

Molecular Simulation of Gas-Water Competitive Adsorption in Shale Reservoirs

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Abstract

Fracturing is needed to increase shale gas production due to the low porosity and permeability of shale reservoirs. As the main component of fracturing fluid, water is indispensable in the production and development of shale gas. This paper studies the invasion mechanism of fracturing fluid in shale reservoirs by simulating the competitive adsorption of methane and water. This study obtains the variation law of adsorption capacity, interaction force, and gas-water distribution under different gas-water ratios of different minerals. The electrostatic force in quartz plays a major adsorption role, and the van der Waals force in kaolinite plays a major adsorption role.

Keywords: methane, water, competitive adsorption, molecular simulation, shale reservoirs

1. Introduction

As unconventional energy, shale gas has very low porosity and permeability of the reservoir. Therefore, in the actual production process, it is necessary to make artificial fractures through volume fracturing to improve shale gas production [1]. Field feedback shows that the flowback rate after fracturing is very low [2,3]. There is no systematic theory for the invasion mechanism of fracturing fluid after fracturing in shale gas reservoirs [4]. Therefore, studying the adsorption mechanism of methane and water in nanopores of shale reservoirs can better understand the occurrence characteristics of shale gas and the mechanism of fracturing fluid invasion in shale reservoirs, which plays an essential role in the production and development of shale gas.

Tan et al. [5] studied the effects of TOC content, clay minerals, water content, and other factors on methane adsorption capacity. The results showed that TOC content was the main one. Deng et al. [6] established a seepage model considering various flow effects to study the influence of adsorption on production capacity. They concluded that the absorption gas accounted for 10-15 % of the total gas production. Xu et al. [7] assessed the adsorption capacity of methane in shale through an

isothermal adsorption experiment. The results showed that the higher the total organic carbon content, the stronger the methane adsorption capacity. The adsorption capacity of organic matter was stronger than inorganic minerals. Chao Li et al. [8] studied the adsorption behaviors of methane and ethane in shale through an isothermal adsorption experiment. The results showed that the organic shale had the largest adsorption capacity for ethane and preferentially adsorbs ethane. The above studies are based on macroscopic experiments and theoretical derivation to study the influence of different factors on shale gas adsorption. It is necessary to describe the occurrence process of shale gas from a microscopic view.

Molecular simulation can simulate the occurrence state of shale gas at the nanoscale and study the interaction mechanism between shale gas and reservoir. Wang et al. [9] studied the competitive adsorption behaviors of carbon dioxide and methane in shale kerogen nanopores by the grand canonical Monte Carlo method. The results showed that carbon dioxide preferentially adsorbs on the kerogen substrate more than methane at different temperatures. Zhao et al. [10] studied methane adsorption in graphite with different pore sizes using the grand canonical Monte Carlo and molecular dynamics methods. The simulation showed that methane molecules formed two adsorption layers with different energy near the wall. Li et al. [11] studied the adsorption behavior and mechanism of methane in clay minerals by molecular dynamics and grand canonical Monte Carlo simulation. The results showed that the crystal structure, chemical composition, and physical properties of minerals would eventually affect the adsorption amount of methane. Li et al. [12] studied the variation of gas in nano-slits and the mechanical theory behind it through the molecular simulation method. They clarified the physical phenomena caused by the nano-scale effect and its variation with pressure.

Although the above studies have obtained the influence of different factors on methane adsorption, most focus on the influence of carbon dioxide and nitrogen on methane adsorption. There is no systematic

and reliable method to study the influence of water on shale reservoir adsorption. In this paper, a sandstone model represented by quartz and a clay model represented by kaolinite has been constructed to study the competitive adsorption of methane and water by molecular simulation. The influence of water on methane adsorption in shale reservoirs under different conditions and the interaction mechanism between fluid and reservoir were studied.

2. Simulation method and model

2.1 Simulation model

The specific cell parameters of the mineral model are shown in Table 1 [13]. The cell model is established based on the data in Table 1. The cell model is used to construct computational models with pore sizes of 1nm, 2nm, 5nm, and 10nm. Figure 1 shows the calculation model (1 nm for example).

