Understanding methane/carbon dioxide partitioning in clay nano- and meso-pores with constant reservoir composition molecular dynamics modeling†

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The interactions among fluid species such as H2O, CO2, and CH4 confined in nano- and meso-pores in shales and other rocks is of central concern to understanding the chemical behavior and transport properties of these species in the earth’s subsurface and is of special concern to geological C-sequestration and enhanced production of oil and natural gas. The behavior of CO2, and CH4 is less well understood than that of H2O. This paper presents the results of a computational modeling study of the partitioning of CO2 and CH4 between bulk fluid and nano- and meso-pores bounded by the common clay mineral montmorillonite. The calculations were done at 323 K and a total fluid pressure of 124 bars using a novel approach (constant reservoir composition molecular dynamics, CRC-MD) that uses bias forces to maintain a constant composition in the fluid external to the pore. This purely MD approach overcomes the difficulties in making stochastic particle insertion–deletion moves in dense fluids encountered in grand canonical Monte Carlo and related hybrid approaches. The results show that both the basal siloxane surfaces and protonated broken edge surfaces of montmorillonite both prefer CO2 relative to CH4 suggesting that methods of enhanced oil and gas production using CO2 will readily displace CH4 from such pores. This preference for CO2 is due to its preferred interaction with the surfaces and extends to approximately 20 Å from them.

Introduction

The interactions among fluid species such as water, carbon dioxide and methane confined in nano- and meso-pores in shales and other rocks is of central concern to understanding the chemical behavior and transport properties of these species in the earth’s subsurface and is of special concern to geological C-sequestration and enhanced production of oil and natural gas.1–6 The behavior of water and cations at mineral surfaces and in the interlayer galleries of expandable clays (smectites) has been studied experimentally and computationally for many years,7–19 and more recently there has been increased interest in carbon dioxide and hydrocarbons.20–44 The mutual interactions between CO2 and CH4 in nano- and meso-scale confinement, however, remain poorly understood. Most simulation studies have focused on single component adsorption in the interlayers of clay minerals. These studies show that the CO2 is more strongly adsorbed to clay minerals than CH4.45–47 Recent Grand Canonical Monte Carlo (GCMC) calculations, for instance, have shown preferential adsorption of CO2 over CH4 in the interlayers of dry Na-montmorillonite and other inorganic shale components as functions of temperature (313–373 K) and pressure (0–20 MPa).47–52 In shales and other sedimentary rocks, pores have a wide range of sizes, and the effects of pore size on CO2/CH4 partitioning are poorly understood. This paper presents the results of a computational molecular dynamics (MD) modeling study of the partitioning of CO2 and CH4 between bulk fluid and slit-like nano- and meso pores from 4 to 73 Å thick and the structure of the fluid in those pores. In contrast to most computational studies of clays, the montmorillonite substrate model here is of finite size (Fig. 1), allowing study of the fluid interaction with the siloxane basal surfaces and the protonated sites on broken edges of the clay layers. The results show that the partitioning of CO2 and CH4 between the bulk fluid
(representing fluid in large pores in shales and other rocks) and the nano- and meso-pores is substantially influenced by the pore thickness, with CO₂ being largely preferred in narrow confined pores. CO₂ is also greatly preferred at the protonated edges of broken clay layers.

The MD simulations were done using a novel approach that uses self-adjusting bias forces to maintain a constant composition in the fluid external to the pore (constant reservoir composition molecular dynamics, CRC-MD). Such self-adjusting bias forces have been used previously to maintain a constant chemical potential of the fluid species in modelling the growth of urea crystals from solution (constant chemical potential MD) and to create a concentration gradient across a membrane for modelling the gas transport and separation of mixtures in membranes (concentration gradient driven MD). The advantages of using a purely MD approach to maintain the composition of dense fluids rather than using the stochastic particle insertion–deletion moves used in grand canonical Monte Carlo and related hybrid approaches, such as dual control volume grand canonical molecular dynamics, have been discussed in detail in ref. 55. Inspired by these studies, we have implemented the CRC-MD method, which has proven to be an efficient way to evaluate partitioning of fluid species between bulk fluid and nano- and meso-pores and also onto the surfaces of finite size solid substrates.

