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Adsorption of Carbon Dioxide, Methane and Their Mixtute by Montmorillonite in the Presence of Water

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Abstract

Using grand canonical Monte Carlo (GCMC) simulations, we study the adsorption behavior of CH₄, CO₂, and their mixtures at 298.15 K and pressures up to 50 bar in Na-, Cs-, and Ca-montmorillonite clays in the presence of water. Montmorillonite clays in the presence of preadsorbed water, preferentially adsorb CO₂ over CH₄ during both pure component and mixture adsorption. The atomistic model we have used, gives good agreement with available single-component experimental adsorption isotherms, for CH₄ and CO₂ molecules adsorbed onto montmorillonite clays in the presence of water. We observe the general trend that the presence of increasing preadsorbed water content in the clay interlayers, reduced adsorption amounts of pure CH₄ and CO₂ molecules. With a relatively large basal spacing ($d = 30 \text{ \AA}$), the favorability of adsorption of CO₂ by montmorillonite at relatively low pressures and intermediate water contents has been demonstrated using simulations. GCMC simulation is also used to assess the effect of water on the adsorption of N₂/CH₄, H₂S/CH₄, CO₂/N₂, and CO₂/H₂S binary mixtures in Na-montmorillonite clay. The ideal adsorbed solution theory is shown to agree well with the observed adsorption capacities and selectivities of mixtures in Na-montmorillonite clay.

1 Introduction

Naturally occurring clay minerals determine the key physical traits such as permeability and certain chemical properties such as gas adsorption of shales¹⁻⁴ and provide a distinctive material for carbon dioxide sequestration⁵⁻⁸ and selective sorption.⁹⁻¹² Shale mineralogy varies widely such that some shales are silt-rich or carbonate-rich whereas others are dominated by clay minerals, for example, illite, chlorite, smectite, and kaolinite.^{4,13,14} Processes such as Knudsen diffusion, slip flow (Klinkenberg effect) and adsorption at the solid matrix can affect permeabilities and Darcy-type flow would be disturbed in case of deviation from the laminar flow.¹⁵ However, none of the above models predict the correct behavior of shale gas production data. Thus in spite of the recent improved success in shale gas production,¹⁶ the underlying adsorption and flow mechanisms in shale media are not well understood.^{17,18} In nature, smectite such as montmorillonite is one of the most common type of swelling clay minerals.¹⁹⁻²⁵ To date, there have been numerous simulation studies on water adsorption and swelling in montmorillonites.²³⁻³⁵ The stable basal d -spacing is around 10 Å for dry clays and increases upon interaction with water to the range 11.5-12.5 Å forming a fully saturated monolayer (1W) water arrangement.^{24,27,29-32,36} Due to intake of more water, the d -spacing can increase to the next stable state (14.5-15.5 Å) where water forms a bilayer (2W) structure. Likewise, measured basal d -spacings for three layers of water (3W) are in the range 18.0-19.1 Å. In recent years, molecular modeling of the structure and dynamics of the water-methane mixture in the interlayer region of smectites has attracted interest.^{18,37-41} These simulations demonstrated that montmorillonite surfaces facilitate methane hydrate crystallization from aqueous solution in agreement with experiments.⁴²

Geologic sequestration of carbon dioxide has recently emerged as an alternative for reducing greenhouse emissions.^{5-8,20,39,43-47} According to experimental investigations,^{5,8} carbon dioxide adsorption capacity of clay minerals is comparable to that of coal. The swelling of organoclays in the supercritical CO₂ medium is also important

in nanocomposite preparations and applications.^{48,49} Preferential adsorption of ions and molecules on clay minerals such as montmorillonite can be used for ion exchange⁹ and gas selectivity.^{10–12,18,50} The main component of shale gas is methane, but the composition of the shale gas depends on multiple factors, most of which have geological and geochemical origins.⁵¹ An important issue relevant to methane recovery^{1,4} and CO₂ storage capacity^{5,8} in clays involves the effect of the presence of preadsorbed water, which cannot be avoided owing to the hydrophilic nature of the samples. The presence of such adsorbed solvents leads to, for example, a striking increase of gas solubility in porous solids with pore size in the range of nanometers⁵² and modified sorbate intake.⁵³ Experimental studies have considered adsorption on dry^{1,3–6,10} as well as on moisture equilibrated^{1,4,5,8,20,46,54} clays. The mixture adsorption data is typically predicted from pure component adsorption measurements using the capability of approximate methods such as the ideal adsorbed solution theory (IAST).^{55,56} In common practice, IAST can give fair predictions of gas mixture adsorption in many zeolites⁵⁷ and metal-organic frameworks.⁵⁸

Apart from experimental studies, the effect of moisture on gas sorption in montmorillonite clay minerals and the underlying sorption mechanisms have also been examined in computer simulations.^{7,11,18,38,39,44,46,50} Up to now, there are not enough experimental adsorption isotherm data in this field, especially for adsorption on pure clay minerals. Sometimes the difference of experimental conditions and characteristics of clay minerals would make the results of different studies somewhat incomparable. A comparison between experimental (see, for example, ref 1) and simulation studies is made in this work. In our study, Na-, Cs-, and Ca-montmorillonite were specifically selected for the intercalation of CO₂ and CH₄ molecules into wet clays. This is not only with a view to getting new insight into the effect of ionic size and charge on adsorption behavior of CO₂ and CH₄ molecules, but also because they have already been elaborately investigated for pure water adsorption in clays, both experimentally and in molecular simulations. The adsorption of methane or CO₂ upon montmorillonite from mixture containing species (impurities) other than hydrocarbons and water has