Tab. 1 Cell parameters of the mineral model

	a/nm	b/nm	c/nm	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$
kaolinite	0.518	0.890	1.245	90	99.69	90
quartz	0.491	0.491	0.540	90	90	120

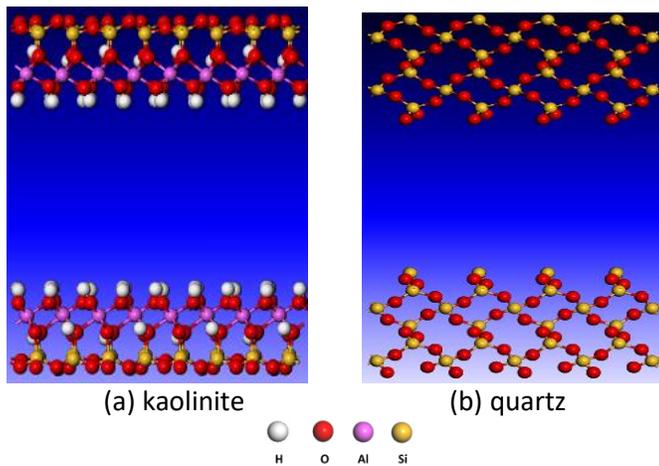


Fig. 1 Calculation Model(1 nm)

2.2 Simulation method

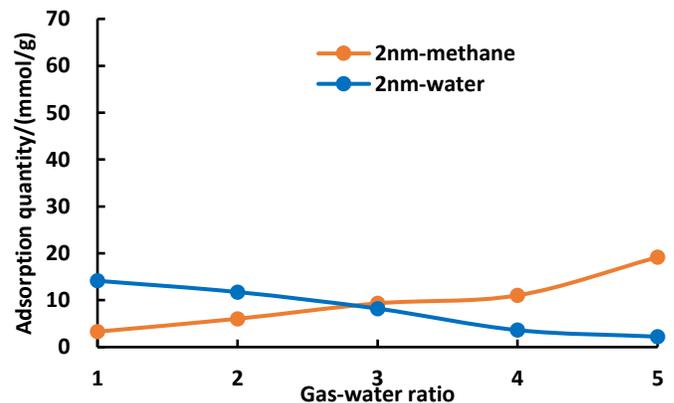
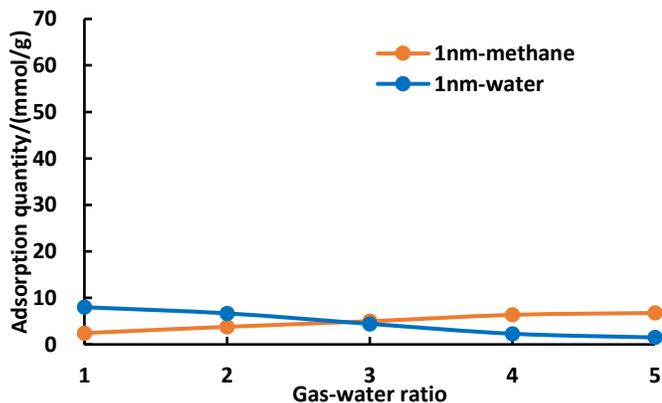
In the adsorption calculation, Universal force field and Monte Carlo method were used for simulation [14]. Monte Carlo algorithm achieves the final equilibrium structure by trying to add, delete, rotate, and move a molecule in the mineral model [15]. 1×10^6 steps first achieved the adsorption equilibrium, and then the adsorption parameters were counted by 1×10^7 steps. The Ewald method was chosen to calculate electrostatic potential energy, and Atom-based algorithm was used to calculate van der Waals force between molecules [16,17].

According to the field production data, the competitive adsorption of methane and water in different pore sizes was simulated at 86 °C and 60 MPa. According to the flowback data, the ratio of gas to water was 1: 1, 2: 1, 3: 1, 4: 1, and 5: 1.

