Mechanisms for kerogen wettability transition from water-wet to CO\textsubscript{2}-wet: Implications for CO\textsubscript{2} sequestration

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A B S T R A C T

Geological CO\textsubscript{2} sequestration (GCS) is an essential building block of the global strategy to alleviate greenhouse gas emissions and mitigate the climate change. Injecting CO\textsubscript{2} into the shale formations can not only reduce carbon emissions but also enhance oil recovery (EOR). Rock wettability is of great importance to CO\textsubscript{2} storage as it determines the efficiency of structural and residual trapping of CO\textsubscript{2} and plays a crucial role in CO\textsubscript{2}-EOR. In this work, molecular dynamics (MD) simulations are adopted to investigate the CO\textsubscript{2}-H\textsubscript{2}O-kerogen systems under various CO\textsubscript{2} pressures. In a vacuum or under low CO\textsubscript{2} pressures, kerogen surface is weakly water-wet thanks to the hydrogen bonding between H\textsubscript{2}O and kerogen. As CO\textsubscript{2} pressure increases, kerogen wettability shifts from water-wet to CO\textsubscript{2}-wet, because more CO\textsubscript{2} molecules accumulate at the H\textsubscript{2}O-kerogen interface and a distinct CO\textsubscript{2} thin film emerges. Density functional theory (DFT) calculations reveal that the O-containing functional groups preferably adsorb H\textsubscript{2}O molecules over CO\textsubscript{2} through hydrogen bonding, which is responsible for the weakly water-wet tendency at low CO\textsubscript{2} pressures. In contrast, the carbon skeleton of kerogen exhibits a stronger affinity to CO\textsubscript{2}, leading to the formation of CO\textsubscript{2} thin film on the kerogen surface. The CO\textsubscript{2} crowding close to the kerogen surface at high CO\textsubscript{2} pressures gives rise to the CO\textsubscript{2}-wet state. This study provides, for the first time, the fundamental mechanism for the kerogen wettability transition from water-wet to CO\textsubscript{2}-wet. The work also indicates that wettability of the mature kerogen is more likely to be CO\textsubscript{2}-wet during GCS, which is unfavorable for capillary trapping of CO\textsubscript{2}, but is favorable for CO\textsubscript{2}-EOR.

1. Introduction

Since the Industrial Revolution, the atmospheric CO\textsubscript{2} concentration has been climbing, reaching the level of ~420 ppm as of May 2021, which is ~50% above the pre-industrial level found in 1850 [1]. As a notorious greenhouse gas, excess amount of atmospheric CO\textsubscript{2} can cause global warming. Geological carbon sequestration (GCS) is a promising way to alleviate CO\textsubscript{2} emissions and forms one of the essential building blocks to reach the net-zero carbon emission target [2]. Shale formations have been considered as one of the ideal sites for GCS [3,4]. The geological conditions of shale formations are optimal for CO\textsubscript{2} storage [5] and the highly impermeable clay-bearing caprocks can also effectively seal the sequestered CO\textsubscript{2} [6]. Furthermore, as GCS is often associated with a high cost, CO\textsubscript{2} enhanced oil recovery (EOR) in shale formations can greatly reduce the financial burden [2].

There are four main geological CO\textsubscript{2} storage mechanisms: structural trapping, where a caprock acts as a seal barrier preventing CO\textsubscript{2} from migrating to shallower zones [7]; residual or capillary trapping, where CO\textsubscript{2} is immobilized by capillary forces in pores and narrow throat in formation rocks [8]; solubility or dissolution trapping, where CO\textsubscript{2} dissolves in the formation water [9]; mineral trapping, where CO\textsubscript{2} reacts with rocks and formation water, forming carbonate minerals [10]. Among these mechanisms, the structural and residual trapping mechanisms are dependent on rock wettability, in which the CO\textsubscript{2}-H\textsubscript{2}O-rock contact angle plays a crucial role [11]. In the residual trapping, a large amount of free CO\textsubscript{2} gas is trapped by a high capillary force which is strongly dependent on the CO\textsubscript{2}-water-rock contact angle, while a water-wet rock is generally favored [12–15].

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Shale media consist of inorganic and organic matters [16]. The inorganic matters include clay, quartz, and carbonate, and are generally considered hydrophilic [17]. The organic matters mainly consist of kerogen with its content up to 10 wt% [18]. Kerogen contains a considerable number of nano-scale pores with some pore throats size as small as 2 nm or less [19]. Such a narrow pore throat can serve as a prime sealing cap associated with an ultra-high capillary pressure for effective and stable structural and residual trapping. While the conventional wisdom is that kerogen is hydrophobic [20,21], a few recent experimental and simulation studies have shown that kerogen can be weakly water-wet [22–25], which might be attributed to the presence of heteroatoms (O, N, and S) in the kerogen structure [5]. Therefore, understanding about the CO₂-water-kerogen contact angle plays an important role in GCS in shale formations. Besides, the CO₂-water-kerogen contact angle is also closely related to Water alternating gas (WAG) flooding in shale formations [26] for EOR.

