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Molecular Dynamics Simulations of Carbon Dioxide, Methane, and Their Mixture in Montmorillonite Clay Hydrates

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Abstract

Molecular dynamics simulations were carried out to study the structural and transport properties of carbon dioxide, methane, and their mixture at 298.15 K in Na-montmorillonite clay in the presence of water. The simulations show that, the self-diffusion coefficients of pure CO$_2$ and CH$_4$ molecules in the interlayers of Na-montmorillonite decrease as their loading increases, possibly because of steric hindrance. The diffusion of CO$_2$ in the interlayers of Na-montmorillonite, at constant loading of CO$_2$, is not significantly affected by CH$_4$ for the investigated CO$_2$/CH$_4$ mixture compositions. We attribute this to the preferential adsorption of CO$_2$ over CH$_4$ in Na-montmorillonite. While the presence of adsorbed CO$_2$ molecules, at constant loading of CH$_4$, very significantly reduces the self-diffusion coefficients of CH$_4$, and relatively larger decrease in those diffusion coefficients are obtained at higher loadings. The preferential adsorption of CO$_2$ molecules to the clay surface screens those possible attractive surface sites for CH$_4$. The competition between screening and steric effects leads to a very slight decrease in the diffusion coefficients of CH$_4$ molecules at low CO$_2$ loadings. The steric hindrance effect, however, becomes much more significant at higher CO$_2$ loadings and the diffusion coefficients of methane molecules significantly decrease. Our simulations also indicate that, similar effects of water on both carbon dioxide and methane, increase with increasing water concentration, at constant loadings of CO$_2$ and CH$_4$ in the interlayers of Na-montmorillonite. Our results could be useful, because of the significance of shale gas exploitation and carbon dioxide storage.
1 Introduction

In nature, smectite such as montmorillonite is one of the most common type of clay minerals that readily swell in the presence of water.\textsuperscript{1–4} Smectites are aluminosilicates consisting of negatively charged layers compensated by solvated cations such as sodium ions. Clays play an important role in extraction of gas and oil from unconventional geological reservoirs such as shale rocks,\textsuperscript{5–13} carbon dioxide storage and sequestration,\textsuperscript{1,14–23} and selective sorption.\textsuperscript{24–27} They are also used commercially\textsuperscript{28,29} as well as in geologic nuclear waste repositories.\textsuperscript{30,31} Understanding the fundamentals of clay-water interfaces is key to the success of those applications. We have specifically focused our study on swelling behavior of Wyoming-type montmorillonite\textsuperscript{2,3} comprising of tetrahedral silica and octahedral alumina sheets that coordinate to form a 2:1 or tetrahedral-octahedral-tetrahedral (TOT) layer. The location of the isomorphous substitution of silicon by aluminium atom in the tetrahedral sheets and aluminium replaced by magnesium in the octahedral sheet determines the distribution of excess negative charge on the clay layer.\textsuperscript{2–4} Apart from the charge distribution, other structural factors influencing the swelling behavior of smectites include the amount of negative charges on the clay layers,\textsuperscript{32,33} the charge and size of the interlayer cations,\textsuperscript{34,35} and vacancies in cis- or trans-octahedral positions.\textsuperscript{36}

The swelling of smectites due to water intake is well understood from previous investigations with an emphasis on montmorillonite.\textsuperscript{2–4,34,37–46} The swelling process typically exhibits two regimes: crystalline swelling at basal $d$-spacings $\lesssim 19$ Å and osmotic swelling corresponding to basal $d$-spacings $\gtrsim 30$ Å.\textsuperscript{47,48} The stable basal $d$-spacing is about 10 Å for dry clays (no water molecules in the interlayer) and increases upon contact with water to the range 11.5-12.5 Å yielding a fully saturated monolayer (1W) water arrangement.\textsuperscript{3,34,37–40,49} Owing to intake of more water, the $d$-spacing can increase to the next stable state (14.5-15.5 Å) where water molecules form a bilayer (2W) structure. Similarly, measured basal $d$-spacings for three layers of water (3W) are in the range 18.0-19.1 Å. Further water incorporation in the interlayer induces
transition from crystalline or discrete swelling to the so-called osmotic swelling, where the basal $d$-spacing increases continuously with water content. As the water content is increased in the interlayer, density profiles show that Na$^+$ ions are able to hydrate thereby less effectively screening the negatively charged, mutually repelling clay surfaces.\cite{3,34,42} While Ca$^{2+}$ ions\cite{37,42} also favor clay swelling, Cs$^+$ ions\cite{39,42} migrate to and bind to the clay surface and act as a clay swelling inhibitor, i.e., Cs-montmorillonites form stable monolayer hydrates in water. The Poisson-Boltzmann treatment to describe the ionic density profile is not valid in the low states of clay hydrations.\cite{50} The various counterions can form, such as, inner-sphere surface complex consisting of ions which are strongly bound to the tetrahedral substitutions, and outer-sphere surface complex which consists of ions loosely associated with the octahedral substitutions.\cite{34} Density maps of water molecules and cations in the interlayers showed the existence of their preferential interaction sites on the surfaces of the clay sheets.\cite{4,50,51} Notably, Na$^+$ counterions have a behavior similar to water hydrogen atoms, preferring oxygen surface atoms to silicon and hexagonal cavity centers.\cite{50,51} The coordination sphere around Ca$^{2+}$ was found to be much more stable than Na$^+$, especially at high water contents.\cite{46} Molecular dynamics (MD) simulations demonstrated that self-diffusion coefficient of water in clay interlayer nanopores decreases from its bulk value as the clay dry density increases in good agreement with the quasielastic neutron scattering (QENS) results.\cite{52,53} Note that a similar behavior was observed for Na$^+$ counterions. The mobility of Na$^+$ in the interlayer was always much greater than that of Ca$^{2+}$ due to their different hydration shells.\cite{46}

An important topic relevant to CO$_2$ storage capacity\cite{14,17} and methane recovery\cite{7,13} in clays involves the effect of the existence of preadsorbed water, which cannot be avoided due to the hydrophilic nature of the samples. The preadsorbed water may render many microporous sorption sites unaccessible to sorbate by occupying the sorption sites or filling pore throats, therefore reducing the storage capacity of clays. X-ray diffraction measurements showed negligible expansion for dry clay samples upon exposure to dry CO$_2$ and that residual water is required to intercalate CO$_2$.\cite{1,21} Expe-
imental investigations have explored gas sorption on both dry\textsuperscript{6,7,13–15,25} and moisture equilibrated\textsuperscript{1,7,13,14,17,22,54} clays. In addition, computer simulations have inspected the effect of water on the adsorption of carbon dioxide and methane in clay minerals, and the underlying sorption mechanisms.\textsuperscript{16,19,20,22,26,55–61} The simulated distributions confirmed that H\textsubscript{2}O, CO\textsubscript{2}, and CH\textsubscript{4} molecules indeed form well-defined layered structures similar to pure 1W, 2W etc. hydration states.

