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Effects of Sulfate Ions on Crude Oil Adsorption/Desorption on Carbonate Rocks: Experimental and Molecular Simulations

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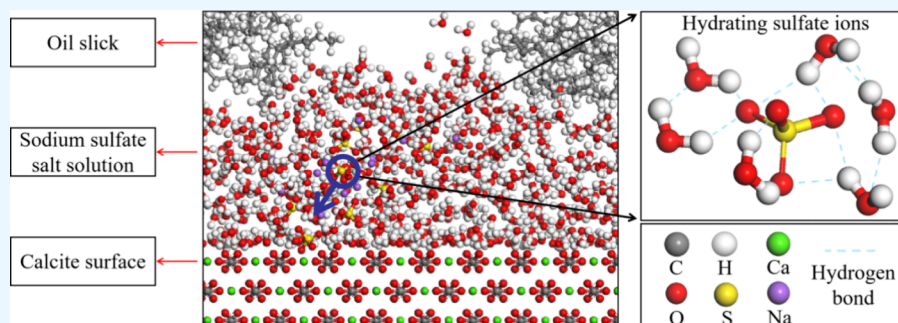
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ABSTRACT: In the background of the strong oil wettability and low production by water flooding in carbonate reservoirs, low-salinity water containing sulfate ions can significantly change the surface wettability of carbonate rocks and thus increase the sweeping area; however, the absorption and desorption mechanisms of the oil film in the carbonate rock surface remain unclear. This paper analyzed the wettability alternation of carbonate rocks' surface in pure water and sodium sulfate solution. At the same time, MD (Materials Studio) software was used to simulate the formation process of the oil film and the effect of sulfate ions on the desorption of the oil film on the surface of carbonate rocks. The experimental results showed that sodium sulfate solution could accelerate the rate from oil-wet to water-wet and the final contact angle (49°) was smaller than that in pure water. The simulation results showed that dodecane molecules moved to the surface of calcite to form a double layer of the oil film and that the oil film near the calcite surface had a high-density stable structure under the van der Waals and electrostatic action. The hydrating sulfate ions above the oil film broke through the double oil film to form a water channel mainly under the action of electrostatic force and a hydrogen bond and then adsorbed on the calcite surface. A large number of water molecules moved down the water channel based on a strong hydrogen bonding force and crowded out the oil molecules on the surface of the calcite, resulting in the oil film detachment. This work aims to explain the interaction of oil molecules, water molecules, and SO_4^{2-} ions at the molecular scale and guide the practical application of low-salinity water flooding in carbonate reservoirs.

1. INTRODUCTION

Carbonate rocks are supersaturated calcium bicarbonate solutions in nature that are precipitated from water. Carbonate reservoirs account for about 60% of the global remaining oil reserves,[1] mainly including limestone and dolomite carbonate rock types,[2,3] among which calcite mineral composition accounts for a relatively high proportion.[4,5] As the heterogeneity of carbonate reservoirs is usually high and the surface has strong oil wetness, the increment of oil production in ordinary water flooding is usually very low,[6] so we consider changing the composition of water flooding and adopting low-salinity solution to displace the remaining oil in the reservoir to increase oil production.

As a new experimental method to enhance oil recovery, low-salinity water flooding has attracted people's attention. By changing the ion type, concentration, and charge quantity of injected water in the rock reservoir, the wettability of the

reservoir can be changed from oil-wet to water-wet and the displacement efficiency of the remaining oil can be improved.[7−9] Ca^{2+} and Mg^{2+} ions in carbonate rocks and Cl^- and SO_4^{2-} ions in low-salinity water are potential-determining ions affecting crude oil displacement.[8] Compared with conventional water flooding, the solution containing sulfate can change the wettability of carbonate rocks and change the wettability to a wetter state.[10] Increasing the concentration of SO_4^{2-} can significantly change the wettability of carbonate reservoirs and significantly improve the oil recovery.[11,12] It can be seen that
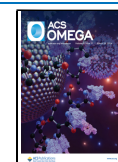
SO_4^{2-} has an impact on the wettability of carbonate reservoirs, but the formation of the oil-wet carbonate surface and the mechanism of SO_4^{2-} salt ion desorption of crude oil have not been clarified.