been rarely studied.^{45,59,60} The objective of our present work was to systematically investigate using grand canonical Monte Carlo (GCMC) simulations the adsorption of pure sorbate molecules such as methane, carbon dioxide, nitrogen and hydrogen sulfide as well as their mixture upon clay minerals in the presence of water. The number of adsorbed water molecules is kept constant in our simulations upon subsequent gas adsorption, because typical hydrophilic pores indicate that water remains adsorbed upon carbon dioxide and methane adsorption.^{1,20,45,61} Preferential sorption of water at the clay surfaces, however, does not mean that the number of adsorbed water molecules has to be kept fixed in the interlayers to study intercalation of other species.^{18,44,50,62} The adsorption isotherms and density profiles of these four molecules, at different basal d -spacings and densities of preadsorbed water in the interlayer of clays, are first obtained from GCMC simulations in the μVT ensemble, where μ is the chemical potential of the adsorbing molecule. For this study, we chose basal spacings $d = 12, 15, 18$, and $30 \text{ \AA}$ covering, for example, the swelling states (at fully saturated water arrangement) $\sim 1W, \sim 2W, \sim 3W$, and $> 3W$, respectively. The simulated d -spacings are similar in spirit to previous studies^{24,25,27,28,34} and consistent with those known for montmorillonites in the atmospheric environment containing sorbate molecules.^{1,5,8,45}

When using pre-determined interlayer distances to study the adsorption of binary and ternary mixtures with one of their components (water) preadsorbed at certain concentrations, the final equilibrated compositions of the mixtures do not necessarily correspond to the thermodynamically stable states. We chose to employ basal spacings of 12 and $15 \text{ \AA}$, for a comparison (see Fig. 2) of our simulated and corresponding experimental data reported by Liu et al.¹ and Romanov⁸ for adsorption of binary mixtures (e.g., $\text{H}_2\text{O}/\text{CO}_2$ and $\text{H}_2\text{O}/\text{CH}_4$) in montmorillonite clays with one of the two components (water) preadsorbed at certain concentrations. Experiments showed that, interaction of montmorillonite clays with variably wet CO_2 (2%-100% saturation of H_2O) at $T = 323.15 \text{ K}$ and $P = 90 \text{ bar}$ can lead to swelling to a d -spacing of $\approx 18.8 \text{ \AA}$.⁴⁵ For the case of adsorption of binary mixture ($\text{H}_2\text{O}/\text{CO}_2$) upon montmorillonite clays at basin conditions and in the absence of preadsorbed water, simulations^{44,62}

reported that the thermodynamically stable structures are characterized with basal d -spacings corresponding to the monolayer ($d \approx 12$ Å) and bilayer ($d \approx 15$ Å) hydration states consistent with experimental behavior.²⁰ Recent simulations employed similar pre-determined interlayer distances for GCMC simulations of adsorption of binary mixtures (e.g., H₂O/CO₂, H₂O/CH₄, and CO₂/CH₄) in clays.^{18,39,50,63} The adsorption simulation using a large basal d -spacing (30 Å) would represent, for example, gas adsorption onto an external montmorillonite surface. Since the experimental data of ternary mixtures are not yet available, we assume that the stable states for ternary mixtures (e.g., H₂O/CO₂/CH₄) are also close to the above selected d -spacings ($\sim 1W$, $\sim 2W$, $\sim 3W$ etc.) over the studied conditions. In addition, IAST based on fitting curves of single component adsorption isotherms is used to predict mixture isotherms, and compared with the corresponding results of our direct molecular simulations. Our simulations show the general trend, that the presence of increasing water molecules in the clay reduced adsorption amounts of pure CH₄ and CO₂ molecules. The favorability of adsorption of CO₂ by montmorillonite clay at relatively low pressures and intermediate water contents has been demonstrated using simulations, which could open new possibilities for tuning the adsorption behavior in clays for CO₂ storage and other applications.

2 Simulation details

The model of clay used is the Wyoming-type montmorillonite^{23,24,26,27,29,31,39} which contains tetrahedral and octahedral substitutions. Wyoming-type montmorillonite is commonly referred as Na-enriched montmorillonite occurring in nature. Texas-type (Ca-enriched) montmorillonite also has tetrahedral and octahedral substitutions. The montmorillonite modeled here has a layer charge of $-0.75e$, approximately 66.6% of which is in the octahedral layer, and the unit cell formula is $M_{0.75/n}(Si_{7.75}Al_{0.25})(Al_{3.5}Mg_{0.5})O_{20}(OH)_4$, where M represents a counterion (Na^+ , Cs^+ , or Ca^{2+}) and n represents the charge on the ion. This clay model is based on the pyrophyllite unit cell structure ($Si_8Al_4O_{20}(OH)_4$)

