Absolute adsorption and adsorbed volume modeling for supercritical methane adsorption on shale

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Abstract
Adsorbed methane significantly affects shale gas reservoir estimates and shale gas transport in shale formations. Hence, a practical model for accurately representing methane adsorption behavior at high-pressure and high-temperature in shale is imperative. In this study, a reliable mathematical framework that estimates the absolute adsorption directly from low-pressure excess adsorption data is applied to describe the excess methane adsorption data in literature. This method provides detailed information on the volume and density of adsorbed methane. The obtained results indicate that the extensively used supercritical Dubinin-Radushkevich model with constant adsorbed phase density underestimates absolute adsorption at high pressure. The adsorbed methane volume increases both the pressure and expands with the temperature. The adsorbed methane density reduces above 10 MPa, and approaches a steady value at high pressure. This study provides a novel method for estimating adsorbed shale gas, which is expected to improve the prediction of shale gas in place and gas production.

Keywords Shale gas · Methane adsorption · Absolute adsorption · Supercritical

1 Introduction
The rapidly increasing production of shale gas due to the advances in horizontal drilling and multistage hydraulic fracturing techniques has attracted growing interest in recent years [1]. In 2019, dry shale gas production accounted for 75% of the U.S. natural gas production, and this value is expected to exceed 90% in 2050, according to the Energy Information Administration (2019) [2].

Shale gas can be stored in three states in shale reservoirs: free and compressed gas within pores and fractures, adsorbed gas on the surfaces of organic matter and minerals, and dissolved gas in water and organic matter. Curtis et al. indicated that adsorbed gas accounts for 20%–85% of the total quantity [3]; Montgomery et al. [4] reported that the percentage of adsorbed gas in the total gas in place (GIP) was as high as 50%–60% in some cases. Hence, it is clear that adsorbed methane constitutes as significant proportion of the total shale gas content. In most shale formations, the burial depth is 2000–4000 m with pressures of up to 25 MPa, and the corresponding temperature can reach 60–100 °C. To evaluate the adsorption of methane on shales, a series of isothermal adsorption experiments were performed under different conditions (see Table 1).

All the commonly used models for high-pressure methane adsorption are based either on the empirical monomolecular layer (e.g., Langmuir-based model) or pore-filling (e.g., D-R-based model) assumption. The Langmuir-based model does not consider the interaction between the adsorbed molecules [14]. The D-R-based model was developed based on the pore filling theory and is only valid for pore diameters below 2 nm [15]. However, numerous investigations have revealed that shale formations include a wide range of pore sizes, from micro- to macropores [16–24].

The aforementioned methods are based on assumptions that the unknown adsorbed phase density remains constant with the changing adsorbed phase volume or that the unknown adsorbed phase volume remains constant with the changing adsorbed phase density [25, 26]. However, molecular dynamics simulations have indicated that the adsorbed phase density is position-dependent in the slit pores and that the adsorbed phase density varies with the increase in pressure [27]. Additionally, the adsorbed phase volume is not constant in ultrahigh-pressure gas adsorption measurements [28, 29, 12]. The hydrostatic pressure...
in the Upper Ordovician to Lower Silurian shale formations in the Sichuan Basin can reach 60 MPa because the depths can exceed 4000 m [30–32]. Recent advancements in devices based on the gravimetric method have widely facilitated the widespread use of high-pressure and ultra-high-pressure methane adsorption measurements. Li et al. analyzed methane adsorption on Paleozoic shale and kerogen from the Sichuan Basin, and reported that the D-R-based model produced large deviations in the experimental data at 30–60 MPa pressure [12]. Lin et al. performed grand canonical Monte Carlo (GCMC) simulations to describe methane adsorption and desorption on reconstructed shale, and noted that the modified Langmuir model failed to represent ultra-high-pressure data [33].

As a result, neither Langmuir-based nor D-R-based models can reflect the physical interpretation of supercritical methane adsorption. Thus, these extensively used models are unsuitable for studying for high-pressure and ultrahigh-pressure methane adsorption. In the last decade, the simplified local density (SLD) model with a specific equation of state (EOS) has been extensively used to represent methane adsorption behaviors in shale [13, 34–37]. However, the SLD model produces relatively large errors at high pressures [13] and is difficult to implement in engineering applications.

