Thermodynamics and Kinetics of CO$_2$/CH$_4$ Adsorption on Shale from China: Measurements and Modeling

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Abstract: CO$_2$-enhanced shale gas recovery (CO$_2$-ESGR) sequesters anthropogenic CO$_2$ and improves the profitability of shale gas exploitation. This work investigated the adsorption behaviors of CO$_2$ and CH$_4$ on shale from China at 20, 40, 60 and 80 $^\circ$C. The pressure ranges for CO$_2$ and CH$_4$ were 1–5 and 1–15 MPa, respectively. The excess adsorbed amount of CH$_4$ increased with increasing pressure from the beginning to the end, while the maximum excess CO$_2$ adsorption was observed at approximately 4 MPa. The absolute average deviations (AADs) of CO$_2$ and CH$_4$, determined by the Langmuir + k model, were 2.12–3.10% and 0.88–1.11%, respectively. Relatively good adsorptivity for CO$_2$ was exhibited when the pressure was less than 5 MPa, which was beneficial to the implementation of CO$_2$-ESGR. With continuous increases in pressure, the adsorption capacity of CO$_2$ was weaker than that of CH$_4$, suggesting that the injected CO$_2$ would reduce the partial pressure of CH$_4$ for CO$_2$-ESGR and the displacement effect would no longer be significant. In addition, the adsorption rate of CO$_2$ was much faster than that of CH$_4$. CO$_2$ was more active in the competitive adsorption and it was advantageous to the efficiency of CO$_2$-ESGR.

Keywords: adsorption; thermodynamic models; CO$_2$-ESGR; high pressures; kinetics

1. Introduction

Carbon capture, utilization, and storage (CCUS) has exhibited great potential in reducing the concentration of atmospheric CO$_2$, and has played an indispensable role in mitigating the severe consequences of global warming [1–8]. CO$_2$-enhanced shale gas recovery (CO$_2$-ESGR) not only creates the opportunity for sequestering anthropogenic CO$_2$, but also improves the feasibility and profitability of shale gas exploitation [9,10]. In order to have a scientific and comprehensive understanding of the process of CO$_2$-ESGR, it is essential to research both the adsorption thermodynamics and kinetic properties of CO$_2$ and CH$_4$, including their different adsorption capacities and adsorption/desorption rates [11–13]. While the kinetic properties of CO$_2$ and CH$_4$ directly determine the feasibility and efficiency of CO$_2$-ESGR, the adsorption capacities of CO$_2$ and CH$_4$ play an important role in accessing CH$_4$ reserves and the maximum amount of CO$_2$ sequestration.

To date, both experimental and numerical simulations have provided theoretical guidance for the implementation of CO$_2$-ESGR [14–17]. Gu et al. [18] investigated the adsorption behaviors of CO$_2$ and CH$_4$ on diverse shales from the Sichuan basin and observed that the adsorption of CH$_4$ on the surface of the shales was mainly as a monolayer as the temperature rose, while that of CO$_2$ gradually changed from a multilayer to a monolayer. Weniger et al. [19] conducted adsorption experiments of CO$_2$ and
CH$_4$ on carbonaceous shales at pressures of up to 25 MPa; the maximum measured excess adsorbed amount was 0.47 mmol/g for CH$_4$ and 0.81 mmol/g for CO$_2$. Chareonsuppanimit et al. [20] measured the adsorption isotherms of three different gases on shales from the Illinois basin, and they revealed that the adsorption capacities of N$_2$, CH$_4$, and CO$_2$ were in the ratio 1:3.2:9.3 at approximately 7 MPa. Du et al. [21] simulated the process of CO$_2$/CH$_4$ displacement by injecting CO$_2$ into shales which were pre-adsorbed by CH$_4$. They showed that CO$_2$ had a relatively larger excess adsorbed amount than CH$_4$, and CO$_2$ had the ability to enhance CH$_4$ recovery from the shale gas reservoir. Although numerous studies have reported the adsorption amounts of CO$_2$ and CH$_4$, literature on the kinetics of CO$_2$/CH$_4$ adsorption on shales is limited.