3. Results and discussions

3.1 Adsorption Quantity

Fig. 2 and Fig. 3 describe the variation of adsorption quantity of kaolinite and quartz for methane and water with a gas-water ratio. It can be seen from Figs. 2 and 3 that the adsorption quantity of methane by kaolinite is greater than that by quartz, and the adsorption quantity of water is less than that by quartz. The adsorption quantity of methane and water increases with pore size. The adsorption quantity of methane increases with the increase of gas-water ratio, and the adsorption quantity of water decreases with the increase of gas-water ratio. When the gas-water ratio is greater than 3: 1, the adsorption quantity of kaolinite for methane is greater than that for water. No matter how the gas-water ratio changes, the water adsorption quantity of quartz minerals is always greater than that of methane due to quartz's strong hydrophilicity.



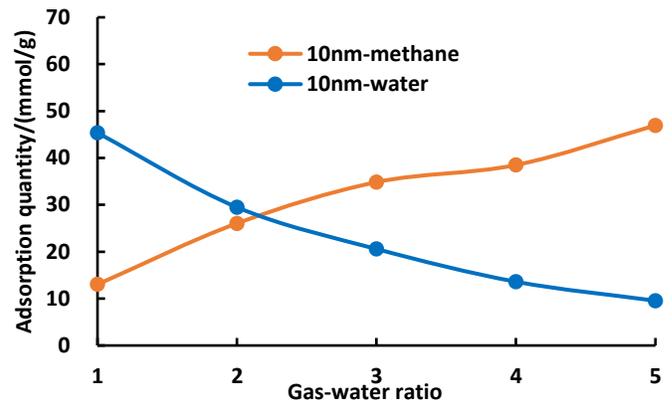
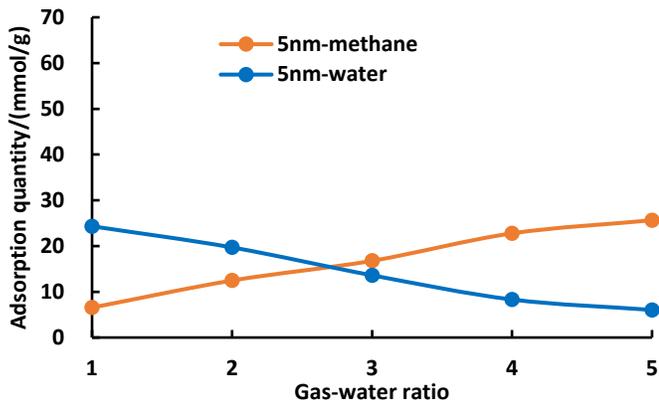


Fig. 2 Change of adsorption quantity of methane and water competitive adsorption with gas water ratio in kaolinite

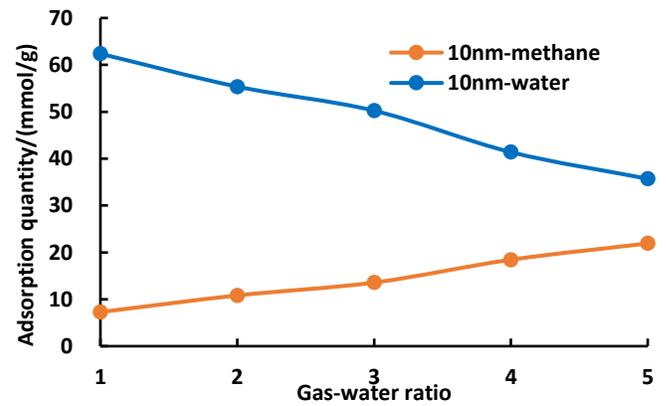
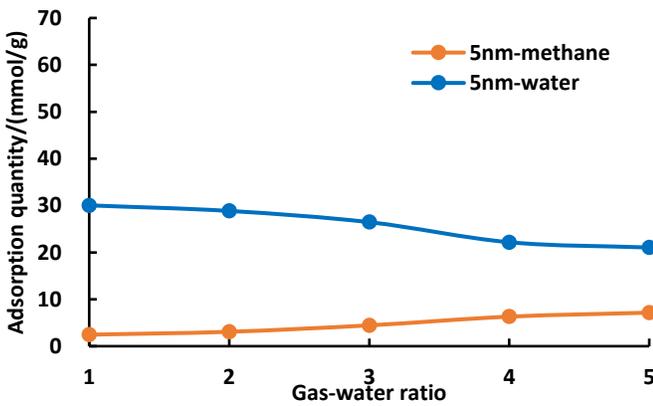
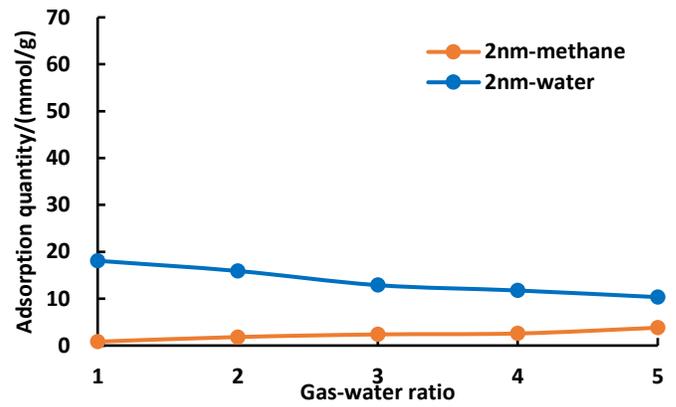
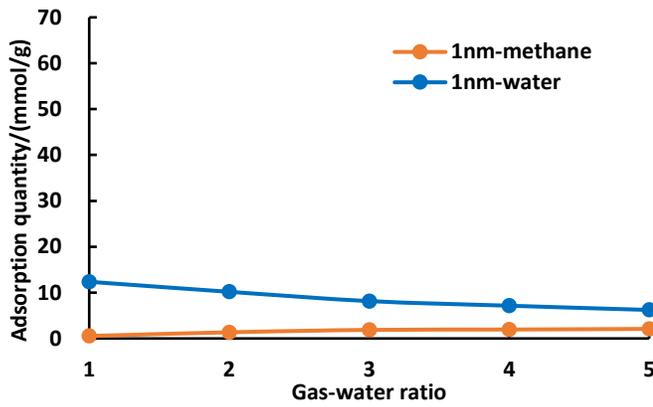