Adsorbed gas is another key parameter for predicting the productivity and working life of a producing shale gas well. The absolute adsorption is needed to estimate the shale gas migration in nanopores and to develop a kinetic model [38]. For an accurate evaluation of the isosteric heat of methane adsorption, the adsorbed methane volume is vital [39]. Although several practical methods to determine the absolute adsorption have been proposed [38, 40, 41], however, all of them involve additional experimental procedures. Thus, to improve the understanding of the shale gas storage and migration, an alternative model that can accurately estimate shale gas adsorption (including excess adsorption, absolute adsorption, adsorbed phase volume, and adsorbed phase density) is essential.

The remainder of this study is structured as follows. First, experimental isotherms from the literature were selected and transformed into a Virial plot to obtain Henry’s constant. The experimental isotherms were then mathematically converted to generalized isotherms and linearized plots. Next, a model of absolute adsorption was established from the linearized plots. Finally, the estimated volume and density of adsorbed methane, absolute adsorption were compared with the conventional models regarding either volume of adsorbed phase or density of adsorbed phase as an unknown constant.

### 2 Data acquisition and methodology

#### 2.1 Data acquisition

The data used in this study were measured by Li et al. [10], using a gravimetric apparatus (ISOSORP-HP Static II, Rubotherm GmbH, Germany). Supercritical methane adsorption was determined at various temperatures (40–120 °C) and at pressures of up to 35 MPa. Samples FC-47, FC-66, and FC-72, which were drilled at different depth from the Niutitang formation (lower Cambrian) in northeast Guizhou Province were ground into grains of 20–50 mesh for their high-pressure methane adsorption to be investigated. Prior to the methane adsorption, about 5–6 g sample was heated for 12 h at 110 °C under approximately 1 kPa to remove the residual gas and moisture. Further details on the samples, including the depth, mineral composition, and pore characteristics, can be found elsewhere [10].

The principal procedures of adsorption measurement are summarized as follows. The methane adsorption was measured at two points: Measurement Point 1 at vacuum \( MP_{1,0} \) (including the weight of sample container and shale sample) and experimental condition \( MP_{1}(p,T) \), and the Measurement Point 2 at vacuum \( MP_{2,0} \) (including the weight of the titanium sinker, sample container and shale sample) and the experimental condition \( MP_{2}(p,T) \) [42]. The density of bulk methane inside the chamber can be expressed as [43]:

| Reference | Pressure | Temperature | Model | Assumption |
|-----------|----------|-------------|-------|------------|
| [5]       | 25 MPa   | 65 °C       | Langmuir based | \( \rho_a \) constant |
| [6]       | 25 MPa   | Up to 150 °C| Langmuir based | \( \rho_a \) constant |
| [7]       | about 27 MPa | 45 °C | Langmuir model | none |
| [8]       | 35 MPa   | Up to 150 °C| D-R based | \( \rho_a \) constant |
| [9]       | 27 MPa   | Up to 82 °C | Langmuir based | \( \rho_a \) constant |
| [10]      | 35 MPa   | Up to 120 °C| Langmuir based; D-R based | \( \rho_a \) constant |
| [11]      | 25 MPa   | 45 and 130 °C| Langmuir model | \( \rho_a \) constant |
| [12]      | 60 MPa   | Up to 140 °C| D-R based | \( \rho_a \) constant |
| [13]      | 30 MPa   | Up to 100 °C| Langmuir based; D-R based | \( \rho_a \) constant |
where the $m_{sk,0}$ and $m_{sk}$ represent the weight of the titanium sinker under vacuum and the experimental condition, respectively, and $V_{sk}$ is the known volume of the titanium sinker. The excess adsorption ($n_{ex}$), i.e., the difference between the absolute adsorption ($n_{abs}$) and the amount that would be present in the same volume at the density of the gas in the bulk phase [41], can be expressed as follow according to the Gibbs definition [44]:

$$n_{ex} = \frac{m_{a} - \rho_{b} V_{a}}{M_{m_{x}}} = \frac{M P_{1}(\rho, T) - M P_{1,0} + \rho_{b} V_{0}}{M_{m_{x}}}$$

where $m_{a}$ is the absolute amount of adsorbed methane; $V_{a}$ is the adsorbed phase volume; $M$ is the mole mass of methane; $m_{x}$ is the weight of the shale sample, and $V_{0}$ is the combined volume of the shale sample and sample container. The values of the $V_{0}$ and $m_{x}$ were determined using high pressure helium gravimetry [44].