**Methods**

In the CRC-MD method, each simulation cell consists of a bulk fluid reservoir, two bias force regions, two composition control regions, two transition regions, and the substrate (clay) + pore assemblage in the center (Fig. 1a). The concentrations of the fluid species in the control regions are maintained at constant values by forces in the bias force regions. These bias forces act in such a way that if the concentration of a given species in a control region is different than the target concentration molecules of that species are moved into or out of the control region from or to the reservoir. A detailed explanation of the functional forms of the bias forces and how they work can be found elsewhere.

The substrate used in the simulations was the expandable smectite clay mineral, montmorillonite, which develops a permanent negative structural charge by the isomorphic substitution of Al³⁺ for Si⁴⁺ in the tetrahedral sheet and Mg²⁺ for Al³⁺ in the octahedral sheet. The model here has a structural formula of M⁺₀.₇₅(Si₄.₇₅Al₀.₂₅)(Al₃.₅Mg₀.₅)O₂₀(OH)₄. The distribution of
the isomorphic substitutions has a quasi-disordered pattern and was prepared using the “Supercell” program, which creates substitutions in accordance with an extension of the Lowenstein’s rule, which forbids tetrahedral Al–OAl and octahedral Mg–O–Mg linkages. The simulated montmorillonite particles have lateral dimensions of \( \sim 73.0 \times 41.4 \) Å along the \( a \) and \( b \) crystallographic axes, respectively, with an orthorhombic unit cell. To create a finite size particle, the montmorillonite structure was cleaved along (010), creating broken edge sites on that surface. On the broken edges, the dangling tetrahedral Al\(^{3+}\) and Si\(^{4+}\) sites are saturated by single OH\(^{-}\) groups, and most of the dangling octahedral Al\(^{3+}\) sites are saturated with 1 OH\(^{-}\) and 1 H\(_2\)O molecules. Meanwhile, according to \textit{ab initio} calculations, when the octahedral Mg\(^{2+}\) sites are saturated with 1 H\(_2\)O molecule and 1 OH\(^{-}\) group, proton transfer reactions occur with the neighboring octahedral Al\(^{3+}\) sites and tetrahedral Si\(^{4+}\) sites to generate octahedral Mg\(^{2+}\) sites saturated with 2 H\(_2\)O molecules (as predicted by the crystal growth theory). A neighboring octahedral Al\(^{3+}\) site with 2 OH\(^{-}\) groups. These coordination environments were used in the clay substrate. Furthermore, the oxygen atoms of the OH\(^{-}\) groups of the broken edge sites were assigned a slightly higher negative charge (-0.9659 [e]) compared to the original CLAYFF\(^{62}\) value (-0.95 [e]). This was done not only to ensure that the broken edges of the montmorillonite particle are electrostatically neutral, but also because the OH\(^{-}\) groups of the edge sites have fewer bond connections compared to those in the interior of the clay structure. Importantly, the two (010) surfaces of this model have different compositions. One contains only unsubstituted tetrahedral Si\(^{4+}\) and octahedral Al\(^{3+}\) sites (left side of the particle in Fig. 1b), whereas the other contains two substituted tetrahedral Al\(^{3+}\) and two octahedral Mg\(^{2+}\) sites (right side of Fig. 1b).

The modeled montmorillonite particle consists of three T–O–T layers which encompass two anhydrous interlayers and expose two external basal surfaces to the pore (Fig. 1a). Because of the 3-dimensional periodic boundary conditions used, only the broken (010) surfaces and the basal surfaces bounding the pore are exposed to the fluid phase. The lateral dimensions of the simulation cell are 300 Å × 41.4 Å (Fig. 1a). The thickness of the slit-like pore between the external basal surfaces (Fig. 1b) were varied from 4 to 73 Å. For pore thicknesses less than 10 Å, the slit-like pore is less than the thickness studied (Fig. 2a and b). At the smallest thickness studied (4.0 Å), neither CO\(_2\) nor CH\(_4\) enters the pore. At a thickness of 6.0 Å, CO\(_2\) fills the pore and there is only a negligible fraction of CH\(_4\) molecules near the entry points. These results are in good agreement with recent experimental and simulation studies that show that the basal spacing required for CO\(_2\) intercalation in the interlayer galleries of smectite clays is less than for CH\(_4\).

