

Original article

Thickened supercritical CO₂ for enhanced shale oil recovery and CO₂ sequestration: A molecular dynamics study

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Abstract:

Shale oil recovery is constrained by oil retention in nanopore networks and at mineral-organic interfaces. Supercritical CO₂ injection has been explored as an enhanced recovery method because it can enter confined pore spaces and interact favorably with shale oil. However, the low viscosity of CO₂ limits its mobility control ability, resulting in low sweep efficiency. Thickening CO₂ with suitable thickeners is therefore a practical strategy to address this limitation. In this study, high-pressure visual observations, viscosity calculations, and molecular dynamics simulations were combined to evaluate the performance of CO₂ thickened with 12-hydroxystearic acid and dimethyl sulfoxide, with emphasis on bulk viscosity, phase compatibility, interfacial partitioning, and confined transport in a mixed-wet kerogen-illite nanopore. High-pressure visual observations confirm the formation of a stable CO₂-rich phase under elevated pressure, and viscosity calculations show a higher viscosity than neat supercritical CO₂. Molecular dynamics simulations reveal that dimethyl sulfoxide and 12-hydroxystearic acid preferentially accumulate near the kerogen-illite walls rather than in the pore interior. This near-wall partitioning modifies the local wall-fluid environment and introduces competitive adsorption with oil components. Interaction-energy analysis indicates that the improved oil-mobilization tendency is associated with weakened wall-oil adhesion rather than enhanced direct CO₂-oil attraction. As a result, near-wall retained oil becomes less dominated by wall adhesion and more susceptible to CO₂-assisted mobilization. Diffusion analysis shows that the thickened formulation reduces the diffusive mobility of oil components while preserving in-plane CO₂ transport. These findings suggest that thickened CO₂ may improve shale oil recovery through a coupled rheological-interfacial mechanism.

1. Introduction

Shale oil has become an increasingly important unconventional oil and gas resource in the global energy system (Hu et al., 2020; Song et al., 2024; Zhao et al., 2024b; Sun et al., 2025). Its efficient development remains challenging because shale formations are characterized by ultralow permeability, abundant nanopores, strong surface heterogeneity,

and complex organic-inorganic mineral compositions (Hu et al., 2020; Xu et al., 2022; Zhang et al., 2024; Dordzie and Balhoff, 2025). These features usually lead to low primary recovery, and hydrocarbons can be strongly retained in nanopore systems (Bao and Zhao, 2021; Wei and Sheng, 2022). Recent integrated core-analysis results further indicate that such retention is associated with lithology, pore architecture, organic-

matter-hosted nanopores, and heavy or adsorbed hydrocarbon fractions, which complicates the distinction between mobile and retained oil in tight shale systems (Mukhametdinova et al., 2026). Carbon dioxide (CO₂) injection has attracted wide attention as a promising strategy for shale oil development. CO₂ can diffuse into nanopores, interact with hydrocarbons, reduce oil viscosity, and promote pore-scale oil mobilization (Song et al., 2024). Understanding the molecular behavior of CO₂ in shale nanopores is therefore essential for improving shale oil recovery and achieving carbon storage (Zhang et al., 2020; Cai et al., 2024; Song et al., 2024). At the same time, CO₂ retention in organic-rich shale pores can contribute to geological CO₂ storage (Kolster et al., 2017; Krevor et al., 2023).

Under typical reservoir conditions, injected CO₂ usually exists as supercritical CO₂ (scCO₂) (Oh et al., 2015). ScCO₂ combines liquid-like density, gas-like diffusivity, and low viscosity, allowing it to enter confined pore spaces and interact with adsorbed hydrocarbons. However, the low viscosity of CO₂ also creates an unfavorable mobility ratio during CO₂ flooding. At the field scale, this can lead to viscous fingering, early gas breakthrough, and gravity override, resulting in poor sweep efficiency (Huppert and Neufeld, 2014; Masalmeh et al., 2025). Increasing the viscosity of the CO₂ is therefore a key strategy for improving mobility control while preserving the high diffusivity and hydrocarbon affinity of scCO₂ (McClain et al., 1996).

Several types of CO₂ thickeners have been developed, including polymers, surfactants, and small-molecule organogelators (Gullapalli et al., 1995; Pal et al., 2022). Among these, 12-hydroxystearic acid (12-HSA) is a promising small-molecule thickener. It can self-associate through intermolecular hydrogen bonding and form a three-dimensional network in suitable solvents (Gullapalli et al., 1995; Terech and Weiss, 1997; Fameau and Rogers, 2020). Since 12-HSA has limited solubility in pure CO₂, a polar cosolvent is needed to improve its compatibility with the CO₂-rich phase. Dimethyl sulfoxide (DMSO) is a suitable cosolvent because it can promote the dispersion of 12-HSA and facilitate the formation of a stable thickened CO₂-rich system (Pellini et al., 2025). Existing experimental and simulation studies have mainly focused on bulk-phase viscosity enhancement, additive solubility, and rheological response (Zhao et al., 2023; Geng et al., 2026). However, bulk thickening alone cannot fully determine the behavior of the system in shale nanopores. Under nanoscale confinement, wall affinity, confinement effects, and competitive adsorption play critical roles in controlling fluid behavior (Bocquet and Charlaix, 2010; Falk et al., 2015).

Shale nanopores are chemically heterogeneous systems in which organic kerogen and inorganic clay minerals provide distinct surface environments (Tian et al., 2019; Song et al., 2022; Neil et al., 2025). This heterogeneity gives rise to mixed wettability and component-specific hydrocarbon retention in shale reservoirs (Subbotina et al., 2023). Oil molecules, especially heavy or surface-active components, tend to form stable adsorption layers near pore walls, while CO₂ may partition differently between the interfacial region and the pore interior (Zhao et al., 2024a; Liu et al., 2025, 2026).

Previous molecular simulation studies have clarified several aspects of pure CO₂-oil interactions, hydrocarbon adsorption, and confined diffusion behavior (Wang et al., 2023; Wu et al., 2024; Zhao et al., 2024c). However, the role of CO₂ thickeners in organic-inorganic mixed nanopores has not been sufficiently resolved. In particular, the coupled effects of thickener partitioning, near-wall oil retention, CO₂-oil competition, wall-fluid interaction, and confined molecular mobility remain poorly understood.

In this study, high-pressure visual experiments and molecular dynamics simulations were combined to investigate the behavior of CO₂ thickened with 12-HSA and DMSO in mixed-wet kerogen and illite slit nanopores. The work was designed to connect macroscopic thickening performance with nanoscale fluid redistribution in shale nanopores, rather than to reproduce a continuous non-equilibrium injection front or a full reservoir-scale displacement process. A multicomponent shale-oil surrogate was introduced to represent hydrocarbons with different molecular structures and retention tendencies. The study first evaluated the stability and viscosity enhancement of the thickened CO₂-rich phase and then compared the confined behavior of neat and thickened CO₂ in terms of molecular partitioning, competitive adsorption, near-wall oil retention, interaction-energy evolution, and in-plane diffusion. Within this framework, the work clarifies how the additives modify the wall-fluid interfacial environment and provides molecular-level evidence for the interfacial mechanism of thickened CO₂ in shale oil recovery.

2. Calculation methods

2.1 Construction of the kerogen-illite slit nanopore model

A mixed-wet kerogen-illite slit nanopore was constructed to represent the organic-inorganic pore environment of shale reservoirs. The solid framework contained illite clay, Type II kerogen, and charge-compensating potassium ions, providing both mineral and organic surface domains for fluid redistribution in confined pores (Sposito et al., 1999). The wall-normal direction was defined as the *z* direction, and the two opposing solid surfaces formed a slit pore with a nominal width of 6 nm.

Background water layers were incorporated near the pore walls to represent the hydrated environment commonly present in shale nanopores (Björneholm et al., 2016). The water content was kept identical in the neat and thickened CO₂ systems so that differences in fluid redistribution could be attributed to the thickeners rather than to changes in initial hydration. During the equilibration and production simulations, the wall atoms were position-restrained to maintain the fixed slit geometry. A molecular snapshot of the kerogen-illite slit nanopore and fluid components is shown in Fig. 1. Detailed structural parameters of the model are provided in Supplementary Table S1.