$$MP_{1,He}(\rho, T) = MP_{1,0} - \rho_{He} V_{0} = m_{x} + m_{c} - \rho_{He} V_{0}$$

where $\rho_{He}$ is the density of Helium, as obtained from Eq. (1), and $m_{c}$ is the known mass of the sample container. Hence, by plotting the $MP_{1,He}(\rho, T)$ against $\rho_{He} V_{0}$ and $m_{c}$ can be obtained from the slope and the intercept, respectively. All the right-hand-side terms of Eq. (2) are known. Notably, there is a large deviation between the determined value (0.4524 mg/g) and model-fitted value (0.3703 mg/g) for the first datum of sample FC-66 at 80°C in the original reference. Hence, while evaluating the experimental data in the following sections, this datum was excluded.

2.2 Henry’s constant and the virial plot

At relatively low pressure, methane adsorption can be described using Henry’s law [45]:

$$n_{abs} = K_{H} P$$

where $K_{H}$ is Henry’s constant (mmol/MPa) and $P$ is the pressure (MPa).

When the adsorption reaches the equilibrium state, in terms of the virial equation, the absolute uptake $n_{abs}$ and equilibrium pressure $P$ can be expressed as:

$$\ln(\frac{P}{n_{abs}}) = \frac{1}{T} \sum_{i} a_{i} n_{abs}^{i} + \sum_{i} b_{i} n_{abs}^{i}$$

where $a_{i}$ and $b_{i}$ are temperature independent parameters. Because Henry’s law is valid only at low pressure, the higher order terms in Eq. (5) can be ignored. When the experimental data before the maximum are optimized by the Universal Global Optimization (1stopt, 7d software, http://www.7dsoft.com/en/), the four temperature independent parameters ($a_{0}, a_{1}, b_{0}$ and $b_{1}$) can be achieved (Table 2), and only the points where the difference between excess sorption and absolute sorption is negligible will fall on the smooth curve, as shown in Fig. 1.

To obtain the Henry’s constant ($K_{H}$), an alternative expression of Eq. (5) was used [46]:

$$\ln(\frac{P}{n_{abs}}) = \ln \frac{1}{a} + 2C_{1} n_{abs}$$

When plot of $\ln(P/n_{abs})$ against $n_{abs}$ was used within the same experimental data which can be well fitted by Eq. (5), a linear relationship is observed for low absolute adsorption values (as shown in Fig. 2 and Table 3); therefore, $\ln (1/a)$ can be obtained by fitting the curve in this region. Henry’s constants obtained at relatively low pressure are then reliable because the difference between the absolute adsorption and excess adsorption in the low-pressure range can be disregarded.

2.3 Evaluation of the absolute from the excess adsorption

Absolute adsorption is the quantity of methane molecules constrained within the shale pore structure. Absolute adsorption is rarely mentioned in the context of methane adsorption at low pressure because absolute and excess adsorption are almost indistinguishable in this case, especially for shales with small adsorption capacity. In case of high-pressure methane adsorption, by contrast, difference between excess and absolute adsorption is considerable, and it is necessary to distinguish them.

The isotherms for methane adsorption under different temperatures can be generalized as a single isotherm by plotting $\ln(1000-n_{ex})$ against $\ln(K_{H}P)$, with $P$ in kPa, as shown in Fig. 3 [47]. To avoid negative results when taking the logarithms, the pressure $P$ as well as the excess adsorption $n_{ex}$ are magnified by a factor of 1000, as depicted in the following figures [48]. As seen in Fig. 3, most of the points in the relatively low methane coverage range are located on a smooth curve, mainly because the difference between

| Sample | $a_{0}$ | $a_{1}$ | $b_{0}$ | $b_{1}$ | RSS |
|--------|--------|--------|--------|--------|-----|
| FC-47  | −2967.48 | 7870.12 | 10.662 | 8.53 | 0.000223 |
| FC-66  | −3031.69 | 6817.71 | 10.539 | −1.35 | 0.000169 |
| FC-72  | −2905.84 | 4411.29 | 9.813 | 0.68 | 0.000267 |

