Micro-storage State and Mechanism of Shale Gas

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Abstract. Shale gas has attracted increasing attention as a new potential source of natural gas in recent years. Accurate micro-storage and mechanism of shale gas is important for defining and describing the adsorption characteristics, gas-in-place estimates. Organic-rich shale gas reservoirs were usually deposited under water environment which has great impact on shale gas adsorption. Different from the widely used solid-gas interface adsorption theory, the pore system in original shale reservoir is divided into solid-gas system and solid-liquid-gas system. In same statement, shale pores have stronger interaction with water molecules than CH₄ molecules, especially in solid-gas system. Water molecules mainly formed as competitive adsorption with shale gas on solid surface (solid-gas system) and liquid water surface (solid-liquid-gas system). Maxim gravitational potential energy, \( \Psi_{\text{max}} \), the distance where \( \Psi_{\text{max}} \) occurs, \( z_{\text{m}} \) and limited pore side, \( D_{\text{L}} \) are given. When pore size \( D < D_{\text{L}} \), no matter in what position the adsorbed molecules is, it force by both sides of the pore silts. When \( D > D_{\text{L}} \), the ratio of unaffected area increases to approximately 100% with pore side. When \( D < 10 \text{ nm} \), the ratio increases rapidly this means that the ratio of free gas increases quickly. When \( D > 50 \text{ nm} \), the ratio of unaffected area almost reaches 100%, which means that the content of free gas is far greater than the adsorbed gas. This study not only provides a new classification of shale pore system, but also can act as a reference to better understanding the adsorption mechanism of shale reservoir.

1. Introduction
Organic-rich shale gas reservoirs were usually deposited under water environment like tidal flats or deep-water basins. Loucks and Stephen [1] studied the sedimentary environment of the Mississippian Barnett Formation of the Fort Worth Basin, pointing out that it was deposited over a 25-m.y. time span in a deeper water foreland basin that had poor circulation with the open ocean. Shale reservoirs usually have certain water saturation, 7~20% for Haynesville, 25~35% for Barnett, 15~35% for Marcellus and even 42% for Eagle Ford[2,3]. While evaluating the reservoir of shale adsorption capacity and adsorbed gas content, the widely used isothermal adsorption experiment commonly uses dry shale samples. This might overestimated the reserves of shale gas. Ross and Bustin [4] compared isothermal adsorption behavior between dry and moisture shale from lower Jurassic Gordondale Member, the sorption capacities under dry conditions are 0.5~4 cm³/g, which is much greater than moisture equilibrated conditions, 0.1~1.6 cm³/g. They found that water occupation of potential sorption sites on clay contents. Recent studies also show that a certain water film remains in liquid phase on the surface of inorganic pores as its systems are water wetting under the formation conditions[5,6]. These recent results demonstrate the need for more consideration in water-gas interaction instead of solid-gas interaction in inorganic pores.
With further exploration and development of shale gas, studies on pore types and storage state in shale reservoir is increasing. Researchers at home and abroad use scanning electron microscope (SEM) to observe the pores in shales. However, classifying the various pore types and typical scale from view of liquid-gas storage state is lacked, which makes the understanding of the shale pores is not comprehensive. In addition, although experiments have confirmed the existence of absorbed gas and free gas in shale reservoirs, the micro-storage state of gas and its mechanical mechanism in various types of pores is not clear. In this study, pore system in shales is divided into two categories from the point of liquid-gas distribution: solid-gas system and solid-liquid-gas system. Mechanical mechanisms of methane and water molecules adsorption in two systems are also competitively calculated. Besides, the affection of pore size in two systems is studied and their interaction distances in shale gas system are also divided.

2. Mechanical analysis of liquid and gas distribution

2.1. Fluid–fluid/solid interaction model
The types of shale pores are complex. Due to the sedimentary environment and process, shale forms different types of pores ranging various scales. From characteristics of gas and water distribution, pore system in shales can be divided into two categories: solid-gas system and solid-liquid-gas system. Gas pores existing in organic matters belong to solid-gas system. In solid-liquid-gas system, extra gas was dissolved in liquid-water or place in the spaces between water molecules.