Liu et al. experimentally investigated CH\textsubscript{4} capture in Ca-rich montmorillonite having a basal $d$-spacing of about 15 Å at 333.15 K, and the adsorption data at various water content were fitted to the Langmuir adsorption model.\textsuperscript{13} The highest sorption capacity was obtained for the Ca-rich montmorillonite pre-heated at 473.15 K, with a maximum value of $\approx 0.25$ mmol/g\textsubscript{clay}. They demonstrated that the adsorbed water occupied the adsorption sites of the clay minerals and reduced the CH\textsubscript{4} adsorption capacity. Similar findings were observed in the experiments of high pressure CH\textsubscript{4} adsorption conducted on dry and moisture equilibrated clay samples.\textsuperscript{7} In recent times, molecular modeling of the structure and dynamics of the water-methane mixture in the interlayer region of smectites has attracted interest.\textsuperscript{20,26,55–57,59–61} These studies showed that montmorillonite surfaces facilitate methane hydrate crystallization from aqueous solution, consistent with experiments.\textsuperscript{62} The simulations also demonstrated that methane molecules lost coordination to surface oxygen with hydration, and became more fully solvated to water molecules. Density maps showed that methane molecules and Na\textsuperscript{+} ions in the interlayers are situated in mutually exclusive regions on the clay surfaces, and distribution of water molecules coincides with the sodium region.\textsuperscript{57} MD simulations showed that the self-diffusion coefficients of methane, water, and sodium ions at 460 K and 900 bar increased with an increase of basal spacing.\textsuperscript{60} These results are correspondingly larger than those obtained at the ground level.\textsuperscript{6,57,59}

According to experimental studies, carbon dioxide adsorption capacity of clay minerals is comparable to that of coal.\textsuperscript{14,17} The adsorption of CO\textsubscript{2} upon Na-rich Wyoming montmorillonite having a basal $d$-spacing of about 12 Å at 328.15 K and relative humidity (RH) of 20\% (0-1 W) resulted in limited uptake at low pressures.\textsuperscript{17} The CO\textsubscript{2}
sorption isotherms of dehydrated Na-rich Wyoming montmorillonite as well as Ca-rich Texas montmorillonite measured at 318.15 K produced typically higher excess sorption values than the corresponding samples with water content. Recent investigations combining in situ experiment and theory showed that for montmorillonite clays, CO$_2$ intercalation peaks from $\approx$ 0W to 1W equivalent hydration states, and then decreases with further hydration.$^{63,64}$ Other studies also suggest that clay-CO$_2$ interactions become more favorable in sub- to single-hydrated montmorillonite systems, when compared to $\gtrsim$ 2W hydration states.$^{65,66}$ The position of the isomorphic substitutions in the tetrahedral sheets is a key factor in determining the CO$_2$ distribution in the interlayer projected on a plane parallel to the internal surfaces of clay.$^{66}$ In the absence of tetrahedral substitutions, CO$_2$ molecules develop a periodic pattern reminiscent of ditrigonal rings of the basal surfaces.$^{19}$ CO$_2$ intercalation into Na-montmorillonite at a temperature 348.15 K, and pressures 25 and 125 bar indicated that the more CO$_2$ molecules in the interlayer, the smaller the self-diffusion coefficient of all species.$^{19}$ The extent of adsorption of water, carbon dioxide and methane molecules in clays typically increases with cation-water hydration energy (e.g., Ca$^{+2}$ > Na$^+$ > Cs$^+$).$^{37,38,42,45,67}$ At the same time, little is known about the molecular details of ternary water/CO$_2$/CH$_4$ mixture intercalation in the interlayer of smectite clays.$^{68–70}$

Our studies indicated that molecular simulations represent a useful tool to generally explore the chemical and surface interactions.$^{67,71,72}$ In the present study, molecular dynamics simulations are used to investigate the structural and transport properties of CO$_2$, methane, and their mixture in hydrated Na-montmorillonite at preadsorbed water content and 298.15 K. Our results cover the experimental RH region, where swelling and shrinking normally occur. For this study, we chose basal spacings as $d = 12, 15, 18$, and 30 Å covering, for example, the swelling states (at fully saturated water arrangement) $\approx 1W$, $\approx 2W$, $\approx 3W$, and $> 3W$, respectively. Recent molecular simulations used similar pre-determined interlayer distances for the study of adsorption of binary mixtures (e.g., water/CO$_2$, water/CH$_4$, and CO$_2$/CH$_4$) in clays.$^{20,56,68}$ When employing pre-determined basal distances to investigate binary and ternary mixtures,
the final equilibrated composition of the system does not necessarily correspond to the thermodynamically stable state. Liu et al.\textsuperscript{13} and Romanov\textsuperscript{17} demonstrated, however, that stable basal spacings of $\approx 12$ and $15$ Å exist during the adsorption of binary mixtures (e.g., water/CO\textsubscript{2} and water/CH\textsubscript{4}) in montmorillonite clays with one of the two components (water) preadsorbed at certain concentrations. Molecular simulations\textsuperscript{19,66} of binary mixture (water/CO\textsubscript{2}) intercalated in Na-montmorillonite clays at basin conditions reported that the thermodynamically stable structures are characterized with basal distances corresponding to the monolayer ($d \approx 12$ Å) and bilayer ($d \approx 15$ Å) hydration states consistent with experimental behavior.\textsuperscript{1} The interaction of montmorillonite clays with variably wet CO\textsubscript{2} (2\%-100\% saturation of H\textsubscript{2}O) at $T = 323.15$ K and $P = 90$ bar can lead to swelling to a $d$-spacing of $\approx 18.8$ Å.\textsuperscript{21} The simulations using a large basal $d$-spacing (30 Å) would represent, for example, gas interaction with an external montmorillonite surface or osmotic swelling.\textsuperscript{47,48} The rest of this paper is organized as follows. In section 2 we describe the model and the simulation method. In sections 3.1 and 3.2, we present simulation results for the binary (water/CO\textsubscript{2} and water/CH\textsubscript{4}) and the ternary (water/CO\textsubscript{2}/CH\textsubscript{4}) mixtures, respectively. Section 4 summarizes our conclusions and gives an outlook for further works.

2 Simulation details

All MD simulations were carried out with the LAMMPS code.\textsuperscript{73} The clay model is based on the pyrophyllite unit cell structure (Si\textsubscript{8}Al\textsubscript{4}O\textsubscript{20}(OH)\textsubscript{4}) and the position of the atoms in this unit cell is obtained from Skipper et al.\textsuperscript{2} Our simulation box is made up of two parallel TOT clay layers, each containing replicated pyrophyllite unit cells with dimensions 42.24, 36.56, and 6.56 Å along $x$, $y$, and $z$ directions, respectively. Therefore, the simulation supercell of orthorhombic symmetry ($\alpha = \beta = \gamma = 90^\circ$) is made up by a total of 64 unit cells ($8 \times 4 \times 2$) with 2560 atoms constituting the mineral portion of the clay phase (Fig. 1). The $z$-dimension of the simulation box $L_z = 2d$, where $d$ is the basal spacing. The clay considered
in this work is the Na-saturated Wyoming-type montmorillonite of unit cell formula: 
\[ \text{Na}_{0.75}(\text{Si}_{7.75}\text{Al}_{0.25})(\text{Al}_{3.5}\text{Mg}_{0.5})\text{O}_{20}(\text{OH})_{4} \]. Based on this formula, each of our clay sheets with 32 unit cells have 16 isomorphic substitutions of Al by Mg ion in the octahedral sheet, 8 isomorphic substitutions of Si by Al ion in the tetrahedral sheets, and 24 compensating \( \text{Na}^{+} \) in the interlayer region. All these substitutions were assigned in a fashion to obey the Loewenstein’s rule (e.g., neighboring Al-O-Al avoidance). Periodic boundary conditions are employed in all three spatial dimensions. In our simulations, clay particles are considered to be rigid.

All atoms in the system interact via the pairwise additive Lennard-Jones (LJ) 12-6 function representing the van der Waals energy term:

\[
U_{\text{LJ}}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right],
\]

(1)

where \( r_{ij} \) is the distance between the centers of \( i \) and \( j \) atoms. The parameter \( \varepsilon_{ij} \) controls the strength of the short-range interactions, and the LJ diameter \( \sigma_{ij} \) is used to set the length scale. The LJ parameters \( \sigma_{ij} \) and \( \varepsilon_{ij} \) are deduced from the conventional Lorentz-Berthelot combining rules:

\[
\sigma_{ij} = \frac{\sigma_{i} + \sigma_{j}}{2},
\]

(2)

\[
\varepsilon_{ij} = \sqrt{\varepsilon_{i}\varepsilon_{j}}.
\]

(3)

The charged atoms are interacting with each other via the unscreened Coulomb potential

\[
U_{\text{Coul}}(r_{ij}) = \frac{q_{i}q_{j}}{4\pi\varepsilon_{0}r_{ij}},
\]

(4)

where \( q_{i} \) and \( q_{j} \) are the partial charges of the atoms \( i \) and \( j \), respectively, and \( \varepsilon_{0} \) is the dielectric permittivity of vacuum.