Results and discussion

The mole fractions and number densities of CO\(_2\) and CH\(_4\) molecules in the pores vary greatly depending on the pore thickness (Fig. 2a and b). At the smallest thickness studied (4.0 Å), neither CO\(_2\) nor CH\(_4\) enters the pore. At a thickness of 6.0 Å, CO\(_2\) fills the pore and there is only a negligible fraction of CH\(_4\) molecules near the entry points. These results are in good agreement with recent experimental and simulation studies that show that the basal spacing required for CO\(_2\) intercalation in the interlayer galleries of smectite clays is less than for CH\(_4\).
due to steric effects. 6,31,32,38,39 At a pore thicknesses of 7.5 Å some CH₄ enters the pore, and the CO₂/CH₄ ratio decreases rapidly with increasing pore thickness up to 33.0 Å (Fig. 2a). At larger pore thickness, the CO₂/CH₄ ratio decreases less rapidly and slowly approaches the composition in the control regions (2 molecules per nm³), although for the thicknesses studied here it never reaches the control region composition. The number density of CO₂ molecules in the pores is always larger than in the control region, with the highest value of ~8.2 molecules per nm³ at 9.0 Å and progressively smaller values at larger thicknesses. In contrast, the CH₄ density increases with thickness to 33.0 Å and then decreases with increasing thickness. However, it is never much greater than the value in the control region of 2 molecules per nm³. (Fig. S1, ESI, † shows that the fluid compositions in the control regions were kept at the target values with great accuracy throughout the production runs.) These changes highlight the important conclusion that pores with dimensions of 1 to a few nm bounded by basal clay surfaces preferentially incorporate CO₂ relative to CH₄, with the smallest pores showing the greatest preference (Fig. 2b). These results are in agreement with recent GCMC simulation studies of CO₂/CH₄ adsorption in the interlayers of Na-montmorillonite at 318 K and Pfluid = 0 to 300 bars. 48 Importantly, the CO₂/CH₄ ratios at small pore sizes (<23.0 Å) are in excellent agreement with the selectivity parameters obtained from recent GCMC simulation studies at similar thermodynamic conditions (323 K and Pfluid = 100 bar). 49

Fig. 2 (a) Computed mole fractions of CO₂ (black) and CH₄ (red) molecules and the CO₂/CH₄ ratio (gold) as functions of pore thickness. Solid and dashed lines correspond to left and right y axis, respectively. (b) Number density of the fluid species within the pore region bounded by the oxygens of the montmorillonite basal surfaces.

The probability density profiles (PDPs) of CO₂ and CH₄ in the pores perpendicular to their surfaces show that the changes in their concentrations with pore thickness are due to preferential sorption of CO₂ and structuring of the fluid near the pore surfaces (Fig. 3). Significant structuring of the fluid into three discernable layers extends to ~15.0 Å from each pore surface, with CO₂/CH₄ ratios larger than in the composition control regions extending to ~20 Å from the surfaces. At a pore thickness of 6.0 Å, the CO₂ molecules are located at the mid-plane of the pore (3.0 Å from each surface), as expected since this thickness corresponds to a clay interlayer with 1 layer of intercalated molecules. 32 At a pore thickness of 7.5 Å, the CO₂ begins to form two layers, and the small amount of CH₄ is at the middle of the pore. At 9.0 Å there are two well developed layers of CO₂ and CH₄. At 12.3 Å a third layer of CO₂ and CH₄ begins to develop, and the layer of CO₂ nearest the surfaces develops a shoulder. At 15.6 Å the central layer begins to split into two, and at 20.5 Å a fifth layer begins to develop. By 43.0 Å the fluid structuring near the surfaces is fully developed, and the CO₂ and CH₄ concentrations in the middle of the pore are essentially equal. At 73.0 Å the concentrations in the central region of the pore are close to those in the control volume, 2 molecules per nm³. For all pore thicknesses greater than 33.0 Å the fluid at each surface is structured into three layers of CO₂ and CH₄ with maxima near 3.0, 6.8, and 10.4 Å and peak densities that decrease with increasing distance from the surface. The PDP’s are in good agreement with those from GCMC simulation studies of single component adsorption in slit nanopores in Na-montmorillonite at 323 K and Pfluid = 100 bars with a thickness of ~21.0 Å 49 and also in interlayers of Na-montmorillonite at 298 K and Pfluid = 40 bars. 45,46 Such three-layer structures commonly occur near surfaces for many fluids, including H₂O. 72