with the position of the atoms in the unit cell of the clay taken from Skipper et al.²³ In order to minimize finite size effect, the simulation box is made up of two tetrahedral-octahedral-tetrahedral (TOT) clay layers,²⁴ each containing replicated pyrophyllite unit cells ($8 \times 4 \times 1$) with dimensions 42.24, 36.56, and 6.56 Å along x , y , and z directions, respectively. The simulation supercell of orthorhombic symmetry ($\alpha = \beta = \gamma = 90^\circ$), thus consists of two TOT clay layers made up by a total of 64 unit cells. Periodic boundary conditions were employed in all three spatial dimensions. The two TOT clay layers are parallel to each other and considered to be rigid molecules. At the start of each simulation, the water molecules and counterions were placed at random within the interlayer region. The sorbate molecules are permitted to move in and out of the simulation box, while the number of preadsorbed water molecules and counterions are kept constant during GCMC simulations. Note, however, that the dynamics of preadsorbed water molecules and counterions are allowed. The z dimension of the simulation box $L_z = 2d$, where d is the basal spacing which is the sum of the clay layer thickness and the interlayer space. The distance along z direction between planes through the centers of the inner oxygen atoms of two adjacent TOT layers defines the interlayer spacing. As in previous simulations,^{24,27,39} the clay layer of Wyoming-montmorillonite was constructed by introducing in each clay sheet 16 isomorphic substitutions of trivalent Al atoms by divalent Mg atoms in the octahedral sheet, 8 isomorphic substitutions of tetravalent Si atoms by trivalent Al atoms in the tetrahedral sheets, and 24 compensating monovalent sodium or cesium ions in the interlayer region (12 in the case of Ca-montmorillonite). All these substitutions were assigned in a fashion to obey the Loewensteins rule (neighboring Al-O-Al avoidance).²⁶ Here we are using the capability of the CLAYFF force field²⁹ which represents more realistically the local charge inhomogeneities formed around each specific substituted site in the clay configuration.²⁶ Further details of the force fields (Table S1), simulation method, validation of simulation model, isotherm equations used to fit our pure component simulation data, and IAST are provided in the Supporting Information.

3 Results and discussion

3.1 Single component adsorption of CH₄, CO₂, N₂, and H₂S in the presence of preadsorbed water

GCMC simulations were performed to calculate single-component adsorption isotherms for methane, carbon dioxide, nitrogen and hydrogen sulfide in variably hydrated montmorillonite at 298.15 K. The computed isotherms at basal d -spacings of 12, 15, 18 and 30 Å are shown in Fig. 1 as symbols. Tables S2-S5 in the Supporting Information also provide the average number of pure adsorbates (CH₄, CO₂, N₂, and H₂S, respectively) in each simulation. We report in our simulations, the total uptake or amount adsorbed unless otherwise stated. In addition, density of water is reported as the mass of water molecules in an interlayer in g per interlayer volume (simulation cell area $\times$ ($d - 6.56$) Å) in cm³. For example, in ambient conditions and for basal d -spacings of 12, 15, and 18 Å, we have obtained ≈ 0.52 , 0.71, and 0.80 g/cm³ of saturated water densities in the interlayer space of Na-montmorillonite clay, respectively (see Fig. S1, Supporting Information). Over the basal d -spacings and pressure range considered in our study, the presence of increasing water molecules in the clay typically reduced the sorbate adsorption. Fig. 1 shows not only the data of our GCMC simulations but also the best fits (lines) to these isotherm curves. Fits of the single-component isotherms using equations, such as Langmuir model,⁵⁶ are needed to predict the adsorption isotherms of gas mixtures using IAST (see next section).

The simulated adsorption isotherms and the experimental one are compared in Fig. 2. In order to convert the total adsorbed amounts of our GCMC simulations to the excess quantities (see eq. S9, Supporting Information), Fig. S2 in the Supporting Information provides estimate of accessible pore volume, obtained by GCMC simulations of helium adsorption in montmorillonite clays, as a function of basal d -spacing at various densities of water. Liu et al. experimentally studied CH₄ adsorption upon 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 model.¹ The highest sorption capacity was obtained for the Ca-rich montmorillonite pre-heated at 473.15 K, with a maximum value of ≈ 0.25 mmol/g_{clay}. They demonstrated that the adsorbed water occupied the adsorption sites of the clay minerals and reduced the CH₄ adsorption capacity. Their observation is in good qualitative agreement with our simulation result, that the CH₄ adsorption capacity decreased with the increasing moisture content. Note that, in the experimental study described by Liu et al.,¹ both the water molecules from inside and outside the interlayer space were considered, but only interlayer water adsorption is considered in this study. Besides, the experiments do not provide clear distinction between sorption within the interlayer space and on the external surface. Therefore, using the preadsorbed water content as a fitting parameter, the simulated methane isotherms were fitted to match the corresponding experimental ones. Similar findings were obtained in the experiments of high pressure CH₄ adsorption conducted on dry and moisture equilibrated montmorillonite samples.⁴

Experimental study of CO₂ capture in Na-rich Wyoming montmorillonite (SWy-2) 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 adsorption at low pressures.⁸ The CO₂ sorption isotherms of dry Ca-rich Texas montmorillonites as well as Na-rich Wyoming montmorillonite measured at 318.15 K yielded typically higher excess sorption values than the corresponding samples with moisture content.⁵ Recent studies combining in situ experiment and theory by Schaefer et al. showed that for montmorillonite clays, CO₂ intercalation peaks from $\sim 0W$ to $1W$ equivalent hydration states, and then decreases with further hydration.⁶⁴ These above-mentioned experiments are in qualitative agreement with our GCMC simulation results (see, e.g., Figs. 1 and 2). Separate GCMC simulations of adsorption of pure water ($\mu_{H_2O}VT$) in the clay corresponding to the one used for experimental studies under the room conditions of 20% RH,⁸ provided a water content in the interlayers ≈ 0.4 g/cm³, which is used as a fitting parameter in Fig. 2 (Assuming that the vapor is an ideal gas, $RH/100 \approx \exp(\mu/k_B T)/\exp(\mu_0/k_B T)$, where μ_0 is the water chemical potential at saturated RH³³ and the chemical potential of SPC/E

water $\mu_0 \approx -43.1$ kJ/mol under ambient conditions (100% RH)³⁰). Recent computer simulation studies showed that clay-CO₂ interactions become more favorable in sub- to single-hydrated montmorillonite systems, when compared to $\gtrsim 2W$ hydration states, which is consistent with our results.⁶⁰