Fig. 3 Change of adsorption quantity of methane and water competitive adsorption with gas water ratio in quartz

3.2 Adsorption Heat

The adsorption heat is the thermal effect in the adsorption process [18]. The size of the adsorption heat can reflect the stability of the adsorption system. The greater the adsorption heat's absolute value, the more stable the adsorption is [19]. Fig. 4 and Fig. 5 show the variation of methane and water adsorption heat with a gas-water ratio. The adsorption heat of methane and water decreases with the pore size increase. The adsorption heat of kaolinite to methane is greater than that of quartz, and the adsorption heat of kaolinite to water is less than that of quartz to water. The adsorption quantity and heat results show that kaolinite is lipophilic

and quartz is hydrophilic. Tian also found that kaolinite is more lipophilic than quartz [20,21]. The adsorption heat of methane decreases with the increase of the gas-water ratio. With the increase of gas-water ratio, the adsorption quantity of methane increases, the interaction between methane increases, and the adsorption force of pore surface on methane decreases, reducing methane adsorption stability, so the adsorption heat decreases. The adsorption heat of water also decreases with the increase of the gas-water ratio. According to the results of adsorption quantity, with the increase of gas-water ratio, the adsorption amount of water decreases, resulting in the decrease of adsorption heat.

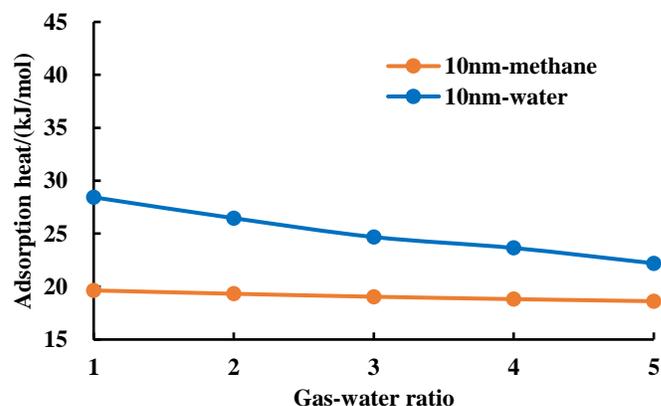
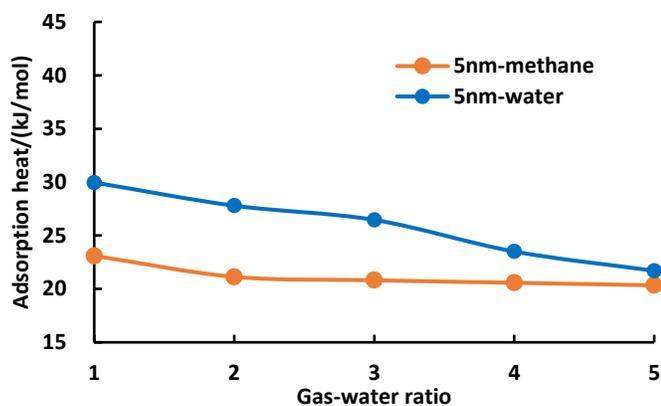
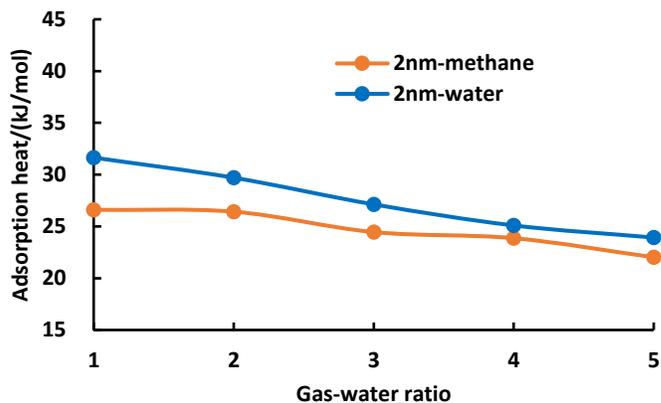
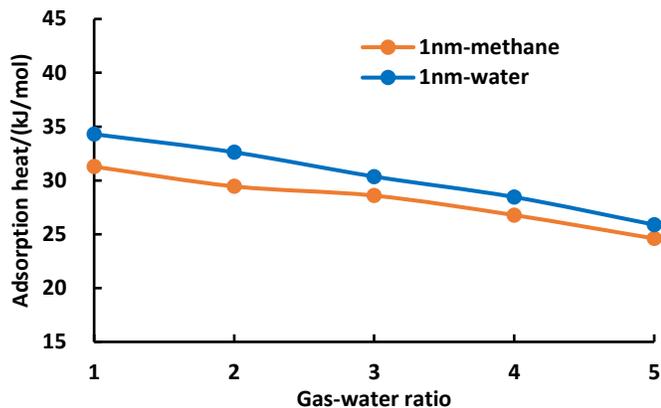


Fig. 4 Change of adsorption heat of methane and water competitive adsorption with gas water ratio in kaolinite

