Displacement Mechanism of Oil in Shale Inorganic Nanopores by Supercritical Carbon Dioxide from Molecular Dynamics Simulations

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ABSTRACT: Supercritical CO2 (scCO2), as an effective displacing agent and clean fracturing fluid, exhibits a great potential in enhanced oil recovery (EOR) from unconventional reservoirs. However, the microscopic translocation behavior of oil in shale inorganic nanopores has not been well understood yet in the scCO2 displacement process. Herein, nonequilibrium molecular dynamics (NEMD) simulations were performed to study adsorption and translocation of scCO2/dodecane in shale inorganic nanopores at different scCO2 injection rates. The injected scCO2 preferentially adsorbs in proximity of the surface and form layering structures due to hydrogen bonds interactions between CO2 and —OH groups. A part of scCO2 molecules in the adsorption layer retain the mobility, due to the cooperation of slippage, Knudsen diffusion, and imbibition of scCO2. The adsorbed dodecane are separated partly from the surface by scCO2, as a result the competitive adsorption between scCO2 and dodecane, and thus enhancing the mobility of oil and improving oil production. In the scCO2 displacement front, interfacial tension (IFT) reduction and dodecane swelling enhance the mobilization of dodecane molecules, which plays the crucial role in the CO2 EOR process. The downstream dodecane, adjacent to the displacement front, is found to aggregate and pack tightly. The analysis of contact angle, meniscus, and interfacial width shows that the small scCO2 injection rate with a large injection volume is favorable for CO2 EOR. The morphology of meniscus changes in the order convex—concave—CO2 entainment with the increase of the injection rate. The microscopic insight provided in this study is helpful to understand and effectively design CO2 exploitation of shale resources.

1. INTRODUCTION

The growing demand for crude oil has inspired the innovative technologies to develop enhanced oil recovery (EOR) methods involving the injection of CO2, N2, hydrocarbon gases, or chemicals into oil reservoirs. Among these EOR methods, CO2 EOR has become increasingly important because CO2 flooding can effectively improve the oil recovery factor (RF) and considerably mitigate greenhouse gas emissions.1 The oil recovery rate can be enhanced by 8–16% of the OOIP through CO2 tertiary processes.2,3 CO2 injection, in contrast to water flooding, is recognized as a promising agent to EOR in shale reservoirs due to favorable properties such as low viscosity and high injectivity.4 Gamadi et al. studied cyclic CO2 injection for improving oil recovery and observed a maximum increase of recovery from 33% to 85%.5 CO2, as the clean fracturing fluid, can create better fractured networks compared to water.6,7

The commonly recognized oil recovery mechanisms include oil viscosity reduction, oil swelling, interfacial tension (IFT) reduction, and light-hydrocarbons extraction.8,9 The CO2 EOR process is quite different for shale reservoirs because CO2 is expected to flow through natural and produced fractures rather than the nonfractured rock matrix. Hawthorne et al. showed that mobilization of light oil components into CO2 is a dominant recovery process rather than dissolution of CO2 into bulk oil.10 Alharthy et al. indicated that molecular diffusion and adective mass migration across the fracture-matrix interface are the main mechanisms for incremental production of oil in shale nanopore.11,12 Tovar et al. reported that the main recovery mechanism is the vaporization of the hydrocarbons into CO2.13 Wang et al. found that the dissolution of CO2 induces an increase in oil/gas relative permeability due to the reduced viscosity of CO2 saturated oil phase.13 However, it is difficult to speculate the exact mechanism based on experiments due to the universal existence of nanopores in shale 2–100 nm.14–17 In nanopores, microstructural, dynamical, and thermophysical behaviors of the confined fluids differ dramatically from their bulk counterparts. The transport properties in nanochannel is significantly affected by the width of channel, system temperature, hydrophobicity/hydrophilicity, and roughness of wall.18–20 The stress anisotropy is also observed in a fluid confined in a nanochannel.21 These behaviors result from the molecular asymmetry between fluid—fluid and fluid—solid interactions displaying inhomogeneous density distributions of the local fluid, which can be demonstrated by molecular simulation techniques.22–24 Thu et al. investigated structural and dynamic properties of pure propane and the relation

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between structure and dynamics of CO₂−C₆H₁₄ mixtures in slit-shaped silica pores using molecular dynamics (MD) simulations. Wu et al. and Yuan et al. investigated displacement of methane with CO₂ in carbon nanochannels from MD simulations. Jin et al. studied methane flow in shale nanopores by nonequilibrium molecular dynamics (NEMD) simulations. Wang et al. investigated octane transport in shale inorganic nanopores from NEMD simulations. The results showed that much progress has been achieved in adsorption and transport of oil or gas in nanopores. However, it remains challenging for adsorption, migration, interfacial and confinement properties of scCO₂/oil during the CO₂ driving oil transport process inside shale nanopores.