The adsorbed amounts of sorbate molecules in the clay-water system under identical conditions show the following general order: H₂S > CO₂ > CH₄ > N₂ (see Fig. 1). A similar trend was noted in recent experimental studies dedicated to montmorillonite clays.⁵⁹ The adsorption isotherms for zeolites also displayed a similar behavior.⁶⁵ Polar H₂S has much more affinity to the hydrophilic montmorillonite framework than any other sorbate molecules considered in this work. In this study, we assume that H₂S is adsorbed physically to the clay.^{65,66} CO₂ molecule essentially by virtue of its, e.g., quadrupole moment which is about three times larger than N₂,^{57,65} interacts more strongly with the electrostatic field defined by the clay hydrate. CH₄ has zero quadrupole moment, but higher polarizability than N₂ which is responsible for their above observed order.^{65,67} The above adsorption order is affected, however, by the selection of a relatively small basal spacing (e.g., for the case of $d = 12$ Å, N₂ > CH₄, possibly due to the comparatively significant quadrupole moment of the former). In the absence of intermolecular interactions and surface energetic heterogeneity, the isosteric heat⁶⁸ (see Supporting Information) should be constant at all loadings. The isosteric heats of adsorption of pure adsorbate molecules calculated by using the Clausius-Clapeyron relation (lines) and the fluctuations of the energy (symbols), at a basal d -spacing of 18 Å and a water content of 0.4 g/cm³ in the Na-montmorillonite, are shown in Fig. S3 in the Supporting Information. It is clear from Fig. S3 that the isosteric heats decrease in the order of H₂S > CO₂ > CH₄ > N₂, which is attributed mainly to weakening of fluid-solid interaction. This result is also consistent with the preferentially adsorbed order, according to the isotherms presented in Fig. 1. We also observe a monotonic increase of the isosteric heats of adsorption of various adsorbates as a function of their loading. This is typically due to favorable adsorbate-adsorbate intermolecular interactions and a relatively homogeneous adsorbent surface. Thus, the

stronger the adsorbate-adsorbate interaction, the quicker the curve rising trend.

Other than high uptake capacities, clays exhibit type IV isotherms in the International Union of Pure and Applied Chemistry (IUPAC) classification, for CO_2 and H_2S molecules over the studied pressure range at a basal d -spacing of 30 Å, as illustrated in Figs. 1h and 1p, respectively. The position of the adsorption step is temperature dependent, and moves to higher bulk pressure with increasing temperature (see Fig. S4 in the Supporting Information). In contrast, adsorption isotherm behavior of CH_4 and N_2 at this basal d -spacing was not significantly different, in comparison with the corresponding ones at small separations (basal d -spacings of 12, 15 or 18 Å). Adsorption isotherm, such as the IUPAC type IV, indicates multilayer formation followed by condensation in the pore.^{56,69} Therefore, to explore the distribution of the various species in the interlayer space of the clay, number density profiles were calculated at bulk pressure $P = 20$ bar and with 0.4 g/cm^3 of preadsorbed water. Fig. 3 displays the resulting average density profiles of various sorbate molecules computed along the z -axis (perpendicular to the Na-montmorillonite surface). The corresponding distributions of water (oxygen atoms) and sodium ions are shown in Figs. S5-S8 in the Supporting Information. The distributions of sorbate molecules indicate layered structures similar to pure hydration states such as 1W, 2W, etc. A very high peak is obtained for the first-layer adsorption in almost all cases, which indicates that the strong solid-fluid interaction causes the molecules to pack much closer to the clay surface. In general, the profiles of CH_4 (Fig. 3a) and N_2 (Fig. 3c) are very similar over the studied conditions. As seen in Figs. 3b and 3d, pronounced changes occur in the density profiles of CO_2 and H_2S with increasing basal d -spacing. The distributions indeed confirm that at a basal d -spacing of 30 Å, CO_2 and H_2S molecules significantly accumulate in the middle of the interlayer region of the clay. H_2S molecules form well-defined layered structures and CO_2 molecules also adsorb in multilayers here. The profiles obtained for CH_4 and CO_2 in clays are in good qualitative agreement with previous simulations.^{39,44,46,50} We obtained mostly hydrated sodium ions using the rigid clay model, in qualitative agreement with previous simulation results (see Figs. S5-S8 in

the Supporting Information).^{25,44,46,50}

Very interestingly, we found that the presence of a high water content in the clay is also favorable for the adsorption of carbon dioxide, for a basal d -spacing of 30 Å (see Figs. 1h and S4 in the Supporting Information). The obvious trend in these plots is that, at relatively high pressures, the effect of increased water is to reduce CO₂ uptake (see, for example, Fig. 1h). The opposite effect is observed only at relatively low pressures, and even then only the intermediate amounts of water show this enhancement. These predictions could open new possibilities for tuning the adsorption in clays for CO₂ sequestration and other applications. The multilayer adsorption observed in clay hydrates, for example, could potentially provide a mechanism by which to adsorb CO₂ selectively from gas mixtures at conditions close to those existing in subsurface geological reservoirs and cap rocks. Note that, the relevant P/T conditions based on lithostatic pressure and geothermal gradient significantly differ from those used in this work.^{18,37,44,62} The temperature regimes are much warmer and pressure could be higher (Fig. S4 in the Supporting Information, for example, displays the trend of the gas uptake as a function of temperature and pressure). The temperature, 298.15 K would generally refer to the near-surface geological conditions.^{39,50,63} A similar behavior is predicted for H₂S at a basal d -spacing of 30 Å (see Fig. 1p). In graphene-oxide systems, however, the same phenomena have been reported using combined experiment and simulation studies.⁷⁰ Jin and Firoozabadi also observed using GCMC molecular simulations that when $P \lesssim 40$ bar, CO₂ sorption in montmorillonite clays at a basal d -spacing of 46.56 Å, is comparable for preadsorbed water contents of 0.4 g/cm³ and 0.6 g/cm³, and slightly higher sorption is observed at water content of 0.6 g/cm³.³⁹ Loring et al.⁷¹ reported that the sorbed CO₂ concentration in monmorillonite clays increased dramatically at sorbed H₂O concentrations from 0 to 4 mmol/g. Sorbed CO₂ then decreases as sorbed H₂O increases above 4 mmol/g. Adsorption is a process that is a balance between energetic and entropic contributions. Such arguments have been used previously to describe competitive CO₂/CH₄ adsorption in nanoporous materials of varying porosity.⁷² Consistent with the above observed adsorption preference for