Currently, the application system of molecular dynamics simulation (MDS) is becoming more and more mature,[13,14] which can characterize the interaction forces between different complex systems on a molecular scale,[15,16] including electrostatic force, Coulomb force, and van der Waals force, and describe the dynamics, energy, relative concentration, and other characteristics of complex systems in detail.[17] Molecular dynamics can be used to simulate the process of oil film adsorption and desorption on the surface of carbonate rocks and explain the mechanism of wettability change on the surface of carbonate rocks from the perspective of the digital model and the molecular scale.

In this paper, carbonate rocks were used as the research object and the treated thin slices were immersed in formation crude oil to form an oil film. The wettability angle of the thin-slice surface in Na_2SO_4 solution and pure water at different times was measured. The amorphous cell (AC) module in the Materials Studio software was used to establish a molecular box consisting of n-dodecane and sodium sulfate, and the MD (Material Dynamic) module was used for MDS. The formation and desorption of the oil film on the carbonate rock surface and the mechanism of wettability alternation were explained. Through the combination of experiment and molecular simulation, the effects of sulfate solution on the surface wettability of carbonate rock were compared from the macroscopic perspective and the mechanism of the wettability change was clarified from the microscopic perspective, which provided a new idea and method for the actual development of the carbonate reservoir.

2. EXPERIMENTS

2.1. Experimental Materials. The carbonate rock core slices used in the experiment were from the Shengli Oilfield. The detailed rock properties obtained by an X-ray diffractometer are shown in Figure 1. The light crude oil with a density of 0.83 g/cm³ and a viscosity of 60 cP at ambient temperature was acquired from a heavy-oil reservoir (15 MPa, 80 °C) in the Shengli Oilfield, Shandong, China. Anhydrous sodium sulfate
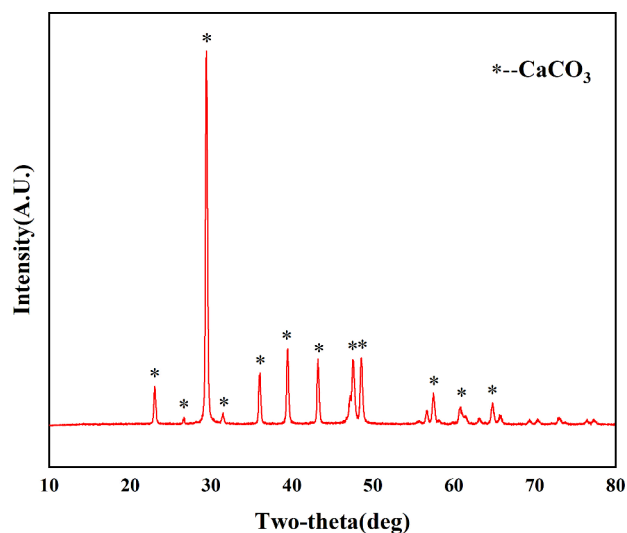

Figure 1. XRD mineral composition analysis diagram.

(AR) and n-heptane (AR) were provided by Sinopharm Chemical Reagent Co., Ltd. The X-ray diffractometer (XRD) was purchased from Dandong Tongda Technology Company. The vacuum-drying oven was produced by Huyue Instrument Equipment Factory. The contact angle measuring instrument was provided by Shanghai Zhongchen Digital Technology Equipment Co., Ltd. Deionized water was also used for this study.

2.2. Main Experimental Steps. *2.2.1. Oil-Wet Surface Formation.*

1. The core sheet was polished with fine sandpaper, washed, and dried with deionized water to ensure that the surface is free of any contaminants.
2. The sheet was dipped in light crude oil and placed in a drying oven at 60 °C.
3. The slices were taken out every other day, washed quickly with n-heptane (C_7H_{16}), and then dried to determine the surface wetting angle of the slices using a contact angle measuring instrument.

2.2.2. Oil-Wet to Water-Wet Process.

1. Typically, low-salinity water flooding has a salinity below 5000 ppm.[18] A 500 ppm sodium sulfate solution was prepared at room temperature, and 0.5 g of chemically pure sodium sulfate (Na_2SO_4) reagent was dissolved in 1 L of pure water.
2. The oil-wet slices were immersed in sodium sulfate solution and pure water respectively for 0, 6, 12, 24, 36, 48, 60, and 72 h. The slices were taken out, and the wetting angles of different solutions and times were measured by a contact angle measuring instrument.