The differences in the structure of the CO₂ and CH₄ layers near the pore surfaces are due to the differences in their interaction with the basal surface of the clay. For the CO₂ layer nearest to the surface, the peak at 3.0 Å is due to CO₂ molecules adsorbed with one OCO₂ located above the center of a ditrigonal cavity on the basal surface and the other OCO₂ located above a Si tetrahedron, as observed in earlier simulation studies of smectite interlayers. 25,31,32 The CO₂ molecules at 3.9 Å are located with their CO₂ closer to a tetrahedral site. This structuring is consistent with the well-known ability of CO₂ to enter smectite clay interlayers. 6,20–28,31–34,37,18,40 In contrast, the lack of structuring in the CH₄ peak nearest the surface and the equal distances between the three layers suggest that these molecules are interacting much more weakly with the surfaces and behave like hard spheres with the layers packed on one top of each other. This conclusion is consistent with the incorporation of CH₄ into the interlayer galleries of expandable clays occurring by a passive, space filling mechanism with basal spacings similar to 7.5 Å. 39

Increasing CO₂ and CH₄ incorporation with increasing pore thickness also greatly effects the coordination of the Na⁺ ions to the pore surfaces (Fig. 3). At 4.0 Å, most of the Na⁺ ions are located at the mid-plane of the pore (near 2.0 Å from each surface) with broad shoulders at 0.5 Å from each surface. Based on previous simulation studies by Greathouse et al., 11 the Na⁺ ions at 0.5 Å are located above the centers of ditrigonal cavities, and those at 2.0 Å are adsorbed near the Si/Al tetrahedra. At 6.0 Å, where CO₂ begins to fill the pore, more Na⁺ occur above the ditrigonal cavities, and as the pore thickness increases progressively more occur on these sites. At larger pore thicknesses...
The Na⁺ ions located at 2.0 Å from the surfaces are adsorbed only near tetrahedral Al³⁺ sites. As near the basal surfaces bounding the pores, the concentrations of CO₂ and CH₄ on the surfaces of the broken edges of the clay layers are greater than in the control volumes, and CO₂ is preferentially associated with the surface (Fig. 4). The layered structure of the fluid near the broken edge surfaces is also generally similar to that on the basal surfaces, and concentrations greater than in the control regions extending to ~20 Å from the surface. The concentrations of CO₂ and CH₄ in the well-defined layers near the broken surfaces are, however, significantly lower than above the basal surfaces (compare values in Fig. 4b with those in Fig. 3), suggesting that both are attracted less strongly to the protonated edge sites than to basal siloxane surfaces. The PDP’s show three peaks for CO₂ (1.7 Å, 2.8 Å and 6.3 Å) and two peaks for CH₄ (3.4 Å and 6.7 Å). The positions of the two peaks for CH₄ are the same as above the basal surfaces, again illustrating the weak, non-specific interaction of CH₄ with silicate surfaces. In contrast, the positions of the two peaks for CO₂ are significantly closer to the broken edge surfaces. Recent GCMC simulation studies showed a greater preference for CO₂ relative to CH₄ in hydroxylated pores in quartz, which the authors attributed to stronger interaction of CO₂ with the protonated sites. The origin of this difference will require substantial additional work, but we note that in the results here the differences between the two broken (010) surfaces with differently substituted octahedral and tetrahedral sites are not significant. Note that in these simulations the structuring of the fluid above the broken surfaces does not depend on pore size, since the broken surfaces face the transition region, for which the thickness is independent of pore size. The PDP’s of the fluid species parallel to the broken edges (sum of all molecules within 15.0 Å of the surface) further illustrate the preferential association of CO₂ with the broken edges (Fig. 4a). These plots also demonstrate that the effects of the surface extend only ~10 Å into the fluid in the transition region above the opening of the pore.
Conclusions

