Monte Carlo simulations are employed to investigate the nature of competitive cage occupancy in CO$_2$/CH$_4$, CO$_2$/N$_2$, and N$_2$/CH$_4$ mixed sI hydrates. To represent the results, total and partial occupancy isotherms will be used, which allow to elucidate the effects of gas mixture composition and pressure on the composition of binary hydrates, to obtain the distribution of gas molecules over various types of cavities and to calculate selectivity of the hydrate framework to the components of the gas mixture.

**SIMULATION DETAILS**

*Molecular Simulations*

Simulation of hydrate framework occupancy was performed by grand canonical Monte Carlo method using in-house software. The dispersion interactions in the system were described by Lennard-Jones potential, while electrostatic interactions between effective atomic charges were taken into account via Coulombic potential. Three-dimensional periodic boundary conditions were implemented to model a bulk hydrate phase. The nearest image convention was used to evaluate the interaction energies.

All-atom rigid models of water and gas molecules were chosen for the simulation, namely, TIP4P/ice for H$_2$O [28], OPLS-AA for methane [29] and TraPPE for carbon dioxide and nitrogen [30].

Hydrate framework was represented by $4 \times 4 \times 4$ unit cells of structure I with 2944 water molecules (Fig. 1). In total, the simulation cell contained 512 cages available to gas molecules, including 128 small cages and 384 large cages. Hydrate framework was completely rigid and did not change during the simulation.

The occupancy of hydrate was studied at 270 K and pressures from 1 to 50–70 atm, depending on the system. Three binary gas mixtures were considered: CO$_2$/CH$_4$, CO$_2$/N$_2$, N$_2$/CH$_4$ with 10, 30, 50, 70, or 90 mole percent of the first component.

From a methodological point of view, the investigation of hydrate framework filling resembles gas adsorption simulations by grand canonical Monte Carlo method, i.e., the chemical potentials of the gases control the amount of gas in the solid. The chemical potential values providing the necessary compositions of gas mixtures within the desired range of pressures were obtained from a large set of preliminary simulations for bulk gas mixtures without the hydrate framework. Monte Carlo simulation length varied from 15–20 million steps for preliminary bulk gas calculations to 30 million steps for hydrate simulations. All computed properties were averaged over the equilibrated part of trajectory, which was no shorter than 15 million steps.

**Occupancy**

The amount of gas contained in hydrate is described by occupancy $\Theta$, which is defined as the number of gas molecules divided by the number of cages:

$$\Theta = \frac{N_{\text{gas}}}{N_{\text{cages}}}.$$  

For the calculation of the total occupancy $N_{\text{gas}}$ is the total amount of all gas molecules in the system, while for the partial occupancy the number of molecules of a particular gas is used. In a similar manner, for the calculation of the total occupancy the number
of all types of cages in the framework is used (512 in this work), but when the occupancy of a particular type of cages is evaluated, \( N_{\text{cages}} \) is the number of corresponding cages in the simulation cell (128 for small cages and 384 for large cages).

**Selectivity**

Selectivity of hydrate framework to a component of the binary gas mixture is defined in the same way as in adsorption simulations and is described by selectivity coefficient \( S_i \), which is the ratio of gas mole fractions in hydrate and in the gas phase:

\[
S_i = \frac{x_i}{x_j}_\text{hydrate} / \frac{x_i}{x_j}_\text{bulk},
\]

where \( S_i \) is the selectivity coefficient towards the component \( i \), \( x_i \) and \( x_j \) are the molar fractions of the mixture components \( i \) and \( j \). The selectivity coefficients to carbon dioxide \( S_{\text{CO}_2} \) (\( \text{CO}_2/\text{CH}_4 \) and \( \text{CO}_2/\text{N}_2 \) hydrates) and to methane \( S_{\text{CH}_4} \) (\( \text{N}_2/\text{CH}_4 \) hydrate) were calculated.