Here we employ the CLAYFF force field which more realistically represents the local charge inhomogeneities formed around each specific substituted site in the clay layers. The CLAYFF force field that consists of nonbonded (electrostatic and van der Waals) terms predicts structural and dynamic properties of clays in fair agreement with experiments. Water is represented by the simple point charge (SPC)
model with flexible intramolecular interactions. This model approximates water by three sites with each site represented by a LJ sphere with an embedded central point charge, and the O-H bond length is allowed to fluctuate according to the harmonic term

\[ U_{\text{bond stretch}}(r_{ij}) = \frac{1}{2} k_r (r_{ij} - r_0)^2, \]  

where \( k_r = 1108.27 \, \text{kcal/mol/Å}^2 \) is the force constant and \( r_0 = 1 \, \text{Å} \) is the equilibrium bond length. The H-O-H bond angle is allowed to fluctuate according to the bending potential

\[ U_{\text{angle bend}}(\theta) = \frac{1}{2} k_\theta (\theta - \theta_0)^2, \]

where \( k_\theta = 91.54 \, \text{kcal/mol/rad}^2 \) is the force constant, \( \theta \) is the bond angle, and \( \theta_0 = 109.47^\circ \) represents the equilibrium bond angle. Similarly, each carbon dioxide molecule is modeled using the flexible force field developed by Cygan et al. such that the equilibrium C-O bond length is 1.162 Å, \( k_r = 8443 \, \text{kJ/mol/Å}^2 \), the equilibrium O-C-O bond angle \( \theta_0 = \pi \, \text{rad} \), and \( k_\theta = 451.9 \, \text{kJ/mol/rad}^2 \). Methane (single-site) is represented by the TraPPE force field and \( \text{Na}^+ \) is modeled using the parameters proposed by Smith and co-workers.

Grand canonical Monte Carlo (GCMC) algorithm was employed to simulate the adsorption of \( \text{CH}_4 \), \( \text{CO}_2 \), and their mixture at 298.15 K and bulk pressures up to 50 bar, in Na-montmorillonite clays in the presence of preadsorbed water. Excess sorption measured in experiments would mostly be related to sorption due to swelling. As in the case of previous studies, our GCMC simulation did not take into account explicit swelling. The sorbate molecules were permitted to move in and out of the simulation box (\( \mu VT \)), and the number of preadsorbed water molecules and counterions were kept constant during GCMC simulations. Note, however, that the dynamics of preadsorbed water molecules and counterions were allowed. The chemical potentials of sorbate molecules needed in the GCMC simulations were computed from the \( NPT \) ensemble Monte Carlo simulations, using the Widom’s insertion method. Those results are in good agreement with the values obtained from the Peng-Robinson equation of state. The imposed chemical potentials or equivalently the fugacities of...
CO$_2$ and CH$_4$ molecules for the corresponding pressures in the binary adsorption cases (water/CO$_2$ and water/CH$_4$) are provided in the Supporting Information of our previous work.$^{67}$ Further, the partial pressure of each component in the bulk CO$_2$/CH$_4$ mixture was obtained as $x_i P$, where $x_i$ is the mole fraction of the component. The final configurations obtained from these GCMC simulation studies were used as the initial configurations in our MD simulations. Equilibration runs of 1 ns were carried out in the $NVT$ ensemble at $T = 298.15$ K, followed by 2 ns production runs in the $NVE$ ensemble. The use of the $NVE$ ensemble ensures that dynamical properties, such as self-diffusion coefficients, are not biased by the extended system algorithms used to produce constant-temperature ensemble.$^{4,74}$ Three independent trajectories each of length 3 ns per simulation were computed to achieve good statistical averages. The equations of motion were integrated using the velocity Verlet algorithm with a time step of 1 fs. Temperature was controlled by a Noé-Hoover thermostat$^{74}$ with a relaxation time of 0.1 ps and a drag value of 1.0. The nonbond terms were handled with a cutoff at 9.5 Å. The extra skin distance for building neighbour lists was set to 2 Å. The long-range van der Waals interactions were included via tail corrections. The long-range part of the electrostatic interactions was treated using the particle-particle particle-mesh (PPPM) method with a precision value of $10^{-5}$ and a grid order value of 5. The differences of system temperatures from the preset value during $NVE$ production runs were mostly negligible (typically $< 1\%$).

To estimate the self-diffusion coefficients of the interlayer species, the Einstein relation was employed:

$$D_{xy} = \lim_{t \to \infty} \frac{1}{4N_m t} \left\langle \sum_{j=1}^{N_m} [r_j(t) - r_j(0)]^2 \right\rangle,$$  

(7)

where $N_m$ is the number of a selected species, and $r_j(t)$ is the center-of-mass position of the $j$th species at time $t$. The self-diffusion coefficients were thus obtained from the linear slope of the mean square displacements (MSDs) as a function of the simulation time. The MSDs of the molecules and ions were evaluated using the 2 ns equilibrated atomic trajectories from the $NVE$ ensemble simulations with 0.8 ps sampling. Dif-
ferent restart points in the analysis were taken to check the convergence. Note that, $D_{xy}$ values in clay interlayer nanopores were insensitive to the size of the simulation cell. Further details of the force fields (see Table S1) and validation of our simulation model using water-saturated Na-montmorillonite (see Figs. S1-S7, Supporting Information) are provided in the Supporting Information. The diffusion coefficients obtained in our simulations (Fig. S7, Supporting Information) are in good agreement with experimental results as well as with other MD simulation results (see discussion below).

3 Results and discussion

3.1 Water/CO$_2$ and water/CH$_4$ binary mixtures in Na-montmorillonite

3.1.1 Atomic density profiles

In order to explore the distribution of the various species in the interlayer space of the clay, number density profiles were estimated for carbon dioxide and methane in variably hydrated Na-montmorillonite at 298.15 K. The final configurations reported from the GCMC simulation study of adsorption of CO$_2$ and CH$_4$ by Na-montmorillonite in the presence of preadsorbed water, were used as the initial configurations in our NVT simulations. Fig. 2 displays the average density profiles of carbon dioxide (carbon atoms) and methane molecules computed along the $z$-axis (perpendicular to the Na-montmorillonite surface) at compositions obtained for a bulk pressure of 20 bar each. Figs. 2a and c report the profiles of different species adsorbed at a preadsorbed water content of 0.2 g/cm$^3$, while Figs. 2b and d represent a preadsorbed water content of 0.4 g/cm$^3$. Note that, in ambient conditions and for basal $d$-spacings of 12, 15, 18, and 30 Å, we obtained $\approx 0.52$, 0.71, 0.80, and 0.97 g/cm$^3$ of saturated water densities in the interlayer space of Na-montmorillonite clay, respectively. Figs. S8-S11 and S12-S14 in the Supporting Information provide the corresponding distributions of water oxygens and sodium ions in the interlayers of the Na-montmorillonite-water-CO$_2$ and the Na-
montmorillonite-water-CH₄ systems, respectively. Methane adsorption in the presence of water and with d-spacing of 12 Å is not considered in our work because the amount of adsorbed CH₄ in this case is relatively very small for the investigated water densities (e.g., only about four CH₄ molecules per supercell at the highest considered pressure of 50 bar and water density of 0.2 g/cm³). Therefore, using our current system size, much longer simulations would be required to obtain statistically reliable estimates of, e.g., diffusion coefficients of methane at d = 12 Å and for the investigated water densities. The adsorption of sodium ions onto montmorillonite occur mostly as both inner- and outer-sphere surface complexes (see also Fig. S1a, Supporting Information). The overall distributions of sodium ions are not affected significantly by the presence of CO₂ or methane under the studied conditions. Further, the distributions confirm that carbon dioxide, methane, and water molecules indeed form well-defined layered structures similar to pure hydration states such as 1W, 2W, etc. in ambient conditions (see Fig. S1b, Supporting Information).