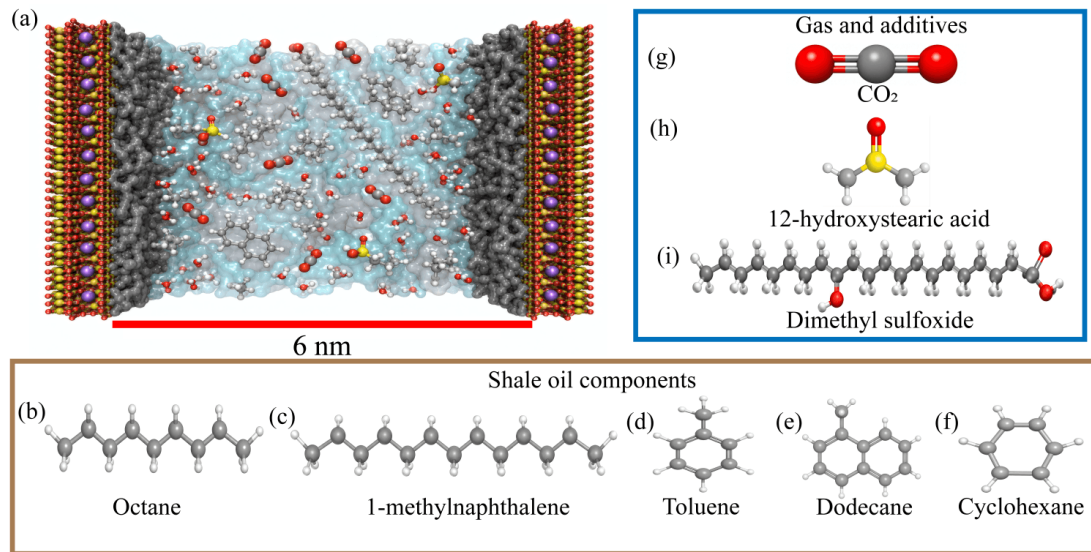


Fig. 1. Molecular model of the mixed-wet kerogen-illite slit nanopore and confined fluid components: (a) Kerogen-illite slit nanopore, (b) octane, (c) 1-methylnaphthalene, (d) toluene, (e) dodecane, (f) cyclohexane, (g) CO₂, (h) 12-HSA and (i) DMSO.

Table 1. Molecular composition of the neat and thickened scCO₂ systems at different state points.

State point	Temperature (K) and pressure (MPa) label	Number of CO ₂ in Model 1	Number of CO ₂ in Model 2	Number of DMSO in Model 2	Number of 12-HSA in Model 2
S1	328, 15	1,700	1,700	402	23
S2	338, 22	1,950	1,950	461	26
S3	348, 29	2,080	2,080	493	28
S4	358, 36	2,170	2,170	514	29
S5	368, 43	2,240	2,240	529	30
S6	378, 50	2,290	2,290	542	31
S7	388, 57	2,330	2,330	552	31
S8	398, 64	2,370	2,370	560	32
S9	408, 71	2,400	2,400	568	32

Notes: The water content was fixed at 5 wt% in both systems.

2.2 Fluid composition and pressure-equivalent molecular loading

Two sets of confined pore systems were constructed. Model 1 represents the neat scCO₂ case without thickeners. Model 2 represents the thickened scCO₂ case containing CO₂, DMSO, and 12-HSA. The shale-oil phase was represented by five components: Octane, toluene, cyclohexane, 1-methylnaphthalene, and dodecane. The molecular numbers of these components were kept constant across all simulations to enable direct comparison among different state points and between the neat and thickened scCO₂ cases. The shale-oil composition consisted of 90 octane molecules, 60 toluene molecules, 45 cyclohexane molecules, 45 1-methylnaphthalene molecules, and 60 dodecane molecules.

Instead of imposing pressure directly through a barostat in the confined pore, each temperature-pressure state was

represented by a pressure-equivalent molecular loading. The number of CO₂ molecules increased with bulk reservoir pressure. For the thickened scCO₂ system, the numbers of DMSO and 12-HSA molecules were adjusted consistently with the CO₂ loading while maintaining approximately 18 wt% 12-HSA in DMSO. This procedure avoided direct pressure coupling to the restrained kerogen-illite wall while retaining the density/loading effect associated with different reservoir pressure states. The complete molecular loading scheme is listed in Table 1. In Model 1, DMSO and 12-HSA were absent. In both models, the shale oil composition and the water layers were kept unchanged at all state points. Therefore, the difference between Model 1 and Model 2 directly reflects the molecular effect of the scCO₂ formulation thickened with 12-HSA and DMSO.

2.3 Force-field assignment and simulation protocol

Classical force fields were assigned to all solid and fluid components, with detailed parameter sources listed in Supplementary Table S2. Confined pore production was performed using a fixed-geometry constant-volume protocol because the kerogen-illite walls were position-restrained, making direct pressure coupling inappropriate for this restrained slit-pore system. Pressure effects were therefore represented by pressure-equivalent molecular loading. Each system was minimized, equilibrated, and then simulated at the corresponding state point, with three independent trajectories generated for uncertainty estimation.

2.4 Analysis methods

To simplify the mathematical notation, compact symbols are used in the following analyses. The subscript i identifies a fluid component, j refers to another interacting group, C represents CO₂, w denotes the near-wall region, W indicates the pore wall, and c denotes the pore-core region. Full component names are retained in the text, tables, and figure captions, while long words are not used as mathematical subscripts.

2.4.1 Viscosity calculation

The dynamic viscosity of the neat and thickened CO₂ systems was evaluated to validate the rheological response of the 12-HSA/DMSO thickened formulation. The viscosity of neat scCO₂ was compared with the reference CO₂ viscosity recommended by National Institute of Standards and Technology. Two independent methods were used: The Green-Kubo method and the Einstein-Helfand method. In the Green-Kubo formalism, the shear viscosity is obtained from the time integral of the autocorrelation function of the off-diagonal pressure tensor components (Green, 1954; Kubo, 1957):

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle \delta P_{\alpha\beta}(0) \delta P_{\alpha\beta}(t) \rangle dt \quad (1)$$

where η is the shear viscosity; $P_{\alpha\beta}(\alpha \neq \beta)$ are the off-diagonal components of the microscopic pressure tensor; α and β denote the Cartesian directions x , y , and z ; $\delta P_{\alpha\beta}(t)$ is the fluctuation of the off-diagonal pressure tensor from its equilibrium average, defined as $\delta P_{\alpha\beta} = P_{\alpha\beta} - \langle P_{\alpha\beta} \rangle$; V is the instantaneous simulation volume; T is the absolute temperature; k_B is the Boltzmann constant; and t is the correlation time.

The Einstein-Helfand method calculates viscosity from the long-time slope of the mean-square displacement of the Helfand moment (Helfand, 1960):

$$\eta = \frac{1}{2Vk_B T} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\{ \left\langle [G_{\alpha\beta}(t) - G_{\alpha\beta}(0)]^2 \right\rangle \right\} \quad (2)$$

where $G_{\alpha\beta}$ is the Helfand moment associated with the corresponding stress component. Agreement between the Green-Kubo and Einstein-Helfand results was used to assess the reliability of the viscosity calculations.

Because viscosity is a bulk rheological property, the viscosity calculations were used to characterize the neat and thickened CO₂-rich fluid formulations rather than to define a true

pore-scale viscosity inside the kerogen-illite slit. The confined pore simulations were used for molecular redistribution, near-wall retention, interaction-energy, and diffusion analyses.

2.4.2 Density profiles and near-wall retention metrics

To replace qualitative scatter-type spatial distribution plots with quantitative structural descriptors, component-resolved mass-density profiles were calculated along the z direction, which is normal to the slit-pore walls. For each bin, the mass density of component i was calculated from the number of molecules located in the bin, the molecular weight of the component, and the bin volume (Huang et al., 2024):

$$\rho_i(z) = \frac{n_i(z)M_i}{V_b} 1.66054 \quad (3)$$

where $\rho_i(z)$ is the local mass density of component i in the z -direction bin, in kg/m³; $n_i(z)$ is the number of molecules of component i in the bin; V_b is the bin volume, in nm³; M_i is the molecular weight of component i , g/mol. The coefficient 1.66054 accounts for Avogadro's constant and converts molecules nm⁻³ and g/mol into kg/m³.