The wettability of the rock can be reflected by the contact angle. Usually, the contact angle formed by the liquid−solid interface is measured and determined geometrically. The conventional wetting angle is classified as water-wet: 0−75°, neutral wetting: 75−105°, oil-wet: 105−180°.[19]

3. MOLECULAR SIMULATION

3.1. Software Simulation and Modules. The Forcite module of the simulation software Materials Studio 2017 was used to calculate the molecular interaction force and energy and analyze the adsorption and desorption process of the oil film on the surface of calcite. The COMPASSII force field of the module was used to set the charge of different ions, and the motion of several single molecules and their condensed state were accurately predicted by the van der Waals force, electrostatic force, and hydrogen bond interaction. The AC module of the simulation software of Materials Studio 2017 adopts the Monte Carlo method to build an amorphous model such as a polymer blending model and a solution model of various components and different proportions.

3.2. Main Simulation Steps. *3.2.1. Oil-Wet Surface Formation.*

1. The (104) face of the calcite cell was cut out and expanded. The formed supercell was used as the basic reaction surface. A 2 nm vacuum layer was added to eliminate the effect of the periodic boundary. The size of the supercell was 24.29 Å × 49.90 Å × 33.70 Å, as shown in Figure 2a.
2. The AC module was used to construct the box containing 25 dodecanes ($C_{12}H_{26}$) oil molecules,[20,21] as shown in Figure 2b. The oil molecule (dodecane) is so weakly polar

(a) Calcite surface (b) Double layer oil film (c) Overall conformation diagram
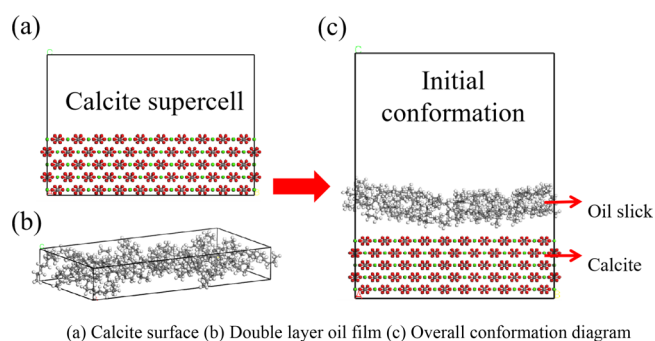
Figure 2. Structure of the oil-wet simulation system on the calcite surface.

that it can be considered a nonpolar molecule, which was placed on the surface of the calcite supercell, and a 3 nm vacuum layer was added, as shown in Figure 2c.

3. Calcite supercells were frozen, and the Geometry Optimization task was used in the Forcite module to perform geometric optimization with the steepest descent. Molecular dynamics relaxation (T = 298.15 K, t = 5 ns) was simulated under the canonical ensemble (NVT) of the dynamic task.

3.2.2. Oil-Wet to Water-Wet Process.

1. An AC module was used to construct the box containing 700 water molecules, 20 Na^+ ions, and 10 SO_4^{2-} ion salt solution, as shown in Figure 3a.
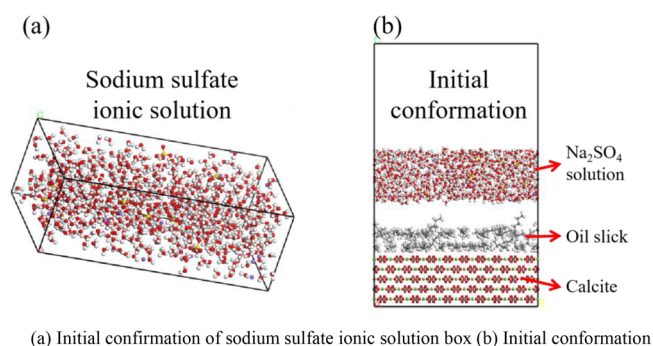

(a) Initial confirmation of sodium sulfate ionic solution box (b) Initial conformation

Figure 3. Initial model of oil film desorption.

2. The salt solution box was placed above the oil film, and a 3 nm vacuum layer was added to eliminate the effect of the periodic boundary, as shown in Figure 3b. To demonstrate the effectiveness of the SO_4^{2-} ion, a pure-water solution box composed of 700 water molecules was compared.

3. The steepest-descent method was used to perform geometric optimization, obtain the optimal structural model, and simulate molecular dynamics relaxation (T = 298.15 K, t = 2 ns) under the canonical ensemble (NVT). The structure diagram of pure water and sodium sulfate solution at the same time was recorded. The overall process of molecular simulation is shown in Figure 4.

