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Full Length Article

Effect of water on methane adsorption on the kaolinite (0 0 1) surface based on molecular simulations

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ABSTRACT

CH_4 adsorption isotherms of kaolinite with moisture contents ranging from 0 to 5 wt% water, the effects of water on maximum adsorption capacity, kaolinite swelling, and radial distribution function were modelled by the implementing combined Monte Carlo (MC) and molecular dynamics (MD) simulations at 293.15 K (20 °C) and a pressure range of 1–20 MPa. The simulation results showed that the absolute adsorption of CH_4 on both dry and moist kaolinite followed a Langmuir isotherm within the simulated pressure range, and both the adsorption capacity and the rate of CH_4 adsorption decreased with the water content increases. The adsorption isosteric heats of CH_4 on kaolinite decreased linearly with increasing water content, indicating that at higher water contents, the interaction energy between the CH_4 and kaolinite was weaker. The interaction between kaolinite and water dominates and was the main contributing factor to kaolinite clay swelling. Water molecules were preferentially adsorbed onto oxygen and hydrogen atoms in kaolinite, while methane showed a tendency to be adsorbed only onto oxygen. The simulation results of our study provide the quantitative analysis of effect of water on CH_4 adsorption capacity, adsorption rate, and interaction energy from a microscopic perspective. We hope that our study will contribute to the development of strategies for the further exploration of coal bed methane and shale gas.

1. Introduction

Clay minerals have large surface areas (approximately 800 $m^2 g^{-1}$) and micropore to mesopore structures that can significantly affect the adsorption properties of porous media such as shale and coal [1,2]. Kaolinite is one of the most abundant components in clay minerals [3–5], and understanding the interaction between kaolinite and methane molecules is important for research in the fields of shale gas and coal bed methane.

Some coal bed methane and shale gas reservoirs are water saturated [6,7], and the clay minerals that have similar silicoaluminate crystallographic layers with Al—O octahedra and Si—O tetrahedra are hydrophilic [8–10]. Water molecules can be adsorbed onto the surface of the clay mineral without difficulty, which can decrease the total methane sorption of clay minerals [11]. Hence, preloaded water can substantially decrease the total amount of methane adsorbed onto clay-rich rocks [12]. Ross et al. [13] found that the adsorbed capacities of water-saturated montmorillonite and illite were lower than under dry conditions. Ross and Bustin [12] found that at low pressures (6 MPa), the CH_4 adsorption capacities of illite and montmorillonite were lower than that of kaolinite on a moisture-equilibrated basis but were significantly higher than that of kaolinite under dry conditions. Moreover, a few clay minerals, e.g., montmorillonite clay, are able to further enhance the interaction between clay molecules and methane molecules because of the cation-exchange capacity of montmorillonite clay [14].

Some molecular simulations have been carried out on the adsorption of gas in dry and moist clays. Billemont et al. [15] used grand canonical Monte Carlo (GCMC) simulations to consider the influence of water on methane sorption in porous carbons and observed that water molecules have a higher free energy barrier than methane molecules, which cannot displace the water molecules, and the preloaded water molecules notably decreased the adsorption capacity of methane. Jin et al. [16] also utilized GCMC simulations to research the influence of water on methane sorption in montmorillonite clay. However, to our knowledge, no computational and theoretical research has been carried out on the influence of water content on methane sorption in other clay minerals such as kaolinite and illite. Therefore, in this paper, we used the GCMC and molecular dynamics (MD) methods to research the effect of water on methane adsorption in kaolinite over a pres-

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sure range of 1–20 MPa and with pre-adsorbed water contents of 0–5 wt% simulated at 293.15 K. Molecular simulations can reveal the absolute adsorption isotherms, interaction energy, isosteric heat of adsorption, kaolinite swelling, adsorbed phase density, and radial distribution functions between the surface of kaolinite and CH_4. The objectives of this work were to better understand CH_4/water/kaolinite clay interactions and to shed light on the influence of water on the adsorption capacity and kaolinite swelling of CH_4 on kaolinite surfaces at the atomic level. The findings of this study are also expected to shed light on the details of coal bed methane and shale gas adsorption.

2. Simulation methods

2.1. Models

We use methane to represent coal bed gas and shale gas because methane is the main component of coal bed gas and shale gas. Here, we mainly consider the case of methane in hydrated kaolinite. Methane is represented by an all-atom model [17,18]; the C—H bond length and the C—H bond angle were calculated to be 0.109 nm and 109°28′, respectively, as shown in Fig. 1. Water is represented by a simple point charge model [19]; the H—O bond length and the H—O—H bond angle were calculated to be 0.079 nm and 104°6′, respectively, as shown in Fig. 2.

The kaolinite mineral consists of 1:1 dioctahedral layers. The dioctahedral layers consist of a sheet of corner-sharing SiO_4 tetrahedra and a sheet of edge-sharing AlO_6 octahedra linked by common oxygen atoms parallel to the (0 0 1) sheet with a composition of $Si_4Al_4O_{10}(OH)_8$ [20]. The kaolinite structure used here was that determined experimentally by Bish and Von Dreele [21], and the space group symmetry C1 presents the following kaolinite lattice parameters: a = 0.515 nm, b = 0.894 nm, c = 0.739 nm, $\alpha = 91.93°$, $\beta = 105.05°$, and $\gamma = 89.80°$. The kaolinite model is shown in Fig. 3, and the atom positions have been used in kaolinite adsorbed water simulations and verification by comparison with experimental results [22,23].