The near-wall region was defined as the region within 0.50 nm from each solid-fluid interface. The pore-core region was defined as the remaining central part of the accessible pore. For each component, the near-wall fraction was calculated as (Guo et al., 2022):

$$f_i = \frac{n_i^w}{n_i} \quad (4)$$

where f_i is the near-wall fraction of component i ; n_i^w is the number of molecules of component i in the near-wall region, and n_i is the total number of molecules of component i in the accessible pore. The near-wall enrichment factor was calculated as (Guo et al., 2022):

$$R_i = \frac{\rho_i^w}{\rho_i^c} \quad (5)$$

where R_i is the near-wall enrichment factor of component i ; and ρ_i^w and ρ_i^c are the average mass densities of component i in the near-wall and pore-core regions, respectively. A value of $R_i > 1$ indicates preferential near-wall enrichment, $R_i \approx 1$ indicates an approximately uniform distribution, and $R_i < 1$ indicates depletion near the wall. For CO₂, the near-wall immobilized fraction was calculated using the same near-wall definition (Guo et al., 2022):

$$f_C = \frac{n_C^w}{n_C} \quad (6)$$

where f_C is the near-wall fraction of CO₂; n_C^w is the number of CO₂ molecules located in the near-wall region, and n_C is the total number of CO₂ molecules in the accessible pore. This dimensionless descriptor was used to evaluate CO₂ retention near the pore walls under confinement.

2.4.3 Interaction-energy analysis

To quantify molecular affinities among CO₂, shale-oil components, additives, and the pore wall, pairwise interaction energies were calculated using GROMACS energy-group decomposition. The interaction energy between two groups i

and j was defined as the sum of the short-range Lennard-Jones and short-range Coulombic contributions (Lindahl et al., 2001; Guo et al., 2022):

$$E_{ij} = E_{ij}^L + E_{ij}^Q \quad (7)$$

where E_{ij} is the nonbonded interaction energy between molecular groups i and j ; E_{ij}^L is the short-range Lennard-Jones contribution, and E_{ij}^Q is the short-range Coulombic contribution. The indices i and j denote the selected interacting groups, such as the pore wall, CO₂, shale-oil components, DMSO, or 12-HSA.

Negative values indicate attractive net interactions. Because the reciprocal-space contribution of PME cannot be uniquely decomposed into individual group pairs, the pairwise interaction energies are reported using the short-range Lennard-Jones and Coulombic terms. The same procedure was applied to all systems, allowing consistent comparison among components and state points. The analyzed interactions included wall-oil, CO₂-oil, wall-CO₂, wall-DMSO, wall-12-HSA, CO₂-DMSO, CO₂-12-HSA, and DMSO-12-HSA. These interactions were used to interpret component-specific near-wall retention, additive-assisted interfacial restructuring, and the relative mobilization tendency of different shale-oil components.

2.4.4 Energy-based CO₂-oil mobilization tendency index

To connect the interaction-energy results with the observed near-wall oil retention behavior, an energy-based CO₂-oil mobilization tendency index was calculated for each shale-oil component. For oil component i , the index was defined as (Guo et al., 2022):

$$\Psi_i = \frac{|E_{Ci}|}{|E_{Wi}|} \quad (8)$$

where Ψ_i is the energy-based mobilization tendency index of oil component i , E_{Ci} is the interaction energy between CO₂ and oil component i ; E_{Wi} is the interaction energy between the wall and oil component i . When $\Psi_i > 1$, the CO₂-oil attraction is stronger than the wall-oil adhesion, indicating a greater thermodynamic tendency for the oil component to interact with the CO₂-rich phase rather than remain attached to the wall. When $\Psi_i < 1$, wall-oil adhesion dominates, indicating stronger near-wall retention. Therefore, Ψ_i is used as a descriptive energy-based oil mobilization descriptor. It is not a direct oil recovery factor, not a displacement efficiency, and not a substitute for a non-equilibrium injection simulation. Instead, it provides a molecular-scale measure of the relative competition between CO₂-oil affinity and wall-oil adhesion under equilibrium confined-pore conditions.

2.4.5 Mean-square displacement and in-plane diffusion coefficient

At nanometer scales, transport can depart from continuum descriptions as wall interactions and molecular-scale structuring become increasingly important (Kavokine et al., 2021). The mobility of CO₂, oil components, DMSO, and 12-HSA in the confined slit pore was quantified using the mean-square

displacement method. Because the z direction is strongly constrained by the slit geometry, the in-plane diffusion coefficient D_{xy} was used as the primary mobility descriptor. Molecular centers of geometry were used to calculate component-resolved displacements. The in-plane mean-square displacement was calculated as (Calandrini et al., 2011):

$$MSD_{xy}(t) = \langle [x(t) - x(0)]^2 \rangle + \langle [y(t) - y(0)]^2 \rangle \quad (9)$$

where $MSD_{xy}(t)$ is the in-plane mean square displacement at time t ; $x(t)$ and $y(t)$ are the molecular coordinates in the two directions parallel to the pore walls at time t ; $x(0)$ and $y(0)$ are the corresponding initial coordinates.

The in-plane diffusion coefficient was then obtained from the linear region of the MSD curve (Calandrini et al., 2011):

$$D_{xy} = \frac{1}{4} \frac{d}{dt} MSD_{xy}(t) \quad (10)$$

where D_{xy} is the in-plane diffusion coefficient of the selected component; $MSD_{xy}(t)$ is the in-plane mean square displacement at time t ; and t is the diffusion time; x and y are the corresponding initial coordinates; d is an infinitesimal change in the in-plane mean square displacement; and dt is an infinitesimal time interval.

Before diffusion analysis, trajectories were processed using a no-jump treatment to remove periodic boundary artifacts. The fitted diffusion coefficients were reported in m²/s. The comparison of D_{xy} between neat and thickened scCO₂ systems was used to evaluate the mobility-control effect of the thickener and to determine whether CO₂ retained sufficient molecular mobility under confinement.

2.4.6 Statistical analysis and uncertainty estimation

For each temperature-pressure state and each model, three independent simulations were performed. The reported density profiles, near-wall fractions, enrichment factors, CO₂ near-wall immobilized fractions, interaction energies, mobilization tendency indices, and diffusion coefficients were calculated independently from each trajectory and then averaged. Error bars represent the standard deviation among the three independent simulations (Calandrini et al., 2011):

$$\sigma = \sqrt{\frac{1}{r-1} \sum_{k=1}^r (a_k - \bar{a})^2} \quad (11)$$

where σ is the sample standard deviation; $r = 3$, a_k is the value from the k -th independent simulation, and $\bar{a}$ is the average value. This procedure was used to assess the reproducibility of the molecular redistribution, interaction-energy, and diffusion results.

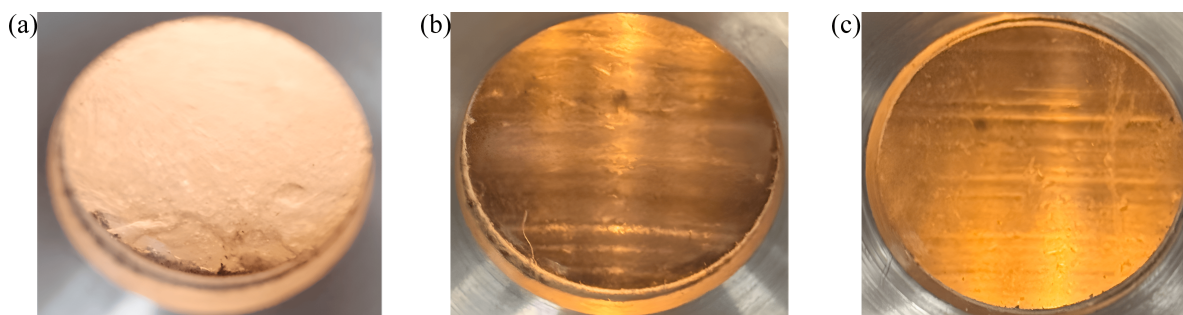
3. Results and discussion

3.1 Viscosity validation and rheological response of neat and thickened CO₂

Before analyzing confined-pore redistribution, the phase compatibility and rheological response of the CO₂ formulation thickened with 12-HSA and DMSO were evaluated. Visual observations show that the formulation has limited apparent

Table 2. CO₂ near-wall immobilized fraction in neat and scCO₂ system thickened with 12-HSA and DMSO.