The RSS signifies residual sum of squares, mmol²/g².
The absolute adsorption ($n_{abs}$) is known to increase monotonically with increasing pressure for the physisorption system [9]. The smooth curves in Fig. 3 describe the range of $n_{abs}$ are indistinguishable to $n_{ext}$, all the generalized isotherms in Fig. 3 can be represented by a Langmuir-type equation empirically [39, 49–51]:

$$
\ln\left(\frac{P}{n_{ads}}\right) = \ln\frac{1}{n_{ads, max}} + \frac{B}{n_{ads, max}}
$$

where $P$ is the pressure, $n_{ads}$ is the amount adsorbed, and $n_{ads, max}$ is the maximum amount adsorbed.
where $Y = \ln (1/\ln(K_{HF}P))$, and $\alpha$ and $\beta$ are undetermined parameters. Set $E = \ln Y = \ln([-\ln(1000-n_{ex})])$ and $F = 1/bX = 1/[b \cdot \ln(K_{HF}P)]$, the Eq. (7) can be expressed as:

$$E = \ln Y = \ln \alpha - \ln(1 + F)$$

The $\ln (1 + F)$ can be expended as a Taylor series:

$$\ln(1 + F) = F - \frac{1}{2}F^2 + \frac{1}{3}F^3 - \cdots + \frac{(-1)^{n+1}}{n}F^n$$

Ignoring the higher order right-hand terms in Eq. (10), because $|F| < 1$, we obtain

$$E = \ln \alpha - F$$

As clearly indicated in Eq. (11), when plotting $E$ (i.e. $\ln([-\ln(1000-n_{ex})])$ against $1/\ln(K_{HF}P)$, there must be a linear relationship in the low methane coverage range, namely, the relatively low-pressure range. Absolute adsorption is indistinguishable to excess adsorption in the low methane coverage range because $\rho_a$ is negligible compared with $\rho_a$. The linear plots in Fig. 4 can be regarded as the absolute adsorption.

Taking $1/\ln(P)$ as the X-axis and $\ln([-\ln(1000-n_{ex})])$ as the Y-axis in the linear region of Fig. 4, the linear plots in Fig. 4 can all be expressed using a linear equation [52]:

$$\ln \left[ \frac{X_i (1 - X_b)}{X_b (1 - X_i)} \right] + \left[ \frac{z_0 (X_i - X_b)}{X_b (1 - X_i)} \right] \frac{E}{kT} + \left[ \frac{z_2 (X_{i+1} - 2X_i + X_{i-1})}{kT} \right] \frac{E}{kT} = 0, i = 2, 3, ...$$

| Temperature | FC-47 | FC-66 | FC-72 |
|-------------|-------|-------|-------|
| 40 °C       | $y = 31.895x + 1.3245$ (R² = 0.999); | $y = 19.904x + 0.9657$ (R² = 0.996); | $y = 14.203x + 0.5711$ (R² = 0.998); |
|             | $K_{HF} = 0.266$; | $K_{HF} = 0.3807$; | $K_{HF} = 0.565$; |
| 60 °C       | $y = 28.869x + 1.7777$ (R² = 0.999); | $y = 18.752x + 1.4721$ (R² = 0.998); | $y = 13.75 + 1.1427$ (R² = 0.999); |
|             | $K_{HF} = 0.169$; | $K_{HF} = 0.229$; | $K_{HF} = 0.319$; |
| 80 °C       | $y = 29.547x + 2.2955$ (R² = 0.997); | $y = 17.543x + 1.9681$ (R² = 0.990); | $y = 13.24x + 1.5324$ (R² = 0.998); |
|             | $K_{HF} = 0.100$; | $K_{HF} = 0.1397$; | $K_{HF} = 0.216$; |
| 100 °C      | $y = 28.096x + 2.7602$ (R² = 0.990); | $y = 16.749x + 2.4657$ (R² = 0.992); | $y = 14.014x + 1.8769$ (R² = 0.992); |
|             | $K_{HF} = 0.0635$; | $K_{HF} = 0.0850$; | $K_{HF} = 0.153$; |
| 120 °C      | $y = 29.942x + 3.0996$ (R² = 0.989) | $y = 17.131x + 2.7393$ (R² = 0.990); | $y = 12.504x + 2.4394$ (R² = 0.993); |
|             | $K_{HF} = 0.045$; | $K_{HF} = 0.0646$; | $K_{HF} = 0.087$; |

