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Role of interfacial tension on wettability-controlled fluid displacement in porous rock: A capillary-dominated flow and how to control it

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Abstract:
Oil displacement by spontaneous imbibition is a capillary-governed process, in which wettability controls fluid displacement direction. Capillarity is a driving force to enhance oil displacement in water-wet system, while in oil-wet system capillarity is a resisting one. To promote oil displacement, the former requires high capillarity, but the latter opposes. Such requisites are hypothesized to be alternatively achieved by manipulating an oil-water interfacial tension, without altering wetting character. In this study, spontaneous imbibition was conducted with a set of specifically designed imbibing fluids. Brines at different valencies were meticulously selected to attain desired wettabilities: monovalent brine establishes a water-wetting while divalent brine provides an oil-wet characteristics. A non-ionic surfactant, Triton X-100, was intentionally chosen to solely reduce interfacial tension, with negligible change in wettability. By mixing each brine with the surfactant, high-interfacial tension and low-interfacial tension imbibing fluids at the same wettability for the two wetting regions were obtained, and hence the hypothesis can be examined. For water-wet system, reduced interfacial tension attributed to a weakened driving capillary force to oil displacement, and hence lower oil displaced. On the contrary in oil-wet system, reduction in resisting capillary force as contributed from a reduced interfacial tension displaced greater oil. The results demonstrate how the capillary-driven fluid displacement can be manipulated by the interfacial tension change only, without a challenge of altering wettability. With results obtained from both wetting regions, a correlation between capillarity and ultimate oil displacement was also observed.

1. Introduction

One of multiphase flow mechanisms in porous media is spontaneous imbibition, which is essential to fluid displacement applications. Imbibition phenomenon has been considered as a mechanism that principally attributes to immiscible fluid displacement in tight porous media, e.g., oil production from low-permeability reservoir (Hamida and Babadagli, 2007). Owing to pore sizes at micron and submicron in tight rock, fluid displacement is mostly dominated by capillarity (Gu et al., 2017; Cai et al., 2021; Wang et al., 2023) which can be quantified by capillary pressure (P_c) that either restrains or imbibes fluid into those small-pore networks. Apart from the nature of pore configuration, the P_c also depends on

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wettability and fluid-fluid interfacial tension (σ), as expressed by (Thomas, 1805; Blunt, 2017):

$$P_c = \frac{2\sigma \cos\theta}{r} \tag{1}$$

where r is the average pore radius of porous rock and θ is the three-phase contact angle, which characterizes the wettability and defined through wetting phase. It is important to note that number "2" in Eq. (1) refers to "circular" cross-section characteristics of pore configuration, where other pore geometry differs (Blunt, 2017). It has been well concluded and experimentally demonstrated that P_c is a wettability-controlled factor (Sukee et al., 2022a), see Eq. (1), and hence also the spontaneous imbibition process. This emphasizes a crucial role of wettability: positive P_c as of water-wet ($\theta < 90°$) and negative P_c as of oil-wet ($\theta > 90°$). Our previous experimental study has revealed that at a given "capillary-dominated" flow (i.e., spontaneous imbibition) positive P_c improves oil displacement, while negative P_c opposes the process. P_c was also shown to be influenced by change in σ, through previous works conducted with simultaneous changes on θ and σ (Massarweh and Abushaikha, 2020; Deng et al., 2021; Liu et al., 2022; Sukee et al., 2022b) and yet a decoupled role of σ is to be investigated.

Many efforts focus on changing wettability toward strongly water-wet (Jarrahian et al., 2012; Hou et al., 2020; Tu and Sheng, 2020; Ekechukwu et al., 2021) with aim to secure a strong positive capillarity to displace more "trapped oil". Chemical additives, namely surfactants, alkalis, nanoparticles, and low-salinity brines, are typically considered as displacing fluids, with anticipation to reverse oil-wet reservoir to be water-wet. Anionic surfactants have a great potential to convert oil-wet to be water-wet in sandstone rock due to strengthening electrostatic repulsion between the oil-water and solid-water interfaces (Standnes and Austad, 2000; Jarrahian et al., 2012; Tangparitkul et al., 2018). Nanofluids have been reported to improve submicroscopic oil displacement due to structural disjoining pressure, hence water-wet attained (Zhang et al., 2014; Tangparitkul et al., 2018). Low-salinity brines or "ion-tuned" fluids are also great displacing fluids to change wettability toward water-wet since some salt cations (e.g., Na^+) effectively hydrate and lead to construct the hydration forces between the oil-water and solid-water interfaces (Tangparitkul et al., 2021; Sukee et al., 2022a).

Some studies also considered an approach for σ reduction as a mechanism to enhance fluid displacement (Sheng, 2013; Xu et al., 2019; Saira and Le-Hussain, 2021; Deng et al., 2023b; Li et al., 2023). Since petroleum reservoirs are typically oil-wet, reduced σ results in less negative capillary allowing more "trapped oil" to be displaced. Surfactants are very effective chemicals to reduce the σ by adsorption at the oil-water interface (Mohapatra et al., 2014; Hosseininoosheri et al., 2016), leading to a weakening of negative capillary that retains the trapped oil. However, significantly reduced σ could also lead to change in wettability (θ) due to the interfacial energies of the three-phase (oil-water-rock) rebalancing, as described by the Thomas's law (Thomas, 1805). Such changes effectively lead to a coupled contribution from both σ reduction and wettability alteration, as discussed above, which appear to not always favor the fluid displacement (Chen and Mohanty, 2015; Xu et al., 2019; Deng et al., 2023a).

Previous research with capillary-dominated oil displacement normally considered a contribution from simultaneous changes in wettability and σ, some of which are summarized in Table 1. By examining different chemical additives or even the mixtures thereof, incremental oil recovery could be justified with the observed changes in θ and σ, though a controversy revealed. Sukee et al. (2022a) observed opposite results of oil recovery using different brines, one of which increased but another decreased, although both θ and σ decreased in the same manner. When compared to other work (Sukee et al., 2022b), attaining the same degree of wettability (oil-wet) also found contradict results on oil recovery, with a quarter of difference in σ reduction. This reflects an insufficient wettability-dependence for justification of resulted oil displacement, and yet implies the understanding on σ involvement and its sole investigation.