The CO₂-water-rock contact angle is dependent on temperature [27–29], pressure [27,30–32], rock type [33], pore structure and connectivity [34–36] and salt concentration [28,37,38], among other factors. Chiquet and coworkers [30] measured CO₂-water-quartz and CO₂-water-mica contact angles under different pressures, and found that as pressure increased from 0 to 11 MPa at 288 K, large increases in the contact angles were observed in the order of 15–25° for quartz and 40–50° for mica. As a result, these two substrates shifted from a water-wet state under a low CO₂ pressure to an intermediate-wet state under a high CO₂ pressure at 288 K. They suggested that the wettability alteration was caused by the pH reduction as well as the increase in CO₂ pressure. Similar phenomena of rock wettability transition were also reported by other experimental studies in the CO₂-water-quartz [31,39] and the CO₂-water-mica [27] systems. Much less attention has been paid to the contact angles of CO₂-water-organic rock systems. Arif et al. [40] measured the contact angles of CO₂-water-coal systems and reported that when the pressure increased from 0.1 MPa to 20 MPa at 323 K, the advancing contact angle increased from 47° to 141° and the receding contact angle increased from 42° to 129°. They explained that the increased contact angle was related to the increased CO₂ adsorption under higher pressure. As for the CO₂-water-kerogen system, Ho et al. [25] reported that the water contact angle on kerogen surface was 42.8° in the absence of CO₂, while the contact angle was 180° when the CO₂ pressure was 200 atm at 300 K, indicating that the kerogen wettability shifted from water-wet to CO₂-wet. They observed that CO₂ formed a thin film on the kerogen surface which might facilitate the wettability change. However, their work focused on CO₂ effects on the water flow in the kerogen nanochannel and paid little attention to the CO₂-induced wettability transition mechanism. While these works reported contact angles in CO₂-water-rock systems over a wide range of pressure, temperature and rock chemistry, there is a lack of direct investigations into the interactions between water and kerogen in the absence/presence of CO₂. Making the underlying mechanisms of kerogen wettability transition remain elusive.

A comprehensive understanding of the wettability in CO₂-water-kerogen systems is needed for geological CO₂ sequestration and CO₂-EOR as kerogen is the main constituent of organic matters in shale. In this work, we study interfacial phenomena and evaluate contact angles in CO₂-water-kerogen systems using molecular dynamics (MD) simulations under typical GCS conditions. The contact angle in the CO₂-H₂O-kerogen system increases until reaching 180° as CO₂ pressure increases. The interfacial configurations, density profiles and hydrogen bond densities are carefully analyzed. Moreover, the effect of kerogen heteroatoms on the CO₂-induced contact angle transition is explained by the first-principle density functional theory (DFT) calculations. The work provides a fundamental understanding about CO₂-H₂O-kerogen interactions and reveals the underlying mechanism of wettability variability from sub-atomic and molecular perspectives.

2. Methodology

2.1. Molecular dynamics simulations

The schematic representation of the CO₂-H₂O-kerogen system is shown in Fig. 1. A typical simulation system consists of a cylindrical water droplet residing on the kerogen surface in a CO₂ environment. The simulation box has the dimensions of 110 × 135 × 172 Å². The simulation domain is tested to be large enough to eliminate any finite size effect. The cylindrical droplet geometry is employed to avoid the line tension effect [41]. The kerogen surface slab is constructed by MD simulations following the procedures reported in our previous works [42–45]. The Type II-D kerogen molecular model proposed by Ungerer et al. [46] is chosen to represent mature kerogens in shale formations. During the simulation, the kerogen structures are modelled using the consistent valence force field (CVFF) [47]. The final size of the kerogen slab is 110 × 135 × 36.5 Å². The density of the simulated kerogen is 1.19 g/cm³, which falls within the range of experimental values of type II kerogen of 1.18–1.35 g/cm³ [48]. Then, a water droplet consisting of 8,000 H₂O molecules is placed on top of the kerogen surface. Fig. S1 in the Supporting Information (SI) shows the initial configuration of the H₂O-kerogen system in the absence/presence of CO₂. The number of CO₂ molecules in the surrounding CO₂ phase ranges from 0 to 23,300 to represent various pressure conditions ranging from 0 to 60 MPa. The CO₂ density far away from the H₂O droplet and kerogen surface is used to dictate the pressure P by comparing to the NIST Chemistry Webbook [49]. Table S1 summarizes the number of H₂O and CO₂ molecules in the simulation systems. For each case, the values of pressure and the uncertainties were the average value and the standard deviation, respectively, calculated from 5 independent estimates obtained by dividing the 5 ns production run into segments of 1 ns.