In this work, nonequilibrium molecular dynamics (NEMD) simulations were performed to study the microscopic mechanism of scCO₂ displacing oil inside the shale inorganic nanopore. First, we investigate the adsorption and transport of scCO₂ in the nanopore. Then, we examine detachment and translocation of dodecane in the nanopore. In addition, we study the effects of IFT and oil volume swelling on oil migration in the nanopore. Finally, we investigated the effect of injection rate on the transport of scCO₂ and dodecane in the nanopore. Our results would help to understand and design effective CO₂ exploitation of shale resources as well as provide physical insight into CO₂ storage, nanoscale fluid flow, and surface cleaning.

2. MODELS AND METHODOLOGY

To construct MD simulation models, the nanopore with a diameter of 30 Å was created by digging a cylindrical hole in a cristobalite supercell in the size of 42.96 x 42.96 x 153 Å. The nanopore with hydroxylated surfaces of silica was fixed in all simulations. Initially, 90 dodecane molecules represent oil which were placed inside the left end of the nanopore. An equilibrium MD simulation was carried out for 2000 ps to obtain a steady-state distribution of oil in the nanopore (Supporting Information, Figure S1). Then the nanopore was connected with 2197 CO₂ molecules, which randomly distributed in a cuboid system with edge dimension of 42.96 x 42.96 x 106 Å. Periodic boundary conditions (PBC) were applied in three dimensions. A vacuum of 26 Å long was constructed along the z direction to eliminate the boundary effect. The created model is shown in Figure 1.

All MD simulations were performed using LAMMPS software in the NVT ensemble with a time step of 1 fs. The Nosé–Hoover thermostat was employed to control the temperature at 318 K. The nanopore was modeled with the consistent valence force field (CVFF). CO₂ was modeled with the EPM2 model which was successfully demonstrated to reproduce critical point of CO₂ in experiments. The dodecane representing oil was modeled by the CHARMM force field. The cutoff of nonbonded interaction was set to be 9.5 Å. Long-range electrostatic interaction was calculated using the Ewald summation method. The precision of calculation was 0.0001. The nonbond energy was between two atoms i and j was the sum of Lenard-Jones (12) and electrostatic potential energy:

\[
E_{ij} = \frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}} + 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]
\]

where qi and qj were the charges of the atoms i and j, respectively; rij represented the separation between two atoms i and j, and σij and εij represented the LJ potential well depth and the zero-potential distance. The interaction between different types of atoms was determined by the Lorentz–Berthelot rule: σij = (σii + σjj)/2 and εij = (εii εjj)1/2. σ and ε values employed in the interaction calculations are given in Table 1 of the Supporting Information.

NEMD simulations were performed to simulate the process of dodecane displaced by scCO₂ in the nanopore. A rigid graphene sheet was placed at the left side of scCO₂, and moved at rates of 2, 4, 6, 8, and 10 m/s in the z direction, which drove scCO₂ to enter into the nanopore and displace dodecane molecules. Corresponding to the injection rates, the simulations times were 4.0, 2.0, 1.5, 1.0, and 0.8 ns, respectively.