The profiles of carbon dioxide molecules (Figs. 2a and b) exhibit quite similar qualitative agreement to those reported at nonsaturation or fully saturation. GCMC and MD simulations by Botan et al. showed that, CO₂ molecules in the interlayers of hydrated Na-montmorillonite hardly influence the distribution of other atoms. This observation is consistent with our simulation results over the investigated basal d-spacings and pressure/loading range. Gibbs ensemble Monte Carlo and NPT simulations, both of which take into account the effects of interlayer volume change, have shown that the incorporation of CO₂ molecules into the interlayer region modified the water and Na⁺ profiles, however, mostly due to swelling. Fig. 2c reports the profiles of methane adsorbed at a preadsorbed water content of 0.2 g/cm³, which, upon addition of more preadsorbed water molecules, start to form relatively low peaks (Fig. 2d). A high peak is obtained for the first-layer adsorption in almost all cases, which indicates that the strong methane-solid interaction causes the molecules to pack much closer to the clay surface. This behavior is consistent with previous studies on clays under near-surface geological conditions and that observed at basin conditions.
Our simulations show that methane molecules in the interlayer region of hydrated Na-montmorillonite hardly affect the distribution of other atoms. It is evident from the simulated profiles that CO$_2$ molecule essentially by virtue of its, e.g., quadrupole moment, has much more affinity to the hydrophilic montmorillonite framework than the methane molecule. Under identical conditions, therefore, carbon dioxide molecules exhibit a higher adsorbed amount and lie closer to the clay surface than molecules of methane. We find that the adsorption amounts of CH$_4$ and CO$_2$ in the clay interlayers, generally increase with an increase in basal spacing or bulk pressure. At low-pressure range (typically, \(\lesssim 20\) bar), however, the adsorption amounts of carbon dioxide and methane in the small pores is higher than that of the corresponding larger ones.\textsuperscript{67,68} This phenomenon is due to the relatively stronger fluid-clay interaction in the small pores, and becomes negligible for high water contents. The presence of increasing water molecules in the clay, in general, reduces adsorption amounts of pure CO$_2$ (Figs. 2a and b) and CH$_4$ (Figs. 2c and d), possibly because preadsorbed water render many sorption sites unaccessible to sorbate by occupying the sorption sites or filling interlayer space. In contrast, with a relatively large basal spacing (\(d = 30\) Å), our results (see, e.g., Figs. 2a and b) show the favorability of adsorption of CO$_2$ by montmorillonite at relatively low pressures and intermediate water contents.\textsuperscript{20,67} This enhancement is attributed to the multilayer adsorption of CO$_2$ molecules in the clay interlayers.\textsuperscript{20,67} In addition, the clay-CO$_2$ interaction was shown to be more favorable in sub- to single-hydrated montmorillonite systems, when compared to > 2W hydration states.\textsuperscript{63,65,66}

As an aside, we note that an increase of CO$_2$ adsorption capacity in the presence of water has been previously reported in adsorbents, such as metal-organic frameworks,\textsuperscript{76} single-walled carbon nanotubes,\textsuperscript{77} and mesoporous carbons.\textsuperscript{78} At the same time, the increase of water content results in a very slight enhancement of CH$_4$ intake at low pressures and \(d = 30\) Å (Figs. 2c and d). The main characteristic of the enhanced intake is an increase in CO$_2$ or methane density with water, also away in \(z\)– direction from the first closest adsorption layer near to the clay surface.

The coordination numbers of Na-O$_w$, Na-O$_s$, and Na-O$_c$ in the Na-montmorillonite-
H$_2$O-CO$_2$ system and of Na-O$_w$ and Na-O$_s$ in the Na-montmorillonite-H$_2$O-CH$_4$ system are provided in Table S2 and Table S3 (Supporting Information), respectively, where O$_w$ denotes the water oxygen atom, O$_s$ represents the surface oxygen atom of clay sheet, and O$_c$ stands for oxygen atom in CO$_2$. These numbers are obtained from the integral of the corresponding radial distribution function profiles$^{67}$ from the position starting at $r = 0$ to the position where the first minimum locates after the first peak, and further support that the presence of CO$_2$ and CH$_4$ molecules in the interlayers of hydrated Na-montmorillonite hardly influence the behavior of other atoms under the studied conditions. The coordination numbers obtained here are consistent with previous results reported for similar conditions$^{57}$ (Table S3, Supporting Information). We observe relatively low probabilities of CO$_2$ participation in the first hydration shell of Na$^+$ ions. A similar observation was reported at elevated temperature and pressure.$^{58}$

### 3.1.2 Preferential adsorption sites

The main factors affecting the distribution of sorbate molecules in the interlayer include the size and charge of the interlayer cations,$^{35,46}$ the positions of the isomorphic substitution in the clay sheets,$^{57,58,66}$ and the ditrigonal ring locations of the basal surfaces.$^{50,51,66}$ To understand the molecular structure of adsorbed layers of the different species in the interlayers and to identify the preferential adsorption sites on the montmorillonite substrate, we calculated in-plane ($xy$) density distributions. All these calculations were performed for each molecule found within either the first closest adsorption layer (monolayer) near to the clay surface or away from it (see, e.g., Fig. 2). The computed distributions of carbon dioxide (carbon atoms) at a basal $d$–spacing of 12 Å and methane at a basal $d$–spacing of 15 Å, each with compositions obtained for a bulk pressure of 20 bar are shown in Fig. 3. Figs. S15-S22 and S23-S28 in the Supporting Information provide the corresponding distributions of water oxygens and sodium ions, and additionally, the distributions of different species in the interlayer of the Na-montmorillonite-water-CO$_2$ and the Na-montmorillonite-water-CH$_4$ systems,
respectively, at identical conditions and for the other investigated basal spacings.

Sodium ions coordinated to the inner-sphere surface complexes are associated only with the sites of the isomorphic substitution in the tetrahedral sheets. Inner-sphere surface complexes of $\text{Na}^+$ with tetrahedral charge sites persist in all hydrates. Our results show that, sodium ions in the outer-sphere surface complexes at a basal $d$—spacing of 12 Å seem to avoid the sites of the isomorphic substitution in the tetrahedral sheets. At a relatively low water content of 0.2 g/cm$^3$, the instantaneous spatial distribution of the clustered water molecules along the montmorillonite surface is correlated with the sites of both tetrahedral and octahedral substitutions. Water molecules show a great tendency to spread along the surface, as the water content is increased to 0.4 g/cm$^3$. This trend is consistent with all the investigated hydrates. In the case of pure hydration states (fully saturated), water molecules near the surface develop a periodic pattern reminiscent of ditrigonal rings of the basal surfaces$^{50,51}$ (Figs. S2-S5, Supporting Information). While for $d \geq 15$ Å, the distribution of sodium ions in the outer-sphere surface complexes is similar to water. These results are in good agreement with previous simulations which have shown that outer-sphere surface complexes with octahedral charge sites found in the one-layer hydrate partially dissociated into an incipient diffuse layer in the two- and three-layer hydrates.$^{34,51}$ Note also that, the presence of $\text{CO}_2$ and $\text{CH}_4$ molecules in the studied pressure/loading range hardly affects the horizontal distribution behaviors of water and sodium ions in Na-montmorillonite, when compared to the corresponding pure cases (data not shown).