Throughout the simulations, the kerogen surface is held stationary, while H₂O and CO₂ molecules can move freely. The H₂O molecules are described by the SPC/E model [50], while we use the rigid TraPPE model to represent the CO₂ molecules [51]. The combination of SPC/E-TraPPE force fields has been proven to be very accurate for describing CO₂-H₂O interaction in the temperature range 323.15–478.15 K and pressures up to 100 MPa [52], in comparison with the experimental data [53]. The Lorentz-Berthelot mixing rules [54] are employed to calculate the interactions between unlike atoms. The non-bonded interactions are represented by the pairwise Coulomb potential and Lennard-Jones (LJ) potential. A cutoff radius of 1 nm is used to compute the LJ interactions with the analytical tail corrections [55]. The long-range electrostatic potential is computed using the PPPM integrations [56]. Periodic boundary conditions are applied in both the x- and y-directions. In the z-direction, a virtual wall is placed at the top of the simulation box which is far away from the H₂O droplet and kerogen surface to confine the CO₂ molecules. The fluid-virtual wall interaction is given by [57,58],

\[
w(z) = \left\{ \begin{array}{ll}
\epsilon_g \left[ \frac{2}{15} \left( \frac{\sigma_g}{z} \right)^9 - \left( \frac{\sigma_g}{z} \right)^3 \right], & z < z_{\text{min}} \\
0, & z \geq z_{\text{min}}
\end{array} \right.
\]  

(1)

where z denotes the distance between the fluid molecule and the wall, \( \epsilon_g \) and \( \sigma_g \) are obtained from the Lorentz-Berthelot mixing rules of energy and size parameters of CO₂ molecules, respectively. The potential was cut and shifted at its minimum, to ensure that the virtual wall only exerts repulsive force to CO₂ molecules. A vacuum with the same sizes in x- and y-directions and three times of the length of the simulation box in the z-direction is inserted to avoid the artificial influence from the periodic images in the z-direction [55,59]. The entire simulation box including the vacuum space is shown in Fig. S2.

All MD simulations are carried out using the open-source package LAMMPS [60]. The time step is 1 fs. All systems are initially equilibrated for 10 ns in the NVT ensemble and the temperature is maintained at 330
We use DFT to investigate the interactions among CO₂, H₂O and the surface functional groups on kerogen. Competitive adsorption of H₂O and CO₂ on different functional groups are simulated and the role of the main functional groups in the H₂O-CO₂ co-adsorption is studied. The first-principle DFT with dispersion correction of D3 scheme (DFT-D) calculations is implemented in Vienna ab-initio Simulation Package (VASP) [62,63]. All the geometries for modelling are established in MedeA 3.1 from the Materials Design. The projector augmented-wave (PAW) [64] method and the generalized-gradient-approximation (GGA) [65] exchange-correlation functional in the form of Perdew–Burke–Ernzerhof (PBE) [66] are employed in all the calculations. The electronic wave function is expanded on a plane-wave basis with the energy cutoff of 600 eV to converge the relevant quantities. The Brillouin zone is sampled using a \( \Gamma \times \Gamma \times \Gamma \) Monkhorst-Pack k-point with a density at the H₂O-kergon interface gradually increases and a distinct dew film emerges at 44.40 MPa, which separates the water droplet from the kerogen surface. Within the kerogen matrix, gray, white, red, blue and purple dots represent C, H, O, N and S atoms, respectively. O and H atoms in H₂O molecules are represented by red and white spheres, respectively; CO₂ molecules are represented by green sticks. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 1. Schematic representation of a cylindrical water droplet consisting of 8000 H₂O molecules on the kerogen surface in the presence of the CO₂ phase. Within the kerogen matrix, gray, white, red, blue and purple dots represent C, H, O, N and S atoms, respectively. O and H atoms in H₂O molecules are represented by red and white spheres, respectively; CO₂ molecules are represented by green sticks. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1: Simulation settings in CO₂-H₂O-Kerogen systems.

