



Thermodynamics and Kinetics of CO₂/CH₄ Adsorption on Shale from China: Measurements and Modeling

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Received: 8 January 2019; Accepted: 8 March 2019; Published: 13 March 2019



Abstract: CO₂-enhanced shale gas recovery (CO₂-ESGR) sequestrates anthropogenic CO₂ and improves the profitability of shale gas exploitation. This work investigated the adsorption behaviors of CO₂ and CH₄ on shale from China at 20, 40, 60 and 80 °C. The pressure ranges for CO₂ and CH₄ were 1-5 and 1-15 MPa, respectively. The excess adsorbed amount of CH₄ increased with increasing pressure from the beginning to the end, while the maximum excess CO2 adsorption was observed at approximately 4 MPa. The absolute average deviations (AADs) of CO₂ and CH₄, determined by the Langmuir + k model, were 2.12–3.10% and 0.88–1.11%, respectively. Relatively good adsorptivity for CO₂ was exhibited when the pressure was less than 5 MPa, which was beneficial to the implementation of CO₂-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 CH₄ for CO₂-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 CO₂-ESGR.

Keywords: adsorption; thermodynamic models; CO₂-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]. CO₂-enhanced shale gas recovery (CO₂-ESGR) not only creates the opportunity for sequestrating anthropogenic CO₂, 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 CO₂ and CH₄, 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 CO₂-ESGR, the adsorption capacities of CO₂ and CH₄ play an important role in accessing CH₄ reserves and the maximum amount of CO₂ 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 CH₄ on diverse shales from the Sichuan basin and observed that the adsorption of CH₄ on the surface of the shales was mainly as a monolayer as the temperature rose, while that of CO₂ gradually changed from a multilayer to a monolayer. Weniger et al. [19] conducted adsorption experiments of CO2 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 N₂ 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 1. Compositional analysis of the shale sample.

| Ultimate Analysis (Dry wt % Basis) | | | | Proximate Analysis (wt %) | | |
|------------------------------------|-------|-------|-------|---------------------------|-------|------|
| Ν | С | S | Н | Moisture | Ash | TOC |
| 0.732 | 24.66 | 3.001 | 2.161 | 4.04 | 57.88 | 4.91 |

Both the BET surface area and pore distribution of the shale sample were determined by measuring the N₂ adsorption/desorption isotherms at a temperature of 77 K. Figure 1a displays the N₂ adsorption (solid) and desorption (hollow) isotherms, and the BET surface area of the shale was $60.76 \text{ m}^2/\text{g}$. The pore size distribution of the shale revealed the presence of extensive micropores and mesopores (Figure 1b) which were the key to CO₂ and CH₄ adsorption.



Figure 1. (a) N₂ 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 CO₂ and 1–15 MPa for CH₄, respectively, using a high-pressure volumetric analyzer (HPVAII-200). The HPVAII 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 $\pm 0.04\%$ and $\pm 0.15\%$, 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) HPVA II-200.

The adsorbed amounts of CO₂ and CH₄ 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 (CO₂ or CH₄) experiment was carried out automatically by the HPVA II-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:

$$V_{AFS} = V_{xU} + V_{xL} + V_S, \tag{1}$$

where V_{xU} represents the upper-stem volume, around 3.5 cm³, and V_{xL} and V_s are the lower-stem volume and the adsorption cell volume, respectively.



Figure 3. Three sections of the sample tube.

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:

$$n_D = \frac{P_A V_{LP}}{T_A z_A R} - \frac{P_B V_{LP}}{T_B z_B R},\tag{2}$$

where V_{LP} represents the low pressure manifold volume, 46.7791 cm³.

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

$$V_{SxL} = V_S + V_{xL}.$$
(3)

Knowing the pressure and temperature of the adsorption cell before ($P_{s0} = 0$ and T_{s0}) and after injection (P_{s1} and T_{s1}), allowed for the calculation of V_{SxL} and ultimately V_{AFS} from the following expression:

$$n_D + \frac{P_{s0}V_{xU}}{T_A z_{xU0}R} + \frac{P_{s0}V_{SxL}}{T_{s0} z_{s0}R} = \frac{P_{s1}V_{xU}}{T_B z_{xU1}R} + \frac{P_{s1}V_{SxL}}{T_{s1} z_{s1}R}.$$
(4)