State point	Temperature (K) and pressure (MPa) label	Neat scCO ₂ system	Standard deviation	12-HSA/DMSO-thickened scCO ₂ system	Standard deviation
S1	328, 15	0.124	0.0021	0.147	0.0071
S2	338, 22	0.126	0.0014	0.127	0.0035
S3	348, 29	0.130	0.0046	0.128	0.0034
S4	358, 36	0.136	0.0030	0.119	0.0036
S5	368, 43	0.136	0.0020	0.107	0.0047
S6	378, 50	0.136	0.0020	0.110	0.0033
S7	388, 57	0.148	0.0056	0.111	0.0052
S8	398, 64	0.151	0.0047	0.102	0.0038
S9	408, 71	0.151	0.0054	0.099	0.0019

**Fig. 2.** Visual phase behavior of the 12-HSA/DMSO solution in scCO₂: (a) Turbid mixture at low temperature and low pressure, (b) clear CO₂-rich phase under elevated temperature and pressure after stirring and (c) stable clear phase after 24 h of static equilibration.

compatibility at the lowest state point, where the mixture remains turbid and CO₂ bubbles are visible. This state point is therefore treated as a lower-bound condition rather than an optimal single-phase condition. At higher state points, the mixture becomes optically clear after stirring and remains stable after static equilibration, which confirms the formation of a stable CO₂-rich phase under elevated-pressure conditions. The windowed high-pressure view cell setup and the visual procedure used to assess the phase compatibility of the scCO₂ formulation containing 12-HSA and DMSO are described in Supplementary Appendix C, and representative visual observations are shown in Fig. 2. The simulated viscosity results further confirm the intended rheological contrast between neat and thickened CO₂. The calculated viscosity of neat scCO₂ agrees with the reference trend from the National Institute of Standards and Technology, indicating that the molecular model reproduces the low-viscosity character of scCO₂. After adding 12-HSA/DMSO formulation, both the Green-Kubo and Einstein-Helfand methods predict a substantial viscosity enhancement, and the two methods yield nearly identical trends. The complete numerical values are provided in Supplementary Fig. S1. The viscosity enhancement is attributed to additive-assisted molecular association in the CO₂-rich phase. DMSO improves the compatibility of 12-HSA with the CO₂-

rich environment, while 12-HSA contributes to intermolecular association and network-like structuring. This interpretation is consistent with the general behavior of low-molecular-weight gelators, which form networks through the self-assembly and entanglement of one-dimensional supramolecular structures (Draper and Adams, 2017). These results validate the rheological basis for mobility control and provide the bulk fluid reference for the subsequent confined-pore redistribution analysis.

3.2 CO₂ distribution and near-wall immobilization in kerogen-illite slit nanopores

After validating the viscosity enhancement of the scCO₂ formulation thickened with 12-HSA and DMSO, the spatial distribution and near-wall retention of CO₂ in the kerogen-illite slit nanopore were analyzed. Because the production simulations were performed under fixed-geometry constant-number, constant-volume, and constant-temperature conditions, the CO₂ retention behavior is discussed here in terms of the *z*-direction density profile and the near-wall retained CO₂ fraction, rather than as a reservoir-scale sequestration efficiency. The density profiles are shown in Fig. 3, and the corresponding near-wall immobilized fractions are summarized in Table 2.

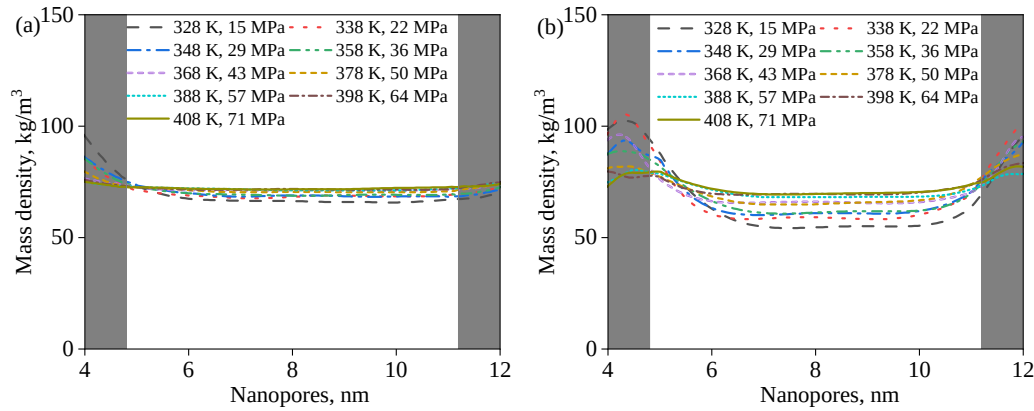


Fig. 3. CO₂ mass-density profiles along the *z*-axis in kerogen-illite slit nanopores: (a) Neat scCO₂ system and (b) 12-HSA/DMSO-thickened scCO₂ system.

For the neat scCO₂ system, the CO₂ density profiles show that CO₂ molecules can occupy the entire slit pore, with only moderate near-wall enrichment (Fig. 3(a)). At the low-temperature and low-pressure state, the CO₂ density near the wall is higher than that in the pore center, indicating preferential accumulation at the solid-fluid interface. As the temperature-pressure state increases, the density profile becomes progressively flatter. This indicates that CO₂ is more broadly distributed across the pore space at higher state points. The maximum near-wall density decreases from approximately 109 kg/m³ at 328 K and 15 MPa to approximately 80 kg/m³ at 408 K and 71 MPa, showing that the local near-wall enrichment weakens as the system approaches higher pressure-equivalent loading.

Although the near-wall enrichment becomes less pronounced at high state points, the near-wall retained CO₂ fraction in the neat scCO₂ system increases from 0.124 at 328 K and 15 MPa to 0.151 at 408 K and 71 MPa (Table 2). This indicates that, under neat scCO₂ conditions, the increasing pressure-equivalent CO₂ loading enhances the population of CO₂ molecules retained in the near-wall region. Therefore, neat scCO₂ exhibits two simultaneous features: Its density profile becomes more spatially uniform at high state points, but the fraction of CO₂ molecules located in the near-wall region increases because of the larger CO₂ loading and greater wall-accessible occupancy.

The CO₂ distribution changes after introducing the 12-HSA/DMSO formulation (Fig. 3(b)). At 328 K and 15 MPa, the thickened system shows a relatively strong near-wall CO₂ enrichment, and the CO₂ near-wall immobilized fraction reaches 0.14728 ± 0.00713 , which is higher than that of neat scCO₂ at the same state point. This behavior is consistent with the visual-cell observation discussed in Section 3.1: The 12-HSA/DMSO formulation has poor apparent compatibility with scCO₂ at the lowest temperature-pressure condition. Under this limiting condition, incomplete phase compatibility and interfacial accumulation of the additives can promote local CO₂ clustering near the wall. At higher temperature-pressure states, the behavior becomes clearly different. The CO₂ density profiles in the thickened system gradually flatten, and the near-wall CO₂ peak weakens. Correspondingly, the near-wall

retained CO₂ fraction decreases from 0.147 at 328 K and 15 MPa to 0.099 at 408 K and 71 MPa. This decline indicates that, once the 12-HSA/DMSO formulation becomes better dispersed under elevated conditions, CO₂ is less confined to the near-wall region and becomes more distributed within the pore interior.

A direct comparison between the neat and thickened systems further highlights the role of the additives. At the lowest temperature-pressure state point, the near-wall retained CO₂ fraction in the thickened system is approximately 18% higher than that in the neat scCO₂ system. However, this relationship reverses as the state point increases. From 348 K and 29 MPa onward, the thickened system consistently shows a lower near-wall retained CO₂ fraction than neat scCO₂. At 408 K and 71 MPa, the value decreases from 0.151 in the neat system to 0.099 in the thickened system, corresponding to a reduction of approximately 34%. Averaged over all nine state points, the thickened system yields a lower CO₂ near-wall immobilized fraction than neat scCO₂, with an average decrease of approximately 15%.