In good agreement with a most recent simulation study,$^{66}$ $\text{CO}_2$ molecules clearly tend to locate in the areas away from the charge originating due to the isomorphic tetrahedral substitutions (Figs. 3a-b). As the water content increases from 0.2 (Fig. 3a) to 0.4 g/cm$^3$ (Fig. 3b), water displaces more $\text{CO}_2$ molecules from near the sites of the substitutions in the clay sheets. The spatial distribution of $\text{CO}_2$ molecules in Na-montmorillonite is also correlated with the positions of the substitutions in the octahedral sheets. However, any correlation of $\text{CO}_2$, water or sodium ions with the octahedral substitutions is expected to disappear,$^{66}$ e.g., upon reaching the saturated
RH. We observe a similar distribution behavior of CO$_2$ molecules close to the clay surfaces as above at basal $d$–spacings of 15, 18, and 30 Å, while such a behavior persists, albeit to a much lesser extent, also away from the clay surfaces at basal $d$–spacings of 18 and 30 Å. To improve the statistics, the horizontal positions of an atom closer to the clay surface than a fixed cutoff distance are registered and brought back to the unit cell of the sheet (data not shown). Indeed, carbon atom in a CO$_2$ molecule near the clay surface has a tendency to occupy the ditrigonal cavities. Note that, the specific patterns of sorbate distribution on the clay surface depend on properties such as turbostratic stacking and registry motion of clay sheets, which were not considered in our study.

Consistent with previous simulation work, methane molecules (Figs. 3c-d) and Na$^+$ ions in the interlayers are positioned in mutually exclusive regions on the clay surfaces, and, as mentioned above, distribution of water coincides with the sodium region. This result can be explained by considering that sodium ion has a larger hydration energy than methane, and methane is hydrophobic in nature. As with CO$_2$, an increase in the water content from 0.2 (Fig. 3c) to 0.4 g/cm$^3$ (Fig. 3d), favors displacement of CH$_4$ molecules by water from near the sites of the substitutions in the clay sheets. We find a similar distribution behavior of CH$_4$ molecules close to the clay surfaces at basal $d$–spacings of 18 and 30 Å, while such a behavior persists, albeit diminished, also away from the clay surfaces at a basal $d$–spacing of 30 Å. Methane molecule near the clay surface also has a tendency to occupy the ditrigonal cavities. Inspection of the in-plane density maps reveals that while CO$_2$ molecules occupy more than one of the identified cavity patches of a ditrigonal ring, hydrophobic CH$_4$ molecules occupy only the larger region.

Monte Carlo simulations by Park and Sposito found methane molecule surmounted by a clathrate-like water structure, while below it was a hexagonal ring of clay surface oxygens. The locations of the isomorphic substitution in the clay sheets, thus tend to inhibit the active involvement of the clay mineral surface in promoting methane clathrate formation (Figs. 3c-d). As the tetrahedral negative charge site is closer to
the outer surface and is more effective in confining water, therefore, the final stable state of the mixture hydrate depends on the interplay between those two effects, in addition to the associated swelling. For example, simulation studies reported that the type of clay influence the stability of the smectite-hydrate complexes, being more feasible to form those complexes on octahedrally charged smectites like montmorillonite than in tetrahedrally charged like beidellite.

3.1.3 Orientations of water and CO$_2$

Smit and coworkers have studied in detail the orientation of water dipoles in montmorillonite systems at varying relative humidities. For hydrates with a basal spacing of $d \approx 12$ Å, the water dipole oriented parallel (90°) to the closest clay platelet, while for $d \gtrsim 12.5$ Å, they saw a preferred angle of the water dipole with the normal vector of the closest clay platelet of $\approx 135°$. These observations with regard to orientation of water dipoles in Na-montmorillonite are also in good agreement with our mixture data (Fig. S29, Supporting Information). Note also that, the presence of CO$_2$ and CH$_4$ molecules in the studied systems, hardly affects the orientation of water dipoles, when compared to the corresponding pure cases (data not shown). With an increase in the water content, we observe a shift of the tilted orientation of water dipoles near the surface at $d > 12$ Å toward a normal distribution centered around 90° (see also Fig. S6, Supporting Information). A comparison of the dipole orientations in Na-montmorillonite with those of the corresponding neutral pyrophyllite system (Fig. S30, Supporting Information) shows that sodium ions are possibly responsible for the deviation of the normal distributions centered around 90° observed in the former. Note that, the presence of at least an additional water layer above the existing monolayer on the surface, which allows hydrogen bond formation between those two layers, is an essential condition for obtaining the bimodal distribution of dipoles near to the clay surface.

Based on the in-plane density maps, a parallel orientation was proposed for CO$_2$ molecules along the surface in hydrated Na-montmorillonite at basin conditions. Myshakin et al. examined the distribution of angles between the CO$_2$ axial orientation
and the axis perpendicular to the clay surfaces. At each water/CO$_2$ compositions corresponding to 1W, 2W, and 3W hydration states, a normal distribution centered around 90° was obtained, indicating that the carbon dioxide molecules were preferentially oriented parallel to the confining clay surfaces. With increasing number of water-CO$_2$ layers, the CO$_2$ molecules explored a wider range of angles consistent with our simulations (Fig. 4). The addition of more water into the clay systems while keeping $d$ constant, hardly affects the spread of the distribution of these angles in the proximity of the surfaces (data not shown). The favorable interactions of carbon and oxygen atoms of the CO$_2$ molecule with the surface oxygen and silicon atoms, respectively, basically defines its parallel orientation. A comparison of the orientations of CO$_2$ molecules in Na-montmorillonite with those of the corresponding neutral pyrophyllite system (see Fig. S31, Supporting Information) shows that sodium ions also play a significant role in favoring the parallel orientation of CO$_2$ molecules in the former case. Such behavior has been previously reported, in the study of carbon dioxide in dry Na-montmorillonite clays.

3.1.4 Dynamical properties

The diffusion coefficients of ions and water computed at RH of 100% in Na-montmorillonite are provided in Fig. S7 of the Supplementary Information. In this study, all the reported diffusion coefficients of the different species, unless otherwise stated, are normalized by the corresponding bulk diffusion coefficients at about 298.15 K. The bulk diffusion coefficients of Na$^+$, H$_2$O, CO$_2$, and CH$_4$, are 1.34, 2.30, 2.00, and $1.49 \times 10^{-9}$ m$^2$/s, respectively. Also, all the diffusion coefficients are compared at constant water content and basal $d$-spacing, unless otherwise mentioned. The diffusion coefficients of sodium ions are in agreement with those reported using a similar Wyoming type montmorillonite. The diffusion coefficients of water are also in close agreement with previous simulation results and experimental values obtained using QENS spectroscopy for interlayer water in montmorillonite. These results show that the diffusion coefficient values of water and Na$^+$ in smectites increase with basal spac-
ing, as expected. The trend is similar to that observed for water diffusion in planar nanopores between silica surfaces\textsuperscript{81} and mica surfaces.\textsuperscript{82} These simulations showed that the diffusion coefficient values of different species under sub-nanometer confinement decrease by about one to three orders of magnitude under the extreme confinement, as compared to its bulk value.

Typical MSDs of various sorbate molecules in the clay interlayer are provided in Fig. S32, Supporting Information. Fig. 5 reports the resulting in-plane diffusion coefficients of CO\textsubscript{2} (carbon atoms) and CH\textsubscript{4} molecules in the interlayers of Na-montmorillonite for the different water/CO\textsubscript{2} and water/CH\textsubscript{4} binary mixture compositions in the pore, respectively, outputted by the GCMC simulations.\textsuperscript{67} Fig. S33 in the Supporting Information provides the corresponding diffusion coefficients of water oxygens and sodium ions. Tables S4-S5 in the Supporting Information also provide the diffusion coefficients of these different adsorbates in each simulation. The diffusion coefficients obtained here are consistent with previous results\textsuperscript{57} reported at similar conditions (Table S5, Supporting Information). The diffusion coefficients of sodium ions and water in mixtures are also smaller than their corresponding bulk values typically due to the confinement effect of clay surfaces. Similar to previous studies,\textsuperscript{19,22,57} at a relatively low constant loading of CO\textsubscript{2} or CH\textsubscript{4} in the clay interlayers, the diffusion coefficients of sodium ions and water decrease due to the less hydrated environment. This is because water molecules effectively screen the surface charges and this effect increases with water. The increase in loading of CO\textsubscript{2} or CH\textsubscript{4} in the clay interlayers, even further reduced those diffusion coefficients. The deviation of the diffusion coefficients of water at \(d = 30\) Å from this general behavior is due to, e.g., its multilayer adsorption.

