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A Multi-Scale Modeling of CH₄ and H₂O Adsorption on Coal Molecules and the Water Blocking Effect in Coalbed Methane Extraction

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Abstract: Coalbed methane (CBM) is of great economic value. However, at the same time, CBM is facing a multitude of technological challenges. The water blocking effect (WBE) is one of the physical effects that controls the production of CBM. To alleviate WBE, it is necessary to study its mechanisms at the molecular level. In this study, we used a combined first-principles calculation and molecular simulation approach to investigate the adsorption and diffusion of both methane and water in coal. The results suggest that water does not compete with methane in the adsorption on coal surfaces, yet the presence of water significantly slows down the diffusion of methane within the micropores of coal. This work not only explains the fundamental mechanisms of the WBE but also provides a simulation framework for building strategies to alleviate WBE.

Keywords: coalbed methane (CBM); density functional theory (DFT); adsorption; molecular dynamics; water blocking effect (WBE)

1. Introduction

Coalbed methane (CBM) is one kind of natural gas found in a coal reservoir [1]. A report by Mastalerz et al. shows that, in 2014, the global CBM production reached over 240 billion cubic meters [2]. Despite its large production and considerable economic value, CBM is fundamentally different from the conventional gas, and its production put forward numerous scientific and technical challenges [3,4]. It is generally presumed that gas holding capacity and permeability are two important factors which characterize a CBM reservoir. The former factor determines the gas capacity of the reservoir, while the latter one suggests the easiness of gas extraction [1]. Moreover, CBM is often found with other components, including water and carbon dioxide, in the coal reservoir. Water can also be introduced into the coalbed via hydraulic fracturing during well development processes. Therefore, a study on the adsorption and diffusion behaviors of methane on coal, especially in the presence of water, can generate a better understanding of CBM reservoirs and provide insights on the development of the exploration technologies.

Methane adsorption in the coal matrix has been widely studied at the molecular level by using both first-principles methods [5–10] and molecular simulation techniques [11–16]. These works provide valuable insights into the mechanisms of methane adsorption and diffusion in the coal matrix. However, there are still several topics which are not fully discussed, as follows: 1. The molecular models for coal used in previous first-principles studies are often simplified as graphene or a single carbon sheet, while the effect of other functional groups in coal is neglected. 2. The effect of water, including its

competitive adsorption with methane and its effect on methane diffusion, is not fully covered. However, in engineering practice, it has been found that the water blocking effect (WBE) is one of the major reasons that limit the production rate of CBM wells [17–20]. 3. The effect of microstructures, including micropores, are usually not considered in previous molecular models, although it is generally believed that methane is held within micropores in the CBM reservoirs.

In this study, we aim at bridging these gaps above by performing a combined density-functional theory (DFT) and molecular dynamics (MD) study, with emphasis on the effect of functional groups in coal, the competitive adsorption between water and methane, and the desorption and diffusion of methane with micropores in the presence and absence of water. In Section 3.2.1, insights generated from DFT calculations on the adsorption of methane and water on different sites of coal are presented, and in Section 3.2.2, the diffusion of the CH₄/H₂O system within micropores of coal is analyzed.

2. Materials and Methods

2.1. DFT Calculations

We used plane-wave density functional theory (DFT) to predict the adsorption behaviors of methane and water on the coal surfaces at the molecular level. All calculations were performed using the DMol³ program in the Materials Studio software package. (Version 2017 R2, Dassault Systèmes BIOVIA, San Diego, 5005 Wateridge Vista Drive, CA, USA) [21,22]. The Perdew–Burke–Ernzerhof (PBE) [23] form of the generalized gradient approximation (GGA) was used as the exchange–correlation functional. Grimme’s DFT-D method was adopted to account for the dispersion effect [24]. We also tested other forms of functionals, including revised PBE (RPBE) [25] and Becke–Lee–Yang–Parr (BLYP) [26] forms of GGA functionals, as well as two typical higher-level meta-GGA functionals, namely m11-L [27] and revtpss [28], but found that PBE coupled with DFT-D can closely reproduce the well-established adsorption energy value of methane on the surface of graphene, while keeping the computational cost reasonably low. A detailed comparison between functionals is given in Section 3.1.1. The triple numerical plus polarization (TNP) basis set (version 4.4) was used in all DFT calculations [21]. All other parameters related to the electronic and geometric steps were set to the default values at the fine level provided by the DMol³ program.