This trend suggests that the 12-HSA/DMSO additives modify the near-wall environment and alter how CO₂ partitions between the interfacial region and the pore interior. In the neat scCO₂ system, CO₂ directly accesses the kerogen-illite interface and gradually accumulates in the near-wall region as the CO₂ loading increases. In the thickened system, DMSO and 12-HSA are incorporated into the interfacial region and partially populate the near-wall space, thereby reducing the relative fraction of CO₂ residing near the wall under elevated temperature-pressure conditions. Therefore, the role of the thickened formulation is not to enhance interfacial CO₂ accumulation. Rather, it reduces wall-localized CO₂ enrichment and promotes a more spatially extended CO₂ distribution within the accessible pore volume at most reservoir-relevant state points.

3.3 Near-wall retention and enrichment of shale-oil components

Component-resolved near-wall fractions and enrichment factors were used to quantify the partitioning of shale-oil

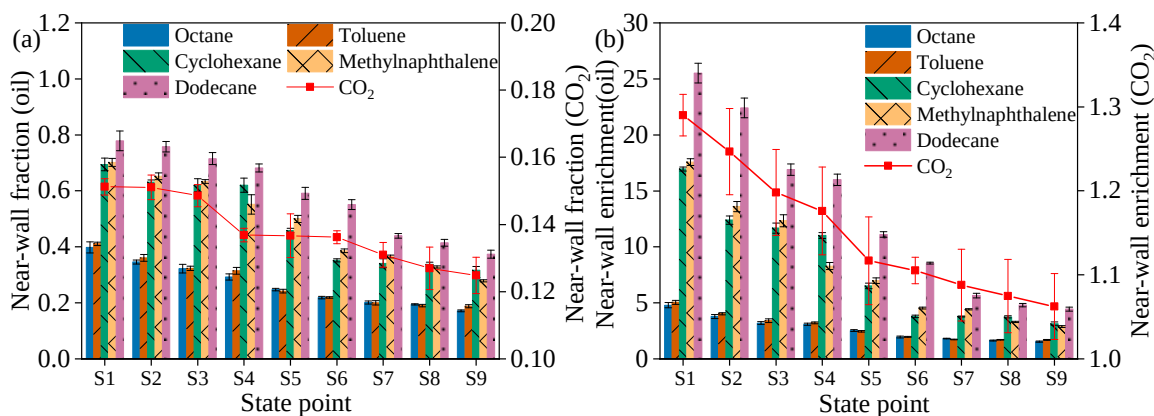


Fig. 4. Near-wall fraction and near-wall enrichment factor for CO₂ and shale-oil components in the neat scCO₂ system: (a) Near-wall fraction and (b) near-wall enrichment factor.

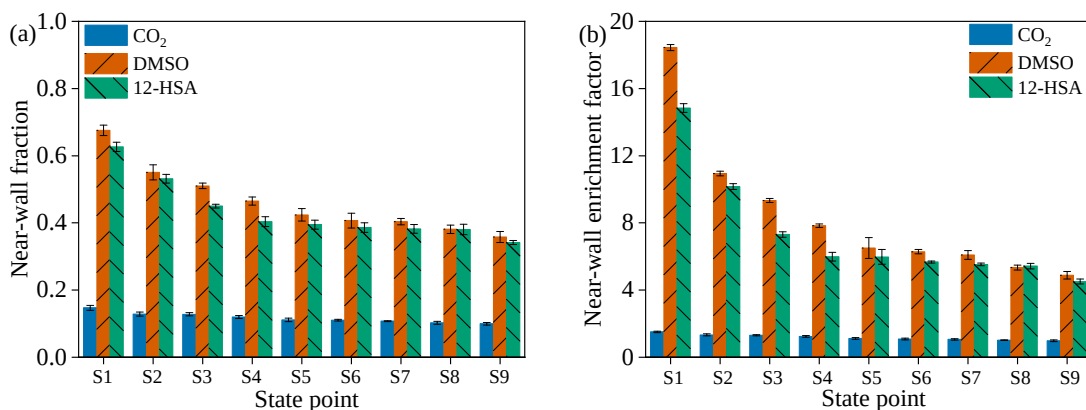


Fig. 5. Near-wall fraction and near-wall enrichment factor for CO₂, DMSO, and 12-HSA in the 12-HSA/DMSO-thickened scCO₂ system: (a) Near-wall fraction and (b) near-wall enrichment factor.

molecules between the wall region and the pore interior. These descriptors quantitatively characterize interfacial retention and complement the z -axis density profiles of individual oil components shown in Supplementary Figs. S2-S6. The complete numerical values of the near-wall fractions and enrichment factors are provided in Supplementary Tables S3-S6. The results for the neat scCO₂ system are shown in Fig. 4, whereas the additive distribution and oil-component redistribution in the thickened system are shown in Figs. 5 and 6, respectively.

In the neat scCO₂ system, all shale-oil components accumulate preferentially near the kerogen-illite wall, but the retention strength depends strongly on molecular structure. Dodecane, 1-methylnaphthalene, and cyclohexane show stronger near-wall enrichment, whereas octane and toluene are less concentrated at the interface. As the state point increases, both the near-wall fraction and enrichment factor of the oil components decrease, indicating a reduction in the contrast between the near-wall and bulk regions and enhanced redistribution from the wall region toward the pore interior. The density profiles in Supplementary Figs. S2-S6 support this interpretation, showing that the near-wall density peaks become weaker and broader at higher state points.

After adding the 12-HSA/DMSO formulation, the near-wall partitioning pattern changes substantially. DMSO and

12-HSA preferentially localize near the kerogen-illite walls, indicating that the additives actively participate in the interfacial region rather than remaining uniformly distributed in the pore interior. This additive-rich near-wall layer alters the retention behavior of shale-oil components in a component-specific manner. The strong near-wall retention of dodecane is clearly suppressed, and the retention of 1-methylnaphthalene is partially weakened. Octane shows a more moderate response, whereas toluene and cyclohexane exhibit more component-specific responses to the reorganized interfacial environment.

These results indicate that the thickened formulation does not simply remove all oil components from the wall. Instead, it induces selective interfacial redistribution controlled by molecular structure and wall-fluid affinity. In the neat scCO₂ system, oil retention is mainly governed by the competition between wall-oil adhesion and CO₂-oil affinity. In the thickened system, DMSO and 12-HSA enrich near the wall, partially weaken the original wall-oil adhesion, and reshape the local adsorption environment. This interfacial restructuring preferentially weakens the retention of strongly wall-associated heavy components, such as dodecane and 1-methylnaphthalene, while allowing cyclic and aromatic molecules to retain distinct component-specific responses.

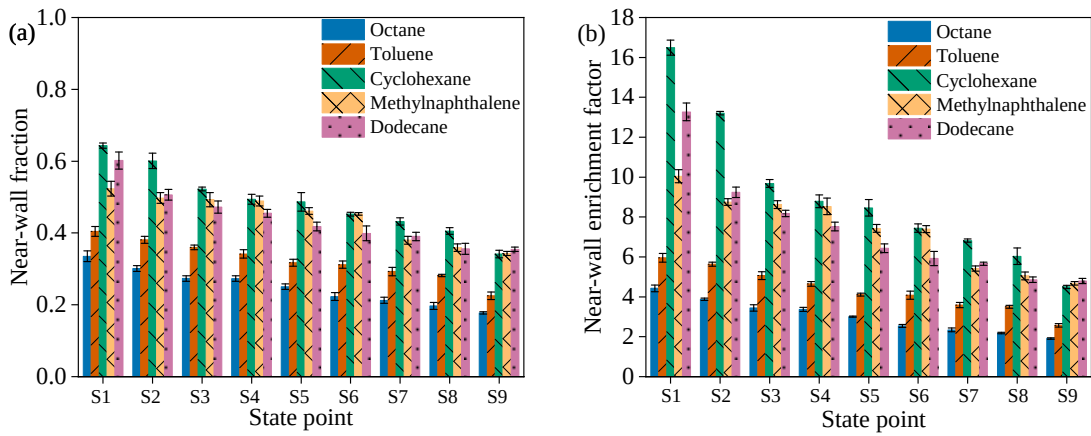


Fig. 6. Near-wall fraction and near-wall enrichment factor of shale-oil components in the 12-HSA/DMSO-thickened scCO₂ system: (a) Near-wall fraction and (b) near-wall enrichment factor.

