Calculating the absolute adsorption of high-pressure methane on shale by a new method

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Abstract
Currently, many adsorption experiments of methane on shale have been done to understand adsorption characteristics of methane on shale, but those experiments’ pressure and temperature are far less than reservoir pressure and temperature; therefore, we carried out the experiments of methane adsorption on shale at 75.6°C and 95.6°C with 0–50 MPa pressure range to study the adsorption characteristics of shale under reservoir condition. We also build a new method to calculate the real (absolute) adsorption of methane on shale. Results present that the characteristics of excess adsorption isotherm under high pressure is different from the characteristics of excess isotherm under low pressure; adsorption obtained by adsorption experiment increases with pressure going up until reaching a peak and then declines with further increase in pressure. We build a new method to calculate the absolute adsorption by assuming that the adsorption phase volume approximately equals to the total volume occupied by adsorbed molecule, and the results calculated by our method show this method is reasonable and effective.

Keywords
Shale, adsorption, high pressure, methane

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Introduction

As the development of shale gas is expanding, it attracts many researchers’ attention and makes them start to research some mechanism of developing shale gas. Shale gas as a significant resource has a unique feature to storage in shale with adsorption phase and free phase. Obviously, the gas content of shale consists of free gas and adsorbed gas. Many studies have proved that adsorption gas takes up 20–85% of the total gas content (Li et al., 2011; Wang et al., 2013; Xiong et al., 2012). So, it is vital to understand the methane adsorption characteristics of shale and to calculate the adsorption.

Until now, many adsorption researches have been carried out to acquire some important adsorption properties of shale. Schettler and Parmely (1990, 1991) studied the characteristics of methane adsorption on shale through adsorption experiments, which indicates that methane is adsorbed by kerogen and various clay minerals and adsorbents have different sorption capacities for their different specific surface areas; the adsorption capacity of some Devonian shale has positive correlation with total organic carbon (TOC; Schettler and and Parmely, 1990, 1991). Lu et al. (1995) found that illite’s sorption plays a key role and shale contains less adsorbed methane with less TOC and a higher temperature. Li et al. (2001) and Nuttal et al. (2005) expressed their belief that organic materials contain more adsorbed gas than clay minerals by conducting adsorption experiment with CH$_4$ and CO$_2$. Strapoc et al. (2010) and Wang et al. (2009) reported that minerals, organic matter, vitrinite reflectance (Ro), and micro-pore volume of shale have impact on adsorption characteristics; monolayer adsorption theory may not be suitable to calculate the total gas content of shale precisely; it is also reported that kerogen in Posidonia shales plays an important role in methane adsorption while sorption of CO$_2$ is mainly due to non-organic materials (Hartman et al., 2011; Rexer et al., 2014). Adsorption experiments on shale were carried out under pressure from 1.0 to 25 MPa at 46°C, and results showed that methane sorption capacity increased with TOC content and moisture content can reduce sorption capacity of shale (Tan et al., 2014).

Although these studies are significant, all the pressure of adsorption experiments almost are less than the reservoir pressure, so these isotherms cannot describe the adsorption feature of reservoir rock; therefore, people need to carry out some adsorption experiments under reservoir pressure to study the adsorption characteristics of reservoir shale.

It is well known that shale gas adsorption belongs to supercritical fluid (SCF) adsorption, because a reservoir’s temperature usually is far greater than the critical temperature of each component in shale gas. Generally, there are some methods to study SCF adsorption, but the mechanism of SCF adsorption is not completely established for lacking abundant and accurate experiment data and a perfect theory. Therefore, the state and structure of SCF adsorbed phase are not sufficiently understood and the density and volume of adsorbed phase are unknown exactly. Naturally, absolute adsorption cannot be calculated with an appropriate theory.

