# Effect of water on methane and carbon dioxide sorption in clay minerals by Monte Carlo simulations

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## ABSTRACT

Shale is mainly composed of: (1) inorganic, and (2) organic materials. As an important constituent of inorganic matter, clay minerals may affect gas-in-place of shale permeable media. Clay minerals are hydrophilic. Hydrophilicity may affect pore space saturation with water in shale media. In this work, we investigate the effect of water on methane and $CO_2$ sorption in clay minerals by using grand canonical Monte Carlo simulations. Our investigation reveals that water may significantly reduce methane and $CO_2$ sorption in clay nanopores. In small pores (1 nm), water and $CO_2$, and water and methane adsorbed in the same layer. In large pores (>2 nm), water molecules adsorb on the first layer, and $CO_2$ and methane form a weak second layer adsorption. $CO_2$ unlike methane both in pure and low water content conditions may form multi-layer adsorption at high pressure. Multilayer adsorption results in significant increase of sorption with pressure. Langmuir adsorption model cannot be used for such descriptions. Our study on sorption of $CO_2$ and water mixtures in clay minerals shows that with a small amount of water in the domain outside the nanopores, $CO_2$ sorption is significantly reduced. In larger pores (>2 nm), gas molecules mainly accumulate in the middle of the pores.

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## 1. Introduction

Shale is composed of two distinct materials: organic and inorganic. The organic materials are mainly composed of kerogen, which is a mixture of organic chemical compounds. Organic matter in shale increases porosity [1] and the porosity of kerogen can be as high as 50% of the total porosity [2]. A study [3] suggests that gas sorption and dissolution in organic materials may significantly contribute to gas-in-place in shale gas reservoirs. In some organic-rich shale reservoirs, there is a strong correlation between methane sorption to the total organic content (TOC) [3–5]. Thermally mature kerogen may have larger micropore volume than that of immature kerogen resulting in higher ratio of gas sorption capacity [1].

In addition to organic matter, clay minerals may provide additional sorption capacity due to high internal surface area [6]. A few studies have reported that the clay mineral composition and its microporous structure may increase gas sorption capacity of organic-rich shales [7–9]. There are indications that clay minerals affect sorption in clay-rich shales [3,7,10–13]; clay minerals have micropore-to-mesopore structures which provide additional

surface areas for gas sorption depending on the pore structures and clay chemical compositions [3]. Experimental and computational works [7,14] have shown that gas sorption in clay minerals can be comparable to shale rocks. Clays are generally made of large particles formed by stacks of sheets [15]. They are hydrophilic and moisture may occupy the surface sites.

Some shale gas reservoirs are water-saturated [16]. Preloaded water in clay-rich shales significantly reduces gas sorption [3] and even in the organic-rich shales, gas sorption capacity can be greatly reduced because of the moisture [17]. While kerogen is generally hydrophobic, clay minerals are hydrophilic; water can be easily adsorbed onto clay mineral surfaces reducing the total gas sorption capacity of shale. Experimental work [7] in clay minerals show that sorption capacity under moisture-equilibrated condition is substantially lower than that under the dry conditions. There are extensive experimental and computational works [18–28] on the effect of water on gas sorption in porous media, such as coals. The methane sorption capacity of moisture-equilibrated coals is substantially lower than the dry samples [20,29]. The adsorption of water is related to the hydrophilic sites from the oxygen-containing functional groups with a reduction of the available pore volume for gas sorption [27]. There are very limited studies on the effect of moisture on gas sorption in clay minerals and the underlying

mechanisms. In contrast to coals, water association with clay surfaces is even stronger due to various partial/full charges of surface atoms. Additionally, some clay minerals, such as montmorillonite clay, have an cation-exchange ability to further enhance the hydrophilicity [30].