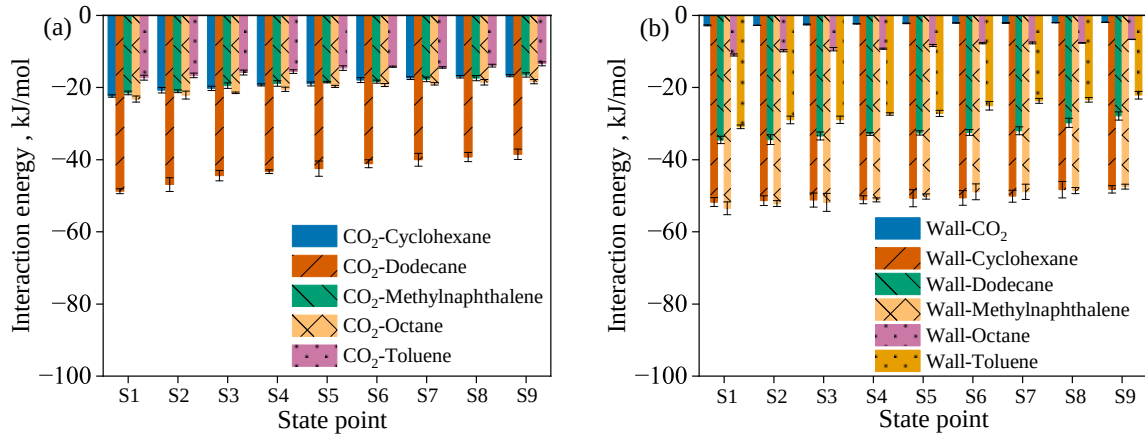


Fig. 7. Normalized interaction energies per target molecule in the neat scCO₂ system: (a) CO₂-shale-oil interaction energies and (b) wall-CO₂ and wall-shale-oil interaction energies. More negative values indicate stronger attractive interactions.

3.4 Interaction energies and energy-based oil mobilization tendency

The normalized interaction energies per target molecule are shown in Figs. 7 and 8. The energy-based CO₂-oil mobilization tendency index calculated from these interaction energies is shown in Fig. 9.

In the neat scCO₂ system, CO₂ shows attractive interactions with all oil components, but the interaction strength is component-specific. Dodecane and octane show stronger CO₂-oil attraction than the cyclic and aromatic oil components. For example, the CO₂-dodecane interaction decreases in magnitude from -48.70 ± 0.68 kJ/mol at 328 K and 15 MPa to -38.49 ± 1.47 kJ/mol at 408 K and 71 MPa, while CO₂-octane changes from -23.16 ± 0.84 to -18.33 ± 0.58 kJ/mol. Toluene shows the weakest CO₂-oil attraction among the five oil components. These results indicate that neat scCO₂ has stronger affinity for linear alkanes than for aromatic or cyclic molecules. However, CO₂-oil attraction alone does not determine oil mobilization because oil molecules also interact with the kerogen-illite wall. In the neat scCO₂ system, wall-oil interactions are especially strong for cyclohexane, 1-methylnaphthalene, and dodecane.

After adding the 12-HSA/DMSO formulation, the direct CO₂-oil interactions become slightly weaker than those in the neat scCO₂ system. For example, CO₂-dodecane changes from -43.26 ± 0.76 to -34.12 ± 0.70 kJ/mol over the state range, and CO₂-octane changes from -20.64 ± 0.80 to -15.95 ± 0.19 kJ/mol. This reduction is expected because DMSO and 12-HSA partially incorporated into the CO₂-rich fluid environment, which modifies the local molecular environment around CO₂ and weakens its direct interactions with oil molecules. Nevertheless, the thickened system still improves the relative oil mobilization tendency because wall-oil adhesion is weakened more strongly than CO₂-oil attraction. The additive-related interaction energies support this interpretation. DMSO and 12-HSA show strong attraction to the wall and to each other. Specifically, the wall-DMSO, wall-12-HSA, and DMSO-12-HSA interaction energies are strongly negative, indicating strong attractive interactions among the additives and between the additives and the wall. These attractive interactions are consistent with the preferential localization of the additive system in the near-wall interfacial region.

In the neat scCO₂ system, octane and dodecane show $\Psi_i > 1$ over all state points, indicating favorable CO₂-assisted

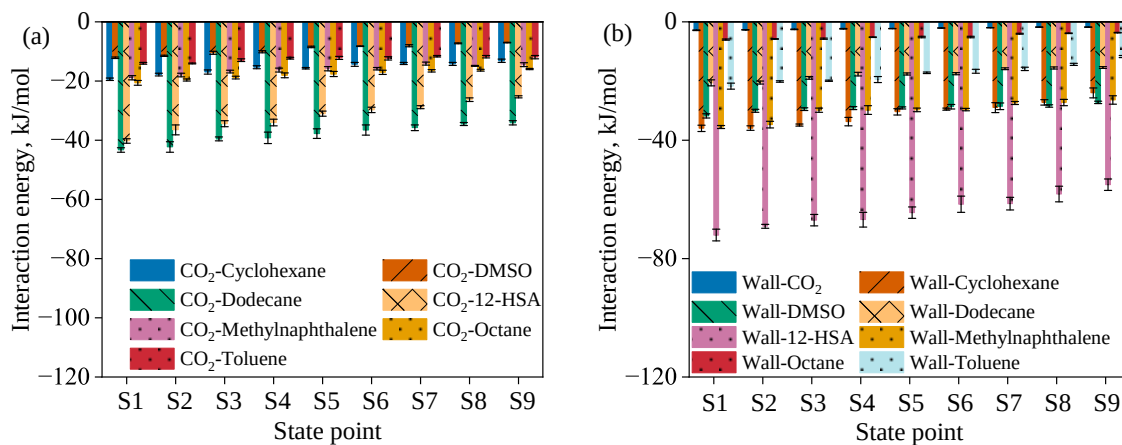


Fig. 8. Normalized interaction energies per target molecule in the 12-HSA/DMSO-thickened scCO₂ system: (a) CO₂-shale-oil, CO₂-DMSO, and CO₂-12-HSA interaction energies and (b) wall-CO₂, wall-shale-oil, wall-DMSO, and wall-12-HSA interaction energies.

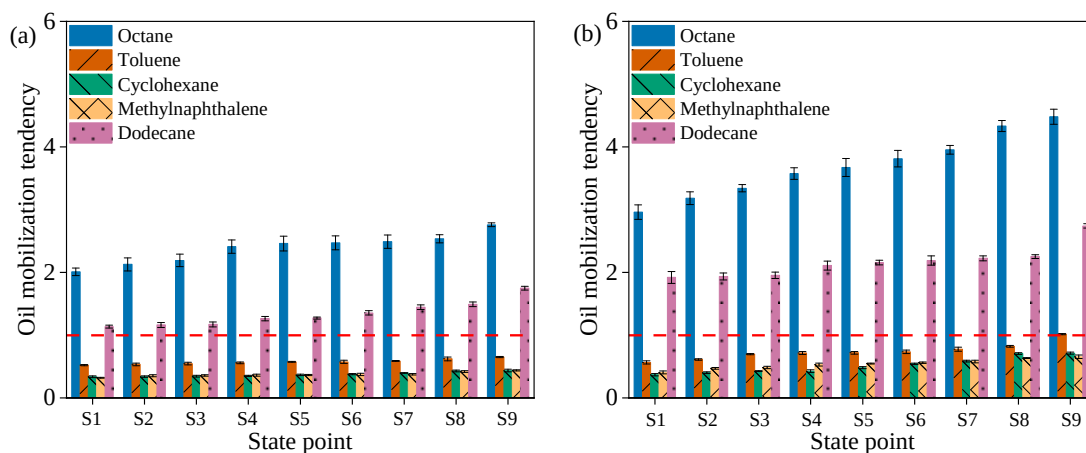


Fig. 9. Energy-based tendency index for CO₂-driven mobilization of shale-oil components: (a) Neat scCO₂ system and (b) 12-HSA/DMSO-thickened scCO₂ system.