After analysis of the ambient free space, the adsorption cell was heated to the experimental temperature. Once equilibrium had been reached, the new pressure and temperature of the adsorption cell (P_{s2} and T_{s2}) were measured, and the amount of helium injected into the adsorption cell (n_D') at the experimental temperature was calculated in the same way as at room temperature. An extra temperature zone (T_{AM}) was introduced, and a new expression was created to solve V_s and V_{xL} at the experimental temperature, as follows:

$$n_D' + \frac{P_{s0}V_{xU}}{T_A z_{xU0}R} + \frac{P_{s0}V_{xL}}{T_{AM} z_{xL0}R} + \frac{P_{s0}V_S}{T_{s0} z_{s0}R} = \frac{P_{s2}V_{xU}}{T_B z_{xU2}R} + \frac{P_{s2}V_{xL}}{T_{AM} z_{xL2}R} + \frac{P_{s2}V_S}{T_{s2} z_{s2}R}.$$
(5)

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 (CH₄ or CO₂) 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 (CH₄ or CO₂) injected into the adsorption cell (n_{dosed}) was obtained from the following expression:

$$n_{dosed} = \frac{P_1 V_{HP}}{T_1 z_1 R} - \frac{P_2 V_{HP}}{T_2 z_2 R},\tag{6}$$

where V_{HP} is the high pressure manifold volume, 27.0903 cm³.

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

$$n_{Nads} = \frac{P_S}{R} \left(\frac{V_S}{z_S T_S} + \frac{V_{xL}}{z_{xL} T_{AM}} + \frac{V_{xU}}{z_{xU} T_{xU}} \right),$$
(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_{dosed} and n_{Nads} , the excess adsorbed amount of gas (n_{ex}) was calculated using the following equation:

$$n_{ex} = n_{dosed} - n_{Nads}.$$
 (8)

2.4. Adsorption Rate Calculations

 M_t/M_{∞} 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_{∞} was obtained from following expression:

$$y = \frac{M_t}{M_\infty} \approx \frac{P_0 - P_t}{P_0 - P_\infty},\tag{9}$$

where P_0 represents the original pressure after injection, and P_t and P_{∞} represent the pressures at time t and at equilibrium, respectively. Based on Fick's II law, the kinetics of CO₂/CH₄ 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:

$$\frac{M_t}{M_{\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \pi^2 D_e t\right) n = 1, 2, 3 \dots \infty.$$
(10)

When $0.0025 \le y = M_t / M_{\infty} \le 0.8$,

$$f_1(y) = 0.286 \times 8.151^y \times y^{1.453}.$$
(11)

When $0.8 \le y = M_t / M_{\infty} \le 0.9$,

$$f_2(y) = (0.285 - 0.284 \times y) / (1 - 1.927 \times y + 0.927 \times y^2).$$
(12)

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

$$\pi^2 D_e t = f_1(y) = f_2(y). \tag{13}$$

It should be noted that the effective diffusion coefficient (D_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:

$$n_{ex} = n_L \left(1 - \frac{\rho_g}{\rho_a} \right) \frac{\rho_g}{\rho_g + \rho_L} + k \rho_g \left(1 - \frac{\rho_g}{\rho_a} \right), \tag{14}$$

where ρ_g represents the free phase density of the actual gas, which is obtained from PV = zRT. The absorbed phase densities ρ_a for CO₂ and CH₄ were 1.027 and 0.421 g/cm³ 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 ρ_L . The parameters n_L , ρ_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

$$\ln\left[\frac{x_t(1-x_g)}{x_g(1-x_t)}\right] + z_0(x_t - x_g)\frac{\varepsilon_{ii}}{kT} + z_2(x_{t+1} - 2x_t + x_{t-1})\frac{\varepsilon_{ii}}{kT} = 0, t = 2, 3, \dots n.$$
(15)

In this equation, k represents the Boltzmann constant and ε_{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:

$$x_t = \frac{\rho_t}{\rho_a}, x_g = \frac{\rho_g}{\rho_a},\tag{16}$$

where ρ_t represents the adsorbed phase density in layer t and ρ_g represents the bulk phase density.