Among the past studies some researchers tried their best to investigate the relation between the absolute adsorption and excess adsorption. Murata and Kaneko (2000) calculated the absolute adsorption of supercritical methane by using the mean density of the adsorbed phase which is determined by excess adsorption isotherm. And this method completely removed the maximum of excess isotherms. But during the calculation they assumed the absolute adsorption isotherm is Langmuir type to acquire two important parameters, and it is not sure that if Langmuir equation can describe the absolute adsorption of SCF, especially high-pressure adsorption of SCF, so this method has an obvious defect. Nikolaev and Dubinin (1958) and
Reich et al. (1980) tried to improve the method of considering adsorbed phase density as liquid density; they assumed that adsorbed phase consists of molecules which have the Van der Waals exclusion value $b$, but they failed. Neimark and Ravikovitch (1997) and Salem et al. (1998) calculated the absolute adsorption by presuming the volume of the adsorbed phase as the pore volume, and they got a monotone adsorption isotherm for porous materials, but the method cannot be applied to non-porous materials and treat pore volume as the volume of adsorbed phase for none definite reason. Myers and Monson (2002) tried to achieve the link between absolute adsorption and excess adsorption by acquiring the accurate void volume of experimental system, but this volume cannot be acquired precisely by experiment. Do and Do (2003) proposed a method to use the integration of a pore volume distribution to calculate the adsorbed phase volume, and they treated the radius of the pore below which the adsorption density is different from the bulk density everywhere as the limit of integration. How to get the right value of the radius for different temperature and pressure still is uncertain, so this method faces a technological problem.

So far there is no proper way to calculate the absolute adsorption of SCF. Though the absolute adsorption can be acquired by experiment, it is an extremely complicated work and has no wide range of applications (Keller et al., 2003). Hence, people need a better approach to obtain the absolute amount of adsorption for avoiding those problems.

In this article, we conducted several adsorption experiments to study the adsorption feature of methane on shale with 75.6°C and 95.6°C and a pressure range of 0–50 MPa. We also develop an original method to calculate the absolute amount of methane adsorption on shale.

**Adsorption experiments**

**Materials**

The experimental samples are Longmaxi Formation shale, from Southern Sichuan Basin, China. The reservoir temperature is about 95.6°C and pressure is about 49 MPa. Methane and helium with purity 99.999% are used in the adsorption experiment. The samples are crushed into particle sizes of 60–100 mesh, and then dried until the weight is stable.

We obtain the mineralogical composition of these samples by X-ray diffraction with D8-DISCOVER apparatus and the T 5163-2010 criteria. Table 1 presents the mineral composition, TOC percentage, and water saturation of these samples. The corresponding pore size distribution (PSD) of the sample we recognize that the shale sample mainly contains micropores and meso-pores.

| No. | Porosity (%) | Water saturation (%) | Organic matter (%) | Quartz | Potassium feldspar | Plagioclase | Calcite | Dolomite | Pyrite | Clay content (%) |
|-----|--------------|----------------------|--------------------|--------|-------------------|-------------|---------|----------|--------|------------------|
| 1   | 4.1          | 35                   | 1.43               | 36     | 2                 | 5           | 7       | 3        | 2      | 45               |
| 2   | 4.8          | 40                   | 3.71               | 28     | \                | 8           | 10      | 14       | 3      | 36               |

TOC: total organic carbon.
**Experiment**

Volumetric method was used to measure the excess adsorption isotherms with GAI-100 instrument. The test pressure of the apparatus ranges from 0 to 69 MPa with a precision of 0.01 MPa; the highest test temperature was 177°C with a precision of 0.1°C. A sketch of GAI-100 is shown in Figure 2. The procedures of preparing experiment in detail are based on Xiong et al. (2016).

Adsorption experiments were carried out at temperature 75.6°C and 95.6°C with a pressure range of 0–50 MPa. Prior to adsorption experiment, sample cylinder and expansion cylinder were vacuumed and the oil bath was heated until the oil temperature was kept constant. Firstly, close Valve 2 that connects the sample cylinder, and open the valve of expansion cylinder and pump methane into expansion cylinder to a pre-set pressure, then close the valve of expansion cylinder. Secondly, record the pressure data when the pressure of expansion cylinder stabilizes (varying within the range of 0–5 lbf/in²). Thirdly, open Valve 2, let gas flow from the expansion cylinder to the sample cylinder. Record pressure data until the pressure variation is less than 5 lbf/in². Finally, calculate the excess adsorption isotherms based on the temperature and pressure data (Xiong et al., 2016).

**Adsorption isotherm analysis**

Figures 3 and 4 present the results of adsorption experiments. Excess adsorption reaches a peak point with an increase in pressure and then declines when the pressure continues to increase further, which means these isotherms have the same characteristics of SCF high-pressure adsorption isotherm (Chen et al., 1997; Xing et al., 2002; Zhou et al., 2000). The
Figure 2. The schematic of GAI-100 adsorption apparatus.