3. RESULTS AND DISCUSSIONS

3.1. Adsorption and Transport of CO₂. To characterize the adsorption of CO₂ in Figure 2A, we report results for the radial number profiles of CO₂ in the nanopore at the injection rate of 2 m/s for 100, 800, 1000, and 1500 ps, respectively. The profile exhibits two well-defined peaks at 14 and 11 Å, indicating the formation of two adsorbed monolayers of CO₂ in the range of 9 Å to the nanopore surface. The ordering construction at 14 and 11 Å is a result of the small dimensions of the nanochannel as described in works of Giannakopoulos and Holland. The time evolution of the profile shows the increase in the CO₂ number in the first layer (14 Å), the second layer (11 Å), and the central area of the pore. This is well understood because the movable graphite plate squeezes more and more CO₂ into the nanopore as time is longer. However, the peaks of two adsorbed layers, especially for the first layer, increase rapidly compared to the central area. The increment in these three regions is evidently observed to follow the sequence the first layer > the second layer > the central area. It indicates that CO₂ molecules preferentially adsorb in proximity of the surface, form layering structures, and subsequently fill the nanopore. It suggests that two typical stages, before and after pore filling, are involved in the adsorption process.

The strong layering of CO₂ molecules in the nanopore, clearly depicted as higher peaks in the corresponding radial profiles, depends on the nature of the solid surface and CO₂. This behavior results from the favorable hydrogen bonds formed by O atoms in CO₂ with H atoms in –OH groups. Moreover, supercritical CO₂ becomes more polar albeit CO₂ is normally nonpolar. This also enhances the electrostatic interaction between CO₂ and the surface, leading to more CO₂ adsorbing on the surface. In this work, a hydrogen bond is defined to exist if the O–O distance is less than 3.5 Å and simultaneously the angle of H–O–O is less than 30°. To
visualize the hydrogen bond, a typical snapshot is described by the inserted Figure 2a. It shows the formation of hydrogen bonds between CO2 and the hydroxylated surface located at different positions. Inserted Figure 2b depicts time evolution of the number of hydrogen bonds. It is evident that the number of hydrogen bonds increases with time, demonstrating the strong interaction between CO2 and the surface responsible for the adsorption of CO2, consistent with the tendency in Figure 2A.

To visualize transport of CO2 molecules, the typical snapshots for CO2 in the nanopore are provided in Figure 2B. It shows that CO2 molecules advance faster along the hydroxylated surface than in the nanopore center. To quantify CO2 migration in the nanopore, the velocity profiles of CO2 in the nanopore as a function of the distance from the solid surface are presented in Figure 2C at 1000 and 2000 ps. Two symmetrical distinct peaks of the velocity profiles occur in the vicinity of the solid surface, showing CO2 molecules move forward faster along the solid surface than in the center of the nanopore. The steric hindrance of dodecane molecules results in that the CO2 velocity in the central area slows down. However, the results also show that the adsorbed CO2 molecules are not immobile but still retain their mobility. Nonzero CO2 velocity on the surface means the slip effect contributing to the flow enhancement of CO2 near the surface. Knudsen diffusion also improves the migration of adsorbed CO2 due to much smaller nanopore size than the mean free path of CO2 molecules. In addition, the hydroxylated surface is CO2-philic due to that CO2 can displace water from the surface with silanol groups. This aids imbibition of CO2 into the hydroxylated nanopore. To investigate the effect of injection rate on adsorption, we present the radial profiles of CO2 molecules in the nanopore at different injection rates with same injection volume, as shown in Figure 2D. Two peaks occur at 14 and 11 Å, indicating two adsorbed layer structures for CO2 molecules and no effect of injection rate on the location of the adsorbed layer. Peak heights of the profiles decrease with the increase in the injection rate, suggesting that CO2 adsorption enhances at low injection rate and weakens at high rate. Because of constant injection volume and cross section area of the nanopore, low injection rate means low CO2 loading per unit time, low injection pressure, and long interaction time between CO2 and the surface. The influence of temperature on the adsorption number of CO2 is investigated as shown in Supporting Information Figure S2. It is found that two adsorbed layers of CO2 on the surface occurring at 14 and 11 Å, but temperature has no evident effect on the location of the adsorbed layer. In addition, the peaks decrease with the increase of temperature. This can be ascribed to the higher mobility of CO2 at high temperature and thus the fewer number of CO2 intend to adsorb on the rock. Similar results have been previously reported by Giannakopoulos et al. Thus, at low injection rate, more CO2 molecules strongly adsorb on the solid surface. While at high injection rate, more CO2 molecules migrate in the central area of the nanopore, reducing the adsorption on the solid surface. To study the effect of the injection rate on the velocity profile, the velocity profiles of CO2 at the rates of 2, 4, and 8 m/s are calculated, respectively, as shown in Figure S3 of Supporting Information. It shows that curvature of parabola decreases with the increase of injection rate. Obviously, with the increase in the injection rate, the velocity of CO2 in the central area of the pore increases rapidly while the velocity of CO2 near the surface decreases especial for the larger injection rate of 8 m/s. The similar results have also been reported by