The diffusion coefficients for CO\textsubscript{2} decrease as its loading increases (Fig. 5), possibly because of steric hindrance. Similarly, at constant loading of CO\textsubscript{2}, the diffusion coefficients for CO\textsubscript{2} decrease as water concentration increases. While, under identical conditions, the diffusion coefficients for CO\textsubscript{2} increase with increasing interlayer space. A similar behavior is observed for methane, in the case of water/CH\textsubscript{4} mixture (Fig. 5). The self-diffusion results of CO\textsubscript{2} and CH\textsubscript{4} match the type I behavior as classified
by Kärger and Pfeifer.\textsuperscript{83} The transport of CO\textsubscript{2} and CH\textsubscript{4} across nanoporous materials showed that steric hindrance causes a decrease in self-diffusion coefficient as loading increases for each substance.\textsuperscript{83–85} The self-diffusion coefficient of very strongly adsorbed CO\textsubscript{2} molecules near the surface -OH groups of the solid silica substrate and in zeolite imidazolate frameworks (ZIFs) displayed, however, a maximum at intermediate loadings, while that of pure hydrocarbons in nanopores typically decreased with increasing loading.\textsuperscript{26,83–87} It is seen that in most cases the diffusion coefficients of CO\textsubscript{2} and CH\textsubscript{4} under our employed different conditions are larger than their corresponding bulk values. As in previous simulations,\textsuperscript{26,57} we attribute this very high mobility of CO\textsubscript{2} and CH\textsubscript{4} molecules to the less hydrated environment in the clay interlayer. The diffusion coefficients of CO\textsubscript{2} and CH\textsubscript{4} molecules are below their corresponding bulk values due to factors such as the confinement effect of clay surfaces and increase of loading. Previous simulations reported $D_{xy}/D_{\text{bulk}}$ of CO\textsubscript{2} from $\approx 0.03$ to 0.3, for the different water/CO\textsubscript{2} compositions, basal $d$-spacings in the range $\approx 12$ (1W) to 15 Å (2W), and basin conditions.\textsuperscript{19,22} Incidentally, we also find that $D_{xy}/D_{\text{bulk}}$ values of CO\textsubscript{2} are $\approx 0.03$ and 0.4 for $d = 12$ and 15 Å, respectively, at their highest considered water contents and loadings (see Figs. 5a-b and Table S4). Additionally, the lateral diffusion coefficient for CO\textsubscript{2} at $d \approx 18$ Å attained a value ($4.23 \times 10^{-9}$ m\textsuperscript{2}/s) comparable to that measured for diffusion of CO\textsubscript{2} in bulk water,\textsuperscript{22} which is again consistent to our work (see our results for a water content of 0.6 g/cm\textsuperscript{3}, in Fig. 5c and Table S4). Note that the diffusion coefficients of both water and CO\textsubscript{2} increased with increasing loading of CO\textsubscript{2}, due to the associated expansion of the interlayer space, which is not explicitly included in our simulations.\textsuperscript{22}

The diffusion coefficients of CH\textsubscript{4} molecules and, to a very lesser extent, CO\textsubscript{2} molecules at constant loadings of CH\textsubscript{4} and CO\textsubscript{2} molecules in the clay interlayers, respectively, are mostly much higher than those of corresponding water molecules (see Tables S4-S5), which is in good accordance with the observed fluid-clay interaction energies\textsuperscript{67,68} and preferential adsorption to the pore walls (see Fig. 2).\textsuperscript{19,20,22,57,66–68} Previous simulations reported the ratios of diffusion coefficients of CO\textsubscript{2} to water for
states \( \leq 3W \), in the range \( \approx 0.5 \) to \( 4.0 \),\(^{19,22}\) which are close to our corresponding results at the highest considered water contents (e.g., 0.4 and 0.6 g/cm\(^3\)). Likewise, high diffusion coefficients of methane in the clay interlayer are in agreement with those reported by Rao and Leng.\(^{57}\) For example, they obtained the ratios of diffusion coefficients of CH\(_4\) to water for states from \( \approx 2W \) to \( 3W \), in the range \( \approx 0.5 \) to \( 16.0 \), consistent with our results, e.g., at the highest considered water contents (0.4 and 0.6 g/cm\(^3\)). Such high values of the diffusion coefficient of methane in dry clay samples have also been reported.\(^{6,26}\) Cha et al. reported the dissociation of methane hydrate at about ambient temperature and lower pressure (\( \lesssim 50 \) bar) in the presence of bentonite which is mainly Na-montmorillonite, than observed for the same process in water alone.\(^{62}\) The diffusion coefficients of methane we obtained are lower than its bulk value and that of water, e.g., at \( d = 18 \) Å and the highest studied water content (0.6 g/cm\(^3\)). This suggests that only those system contains a stable methane clathrate.\(^{59,62}\) At the same conditions, the diffusion coefficients of CO\(_2\) are, however, of the same order of magnitude as its bulk value and that of water, making the montmorillonite-CO\(_2\) hydrate a relatively less stable system. Furthermore, MSDs and adsorption energies supported that smectite-methane hydrate complexes are more stable than smectite-CO\(_2\) complexes.\(^{69}\)

### 3.2 Water/CO\(_2\)/CH\(_4\) ternary mixture in Na-montmorillonite

#### 3.2.1 Atomic density profiles

We also carried out MD simulations of ternary water/CO\(_2\)/CH\(_4\) mixture in Na-montmorillonite clay at 298.15 K. The final configurations obtained from the GCMC simulation study of adsorption of, e.g., equimolar CO\(_2\)/CH\(_4\) binary mixture by Na-montmorillonite in the presence of preadsorbed water,\(^{67}\) were used as the initial configurations in our NVT simulations. In order to examine the distributions of the different species in the interlayer space of the clay, number density profiles were calculated for carbon dioxide and methane in variably hydrated Na-montmorillonite. Fig. 6 shows the average den-
sity profiles of carbon dioxide (carbon atoms) and methane molecules in the ternary mixture computed along the z-axis at compositions obtained for a bulk pressure of 20 bar (equimolar CO₂/CH₄). Figs. S34-S36 in the Supporting Information provide the corresponding distributions of water oxygens and sodium ions. Figs. 6a and c represent the profiles of the various species adsorbed at a preadsorbed water content of 0.2 g/cm³, while Figs. 6b and d report a preadsorbed water content of 0.4 g/cm³. The distributions confirm that carbon dioxide, methane, and water molecules here form well-defined layered structures, similar to the behavior of pure hydration states or binary mixture (water/CO₂ and water/CH₄) profiles described in the previous section. Again, sodium ions mostly occur as inner- and outer-sphere surface complexes.

The density profiles of carbon dioxide and methane molecules in the ternary mixture demonstrate that the clay material has a high adsorption selectivity for carbon dioxide over methane (Fig. 6). This observation is consistent with our simulation results over the studied basal d-spacings and pressure/loading range. A recent study also reported that, CO₂ molecules with enhanced adsorption strength are able to competitively replace CH₄ molecules within the clay samples in their dehydrated states. As is clearly evident from these profiles, CO₂ and CH₄ molecules in the interlayers of hydrated Na-montmorillonite hardly influence the distribution of other atoms. The features of the profiles of the binary mixtures are mostly conserved for the ternary mixture, over the studied conditions. For example, the presence of increasing water molecules in the clay, in general, reduces adsorption amounts of both CO₂ (see Figs. 6a and b) and CH₄ (see Figs. 6c and d) molecules. The density profiles show that the favorability of adsorption of CO₂ and, to a very lesser extent, CH₄ by montmorillonite observed in the binary mixture case (see Fig. 2), at relatively low pressures, intermediate water contents, and large basal d-spacings is retained during the ternary mixture adsorption. Similarly, the density peak of CO₂ is closer to the clay surface, as compared with CH₄. A notable exception is that, methane molecules now have lower densities near to the clay surface relative to the bulk at d = 30 Å. This result is expected due to the stronger affinity of water and CO₂ toward the surface than methane.
3.2.2 Preferential adsorption sites

To identify the preferential adsorption sites on the montmorillonite substrate of the different species of the ternary mixture, we calculated in-plane (xy) density distributions. All these calculations were performed again for each molecule found within either the first closest adsorption layer (monolayer) near to the clay surface or away from it (see, e.g., Fig. 6). The computed distributions of carbon dioxide (carbon atoms) and methane molecules in the ternary mixture at a basal $d$–spacing of 15 Å and compositions obtained for a bulk pressure of 20 bar (equimolar CO$_2$/CH$_4$) are shown in Fig. 7. Figs. S37-S42 in the Supporting Information provide the corresponding distributions of water oxygens and sodium ions, and additionally, the distributions of different species in the interlayer of the Na-montmorillonite-water-CO$_2$-CH$_4$ system at identical conditions and for the other investigated basal spacings.