Coal is a chemical complex consists of C, O, H, N, and S. It does not have a fixed molecular structure and can be subdivided into different types, including anthracite coals, bituminous coals, subbituminous coals, and lignite coals, depending on the concentration of the C element [29]. In this study, we focused on bituminous coals and selected three classical molecular models, which are shown in Figure 1a–c, to simulate the coalbed. In this paper, these three models in Figure 1a–c are referred to as Given type 1 model (G1) [30], Given type 2 model (G2) [31], and Fuchs–Sandoff (FS) model [32], respectively, according to their original references. We chose these three models because they contain a wide range of structural elements and functional groups, including but not limited to aromatic planes, alkane chains, hydroxyl groups, carbonyl groups, and pyridine. These models can represent different structures of coal molecules. As shown later in Section 3.1, although our calculations were based on these three bituminous coals molecules, the results are general and can be extended to other types of coals.

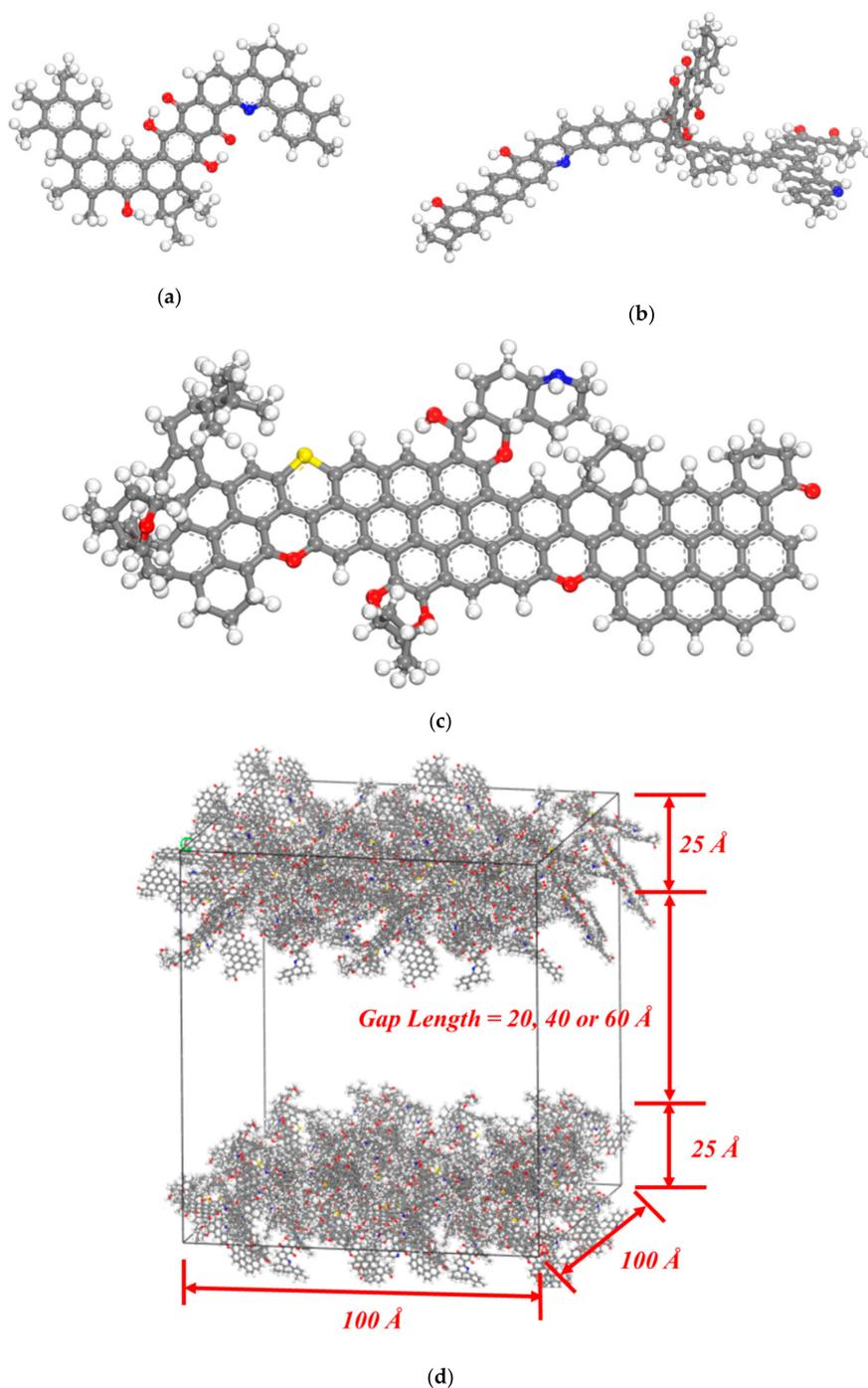


Figure 1. Molecular models for coal used in this study. (a) The Given type 1 (G1) model, (b) the Given type 2 (G2) model, and (c) the Fuchs-Sandoff (FS) model were used in the first-principles density-functional theory (DFT) calculations, while the large-cell model in (d) was used in molecular dynamics (MD) studies.