![Figure 2](image-url)
Duan et al. It indicates that CO₂ molecules preferentially adsorb in proximity of the surface and subsequently fill the nanopore. Therefore, two typical stages, before and after pore filling, are involved in the adsorption process. We can infer that the flow in the central area of the nanopore will be dominant when it reaches saturated adsorption and steady flow state. The results reveal that adsorption of fluids on the surface plays a significant influence on their transport in a nanopore.

3.2. Detachment and Transport of Dodecane. 3.2.1. Detachment of Dodecane. In Figure 3A, we report the radial profiles of molecular number for dodecane in the nanopore at 100, 800, 1000, and 1500 ps, as CO₂ injection rate is 2 m/s. There is a distinct peak at 13 Å corresponding to the adsorbed dodecane layer. The peak of the adsorbed layer decreases with CO₂ injection time, implying parts of adsorbed dodecane molecules are gradually detached from the surface. The detached dodecane molecules transfer to the central area of the nanopore and thus increases the amount of dodecane there, shown by the rising curves of the central area. The results reveal that adsorption of fluids on the surface plays a significant influence on their transport in a nanopore.

![Figure 3. (A) Radial distribution of number density of CO₂ at gas injection rate of 2 m/s at 100, 800, 1000, and 1500 ps; inset shows the interaction energy between CO₂ and the surface (black line), and that between dodecane and the surface (red line). (B) Snapshots of the process of CO₂ detach dodecane in the nanopore at 1, 30, 50, and 150 ps. (C) Snapshots of CO₂ displacing dodecane at gas injection rate 2m/s at (a) 1, (b) 200, (c) 500, and (d) 5000 ps. (D) Density distribution of dodecane molecules (a) in the miscible zone and (b) in the oil zone at 1, 500, and 1000 ps at the injection rate of 2 m/s.](image)

The dodecane detachment is highly linked to the adsorption of CO₂ on the surface. Comparing Figure 3A with Figure 2A, we observe the dodecane peak is always farther from the surface than the peak of the first adsorption layer of CO₂, also indicating preferential CO₂ adsorption on the surface. Then, the average adsorption strength of CO₂ to the hydroxylated surface plays a crucial role in dodecane detachment or dodecane transport process. To evaluate the average adsorption strength of CO₂ molecules, we calculate the interaction energy between CO₂ molecules and the nanopore surface from eq 2.49

\[
E_{\text{CO}_2/\text{rock}} = \frac{E_{\text{total}} - (E_{\text{CO}_2} + E_{\text{rock}})}{N_{\text{CO}_2}}
\]

where \(E_{\text{CO}_2/\text{rock}}\) is the interaction energy between CO₂ molecules and the surface, \(N_{\text{CO}_2}\) is the number of CO₂ molecules, \(E_{\text{CO}_2}\) and \(E_{\text{rock}}\) represent the energy of CO₂ and the rock surface, and \(E_{\text{total}}\) denotes the total energy of the system containing CO₂. Similarly, we can calculate the interaction energy between dodecane and the surface to characterize the average adsorption strength of dodecane molecules. The inset in Figure 3B depicts the variation of the interaction energy of surface-CO₂ and that of surface-dodecane. It can be found that the interaction energy between CO₂ and surface increases with CO₂ injection time, in agreement with the trend of increasing hydrogen bonds in inserted Figure 2B. It indicates the enhancement of CO₂ adsorption on the surface. However, the interaction energy between dodecane and surface reduces, meaning the extent of dodecane adsorption on the surface decreases. After 2300 ps, the interaction energy between
CO\(_2\) and the surface is larger than that between dodecane and the surface. It suggests that the capability of CO\(_2\) to adsorb on the surface is stronger than dodecane. It is a favorable effect on the dodecane detachment.

3.2.2. Transport of Dodecane. From the above analysis of dodecane detachment, we conclude that one of the transport mechanisms for oil in shale is that adsorbed dodecane molecules are detached partly from the surface and migrate into the central area of the nanopore. To further visualize transport of dodecane molecules inside the nanopore, several typical snapshots for the process of CO\(_2\) displacing oil at injection rate of 2 m/s are presented in Figure 3C. It shows that dodecane molecules move to the right of the nanopore and are gradually expelled from the nanopore.