The in-plane distributions of water and sodium ions in the ternary mixture are hardly different from the corresponding binary mixture cases (see previous section). The distribution of methane coincides with the CO$_2$ region showing that these molecules can coexist near the clay plane. Besides that, methane and carbon atom in a CO$_2$ molecule near the clay surface again have a tendency to occupy the ditrigonal cavities (see, e.g., Fig. S43, Supporting Information). An increase in the water content from 0.2 (Figs. 7a and c) to 0.4 g/cm$^3$ (Figs. 7b and d), favors displacement of both CO$_2$ and CH$_4$ molecules by water from near the sites of the substitutions in the clay sheets. We observe a similar distribution behavior of CO$_2$ and CH$_4$ molecules close to the clay surfaces at basal $d$–spacings of 18 and 30 Å, while such a behavior persists, albeit diminished, also away from the clay surfaces at a basal $d$–spacing of 30 Å for CH$_4$, and at basal $d$–spacings of 18 and 30 Å for CO$_2$ molecules. In passing, note that the behavior of the orientations of water dipoles and CO$_2$ in the ternary mixture (Figs. S44 and S45, Supporting Information) is very similar to the corresponding binary mixture cases over the studied conditions.
3.2.3 Dynamical properties

The main factors affecting the self diffusion coefficients of sorbate molecules in a confined mixture include such as steric hindrance of the motion of a tagged particle by neighboring particles as the loading increases, momentum transfer correlations, wherein the faster diffusing species diffuses slower in the mixture relative to the pure component and the slower diffusing species diffuses faster in the mixture than in the pure state, and preferential adsorption. Fig. 8 reports the in-plane diffusion coefficients of CO$_2$ and CH$_4$ molecules in the interlayers of Na-montmorillonite for the different water/CO$_2$/CH$_4$ ternary mixture compositions in the pore outputted by the GCMC simulations. Table S6 in the Supporting Information also provides the diffusion coefficients of these molecules in each simulation. The most important observation from our results is that the diffusion of CO$_2$, at constant loading of CO$_2$, is not much affected by CH$_4$ for the investigated mixture compositions (Figs. 8a-c). The response of CH$_4$ to CO$_2$, at constant loading of CH$_4$ is, however, quite different from the effect of CH$_4$ on CO$_2$, because the presence of adsorbed CO$_2$ reduces very significantly the diffusion coefficients of CH$_4$ (Figs. 8d-f), and relatively larger decrease in those diffusion coefficients are seen at higher loadings. For example, a mixture of CO$_2$/CH$_4$ with bulk composition of 20:80 in the presence of water, leads to a maximum decrease of only about 20% in the self-diffusion coefficients of CO$_2$ from its corresponding values of pure states over the studied conditions. While a mixture of CO$_2$/CH$_4$ even with bulk composition of 20:80 shows a decrease, e.g., by a factor as high as about 4 in the self-diffusion coefficient of CH$_4$ (basal d–spacing of 15 Å, water content of 0.2 g/cm$^3$, and loading of $\approx$ 20 CH$_4$ molecules per supercell) from its corresponding value of pure state. This decrease in the diffusivity becomes quite marked as the contribution of CO$_2$ to the bulk composition of CO$_2$/CH$_4$ mixture increases further, reflecting the severe steric hindrance posed to a diffusing CH$_4$ molecule by other adsorbed molecules in those cases.

In montmorillonites, CO$_2$ is very strongly preferred over CH$_4$ at all loadings, as
is evident from the above described density profiles. Therefore, the adsorbed mixture is very \( \text{CO}_2 \) dominant relative to \( \text{CH}_4 \) and the distribution of \( \text{CO}_2 \) in the mixture is not dramatically perturbed from that of the pure fluid due to loading of methane. For this reason, the diffusion coefficients of \( \text{CO}_2 \) in the pore is largely independent of the fraction of \( \text{CH}_4 \) in the bulk mixture, at all investigated conditions (see Figs. 8a-c). As demonstrated above, \( \text{CO}_2 \) molecules introduced in the interlayer space of the Na-montmorillonite preferentially adsorb to the surface and in this way screen these possible attractive sites for \( \text{CH}_4 \). Such a microscopic behavior should lead to an enhancement of the diffusion coefficient of methane molecules. However, \( \text{CO}_2 \) molecules simultaneously occupy and/or crowd the interlayer space and consequently reduce the effective diffusing space for \( \text{CH}_4 \) molecules. At low loadings of \( \text{CO}_2 \), the combination of both effects leads to a very slight decrease in the self-diffusion coefficients of \( \text{CH}_4 \) molecules, while at higher loadings of \( \text{CO}_2 \), the steric hindrance effect becomes much more important and the self-diffusion coefficients of \( \text{CH}_4 \) molecules significantly decrease (see Figs. 8d-f). Water preferentially binds to the clay surface and therefore, similar effects of water on both carbon dioxide and methane, increase with increasing water content at constant loadings of \( \text{CO}_2 \) and \( \text{CH}_4 \). Because of this, the diffusion coefficients of \( \text{CO}_2 \) and \( \text{CH}_4 \) decrease with an increase in water content (see Fig. 8). A similar observation was reported for the self-diffusion properties of \( \text{CH}_4 \) in \( \text{CO}_2/\text{CH}_4 \) binary mixtures within NaY zeolite.\(^{89}\) In contrast, ZIFs showed that the diffusivity of \( \text{CH}_4 \) is essentially independent of the loading of \( \text{CO}_2 \) in the \( \text{CO}_2/\text{CH}_4 \) mixture, while \( \text{CO}_2 \) diffusivity significantly decreased with an increase in loading of \( \text{CH}_4 \) due to differences in adsorption site preferences.\(^{87}\) Also, carbon dioxide enhanced the self-diffusion coefficients of hydrocarbons such as methane and butane possibly by decreasing their diffusion activation energies due to the competitive adsorption of carbon dioxide on the pore surfaces.\(^{86,90}\)

As discussed in the previous section, the montmorillonite-\( \text{CO}_2 \) hydrate complex, e.g., at a basal \( d \)-spacing of 18 Å is relatively unstable, and therefore the replacement of \( \text{CH}_4 \) in a montmorillonite-\( \text{CH}_4 \) clathrate by \( \text{CO}_2 \) due to preferential attractive ac-
cumulation of CO$_2$ molecules on the clay surfaces (see Figs. 1, 6, and 7) may result in an unstable system. In agreement to our findings, the simulated smectite-CH$_4$ hydrate complexes were reported to be more stable than the smectite-CO$_2$-CH$_4$ mixed and the smectite-CO$_2$ hydrate complexes for a basal $d$-spacing of $\approx 22$ Å.$^{69}$ Taking into account explicit swelling, along with, e.g., the stability analysis of the ternary mixture based on swelling free energy$^{19,58,66}$ and further experiments should shed more light into such effects. Our simulations do not probe clay flexibility, chemical reactions, and pore-network-scale geometric effects such as pore-size variability, pore connectivity, and tortuosity.$^{51,53}$ However, as with water,$^{51,53}$ we hope that our simulated diffusion coefficients can be compared to the macroscopic values calculated from experimental work on hindered motion of carbon dioxide and methane through a clay membrane.