2.2. Molecular Simulation

Molecular simulation methods were used to study the desorption and diffusion of CH_4 in coalbed. The coalbed model used in this study is shown in Figure 1d, which is a large periodic cell with both length and width being 100 Å. This model was obtained from an amorphous cell construction from 80 G1 molecules, 80 FS molecules, and 8 G2 molecules. The cell contains 16,736 C atoms, 13,712 H atoms, 1200 O atoms, 176 N atoms, 80 S atoms, and, therefore, totally 31,904 atoms. The upper and

lower part of the amorphous cell was separated by 20 Å, 60 Å and 100 Å, respectively, to create a gap which represents micropores in the coalbed where CH₄ and H₂O can be adsorbed.

Methane and water were represented by full atomic models. The COMPASS forcefield was used in this work [33]. Electrostatic interactions were calculated by using forcefield assigned charges. The summation methods for electrostatic and van der Waals interactions were Ewald and atom-based, respectively.

Grand canonical Monte Carlo (GCMC) simulations were used to calculate the adsorption isotherms of CH₄, H₂O and the mixture of CH₄ and H₂O at various pressures in coalbed with different pore sizes. The temperature was fixed at 318.15 K (45 °C) since this is a typical coalbed temperature in coalbed gas extraction processes. For each case, 10⁴ configurations at equilibrium were generated and the configuration with the lowest energy was used as the initial input in a MD simulation.

The MD simulations were performed in the constant-temperature, constant-volume (NVT) ensemble with a Nosé–Hoover thermostat to calculate the diffusivities [34]. The cutoff radius of 15.5 Å and time step of 1 fs were used. During simulations, the coalbed model atoms were kept fixed. The diffusion coefficients were calculated by the mean squared displacement (MSD) based on the Einstein relation given by Equation (1).

$$D = \lim_{t \rightarrow \infty} \frac{1}{6tN} \sum_{k=1}^N |r_k(t) - r_k(0)|^2, \quad (1)$$

where N is the number of CH₄ molecules, and $r_k(t)$ is the position of the C atom of the k -th CH₄ molecule at time t .

3. Results and Discussion

3.1. DFT Calculated CH₄ and H₂O Adsorption on Coal

3.1.1. CH₄ and H₂O Adsorption on Graphene

Graphene, or a single layer of carbon rings, was often used as a simplified model for coal in previous studies [5,9,35]. In this work, CH₄ and H₂O adsorptions on graphene were tested in order to validate our computational methods, as well as to provide a baseline for the binding affinity to CH₄ and H₂O.

The most stable adsorption geometries of CH₄ and H₂O on graphene predicted by the PBE functional with DFT-D dispersion corrections are shown in Figure 2. Table 1 lists the adsorption energies (E_{ads}) calculated by the PBE+DFT-D and other methods, along with the distances between the graphene plane and the CH₄ or H₂O molecules.

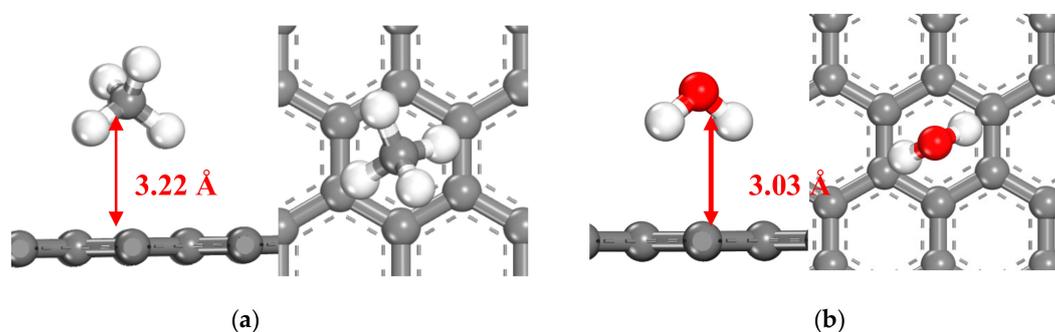


Figure 2. Most stable adsorption geometries of (a) CH₄ and (b) H₂O on graphene.