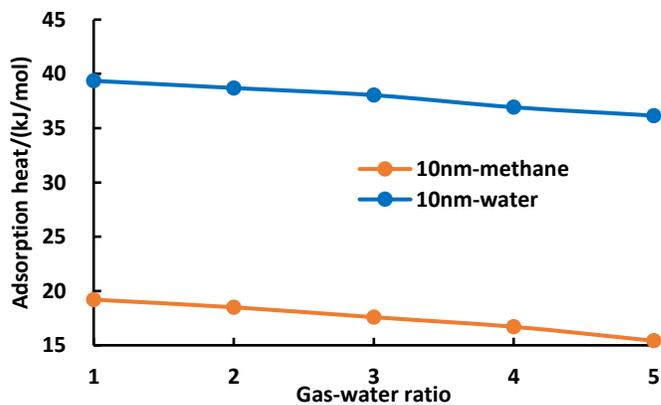
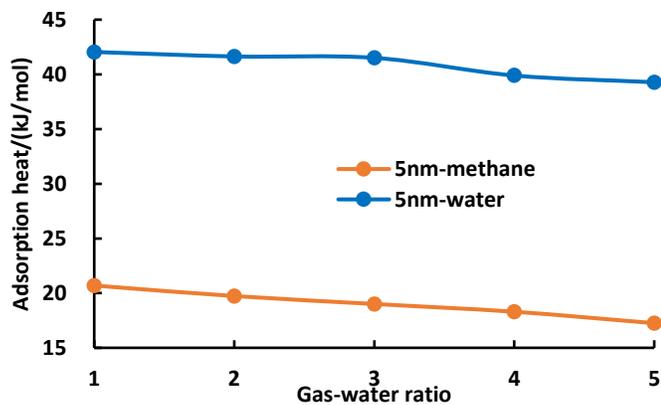
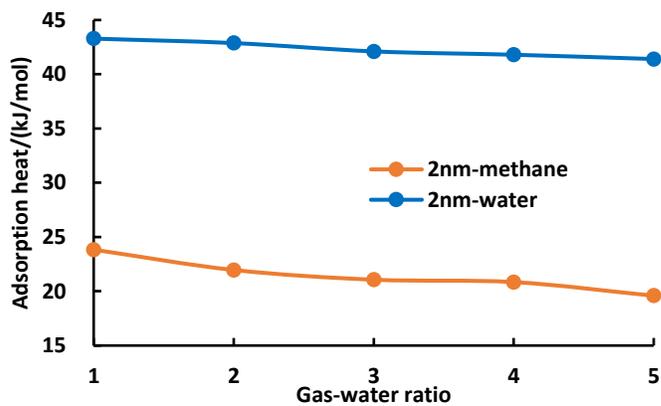
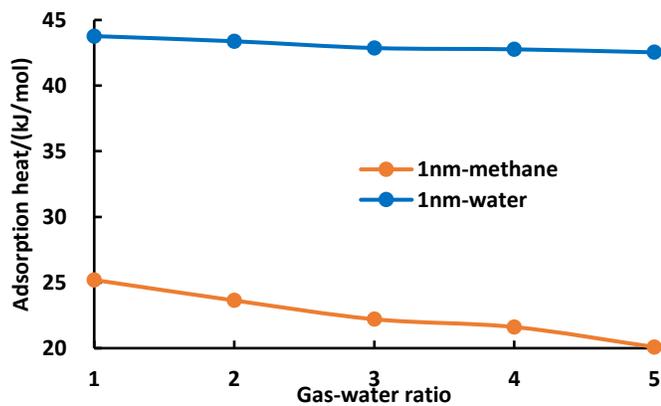


Fig. 5 Change of adsorption heat of methane and water competitive adsorption with gas water ratio in quartz

3.3 Relative Density Distribution

Figures 6 and 7 describe the relative density distribution of methane and water in a 1 nm aperture at

different gas-water ratios. Methane in kaolinite minerals is distributed on the upper and lower surfaces of pores. The adsorption density decreases with the increase of the gas-water ratio. Water initially gathers at the center of kaolinite pore size. With the increase of gas-water ratio, two symmetrical adsorption layers form on the upper and lower surfaces of pore size. Sui obtained similar conclusions by simulating the adsorption of

methane and water on montmorillonite [22]. When the gas-water ratio is 1: 1, methane in quartz minerals is concentrated in the center of the pore diameter to form two main aggregation layers. As the gas-water ratio increases, methane molecules gather on the pore's surface, while water molecules remain concentrated in the central distribution of the pore.

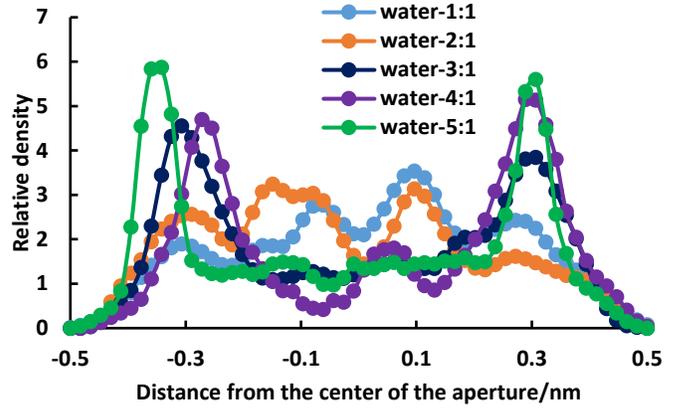
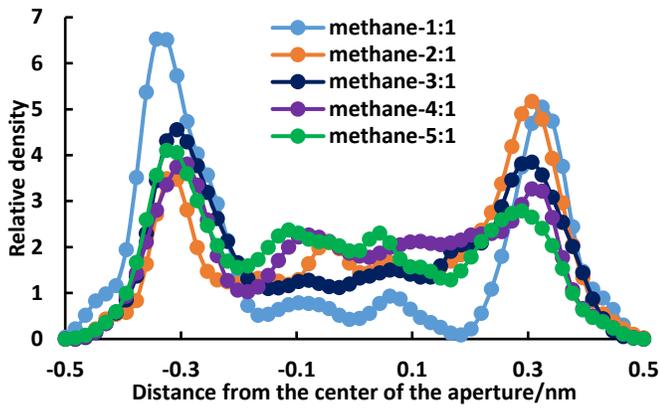