Computational molecular modeling of the partitioning of supercritical CO₂ and CH₄ between bulk fluid and nano- and meso-pores 4 to 73 Å thick bounded by the basal surfaces of the expandable clay mineral montmorillonite show that both species are preferentially incorporated into the pores with the preference for CO₂ much greater than for CH₄. This behavior is due to the association of the fluid species with the clay surface and with a much greater preference of the surface for CO₂ relative to CH₄. Structuring of the fluid extends to ~15 Å from the surface, and the CO₂/CH₄ ratio is greater than in the control region to ~20 Å from the surface. The total CO₂/CH₄ ratio in the pores is greatest at a pore thickness of 6 Å, decreases rapidly to 33 Å, and then gradually approaches the bulk value at larger thickness. Even at a pore thickness of 73 Å, however, it has not reached this value. The behavior of CO₂ and CH₄ on protonated, charge-neutral broken (010) edges of the clay layers is broadly similar, but the concentrations of the fluid species near these surfaces are lower than near the basal surfaces, suggesting that they have weaker interactions with protonated edge sites than with siloxane basal surfaces.

The calculations were done at 323 K and a total fluid pressure of 124 bars using a novel approach (constant reservoir composition molecular dynamics, CRC-MD) that maintains a constant composition in the fluid external to the pore. In this method, bias forces are employed to maintain the target composition of the external fluid, here 2 molecules per nm³.49–51 This purely MD approach overcomes the difficulties in making stochastic particle insertion–deletion moves in dense fluids encountered in grand canonical Monte Carlo and related hybrid approaches. The simulation cell contains a finite size solid substrate, and the approach can be readily applied to many kinds of porous materials such as zeolites, MOFs and C-based materials. It can also be readily applied to pores bounded by non-porous materials, such as silicates and carbonates.

The results here clearly show that nano- and meso-pores in shales bounded by clay minerals have a preference for CO₂ relative to CH₄ and thus methods of enhanced petroleum production such as CO₂ floods or the use of CO₂-based fracking fluids should readily displace CH₄ from such pores. The results are in good agreement with previous experimental and computational, high T and P studies that show that there can be an energetic driving force for CO₂ incorporation in the interlayer galleries of expandable clay minerals, whereas CH₄ enters these spaces by a passive, space filling mechanism.3,6,32,38,39,49 The thickness of the surface layer in which the fluid is structured (~15 Å) is similar to that in which H₂O is structured on oxide and hydroxide surfaces,72,73 suggesting that computational modeling of geochemically relevant fluids in nano- and meso-pores bounded by such materials need only include pores with thicknesses less than a few nm to capture the essential features of their behavior. The results parallel the preference of other inorganic shale components (e.g., calcite and quartz) for CO₂ relative to CH₄, suggesting that for oxide and oysalt materials, CH₄ adsorption is relatively weak and its filling of pores bounded by them occurs by a passive, space filling mechanism.48–52 The organic component of shale known as kerogen is commonly thought to contain much of the CH₄, but recent GCMS studies support the conclusion that although it prefers CO₂ relative to CH₄, the behavior of these species is strongly dependent on the chemical composition, functionality, moisture content and pore structure of the kerogen.74,75 Overall, the structure, dynamics and energetics of the adsorption environments of CO₂, CH₄, other hydrocarbons, and H₂O in kerogen have not been well explored, and the CRC-MD methods used here can be readily applied to help address these important questions.

Conflicts of interest

There are no conflicts to declare.

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