Molecular simulations [14,31,32] have been conducted in relation to gas sorption in dry clay minerals. In a recent work, we have applied grand canonical Monte Carlo (GCMC) simulations to investigate methane and $CO_2$ sorption in clay nanopores [14]. Due to the chemical heterogeneity, the structural and thermodynamic properties in clays are significantly different from that in conventional carbonaceous materials [14]. Coasne et al. [18] used the GCMC simulations to study the effect of water on sorption of methane and carbon dioxide in the slit-pore like nanoporous carbons. They preloaded water in carbon nanopores; the amount of water stayed constant in the process of gas sorption due to the high free energy barrier to desorb preadsorbed water and found that water greatly reduces gas sorption capacity, especially for methane. Coasne et al. [19] also investigated the effect of water on methane and carbon dioxide sorption in disordered porous carbons and observed a higher decrease in the sorption of methane than carbon dioxide. In both studies, the authors explained higher reduction of methane adsorption because of stronger interaction of $CO_2$–$H_2O$ than methane–$H_2O$ interaction. Very recently, Zhang et al. [33] used computer simulations to study methane sorption in dry and moist coals. They reported that methane sorption capacity decreases as moisture content increases. In contrast to carbonaceous materials, computational studies on the effect of water on gas sorption in clay minerals are limited. Botan et al. [34] used Monte Carlo and molecular dynamics simulations to study the structural and thermodynamic properties of carbon dioxide in hydrated sodium montmorillonite. The effect of water was not included in their work. To best of our knowledge, no computational and theoretical investigations have been made on the effect of water on gas sorption in clay minerals.

In this work, we use GCMC simulations to investigate the effect of water on methane and $CO_2$ sorption in clay-like slit pores. Methane is the main constituent of natural gases. Carbon dioxide is often present in the subsurface. Similar to gas sorption modeling in carbonaceous materials, we assume that the inter-pore interactions are negligible and gas adsorbs in nanometer slit-like pores. The solid surface in our work has a structure and charge of the montmorillonite clay consisting of two tetrahedral sheets fused to an octahedral sheet [35]. Montmorillonite clay has a large internal surface area, and shows a strong cation-exchange capacity [7]. It is one of major constituents of clay minerals in shale [3]. Montmorillonite clay consists of negatively charged silicate layers with Si atoms replaced by Al atoms in the tetrahedral sheet and Al atoms replaced by Mg atoms in the octahedral sheet [30]. The negative charges are compensated by interlayer counterions [36]. We use a full atomistic pore structure by duplicating the unit cell of montmorillonite clay proposed by Skipper et al. [37] and sodium ions as the interlayer counterions. By incorporating these features, we believe that our GCMC can provide fundamental understandings of the effect of water on gas sorption in clay minerals. This work is continuation of our previous work on gas sorption in dry clay minerals [14]. By combining these two works, we believe insight is provided into the fundamental understanding of gas sorption in clay and the effect of water (or moisture).

The remainder of this paper is organized as follows. In Section 2, we introduce the molecular simulation methods and define the molecular models we use. In Section 3, we investigate the effect of water on methane and $CO_2$ sorption in clay-like slit pores of various sizes and bulk densities of the gas molecules, as well as the preloaded water in the pores. We also study $CO_2$-$H_2O$ mixture