Fig. 6 Relative density distribution of methane and water under different gas water ratios in kaolinite

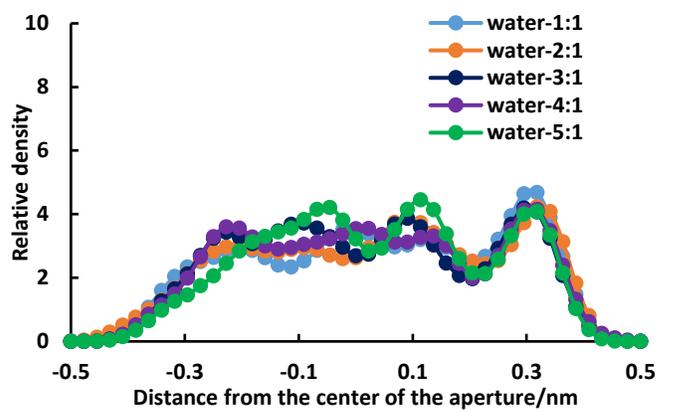
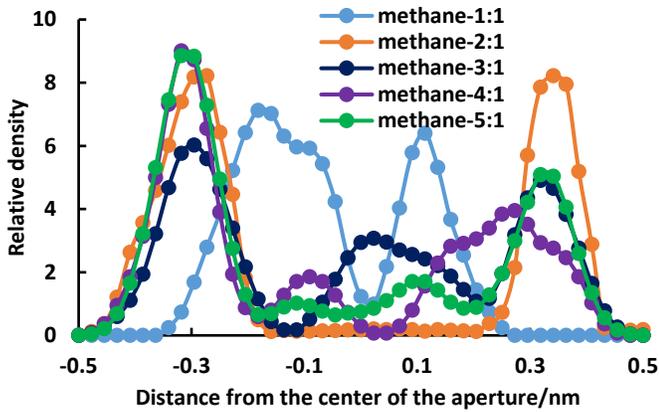


Fig. 7 Relative density distribution of methane and water under different gas water ratios in quartz

3.4 Interaction Energy

As shown in Fig. 8 and Fig. 9, with the increase of gas-water ratio, the proportion of van der Waals energy in total interaction energy in minerals increases, and the proportion of electrostatic energy in total interaction energy decreases. The ratio of electrostatic energy to total interaction energy in quartz minerals is always larger than that of van der Waals energy, indicating that electrostatic force plays a major role in the adsorption of methane and water by quartz minerals. The proportion of electrostatic energy in kaolinite is always smaller than that of van der Waals energy, indicating that kaolinite adsorbs methane and water mainly by van der Waals forces.