In the current study, we aim to systematically examine an influence of σ on the capillary-dominated fluid displacement using spontaneous imbibition, without an influence of wettability alteration. To do this, the oil-water-rock wettability is fixed unchanged while the oil-water σ is not. Such conditions can be achieved by experimenting with specially designed imbibing fluids (i.e., mixtures of brine and surfactant, described below). This allows both positive and negative capillarities to be investigated with two types of σ changes: either decrease or increase, hence the role of σ on wettability-controlled fluid displacement can be elucidated.

2. Materials and experimental methods

2.1 Crude oil and rock samples

Crude oil as an oil phase used throughout the current study was collected from a primary production well at Fang oilfields in Chiang Mai (Thailand). The crude oil was dehydrated and de-gassed before use. The crude oil has density of 854.2 kg/m^3 and viscosity of 18 mPa·s at 50 °C. Chemical compositions of the crude oil notably consist of high wax content (51.0 wt%) with slight asphaltenes (0.05 wt%).

Rock core samples were drilled from sandstone outcrop to 8.5 cm diameter and 15 cm length cylinder, as investigated in our previous study (Sukee et al., 2022a), with reported average pore size of 240 ± 5 µm. Effective porosity of the core samples was determined by liquid saturation method using deionized water. Average porosity is 4.0% which is relatively low, suggesting a capillary control over fluid flow in porous rock.

2.2 Surfactant, brines, and imbibing fluids

Surfactant used in the current study was a non-ionic surfactant Triton X-100 (Labo Chemie, India), with molecular weight of 647 g/mol. A concentration of surfactant solution used in the experiment was prepared at 0.2 mM (about the critical micelle concentration (Yusuf et al., 2021)) to achieve the most reduced interfacial tension and allow a contribution from capillary change distinctly observed. It is noted that the

Table 1. Previous research on oil displacement as contributed by simultaneous changes in wettability and oil-water interfacial tension.

Porous rock	Wettability (θ change (°))	σ change (mN/m)	Change in oil recovery (%) *	Chemical used	References
Sandstone	Oil- to water-wet (118° to 54°)	Increase (0.001 to 0.05)	Increase (3)	KCl brine + SiO_2 nanofluids	Xu et al. (2019)
Sandstone	Oil- to oil-wet (112° to 144°)	Decrease (25 to 0.58)	Decrease (18)	Non-ionic surfactant	Tangirala and Sheng (2019)
Sandstone	Oil- to water-wet (112° to 44°)	Decrease (25 to 0.68)	Increase (9)	Anionic surfactant	Tangirala and Sheng (2019)
Sandstone	Water- to water-wet (20° to 32°)	Decrease (65 to 30)	Increase (33)	NaCl brine	Habibi et al. (2020)
Carbonate	Oil- to water-wet (141° to 32°)	Decrease (20 to 10)	Increase (11)	Alumina nanofluids	Keykhosravi and Simjoo (2020)
Carbonate	Oil- to water-wet (133° to 50°)	Decrease (20 to 3)	Increase (44)	Surfactant	Tu and Sheng (2020)
Carbonate	Oil- to water-wet (123° to 46°)	Decrease (32 to 1.23)	Increase (13)	Anion surfactant	Wang et al. (2020)
Sandstone	Water- to water-wet (22° to 12°)	Decrease (23 to 19)	Increase (10)	Monovalent brines	Zhu et al. (2022)
Sandstone	Water- to water-wet (66° to 44°)	Decrease (36 to 28)	Increase (34)	NaCl brines	Sukee et al. (2022a)
Sandstone	Water- to oil-wet (66° to 131°)	Decrease (36 to 21)	Decrease (20)	$CaCl_2$ brines	Sukee et al. (2022a)
Sandstone	Oil- to oil-wet (171° to 123°)	Decrease (28 to 8)	Increase (27)	Surfactant	Sukee et al. (2022b)

Notes: *Oil recovery compared as contributed from the changes in wettability and interfacial tension reported.

Triton X-100 surfactant was selected intentionally since it does not significantly alter the contact angle of the oil-water-rock system (Li et al., 2020; Sukee et al., 2022b), hence facilitating only effect of the change in the interfacial tension investigated.

Sodium chloride as monovalent salt (NaCl $\geq$ 99.5%, RCI Labscan, Thailand) and calcium chloride as divalent salt ($CaCl_2 \geq 99.5\%$, RCI Labscan, Thailand) were used as received to prepare the brine fluids at 100 mM using deionized water (RCI Labscan, Thailand). Based on our previous observation with the same crude oil-rock-brine system, 100 mM brines secured the wettability system to be water-wet (with NaCl brine; $\theta \sim 32.0°$) and oil-wet (with $CaCl_2$ brine; $\theta \sim 126.9°$) effectively (Sukee et al., 2022a).

To investigate the effect of change in the interfacial tension at each specific wettability on oil displacement, imbibing fluids for spontaneous imbibition experiment were therefore designed into four fluids for the four oil-water-rock characteristics as shown in Table 2.

2.3 Measurements of the oil-water interfacial tension and the three-phase contact angle

The interfacial tension between aqueous solution (i.e., imbibing fluid) and crude oil (σ) was measured by a pendent drop method using an Attension® Theta Optical Tensiometer (TF300-Basic, Biolin Scientific, Finland) at 50 °C. An oil droplet of $\sim$ 10 µL was dispensed at the tip of a stainless inverted needle (gauge 22) using a micro-syringe pump (C201, Biolin Scientific, Finland). The shape of oil droplet was captured at 3.3 fps until no detectable change was observed ($\sim$ 3,600 s), where the steady-state σ was defined and reported.

The three-phase oil-water-rock contact angle (θ) was also measured using An Attension® Theta Optical Tensiometer (TF300-Basic, Biolin Scientific, Finland) at 50 °C by an inverted sessile drop method on aged thin slice rock, with details described in our previous study (Sukee et al., 2022a). The cleaned thin slice of rock was aged with formation water and then crude oil as same as the core samples used for the imbibition experiment (described in the next section). Imbibing fluid was pre-heated to 50 °C and added into the thermal cell to submerge the thin slice. An oil droplet of $\sim$ 5 µL was carefully deposited underneath the thin slice by means of an inverted needle attached to a micro-syringe, and the oil-water-rock contact angle was formed. The contact angle was recorded at 3.3 fps until the steady-state contact angle was attained ($\sim$ 3,600 s). The three-phase contact angle was measured through the imbibing fluid phase from image analysis via the OneAttention software. The average contact angle from the left and right is reported.