The current study not only systematically investigated the adsorption capacities of CO$_2$ and CH$_4$ on shale from China over a wide range of pressures and temperatures, but also compared the kinetic properties of these. First, both the Brunauer–Emmett–Teller (BET) surface area and pore distribution of shale were determined by measuring N$_2$ adsorption/desorption isotherms at a temperature of 77 K. Second, measurements of the gas adsorption of CH$_4$ on shale were made at temperatures of 20–80 °C and pressures of 1–15 MPa. For CO$_2$, the measurements were only conducted at pressures of 1–5 MPa due to equipment limitations. Third, the excess adsorbed amount and the adsorption rate were calculated and discussed. Finally, two different thermodynamic models, the Langmuir + $k$ and Ono–Kondo lattice models, were applied to match the adsorption isotherms.

2. Materials and Methods

2.1. Materials

The purities of both CO$_2$ and CH$_4$ used herein were 99.99%, and the raw shale was derived from Huadian, China. Table 1 shows the results of the ultimate and proximate analysis of the shale sample. The proportion of elemental C was 24.66%, and total organic carbon (TOC) accounted for approximately 4.91% of total shale mass.

<table>
<thead>
<tr>
<th>Ultimate Analysis (Dry wt % Basis)</th>
<th>Proximate Analysis (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>C</td>
</tr>
<tr>
<td>0.732</td>
<td>24.66</td>
</tr>
</tbody>
</table>

Both the BET surface area and pore distribution of the shale sample were determined by measuring the N$_2$ adsorption/desorption isotherms at a temperature of 77 K. Figure 1a displays the N$_2$ adsorption (solid) and desorption (hollow) isotherms, and the BET surface area of the shale was 60.76 m$^2$/g. The pore size distribution of the shale revealed the presence of extensive micropores and mesopores (Figure 1b) which were the key to CO$_2$ and CH$_4$ adsorption.

Figure 1. (a) N$_2$ adsorption (solid) and desorption (hollow) isotherms and (b) pore size distribution of crushed shale.
2.2. Adsorption

Measurements of adsorption were conducted at temperatures of 20, 40, 60 and 80 °C and pressures of 1–5 MPa for CO\(_2\) and 1–15 MPa for CH\(_4\), respectively, using a high-pressure volumetric analyzer (HPVII-200). The HPVII included a data acquisition system, a degas station, and an analysis station (Figure 2). In addition, an exterior bath was employed to regulate temperature. The accuracy of the temperature transducer was 0.01 °C, and the accuracies of the high-pressure and low-pressure transducers were ±0.04% and ±0.15%, respectively. The accuracy of the measurements was greatly improved because the free spaces at both room temperature and experimental temperature were calculated.

![Figure 2. Schematic diagrams of (a) experimental system and (b) HPVII-200.](image)

The adsorbed amounts of CO\(_2\) and CH\(_4\) were calculated through a static volumetric method and the specific experimental procedures were as follows:

1. First, the shale was crushed and sieved before use, and a powder of 0.18–0.25 mm in grain size was obtained. This was dried for 8 h at 105 °C to exclude the effect of moisture on the weight measurement.
2. Then, the powder was weighed and placed into the sample cylinder, which was subsequently attached to the degas station and evacuated overnight at 105 °C to remove the adsorbed moisture and other gases.
3. Next, the cooled cylinder was moved to the analysis station and the manifold was cleaned to avoid contamination by gases in the manifold.
4. Finally, the adsorption of gases (CO\(_2\) or CH\(_4\)) experiment was carried out automatically by the HPVII-200. The experimental data were recorded, and the adsorption isotherms were derived.

2.3. Adsorbed Amount Calculations

The adsorbed amount was determined from the amount of gas dosed into the adsorption cell and the non-adsorbed amount. In order to determine the non-adsorbed amount, we measured the free space, which was the free volume of the adsorption cell excluding shale.

2.3.1. Free Space

The free space was measured using a helium expansion method. At the experimental temperature, the sample tube, which is shown in Figure 3, contained three temperature zones and the free space \(V_{AFS}\) was divided into three volumes:

\[
V_{AFS} = V_{xU} + V_{xL} + V_S, \quad (1)
\]

where \(V_{xU}\) represents the upper-stem volume, around 3.5 cm\(^3\), and \(V_{xL}\) and \(V_S\) are the lower-stem volume and the adsorption cell volume, respectively.
In order to determine $V_{xL}$ and $V_S$, which were two indispensable values in the following adsorbed amount calculations, two mass balances were established at room temperature (298.15 K) and the experimental temperature, respectively.