The absorbed phase densities ρ_a for CO₂ and CH₄ were assumed to be 1.027 and 0.421 g/cm³, respectively [25–29]. In this work, only monolayer adsorption was assumed, for the sake of simplification, and the equation was expressed as

$$\ln\left[\frac{x_1(1-x_g)}{x_g(1-x_1)}\right] + \frac{(7x_1 - 8x_g)\varepsilon_{ii}}{kT} + \frac{\varepsilon_{is}}{kT} = 0,$$
(17)

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

$$n_{ex} = 2C(x_1 - x_g) = 2C(\rho_1 / \rho_a - \rho_g / \rho_a),$$
(18)

where *C* represents a prefactor that correlated with the adsorption capacity and varied with different adsorbents and gases. In this study, the parameters ρ_1 , *C*, and ε_{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_2 and CH_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 cm³) 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 CO₂ and CH₄ adsorption experiments at the same temperature were similar because the free space measurement was completed before the required experimental gas (CO₂ or CH₄) was loaded into the manifold.

Table 2. The adsorption cell volume at experimental temperatures.

| Т (К) | | 293 | 313 | 333 | 353 |
|--------------------------|-----------------|------|------|------|------|
| V_s (cm ³) | CO ₂ | 7.29 | 8.16 | 8.97 | 9.78 |
| | CH ₄ | 7.31 | 8.17 | 8.91 | 9.72 |

A maximum excess adsorbed amount of CO_2 was observed at approximately 4 MPa (Figure 4). A downward trend of excess adsorbed amount of CO_2 at relatively high pressures has also been observed in other studies [32,33]. The relationship can be described using the following correlation:

$$n_{ex} = n_a \left(1 - \rho_g / \rho_a \right), \tag{19}$$

where n_{ex} and n_a represent the excess and absolute adsorbed amounts, respectively. While ρ_a represents the adsorbed phase density, the free phase density is expressed as ρ_g . At the beginning of adsorption, ρ_g was much smaller than ρ_a , and n_{ex} was close to n_a . As, ρ_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 CO₂ molecules. The rapid and large increase in ρ_g may be responsible for the downward trend of n_{ex} . By contrast, the excess adsorbed amount of CH₄ increased with increasing pressure across the entire range of applied pressures. The absence of a maximum in the adsorption isotherm of CH₄ may be attributable to the free phase density, ρ_g , of CH₄, which did not change as much as that of CO₂ with increasing temperature.



Figure 4. The excess adsorbed amounts of CO₂ and CH₄ 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 CO₂ and CH₄ at 1 MPa.

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.

The effective diffusion coefficients (D_e), which reflect the adsorption rate more directly, are listed in Table 3. In this study, D_e of CH₄ at 40 °C was 0.56 × 10⁻³ s⁻¹, and was smaller than that determined in other studies (0.66 × 10⁻³ s⁻¹ at 2 MPa [34] and 0.82 × 10⁻³ s⁻¹ at 3 MPa [35]). This is because

 D_e would increase as the pressure rose. Furthermore, with increasing temperature, the adsorption rates of both CO₂ and CH₄ increased. While D_e of CH₄ at 80 °C was almost 5 times larger than that at 20 °C, D_e of CO₂ was more than 3 times larger than that at 20 °C. In addition, the adsorption rate of CO₂ was much faster than that of CH₄ at all temperatures. Taking 40 °C as an example, D_e of CO₂ (1.65 × 10⁻³ s⁻¹) was almost 3 times larger than that of CH₄ (0.56 × 10⁻³ s⁻¹).

Table 3. The effective diffusion coefficients of CO_2 and CH_4 at 1 MPa.

| $D_e \ (imes 10^{-3} \ { m s}^{-1})$ | 20 °C | 40 °C | 60 °C | 80 °C |
|---------------------------------------|-------|-------|-------|-------|
| CO ₂ | 1.23 | 1.65 | 2.94 | 4.16 |
| CH ₄ | 0.49 | 0.56 | 1.61 | 2.48 |

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

$$AAD\% = \frac{1}{n} \sum_{1}^{n} \left| \frac{n_{ex}_{cal}^{i} - n_{ex}_{exp}^{i}}{n_{ex}_{exp}^{i}} \right| * 100.$$
(20)

Table 4. Parameters and tolerance analysis of the Langmuir + *k* model ^a.