the four adsorbates in terms of polar interactions with the adsorbent, the presence of some water favors adsorption of polar molecules. This factor dominates at low loading, where not much adsorbate is present. However at high loadings, entropic factors dominate because the presence of water occupies pore volume, now not available to the adsorbates.

To gain some insight into why preadsorbed water molecules increase CO₂ adsorption, we examined the number density profiles from the GCMC simulations. The distributions of water, CO₂ and counterions in the interlayer of Na-montmorillonite at a basal d -spacing of 30 Å, $P = 10$ bar, and with 0.2 and 0.4 g/cm³ of preadsorbed water densities are shown in Fig. 4. Also shown are visualizations of these average distributions of molecules in the Na-montmorillonite obtained from GCMC simulation (Fig. S9 in the Supporting Information shows the corresponding profiles of H₂S, but at $P = 2$ bar). Density profiles of atoms in the interlayer region with a water content of 0.2 g/cm³ clearly show separation of CO₂ molecules into two distinct layers, similar to that observed for the water molecules. Further, the sodium cations are solvated within the water layer and mostly remain close to the clay surfaces except a few that are distributed near the midplane of the interlayer region (see Fig. 4a). Inspection of Fig. 4b reveals that at a water content of 0.4 g/cm³, water molecules form layered structures ($> 3W$), and as mentioned above, CO₂ molecules get accumulated in the middle of the interlayer space of the clay as well. Most of the sodium ions are well solvated due to the increase of water content in the interlayer. In contrast to low water content behavior, the sodium ions at this condition are mostly displaced away from the clay surfaces.

To better understand the mechanisms responsible for enhanced adsorption, we calculated the isosteric heats of adsorption of CO₂ from fluctuations of the energy⁶⁸ in our GCMC simulations. Fig. 5 shows the resulting adsorbate-adsorbate (closed symbols) and the fluid-clay contributions (open symbols) to the isosteric heats of adsorption, at a basal d -spacing of 30 Å, and in the presence of 0.2 and 0.4 g/cm³ of preadsorbed water densities. The analysis of the isosteric heat of adsorption clearly shows that,

initially CO₂ molecules adsorb at high-affinity adsorption sites on the clay and subsequent adsorption is at less-favored sites. The fluid-clay isosteric heats of adsorption is approximately of the same order of magnitude for both water densities at all loadings. Therefore, the amount of CO₂ intake is determined by the fluid-fluid interaction. The observation that fluid-clay interactions will be of lesser importance as the adsorbed amount or pressure of CO₂ increases is very reasonable and can be clearly established by plotting the fluid-clay contribution to the potential energy. As shown in the inset to Fig. 5, the fluid-clay energetic contribution will weaken upon an increase in the adsorbed amount of CO₂. It is also clear that, the presence of high water content (0.4 g/cm³) in the clay is energetically less favorable for fluid-clay interaction, in comparison to a water content of 0.2 g/cm³. On the basis of the above analysis and visual inspection of the snapshots, we arrive at the observation that, this enhanced fluid-fluid interaction due to multilayer adsorption of CO₂ (or H₂S) molecules in the clay increases their uptake with the increase of water content.

Isotherms calculated for Na-, Cs-, and Ca-montmorillonite clays indicate a strong dependence of adsorption on the interlayer ion identity (Fig. 1). Under identical conditions, Ca-montmorillonite clay displays the highest adsorption capacity and Cs-montmorillonite the lowest for all isotherms studied. These results appear to be qualitatively correlated with the cation hydration energy, and/or the accessible pore volume (see Fig. S2 in Supporting Information). Note that the extent of water adsorption in clays typically increases with cation-water hydration energy ($\text{Ca}^{+2} > \text{Na}^{+} > \text{Cs}^{+}$).^{27,32,34} In dehydrated montmorillonite, the counterions interact strongly with the clay sheets and are trapped within stable potential wells.⁷³ The radial distribution function between the counterions and tetrahedral oxygen atoms of the dehydrated clay showed strong spatial correlation for Na⁺ in comparison to Ca⁺². Ions such as Ca⁺² and Na⁺ are able to hydrate in the presence of water, thereby becoming separated from the clay surface.^{24,25,27,30,31,33,35,73} In contrast, Cs⁺ ions interact strongly with the rigid clay surface than with the mobile water molecules. The occupation of the surface sites may thus render many such sorption sites inaccessible to sorbate reducing the storage