**RESULTS AND DISCUSSION**

*Total Occupancy and Selectivity of Hydrate Framework*

Occupancy isotherms of the binary \( \text{CH}_4/\text{CO}_2 \) hydrate for gas pressures up to 50 atm are shown in Fig. 2a. For all mixture compositions considered, the total hydrate occupancy is relatively high (more than 0.7) even at low pressures, and grows quickly with increasing pressure. At pressures higher than 25–30 atm the hydrate framework is almost saturated. If the gas mixture contains less than 70% of \( \text{CO}_2 \), the maximum occupancy is close to unity (0.97 or more). For mixtures containing more than 70% of carbon dioxide a significant decrease in total occupancy was observed. The dependence of occupancy on pressure for the \( \text{CO}_2/\text{N}_2 \) mixture is generally the same as for \( \text{CO}_2/\text{CH}_4 \), though the absolute values of \( \Theta \) are somewhat lower.

For the \( \text{N}_2/\text{CH}_4 \) mixture (Fig. 2b), occupancies of the hydrate at pressures below 10 atm are noticeably lower than for \( \text{CO}_2/\text{CH}_4 \) or \( \text{CO}_2/\text{N}_2 \) mixtures. Occupancy isotherms reach saturation at higher pressures than for the two other mixtures (at ca. 30–40 atm).

Along with the total occupancies, partial occupancies were obtained for the components of all three mixtures. The dependences of partial occupancies on pressure are presented in Fig. 3 for mixtures with similar composition (70% of carbon dioxide for \( \text{CO}_2/\text{CH}_4 \) and \( \text{CO}_2/\text{N}_2 \) mixtures, 70% of nitrogen for \( \text{N}_2/\text{CH}_4 \)). For the mixtures containing \( \text{CO}_2 \) the amount of the carbon dioxide in the hydrate drastically exceeds the...
amount of the second component and weakly depends on pressure. Noticeable pressure dependence is observed only for methane partial occupancy. For the N₂/CH₄ mixture with 70% of nitrogen the partial occupancies for both gases are very close, i.e., the mixed hydrate contains more methane as compared to the initial gas phase composition.

The difference between compositions of the hydrate and initial gas mixture can be conveniently described by the selectivity coefficient $S_i$, which is calculated using ratios of gas mole fractions in hydrate and in bulk gas.

Pressure dependence of hydrate selectivity coefficients to CO₂ for CO₂/CH₄ mixtures of various composition is shown in Fig. 4. Under most of the conditions considered, the hydrate framework demonstrates selectivity to carbon dioxide ($S_{CO₂} > 1$), which means that the hydrate contains more CO₂ than the coexisting gas phase. For the mixture containing 90% of CO₂ the hydrate becomes selective to methane ($S_{CO₂} < 1$), i.e., the amount of methane in the hydrate is greater than that in the gas phase. The increase in pressure leads to a slight decrease in selectivity coefficients, which become nearly constant at high pressures.

For the CO₂/N₂ mixture, the behavior of selectivity to CO₂ is qualitatively similar to that for the CO₂/CH₄ mixture. However, the values of $S_{CO₂}$ for the CO₂/N₂ mixed hydrate are two times higher, and the hydrate never becomes selective to the nitrogen. It is worth mentioning that only large cages are selective to carbon dioxide, while in small cages $S_{CO₂}$ is two orders of magnitude lower than in large cavities. The distribution of molecules over the cavities of hydrate framework will be discussed in detail in the next section.

Selectivity of hydrate framework to methane for the N₂/CH₄ mixture is almost unaffected by mixture composition or pressure. The values of $S_{CH₄}$ under the conditions considered in this work were found to be in the range from 2.3 to 2.6.

Qualitatively and quantitatively the results obtained are in good agreement with the available experimental studies [6, 16]. A comparison of calculated and measured [31] selectivity coefficients $S_{CO₂}$ for the CO₂/CH₄ mixture is provided in Table 1.