The absolute adsorption $n_{abs}$ can be expressed as:

$$n_{abs} = \frac{1}{1000} \exp \left[ \exp \left( \alpha + \frac{\beta}{\ln P} \right) \right]$$

The volume of the adsorbed phase can be derived as:

$$V_a = \frac{n_{abs} - n_{ex}}{\rho_g}$$

The bulk methane density $\rho_g$ in Eq. (14) can be calculated using the REFPROP 9.0 software [53]. To date, the absolute adsorption and the volume of adsorbed phase have been obtained from the foregoing mathematical model. The density of adsorbed phase $\rho_a$ can be evaluated:

$$\rho_a = \frac{n_{abs}}{V_a} = \left( \frac{n_{abs}}{n_{abs} - n_{ex}} \right) \rho_g$$

Hence, this model provides a straightforward approach to evaluate the absolute adsorption, density, and volume of adsorbed phase from the experimental excess adsorption. To validate this model, we compare the parameters obtained from this model with the SDR model [10] and Ono-Kondo model.

The Ono-Kondo model process several advantages and it was introduced for representing gas adsorption on shale successfully [54–56]. The Ono-Kondo model for multilayer adsorption can be expressed as [57]:

$$\ln \left[ \frac{X_i (1 - X_b)}{X_b (1 - X_i)} \right] + \left[ \frac{z_0 (X_i - X_b)}{X_b (1 - X_i)} \right] \frac{E}{kT} + \left[ \frac{z_2 (X_{i+1} - 2X_i + X_{i-1})}{kT} \right] \frac{E}{kT} = 0, i = 2, 3, ...$$

Table 3 Fitting results of the virial plots of shale samples

| Temperature | FC-47 | FC-66 | FC-72 |
|-------------|-------|-------|-------|
| 40 °C       | $y = 31.895x + 1.3245$ (R² = 0.999); | $y = 19.904x + 0.9657$ (R² = 0.996); | $y = 14.203x + 0.5711$ (R² = 0.998); |
|             | $K_{HF} = 0.266$; | $K_{HF} = 0.3807$; | $K_{HF} = 0.565$; |
| 60 °C       | $y = 28.869x + 1.7777$ (R² = 0.999); | $y = 18.752x + 1.4721$ (R² = 0.998); | $y = 13.75 + 1.1427$ (R² = 0.999); |
|             | $K_{HF} = 0.169$; | $K_{HF} = 0.229$; | $K_{HF} = 0.319$; |
| 80 °C       | $y = 29.547x + 2.2955$ (R² = 0.997); | $y = 17.543x + 1.9681$ (R² = 0.990); | $y = 13.24x + 1.5324$ (R² = 0.998); |
|             | $K_{HF} = 0.100$; | $K_{HF} = 0.1397$; | $K_{HF} = 0.216$; |
| 100 °C      | $y = 28.096x + 2.7602$ (R² = 0.990); | $y = 16.749x + 2.4657$ (R² = 0.992); | $y = 14.014x + 1.8769$ (R² = 0.992); |
|             | $K_{HF} = 0.0635$; | $K_{HF} = 0.0850$; | $K_{HF} = 0.153$; |
| 120 °C      | $y = 29.942x + 3.0996$ (R² = 0.989) | $y = 17.131x + 2.7393$ (R² = 0.990); | $y = 12.504x + 2.4394$ (R² = 0.993); |
|             | $K_{HF} = 0.045$; | $K_{HF} = 0.0646$; | $K_{HF} = 0.087$; |
Fig. 3 Generalized isotherms for methane adsorption for samples FC-47, FC-66, and FC-72. Data reproduced from literature [10].