When the movable graphite plate moves to the right, it compresses CO\(_2\) to generate a driving force inducing the transport of oil droplet inside the nanopore. With the CO\(_2\) molecules filling the nanopore and occupying the cavity space, the equilibrium of dodecane breaks. The interactions between CO\(_2\) and the solid surface, and between CO\(_2\) and dodecane dominate the structure and the transport of dodecane within the nanopore. The structural variation of oil droplet is also observed in Figure 3(C), showing two distinct zones. One is formed in the displacement front, where CO\(_2\) is miscible with dodecane. The other is the downstream oil zone adjacent to the displacement front. To evaluate the structure of oil droplet, the axial density distribution of dodecane molecules is plotted in Figure 3(D). It shows that the density peak positions shift to the right of the z axis, indicating movement of the oil droplet toward the right side of the nanopore. For the part of oil droplet in the downstream oil zone, the density distribution shows an increasing span of the curve and a decreasing peak. It indicates the oil volume swelling and the interfacial variation, which have a significant influence on oil recovery (we will discuss it in section 3.3). For the part of oil droplet in the downstream oil zone, the density distribution shows a constant span of the curve and an increasing peak. It indicates that dodecane molecules adjacent to the displacement front aggregate and pack tightly, resulting in the formation of an oil column. This is mainly caused by the attractive interaction among dodecane molecules, and the driving force resulting from the oil swelling in the miscible zone and CO\(_2\) flooding. Therefore, the dodecane molecules adjacent to the displacement front migrate forward in the form of an oil column within the nanopore, which is beneficial to the displacement of the oil droplet. In addition, the RDF between C atoms in different dodecane molecules in the downstream oil zone, reported in Figure S4 in the Supporting Information, exhibits the increasing peak and area below the curve with time. The result indicates the higher coordinate number (dodecane) around a dodecane molecule and thus the tighter distribution for dodecane molecules.

3.2.3. Effect of Injection Rate on Detachment and Transport of Dodecane. To quantitatively describe the effect of injection rate on detachment and transport of dodecane, we...
calculate the radial number density, the axial number density and the transport distance of center of mass (COM) for an oil droplet at different injection rates, as shown in Figure 4A–C, respectively.

Figure 4A shows that a distinct peak always occurs at 13 Å for the injection rate of 4, 6, 8, or 10 m/s, which lowers with the decrease in the injection rate. At the injection rate of 2 m/s, no distinct peak occurs in the vicinity of the surface. The results show that small injection rate is of benefit to the detachment of dodecane molecules adsorbed on the surface, while high injection rate is adverse to separate dodecane molecules from the surface. It implies that more residual oil molecules will remain in the nanopore at the higher injection rate, resulting in the loss of oil during the exploiting process. Combining Figure 4A with Figure 2D, we may expect that entrainment or breakthrough of CO₂ will occur at the higher injection rate. In this case, the CO₂ bubble moves steadily and leaves behind a thin oil film close to the surface. The thickening residual oil film in the presence of mass transfer leads to a loss in the oil recovery.

Figure 4B shows that the peak of the axial number density decreases and the span of the curve increases when decreasing the injection rate from 10 to 2 m/s. It indicates looser packing and wider distribution region for dodecane molecules within the nanopore at smaller injection rate. The peak position shifts to the right of the z axis, implying that the displacement distance of the oil droplet increases with the decrease in the injection rate. The results demonstrate that smaller injection rate is preferable to oil displacement in CO₂ flooding, which is also confirmed by Figure 4C. The figure shows the biggest displacement of COM of oil droplet at the injection rate of 2 m/s as CO₂ injection volume is constant. Therefore, a small injection rate with a large gas volume is favorable to CO₂ EOR.