Table 2. Imbibing fluids used for spontaneous imbibition experiment in the current study.

Imbibing fluids	Desired oil-water-rock characteristics	
	Interfacial tension	Wettability
100 mM NaCl	Relatively high	Water-wet
100 mM $CaCl_2$	Relatively high	Oil-wet
100 mM NaCl + 0.2 mM Triton X-100	Relatively low	Water-wet
100 mM $CaCl_2$ + 0.2 mM Triton X-100	Relatively low	Oil-wet

2.4 Oil displacement by spontaneous imbibition

To investigate an immiscible displacement between crude oil and the imbibing fluids (listed in Table 2), spontaneous imbibition process which is governed by capillarity was experimented. Experimental procedure conducted in the current study is based on our previous work (Sukee et al., 2022a), which is briefly described hereafter.

The rock core samples were prepared before each imbibition experiment by cleaning with formation water for 2 days by means of liquid saturation method. Thereafter, the samples were saturated with crude oil and aged for 5 days at 50 °C, where an initial oil saturation was defined. Due to the aging process, an initial wettability of the oil-water-rock system was established to be weakly water-wet, with the measured three-phase contact angle of 66.0° .

An oil-saturated core sample was placed in the Amott cell chamber, then the cell was filled with imbibing fluid immediately to initiate a spontaneous imbibition process. The core sample was hence submerged in an imbibing fluid. Displaced oil (or produced oil) from the core sample was measured periodically at graduated cylinder scale attached to the Amott cell. With a 1-cm-height stainless-wire truss partitioning between the core bottom-end and the cell bed, fluids are allowed to flow upward from bottom-end to configurating a co-current flow direction (Sukee et al., 2022a). The imbibition experiment was conducted in an oven at an operating temperature of 50 °C.

3. Results and discussion

3.1 Crude oil-brine interfacial tension and the three-phase contact angle

Desired oil-water-rock characteristics (i.e., σ and θ) as manipulated by each imbibing fluid (Table 2) were successfully achieved, confirmed by the measured both interfacial properties as reported in Fig. 1 and discussed below.

Fig. 1(a) reports the σ measured against all imbibing fluids. Considering the pair of NaCl and $CaCl_2$ brines (without surfactant added), the measured were relatively high at roughly 33 mN/m. With surfactant included, the σ of the two fluids were reduced to be relatively low at approximately 4 mN/m, $\sim$ 88% reduction compared to the surfactant-free fluids. Such a σ reduction was a contribution from additional (Triton X-100) surfactant adsorption at the crude oil-water interface, which normally screens the brine-induced adsorption of indigenous surface-active species (e.g., asphaltenes and naphthenic acids) (Chávez-Miyauchi et al., 2016a; Ameri et al., 2018).

Comparing between the two brines without surfactant at equivalent concentration (100 mM), slightly lower σ (30.9 mN/m) was obtained in $CaCl_2$ brine than that of NaCl brine (35.0 mN/m), a result of greater $CaCl_2$ brine-induced adsorption of indigenous surface-active species at the oil-water interface as observed in our previous study (Tangparitkul et al., 2021). Such a stronger neutralization effect is due to strongly hydrated Ca-ion and of higher valency than that of Na-ion (Wu et al., 2016; Taylor and Chu, 2018; Tangparitkul et al., 2021).

Steady-state contact angles of all imbibing fluids are shown in Fig. 1(b), illustrating a distinctive dependence on brine valency. Either with or without surfactant added, monovalent NaCl brines clearly secured the oil-water-rock system of water-wetting ($\theta \sim 44°$). Similar to divalent $CaCl_2$ brines, the measured contact angles remained in oil-wet region ($\theta > 90°$), even though a slight reduction ($126.9° \rightarrow 104.6° : \triangle\theta \approx 22°$) was observed when surfactant was added. The resulted θ verify a marginal intervention of Triton X-100 surfactant to alter wettability, but a greater change in the σ, as anticipated (Li et al., 2020; Sukee et al., 2022b).

Influence of brine valency (i.e., emphasized by the non-DLVO hydration forces) on the crude oil-brine-rock wettability has been extensively studied (Tangparitkul et al., 2021; Sukee et al., 2022a), such as in low-salinity enhanced oil recovery (EOR) or ion-engineered waterflooding (Mosallanezhad and Abushaikha, 2021; Saeedi Dehaghani and Ghalamizade Elyaderani, 2021). Highly hydrated cation tends to construct a strongly repulsive disjoining pressure between the oil-water and rock-water interfaces (i.e., increases water film stability), thus displacing oil from substrate and obtaining wettability toward more water-wet. In the current study, initial wettability (66°) was altered primarily based on brine valency at the equivalent brine concentration (100 mM). In NaCl brine systems, the long-range DLVO (van der Waals and electrostatic) forces were screened by the short-range hydration forces resulted from hydrated Na^+ cation (Zhao et al., 2006; Guo and Kovscek, 2019), hence the θ decreased to be $\sim 44°$. However, the θ was found to increase in the $CaCl_2$ brine system owing to divalent ion bridging of indigenous surface-active species (i.e., anionic naphthenic acids) adsorbed on rock substrate via divalent Ca^{2+} cation, thus the interaction is dominated by a long-range attractive hydrophobic forces between the crude oil-brine and substrate-brine interfaces (Ducker et al., 1994;