Table 1. Binding energies and distances of CH₄ and H₂O on the graphene predicted by different DFT functionals and the COMPASS forcefield. For Perdew–Burke–Ernzerhof (PBE) and BLYP functionals, we also tested the effect if no dispersion corrections are considered. Binding energy E_{ads} is defined as $E_{\text{ads}} = E(\text{surface} + \text{adsorbate}) - E(\text{surface}) - E(\text{adsorbate})$. A more negative E_{ads} value means stronger binding. For comparison, values from previous theoretical and experimental studies are also included. RPBE = revised PBE.

Method	CH ₄		H ₂ O	
	E_{ads} (kJ/mol)	Distance (Å)	E_{ads} (kJ/mol)	Distance (Å)
PBE+DFT-D	−24.90	3.22	−31.63	3.03
PBE (no dispersion)	−8.24	3.58	−7.12	3.19
BLYP+DFT-D	−29.24	3.19	−28.26	3.03
BLYP (no dispersion)	−0.63	4.60	−12.54	3.30
RPBE	−4.62	3.96	−6.68	3.64
m11-L	−29.47	2.87	−29.48	3.10
revtpss	−4.59	3.22	−11.37	3.17
COMPASS forcefield	−5.38	3.47	−20.19	3.36
Literature (DFT)	−31.8 [36]	3.36 [36]	−17.4 [37]	3.25 [37]
Experimental	−13.5 [38]	3.03 [38]	−19.0 [39]	-

The binding energy (−24.90 kJ/mol) and distance (3.22 Å) of CH₄ adsorption on graphene predicted by PBE+DFT-D closely match the experimental values of −13.5 kJ/mol and 3.03 Å [38]. They also resemble the values found in previous theoretical calculations; for example, −31.8 kJ/mol and 3.36 Å, as reported by [36]. A similar study based on a smaller carbon model (C₆H₈) predicted the adsorption energy and distance to be −13.3~−13.89 kJ/mol and 3.36~3.39 Å [5].

The results in Table 1 suggest that the dispersion effect is indispensable for the correct prediction of CH₄ and H₂O adsorption since, without dispersion, the interactions between the carbon layer and the small molecules become rather weak so that the equilibrium distances are larger than the experimental value. The results also suggest that PBE+DFT-D can achieve accuracy equivalent to that produced by m11-L, which is a meta-GGA functional and computationally more expensive [27]. Moreover, H₂O adsorption is slightly stronger (−31.63 kJ/mol) than CH₄ adsorption (−24.90 kJ/mol), with both hydrogen atoms facing towards the graphene layer.

As a comparison, we also tested the accuracy of the COMPASS forcefield. For methane adsorption, the COMPASS forcefield predicted value (−5.38 kJ/mol) is slightly weaker than the experimental result (−13.5 kJ/mol) but is qualitatively correct. For H₂O adsorption, COMPASS forcefield generates an adsorption energy (−17.4 kJ/mol) rather close to the experimental value. The results suggest that the accuracy of the COMPASS forcefield is adequate for the molecular simulation calculations performed in this study.

3.1.2. CH₄ and H₂O Adsorption on Coal Molecules

We calculated the adsorption of CH₄ and H₂O on various sites on the three representative coal molecules as described in Section 2. The results suggest that the binding affinity of CH₄ and H₂O to coal is primarily determined by the local chemical environment, i.e., the functional groups, on the coal molecules. Chemical compositions and structures of the portions on the coal molecules which are greater than 5 Å away from the CH₄ or H₂O molecule have little effect on the binding energy. Table 2 enumerates the binding energies of CH₄ versus the functional groups, beside which CH₄ is adsorbed. For each type of adsorption site, several typical adsorption structures are shown, along with their respective adsorption energies. Table 3 gives the same information for H₂O adsorption.

Several observations can be made based on the results in Tables 2 and 3.

1. The most stable adsorption site for CH₄ is above aromatic planes, especially if a CH₄ molecule interacts with more than one aromatic planes, such as the case in row 1 of Table 2. Polycyclic