Figure 3. The excess adsorption isotherms of 1# shale.
The amount of absolute (real) adsorption will increase to saturation as the pressure rises, that is, the isotherm should be monotonically increasing based on adsorption theory (Do and Do, 2003; Zhou and Bai, 2002). Hence, according to the experimental results and theories above, even if the temperature and pressure of adsorption meet the reservoir condition, the excess amount of adsorption obtained by experiment cannot be regarded as the real (absolute) amount of adsorption on shale.

Method to calculate the absolute adsorption

Absolute adsorption and excess adsorption

Based on the definition of excess adsorption and absolute adsorption

\[
n_{\text{abs}} = \int_{V_a} \rho(r) dr = \frac{22.4 \bar{\rho}_a V_a}{M_m} \quad (1)
\]

\[
n_{\text{ex}} = \int_{V_a} (\rho(r) - \rho_{\text{bulk}}) dr = \frac{22.4 (\bar{\rho}_a - \rho_{\text{bulk}}) V_a}{M_m} = n_{\text{abs}} - \frac{22.4 \rho_{\text{bulk}} V_a}{M_m} \quad (2)
\]

where \(n_{\text{abs}}\) is the absolute amount of adsorption for unit mass, m\(^3\)/t; \(V_a\) is the volume of adsorption phase for unit mass, m\(^3\)/t; \(\rho(r)\) is the density profile of adsorbed phase, kg/m\(^3\); \(\bar{\rho}_a\) is the average density of adsorption phase, kg/m\(^3\); \(n_{\text{ex}}\) is the excess amount of adsorption.

**Figure 4.** The excess adsorption isotherms of 2# shale.
for unit mass, \( m^3/t \); \( \rho_{\text{bulk}} \) is the density of bulk fluid, \( \text{kg/m}^3 \); \( M_m \) is molar mass, g/mol. Generally, \( \rho_{\text{bulk}} \) is constant, so we can get the relationship

\[
n_{\text{abs}} = n_{\text{ex}} + \frac{22.4\rho_{\text{bulk}} V_a}{M_m}
\]  

(3)

**Method**

According to equation (3), if we can get \( n_{\text{ex}} \) and \( V_a \), then we can calculate the absolute adsorption. \( n_{\text{ex}} \) can be obtained by adsorption experiment, because adsorption acquired by adsorption experiment (volumetric method or gravity method) is excess (Belmabkhout et al., 2004; Murata and Kaneko, 2000). Therefore, the key to calculate \( n_{\text{abs}} \) is to calculate the \( V_a \) precisely.

Here, we assume the volume of adsorption phase \( (V_a) \) approximately equals to the total volume occupied by adsorbed molecule \( (V_t) \), and \( V_t \) can be calculated by multiplying each adsorbed molecule’s volume with the molecular amount which corresponds to the adsorption obtained by general adsorption experiment. Equation (4) is the expression of \( V_a \)

\[
V_a = V_t = \frac{1000n_{\text{Test}}}{22.4} N_A V_m
\]  

(4)

where \( n_{\text{Test}} \) is the experimental adsorption for unit mass, \( m^3/t \); \( N_A \) is Avogadro constant, \( \text{mol}^{-1} \); \( V_m \) is the volume of each adsorbed molecule, \( m^3 \); \( V_t \), \( m^3/t \).

Hence, equation (3) can be substituted by the following equation (5)

\[
n_{\text{abs}} = n_{\text{ex}} + \frac{22.4\rho_{\text{bulk}} V_a}{M_m} = \left( 1 + \frac{1000\rho_{\text{bulk}} N_A V_m}{M_m} \right) n_{\text{Test}}
\]  

(5)

Assuming \( V_m \) can be calculated by the equation as follow

\[
V_m = \frac{4}{3} \pi R^3
\]  

(6)

where \( R \) is the radius of adsorbed molecule, m.

Now we need a \( R \) with more accurate measurement to compute \( V_a \). Based on the molecular potential energy of methane we find a way to get a reasonable \( R \). Figure 5 tells us that when the distance between two methane molecules is \( R_0 \), there is almost no force between the two molecules, that is, the two methane molecules are in chemical potential balance (Prausnitz et al., 2006). According to this conclusion we assume that the distance between every two adsorbed molecules also is \( R_0 \) when adsorption system reaches the adsorption balance. The diameter of methane molecule is 0.38 nm, then we can get the expression of \( R \) (Figure 6)

\[
R = \frac{R_0}{2} + 0.19
\]  

(7)
The $R_0$ equals to 0.3737 nm through calculation based on the data of Figure 5. Besides that, we take the effect of micro-pore wall and water saturation of shale into consideration. To some extent we think that the wall-effect will decline the value of $R$, so we substitute $R$ with $0.9 R$ when we calculate $V_m$, hence, we get the final equation to calculate the absolute

Figure 5. Interaction potential energy between two methane molecules (Lennard–Jones).