Considering the kaolinite structure model cannot reflect the periodicity and the basal spacing of a natural kaolinite, the 4 × 2 × 2 kaolinite super model was established as the research object; the model size is 2.059 nm × 1.787 nm × 2.519 nm, and the layer spacing is 0.72 nm [24–27], as shown in Fig. 4.

2.2. Force field

The research object is the system consisting of kaolinite and CH_4, in which the total potential energy is composed of the intermolecular energy between kaolinite and CH_4 as well as a non-bonded energy between CH_4 molecules.

Therefore, the Dreiding force field was selected [28], in which the total potential energy E consists of intermolecular energy and non-bonded energy, the formula can be expressed as follows:

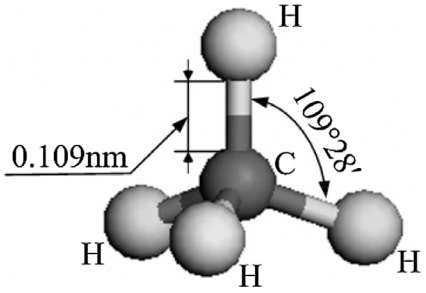

Fig. 1. The molecular model of methane.

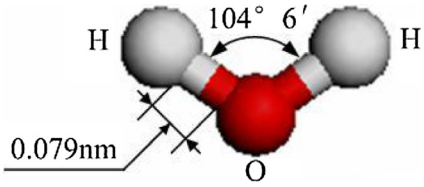

Fig. 2. The molecular model of water.

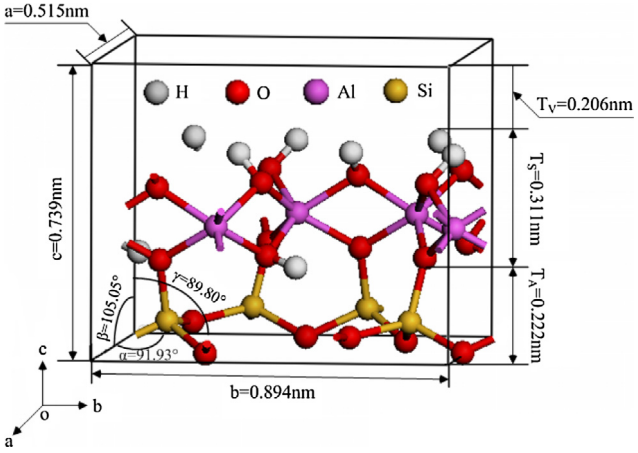

Fig. 3. The molecular model of kaolinite.

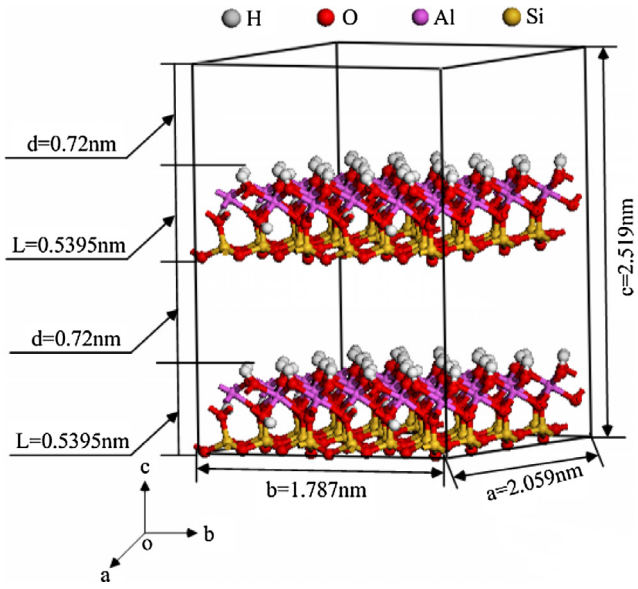

Fig. 4. The 4 × 2 × 2 super molecular model of kaolinite.

$$
\begin{aligned}
E = {} & \underbrace{\frac{1}{2}\sum_i k_b(b_i - b_0)}_{1} + \underbrace{\frac{1}{2}\sum_i k_\theta(\theta_i - \theta_0)}_{2} \\
& + \underbrace{\frac{1}{2}\sum_i v_i(1 + \cos\varphi) + \sum_i v_i(1 - \cos 2\varphi) + v_i(1 + \cos 3\varphi)}_{3} \\
& + \underbrace{\frac{1}{2}\sum_i k_x(x_i - x_0)^2}_{4} + \underbrace{4\sum_i\sum_j \varepsilon_{ij}\left[\left(\frac{\delta_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\delta_{ij}}{r_{ij}}\right)^{6}\right]}_{5} \\
& + \underbrace{\sum_i\sum_j \frac{q_i q_j}{r_{ij}}}_{6} + \underbrace{D_{hb}\left[5\left(\frac{R_{hb}}{R_{DA}}\right)^{12} - \left(\frac{R_{hb}}{R_{DA}}\right)^{10}\right]\cos^4(\theta_{DHA})}_{7}
\end{aligned}
\tag{1}
$$