In order to thoroughly understanding the micro-storage state and mechanism in shale pore-system, it is necessary to study the stress between methane and water molecular with pore slides. The main component of shale gas is methane, therefore, in this study shale gas is assumed as pure methane. It is generally believed that the adsorption of shale gas is physical[11], which means that only intermolecular force exists between adsorbate and adsorbent molecules. The influence of gravity is ignoring because the intermolecular force is much larger than its gravity. The pore system is assumed to be composed of two slit and the adsorbed molecules are inside these two-surface slit, as shown in Figure 1.

![Figure 1. Fluid–fluid/solid interaction model](image)

The molecular potential energy, \( u \), and interaction energy of single-face slit, \( \psi(z) \), was represented by Lee's partially-integrated potential[20], which is widely used in molecular simulation and modelling adsorbed curve (the SLD model). It is clearly assumed in two parts: repulsion, \( u_p \) and attraction, \( u_{at} \), Eq.1, 2.

\[
u = u_p + u_{at} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} + \left( \frac{\sigma}{r} \right)^{6} \right]
\]

(1)
\[
\psi (z) = 4 \pi \rho_{\text{atom}} \varepsilon_{fs} \sigma_{fs}^2 \left\{ \frac{\sigma_{fs}^4}{5 (z)^5} - \frac{1}{2} \sum_{i=1}^{4} \frac{\sigma_{fs}^4}{z + (i-1) \sigma_{fs}^4} \right\}
\]  

(2)

Where \( \varepsilon_{fs} \) is the fluid–solid interaction energy parameter and \( \varepsilon_{ss} \) is the interaction energy of solid–solid. \( z \) is the position of a adsorb molecule. \( \sigma_{ff} \) is the molecular diameter parameter of the adsorbate and \( \sigma_{ss} \) is the carbon interplanar distances parameter, Eq.3, 4. In this work, values of them are following earlier works [18,21,22], as shown in Table 1.

\[
\varepsilon_{fs} = \sqrt{\varepsilon_{ff} \varepsilon_{ss}}
\]

(3)

\[
\sigma_{fs} = \frac{\sigma_{ff} + \sigma_{ss}}{2}
\]

(4)

Eq.2 only describes the potential energy of a single side, but the adsorb molecule effects by both side of the silt in actual process. Therefore, for a two-surface silt which its distance is \( L \), total potential energy a molecule inside it is as follows:

\[
\psi_{\text{total}} = \psi\left(z + \sigma/2\right) + \psi\left(L - z + \sigma/2\right)
\]

(5)

### Table 1. Parameters used in this study

| Types | \( \varepsilon \) | \( \sigma \) |
|-------|------------------|----------|
| C     | 148.6            | 0.373    |
| CH4   | 28               | 0.34     |
| H2O   | 78.2             | 0.3166   |

2.2. Mechanism in solid-gas system

Gas pores exist in organic matter, which is mainly consists of carbon. Therefore, surface of gas pores can be considered as carbon molecules. According to Eq.5 and Table.1, the interaction energies between CH4, water molecules and the surface of different pore sizes (0.5 nm, 2 nm, 5 nm and 20 nm) are calculated, as shown in Figure 2.

Define the boundary distance as \( z_0 \), when the position of a adsorb molecule \( z \) is less than \( z_0 \), potential energy is positive, which means that energy between gas pores and adsorbed molecules is repulsion and gravity on the contrary. The positive energy is increased at first and then decreased while the gravity energy is decreased with the increase of the distance. When pore size is less than 2nm, molecules located in the centre still suffer gravity energy influenced from both sides of the slit. It means that most of the produced gas is adsorbed on the surface of gas pores, rarely forming as free gas. When pore size is larger than 2 nm, the gravity energy suffered by molecules which located in the center approaches zero. The unaffected area increased with the pore size, which also means that the free gas area is increased.