At room temperature, the entire system was evacuated to a vacuum. Subsequently, helium was injected into the system (around 0.08 MPa), and when the pressure became stable, Valve 1 between the manifold and the adsorption cell opened. During this process, the pressure and temperature before injection ($P_A$ and $T_A$) and after injection ($P_B$ and $T_B$) were recorded, and the amount of helium injected into the adsorption cell ($n_D$) was calculated from the following equation:

$$n_D = \frac{P_A V_{LP}}{T_A z_A R} - \frac{P_B V_{LP}}{T_B z_B R},$$

where $V_{LP}$ represents the low pressure manifold volume, 46.7791 cm$^3$.

For the free space analysis at room temperature, because $V_S$ and $V_{xL}$ shared the same temperature and pressure, a new volume $V_{SxL}$ was introduced and expressed as

$$V_{SxL} = V_S + V_{xL}.$$
2.3.2. Adsorbed Amount of Gas

The procedure to determine the adsorption characteristics of the shale was similar to that described for helium expansion. However, instead of using the low-pressure transducer, a high-pressure transducer was used to measure the experimental pressure. The gas (CH\textsubscript{4} or CO\textsubscript{2}) was continuously loaded into the manifold to the preset pressure, automatically and accurately. The pressure and temperature before (\(P_1\) and \(T_1\)) and after injection (\(P_2\) and \(T_2\)) were collected by the data acquisition system, and the amount of gas (CH\textsubscript{4} or CO\textsubscript{2}) injected into the adsorption cell (\(n_{\text{dosed}}\)) was obtained from the following expression:

\[
n_{\text{dosed}} = \frac{P_1 V_{\text{HP}}}{T_1 z_1 R} \left( \frac{V_S}{z_S T_S} + \frac{V_{xT}}{z_{xT} T_{xT}} + \frac{V_{xU}}{z_{xU} T_{xU}} \right),
\]

(6)

where \(V_{\text{HP}}\) is the high pressure manifold volume, 27.0903 cm\textsuperscript{3}.

The amount of non-adsorbed gas (\(n_{\text{Nads}}\)) was calculated using

\[
n_{\text{Nads}} = \frac{P_S}{R} \left( \frac{V_S}{z_St} + \frac{V_{xT}}{z_{xT} T_{AM}} + \frac{V_{xU}}{z_{xU} T_{xU}} \right),
\]

(7)

where \(P_S\) is the pressure of the adsorption cell, and \(T_{xU}\) and \(T_S\) were the temperatures of the upper stem and the adsorption cell, respectively.

Knowing \(n_{\text{dosed}}\) and \(n_{\text{Nads}}\), the excess adsorbed amount of gas (\(n_{\text{ex}}\)) was calculated using the following equation:

\[
n_{\text{ex}} = n_{\text{dosed}} - n_{\text{Nads}}.
\]

(8)

2.4. Adsorption Rate Calculations

\(M_t/M_{\infty}\) is the ratio between the cumulated excess adsorbed amount at time \(t\) and at equilibrium. This is a normalized and widely used parameter that reveals the gas adsorption rate. During the measurements, both the temperature and pressure were recorded and analyzed using a pressure-decay method [22]. \(M_t/M_{\infty}\) was obtained from following expression:

\[
y = \frac{M_t}{M_{\infty}} \approx \frac{P_0 - P_t}{P_0 - P_{\infty}},
\]

(9)

where \(P_0\) represents the original pressure after injection, and \(P_t\) and \(P_{\infty}\) represent the pressures at time \(t\) and at equilibrium, respectively. Based on Fick’s II law, the kinetics of CO\textsubscript{2}/CH\textsubscript{4} adsorption on shale were calculated using the simplified diffusion model proposed by Terzyk and Gauden [23,24]. The effective diffusion coefficient (\(D_e\)) was obtained from the following expressions:

\[
\frac{M_t}{M_{\infty}} = 1 - 6 \times 10^{-8} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \pi^2 D_\text{e} t\right) n = 1, 2, 3 \ldots \infty.
\]