- aromatic planes, which resemble the graphene plane, have slightly stronger bind affinity with CH₄, than monocyclic aromatic planes.
- The most stable adsorption site for H₂O is N atom sites with H₂O can form strong hydrogen bonds with N. However, considering that the percentage of the N element in coal is rather low, the amount of H₂O molecule that can be attracted in coal by N atoms by hydrogen bonding is limited.
 - Water can form hydrogen bonds with O atoms or be adsorbed on aromatic planes, both of which have similar adsorption energies (around -33 kJ/mol). The adsorption of H₂O on aromatic planes is slightly stronger than CH₄ adsorption, which has E_{ads} values around 20 kJ/mol. However, this difference is not large enough to allow the coal surface to have a strong binding preference with H₂O.
 - The presence of substituents on the aromatic rings, such as hydroxyl, carbonyl, -O-, -N=, and -S-groups, often have little influence (<5 kJ/mol) on the adsorption energies of CH₄ and H₂O.
 - The least favorable adsorption sites for both CH₄ and H₂O are alkane groups and chains. It suggests that the molecular surfaces of anthracite coals, which have high carbon concentrations, should have stronger binding affinity with CH₄ and H₂O than bituminous coals, subbituminous coal, and lignite. This observation is consistent with previous findings that methane binding is stronger on larger aromatic planes [5]. However, this observation does not necessarily suggest that anthracite coals have stronger methane holding capacity, since other morphological factors, including pore sizes and specific surface areas, can also influence the methane sorption behaviors of coals.

Table 2. CH₄ adsorption structures and energies on different types of adsorption sites of coal. For each adsorption structure, the adsorption energy (in kJ/mol) and the name of the coal molecule (the codenames G1, G2, and FS refer to Given type 1, Given type 2, and FS, as shown in Figure 1a–c, respectively).

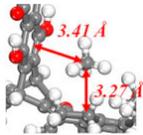
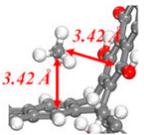
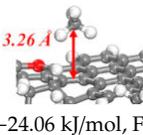
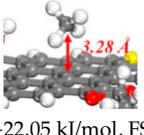
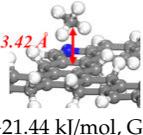
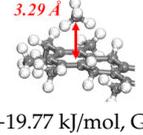
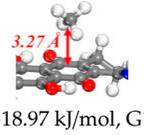
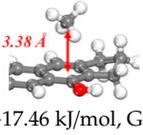
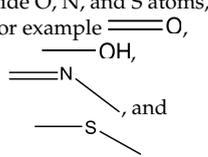
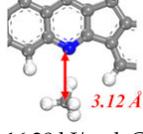
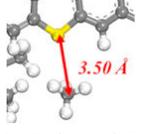
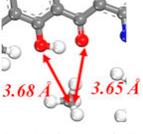
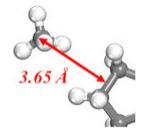
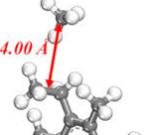
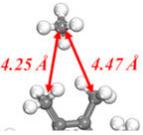
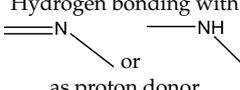
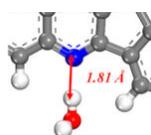
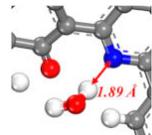
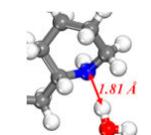
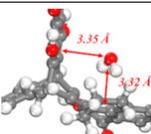
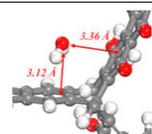
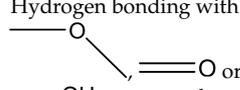
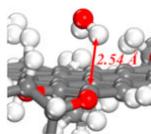
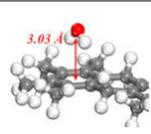
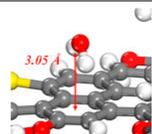
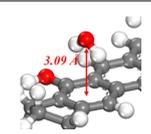
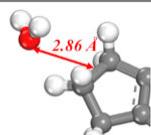
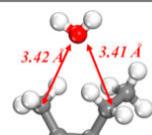
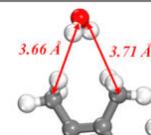
No.	Adsorption Site	Representative Adsorption Structures and Energies		
1	Sandwiched by aromatic planes	 -37.92 kJ/mol, G2	 -27.37 kJ/mol, G2	
2	Above polycyclic aromatic planes such as or	 -24.06 kJ/mol, FS	 -22.05 kJ/mol, FS	 -21.44 kJ/mol, G2
3	Above an aromatic ring with or without substituents	 -19.77 kJ/mol, G1	 -18.97 kJ/mol, G1	 -17.46 kJ/mol, G2
4	Beside O, N, and S atoms, for example  and	 -16.28 kJ/mol, G1	 -14.36 kJ/mol, FS	 -13.26 kJ/mol, G1
5	Beside alkane groups or chains, such as -CH ₃ , -C ₂ H ₅ , -C ₂ H ₄ , ...	 -7.96 kJ/mol, G2	 -7.25 kJ/mol, G1	 -5.90 kJ/mol, G1

Table 3. H₂O adsorption structures and energies on different types of adsorption sites of coal.