4. RESULTS

4.1. Oil Film Adsorption. *4.1.1. Oil Film Adsorption Test.* As shown in Figure 5, the wetting angle of the wafer gradually increased and the growth rate was fast. After the seventh day, the wetting angle increment was small and gradually stabilized. The
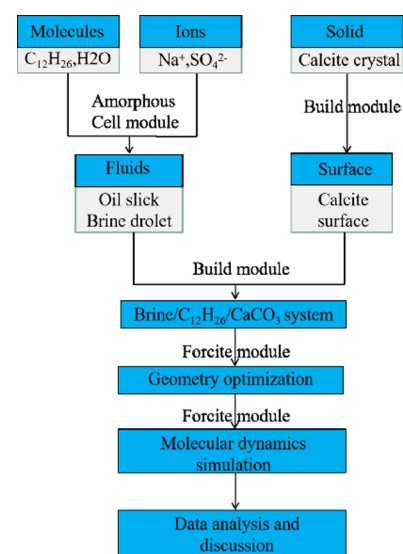

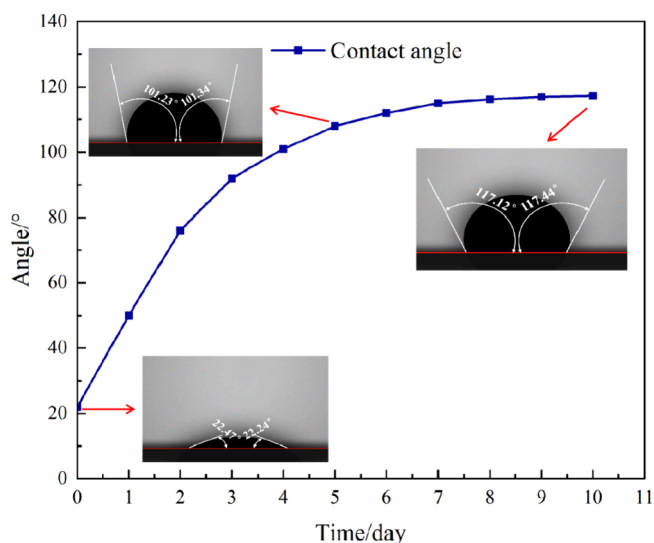**Figure 4.** Molecular simulation flowchart.

Figure 5. Wetting angle over time.

wetting angle changed from the initial 22.36 to 117.28°, indicating that the surface of the wafer became oil-wet.

4.1.2. Molecular Simulation of Oil Film Adsorption. Figure 6a,b shows the movement of dodecane oil molecules to the surface of calcite. It can be seen that dodecane oil molecules gradually approached and finally adsorbed on the surface of calcite over time. The initial irregular dispersion of dodecane oil molecules gradually transformed into an ordered arrangement over time and formed an obvious double-layer arrangement structure, as shown in Figure 6c.

Figure 6d shows the relative concentration distribution curve of oil molecules after the balanced system. The dodecane oil molecules were mainly distributed in the range of 0−1.4 nm from the surface of calcite, and there were two distribution peaks (d1 = 0.30 nm, d2 = 0.73 nm), indicating that the dodecane oil film on the surface of calcite presented a bilayer structure. The relative concentration of oil molecules in the first layer was 12.62, and that in the second layer was 9.84. It can be seen from Figure 8 that the first layer of the double-layer oil film was arranged in a more orderly way and had a more stable structure.
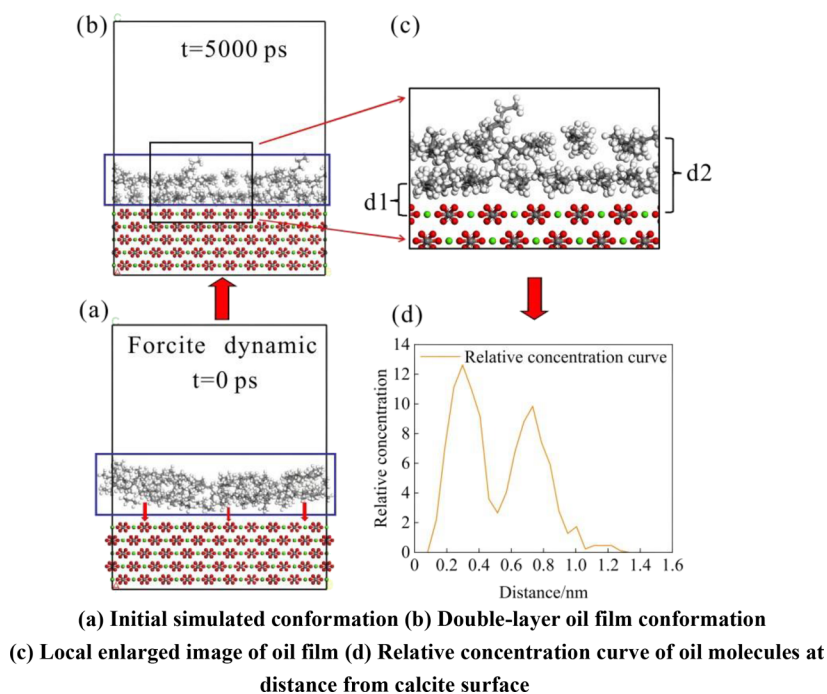
(a) Initial simulated conformation (b) Double-layer oil film conformation
(c) Local enlarged image of oil film (d) Relative concentration curve of oil molecules at distance from calcite surface