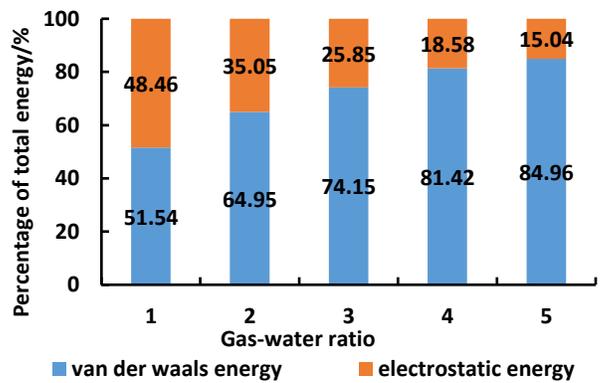


Fig. 8 Proportion of interaction of kaolinite under different gas water ratio

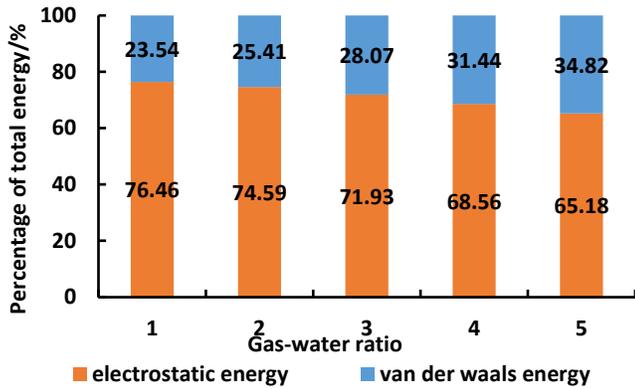


Fig. 9 Proportion of interaction of quartz under different gas water ratio

It can be seen from Fig. 10 and Fig. 11 that van der Waals energy increases with the increase of gas-water ratio, and the electrostatic energy decreases with the increase of gas-water ratio. With the increase of gas-water ratio, the adsorption quantity of methane increases, and the adsorption quantity of water molecules decreases. The adsorption of methane by minerals mainly depends on van der Waals force, and the adsorption of water mainly depends on electrostatic force [11]. Therefore, when the number of methane adsorbed by minerals increases and the number of water molecules decreases, the van der Waals energy representing van der Waals force increases, and the electrostatic energy representing electrostatic force decreases.

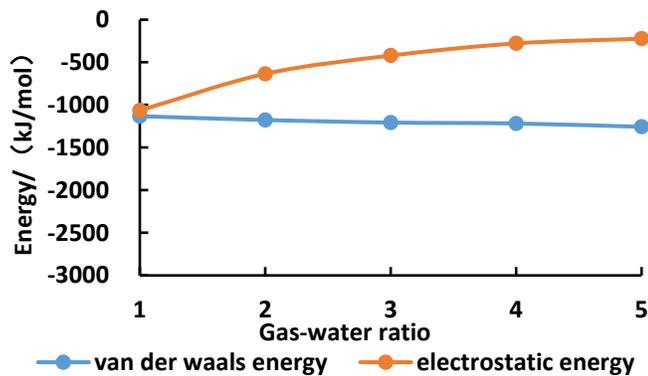


Fig. 10 Relationship between interaction energy and gas water ratio of kaolinite

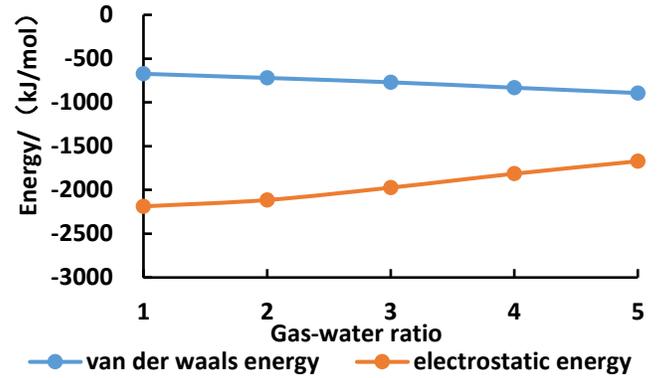


Fig. 11 Relationship between interaction energy and gas water ratio of quartz

4. Conclusions

By simulating the competitive adsorption of methane and water under different pore size spaces and gas-water ratios, it is found that the adsorption quantity of water in the initial state of kaolinite is greater than that of methane. However, with the increase of pore size and gas-water ratio, the adsorption quantity of methane will be greater than water adsorption, and the adsorption quantity of water in quartz has always been greater than methanes. The adsorption stability of minerals for methane and water decreases with the increase of the gas-water ratio. With the increased gas-water ratio, water adsorbs from the pore center to the kaolinite surface, and methane always adsorbs on the pore surface. As the gas-water ratio increases, methane in quartz adsorbs to the upper surface of the pore size, and water molecules adsorb in the center of the pore size. With the increase of gas-water ratio, the van der Waals energy increases, the electrostatic energy decreases, and the proportion of van der Waals energy to the total action energy keep increasing. The electrostatic force in quartz plays a major role in adsorption, and the van der Waals force in kaolinite plays a major role in adsorption.

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6. Reference

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