4 Conclusions

We have completed extensive molecular dynamics simulations to better assess the diffusion behavior of CO$_2$, CH$_4$, and their mixture in Na-montmorillonite clay in the presence of water at 298.15 K. The simulations show that the self-diffusion data of CO$_2$ and CH$_4$ match the type I behavior as classified by Kärger and Pfeifer.$^{83}$ The diffusion coefficients of CO$_2$ in the interlayers of Na-montmorillonite decrease as its loading increases, possibly because of steric hindrance. Similarly, at constant loading of CO$_2$, the diffusion coefficients for CO$_2$ decrease as water content increases. While, under same conditions, the diffusion coefficients for CO$_2$ increase with increasing basal $d$-spacing. Similar behavior is seen with the diffusion behavior of methane in Na-montmorillonite in the presence of water. The self-diffusion coefficients of water and sodium ions, at a relatively low constant loading of CO$_2$ or CH$_4$ in the clay interlayers, decrease due to the less hydrated environment where water molecules less effectively screen the surface charges. The increase in loading of CO$_2$ or CH$_4$ in the clay interlayers, even further reduced those diffusion coefficients. The diffusion coefficients of CH$_4$ molecules and, to a very lesser extent, CO$_2$ molecules are mostly much higher than
those of water molecules, which is in good accordance with the observed fluid-clay interaction energies\textsuperscript{67,68} and preferential adsorption close to the pore walls.\textsuperscript{19,20,22,57,66–68}

An important finding is that the diffusion of CO\textsubscript{2} in the interlayers of Na-montmorillonite, at constant loading of CO\textsubscript{2}, is not much affected by CH\textsubscript{4} for the investigated CO\textsubscript{2}/CH\textsubscript{4} mixture compositions. Through careful analysis of the atomic density profiles of the different species in the interlayers, we attribute this to the preferential adsorption of CO\textsubscript{2} over CH\textsubscript{4} in Na-montmorillonite. While the presence of adsorbed CO\textsubscript{2} molecules, at constant loading of CH\textsubscript{4}, very significantly reduces the self-diffusion coefficients of methane, and relatively larger decrease in those diffusion coefficients are observed at higher loadings. The preferential adsorption of CO\textsubscript{2} molecules to the clay surface screens those possible attractive surface sites for CH\textsubscript{4} which may lead to an enhancement of the diffusion coefficient of methane molecules. However, CO\textsubscript{2} molecules simultaneously occupy the interlayer region and, therefore, decrease the effective diffusing space for CH\textsubscript{4} molecules. The interplay of both effects leads to a very slight decrease in the self-diffusion coefficients of CH\textsubscript{4} molecules at low loadings of CO\textsubscript{2}. The steric hindrance effect becomes much more significant at higher loadings of CO\textsubscript{2} and the self-diffusion coefficients of methane molecules significantly decrease. The simulations show that similar effects of water on both carbon dioxide and methane, increase with increasing water content, at constant loadings of CO\textsubscript{2} and CH\textsubscript{4} in the interlayers of Na-montmorillonite. Our results could be useful, such as for designing separation devices, CO\textsubscript{2} storage, and also for better understanding the behavior of fluids in nanoporous rocks (e.g., shales). In the future, we hope to explore the hydrogen bond dynamics,\textsuperscript{22} residence time of different species,\textsuperscript{22,46} and Poiseuille and electro-osmotic flows in clay nanopores.\textsuperscript{43}

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**Supporting Information**

Additional details of simulation analysis are provided in the Supporting Information.
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Figure 1: Equilibrium snapshot of Na-montmorillonite at $T = 298.15$ K with a preadsorbed water content of 0.4 g/cm$^3$ and in contact with equimolar CO$_2$/CH$_4$ mixture at a bulk pressure of 20 bar. The basal $d$-spacing is 18 Å. Color code: O, red; H, white; Si, yellow; Al, light blue; Mg, light green; Na, dark blue; C, black.
Figure 2: Equilibrium distributions of CO$_2$ (top panels) and CH$_4$ (bottom panels) molecules in the interlayers of Na-montmorillonite at $T = 298.15$ K and a bulk pressure of 20 bar each. The origin corresponds to the clay surface oxygen. The preadsorbed water contents are 0.2 (left panels) and 0.4 g/cm$^3$ (right panels).
Figure 3: Equilibrium distributions (in-plane) of CO$_2$ (top panels) and CH$_4$ (bottom panels) molecules at basal $d$–spacings of 12 and 15 Å, respectively, in the interlayers of Na-montmorillonite at $T = 298.15$ K and a bulk pressure of 20 bar each. The preadsorbed water contents are 0.2 (left panels) and 0.4 g/cm$^3$ (right panels). Bright regions correspond to high density. The positions of Al substitutions in the adjacent tetrahedral layers are indicated by small circles (cyan), while that of Mg in the inner octahedral layer are given by large circles (green).
Figure 4: Equilibrium distribution of orientations of the head-to-tail vector of CO$_2$ molecules relative to the axis perpendicular to clay surface in the interlayers of Na-montmorillonite at $T = 298.15$ K and a bulk pressure of 20 bar. The basal $d$–spacings are (a) 12, (b) 15, (c) 18, and (d) 30 Å, and the preadsorbed water content is 0.2 g/cm$^3$. The origin corresponds to the clay surface oxygen. Bright regions correspond to high probabilities of orientation angles.
Figure 5: Normalized diffusion coefficients of CO$_2$ (squares) and CH$_4$ (circles) molecules in the interlayers of Na-montmorillonite at $T = 298.15$ K and for different water/CO$_2$ and water/CH$_4$ binary mixture compositions in the pore, respectively. The basal $d$–spacings are (a) 12, (b) 15, (c) 18, and (d) 30 Å, and the preadsorbed water contents are 0.2 (black-filled), 0.4 (open), and 0.6 g/cm$^3$ (gray-filled).
Figure 6: Equilibrium distributions of CO$_2$ (top panels) and CH$_4$ (bottom panels) molecules in the interlayers of Na-montmorillonite at $T = 298.15$ K and in contact with equimolar CO$_2$/CH$_4$ mixture at a bulk pressure of 20 bar. The origin corresponds to the clay surface oxygen. The preadsorbed water contents are 0.2 (left panels) and 0.4 g/cm$^3$ (right panels).
Figure 7: Equilibrium distributions (in-plane) of CO$_2$ (top panels) and CH$_4$ (bottom panels) molecules at a basal $d$—spacing of 15 Å in the interlayers of Na-montmorillonite at $T = 298.15$ K and in contact with equimolar CO$_2$/CH$_4$ mixture at a bulk pressure of 20 bar. The preadsorbed water contents are 0.2 (left panels) and 0.4 g/cm$^3$ (right panels). Bright regions correspond to high density. The positions of Al substitutions in the adjacent tetrahedral layers are indicated by small circles (cyan), while that of Mg in the inner octahedral layer are given by large circles (green).
Figure 8: Normalized diffusion coefficients of CO₂ (left panels) and CH₄ (right panels) molecules in the interlayers of Na-montmorillonite at $T = 298.15$ K and for different water/CO₂/CH₄ ternary mixture compositions in the pore. The mole fractions of methane in bulk phase are 0.2 (squares), 0.5 (circles) and 0.8 (triangles). The basal $d-$spacings are 15 (top panels), 18 (middle panels), and 30 Å (bottom panels), and the preadsorbed water contents are 0.2 (filled) and 0.4 g/cm$^3$ (open). The solid (water content of 0.2 g/cm$^3$) and dashed (water content of 0.4 g/cm$^3$) lines represent the diffusion coefficients of CO₂ and CH₄ molecules in the interlayers of Na-montmorillonite for the corresponding water/CO₂ and water/CH₄ binary mixtures, respectively (see Fig. 5).
Table of Contents (TOC) Image

Molecular Dynamics Simulations of Carbon Dioxide, Methane, and their Mixture in Montmorillonite Clay Hydrates

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