Figure 6. Curve of oil film adsorption and relative concentration.
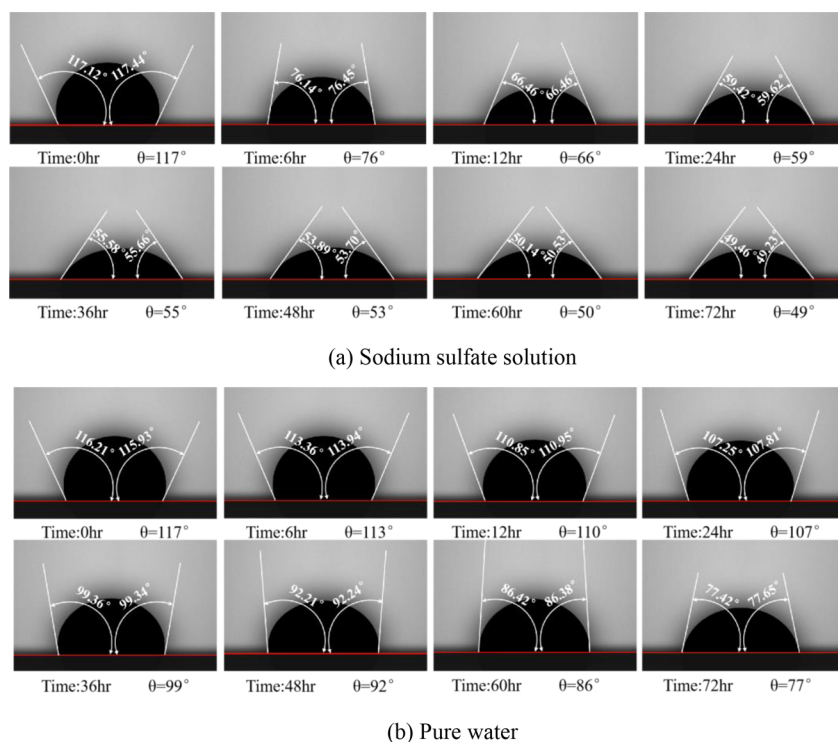

(a) Sodium sulfate solution

(b) Pure water

Figure 7. Changes of the surface wetting angle of carbonate sheet with time in different solutions.

The strong interaction with the calcite surface made the oil-wetting effect more significant.

4.2. Oil Film Desorption. *4.2.1. Wetting Angle Change.* Figure 7 shows the variation of the wetting angle of the carbonate sheet with time in sodium sulfate solution and pure water. Both sodium sulfate solution and pure water reduced the wetting angle of the carbonate sheet surface, and the sheet changed from oil-wet to water-wet. However, in the same period, the wetting angle of the wafer soaked in a sodium sulfate solution changed greatly. Finally, the surface wetting angle of the wafer soaked in sodium sulfate solution was smaller than that of the wafer soaked in pure water ($\theta_{Na2SO4} = 49.35°$, $\theta_{H2O} = 77.45°$). It can be seen that the ions in the sodium sulfate solution play a major role in the surface wettability change of the wafer.