Fig. 4 Linear plots of methane adsorption for samples FC-47, FC-66, and FC-72. Data reproduced from Li et al. [10] (Note the first datum at 80 °C of sample FC-66 are excluded because of the large deviation between the measured data and model fitted data in the reference).
where \( X_i \) is the fraction of occupied adsorption site in the \( i \)th layer; \( X_b \) is the fraction occupied by the bulk phase, and \( X_{i+1} = X_b \); \( \rho_i \) is the density of adsorbed phase in the \( i \)th layer; \( \rho_m \) is the maximum density of adsorbed phase, namely, the density when all the adsorption site are occupied; \( k \) is the Boltzmann constant; \( z_0 \) is coordination number in the bulk; \( z_1 \) is coordination number within any layer; \( z_2 = (z_0 - z_1)/2 \). For a hexagonal configuration of lattice cells, \( z_0 = 8 \), \( z_1 = 6 \), and \( z_2 = 1 \), respectively. \( E/k \) indicates the interaction energy of bulk phase, and \( E_s/k \) describes the interaction energy of adsorbed gas and pore surface. The excess adsorption is [57]:

\[
\ln \left[ \frac{X_i (1 - X_b)}{X_b (1 - X_i)} \right] + (z_1 X_i + z_2 X_2 - z_0 X_b) \frac{E_i}{kT} + \frac{E_s}{kT} = 0, \quad i = 1 \quad \quad (17)
\]

\[
X_i = \frac{\rho_i}{\rho_m} \quad \quad (18)
\]

\[
X_b = \frac{\rho_b}{\rho_m} \quad \quad (19)
\]

Table 4 Fitting parameters for the linear plots in Fig. 3

| Sample | T (°C) | \( \alpha \) | \( \beta \) | \( R^2 \) |
|--------|--------|---------------|---------------|---------|
| FC-47  | 40     | 2.028         | -4.5574       | 0.999   |
| FC-66  | 60     | 2.0864        | -5.2237       | 0.996   |
| FC-72  | 80     | 2.207         | -6.5373       | 0.994   |
| FC-72  | 100    | 2.3484        | -7.9812       | 0.993   |
| FC-72  | 120    | 2.4786        | -9.369        | 0.993   |

Table 5 Fitting results of the monolayer Ono-Kondo model and RMSE of the shale samples

\[
n_{ex} = 2C \sum_{i=1}^{\infty} (X_i - X_b) \quad \quad (20)
\]

where \( C \) is a prefactor related to the active sites of the adsorbent for a specific gas. In the Ono-Kondo model, the \( C, \rho_m, E_s \) and \( E \) are regression parameters. Recent investigation by applying the Ono-Kondo model have showed that the supercritical methane adsorption on shale is monolayer adsorption [56]. In this study, we apply the monolayer scenario of the Ono-Kondo model to represent the experimental data. Obviously, in the monolayer Ono-Kondo model, the \( X_2 \) in Eq. (17) will be replaced as \( X_b \), because the density of the “second layer” equals to the density of bulk methane. The \texttt{lsolve} in MATLAB was used to solve the nonlinear equations (Eq. 17, Eq. 18, Eq. 19, Eq. 20) and the \texttt{lsqcurvefit} in MATLAB was used to fit the experimental data. For monolayer scenario, one can directly obtain the density of adsorbed phase and absolute adsorption via the Ono-Kondo model. We considered the root mean square error (RMSE) [58] to evaluate the disagreement between the model fitted excess adsorption and the experimental results:
\[ RMSE = \sqrt{\frac{1}{m} \sum_{i=1}^{m} (n_{cal} - n_{ex})^2} \]  \hspace{1cm} (21)
is a pore structure parameter. In the presence of micropore-filling; sites will lose the methane molecules under higher temperature implying that some of the adsorption $C_m$ molecules decrease. The parameter also declines with pore surface and the repulsive effect among the bulk gas indicating that attractive effect between the methane and absolute energy of bulk phase ($E/k$) is positive, indicating the bulk repulsive, indicating the attractive force. However, the interaction energy of bulk phase ($E/k$) is positive, indicating that the methane has repulsive force among molecules. The absolute value of $E/k$ and $E/k$ decline with increasing temperature indicating that attractive effect between the methane and pore surface and the repulsive effect among the bulk gas molecules decrease. The parameter $C$ also declines with increasing temperature implying that some of the adsorption sites will lose the methane molecules under higher temperature, resulting in the decline in maximum density $\rho_m$.

