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Methane and carbon dioxide adsorption in clay-like slit pores by Monte Carlo simulations

Zhehui Jin [a], Abbas Firoozabadi [a,b,*]

[a] Reservoir Engineering Research Institute, United States
[b] Yale University, United States

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ABSTRACT

Shale is composed of two distinct permeable media: (1) inorganic, and (2) organic. Both media may contribute to the amount of hydrocarbon and non-hydrocarbon species in shale. In this work, we investigate sorption in clay minerals which may constitute most of the inorganic matter in shale. We represent the inorganic matter by the montmorillonite clays with different charges for different atoms. Sorption of methane and carbon dioxide is investigated by Monte Carlo simulations. In this work, we assume that methane is structureless and CO_2 is assumed to have structure and we assign partial charges to its atoms. Our results indicate that charge affects the orientation of CO_2 molecules close to the surface and plays an important role in CO_2 sorption. Methane sorption is found to be mainly a function of surface area. We also incorporate cation exchange in clay description and model its effect on sorption. Cation exchange increases CO_2 sorption at low pressure significantly and as pressure increases, the effect becomes less pronounced. Cation exchange also affects orientation of CO_2 molecules near the surface. Results from our simulation are expected to provide insight into phase behavior in clays, a major constituent of shale media.

1. Introduction

Shale gas is an important unconventional energy resource; it has had a game changing effect on natural gas supply in the US in recent years. Despite the huge impact, we know very little on some fundamental aspects related to the phase behavior and local species distribution in shale permeable media. The fluid samples from shale light oil formations may be highly undersaturated. However, when production starts, the ratio of gas to liquid may increase significantly. Such a phase behavior is drastically different from that in conventional formations. The modeling of phase behavior in shale gas and shale light oil formations provides knowledge related to well production rate. In the literature, there is neither a molecular model nor a macroscopic-based model that can describe phase behavior in shale formation.

One of the challenges in the shale gas and shale light oil formations is well productivity and gas-in-place (GIP) estimation [1]. The contribution of the adsorbed gas to the total GIP can be as much as 60% [2]. However, there is currently no sound theory to predict the sorbed gas in shale media mainly due to complex nature of shale media. Shale is comprised of two distinct parts: inorganic and organic materials. The organic material is mainly composed of kerogen, which is a mixture of organic chemical compounds. A study [3] suggests that gas sorption and gas solubility in organic materials may provide bulk of the gas-in-place in shale gas reservoirs. The common belief is that the amount of adsorbed gas is proportional to the content of organic matter. A number of papers present data relating a correlation between methane sorption to the total organic content of organic-rich shales [3–5].

A few studies have shown that the clay mineral composition and its micropore structure also affect gas sorption of organic-rich shales [6–8]. There are indications that clay minerals affect sorption in clay-rich shales [9–11]; sorption in clay-rich shales can be comparable to that of total-organic-carbon (TOC) shales. Clay minerals have micropore-to-mesopore structures which provide surface area for gas adsorption depending on the pore structures and clay chemical compositions. The surface area of shale rocks is in the range of 5–50 m^2/g [3]. The surface area of clay minerals is reported to be in the range of 10–25 m^2/g [12]. The surface areas in shale and clay minerals are, therefore, comparable. The clay-rich shales provide a significant portion of mesoporosity [3]; we may not therefore predict the GIP in shales only based on the TOC contents. Experimental work [13] has shown that pores of 1–2 nm width in the interlayers of clay minerals provide the adsorption sites for gases due to large surface area. In this microscopic scale, the properties of species are greatly different from that in bulk. Unlike simple carbonaceous porous media, clay minerals exhibit morphological

* Corresponding author at: Reservoir Engineering Research Institute, United States. Tel.: +1 650 326 9259.
E-mail address: af@rerinst.org (A. Firoozabadi).

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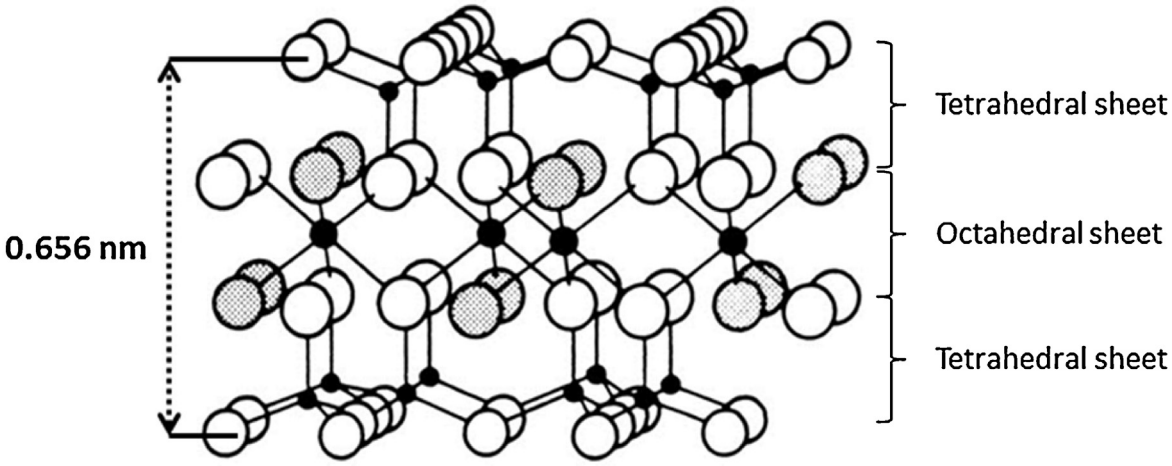