In addition, the adsorbed ability between gas pore and water is stronger than it with CH4, as show in Figure 2. Define the maxim gravity energy is \( \psi_{\text{max}} \) and its position is \( z_{\text{max}} \). \( \psi_{\text{max}} \) between gas pore and water is about 1.6 times stronger than that with CH4. Therefore, shale gas forms as adsorb state when pore side is less than 2 nm and the content of free gas is increased with the pore size. Water molecules, which rarely exit in gas pores is competitive adsorb with CH4. Gas pores preferentially adsorb water molecules, which occupy a certain amount of effective adsorption sites.
2.3. Mechanism in solid-liquid-gas system

In solid-liquid-gas system, pore slides is usually covered by a certain water film. Gases, like CH$_4$ and water molecules, are adsorbed on the surface of the water film. Therefore, surface of the slit can be considered as water molecules in mechanism calculation of solid-liquid-gas system. According to Eq.5 and Table.1, the interaction energies between CH$_4$, water molecules and the surface of different pore sizes (0.5 nm, 2 nm, 5 nm and 20 nm) are calculated, as shown in Figure 3. The tendency of potential energy in solid-liquid-gas system is similar with that in solid-gas system, but the value of $z_0$, $z_{\text{max}}$ and $\Psi_{\text{max}}$ is different.

![Potential energy diagrams for solid-gas system](image1)

![Potential energy diagrams for solid-liquid-gas system](image2)
2.4. Competitive analyses

Competitive analyses of the adsorb mechanism between solid-gas system and solid-liquid-gas system is shown in Figure 4. The potential energy in solid-gas system is stronger than that in solid-liquid-gas system. Values of $\Psi_{\text{max}}$, $z_m$, $z_L$, etc is listed in Table 2.

Defining limit pore size as $D_L = 2 \times z_L$, when pore size $D < D_L$, no matter in what position the adsorbed molecules is, it is forced by both sides of the pore silts. When $D > D_L$, the ratio of unaffected area increases to approximately 100% with pore side, as shown in Figure 5. When $D$ is less than nearly 10nm, the ratio increases rapidly this means that the ratio of free gas increases quickly. When $D$ is 10nm~50nm, the increase range of unaffected area is very few. When $D > 50$ nm, the ratio of unaffected area is ~100%, which means that the content of free gas is far greater than the adsorbed gas.

| Types | Solid-gas system | Solid-liquid-gas system |
|-------|------------------|------------------------|
|       | C-CH$_4$ | C-H$_2$O | H$_2$O - CH$_4$ | H$_2$O - H$_2$O |
| Repulsion area | <0.115 | <0.105 | <0.120 | <0.11 |
| $\Psi_{\text{max}}$ (J) | $1.822 \times 10^{-20}$ | $2.827 \times 10^{-20}$ | $1.144 \times 10^{-20}$ | $1.762 \times 10^{-20}$ |
| $z_m$ (nm) | 0.170 | 0.155 | 0.170 | 0.155 |
| $z_L$ (nm) | 0.940 | 1.030 | 0.730 | 0.820 |
| $D_L$ (nm) | 1.880 | 2.060 | 1.460 | 1.640 |

3. Conclusions

Adsorption mechanism of CH$_4$ and water molecules of different pore sizes (0.5 nm, 2 nm, 5 nm and 20 nm) in solid-gas system and solid-liquid-gas system are analysed separately. The potential energy is stronger in solid-gas system than that in solid-liquid-gas system. Interaction energies both increase at...
first and then decrease while the gravity energy decreases with the increase of the distance. Besides, adsorption ability between gas pore and water is stronger than that with CH₄.

Shale gas reservoir is a complex solid-liquid-gas system. It has a stronger interaction with water molecules than CH₄ molecules, especially in solid-gas system. Water molecules mainly formed as competitive adsorption with shale gas on solid surface (solid-gas system) and liquid water surface (solid-liquid-gas system). Maxim gravitational potential energy, \( \Psi_{\text{max}} \), the distance where \( \Psi_{\text{max}} \) occurs, \( z_m \) and limited pore side, \( D_l \), are given. In addition, shale pores whose size \( D < 50 \) nm often adsorb large amount of shale gas, and are nearly 100% filled by free gas when \( D > 50 \) nm.

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