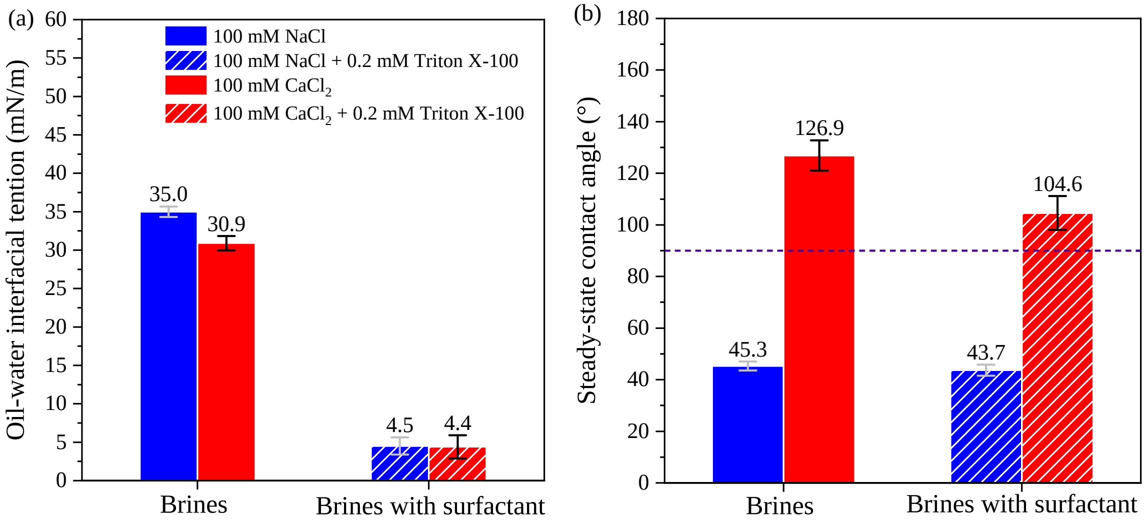

Fig. 1. Interfacial characteristics of each crude oil-water-rock system as obtained from each imbibing fluid: (a) the oil-water interfacial tension and (b) the steady-state contact angle. Dash line in (b) separates wettability regions: water-wetting ($\theta < 90°$) and oil-wetting ($\theta > 90°$). Error bars are standard derivation.

Liu et al., 2005; Zhang et al., 2018).

3.2 Oil displacement results

Dynamic oil displacement by different imbibing fluids is shown as oil recovery in Fig. 2. General observation is that crude oil was recovered or "displaced" by imbibing fluid immediately at great amount (30 h $< t <$ 50 h) after the imbibition test was executed. Oil displacement was thereafter gradually proceeded at later period until negligible oil produced was observed (i.e., the steady state), where ultimate oil displacement is defined ($t \sim$ 150 h), see Fig. 2(c).

To systematically compare a capillary influence of the imbibing fluids, a pair of water-wetting fluids (NaCl brines) are first considered, see Fig. 2(a). Water-wet with high σ (100 mM NaCl) fluid displaced crude oil form rock effectively, with high amount of oil being displaced rapidly at initial period of imbibition, see Fig. 2(b). When incorporated with low σ, water-wet fluid (100 mM NaCl + 0.2 mM Triton X-100) rather diminished its displacing ability, with oil displacement at the steady state reduced greatly by $\sim$ 66% and displacement speed five-fold reduced (Fig. 2(b)), when compared to its counterpart of water-wet with high-σ fluid. This demonstrates a contribution of σ reduction when capillarity is a driving force to fluid displacement (as in this water-wet case), the higher the capillary force the greater the fluid displacement. In other words, water-wet system does not need an σ reduction but rather an σ increase to enhance fluid displacement.

Considering a pair of oil-wetting fluids ($CaCl_2$ brines), much lower oil displacements are observed as shown in Fig. 2(a) since the oil-wet controlled system does not favor fluid displacement in general. Oil-wet with high σ (100 mM $CaCl_2$) fluid barely displaced any oil from rock core, no produced oil observed. When mixed with surfactant (100 mM $CaCl_2$ + 0.2 mM Triton X-100), a relatively low σ attained led to an obvious improvement on oil displacement. The oil-wet with low-σ imbibing fluid yielded $\sim$ 16% oil recovery, with displacement speed similar to that of water-wet with low-σ fluid, see Fig. 2(b). This substantiates a contribution of σ reduction to fluid displacement when capillary system is oil-wet, i.e., a resisting capillary force to fluid displacement. As the oil displacement results revealed, a reduced resisting capillary force, as induced by the decreased σ, promoted oil displacement by weakening an oil-wet hindrance.

It is noted that even attaining the same σ ($\sim$ 4 mN/m, Fig. 1(a)), the oil-wet imbibing fluid (θ = 104.6°) still could not compete with the water-wet system (θ = 43.7°). This stressed that capillary-governed fluid displacement is indeed a "wettability-controlled" process (Cheng et al., 2022).

In addition, surfactant influence on fluid displacement behavior was found to be screened by the brine fluids. Additional imbibition experiment was performed with surfactant-only fluid (0.2 mM Triton X-100) and resulted in terribly less oil displacement (three-fold to seven-fold when compared to the other surfactant-added imbibing fluids, see Fig. S1 in Supplementary Material). This again confirms a wettability-controlled and capillary-driven fluid displacement, even though magnitude of such a "control" can be manipulated by a degree of σ change.

3.3 Fluid displacement mechanisms

With knowing that a capillary-driven immiscible fluid displacement is a wettability-controlled process, conventional chemical enhancement for fluid displacement in porous media (e.g., EOR) is usually achieved by reducing the fluid-fluid σ since wettability of the system typically hinders the displacement. An increasing number of recent research also explored the wettability change by chemical additives (Chávez-Miyauchi et al., 2016b; Massarweh and Abushaikha, 2020; Burgan and Jellah, 2021), with some studies even proposed displacing chemical fluids that could both reduce the σ and