The maximum deviation of calculated selectivity coefficients from the experimental values is about 35%, which can be at least partially attributed to the difference in temperatures and mixture compositions used in experiments and simulations. Though the pri-
mary trends are similar in both cases, simulation data suggest a somewhat more pronounced increase of the \( S_{CO_2} \) values with increasing pressure and decreasing CO\(_2\) content.

The observed difference in the behavior of N\(_2\)/CH\(_4\) mixture and CO\(_2\)-containing mixtures is due to the nature of carbon dioxide. Possessing a noticeable quadrupole moment, carbon dioxide interacts with water molecules much stronger than non-polar molecules of nitrogen or methane. Therefore, carbon dioxide preferentially occupies the hydrate cages, which can be seen from partial occupancies (Fig. 3) and selectivity coefficients (Fig. 4). Moreover, even at low pressures the occupancy of hydrate by CO\(_2\) molecules is quite close to the saturated framework occupancy. Weaker interactions of water with CH\(_4\) and N\(_2\) molecules lead to low occupancies at pressures below 15 atm (Fig. 2a, b). As one can see from Fig. 2b, the most 'unfavorable' gas for the filling of sI hydrate is nitrogen. Thus, the difference in hydrate occupancy caused by interactions of guest molecules with water is more pronounced at low pressures, while at higher pressures the occupancy mostly depends on the size of gas molecules.

While the low-pressure region on the occupancy isotherms is important for obtaining a complete description of the behavior of the simulated systems, it is located outside the experimentally observed hydrate stability zone. CO\(_2\)/CH\(_4\) hydrate stability zone at 273.7 K is located above 14 and 25 atm for mixtures containing 79 and 10% of CO\(_2\), respectively [32]. For the CO\(_2\)/N\(_2\) mixture (25% CO\(_2\)) at 274 K hydrates are observed at 59 atm, though this pressure value was found to decrease significantly when the temperature increases [33]. For the N\(_2\)/CH\(_4\) mixture at 273 K the stability limit increases from 35 to ca. 140 atm with increasing nitrogen content in the mixture, but at the temperature of 270 K, for which the simulations were carried out in this study, the pressures should also be lower [34]. It is worth noting that these experimental pressures cannot be directly applied to simulations as the pressure values obtained by experiment and simulation may differ significantly. However, the exact location of the lower stability limit is not a high-priority issue for this particular study, and further discussion will rely predominantly on simulation data obtained for high occupancies and high pressures, i.e., for conditions under which the hydrate should be definitely stable.

**Cage Occupancies**

As shown in Fig. 2, total occupancies reach saturation at high pressures, namely, at ca. 50 atm for CO\(_2\)/CH\(_4\) and CO\(_2\)/N\(_2\) hydrates and ca. 70 atm for N\(_2\)/CH\(_4\) hydrate. Thus, maximum occupancies can be estimated for each mixture composition. Maximum occupancies of the large and small cages can also be evaluated separately. The result is shown in Fig. 5.

It was found that total maximum occupancies of the hydrate framework are the highest for CO\(_2\)/CH\(_4\) and N\(_2\)/CH\(_4\) mixtures and are very similar to each other. Maximum occupancy of CO\(_2\)/N\(_2\) mixed hydrate is lower due to unfavorable filling of small cages. Large cages are almost fully occupied under all conditions. Occupancy of small cages is much lower and decreases with increasing CO\(_2\) content in the mixture.

The results obtained can be explained by the partial gas occupancies (Fig. 6). Partial occupancy of small cages by carbon dioxide is close to zero, thus all CO\(_2\) molecules reside in large cages (Fig. 6a, b). The filling of small cages by carbon dioxide rises for the mixtures with 90% of CO\(_2\), which is accompanied by a sharp decrease of the content of the second component in small cages. At such mixture composition (90% CO\(_2\)) the number of molecules of the second component in large cages is negligible. In CO\(_2\)/N\(_2\) and CO\(_2\)/CH\(_4\) hydrates nitrogen and methane fill both large and