| | Т (К) | п | n_L (mmol·g ⁻¹) | $ ho_L$ (g·cm ⁻³) | k (cm ³ ·g ⁻¹) | AAD |
|-----------------|--------|----|-------------------------------|-------------------------------|---------------------------------------|-------|
| CO ₂ | 293.20 | 9 | 3.0430 | 0.0824 | -5.9953 | 3.10% |
| | 312.79 | 9 | 3.2252 | 0.0959 | -7.5770 | 2.54% |
| | 333.11 | 9 | 5.6648 | 0.1526 | -15.5211 | 2.47% |
| | 353.35 | 9 | 8.9370 | 0.2184 | -21.9797 | 2.12% |
| CH ₄ | 293.13 | 12 | 0.5244 | 0.0149 | 8.6347 | 1.11% |
| | 313.14 | 12 | 0.4471 | 0.0222 | 9.9930 | 1.03% |
| | 333.32 | 12 | 0.3960 | 0.0236 | 10.3226 | 0.88% |
| | 353.33 | 12 | 0.4460 | 0.0266 | 8.5970 | 1.06% |

^a *n*: Number of data points estimated. AAD, absolute average deviation.

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

| | Т (К) | n | $ ho_1$ (g·cm ⁻³) | C (mmol·g ⁻¹) | ε_{is}/k (K) | AAD |
|-----------------|--------|----|-------------------------------|---------------------------|--------------------------|-------|
| CO ₂ | 293.20 | 9 | 0.6867 | 0.9435 | -1066.2 | 3.11% |
| | 312.79 | 9 | 0.6249 | 0.8418 | -1088.7 | 2.70% |
| | 333.10 | 9 | 0.6004 | 0.7022 | -1152.1 | 3.79% |
| | 353.35 | 9 | 0.5330 | 0.7196 | -1121.1 | 3.08% |
| CH ₄ | 293.13 | 12 | 0.2476 | 1.7363 | -483.3 | 3.51% |
| | 313.14 | 12 | 0.1944 | 2.5245 | -363.7 | 2.91% |
| | 333.32 | 12 | 0.1734 | 2.7091 | -351.4 | 2.40% |
| | 353.31 | 12 | 0.1735 | 2.1090 | -420.5 | 1.31% |

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 CO₂ and CH₄ were 2.12–3.10% and 0.88–1.11%, respectively. For the Ono–Kondo model, the AADs of CO₂ and CH₄ were 2.70–3.79% and 1.31–3.51%, respectively. Meanwhile, the interaction energy

 ε_{is}/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 CO_2 and CH_4 on shale from China, and two different thermodynamic models were employed to match the adsorption isotherms.

- (1) The excess adsorbed amount of CH_4 increased with increasing pressure across the complete range of experimental pressures applied. By contrast, a maximum excess adsorbed amount of CO_2 was observed at approximately 4 MPa.
- (2) With increasing temperature, the time to reach equilibrium of both CO_2 and CH_4 decreased and, therefore, the adsorption rates rose for both gases. CO_2 exhibited a larger adsorption rate than CH_4 . The effective diffusion coefficient D_e of CO_2 (1.65 × 10⁻³ s⁻¹) was almost 3 times larger

than that of CH₄ ($0.56 \times 10^{-3} \text{ s}^{-1}$) at 40 °C. This may be attributed to the higher affinity between shale and CO₂, making it easier for CO₂ 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 CO₂ and CH₄ were 2.12–3.10% and 0.88–1.11%, respectively. The trend of peaking at approximately 4 MPa for CO₂ was accurately modeled. From the Ono–Kondo model, the AADs of CO₂ and CH₄ were 2.70–3.79% and 1.31–3.51%, respectively. The interaction energy ε_{is}/k between CO₂ and shale in the Ono–Kondo model was 2–3 times larger than that between CH₄ and shale, which is indicative of a stronger affinity between CO₂ and shale than between CH₄ and shale. This also may account for the relatively larger adsorption rate for CO₂.

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.

Author Contributions: Y.C. conducted the experiments and processed the data. All authors were involved in analyzing the data and writing the paper.

Funding: This research was funded by the National Key Research and Development Program of China (Grant 2016YFB0600804), National Natural Science Foundation of China (Grant 51576031, 51436003, and 51622603) and the Fundamental Research Funds for the Central Universities (Grant DUT18LAB22).

Acknowledgments: The authors appreciate the Qingdao Standard Testing Co., Ltd., which provides the testing report of sample.

Conflicts of Interest: The authors declare no conflict of interest.

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