4.2.2. Oil Film Desorption Model. 8 shows the motion path of the sodium sulfate solution and the process of oil film desorption. Hydrating sulfate ions form hydrated sulfate ions
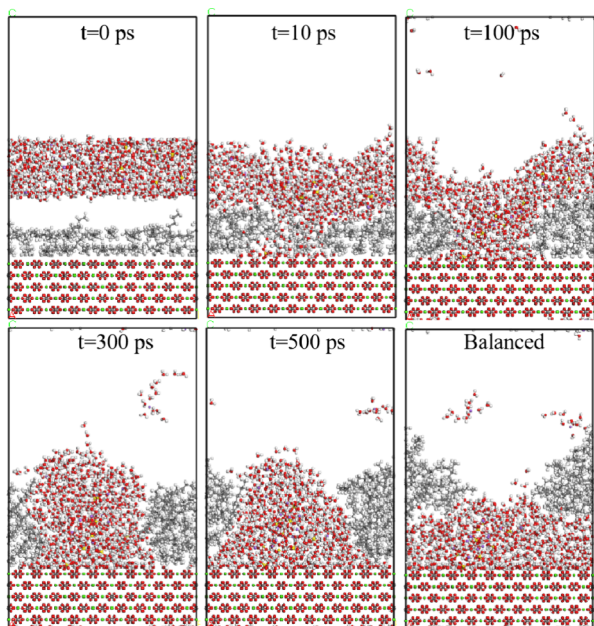
Figure 8. Motion trajectories of molecules in the system.

with six water molecules by hydrogen bonding. Under the action of electrostatic force and van der Waals force, water molecules and hydrated sulfate ions move to the surface of calcite, break through the oil film layer by layer, form water channels, and adsorb on the surface of calcite. Under the action of hydrogen bonding, a large number of water molecules move to the surface of calcite through water channels and accumulate layer by layer. Over time, the water channel widens, and at the same time, the water molecules adsorb and diffuse on the surface, forming a water film that separates the dodecane molecules from the calcite surface. The thickness of the water film increases gradually until the double-layer oil molecules are completely desorbed.

As shown by the relative concentration curve in Figure 9, the relative concentration of water molecules near the calcite surface
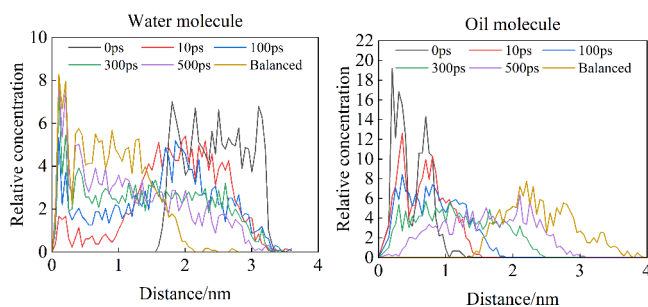

Figure 9. Molecular relative concentration changes with molecular distance from the calcite surface.

increases over time and gradually presents a hierarchical pattern while the relative concentration of oil molecules gradually decreases. When the equilibrium state is reached, the relative concentration of water molecules near the surface reaches the maximum value while the relative concentration of oil molecules is 0, indicating that the oil film has completely separated from the calcite surface and is replaced by water film molecules, which further proves that the wettability of the calcite surface changes from oil-wet to water-wet.

Figure 10 shows that dodecane oil molecules did not completely escape from the surface of calcite in the system
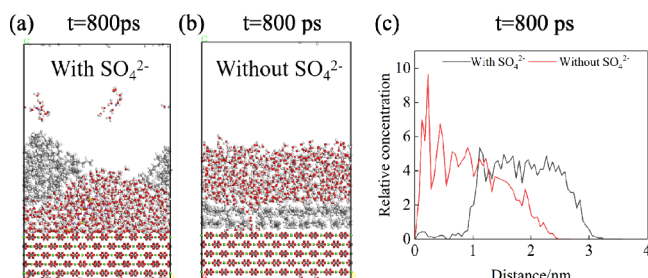

Figure 10. Comparison of instantaneous system conformation and relative concentration.

without sulfate ions while dodecane oil molecules did completely escape from the surface of calcite in the system containing sulfate ions at the same time. By comparison of the system conformation, it is shown that the presence of sulfate ions accelerates the oil film desorption, that is, the change of surface wettability.