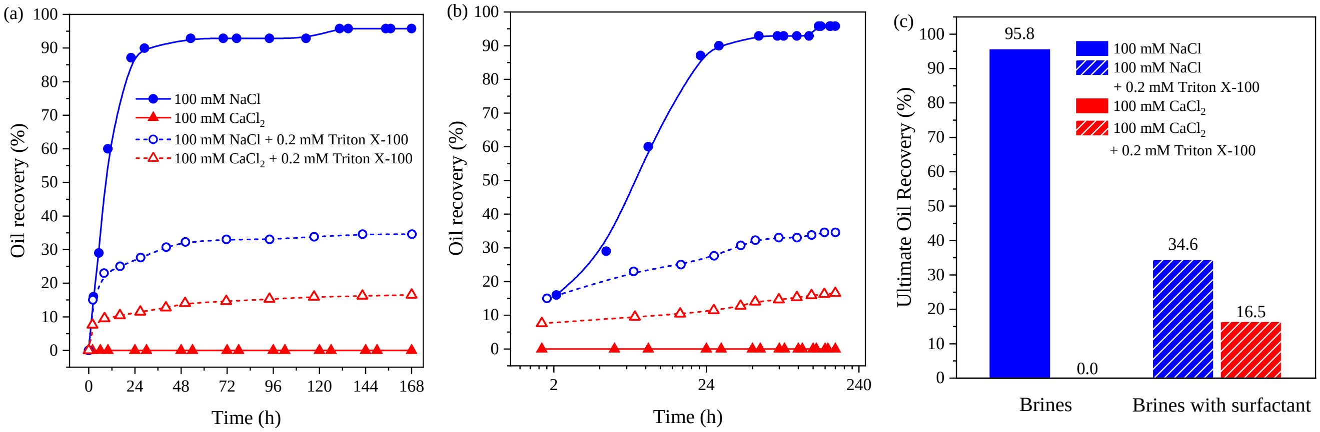

Fig. 2. Oil recovery results from oil displacement experiment as a function of time and various imbibing fluids: (a) comparison among four imbibing fluids with (b) the result re-plotted on semi-log scale and (c) ultimate oil recovery results from each imbibing fluid. For 100 mM CaCl$_2$ fluid, no oil recovery (0.0%) was observed. Lines to guide the eye.

alter wettability simultaneously (Xu et al., 2019; Burgan and Jellah, 2021). Such a simultaneous change to both σ and wettability could diminish fluid displacement if their contributions contradict each other.

Hence, contribution to change in those two factors needs a holistic consideration, which can be assessed by using dimensionless numbers, including capillary number (N_C) and inverse Bond number (N_B^{-1}) (Jacquin and Adler, 1985; Meng et al., 2016; Xu et al., 2019). The capillary number is a viscous to capillary forces ratio:

$$N_C = \frac{\mu V}{\sigma \cos\theta} \tag{2}$$

where μ is the oil viscosity, and V the characteristic fluid velocity (taken to be 1 × 10^{-6} m/s, (Berg and Ott, 2012). The inverse Bond number is defined as a ratio of capillary to gravitational forces:

$$N_B^{-1} = \frac{\sigma \cos\theta}{r \triangle \rho g H} \tag{3}$$

where $\triangle\rho$ is the density difference between crude oil and water phases, g the gravity acceleration constant, and H the core length characteristic taken to be the core height.

The dimensionless numbers (N_C and N_B^{-1}) and P_c (Eq. (1)) for each imbibition experiment were calculated and reported in Table 3. It is obvious that all resulted N_{Ca} were substantially low ($< 5.5 \times 10^{-6}$), indicating a dominant capillary-control rather than a viscous advection (Austad et al., 1998) as previously discussed. The other two quantities (N_B^{-1} and P_c) however show a dramatic variation in different imbibing fluids. Negative N_B^{-1} and P_c reflect a resisting capillarity due to oil-wet system (i.e., $\theta > 90°$, see Fig. 1(b)), and vice versa for being positive of a driving capillarity.

With same fluid-rock system studied by spontaneous imbibition in our previous work (Sukee et al., 2022a), the displacement results were found to depend on brine valency and concentration (as of imbibing fluid) which is contributed from changes in σ and θ, though no surfactant was used to reduce the σ significantly. To better illustrate the fluid displacement mechanism, the N_B^{-1} and P_c values from both previous and current studies were plotted against residual oil saturation (i.e., non-displaced or "trapped" oil: S_{or}) to correlate their relations, as shown in Fig. 3.

Residual oil saturation was found to be inversely proportional to both P_c (Fig. 3(a)) and N_B^{-1} (Fig. 3(b)). Considering P_c, negative values of oil-wet system are weakened by decreasing in σ, which leads to improving on fluid displacement (less residual oil saturation). While in water-wet system with positive P_c, higher σ is evidenced to displace more fluid (higher oil displacement or lesser residual oil). For example, when compares 100 mM NaCl fluid to 100 mM NaCl + 0.2 mM Triton X-100 fluid (Fig. 3(a)), strong reduction in σ decreased P_c from 494.8 to 54.2 Pa and hence resulted in much less fluid displacement, see Table 3.

General observation of N_B^{-1} is similar to that of P_c. One distinctive different to note is that much reduced σ led to relatively low absolute N_B^{-1} values ($\left|N_B^{-1}\right| < 1$) of which the capillary term ($\sigma\cos\theta$) is screened by the gravitational contribution ($r \triangle \rho g H$), see Eq. (3). In this range of low $\left|N_B^{-1}\right|$, the gravitational force likely plays a part in the fluid displacement process in addition to the capillarity (Xu et al., 2019) (shaded strip in Fig. 3(b)).

With good correlations between residual oil saturation (S_{or}) and (i) P_c and (ii) N_B^{-1} observed in Fig. 3, data fitting to semi-empirical function was performed and resulted as follows:

$$S_{or} = -0.0001(P_c)^2 - 0.0888(P_c) + 81.5810 \tag{4}$$

$$\begin{aligned} S_{or} = & -1.4666(N_B^{-1})^3 - 3.3009(N_B^{-1})^2 \\ & - 17.06(N_B^{-1}) + 78.289 \end{aligned} \tag{5}$$

The P_c correlation is fitted with quadratic function where R^2 is 0.91, while the N_B^{-1} correlation is a third-order polynomial function with R^2 of 0.88.

4. Conclusions

Capillary-governed oil displacement has been examined via spontaneous imbibition experiment using specially designed

Table 3. Measured crude oil-water-rock interfacial characteristics (σ and θ), dimensionless numbers (N_C and N_B^{-1}), and P_c for each imbibing fluid with ultimate oil displacement results.