**Table 1**
Atomic positions and effective charges in the unit cell.

| Atom | $x$ (nm) | $y$ (nm) | $z$ (nm) | $q$ (e) |
|---|---|---|---|---|
| O | 0.264 | 0.0 | 0.328 | −0.8 |
| O | 0.132 | 0.228 | 0.328 | −0.8 |
| O | 0.396 | 0.228 | 0.328 | −0.8 |
| O(OH) | 0.0 | 0.0 | 0.106 | −1.7175 |
| H(OH) | 0.08815 | 0.0 | 0.1434 | 0.7175 |
| Si | 0.264 | 0.152 | 0.273 | 1.2 |
| Si | 0.0 | 0.305 | 0.273 | 1.2 |
| O | 0.264 | 0.152 | 0.106 | −1.0 |
| O | 0.0 | 0.305 | 0.106 | −1.0 |
| Al | 0.44 | 0.152 | 0.0 | 3.0 |
| Al | 0.44 | −0.152 | 0.0 | 3.0 |
| O | 0.0 | 0.457 | 0.328 | −0.8 |
| O | 0.396 | 0.685 | 0.328 | −0.8 |
| O | 0.132 | 0.685 | 0.328 | −0.8 |
| O(OH) | 0.264 | 0.457 | 0.106 | −1.7175 |
| H(OH) | 0.35215 | 0.457 | 0.1434 | 0.7175 |
| Si | 0.0 | 0.609 | 0.273 | 1.2 |
| Si | 0.264 | 0.762 | 0.273 | 1.2 |
| O | 0.0 | 0.609 | 0.106 | −1.0 |
| O | 0.264 | 0.762 | 0.106 | −1.0 |
| Al | 0.704 | 0.609 | 0.0 | 3.0 |
| Al | 0.704 | 0.305 | 0.0 | 3.0 |
| O | 0.088 | 0.914 | −0.328 | −0.8 |
| O | 0.22 | 0.686 | −0.328 | −0.8 |
| O | −0.044 | 0.686 | −0.328 | −0.8 |
| O(OH) | 0.352 | 0.914 | −0.106 | −1.7175 |
| H(OH) | 0.26385 | 0.914 | −0.1434 | 0.7175 |
| Si | 0.088 | 0.762 | −0.273 | 1.2 |
| Si | 0.352 | 0.609 | −0.273 | 1.2 |
| O | 0.088 | 0.762 | −0.106 | −1.0 |
| O | 0.352 | 0.609 | −0.106 | −1.0 |
| O | 0.352 | 0.457 | −0.328 | −0.8 |
| O | −0.044 | 0.229 | −0.328 | −0.8 |
| O | 0.22 | 0.229 | −0.328 | −0.8 |
| O(OH) | 0.088 | 0.457 | −0.106 | −1.7175 |
| H(OH) | −0.00015 | 0.457 | −0.1434 | 0.7175 |
| Si | 0.352 | 0.305 | −0.273 | 1.2 |
| Si | 0.088 | 0.152 | −0.273 | 1.2 |
| O | 0.352 | 0.305 | −0.106 | −1.0 |
| O | 0.088 | 0.152 | −0.106 | −1.0 |

sorption in clay nanopores of different sizes. In Section 4, we summarize the key conclusions and discuss implications.

## 2. Simulation method

### 2.1. Molecular model

We use a fixed solid surface of montmorillonite clay as a 2:1 clay mineral with the unit cell formula $Na_{0.75}(Si_{7.75}Al_{0.25})(Al_{3.5}Mg_{0.5})O_{20}(OH)_4$[30]. The simulation cell contains two 32-clay unit cells resulting in a clay patch of $4.224 \times 3.656$ nm with a thickness of 0.656 nm separated by a fixed distance to represent a clay nanopore. The positions and charges of the sites in the unit cell of the clay are shown in Table 1 [37]. These positions and charges [37] have been widely used in simulations of water sorption in clay and validated by comparing to experimental data [30,38,39]. The unit cell is replicated to form the clay sheet we use in the simulations. Each of our clay sheets has 16 isomorphous replacements of trivalent Al atoms by divalent Mg atoms in the octahedral sheet, 8 isomorphous replacements of tetravalent Si atoms by trivalent Al atoms in the tetrahedral sheet, and 24 compensating monovalent sodium ions in the interlayer region [30]. In our simulation, the sheets are considered as rigid molecules; no bending potential is considered for clay sheets. The two clay sheets form a slit-like nanopore structure and sodium ions, water and gas molecules are distributed within the pore.

Methane, carbon dioxide and water molecules are simulated by using the TraPPE [40], EPM2 [41] and SPC-E [42] model,