capacity of clays. Simulated radial distribution functions describing ion-water oxygen ($\text{O}_{\text{H}_2\text{O}}$) spatial correlations in the interlayer of Na-, Cs-, and Ca-montmorillonite at a basal d -spacing of 15 Å, bulk pressure of methane $P = 20$ bar, and in the presence of 0.6 g/cm³ of preadsorbed water are compared in Fig. 6 (Fig. S10 in the Supporting Information provides corresponding distributions of CO_2 , N_2 , and H_2S cases). The ion-water radial distribution functions of Na-montmorillonite clay hydrates containing CO_2 or CH_4 are in fair agreement with previous simulations.^{38,44,50} According to this distribution, both Ca- $\text{O}_{\text{H}_2\text{O}}$ and Na- $\text{O}_{\text{H}_2\text{O}}$ spatial correlations show sharp peaks in $g(r)$ near ≈ 2.4 Å and ≈ 4.4 Å, evidently because of Ca^{+2} and Na^+ solvation effects that has been observed also for pure water in montmorillonite.^{25,44,73} However, this kind of structure in $g(r)$ is relatively weak in the Cs-montmorillonite, suggesting that solvation interactions are important in organizing interlayer water and ions. Typically, sorbate molecules hardly influence⁴⁴ the distribution of other atoms (see also, Fig. S10 in the Supporting Information). Experimentally determined CH_4 adsorption capacity of Na-montmorillonite was found to be lower than that of Ca-Montmorillonite,^{1,4,10} however, possibly because the interlayer distance of Na-montmorillonite is smaller than the size of CH_4 . The highest sorption capacities of CH_4 obtained in the experiments for Ca-rich and Na-rich montmorillonites were ≈ 0.25 and ≈ 0.08 mmol/g_{clay}, respectively (see Fig. 2).^{1,4} The CO_2 sorption isotherms of both dry and moisture containing clays also obtained the highest sorption capacities for Ca-rich montmorillonite.^{5,64}

3.2 Adsorption of CO_2/CH_4 , N_2/CH_4 , $\text{H}_2\text{S}/\text{CH}_4$, CO_2/N_2 , and $\text{CO}_2/\text{H}_2\text{S}$ mixtures in the presence of preadsorbed water

We also carried out GCMC simulations of adsorption of binary mixtures in Na-montmorillonite clay at 298.15 K. Figs. 7a-c show the behavior of CO_2/CH_4 , N_2/CH_4 , and $\text{H}_2\text{S}/\text{CH}_4$ binary mixtures, respectively, as computed using GCMC simulations (symbols) at various bulk mole fractions of CH_4 , a basal d -spacing of 18 Å, and in the presence of 0.4 g/cm³ of preadsorbed water (see also Table S6, Supporting Information). Consistent with

the single-component isotherms described in the previous section, Na-montmorillonite selectively adsorbs all sorbate molecules considered, except N_2 , relative to CH_4 . Our GCMC simulations demonstrate that small amounts of H_2S are able to extremely diminish CH_4 adsorption upon montmorillonite over the studied pressure range (Fig. 7c). The smooth lines in Figs. 7a-c represent the isotherms predicted by applying IAST to the single-component isotherms described previously. In IAST, there is no constraint on the mathematical formulation of the single-component adsorption isotherm, as the integration (see eq. S12 in the Supporting Information) can be done analytically or with a numerical procedure. The qualitative agreement between the GCMC data and the IAST predictions in Fig. 7 demonstrates that, the later coupled to the single-component adsorption fits is a good candidate to predict the binary adsorption behavior of gas mixtures in clays across the pressure range studied. The accuracy of IAST here extends to adsorbed mixtures in equilibrium with gas phases that have low or moderate CH_4 partial pressures. The IAST model also predicted the bisolute competitive sorption data favorably in modified montmorillonite.⁷⁴ The IAST, however, is known to fail to capture even qualitative features for certain non-ideal mixtures or high pressures.⁷² The discrepancy between our calculated adsorption selectivity with IAST and with GCMC simulations is more significant for $\text{H}_2\text{S}/\text{CH}_4$ selectivity (see below) as the size and electronic character of H_2S and CH_4 are significantly different.

The selectivity is a key and sensitive parameter to quantify the competitive adsorption between two components.^{11,57} For example, ethane selectivity against methane in montmorillonite reduced with increase in pore size or pressure.¹¹ The selectivity $S_{\text{A/B}}$ in a binary mixture of components A and B is defined as

$$S_{\text{A/B}} = \frac{x_{\text{A}}/y_{\text{A}}}{x_{\text{B}}/y_{\text{B}}}, \quad (1)$$

where x_{A} (y_{A}) and x_{B} (y_{B}) are the mole fractions of components A and B in the adsorbed phase (bulk phase), respectively. This quantity can easily be computed directly using results from mixture GCMC simulations as well as using IAST. The resulting GCMC simulation data (symbols) and IAST predictions (lines) are shown in the cor-

responding Figs. 7d-f. All the predicted selectivity values from IAST are in quite good agreement with the simulated values as shown in Figs. 7d-f. The IAST predicted $\text{H}_2\text{S}/\text{CH}_4$ selectivity, displayed the highest deviation among the three cases that we tested here, overestimating the simulation results by factors as high as only ≈ 1.2 , at the highest investigated pressure (see Fig. 7f). Inspection of Figs. 7d and f shows that, CO_2 and H_2S molecules have higher affinity for the montmorillonite surface than methane, a finding consistent with earlier observations (see Fig. S3, Supporting Information). In addition, the simulation and IAST results of CO_2/CH_4 and $\text{H}_2\text{S}/\text{CH}_4$ selectivities increase as the bulk phase pressure is increased. By contrast, methane has a higher affinity for the montmorillonite surface than nitrogen, and the N_2/CH_4 selectivity decreases as the bulk phase pressure is increased.