No.	Adsorption Site	Representative Adsorption Structures and Energies		
1	Hydrogen bonding with  or as proton donor	 1.81 Å -54.33 kJ/mol, G2	 1.89 Å -48.48 kJ/mol, G1	 1.81 Å -46.06 kJ/mol, FS
2	Sandwiched by aromatic planes	 3.35 Å 3.32 Å -41.30 kJ/mol, G2	 3.36 Å 3.12 Å -33.87 kJ/mol, G2	
3	Hydrogen bonding with  or OH as proton donor or acceptor	 2.54 Å -33.54 kJ/mol, FS	 2.01 Å -33.49 kJ/mol, G2	 2.80 Å 2.08 Å -31.39 kJ/mol, G1
4	Above monocyclic or polycyclic aromatic planes	 3.03 Å -33.49 kJ/mol, G1	 3.05 Å -32.40 kJ/mol, FS	 3.09 Å -29.47 kJ/mol, G2
5	Beside alkane groups or chains such as -CH ₃ , -C ₂ H ₅ , -C ₂ H ₄ -, ...	 2.86 Å -9.38 kJ/mol, G2	 3.42 Å 3.41 Å -9.19 kJ/mol, G1	 3.66 Å 3.71 Å -8.04 kJ/mol, G1

The above observations were made based on the assumptions that an isolated CH₄ or H₂O molecule was adsorbed on the surface. In fact, both CH₄ and H₂O can be present on the surface at the same time. In the next section, we examine the co-adsorption of CH₄ and H₂O.

3.1.3. Co-Adsorption of CH₄ and H₂O on Coal Molecules

As demonstrated in Section 3.1.2, both CH₄ and H₂O prefer aromatic planes over alkane chains. Therefore, CH₄ and H₂O may be adsorbed competitively on the aromatic planes of coal. To quantitatively investigate their intermolecular interactions, we examined the co-adsorption of CH₄ and H₂O and calculated the adsorption energy of CH₄ in the presence of a nearby H₂O and vice versa. The geometries and energies of six co-adsorption structures are shown in Figure 3.

A comparison between Figure 3a,c and row 4 of Table 3 suggest that the presence of a nearby CH₄ has a negligible influence on the adsorption of H₂O, even if the distance between CH₄ and H₂O is as small as 3.43 Å. The same conclusion holds for CH₄ adsorption. As shown in Figure 3d,f and row 2 of Table 2, the adsorption energy of CH₄ above aromatic planes is around 22 kJ/mol, regardless of whether a nearby H₂O molecule is present.

The results in Figure 3 suggest CH₄ and H₂O have rather weak interactions. They will neither enhance nor weaken the adsorption of each other. The results also imply that H₂O does not have the ability to dispel CH₄ from the coal surface if CH₄ is already adsorbed on the surface. Water is usually found in CBM wells. In some cases, water coexists with coal in the well, and the CBM well needs to be dewatered before the extraction. In other instances where the CBM wells are fractured, external water is introduced through the fracturing fluid. This conclusion implies that water does not facilitate the desorption of CH₄ from the coalbed. In Section 3.2, the effect of water on the desorption of CH₄ from the coal surface is further investigated from the MD point of view.