| P (MPa) | Number of H₂O molecules | Number of CO₂ molecules |
|---------|-------------------------|-------------------------|
| 0       | 8000                    | 0                       |
| 0.65 ± 0.01 | 8000                  | 478                     |
| 4.66 ± 0.04 | 8000                  | 2962                    |
| 8.66 ± 0.03 | 8000                  | 6613                    |
| 11.24 ± 0.04 | 8000                  | 10,699                  |
| 15.95 ± 0.05 | 8000                  | 16,000                  |
| 34.26 ± 0.09 | 8000                  | 20,760                  |
| 44.42 ± 0.08 | 8000                  | 22,000                  |
| 59.36 ± 0.08 | 8000                  | 23,300                  |

K by using the Nosé–Hoover thermostat [61] with a damping constant of 100 fs. The system is considered to reach equilibrium when little fluctuation can be observed in the density distributions. Then, production runs of 5 ns are conducted and the trajectory snapshots are analyzed to obtain the CO₂-H₂O-kerogen contact angle. Further details regarding the contact angle measurement can be found in the SI.

2.2. DFT calculations

The energy defined by the following equation is used to evaluate the total interactions of the adsorbates, with the assumption that the variation of adsorption energies over different adsorption sites is negligible.

\[
E_{\text{tot}} = E_{\text{substrate}} - E_{\text{adsorbate}}
\]

(2)

where \( E_{\text{total}} \) is the total energy of the substrate with the adsorbed gas molecule, \( E_{\text{substrate}} \) denotes the energy of the bare substrate and \( E_{\text{adsorbate}} \) is the energy of the isolated gas molecule. It is widely accepted that the most negative adsorption energy means the most stable configuration.

The energy defined by the following equation is used to evaluate the total interactions of the adsorbates, with the assumption that the variation of adsorption energies over different adsorption sites is negligible.

\[
E_{\text{int}} = E_{\text{tot}} - E_{\text{CO}_2} - E_{\text{H}_2\text{O}}
\]

(3)

where \( E_{\text{int}} \) is the total co-adsorption energy for the whole system, \( E_{\text{CO}_2} \) and \( E_{\text{H}_2\text{O}} \) are the total adsorption energies for CO₂ and H₂O, respectively.

3. Results and discussion

In this section, we first calculate the CO₂-H₂O-kerogen contact angle in the absence or presence of CO₂. The effect of CO₂ pressure on the contact angles is analyzed in detail. Then, the underlying mechanisms of kerogen wettability transition induced by the CO₂ pressure increase are discussed via MD and DFT simulations.

3.1. Contact angles on kerogen surface

Two examples of representative equilibrium snapshots and the corresponding two-dimensional (2-D) density contours of water droplets at 0 MPa and 11.24 MPa and 330 K are plotted in Fig. 2a and b. The 2-D density contours of H₂O and CO₂ under the other pressures are given in Fig. S4. When \( P \leq 4.66 \text{ MPa} \), the water droplet resides on the kerogen surface and two distinct H₂O adsorption layers are observed on the kerogen surface. The formation of H₂O layering structures can be attributed to the hydrogen bonding between H₂O and kerogen hetero-atoms as we will discuss below as well as the entropic effect [68]. As \( P \) increases, the two layers become less prominent and the H₂O density distributions close to the kerogen surface become more uniform. At \( P = 44.40 \text{ MPa} \), the water droplet is completely detached from the kerogen surface.

\[
P \text{ versus } \theta \text{ is plotted in Fig. } 2c. \text{ The kerogen wettability can}
\]
Fig. 2. Water droplet on the kerogen surface at 330 K and at (a) 0 MPa; (b) 11.24 MPa; equilibrium snapshots (left) and 2-D water density contour plots (right). The density is given in the unit of Å⁻². The dashed lines denote the contour profiles of water: \( \rho_w(x, z) = 0.5 \rho_b \). (c) \( \text{CO}_2 \)-\( \text{H}_2\text{O} \)-kerogen contact angle as a function of \( \text{CO}_2 \) pressure.

be classified into five different conditions according to \( \theta \) based on the definitions given in Ref. [7]. \( \theta \) shifts from 60.4° ± 0.2° to 71.0° ± 1.9° when \( P \) increases from 0 MPa to 0.65 MPa. Then, \( \theta \) reaches 137.9° ± 0.8° at 15.95 MPa, after which \( \theta \) continues to increase but with a reduced rate until \( \theta \) reaches 180° at 44.42 MPa. \( \theta \) remains at 180° when further increasing \( P \) to 59.4 MPa. As \( P \) increases, the kerogen wettability shifts from a weakly \( \text{H}_2\text{O} \)-wet state to a strongly \( \text{CO}_2 \)-wet state. Similar trends were observed in \( \text{CO}_2 \)-\( \text{water} \)-quartz systems [69]. Combined with the analysis on \( \text{CO}_2 \) density contour plots (Fig. 5d and f), the effect of \( \text{CO}_2 \) pressure on \( \theta \) can be attributed to the accumulation of \( \text{CO}_2 \) molecules at the \( \text{H}_2\text{O} \)-kerogen interfaces.