(10)

When \(0.0025 \leq y = M_t/M_{\infty} \leq 0.8\),

\[
f_1(y) = 0.286 \times 8.151 y \times y^{1.453}.
\]

(11)

When \(0.8 \leq y = M_t/M_{\infty} \leq 0.9\),

\[
f_2(y) = (0.285 - 0.284 \times y) / \left(1 - 1.927 \times y + 0.927 \times y^2 \right).
\]

(12)

When \(f_1(y) = f_2(y)\),

\[
\pi^2 D_\text{e} t = f_1(y) = f_2(y).
\]

(13)

It should be noted that the effective diffusion coefficient (\(D_\text{e}\)) in this work was assumed as a mean value that was not influenced by the time and gas concentration.
3. Modeling

3.1. Langmuir + k Model

The Langmuir model is a common and widely used expression to study adsorption behavior. It was originally proposed assuming there was an equilibrium between the free gas molecules and the adsorbed gas molecules at the adsorption spot, and then modified by Sakurovs et al. [25] using gas density, rather than pressure, as the independent variable. In addition, the ‘Henry’ absorption coefficient \( k \) was introduced, and the thermodynamic equilibrium equation of the Langmuir + \( k \) model was expressed as:

\[
 n_{ex} = n_L \left( 1 - \frac{\rho_g}{\rho_a} \right) \frac{\rho_g}{\rho_g + \rho_L} + k \rho_g \left( 1 - \frac{\rho_g}{\rho_a} \right),
\]

where \( \rho_g \) represents the free phase density of the actual gas, which is obtained from \( PV = zRT \). The absorbed phase densities \( \rho_a \) for CO\(_2\) and CH\(_4\) were 1.027 and 0.421 g/cm\(^3\) respectively [25–29]. Furthermore, the adsorption capacity of the surface was expressed by \( n_L \), and the gas density (when adsorption was half the maximum) was expressed by \( \rho_L \). The parameters \( n_L, \rho_L, \) and \( k \) were obtained from regression fitting.

3.2. Ono–Kondo Lattice Model

The Ono–Kondo lattice model was established using lattice theory, which is more applicable to fitting high-pressure adsorption isotherms. It was improved by Sudibandriyo et al. [30,31] and the equilibrium equation was expressed as:

\[
 \ln \left[ \frac{x_t (1 - x_g)}{x_g (1 - x_t)} \right] + z_0 (x_t - x_g) \frac{\varepsilon_{ii}}{kT} + z_2 (x_{t+1} - 2x_t + x_{t-1}) \frac{\varepsilon_{ii}}{kT} = 0, t = 2, 3, \ldots n.
\]

In this equation, \( k \) represents the Boltzmann constant and \( \varepsilon_{ii}/kT \) represents the fluid–fluid interaction energy. Furthermore, \( x_t \) and \( x_g \) are the proportions of the adsorption spots taken up by the adsorbed gas molecules in layer \( t \) and by the fluid molecules, respectively. These were expressed as follows:

\[
 x_t = \frac{\rho_t}{\rho_a}, x_g = \frac{\rho_g}{\rho_a},
\]

where \( \rho_t \) represents the adsorbed phase density in layer \( t \) and \( \rho_g \) represents the bulk phase density.

The absorbed phase densities \( \rho_a \) for CO\(_2\) and CH\(_4\) were assumed to be 1.027 and 0.421 g/cm\(^3\), respectively [25–29]. In this work, only monolayer adsorption was assumed, for the sake of simplification, and the equation was expressed as

\[
 \ln \left[ \frac{x_1 (1 - x_g)}{x_g (1 - x_1)} \right] + \frac{(7x_1 - 8x_g)\varepsilon_{ii}}{kT} + \frac{\varepsilon_{is}}{kT} = 0,
\]

where \( \varepsilon_{is}/kT \) represents the fluid–solid surface interaction energy. The thermodynamic expression of the Ono–Kondo lattice model was as follows:

\[
 n_{ex} = 2C (x_1 - x_g) = 2C (\rho_t / \rho_a - \rho_g / \rho_a),
\]

where \( C \) represents a prefactor that correlated with the adsorption capacity and varied with different adsorbents and gases. In this study, the parameters \( \rho_1, C, \) and \( \varepsilon_{is}/k \) were obtained from the regression fitting while other parameters were obtained from published values [29,31].
4. Results and Discussion