mobilization, whereas Ψ_i values for toluene, cyclohexane, and 1-methylnaphthalene remain below unity, indicating dominant wall-controlled retention. After adding the 12-HSA/DMSO formulation, Ψ_i values are higher than those in the neat scCO₂ system at the corresponding state points for all oil components. This comparison indicates that the formulation weakens wall-controlled retention and shifts the balance toward CO₂-assisted mobilization. However, the extent of this shift remains component-dependent. Octane and dodecane retain $\Psi_i > 1$ in the thickened system, while Ψ_i for toluene approaches unity only at the highest state point. Ψ_i values for cyclohexane and 1-methylnaphthalene remain below unity even after thickening, although they are higher than those in neat scCO₂. Overall, the 12-HSA/DMSO formulation mitigates wall-controlled retention but does not fully overcome the strong wall affinity of cyclohexane and 1-methylnaphthalene.

3.5 Confined diffusion and molecular mobility

The in-plane diffusion coefficient D_{xy} was calculated to evaluate the molecular mobility of CO₂ and shale-oil components in the kerogen-illite slit nanopore. Because the z

direction is constrained by the solid walls, D_{xy} provides a more appropriate descriptor of molecular migration within the pore than a three-dimensional diffusion coefficient. The results for the neat scCO₂ and scCO₂ system thickened with 12-HSA and DMSO are shown in Fig. 10.

In the neat scCO₂ system, CO₂ remains the most mobile species throughout the investigated temperature and pressure range. Its in-plane diffusion coefficient increased from 5.48×10^{-8} m²/s at 328 K and 15 MPa to 6.46×10^{-8} m²/s at 408 K and 71 MPa, indicating that CO₂ maintains high lateral mobility even under nanoscale confinement. This mobility is substantially higher than that of the shale-oil components, whose diffusion coefficients are generally several-fold to more than one order of magnitude lower. At 328 K and 15 MPa, octane is the fastest-moving oil component, with a D_{xy} value of 1.14×10^{-8} m²/s. This relatively high mobility is consistent with its weaker near-wall retention and stronger energy-based mobilization tendency discussed above. Toluene shows a lower but still measurable lateral diffusivity of 3.43×10^{-9} m²/s, while dodecane diffuses more slowly, with $D_{xy} = 1.37 \times 10^{-9}$ m²/s. The lowest mobilities are observed for cyclohexane and

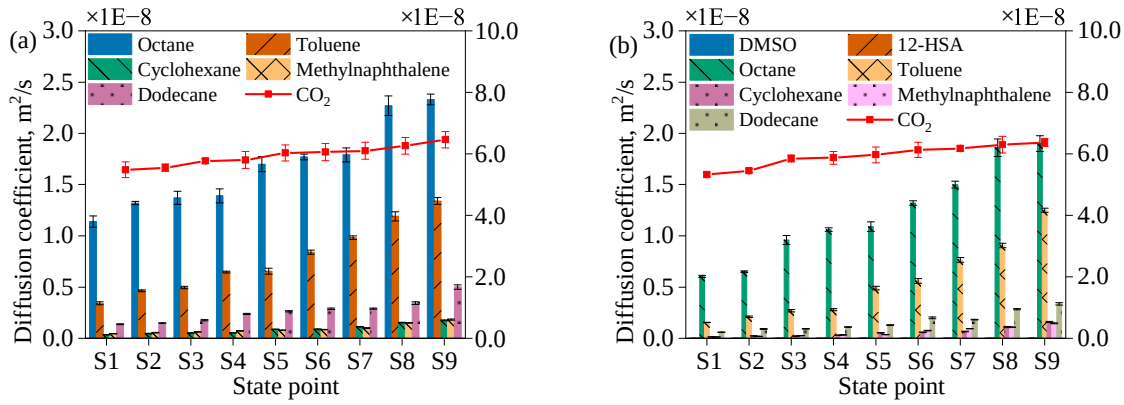


Fig. 10. In-plane diffusion coefficients D_{xy} of CO_2 and shale-oil components in kerogen-illite slit nanopores: (a) Neat scCO_2 system and (b) 12-HSA/DMSO-thickened scCO_2 system. Error bars represent standard deviations from three independent simulations.

1-methylnaphthalene, with D_{xy} values of 4.60×10^{-10} and $3.45 \times 10^{-10} \text{ m}^2/\text{s}$, respectively. These differences show that oil mobility in the neat scCO_2 system is controlled not only by molecular size but also by molecular geometry and wall affinity. Octane exhibits higher mobility in the confined pore because it is less strongly immobilized near the kerogen-illite wall. By contrast, cyclohexane and 1-methylnaphthalene are more strongly affected by wall-controlled retention, which limits their lateral displacement. This is consistent with their $\Psi_i < 1$ behavior in the energy-based mobilization analysis.

With increasing the temperature-pressure state, the diffusivity of all oil components increases in the neat scCO_2 system. At 408 K and 71 MPa, D_{xy} reaches $2.33 \times 10^{-8} \text{ m}^2/\text{s}$ for octane, $1.34 \times 10^{-8} \text{ m}^2/\text{s}$ for toluene, $5.01 \times 10^{-9} \text{ m}^2/\text{s}$ for dodecane, $1.82 \times 10^{-9} \text{ m}^2/\text{s}$ for 1-methylnaphthalene, and $1.75 \times 10^{-9} \text{ m}^2/\text{s}$ for cyclohexane. These results indicate that higher state points promote the in-plane mobility of the confined oil molecules. This is consistent with the weakening of near-wall enrichment at high temperature-pressure loading, because oil molecules that are less strongly confined to the adsorption layer can more readily migrate within the pore plane. In the presence of the 12-HSA/DMSO formulation, the diffusivity of CO_2 remains high and changes only slightly relative to the neat scCO_2 system. In the thickened system, D_{xy} for CO_2 ranges from 5.32×10^{-8} to $6.37 \times 10^{-8} \text{ m}^2/\text{s}$ over the nine state points. The average CO_2 diffusivity is nearly unchanged, with values of 5.94×10^{-8} and $5.95 \times 10^{-8} \text{ m}^2/\text{s}$ in the thickened and neat system, respectively, corresponding to a difference of less than 1%. This indicates that, although the 12-HSA/DMSO formulation greatly increases the dynamic viscosity of the CO_2 -rich phase, CO_2 itself still retains strong in-plane molecular mobility in the slit pore. In other words, the thickened formulation provides a mobility control effect without significantly suppressing the pore-scale migration of CO_2 .

The oil components, however, show a clear reduction in diffusivity in the presence of the 12-HSA/DMSO formulation. At 328 K and 15 MPa, this reduction is observed for all oil components: D_{xy} decreases from 1.14×10^{-8} to $6.05 \times 10^{-9} \text{ m}^2/\text{s}$ for octane, from 3.43×10^{-9} to 1.55×10^{-9}

m^2/s for toluene, from 1.37×10^{-9} to $6.05 \times 10^{-10} \text{ m}^2/\text{s}$ for dodecane, from 3.45×10^{-10} to $1.39 \times 10^{-10} \text{ m}^2/\text{s}$ for cyclohexane, and from 4.60×10^{-10} to $1.32 \times 10^{-10} \text{ m}^2/\text{s}$ for 1-methylnaphthalene. Overall, at the lowest temperature-pressure state point, D_{xy} values of the oil components are reduced by approximately 47%–71% after thickening, depending on molecular structure.