We have seen that at a basal d -spacing of 30 Å, CO_2 and H_2S exhibit multilayer adsorption pattern (see, e.g., Figs. 3b and d). In Figs. 8a-c, the GCMC simulation results (symbols) of the binary isotherms are compared to IAST (lines) for the adsorption of CO_2/CH_4 , CO_2/N_2 , and $\text{CO}_2/\text{H}_2\text{S}$ mixtures, respectively, at various bulk mole fractions of CO_2 , a basal d -spacing of 30 Å, and in the presence of 0.2 g/cm^3 of preadsorbed water (see also Table S7, Supporting Information). The selectivity estimates coming from GCMC simulations (symbols) and IAST (lines) are shown in the corresponding Figs. 8d-f. The IAST results calculated by neglecting any nonideality, still successfully forecasts the same qualitative behavior in adsorbed amount and selectivity as the GCMC simulations for majority of these binary mixtures. However, the IAST predictions, for example, underestimate the corresponding mixture GCMC results of CO_2/CH_4 and CO_2/N_2 selectivities, as the bulk phase pressure is increased. This is expected, because the performance of IAST has been shown to degenerate for mixtures of molecules of differing sizes and polarities.^{57,58} As a consequence of the significant disparity in the interaction strengths between molecules in a mixture of adsorbates of differing polarities, the average deviations between IAST and GCMC results ranged from 30 to 67%.⁵⁸ The selectivity of CO_2/N_2 in the clay system, obtained using IAST, showed the highest deviation among the three cases that we tested, underestimating

the simulation results by factors as high as ≈ 2.2 , at the highest studied pressure (see Fig. 8e). The CO_2/CH_4 selectivity increases as the bulk phase pressure is increased at a basal d -spacing of 30 Å (Fig. 8d). This behavior is similar to the above case (Fig. 7d), and indeed of potentially great practical importance for CO_2 utilization and storage, such as, in shale gas reservoirs.⁵⁹ A comparison between the single-component (Fig. 1h) and corresponding mixture isotherm data of CO_2 molecules (Figs. 8a-c) indicates that, the multilayer adsorption behavior of CO_2 is almost unaffected by the presence of CH_4 , N_2 or H_2S , over the entire range of conditions we considered. Overall, water does not affect the pore-filling mechanisms of various binary mixtures we studied, by comparison with the corresponding pure ones (compare, e.g., Fig. 1 with Figs. 7 and 8). This is because, as in the case of pure CH_4 , CO_2 , N_2 , and H_2S adsorption in the presence of water (Fig. 1), the coadsorption isotherms (Figs. 7 and 8) are either type I or type IV according to the IUPAC classification. To summarize this section, we have tested IAST for various gas mixtures in clays. Using IAST requires the availability of single component adsorption isotherms, which can be readily estimated using GCMC simulation. The comparisons indicate that, we can potentially use IAST as a useful tool for rationalizing the mixture adsorption behavior in montmorillonite.

Empirical potentials based on electrostatic and van der Waals couplings are useful and reliable to describe the interaction of clay layer with cations, water molecules and inert gas (e.g., CH_4 and N_2). But in the case of CO_2 and H_2S , the use of classical potentials needs to be validated. In the presence of water, CO_2 is known to dissolve and form carbonic acid, increasing the pH of the confined water molecules, and partially destroy the clay network. Furthermore, H_2S is a weak acid able to react with alkali ions. All these reactions are not described in the present study.

4 Conclusions

We have completed extensive grand canonical Monte Carlo simulations to better assess the adsorption behavior of CH_4 , CO_2 , and their mixtures in Na-, Cs-, and Ca-

montmorillonite clays in the presence of water. We have shown that CO_2 uptake and its selectivity over CH_4 in the clays can also be significantly increased with the increase of water content in the interlayer which is attributed to the multilayer adsorption of CO_2 molecules in the clay. This result could open new potentials for tuning the adsorption behavior of clays for CO_2 storage and other applications.

The atomistic model we have used, gives good agreement with single component experimental isotherms of CH_4 and CO_2 .^{1,8} In general, the presence of increasing water molecules in the clay reduced adsorption amounts of pure CH_4 and CO_2 , possibly because preadsorbed water render many sorption sites inaccessible to sorbate by occupying the sorption sites or filling interlayer space. The Ca-montmorillonite clay displayed the highest adsorption capacity and the Cs-montmorillonite the lowest, for all single component isotherms studied, consistent with the order of increasing cation hydration energies. The Na-montmorillonite clay preferentially adsorbs CO_2 over CH_4 during both pure component and mixture adsorption, and the CO_2/CH_4 selectivity is observed to increase as the bulk phase pressure is increased. Further, GCMC simulations were performed to estimate the effect of water on the adsorption of N_2/CH_4 , $\text{H}_2\text{S}/\text{CH}_4$, CO_2/N_2 , and $\text{CO}_2/\text{H}_2\text{S}$ binary mixtures in Na-montmorillonite clay. We found that water does not seem to affect the pore-filling mechanisms in all investigated binary mixtures, by comparison with the corresponding pure cases. On the basis of the single-component CH_4 , CO_2 , N_2 , and H_2S isotherms, that showed the order of adsorption capacities following the order of their polarizabilities, binary mixture adsorption and selectivity were predicted using the IAST. Reasonably good agreement with IAST is obtained for the observed adsorption capacities and selectivities of binary mixtures in the clay. We plan to expand the work on clay to include the basin conditions, the estimation of dynamic properties, and the stability analysis of these binary ($\text{H}_2\text{O}/\text{CO}_2$ and $\text{H}_2\text{O}/\text{CH}_4$) and ternary ($\text{H}_2\text{O}/\text{CO}_2/\text{CH}_4$) mixtures based on swelling free energy.⁴⁴

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Supporting Information

Additional details of simulation method and analysis are provided in the Supporting Information.