3.2. Density distributions

\( \text{H}_2\text{O} \) and \( \text{CO}_2 \) density distributions normal to the kerogen surface as well as the snapshots of the \( \text{CO}_2 \)-\( \text{H}_2\text{O} \)-kerogen systems are displayed in Figs. 3–5. In Fig. 3a, we depict the \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) density profiles along the center of the water droplet at 4.66 MPa. The density profiles are averaged over a 12 Å-wide strip in the center along the \( z \)-direction as illustrated in Fig. 3. The topmost atom of the kerogen slab is defined as the origin in the \( z \)-direction. The uneven kerogen surface is responsible for the non-zero density at \( z < 0 \). Close to the kerogen surface, two prominent \( \text{H}_2\text{O} \) density peaks can be observed at \( z = 0.24 \) nm and \( z = 0.54 \) nm with their values at 1.15 and 1.03 g/cm³, respectively, in line with the layering structures observed in Fig. 2. The \( \text{H}_2\text{O} \) density regresses to its bulk value (0.97 g/cm³) inside the droplet. On the other hand, \( \text{CO}_2 \) density profiles render two distinct peaks: one located at the \( \text{H}_2\text{O} \)-kerogen interface; the other one at the \( \text{H}_2\text{O} \)-\( \text{CO}_2 \) interface. The peak in the vicinity to the kerogen surface indicates the accumulation of \( \text{CO}_2 \) due to the \( \text{CO}_2 \)-kerogen interactions which are largely hydrophobic interactions. In addition, \( \text{CO}_2 \) is dissolved within the \( \text{H}_2\text{O} \) droplet. Away from the \( \text{H}_2\text{O} \) droplet, \( \text{CO}_2 \) density regresses to its bulk value. To better understand the structural properties of the \( \text{CO}_2 \)-\( \text{H}_2\text{O} \)-kerogen system, in Fig. 3b and Fig. 3c, we present the corresponding snapshots showing the entire system and a close-up view of the \( \text{H}_2\text{O} \)-kerogen interface region. They show that a number of \( \text{CO}_2 \) molecules accumulate at the \( \text{H}_2\text{O} \)-kerogen interface.

Fig. 4(a) Mass density profiles of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) averaged over the 12 Å-wide strip normal to the kerogen surface at 15.95 MPa. The snapshot of (b) the entire system; (c) a close-up view of \( \text{H}_2\text{O} \)-kerogen interface region. The color code is the same as Fig. 1.

The thin \( \text{CO}_2 \) film at the \( \text{H}_2\text{O} \)-kerogen interface continues to grow as \( \text{CO}_2 \) pressure reaches 34.26 MPa as shown in Fig. 5a. Comparing to Fig. 4a, the peak value in \( \text{CO}_2 \) density profiles in the vicinity of kerogen surface further increases. As a result, \( \text{H}_2\text{O} \) is depleted from the kerogen surface. The enrichment of \( \text{CO}_2 \) at the \( \text{CO}_2 \)-\( \text{H}_2\text{O} \) interface disappears at high pressures, in line with previous work [70]. As shown in Fig. 5b, the water droplet is almost completely detached from the kerogen surface and a distinct \( \text{CO}_2 \) film can be observed. In contrast to Fig. 3c and Fig. 4c, more \( \text{CO}_2 \) molecules accumulate at the \( \text{H}_2\text{O} \)-kerogen interface.

To reveal the pressure effect on the shape of water droplet, the evolution of droplet contour profiles, defined as the boundary between...
the droplet and the surrounding where the H₂O mass density equals the CO₂ mass density, is depicted in Fig. 6. It is apparent that as the CO₂ pressure increases, the radius of the water droplet decreases. During this process, the kerogen surface turns from H₂O-wet to CO₂-wet. To quantify the relation between the CO₂ pressure and the CO₂ thin film at the H₂O-kerogen interface, the CO₂ film thickness δ is computed. Due to the roughness of the kerogen surface, it is difficult to distinguish the actual δ. Therefore, we define the intersection of the contour profile and the dashed line in Fig. 6 at 0 MPa as the zero reference (δ = 0). The distance from the intersection to δ = 0 is regarded as an indicator of δ. δ as a function of the CO₂ pressure is displayed in the inset of Fig. 6. The CO₂ film thickness first rapidly increases to 0.30 nm at 0.65 MPa, then the increasing rate slightly declines until 15.95 MPa and the CO₂ film thickness eventually reaches a plateau when the CO₂ pressure further increases to 44.42 MPa. Increase in CO₂ film thickness can be attributed to increasing CO₂ adsorption on kerogen surface with increasing CO₂ pressure. The plateau occurs when a complete adsorption layer is formed. As the water droplet leaves the kerogen surface at a higher pressure indicating a completely CO₂-wet state, we only report the film thickness until 44.42 MPa.