\[ n_{ex} = n_{\infty} \left\{ -D \ln \left( \frac{\rho_a}{\rho_g} \right) \frac{RT}{2} \right\} \left( 1 - \frac{\rho_g}{\rho_a} \right) \]  
\[ n_{abs} = n_{\infty} \left\{ -D \ln \left( \frac{\rho_a}{\rho_g} \right) \frac{RT}{2} \right\} \]  

Figure 7 Average densities of the adsorbed methane calculated at pressures above 15 MPa and adsorbed methane densities from literature (The colored spheres represent the data from this study, whereas the hollow circles denote data from literature [10]. The dot-dashed line denotes the liquid methane density at the boiling point (26.35 mol/L at -162 °C))

3 Results and discussion

3.1 Excess adsorption isotherms

The model evaluation results verify that both the monolayer Ono-Kondo model and the SDR model can represent methane adsorption; the monolayer Ono-Kondo model has an RMSE below 0.00137 mmol/g (Table 5), which is equivalent to the original SDR model (Eq. 22) based on the assumption that the unknown adsorbed density is constant. The interaction energy of adsorbed gas and pore surface ($E_n/k$) is negative, indicating the attractive force. However, the interaction energy of bulk phase ($E/k$) is positive, indicating that the methane has repulsive force among molecules. The absolute value of $E_n/k$ and $E/k$ decline with increasing temperature indicating that attractive effect between the methane and pore surface is magnified because the difference in the adsorbed phase density overestimated and underestimated the volume of adsorbed methane at low and high pressure, respectively. Therefore, the volumes of adsorbed phase calculated by the SDR model are all smaller than the micropore volumes $V_{mic}$ (horizontal red solid line in Fig. 5) and their total pore volumes $V_{total}$ (horizontal blue solid line in Fig. 5) [10].

3.2 Adsorbed methane density and volume

As both the adsorbed methane volume and adsorbed methane density have remained unmeasurable, it is imperative to develop a robust method to estimate the adsorbed methane volume and adsorbed methane density. The model adopted in this study provides information on the absolute adsorption firstly and the adsorbed phase volume, and the adsorbed phase density can be evaluated from Eq. (14) and Eq. (15), respectively. The adsorbed methane volume as a function of the temperature and pressure is depicted in Fig. 5. As the uncertainty in the volume evaluated using Eq. (14) is considerably higher at relatively low pressure than that in the relatively high-pressure range, to better demonstrate the trend of the adsorbed volume, only parts of the volume are displayed in Fig. 5 for pressures above 5 MPa. This is due to the low bulk methane density $\rho_g$ at relatively low pressure; any small difference between the determined excess adsorption and absolute adsorption can lead to large deviations in the adsorbed methane volume. The adsorbed methane volume increases steeply at moderate pressure and approaches the maximum value. Additionally, the adsorbed phase volume expands slightly with increasing temperature; this is mainly attributable to the liquid-like characteristic of the adsorbed phase [59]. Interestingly, the adsorbed volumes of these three samples are fall between their micropore volumes $V_{mic}$ (horizontal red solid line in Fig. 5) and their total pore volumes $V_{total}$ (horizontal blue solid line in Fig. 5) [10]. Notably, the routinely applied SDR model with the assumption of constant adsorbed phase density underestimated and approached the volume of adsorbed methane at low and high pressure, respectively. Therefore, the volumes of adsorbed phase calculated by the SDR model are all smaller than the micropore volumes $V_{mic}$. Another interesting finding is that the volumes of the adsorbed phase calculated by using the monolayer Ono-Kondo model (solid triangles in Fig. 5) remain constant with increasing pressure and are numerically close to the micropore volumes $V_{mic}$. Analogously, the assumption that the volume of adsorbed methane is a constant regardless of the temperature and pressure also leads to an inaccurate estimation of the adsorption capacity of methane.