The excess adsorbed amounts and adsorption rates of CO\textsubscript{2} and CH\textsubscript{4} on shale from China were measured and calculated. Furthermore, the Langmuir + k and Ono–Kondo lattice models were employed to match the adsorption isotherms and the results from fitting the models were compared and discussed.

4.1. Adsorption Capacity

The values of the free space ($V_{AFS}$) measured in all adsorption experiments were similar (approximately 20 cm\textsuperscript{3}) because $V_{AFS}$ was obtained from the analysis at room temperature. The lower-stem volume ($V_{XL}$) and adsorption cell volume ($V_{S}$) were calculated through the analysis at experimental temperature. As we can see in Table 2, the temperature difference between the lower stem and the adsorption cell caused the measured value of $V_{S}$ to no longer be constant and, instead, it increased with the rising temperature. At this time, it was more like an effective volume, because the actual amount of gas stored in the adsorption cell was influenced by temperature. Furthermore, the $V_{S}$ values of the CO\textsubscript{2} and CH\textsubscript{4} adsorption experiments at the same temperature were similar because the free space measurement was completed before the required experimental gas (CO\textsubscript{2} or CH\textsubscript{4}) was loaded into the manifold.

Table 2. The adsorption cell volume at experimental temperatures.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>293</th>
<th>313</th>
<th>333</th>
<th>353</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{S}$ (cm\textsuperscript{3})</td>
<td>CO\textsubscript{2}</td>
<td>7.29</td>
<td>8.16</td>
<td>8.97</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{4}</td>
<td>7.31</td>
<td>8.17</td>
<td>8.91</td>
</tr>
</tbody>
</table>

A maximum excess adsorbed amount of CO\textsubscript{2} was observed at approximately 4 MPa (Figure 4). A downward trend of excess adsorbed amount of CO\textsubscript{2} at relatively high pressures has also been observed in other studies [32,33]. The relationship can be described using the following correlation:

$$n_{ex} = n_a \left(1 - \frac{\rho_g}{\rho_a}\right),$$

(19)

where $n_{ex}$ and $n_a$ represent the excess and absolute adsorbed amounts, respectively. While $\rho_a$ represents the adsorbed phase density, the free phase density is expressed as $\rho_g$. At the beginning of adsorption, $\rho_g$ was much smaller than $\rho_a$, and $n_{ex}$ was close to $n_a$. As $\rho_g$ increased extremely rapidly with increasing pressure, $n_a$ increased moderately and eventually remained stable once the majority of adsorptive sites of shale were occupied by CO\textsubscript{2} molecules. The rapid and large increase in $\rho_g$ may be responsible for the downward trend of $n_{ex}$. By contrast, the excess adsorbed amount of CH\textsubscript{4} increased with increasing pressure across the entire range of applied pressures. The absence of a maximum in the adsorption isotherm of CH\textsubscript{4} may be attributable to the free phase density, $\rho_g$, of CH\textsubscript{4}, which did not change as much as that of CO\textsubscript{2} with increasing temperature.

Figure 4. The excess adsorbed amounts of CO\textsubscript{2} and CH\textsubscript{4} on the shale sample.
4.2. Adsorption Rates

During the experiment, the chamber pressure increased from the lowest to the highest preset values automatically after each measurement was completed. As the presence of adsorbed gas at every pressure step may affect the adsorption rate at each subsequent pressure step, only the adsorption rate at the first preset pressure (1 MPa) was analyzed because the sample cylinder was originally exposed to vacuum prior to the application of the first pressure and before the adsorption started. With increasing temperatures, the time to reach equilibrium of both CO$_2$ and CH$_4$ decreased, which was indicative of increasing rates of adsorption (Figure 5). That was because the increase in temperature resulted in increased Brownian motion.