Fig. 4. shows the density profiles of H₂O and CO₂ as well as the corresponding snapshots at 15.95 MPa. In Fig. 4a, a sharp peak at z = 0.14 nm is observed in the CO₂ density profile, which highlights the strong accumulation of CO₂ at H₂O-kerogen interfaces, consistent with the finding of Ho et al. [25]. As a result, the H₂O layering structures in the vicinity of kerogen surface become less prominent. This phenomenon can be explained by the snapshots shown in Fig. 4b and c. On the other hand, the enrichment of CO₂ at CO₂-H₂O interface becomes less significant.

Fig. 5. (a) Mass density profiles of H₂O and CO₂ averaged over the 12 Å-wide strip normal to the kerogen surface at 34.26 MPa. The snapshot of (b) the entire system; (c) a close-up view of H₂O-kerogen interface region. The color code is the same as Fig. 1.

Fig. 6. Water droplet contour profiles as a function of CO₂ pressure. Inset: CO₂ film thickness as a function of CO₂ pressure. The dashed line represents the center of the water droplet.
3.3. Hydrogen bond analysis

To further reveal the changes in the water affinity to the kerogen surface with increasing CO\textsubscript{2} pressure, the hydrogen bonds between water and kerogen surface are analyzed. The geometric criterion proposed by Luzar and Chandler [71] is adopted. A hydrogen bond exists if the distance between the donor and acceptor is less than 0.35 nm with the hydrogen-donor–acceptor angle less than 30°. A recent research [72] reported that the strongest interaction between H\textsubscript{2}O and kerogen is contributed by hydrogen bonds in which H\textsubscript{2}O serves as a donor and the heteroatoms (N, O, and S) in kerogen serve as an acceptor. The N atom shows the highest affinity to H\textsubscript{2}O, followed by O and S. In this work, the number of hydrogen bonds between H\textsubscript{2}O and the kerogen heteroatoms is calculated and averaged over the 5-ns production runs. As shown in Fig. 7, it is evident that as CO\textsubscript{2} pressure increases, the total number of hydrogen bonds drops gradually. The results demonstrate that the intrusion of CO\textsubscript{2} into the H\textsubscript{2}O-kerogen interface greatly diminishes the H\textsubscript{2}O-kerogen affinity. In all cases, the O atoms provide the largest fraction of hydrogen bonds (at least 77%), while the S atoms make little contribution. The large hydrogen bond number for O atoms may result from their abundance in kerogen as highlighted in the inset in Fig. 7. The number of O atoms is 2.25 times that of N atoms. The important role of O content in kerogen wettability was also reported by Hu et al. [21]. They found that kerogen wettability may shift from hydrocarbon-wet to water-wet by increasing the number of carbonyl (–C=O) groups on the graphene surface. With the O/C ratio at 20%, the graphene surface with heterogeneously-distributed carbonyl groups is completely water-wet.