The uncertainty of $\rho_a$ is magnified because the difference between $n_{abs}$ and $n_{ex}$ is negligible at low pressure region. It is difficult to determine a reasonable value for $\rho_a$ at relatively low pressure because $(n_{abs} - n_{ex})$ is present in the denominator of Eq. (15) [58]. However, the value of $\rho_a$ at high pressure is more reliable and is nearly constant (Fig. 6). As illustrated in Fig. 6, the adsorbed methane density exhibits a
slight reduction above 10 MPa and most of the values are lower than the liquid methane density at the boiling point (26.35 mol/L at -162 °C), which is widely accepted as the upper limit of the adsorbed density [60, 61]. The slight reduction of the adsorbed phase density might be attributable to the preferential adsorption at different pressures. At low pressure, the methane molecules are preferentially adsorbed on the surfaces of micropores with higher potential. At a given pressure, the adsorbed phase density in the micropores is higher than that in the mesopores [27]. As the pressure increases, the methane molecules are adsorbed on the surface of fine-mesopores which causes the adsorbed density to decrease slightly. At the same temperature, the densities of adsorbed phase at pressure above 15 MPa are arranged from largest to smallest in the order of the SDR model, the monolayer Ono-Kondo model, and evaluated in this study.

The average values of the adsorbed density of methane at pressures above 15 MPa are plotted in Fig. 7, which shows that all the calculated densities are lower than the liquid methane density (26.35 mol/L at -162 °C). The adsorbed methane density obtained using the SDR model is always higher than all the density values obtained in this study. In all models, the density decreases linearly with the temperature. This is attributable to the decrease in absolute adsorption and the increase in the adsorbed methane volume with increasing temperature and to the reduction in the density of the liquid-like adsorbed phase with increasing temperature.

### 3.3 Absolute methane adsorption

It is essential to evaluate shale gas reservoir accurately and acquire more knowledge on methane transport in shale micropores. In nanometer-diameter pores, in particular, surface diffusion of the adsorbed methane can be the main contributor to the total methane flux [62, 63]. Considering methane transport in kerogen pores as an example, the contribution of the adsorbed layer will be more than 60% of the total mass flux, when the pore diameter is less than 2 nm [64]. The absolute adsorption forecast using Eq. (13) and that obtained using the original SDR model from literature [10] and the monolayer Ono-Kondo model are depicted in Fig. 8. In all the cases, the absolute adsorption decreases as the temperature increase because adsorption is an exothermic process.
At a relatively low-pressure range, both the SDR model, the monolayer Ono-Kondo model and the model adopted in this study can represent excess adsorption, which is consistent with the fact that absolute and excess adsorption are approximately identical; however, absolute adsorption increases throughout the entire pressure range. At a higher pressure range, absolute adsorption is consistently higher than the corresponding experimentally measured values. The routinely adopted SDR model with constant adsorbed methane density and the monolayer Ono-Kondo model with constant adsorbed volume underestimate absolute adsorption under high pressure. This inconformity in the absolute adsorption is primarily caused by (i) the SDR and the monolayer Ono-Kondo model’s underestimation of the adsorbed methane volume at high pressures, and (ii) calculation of absolute adsorption as the sum of the excess and the product of the adsorbed phase volume and bulk methane density.

4 Conclusions

In this study, a series of methane adsorption isotherms at pressures of up to 35 MPa and temperatures of up to 120 °C were analyzed using a mathematical method. This method evaluates absolute adsorption on the basis that absolute and excess adsorption are approximately equivalent at relatively low pressure and then increase over the entire pressure range. This model can estimate the adsorbed phase volume, adsorbed phase density, and absolute adsorption from experimental adsorption data. The main results can be summarized as follows:

1. A mathematical framework provides an alternative method to evaluate high-pressure methane adsorption isotherms (up to 35 MPa and 120 °C) for three Niutitang shales in Guizhou Province, China with a variational adsorbed density and adsorbed volume with temperature and pressure. The absolute adsorption, adsorbed volume and adsorbed density can be evaluated from the experimental excess data.

2. The adsorbed methane volume increased rapidly in the moderate pressure range and approached a maximum at high pressure. For all the samples, the adsorbed methane volume expanded slightly as temperature increased, and the adsorbed methane volumes fall into the range of the micropore volume and total pore volume.

3. The adsorbed methane density decreased at pressures above 5 MPa and approached a constant at high pressure. The density at high pressure was lower than the liquid density of methane at its boiling temperature. The SDR-based model with a constant adsorbed phase density and the monolayer Ono-Kondo model overestimated the adsorbed phase density and underestimated the adsorbed volume and absolute adsorption at high pressure region.

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Data availability The data that support the findings of this study are available on request from the corresponding author.

Declarations

Conflict of interest The authors declare no conflict of interest.

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