Imbibing fluids	σ (mN/m)	θ (°)	N_C (-)	N_B^{-1} (-)	P_c (Pa)	Ultimate oil recovery (%)
100 mM NaCl	35.0	32.0	6.1×10^{-7}	1.55	494.8	95.8
100 mM $CaCl_2$	30.9	126.9	-9.7×10^{-7}	-1.41	-309.4	0.0
100 mM NaCl + 0.2 mM Triton X-100	4.5	43.7	5.5×10^{-6}	0.22	54.2	34.6
100 mM $CaCl_2$ + 0.2 mM Triton X-100	4.4	104.6	-1.6×10^{-6}	-0.08	-18.5	16.5

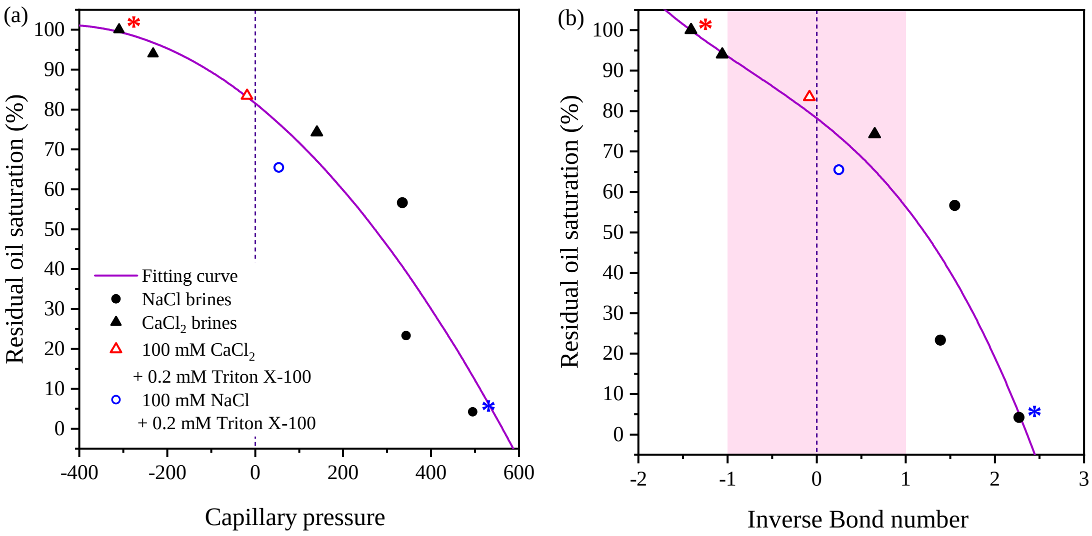

Fig. 3. Correlations between residual oil saturation and: (a) capillary pressure and (b) inverse Bond number. Data plotted includes the results from the current imbibing fluids and other brine fluids from the previous study by Sukee et al. (2022a). Solid symbols with star indicate 100 mM brines (no surfactant-added) for comparison with the equivalent brines but surfactant-added (hollow symbols). Vertical dash lines separate negative and positive regions. Shaded strip in (b) indicates low inverse Bond number region (-1 to +1), where gravitational force likely comes into play.

imbibing fluids (i.e., mixtures of brine and surfactant) to allow "decoupled" contributions from wettability and oil-water interfacial tension investigated since both are likely attribute to capillarity simultaneously. For the water-wet system, reduction in σ tremendously demoted oil displacement by 61.3% as a result of a reducing capillary "driving force". An opposite result was however found in the oil-wet system, where the same degree of σ reduction has improved oil displacement by 16.5% owing to a reducing capillary "resistance". At both regimes of wetting, the σ has demonstrated its vital role in controlling fluid displacement-either elevates or obstructs it.

With the findings summarized above, it is obvious that wettability does govern the fluid displacement "direction"-either driving (water-wet) or resisting (oil-wet) capillarity-but the σ could control the displacement "magnitude" of both directions. As hypothesized, such directions favor different σ magnitudes and hence any change in the σ would directly modify the capillarity at some degree, assuming no wettability alteration. This hypothesis has been demonstrated and proven in the current study. A novel concept of such a σ role on "controlling" fluid displacement is present. High σ is required for a water-wet system, while low σ is needed in an oil-wet one, if improving fluid displacement (e.g., EOR) is anticipated.

Controversy in some studies (Tangirala and Sheng, 2019; Xu et al., 2019) was likely due to an insufficient assessment on controlling mechanisms, particularly a capillarity contribution. Both interfacial phenomena have normally been considered by rough and qualitative data, whilst the current work has rather decoupled and focused on an individual σ role quantitatively-that could solely and even robustly govern the fluid displacement. With equivalent degree of wettability attained, contradict results from the studies by Sukee et al. (2022b) are found, with the latter obtained incremental oil but the former did not. This was likely due to a screening of σ contribution over wettability since the latter work has a capillary resisting force less than the former, thus greater oil displacement obtained. Oil recovery results from a recent study by Deng et al. (2023b) using various surfactant mixtures can be further exemplified with rigorous explanation by our current findings. When compared three surfactant fluids that secured water-wetting ($\theta = 30° - 60°$; the capillary is all driving force), the greater the reduction in σ (4 mN/m $\rightarrow$ 0.63 mN/m $\rightarrow$ 0.01 mN/m) led to the lower the oil recovery (24% $\rightarrow$ 13% $\rightarrow$ 10%), echoing a vital role of σ over the wettability alteration on the oil displacement.

Toward more efficient fluid displacement in subsurface reservoir (Krevor et al., 2023; Tangparitkul et al., 2023), design to change interfacial properties, namely wettability and fluid-fluid interfacial tension, has to be holistically considered but not vaguely. Simultaneous changes in both properties may not result in the best fluid displacement, but could rather obstruct the fluid flow. Future work should investigate more on additives (e.g., chemicals) to displacing fluid that could function selectively as anticipated. Some porous reservoirs might simply need σ change without wettability alteration to the best improved fluid displacement. For example, petroleum reservoirs are typically oil-wet, where only reduction in σ is simply required for EOR rather than coupled changes in wettability and σ. On the contrary in CO_2 geological storage application, typical pristine saline formations, mostly strong water-wet (Bachu, 2015; Ringrose et al., 2021), would require a lower σ to weaken driving capillary force to the wetting (water) phase, without wettability alteration. For underground hydrogen storage, even more complex consideration on the two properties is expected since hydrogen as a non-wetting phase has to be injected into and redrawn from storing reservoir cyclically (Pan et al., 2021; Zivar et al., 2021), thus a great knowledge gap for further research.

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Supplementary file

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Conflict of interest

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

References

Ameri, A., Esmaeilzadeh, F., Mowla, D. Effect of low-salinity water on asphaltene precipitation. Journal of Dispersion Science and Technology, 2018, 39(7): 1031-1039.