Averaged over all nine state points, the 12-HSA/DMSO formulation reduces D_{xy} by approximately 29% for octane, 36% for toluene, 40% for cyclohexane, 40% for 1-methylnaphthalene, and 41% for dodecane. This reduction reflects the increased resistance to molecular motion in the thickened CO_2 -rich phase and the stronger interfacial structuring induced by DMSO and 12-HSA. The effect is more pronounced for components with larger molecular size or stronger wall retention, such as dodecane, cyclohexane, and 1-methylnaphthalene, than for octane. This agrees with the near-wall retention analysis, which shows that these molecules are more strongly affected by the wall environment and the additive-modified interface. The reduction in oil diffusivity becomes less severe at high temperature-pressure state points. For example, at 408 K and 71 MPa, D_{xy} for octane decreases from 2.33×10^{-8} in the neat system to $1.90 \times 10^{-8} \text{ m}^2/\text{s}$ in the thickened system, corresponding to an approximately 18% reduction. For toluene, D_{xy} decreases only slightly from 1.34×10^{-8} to $1.25 \times 10^{-8} \text{ m}^2/\text{s}$, while D_{xy} for cyclohexane decreases from 1.75×10^{-9} to $1.60 \times 10^{-9} \text{ m}^2/\text{s}$. At high state points, the enhanced thermal motion and increased CO_2 density/loading promote molecular exchange within the pore, even in the presence of the thickeners.

The diffusivity trends are broadly consistent with the interaction energy and mobilization tendency results, while also reflecting the role of molecular size and geometry. Octane, with $\Psi_i > 1$, remains the most mobile oil component in both neat and thickened systems. Cyclohexane and 1-methylnaphthalene, whose Ψ_i values remain below unity, exhibit the lowest diffusivities, confirming that strong wall-controlled retention limits their in-plane motion. Toluene shows an intermediate behavior: Its diffusivity increases strongly with increasing state point, and its Ψ_i value ap-

proaches unity in the thickened system at high temperature-pressure loading. Although dodecane has $\Psi_i > 1$, its diffusivity is lower than that of toluene, indicating that molecular size also imposes transport resistance. These results show that confined oil mobility is governed by the combined effects of CO₂-assisted mobilization, wall-controlled retention, molecular size, and molecular geometry.

3.6 Molecular mechanism and implications for thickened CO₂ in shale nanopores

The results show that the 12-HSA/DMSO-thickened CO₂ system does not uniformly detach shale oil molecules from the kerogen-illite surface. Its effect is better described as a component-selective interfacial redistribution process controlled by the combined influence of viscosity enhancement, additive partitioning, wall-fluid interactions, and molecular mobility. The 12-HSA/DMSO formulation provides the rheological basis for mobility control. Both Green-Kubo and Einstein-Helfand calculations show that the viscosity of the thickened CO₂-rich phase increases by approximately 50-60-fold compared with pure CO₂. Visual-cell observations further confirm the formation of a clear CO₂-rich phase under high-pressure conditions, except at 328 K and 15 MPa, where poor apparent compatibility is observed. The confined pore simulations show, however, that viscosity enhancement accounts for only part of the mechanism. DMSO and 12-HSA also accumulate strongly near the kerogen-illite walls, forming additive-rich interfacial regions instead of being uniformly distributed throughout the pore. This interfacial localization changes the adsorption environment of shale oil components. In the neat scCO₂ system, oil molecules mainly compete with CO₂ for accessible adsorption sites on the pore walls. After DMSO and 12-HSA are added, the additive-rich near-wall layer partly screens direct oil-wall contact and reorganizes the local interaction network. As a result, near-wall retention decreases most clearly for dodecane, and wall enrichment also weakens for 1-methylnaphthalene. Toluene and cyclohexane do not show the same consistent decrease in retention. This means that the thickened formulation causes selective oil redistribution, rather than complete detachment of all oil molecules from the pore surface.

The interaction energy analysis supports this interpretation. In the thickened system, the direct CO₂-oil interaction becomes slightly weaker, whereas the wall-oil interaction weakens more strongly. The relative balance therefore shifts from wall-controlled retention toward CO₂-assisted mobilization. This trend is captured by the energy-based mobilization tendency index, Ψ_i . Octane and dodecane show favorable CO₂-assisted mobilization tendencies, while cyclohexane and 1-methylnaphthalene remain mainly controlled by wall retention. The improved mobilization therefore does not arise from stronger direct CO₂-oil attraction. It is mainly caused by additive-assisted interfacial restructuring, which weakens wall-oil adhesion.

The diffusion behavior further reveals the trade-off introduced by thickening. After adding 12-HSA/DMSO formulation, the in-plane diffusion coefficients of shale oil components

decrease, especially at low and intermediate state points. This agrees with the increased viscosity and stronger interfacial ordering of the confined fluid. CO₂, by contrast, remains the most mobile species in the pore, and its in-plane diffusion coefficient changes only slightly. The thickened formulation therefore improves mobility control without substantially suppressing CO₂ mobility within the nanopore space.

Based on these observations, the molecular mechanism of the 12-HSA/DMSO thickener in kerogen-illite nanopores can be described as a coupled rheology-interface process. The formulation increases the viscosity of the CO₂-rich phase, promotes additive enrichment at the wall-fluid interface, weakens wall-oil adhesion, and selectively improves CO₂-assisted oil mobilization while preserving high CO₂ mobility. This interpretation is more physically meaningful than describing the process as a simple complete-displacement process. It also suggests that the design of CO₂ thickeners for shale nanopores should consider not only bulk viscosity enhancement but also additive partitioning and the regulation of wall-oil interactions at organic-mineral interfaces.

4. Conclusions

This study investigated the molecular behavior of CO₂ thickened with 12-HSA and DMSO in mixed-wet kerogen-illite slit nanopores using high-pressure visual observations and molecular dynamics simulations. The following conclusions can be drawn.

- 1) The 12-HSA/DMSO formulation provides substantial CO₂ thickening. Both Green-Kubo and Einstein-Helfand viscosity calculations show the viscosity of the CO₂-rich phase is approximately 50-60 times higher than that of neat scCO₂. Visual cell observations further confirm the formation of stable CO₂-rich phases under elevated pressure conditions, although compatibility was limited at 328 K and 15 MPa. These results indicate that viscosity enhancement and phase compatibility provide the rheological basis for CO₂ mobility control and are favorable for improving sweep efficiency.
- 2) The thickened formulation modifies the wall-fluid interfacial environment rather than acting only as a bulk viscosity modifier. DMSO and 12-HSA preferentially accumulate near the kerogen-illite walls, while CO₂ remains broadly distributed in the pore. Under most reservoir-relevant state points, the near-wall retained CO₂ fraction is lower in the thickened system than in neat scCO₂.
- 3) The effect of the 12-HSA/DMSO-thickened CO₂ system on shale-oil retention is component-specific. Near-wall retention decreases most clearly for dodecane, and wall enrichment also weakens for 1-methylnaphthalene. In contrast, toluene and cyclohexane show more complex responses, indicating that the thickened formulation promotes component-dependent interfacial redistribution rather than uniform removal of all oil components from the pore wall.
- 4) Interaction-energy and diffusion analyses show that the main molecular mechanism is additive-assisted weakening of wall-oil adhesion. Although direct CO₂-oil at-

traction became slightly weaker after thickening, wall-oil adhesion weakens more strongly, thereby increasing the energy-based oil-mobilization tendency index, Ψ_i , for all oil components. This suggests that near-wall retained oil becomes less controlled by wall adhesion and more accessible to CO₂-assisted mobilization. The thickened system reduced oil-component diffusivity but preserved high in-plane CO₂ mobility, suggesting that the formulation can improve mobility control while maintaining CO₂ transport/mobility within the nanopore.

Taken together, these results show that the 12-HSA/DMSO-thickened CO₂ system may improve shale-oil recovery through two coupled routes: Bulk viscosity, which improves mobility control and sweep efficiency, and additive-induced interfacial regulation, which weakens wall-oil adhesion and contributes to microscopic oil mobilization. The present simulations describe equilibrium molecular redistribution in an idealized slit nanopore rather than a dynamic displacement process. Future work should connect these molecular-scale mechanisms with pore-network and continuum-scale models to evaluate their implications for shale oil recovery and CO₂ storage under realistic reservoir conditions.

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Supplementary file

<https://doi.org/10.46690/ager.2026.08.04>

Conflicts of interest

The authors declare no competing interest.

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