Figure 6. Illustration to calculate $V_m$. 

The $R_0$ equals to 0.3737 nm through calculation based on the data of Figure 5. Besides that, we take the effect of micro-pore wall and water saturation of shale into consideration. To some extent we think that the wall-effect will decline the value of $R$, so we substitute $R$ with $0.9 R$ when we calculate $V_m$, hence, we get the final equation to calculate the absolute
adsorption by combining equation (1) with equation (7)

\[ n_{\text{abs}} = \chi \left( 1 + \frac{0.0984 \rho_{\text{bulk}}}{M_m} \right) n_{\text{Test}} \]  

(8)

where \( \chi \) is water saturation, %.

The absolute adsorption isotherms of 1# and 2# shale are calculated by equation (8) (Figures 7 and 8). These absolute isotherms are totally monotonical increasing, which means this new method is effective and reasonable.

### Discussion

This new method is used to calculate the absolute isotherms of methane on AX-21 activated carbon for testing its effectiveness (the data of methane excess adsorption on AX-21 activated carbon comes from Zhou et al.). Those absolute adsorption isotherms calculated by our method are monotonically increasing and remove the maximum of the excess adsorption isotherms at 0°C and 20°C (Figures 9 and 10). According to the methods which come from other researchers in the “Introduction” section, regarding pore volume (or the density of liquid methane) as the volume of adsorbed phase (or the density of adsorbed phase), we obtain the corresponding absolute adsorption isotherms, and then compare these results with the absolute isotherms of methane on AX-21 activated carbon from Murata and Kaneko (2000) and the absolute isotherms of methane calculated by the new method (Figures 9 to 12).

Besides “pore volume” method, the other methods can remove the maximum of the excess isotherms and obtain the monotonic increasing adsorption isotherm (Figures 9 and 10). The monotone curve of absolute adsorption calculated by treating the adsorbed
Figure 8. Absolute and excess isotherms of methane adsorption on 2# shale.

Figure 9. Excess amount of adsorption and the corresponding absolute adsorption calculated by different methods (0°C).
Figure 10. Excess amount of adsorption and the corresponding absolute adsorption calculated by different methods (20°C).

Figure 11. Excess amount of adsorption and the corresponding absolute adsorption calculated by different methods (−20°C).
phase as liquid-like seems good, but this method cannot be applied to calculate an absolute adsorption isotherm at a lower temperature (Figures 11 and 12). Furthermore, the adsorbed phase cannot be assumed to be liquid-like for supercritical methane. “Pore volume” method can barely obtain the appropriate absolute adsorption isotherm at a lower temperature as well (Figures 11 and 12). It seems that Katsuyuki Murata’s method can be used to calculate the absolute amount of adsorption, but the physical background of its computation process is unclear (Murata and Kaneko, 2000), which means that it must be a pure empirical method.

Generally, the method in our article has a clearer physical mean, a more broad application at different temperature, and at least can obtain reasonable absolute adsorption isotherms of methane on two kinds of materials (shale and AX-21 activated carbon).

**Conclusion**

In the article, we carried out adsorption experiments of methane on shale at 75.6°C and 95.6°C with a pressure range of 0–50 MPa. These adsorption isotherms have the typical characteristics of SCF adsorption. Adsorption obtained by experiment at reservoir temperature and pressure is excess adsorption rather than the real (absolute) adsorption.

We develop an original method for calculating the amount of absolute (real) adsorption. This method is based on clear physical background which assumes that the adsorption phase volume approximately equals to the total volume occupied by adsorbed molecule, and the latter volume can be calculated through adsorption tested by experiment. The absolute adsorption isotherms computed by our new method show the tendency of

![Figure 12. Excess amount of adsorption and the corresponding absolute adsorption calculated by different methods (−40°C).](image-url)

*Figure 12. Excess amount of adsorption and the corresponding absolute adsorption calculated by different methods (−40°C).*
monotonical increase, which means the method is reasonable and effective. By this means the amount of real (absolute) adsorbed gas can be calculated in shale reservoir.

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