3.3. Interfacial Behavior of CO₂ and Dodecane.

3.3.1. Interface between CO₂ and Dodecane. The interfacial behavior, playing an important role in studying two-phase flow, dominates the efficiency of CO₂ EOR lying on the achievement of the miscibility front between CO₂ and oil. Figure 5A shows the formation of the miscible zone as well as the variation of its width as a function of time. The formation of the miscible zone consists of three processes: (1) detached dodecane molecules migrate into CO₂; (2) bulk dodecane molecules dissolve in CO₂; and (3) CO₂ penetrate into bulk dodecane. The processes (1) and (2) indicate the translocation of dodecane molecules in the direction opposite to the flow direction, compressing the domain through which CO₂ molecules permeate into dodecane at the displacement front. This lowers the penetration of CO₂ into dodecane, imparting stability to a displacement process in oil recovery. Thus, mobilization of dodecane molecules into CO₂ has a crucial effect on this zone or interface rather than dissolution of CO₂ into bulk dodecane.

We calculate the width of the interfacial region to examine the variation of the interface between CO₂ and dodecane during CO₂ flooding process, as shown in Figure 5(A). The interfacial region is established by the “10–90” interfacial width characterized by the distance L between two surfaces at the 10% and 90% of the dodecane density along the z axis. It is shown that the interfacial widths at 100 and 800 ps for the injection rate of 2 m/s are L₁ = 20 Å and L₂ = 50 Å, respectively. The obvious increase in the interfacial width means the extension of the coexistent region of CO₂ and dodecane, leading to the reduction in IFT. The lower IFT improves the transport of dodecane molecules, which is favorable for EOR. We also calculate the receding contact angle of oil droplet to examine the morphology of the interfacial meniscus, reported in Figure 5B. The contact angle θ is calculated by eq 3.

\[
\theta = \tan^{-1}\left(\frac{r^2 - h^2}{2rh}\right)
\]

where r is the radius of the nanopore and h is the height of the meniscus, as shown in Figure 5B. The contact angle is plotted in Figure 5B, showing a nearly constant value of 175° due to the hydroxylated surface is oleophobic.

3.3.2. Oil Swelling. When CO₂ is injected into oil-bearing reservoirs, interactions between CO₂ and oil will induce favorable effects on the oil recovery, such as oil volume
swelling, oil viscosity decrease and miscible CO₂-oil. To investigate oil volume swelling stimulated by CO₂, several snapshots are reported in Figure 6A, showing the variation of dodecane volume at an injection rate of 2 m/s. It is observed that three processes contribute to the oil volume expansion, including that (1) adsorbed dodecane molecules are separated from the surface migrating into the displacement front; (2) upstream dodecane molecules adjacent to the interface disturbed by CO₂ disentangle and dissolve into CO₂, offering available space for CO₂ diffusion and thus enhancing their miscibility; and (3) adsorbed dodecane molecules in the downstream front are detached from the surface and subsequently move to the central area of the nanopore, providing available space for the back dodecane molecules. Volume swelling offers an additional driving to expel the downstream oil toward the right of the nanopore. On the other hand, it reduces oil viscosity and thus improves oil mobility. To characterize the enhanced mobility, we calculate the self-diffusion coefficients of dodecane at different time using the mean-squared displacement approach based on the Einstein relation,54 reported in Figure 6B. The result shows that the self-diffusion coefficient increases as the time, indicating the increased mobility of dodecane, as expected.

The volume swelling embodies oil molecule disentanglement and loose distribution in the presence of CO₂, which can be described by the radial distribution function (RDF). Figure 6C,D depict the RDFs between C atoms in different dodecane molecules and that between CO₂ and dodecane, respectively. Figure 6C shows that the peak of RDF and the area below the curve decrease with time. It suggests the decrease in the coordinate number (dodecane) around one dodecane molecule or the loose distribution of dodecane molecules. Opposite tendency is observed in Figure 6D, showing that the coordinate number (CO₂) around one dodecane molecule increases with time. The results imply that more and more CO₂ accumulate around dodecane molecules, resulting in the larger average separation between dodecane molecules. The larger separation among dodecane molecules indicates a reduced oil viscosity and enhanced oil mobility.