3.4. Effect of surface functional groups

H\textsubscript{2}O-CO\textsubscript{2} competitive adsorption on kerogen surface is considered to be the key indicator of kerogen wettability. We conduct DFT calculations to reveal the effect of CO\textsubscript{2} on the adsorption of H\textsubscript{2}O over the key kerogen surface functional groups. The kerogen model predominantly consists of a carbon skeleton doped with H and O atoms, with a small number of N and S atoms. The carbon skeleton constitutes the main structure of kerogen, while the O functional group plays a dominant role in hydrogen bonding between H\textsubscript{2}O and kerogen and their interactions. Herein, graphene and O-doped graphene models are chosen to simulate the representative carbon skeleton and O-containing functional groups on the kerogen surface, respectively. The graphene model is derived from a fully optimized graphite cell and the calculated lattice constants has been validated in Fig. S3. Firstly, we compare the adsorption energy of CO\textsubscript{2} and H\textsubscript{2}O molecules on the graphene surface (carbon skeleton of kerogen). The adsorption energy of H\textsubscript{2}O on the graphene surface is −0.12 eV, which is consistent with the range of −0.07 eV to −0.13 eV found in previous studies [73-77]. The adsorption energy of CO\textsubscript{2} on graphene surface is −0.15 eV, which is lower than that of H\textsubscript{2}O, suggesting that the adsorption of CO\textsubscript{2} on graphene surface is more favorable than H\textsubscript{2}O. Then, we investigate the interaction between H\textsubscript{2}O and graphene surface (carbon skeleton) in the presence of CO\textsubscript{2}. Fig. 8 shows the co-adsorption configurations for H\textsubscript{2}O and CO\textsubscript{2} on the graphene surface, and the interaction energy \(E_{\text{int}}\) as defined in Eq. (3) is listed for each configuration. The \(E_{\text{int}}\) value of one H\textsubscript{2}O molecule on the graphene surface is set at zero as a reference. The \(E_{\text{int}}\) values for co-adsorption of an H\textsubscript{2}O-CO\textsubscript{2} mixture (−0.11 eV) and H\textsubscript{2}O-2CO\textsubscript{2} mixture (−0.24 eV) on the graphene surface are negative, arising from the interactions among CO\textsubscript{2} and H\textsubscript{2}O in both systems. In particular, new hydrogen bonds form between the CO\textsubscript{2} and H\textsubscript{2}O molecules. In addition, the presence of CO\textsubscript{2} molecules shifts the H\textsubscript{2}O molecule away from the graphene surface. The results imply that H\textsubscript{2}O adsorption on the graphene surface is weakened by the presence of CO\textsubscript{2}. Further verification, MD simulations are carried out to obtain the contact angles of water droplets on graphene surface under different CO\textsubscript{2} pressures as shown in Fig. S5. Under the same CO\textsubscript{2} pressure, the contact angle on the graphene surface is larger than that on the kerogen surface. The water droplet is completely detached from the graphene surface at 16.32 MPa, while the same phenomenon occurs at 44.42 MPa for the CO\textsubscript{2}-H\textsubscript{2}O-kerogen system. The results reveal that the aromatic carbon skeleton of kerogen preferably adsorbs CO\textsubscript{2} compared to H\textsubscript{2}O, and CO\textsubscript{2} can form a thin film to deplete H\textsubscript{2}O molecules from the kerogen surface, in line with our MD simulation results in Section 3.2.