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Figure 1: Single-component adsorption isotherms for CH_4 , CO_2 , N_2 , and H_2S molecules on Ca- (squares), Na- (circles), and Cs-montmorillonite (triangles) in the presence of 0.2 (black-filled symbols), 0.4 (open symbols), and 0.6 g/cm^3 (gray-filled symbols) of preadsorbed water at 298.15 K as computed from GCMC simulation. The lines are fitting results to the GCMC simulation data.

Figure 2: Single-component adsorption isotherms for CH_4 molecules on Ca-montmorillonite ($T = 333.15$ K, basal spacing $d = 15$ Å) and CO_2 molecules on Na-montmorillonite ($T = 328.15$ K, basal spacing $d = 12$ Å), observed experimentally^{1,8} (open symbols) and as computed from GCMC simulations (corresponding solid symbols). The arbitrarily chosen preadsorbed water contents in the simulations are 0.4 (squares), 0.5 (triangles), and 0.55 g/cm³ (circles).

Figure 3: Equilibrium distributions of (a) CH_4 , (b) CO_2 (carbon atoms), (c) N_2 (nitrogen atoms), and (d) H_2S (sulfur atoms) molecules in Na-montmorillonite at $T = 298.15$ K and $P = 20$ bar as computed from GCMC simulation. The origin corresponds to the clay surface oxygen. The preadsorbed water content is 0.4 g/cm^3 .

Figure 4: Equilibrium snapshots and density profiles of clay mineral-water-CO₂ system with preadsorbed water contents of (a) 0.2 and (b) 0.4 g/cm³ at $T = 298.15$ K and $P = 10$ bar as obtained from GCMC simulation. In the density profiles, the solid, dashed, and dotted lines represent carbon, water oxygen, and sodium atoms, respectively. Each snapshot shows only one of the two interlayers belonging to the central simulation box, for the purpose of clarity. Color code: O, red; H, white; Si, yellow; Al, light blue; Mg, light green; Na, dark blue; C, black. The basal d -spacing is 30 Å.

Figure 5: Isosteric heats of adsorption (adsorbate-adsorbate) for single-component adsorption of CO₂ molecules on Na-montmorillonite at 298.15 K, computed using GCMC simulations with preadsorbed water contents of 0.2 (filled squares) and 0.4 g/cm³ (filled circles). The open symbols show the corresponding fluid-clay contribution to the isosteric heats. The inset shows fluid-clay contribution to the potential energy (same symbols as in main figure). The basal d -spacing is 30 Å.

Figure 6: The ion-water radial distribution functions for hydrated clays in equilibrium with CH_4 molecules at $T = 298.15$ K and $P = 20$ bar as computed from GCMC simulation. The basal d -spacing and the preadsorbed water content are 15 Å and 0.6 g/cm³, respectively.

Figure 7: Amounts adsorbed for (a) CO₂/CH₄, (b) N₂/CH₄, and (c) H₂S/CH₄ binary mixtures in Na-montmorillonite at 298.15 K, computed using GCMC simulations with CH₄ mole fractions: $y_{\text{CH}_4} = 0.2$ (squares), 0.5 (circles), and 0.8 (triangles). The open symbols represent the amount of CH₄ molecules and solid symbols the amount of either CO₂, N₂ or H₂S molecules adsorbed. The solid curves are the predictions of IAST. The basal d -spacing and the preadsorbed water content are 18 Å and 0.4 g/cm³, respectively. Panels (d)-(f) show selectivities from GCMC simulations (symbols) and IAST (lines) under the same conditions as in panels (a)-(c), respectively: $y_{\text{CH}_4} = 0.2$ (squares, solid lines), 0.5 (circles, dashed lines), and 0.8 (triangles, dotted lines).

Figure 8: Amounts adsorbed for (a) CO₂/CH₄, (b) CO₂/N₂, and (c) CO₂/H₂S binary mixtures in Na-montmorillonite at 298.15 K, computed using GCMC simulations with CO₂ mole fractions: $y_{\text{CO}_2} = 0.2$ (squares), 0.5 (circles), and 0.8 (triangles). The open symbols represent the amount of CO₂ molecules and solid symbols the amount of either CH₄, N₂ or H₂S molecules adsorbed. The solid curves are the predictions of IAST. The basal d -spacing and the preadsorbed water content are 30 Å and 0.2 g/cm³, respectively. Panels (d)-(f) show selectivities from GCMC simulations (symbols) and IAST (lines) under the same conditions as in panels (a)-(c), respectively: $y_{\text{CO}_2} = 0.2$ (squares, solid lines), 0.5 (circles, dashed lines), and 0.8 (triangles, dotted lines).

* Using grand canonical Monte Carlo simulations, we study the adsorption behavior of CH₄, CO₂, and their mixtures at 298.15 K and pressures up to 50 bar in Na-, Cs-, and Ca-montmorillonite clays in the presence of water.

* We observe the general trend that the presence of increasing preadsorbed water content in the clay interlayers, reduced adsorption amounts of pure CH₄ and CO₂ molecules. With a relatively large basal spacing ($d = 30 \text{ \AA}$), the favorability of adsorption of CO₂ by montmorillonite at relatively low pressures and intermediate water contents has been demonstrated using simulations.

* The ideal adsorbed solution theory is shown to agree well with the observed adsorption capacities and selectivities of binary mixtures (e.g., CO₂/CH₄) in Na-montmorillonite clay with preadsorbed water.

* The atomistic model we have used, gives reasonable agreement with available single-component experimental adsorption isotherms for CH₄ and CO₂ molecules, adsorbed onto montmorillonite clays in the presence of preadsorbed water.