| Table 1. Comparison of experimental and calculated selectivity coefficients for sI hydrate to CO\(_2\) (\( S_{CO_2} \)) in CO\(_2\)/CH\(_4\) hydrate |
|---|---|---|---|---|
| **Experiment, 277.15 K [31]** | **Simulation, 270.00 K (this work)** |
| \( P \), atm | % CO\(_2\) | \( S_{CO_2} \) | \( P \), atm | % CO\(_2\) | \( S_{CO_2} \) |
| 23.3 | 64 | 1.88 | 23.3 | 70 | 1.20 |
| 25.2 | 52 | 1.96 | 25.2 | 50 | 1.53 |
| 27.6 | 36 | 2.09 | 27.6 | 30 | 2.06 |
| 35.0 | 11 | 2.15 | 35.0 | 10 | 2.59 |
small cages, the amount of N₂ molecules in cages being much lower than that of CH₄. Obviously, carbon dioxide molecules are too large to be accommodated by small cages in noticeable amounts. Nitrogen and methane molecules are smaller, so they can occupy cages of both types. Thus, in sI hydrate nitrogen behaves more like methane than like carbon dioxide, which is the reason of the similarity in the properties of CO₂/N₂ and CO₂/CH₄ hydrates.

For CO₂/N₂ hydrates, a distribution of gas molecules over different cages, similar to the one obtained in simulations, had been observed experimentally [15]. As shown in [6] for CO₂/CH₄ hydrate, the equilibrium occupancy ratio ($\Theta_{\text{large}}/\Theta_{\text{small}}$) for methane varies from 1.26 (pure CH₄) to 0.23 (very low CH₄ content), which is comparable with the values obtained in this work (0.7 for 90% CH₄ and 0.1 for 10% CH₄).

The results of simulation of the N₂/CH₄ mixed hydrate (Fig. 6c) show that all cages are mostly occupied by methane, except mixtures with the highest nitrogen content (70% or more). The difference in the occupancy of large and small cages by both components is not observed.

It should be noted, that the total maximum occupancies of CO₂/CH₄ and N₂/CH₄ hydrates are very close, but the behavior of partial occupancies is completely different.

CONCLUSIONS

Grand canonical Monte Carlo simulations were carried out to compare the occupancy of structure I hydrate framework by three binary gas mixtures, CO₂/N₂, CO₂/CH₄, and N₂/CH₄, at 270 K and pressures up to 70 atm.

CO₂/N₂ and CO₂/CH₄ mixed hydrates are selective to carbon dioxide, with selectivity coefficients $S_{\text{CO}_2}$ being almost twice higher for the CO₂/N₂ mixture. Carbon dioxide in mixed hydrate predominantly

Fig. 5. Maximum total occupancy of the hydrate framework (filled symbols) and occupancy of the small cages (open symbols) for CO₂/CH₄ (1, 3) and CO₂/N₂ (2, 4) hydrates at 50 atm.

Fig. 6. Partial occupancy of the small (1, 3) and large cages (2, 4) at ca. 50 atm for the (a) CO₂/CH₄ and (b) CO₂/N₂ mixtures, and for the (c) N₂/CH₄ mixture at ca. 70 atm.
occupies large cages and only a minor fraction of small cages ($\Theta_{\text{small}} < 0.1$). Nitrogen and methane show no preference to cage size and can be equally found in cages of either type. $\text{N}_2/\text{CH}_4$ hydrate was found to be selective to methane.

The analysis of the results obtained from simulations leads to the conclusion that methane is unlikely to be completely removed only by the injection of pure carbon dioxide, because the filling of small cages by $\text{CO}_2$ molecules is unfavorable. The injection of $\text{CO}_2/\text{N}_2$ mixture should yield better results because nitrogen, if the mixture contains a sufficiently high amount of $\text{N}_2$ (more than 70%), which closely resembles the typical composition of flue gas.

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**CONFLICT OF INTEREST**

The authors declare that there is no conflict of interest.

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