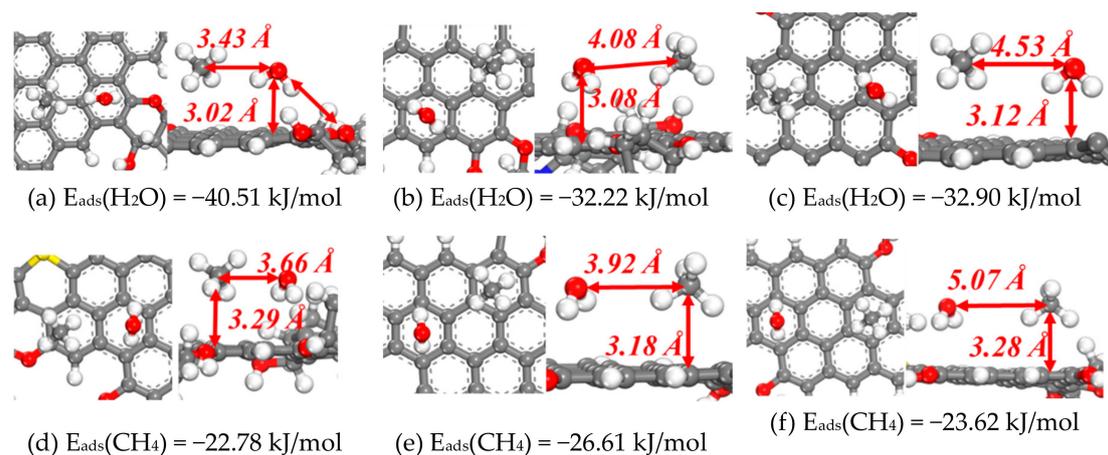


Figure 3. CH_4 and H_2O co-adsorption geometries and energies. Panel (a–c) show different adsorption structures and energies of H_2O with the presence of a CH_4 molecule. Panel (d–f) show the adsorption structures and energies of CH_4 with the presence of an H_2O molecule. For each structure, a top view and a side view are given.

3.2. MD Simulation of CH_4 Desorption and Diffusion in Coalbed

In Section 3.1, we analyzed the adsorption of CH_4 and H_2O on the surface of coal molecules using DFT calculations. However, the results in Section 3.1 are from a static point of view. They provide limited information for the dynamic desorption and diffusion process of CH_4 in a coalbed with the presence of fracturing fluid, which is crucial in coalbed gas extraction processes. In this section, we use MD methods to simulate the desorption and diffusion of CH_4 with and without the presence of H_2O .

3.2.1. Adsorption Isotherms

The adsorption isotherms of CH_4 on coal models with varying pore sizes were tested using the GCMC method. Two sets of calculations were performed. In the first set, the adsorption of pure CH_4 was considered. In the second set, a mixture of CH_4 and H_2O , in which the fugacity of both CH_4 and H_2O are equal to the values marked on the x-axis, was loaded into the cell. Isotherms generated by these two sets of calculations are shown in Figure 4a,b, respectively.

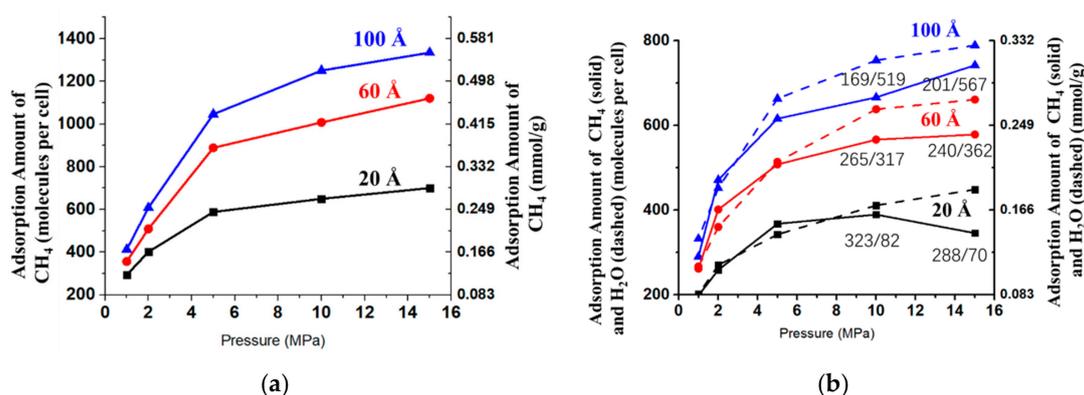


Figure 4. Adsorption isotherms of (a) CH_4 and (b) CH_4 and H_2O in the coalbed model. Blue, red, and black lines refer to the models with 100 Å, 60 Å, and 20 Å pore sizes, respectively. For convenience, the adsorption amounts are measured in units of both the number of molecules per cell and mmol/g (by assuming that the coal has a specific surface area of 50 m^2/g). In (a), CH_4 is the only adsorbate. In (b), both CH_4 (solid lines) and H_2O (dashed lines) with equal fugacity are adsorbed in the cell.

Figure 4a suggests that the adsorption amount increases as the pore size and pressure become larger. However, the adsorption amount of the coalbed structure with 100 Å pore size is much less

than five times of that with the 20 Å pore size. A more careful analysis shows that, under 15 MPa, 300 adsorbed and 1079 free CH₄ molecules are in the 100 Å pore size model, if we consider CH₄ molecules that are within 5 Å of the coal surface to be adsorbed. While in the 60 Å and 20 Å pore size models, the adsorbed/free CH₄ molecules are 392/820 and 498/225, respectively. Therefore, the number of free CH₄ is strictly proportional to the pore size, while at the same time a larger pore size promotes the desorption of CH₄ from the surface when the pressure is kept constant.