Austad, T., Matre, B., Milter, J., et al. Chemical flooding of oil reservoirs 8. Spontaneous oil expulsion from oil- and water-wet low permeable chalk material by imbibition of aqueous surfactant solutions. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 1998, 137(1-3): 117-129.

Bachu, S. Review of CO_2 storage efficiency in deep saline aquifers. International Journal of Greenhouse Gas Control, 2015, 40: 188-202.

Berg, S., Ott, H. Stability of CO_2-brine immiscible displacement. International Journal of Greenhouse Gas Control, 2012, 11: 188-203.

Blunt, M. J. Multiphase Flow in Permeable Media: A Pore-Scale Perspective. Cambridge, UK, Cambridge University Press, 2017.

Burgan, A., Jellah, A. Effect of chemical additives on wettability alteration during chemical EOR: A review. 2021.

Cai, J., Jin, T., Kou, J., et al. Lucas-washburn equation-based modeling of capillary-driven flow in porous systems. Langmuir, 2021, 37(5): 1623-1636.

Chávez-Miyauchi, T. E., Firoozabadi, A., Fuller, G. Nonmonotonic elasticity of the crude oil-brine interface in relation to improved oil recovery. Langmuir, 2016a, 32(9): 2192-2198.

Chávez-Miyauchi, T. E., Firoozabadi, A., Fuller, G. G. Nonmonotonic elasticity of the crude oil-brine interface in relation to improved oil recovery. Langmuir, 2016b, 32(9): 2192-2198.

Chen, P., Mohanty, K. K. Surfactant-enhanced oil recovery from fractured oil-wet carbonates: Effects of low IFT and wettability alteration. Paper SPE 173797 Presented at the SPE International Symposium on Oilfield Chemistry, Texas, USA, 13-15 April, 2015.

Cheng, Z., Zhang, W., Ning, Z., et al. Wettability control on imbibition behavior of oil and water in porous media. Physics of Fluids, 2022, 34: 076603.

Deng, X., Kamal, M. S., Patil, S., et al. Investigation of the coupled effect of IFT reduction and wettability alteration for oil recovery: New insights. ACS Omega, 2023a, 8(13): 12069-12078.

Deng, X., Patil, S., Al Shehri, D., et al. IFT reduction negatively impacts oil recovery when wettability alteration happens. Paper SPE 214178 Presented at the Gas & Oil Technology Showcase and Conference, Dubai, UAE, 13-15 March, 2023b.

Deng, X., Tariq, Z., Murtaza, M., et al. Relative contribution of wettability alteration and interfacial tension reduction in EOR: A critical review. Journal of Molecular Liquids, 2021, 325: 115175.

Ducker, W. A., Xu, Z., Clarke, D. R., et al. Forces between alumina surfaces in salt solutions: Non-DLVO eorces and the implications for colloidal processing. Journal of the American Ceramic Society, 1994, 77(2): 437-443.

Ekechukwu, G. K., Khishvand, M., Kuang, W., et al. The effect of wettability on waterflood oil recovery in carbonate rock samples: A systematic multi-scale experimental investigation. Transport in Porous Media, 2021, 138(2): 369-400.

Gu, X., Pu, C., Huang, H., et al. Micro-influencing mechanism of permeability on spontaneous imbibition recovery for tight sandstone reservoirs. Petroleum Exploration and Development, 2017, 44(6): 1003-1009.

Guo, H., Kovscek, A. R. Investigation of the effects of ions on short-range non-DLVO forces at the calcite/brine interface and implications for low salinity oil-recovery processes. Journal of Colloid and Interface Science, 2019, 552: 295-311.

Habibi, A., Esparza, Y., Boluk, Y., et al. Enhancing imbibition oil recovery from tight rocks by mixing nonionic surfactants. Energy & Fuels, 2020, 34(10): 12301-12313.

Hamida, T., Babadagli, T. Immiscible displacement of oil by water in consolidated porous media due to capillary imbibition under ultrasonic waves. The Journal of the Acoustical Society of America, 2007, 122(3): 1539-1555.

Hosseininoosheri, P., Lashgari, H. R., Sepehrnoori, K. A novel method to model and characterize in-situ bio-surfactant production in microbial enhanced oil recovery. Fuel, 2016, 183: 501-511.

Hou, B., Jia, R., Fu, M., et al. Mechanism of synergistically changing wettability of an oil-wet sandstone surface by a novel nanoactive fluid. Energy & Fuels, 2020, 34(6): 6871-6878.

Jacquin, C., Adler, P. M. The fractal dimension of a gas-liquid interface in a porous medium. Journal of Colloid and Interface Science, 1985, 107(2): 405-417.

Jarrahian, K., Seiedi, O., Sheykhan, M., et al. Wettability alteration of carbonate rocks by surfactants: A mechanistic study. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2012, 410: 1-10.

Keykhosravi, A., Simjoo, M. Enhancement of capillary imbibition by Gamma-Alumina nanoparticles in carbonate rocks: Underlying mechanisms and scaling analysis. Journal of Petroleum Science and Engineering, 2020, 187: 106802.

Krevor, S., de Coninck, H., Gasda, S. E., et al. Subsurface carbon dioxide and hydrogen storage for a sustainable energy future. Nature Reviews Earth & Environment, 2023, 4: 102-118.

Li, R., Manica, R., Lu, Y., et al. Role of surfactants in spontaneous displacement of high viscosity oil droplets from solid surfaces in aqueous solutions. Journal of Colloid and Interface Science, 2020, 579: 898-908.

Li, S., Ye, Z., Wang, J., Tang, L., Lai, N. Effects of fracturing fluid composition and other factors on improving the oil imbibition recovery of shale reservoir. Capillarity, 2023, 9(3): 45-54.

Liu, X., Kang, Y., Yan, L., et al. Implication of interfacial tension reduction and wettability alteration by surfactant on enhanced oil recovery in tight oil reservoirs. Energy Reports, 2022, 8: 13672-13681.

Liu, X., Kang, Y., Yan, L., et al. Interaction forces in bitumen extraction from oil sands. Journal of Colloid and Interface Science, 2005, 287(2): 507-520.

Massarweh, O., Abushaikha, A. S. The use of surfactants in enhanced oil recovery: A review of recent advances. Energy Reports, 2020, 6: 3150-3178.