![Figure 5. Adsorption rates of CO$_2$ and CH$_4$ at 1 MPa.](image)

An equilibrium was reached faster for CO$_2$ than CH$_4$ at all temperatures (Figure 6), and CO$_2$ therefore had a larger adsorption rate than CH$_4$. This may be attributed to the higher affinity between shale and CO$_2$, making it easier for CO$_2$ to diffuse into the micropores on the surface of the shale. CO$_2$ was more active in the competitive adsorption and it was advantageous to the efficiency of CO$_2$-ESGR.

![Figure 6. Comparison of adsorption rates between CO$_2$ and CH$_4$ at different temperatures.](image)

The effective diffusion coefficients ($D_e$), which reflect the adsorption rate more directly, are listed in Table 3. In this study, $D_e$ of CH$_4$ at 40 °C was $0.56 \times 10^{-3}$ s$^{-1}$, and was smaller than that determined in other studies ($0.66 \times 10^{-3}$ s$^{-1}$ at 2 MPa [34] and $0.82 \times 10^{-3}$ s$^{-1}$ at 3 MPa [35]). This is because
would increase as the pressure rose. Furthermore, with increasing temperature, the adsorption rates of both CO\textsubscript{2} and CH\textsubscript{4} increased. While the adsorption rate of CH\textsubscript{4} at 80 °C was almost 5 times larger than that at 20 °C, the adsorption rate of CO\textsubscript{2} was more than 3 times larger than that at 20 °C. In addition, the adsorption rate of CO\textsubscript{2} was much faster than that of CH\textsubscript{4} at all temperatures. Taking 40 °C as an example, the adsorption rate of CO\textsubscript{2} (1.65 × 10\textsuperscript{−3} s\textsuperscript{−1}) was almost 3 times larger than that of CH\textsubscript{4} (0.56 × 10\textsuperscript{−3} s\textsuperscript{−1}).

Table 3. The effective diffusion coefficients of CO\textsubscript{2} and CH\textsubscript{4} at 1 MPa.

<table>
<thead>
<tr>
<th></th>
<th>20 °C</th>
<th>40 °C</th>
<th>60 °C</th>
<th>80 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}</td>
<td>1.23</td>
<td>1.65</td>
<td>2.94</td>
<td>4.16</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>0.49</td>
<td>0.56</td>
<td>1.61</td>
<td>2.48</td>
</tr>
</tbody>
</table>

4.3. Thermodynamic Models

The Langmuir + k and Ono–Kondo lattice models were employed to match the adsorption capacities of shale. The relevant parameters and the tolerance analysis are given in Tables 4 and 5, respectively. The absolute average deviations (AADs) were calculated using

\[
AAD\% = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{n_{\text{cal}}^{i} - n_{\text{exp}}^{i}}{n_{\text{exp}}^{i}} \right| \times 100. \tag{20}
\]

Table 4. Parameters and tolerance analysis of the Langmuir + k model \textsuperscript{a}.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>n</th>
<th>n\textsubscript{L} (mmol·g\textsuperscript{−1})</th>
<th>(\rho_{L}) (g·cm\textsuperscript{−3})</th>
<th>k (cm\textsuperscript{3}·g\textsuperscript{−1})</th>
<th>AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}</td>
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<td>0.0266</td>
<td>8.5970</td>
</tr>
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</table>

\textsuperscript{a} n: Number of data points estimated. AAD, absolute average deviation.

Table 5. Parameters and tolerance analysis of the Ono–Kondo lattice model.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>n</th>
<th>(\rho_{1}) (g·cm\textsuperscript{−3})</th>
<th>C (mmol·g\textsuperscript{−1})</th>
<th>(\varepsilon_{i}/k) (K)</th>
<th>AAD</th>
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<td>2.7091</td>
<td>-351.4</td>
</tr>
<tr>
<td></td>
<td>353.31</td>
<td>12</td>
<td>0.1735</td>
<td>2.1090</td>
<td>-420.5</td>
</tr>
</tbody>
</table>

In Equation (19), n is the number of data points, and the subscripts “exp” and “cal” represent experimental and calculated, respectively.