As discussed in Section 3.3, the O-containing functional groups provide the largest fraction of hydrogen bonds between H\textsubscript{2}O and kerogen. Herein, the H\textsubscript{2}O-CO\textsubscript{2} competitive adsorption on the O-doped graphene surface is also investigated by DFT simulation to reveal the effect of the O-containing functional groups. According to MD simulations, the epoxy O (Oe) has the highest number of hydrogen bonds among all the O-containing functional groups. The average number of hydrogen bonds per Oe atom is 4.6–5.2 times that of other doped O atoms. Therefore, Oe is chosen to be doped on graphene in the DFT calculation. Firstly, the stable configurations of one H\textsubscript{2}O molecule on the O-doped graphene surface are calculated separately. In the most stable H\textsubscript{2}O adsorption configuration, one hydrogen bond is formed between the H\textsubscript{2}O molecule and the O-doped graphene surface with a Hw-Oe distance of 0.192 nm, in which Hw represents the H atom in H\textsubscript{2}O. Moreover, the adsorption energy of one H\textsubscript{2}O molecule (−0.25 eV) on the O-doped graphene surface is much lower than that of CO\textsubscript{2} molecule (−0.18 eV). Then, the adsorption of H\textsubscript{2}O on the O-doped graphene surface in the presence of CO\textsubscript{2} is calculated to investigate the role of CO\textsubscript{2} on H\textsubscript{2}O adsorption on the O-doped graphene surface. The schematic representations for the H\textsubscript{2}O-CO\textsubscript{2} co-adsorption on the O-doped graphene surface are shown in Fig. 9. In the first scenario, two H\textsubscript{2}O molecules are located near the doped Oe site, leading to the formation of two hydrogen bonds: one is between the two H\textsubscript{2}O molecules; the other is between the H\textsubscript{2}O molecule and the doped Oe on the substrate, as shown in Fig. 9a. To illustrate the CO\textsubscript{2} effect, the adsorption of H\textsubscript{2}O on the O-doped graphene surface is modelled in the presence of CO\textsubscript{2} molecules, as shown in Fig. 9b and c. The original adsorption positions of the two H\textsubscript{2}O molecules in the absence of CO\textsubscript{2} are also displayed in green for comparison. As shown in Fig. 9b, the distance between the H\textsubscript{2}O molecules and the substrate only experiences a slight increase. Besides, a small horizontal displacement towards the doped Oe is observed for the CO\textsubscript{2} molecule. Such a trend is more obvious in Fig. 9c, in which two CO\textsubscript{2} molecules are placed near the H\textsubscript{2}O molecules. The results indicate that the O-containing functional group has a strong interaction with H\textsubscript{2}O, which is hardly affected by CO\textsubscript{2}. The presence of CO\textsubscript{2} can even push the H\textsubscript{2}O molecules closer to the functional group.
While this result is seemingly in a stark contrast to the role of CO$_2$ pressure on CO$_2$-H$_2$O-kerogen contact angle as discussed above, we note that the DFT simulations are conducted at the conditions in which there are a very small number of CO$_2$ molecules. It rather endorses the formation of hydrogen bonding between H$_2$O and kerogen surface, and explains why kerogen still behaves as a weakly water-wet [22–25] or intermediate-wet substrate at a relatively low CO$_2$ pressure as shown in Fig. 2. On the other hand, as CO$_2$ pressure further increases, due to the strong interactions between CO$_2$ and carbon skeleton as shown in Fig. 8, more CO$_2$ molecules accumulate in the vicinity of kerogen surface. The formation and constant-growth of CO$_2$ thin film would influence the formation of hydrogen bonding between H$_2$O and kerogen surface. This phenomenon can be attributed to the correlation effect among CO$_2$, H$_2$O and kerogen which can be fully captured by MD simulations. On the other hand, DFT simulations cannot grasp such effect due to high computational costs. The correlation effect stems from intermolecular interactions and molecular configurations and is important when a large number of fluid molecules gather at the interface [78]. For example, a specific fluid molecule distribution close to the substrate is dependent not only on fluid-surface interactions but also molecular configurations of the surrounding fluid. In other words, in a vacuum or at a low CO$_2$ pressure, the CO$_2$-H$_2$O-kerogen contact angle is mainly determined by H$_2$O-kerogen and H$_2$O-H$_2$O interactions which can be revealed from DFT as well as MD simulations, while it is greatly affected by CO$_2$ crowding driven by the hydrophobic interactions at a high CO$_2$ pressure which can only be captured by MD simulations. For further verification, supplementary MD simulations are carried out to calculate the contact angles of water droplets on graphene and O-doped graphene surface (Oe doped) under different CO$_2$ pressures. The results are provided in Fig. S5. Under the same CO$_2$ pressure, the water contact angle on the graphene surface is larger than that on the O-doped graphene surface, and the H$_2$O droplet is totally detached from the graphene surface at 16.32 MPa, while the same phenomenon occurs at 18.77 MPa for the O-doped graphene system. Besides, as shown in Fig. S5c, the density of the CO$_2$ adsorption layer near the graphene surface is larger than that of the O-doped graphene surface under 8.85 MPa. These results further verify the CO$_2$ pressure effects and reveal that CO$_2$ can potentially form a thin film with increasing pressure and repel H$_2$O molecules from the kerogen surface.

4. Conclusions

In this work, the effect of CO$_2$ pressure on the CO$_2$-H$_2$O-kerogen contact angle is investigated through MD and DFT simulations. The simulation results show that the contact angle increases from $60.4^\circ$ to $180^\circ$ when the CO$_2$ pressure increases from 0 to 44.42 MPa. The presence of CO$_2$ results in a gradual transition in the kerogen wettability from H$_2$O-wet to CO$_2$-wet. At low CO$_2$ pressures, CO$_2$ and H$_2$O co-adsorb at the solid–fluid interface. As CO$_2$ pressure increases, a distinct CO$_2$ film is observed at the H$_2$O-kerogen interface, leading to a sharp decline in the number of hydrogen bonds between H$_2$O and kerogen. The H$_2$O-kerogen interaction is dominated by the hydrogen bonding, while the O-containing functional groups on the kerogen surface contribute the majority of hydrogen bonds. According to the DFT calculations, the presence of CO$_2$ pushes the H$_2$O molecule closer to the Oe group on the O-doped graphene substrate. However, on the graphene surface, CO$_2$ has a lower adsorption energy than H$_2$O, while CO$_2$ can push H$_2$O away from the substrate. Therefore, in a vacuum or at a low CO$_2$ pressure, the CO$_2$-H$_2$O-kerogen contact angle is mainly determined by H$_2$O-kerogen and H$_2$O-H$_2$O interactions, while it is greatly affected by CO$_2$ crowding driven by the hydrophobic interactions at a high CO$_2$ pressure. Our work indicates that the highly-matured kerogen with a relatively low O content is prone to wettability change in the presence of CO$_2$. The CO$_2$-wet state at high pressures is unfavorable for CO$_2$ residual trapping, but is favorable for the water alternating gas process for EOR.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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