Meng, Q., Liu, H., Wang, J., et al. Effect of gravity on spontaneous imbibition from cores with two ends open in the frontal flow period. Journal of Petroleum Science and Engineering, 2016, 141: 16-23.

Mohapatra, S. S., Jha, J. M., Srinath, K., et al. Enhancement of cooling rate for a hot steel plate using air-atomized spray with surfactant-added water. Experimental Heat Transfer, 2014, 27(1): 72-90.

Mosallanezhad, A., Kalantariasl, A. Performance prediction of ion-engineered water injection (EWI) in chalk reservoirs using Response Surface Methodology (RSM). Energy Reports, 2021, 7: 2916-2929.

Pan, B., Yin, X., Ju, Y., et al. Underground hydrogen storage: Influencing parameters and future outlook. Advances in Colloid and Interface Science, 2021, 294: 102473.

Ringrose, P. S., Furre, A. K., Gilfillan, S. M. V, Krevor, S., et al. Storage of carbon dioxide in saline aquifers: Physicochemical processes, key constraints, and scale-up potential. Annual Review of Chemical and Biomolecular Engineering, 2021, 12: 471-494.

Saeedi Dehaghani, A. H., Ghalamizade Elyaderani, S. M. Application of ion-engineered persian gulf seawater in EOR: Effects of different ions on interfacial tension, contact angle, zeta potential, and oil recovery. Petroleum Science, 2021, 18: 895-908.

Saira, Y, H., Le-Hussain, F. Effect of alcohol-treated CO_2 on interfacial tension between CO_2 and oil, and oil swelling. Advances in Geo-Energy Research, 2021, 5(4): 407-421.

Sheng, J. Comparison of the effects of wettability alteration and IFT reduction on oil recovery in carbonate reservoirs. Asia-Pacific Journal of Chemical Engineering, 2013, 8(1): 154-161.

Standnes, D. C., Austad, T. Wettability alteration in chalk: 2. Mechanism for wettability alteration from oil-wet to water-wet using surfactants. Journal of Petroleum Science and Engineering, 2000, 28(3): 123-143.

Sukee, A., Nunta, T., Fongkham, N., et al. Effects of brine valency and concentration on oil displacement by spontaneous imbibition: An interplay between wettability alteration and reduction in the oil-brine interfacial tension. Journal of Molecular Liquids, 2022a, 365: 120089.

Sukee, A., Nunta, T., Haruna, M. A., et al. Influence of sequential changes in the crude oil-water interfacial tension on spontaneous imbibition in oil-wet sandstone. Journal of Petroleum Science and Engineering, 2022b, 210: 110032.

Tangirala, S., Sheng, J. J. Roles of surfactants during soaking and post leak-off production stages of hydraulic fracturing operation in tight oil-wet rocks. Energy & Fuels, 2019, 33(9): 8363-8373.

Tangparitkul, S., Charpentier, T. V. J., Pradilla, D., et al. Interfacial and colloidal forces governing oil droplet displacement: Implications for enhanced oil recovery. Colloids and Interfaces, 2018, 2(3): 30.

Tangparitkul, S., Hodges, C. S., Ballard, D. A., et al. Dewetting dynamics of heavy crude oil droplet in low-salinity fluids at elevated pressures and temperatures. Journal of Colloid and Interface Science, 2021, 596: 420-430.

Tangparitkul, S, M., Watchanan Chantapakul, N. P. A realtime autonomous adjusting process for fluid-fluid displacement in CO_2 geological sequestration. Advances in Geo-Energy Research, 2023, 7(2): 71-74.

Taylor, S. E., Chu, H. Metal ion interactions with crude oil components: Specificity of Ca^{2+} binding to naphthenic acid at an oil/water interface. Colloids and Interfaces, 2018, 2(3): 40.

Thomas, Y. An essay on the cohesion of fluids. Philosophical Transactions of the Royal Society of London, 1805, 95: 65-87.

Tu, J., Sheng, J. Experimental and numerical study of surfactant solution spontaneous imbibition in shale oil reservoirs. Journal of the Taiwan Institute of Chemical Engineers, 2020, 106: 169-182.

Wang, H., Cai, J., Su, Y., Jin, Z., Wang, W., Li, G. Imbibition behaviors in shale nanoporous media from pore-scale perspectives. Capillarity, 2023, 9(2): 32-44.

Wang, J., Li, Y., Zhou, F., et al. Study on the effect of wettability on the oil recovery of tight carbonate reservoirs. Paper ARMA-2020-1051 Presented at the 54th U.S. Rock Mechanics/Geomechanics Symposium, physical event cancelled, 28 June-1 July, 2020.

Wu, J., Liu, F., Chen, G., et al. Effect of ionic strength on the interfacial forces between oil/brine/rock interfaces: A chemical force microscopy study. Energy & Fuels, 2016, 30(1): 273-280.

Xu, D., Bai, B., Wu, H., et al. Mechanisms of imbibition enhanced oil recovery in low permeability reservoirs: Effect of IFT reduction and wettability alteration. Fuel, 2019, 244: 110-119.

Yusuf, M., Wathon, M. H., Thanasaksukthawee, V., et al. Adsorption of saponin natural surfactant on carbonate rock and comparison to synthetic surfactants: An enhanced oil recovery prospective. Energy & Fuels, 2021, 35(14): 11193-11202.

Zhang, H., Nikolov, A., Wasan, D. Enhanced oil recovery (EOR) using nanoparticle dispersions: Underlying mechanism and imbibition experiments. Energy & Fuels, 2014, 28(5): 3002-3009.

Zhang, J., Fanghui, L., Yang, H., et al. Effect of ion type on the interaction between polar model oil and mica substrate: A chemical force microscopy study. Energy & Fuels, 2018, 32(10): 10486-10492.

Zhao, H., Long, J., Masliyah, J. H., et al. Effect of divalent cations and surfactants on silica-bitumen interactions. Industrial & Engineering Chemistry Research, 2006, 45(22): 7482-7490.

Zhu, D., Li, B., Li, H., et al. Effects of low-salinity water on the interface characteristics and imbibition process. Journal of Petroleum Science and Engineering, 2022, 208: 109564.

Zivar, D., Kumar, S., Foroozesh, J. Underground hydrogen storage: A comprehensive review. International Journal of Hydrogen Energy, 2021, 46(45): 23436-23462.