5. DISCUSSION

5.1. Formation of Oil Film. In the molecular model constructed in this paper, the charges of the H atom and C atom in an oil molecule are 0.053 and −0.106 e, respectively, and the charge of the Ca atom in calcite is 2 e. On the one hand, due to the strong attraction of positive and negative charges between the Ca atom and the C atom in oil molecules, as well as the attraction between the C atom and H atom in oil molecules, the electrostatic force between atoms keeps the oil molecule close to the surface of calcite.[22−24] On the other hand, the polarity of dodecane oil molecules is very weak. It can be seen that for nonpolar molecules, the van der Waals forces between oil molecules and calcite surface also play a major role in the interaction between oil molecules and calcite surface, as shown in Figure 11. Finally, under the action of electrostatic force and van der Waals force, the oil film spreads on the surface of calcite and presents a double-layer structure.[25−27]
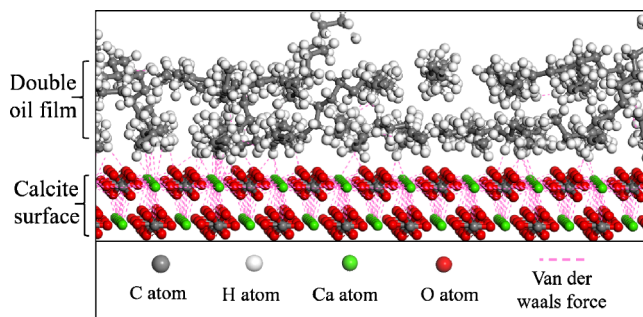

Figure 11. van der Waals force action diagram.

5.2. Desorption of Oil Film. In this paper, the charge quantity of the model is set according to the actual parameters and the surface of calcite is positive. Under the action of hydrogen bonding, as shown in Figure 12, the sulfate ion and six water molecules surrounding it form a hydrated sulfate ion, which is negative.[28,29] There is a strong electrostatic attraction between hydrated sulfate and calcite due to the difference in the electric charge.[30] The charge of the O atom in the water
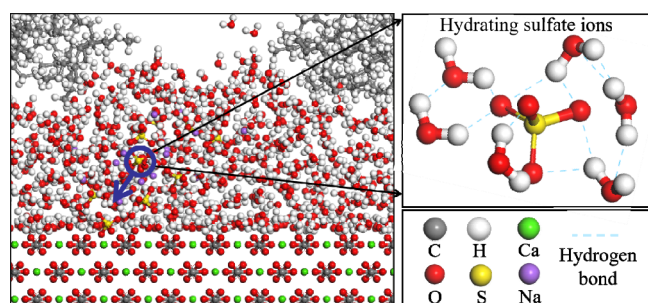
Figure 12. Hydrated sulfate ions and their movements.

molecule is -0.82 e, and the charge of the Ca atom in calcite is 2 e. There is also a certain electrostatic force between water molecules and the calcite surface[24,31,32] and a hydrogen bond force between a large number of water molecules.[33−35] Due to the large charge difference between hydrated sulfate ions and calcite surface, after moving to the calcite surface first, they first contact the second oil film which is loose and far away from the surface and gradually break through and move to the first oil film. After breaking through the first oil film, water molecules and sulfate ions gradually approach the calcite surface and adsorb on the surface under the action of electrostatic force. With the breakthrough of hydrating sulfate ions under the action of hydrogen bonds, a large number of water molecules gradually move to the surface of calcite and gather and the oil film molecules are detached from the surface of calcite to achieve the desorption of the oil film.

6. CONCLUSIONS

Based on experiments and molecular simulation, the formation of oil film on the calcite surface and the mechanism of SO_4^{2-} on the desorption of oil film were studied.

1. When the carbonate rocks were immersed in light oil, the oil film on its surface gradually formed with a wettability angle of $117°$. With the increase of immersing time in Na_2SO_4 solution, the surface of carbonate slices gradually changed from oil-wet to water-wet ($49°$).
2. Under the action of electrostatic force and van der Waals, dodecane molecules gradually approached, adsorbed, and spread on the surface of calcite, resulting in a double-layer oil film.
3. Hydrated sulfate ions broke through the oil film under the action of a strong electrostatic force to form water channels and then adsorbed on the surface of calcite. Under the action of hydrogen bonds, a large number of water molecules accumulated and spread on the surface of calcite along the channel formed by hydrating sulfate ions, crowding out the oil molecules on the surface of calcite and forming oil film desorption.
4. Sulfate ion accelerated the formation of water channels and water film under hydrogen bond and electrostatic force and played an important role in the surface wettability alternation of carbonate rocks.

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Notes
The authors declare no competing financial interest.

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