The Langmuir + k model was able to accurately match the adsorption data and the AADs of CO\textsubscript{2} and CH\textsubscript{4} were 2.12–3.10% and 0.88–1.11%, respectively. For the Ono–Kondo model, the AADs of CO\textsubscript{2} and CH\textsubscript{4} were 2.70–3.79% and 1.31–3.51%, respectively. Meanwhile, the interaction energy
ε/k between CO₂ and shale in the Ono–Kondo model was 2–3 times larger than that between CH₄ and shale, which revealed that there was a larger affinity between CO₂ and shale than between CH₄ and shale. This may also account for the relatively larger adsorption rate of CO₂. Furthermore, the adsorption behaviors of CO₂ and CH₄ on shale were accurately described by the Langmuir + k model (Figure 7) and the trend of peaking at approximately 4 MPa for CO₂ was replicated by the model. It is notable that a downward trend in the predictive isotherms for CO₂ was not apparent in the Ono–Kondo model.

Figure 7. Comparison of adsorption isotherms between CO₂ and CH₄ at different temperatures.

A relatively good adsorptivity for CO₂ was exhibited when the applied pressure was less than 5 MPa (Figure 7) and this was beneficial to the implementation of CO₂-ESGR. This may be attributable to the linear molecular structure of CO₂ and the fact that the molecular dynamics diameter of CO₂ is 0.33 nm, which is slightly smaller than that of CH₄ (0.38 nm). CH₄ cannot diffuse to the ultramicropores on the surface of shale, whereas CO₂ can. Although the adsorption experiments for CO₂ were only performed at pressures of 1–5 MPa, based on existing experimental data, we deduced that with further increases in pressure, the adsorption capacity of CO₂ would be weaker than that of CH₄. This was because CO₂ would achieve a supercritical state and the density of CO₂ would be much larger than that of CH₄. Under this circumstance, the injected CO₂ would reduce the partial pressure of CH₄ for CO₂-ESGR and the displacement effect would no longer be significant.

5. Conclusions

This work examined the adsorption behaviors of CO₂ and CH₄ on shale from China, and two different thermodynamic models were employed to match the adsorption isotherms.

1. The excess adsorbed amount of CH₄ increased with increasing pressure across the complete range of experimental pressures applied. By contrast, a maximum excess adsorbed amount of CO₂ was observed at approximately 4 MPa.

2. With increasing temperature, the time to reach equilibrium of both CO₂ and CH₄ decreased and, therefore, the adsorption rates rose for both gases. CO₂ exhibited a larger adsorption rate than CH₄. The effective diffusion coefficient $D_e$ of CO₂ ($1.65 \times 10^{-3}$ s⁻¹) was almost 3 times larger
than that of CH$_4$ ($0.56 \times 10^{-3}$ s$^{-1}$) at 40 °C. This may be attributed to the higher affinity between shale and CO$_2$, making it easier for CO$_2$ to diffuse into the micropores on the surface of the shale.

(3) The Langmuir + $k$ model predicted the adsorption data well, and the AADs of CO$_2$ and CH$_4$ were 2.12–3.10% and 0.88–1.11%, respectively. The trend of peaking at approximately 4 MPa for CO$_2$ was accurately modeled. From the Ono–Kondo model, the AADs of CO$_2$ and CH$_4$ were 2.70–3.79% and 1.31–3.51%, respectively. The interaction energy $\epsilon/k$ between CO$_2$ and shale in the Ono–Kondo model was 2–3 times larger than that between CH$_4$ and shale, which is indicative of a stronger affinity between CO$_2$ and shale than between CH$_4$ and shale. This also may account for the relatively larger adsorption rate for CO$_2$.

Relatively good adsorptivity for CO$_2$ was exhibited when the pressure was less than 5 MPa and this is beneficial to the implementation of CO$_2$-ESGR. With continuous increases in pressure, the adsorption capacity for CO$_2$ would be smaller than that for CH$_4$. Under this circumstance, the injected CO$_2$ would reduce the partial pressure of CH$_4$ for CO$_2$-ESGR and the displacement effect would no longer be significant. In addition, the adsorption rate of CO$_2$ was much faster than that of CH$_4$ at all temperatures. CO$_2$ was more active in the competitive adsorption and it was advantageous to the efficiency of CO$_2$-ESGR.

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