When a mixture of CH₄ and H₂O was considered, the adsorption amounts of CH₄ and H₂O as functions of pore sizes and pressures are shown in Figure 4b. As represented by the solid curves, the adsorption amount of CH₄ increases as the pressure becomes higher in the models with 100 Å and 60 Å pore sizes, while in the 20 Å model, the adsorption amount of CH₄ slightly decreases as the pressures changes from 10 MPa to 15 MPa. Therefore, in the small pore size case, increasing the pressure of H₂O contributes to the desorption of CH₄ from the coal surface; however, this strategy does not apply to cases where the pore sizes are large.

3.2.2. Diffusivity of CH₄

MD simulations were performed to investigate the diffusivity of CH₄ both in the presence and absence of water. The diffusion coefficients of CH₄ under different pressures and in models with varying pore sizes are shown in Figure 5.

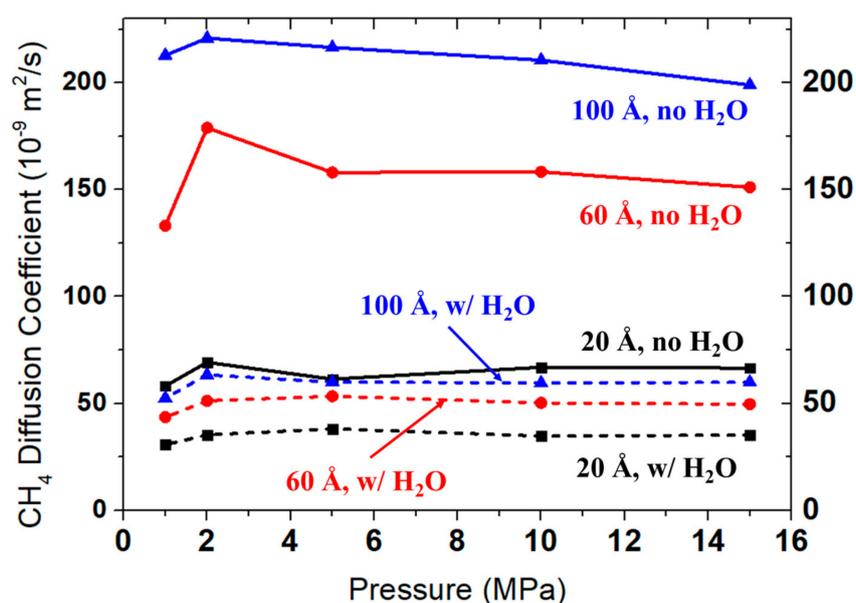


Figure 5. Diffusion coefficients of CH₄ in the coalbed models with varying pore sizes. Solid and dashed lines show the cases where CH₄ alone or a mixture of CH₄ and H₂O is adsorbed in the cell, respectively. Blue, red, and black lines represent the results generated from models with 100 Å, 60 Å, and 20 Å pore sizes, respectively.

The most obvious observation from Figure 5 is that, with H₂O present, the diffusion of CH₄ is significantly impeded. If mixed with H₂O, the diffusion coefficients of CH₄ are reduced to only one fourth to one half compared with the cases when only CH₄ is considered. The reason is that H₂O molecules, which can form a hydrogen-bond network, can partially trap CH₄ molecules to reduce their mobility. This effect, sometimes known as the WBE, can be observed in coalbed extraction processes [38]. Residual fracturing fluid can be present at the entrance of micropores in the coalbed and act like seals to prevent methane from leaving those pores.

The results also suggest that the pressure does not have a strong influence on the diffusivity of CH₄, while the diffusion coefficient of CH₄ is higher in larger pores. In small pores, such as in the 20 Å

case, the rugged surface and small crevices within the pore may trap CH₄ molecules and hinder the movement of CH₄.

4. Conclusions

In this study, we used a combined DFT and molecular simulation approach to study the adsorption and diffusion of methane and water in coal. The results show that the most favorable adsorption sites for methane on coal molecules are aromatic planes. Although water can form hydrogen bonds with O or N atoms in coal, its adsorption energies on aromatic planes, which are the main adsorption sites for methane, are only slightly stronger than that of methane. There is also little mutual influence between water and methane on their separate adsorption energies if they are co-adsorption on the coal surface. These observations suggest water does not compete strongly with methane in the adsorption on coal molecular surfaces. Further MD studies indicate that the WBE on methane diffusion since the diffusivity of methane is significantly reduced when water is present. This study can provide insights into the fundamental reasons behind the WBE. Future works will be focused on the design and verification of strategies that can alleviate the WBE, including the screening of proper surfactants and the removal of water by creating pore negative pressures.

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