3.3.3. Effect of Injection Rate on the Interface between CO₂ and Dodecane. To study the influence of injection rate on the interface between CO₂ and dodecane, we first calculate the receding contact angle of oil droplet at different injection rates, reported in Figure 7A. The corresponding snapshots describing the meniscus morphology are presented in Figure 7B. In order to investigate whether the vacuum area in the right-hand side of the simulation model would influence the morphology of the meniscus or not, we have made a complement to the initial model. The results show that the vacuum space has little or no influence on the morphology of the meniscus when there is enough amount of oil in the nanopore (Supporting Information Figure S5). Figure 7A shows that the contact angle is always larger than 150° due to hydrophilicity of the hydroxylated surface; it is independent of time at constant injection rate; it decreases with the increasing rate due to the weakening adsorption and migration of CO₂ along the surface as the injection rate increases. Figure 7B shows that a high injection rate attenuates the convex extent of interfacial meniscus. The results imply a tendency for the morphology of the meniscus that it would alter in the order convex→concave→CO₂ entrainment when the injection rate gradually increases (Supporting Information, Figure S6).
Then we calculate the interfacial width at the rate of 2 and 8 m/s with same injection volume, plotted in Figure 7C. It shows the effect of injection rate on IFT. The interfacial widths at 2 and 8 m/s are equal to $L_1 = 50$ Å and $L_2 = 25$ Å, respectively. $L_1$ is wider than $L_2$, indicating the lower IFT for $L_1$ than that for $L_2$. Therefore, IFT increases with the increasing injection rate, unfavorable for the translocation of dodecane molecules within the nanopore. We also calculate the RDF between C atoms in different dodecane molecules to examine the effect of injection rate on oil volume swelling, plotted in Figure 7D. It shows that a small injection rate is of benefit to the expansion of oil volume. The peak of RDF and the area below the curve decrease with the injection rate, indicating that the coordinate number around a dodecane molecule also decreases with the injection rate. Consequently, dodecane molecules distribute loosely and the average separation between them increases at smaller CO2 injection rate. This can be observed by comparing the configurations at 10 and 2 m/s inserted in Figure 7D. Because of constant injection volume at different rates, more sufficient interaction between CO2 and dodecane at the small injection rate improves the mobilization of upstream dodecane molecules into CO2, which enhances the volume swelling of dodecane. The volume swelling of upstream dodecane provides additional energy to expel the downstream dodecane toward the right of the nanopore.

4. CONCLUSIONS

In this study, NEMD simulations were carried out to study the microscopic mechanisms of scCO2 displacing oil confined in the shale nanopore at different injection rates. The injected scCO2 preferentially adsorbs on the hydroxylated surface and forms layering structures due to hydrogen bonds between CO2 and −OH groups. However, many adsorbed CO2 molecules still retain their mobility, which may be caused by slippage, Knudsen diffusion, and imbibition of scCO2. Adsorbed dodecane molecules are partly detached from the surface resulting from the competitive adsorption between scCO2 and dodecane, which leads to more moveable oil and thus increasing oil production. The miscible zone is formed by the dodecane molecules separated from the surface, bulk dodecane molecules dissolved in CO2 phase, and CO2 molecules penetrating into dodecane phase. Thus, mobilization of dodecane molecules into CO2 has an important effect on CO2 EOR. The formation of the miscible zone results in IFT reduction and oil volume expansion, which enhance the mobility of oil and have a dominant role in scCO2 driving process. Adjacent to the displacement front, the downstream dodecane molecules aggregate and pack tightly, migrating in the form of oil column favorable to CO2 EOR. With the increase of CO2 injection rate, the contact angle of dodecane phase decreases, the Meniscus convex reduces, and the interfacial width increases. The results reveal that the small injection rate with a large volume is favorable to CO2 EOR. The morphology of meniscus may alter in the order convex−concave−CO2 entrainment when the injection rate gradually increases. The findings are benificial to understand and design effective CO2 exploitation of shale resources as well as may provide physical insight into CO2 storage, nanoscale fluid flow, biological molecules translocation, and so on.

![Figure 7.](image-url)

(A) Contact angle $\theta$ between the dodecane droplet and the surface at different scCO2 injection rate with time. (B) Snapshots of the meniscus curvature at the same injection volume of CO2 but different injection rates of 2, 4, 6, 8, and 10 m/s. (C) Density profile of CO2-dodecane system at injection rate of 2m/s and 8m/s. (D) RDF of C(dodecane)-C(dodecane) at different CO2 injection rate. The inserted snapshots of CO2 displacing oil at the same injection volume but different injection rate (a) 10 and (b) 2 m/s.
Additional experimental results as described in the text (PDF).

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