Fig. 1. The schematic representation of 2:1 layer type clay minerals obtained from Ref. [31]. The open spheres represent O, the shaded spheres represent OH, the small solid spheres depict Si and the large solid spheres are Al.

disorder and heterogeneous chemistry. Such chemical heterogeneity will likely affect gas sorption and sorbed gas phase equilibrium [14]. Currently the underlying mechanisms of gas sorption in clay minerals are not well understood.

Extensive molecular simulation studies [15–18] are reported on water adsorption and swelling in clay minerals. However, gas sorption in clay minerals has been rarely studied. Most of molecular simulations of gas sorption are focused on the activated-carbon slit pores [19–23], where chemical heterogeneity may not be relevant. The chemical heterogeneity of the pores may have significant effect on gas sorption under confinement [14,24–26]. Unlike the conventional carbonaceous materials, due to mineralogy [27], gas sorption in clay minerals not only depends on pore structure but also on the chemical heterogeneity. Experimental research has demonstrated the efficacy of intercalating gas molecules in clays [28]. There are only a handful of molecular simulations on gas sorption in clay minerals. Cygan et al. [29] used *NpT* and *NVT* molecular dynamics (MD) to investigate carbon dioxide intercalation mechanism in the interlayer of montmorillonite clays and the effect of molecular flexibility on diffusion rate of CO_2 in water by a flexible force field. Yang and Zhang [19] used MD in an *NVT* ensemble to study the structure and diffusion of dense CO_2 in clay-like slit pores. The effect of pore structure and chemical heterogeneity on gas sorption and structure in clay minerals has yet to be investigated. A drawback of *NpT* or *NVT* ensemble simulations is that they cannot provide gas content in clays. In this work, we use the grand canonical Monte Carlo (GCMC) simulations to investigate the effect of clay pore structure and chemical heterogeneity on methane and CO_2 sorption in clay-like slit pores. Methane is the main constituent of natural gases. Carbon dioxide can be potentially sequestered in shale formations. It is also found in the subsurface together with methane.

Clays are generally made of large particles formed by stacks of sheets [30]. 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 which has two tetrahedral sheets fused to an octahedral sheet [31] as shown in Fig. 1. Two of the octahedral positions of the montmorillonite clay are filled by the trivalent Al atoms; such an electroneutral 2:1 clay mineral is called pyrophyllite [32]. Montmorillonite clays consist 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 [32]. The negative charges are compensated by interlayer counterions [15,32]. The focus of this work is on gas sorption in a neutral slit-like aluminum-silicate mineral and slit-like montmorillonite clay mineral with cation exchange. We use a full atomistic pore structure of clay by duplicating the unit cell of montmorillonite clay proposed by Skipper et al. [33]. This unit cell has been widely used in molecular simulations of water and hydrate formation in clay minerals [15,32,34–36]. Methane molecule is simulated by single-site Lennard–Jones particles and CO_2 molecule is modeled by three-site particles explicitly considering the short-range van der Waals and long-range electrostatic interactions. By incorporating these features, our GCMC is expected to provide the effect of both pore structure and chemical heterogeneity on gas sorption in clay-like slit pores.

The remainder of this paper is organized as follows. In Section 2, we introduce the molecular simulation methods and define the molecular models. In Section 3, we investigate methane and CO_2 sorption in clay-like slit pores with various pore sizes and bulk pressures of the gas molecules. In Section 4, we summarize the key conclusions and discuss implications.

2. Simulation method

2.1. Model

We use a fixed solid surface of montmorillonite clay as a 2:1 clay mineral. The neutral montmorillonite has the unit-cell formula $Si_8Al_4O_{20}(OH)_4$ [15]. The simulation cell contains two 32-clay unit cells resulting in a clay patch of 4.224 nm × 3.656 nm with a thickness of 0.656 nm separated by a fixed distance to represent a clay nanopore. In molecular dynamics simulations [19], two half-layers of the solid sheets have been used to investigate the structure of dense carbon dioxide in a clay-like slit pore. But in a simulation study of water adsorption in montmorillonite clays, it has been shown that the two-clay-sheets provide more accurate results than the one-clay-sheet, especially at small basal spacings [32]. The positions and charges of the sites in the unit cell of the clay are shown in Table 1 [33]. The positions and charges from Ref. [33] are widely used in simulations of water adsorption in clay and validated by comparing simulations to experimental data [32,35,36]. The unit cell that constitutes the clay sheet in our work is shown in Table 1.

For montmorillonite clay with cation exchange, the unit cell formula is $Na_{0.75}(Si_{7.75}Al_{0.25})(Al_{3.5}Mg_{0.5})O_{20}(OH)_4$ [32]. Based on this formula, each of our clay sheets with 32 unit cells have 16 isomorphous trivalent Al atoms replaced 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