Investigation of the Coupled Effect of IFT Reduction and Wettability Alteration for Oil Recovery: New Insights

Xiao Deng, Muhammad Shahzad Kamal,* Shirish Patil,* Syed Muhammad Shakil Hussain, Mohamed Mahmoud, Dhafer Al-Shehri, and Emad W. Al-Shalabi

Cite This: ACS Omega 2023, 8, 12069−12078

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: Interfacial tension (IFT) reduction and wettability alteration (WA) are both important enhanced oil recovery (EOR) mechanisms. In oil-wet formations, IFT reduction reduces the magnitude of negative capillary pressure, releasing trapped oil. WA changes the negative capillary pressure to positive conditions, helping the entrance of the aqueous phase, and the displacement of the oil phase. In most cases, IFT reduction and WA happen at the same time. However, studies regarding the coupled effect provided different, sometimes conflicting observations. It requires further study and better understanding. In our study, oil-aged Indiana limestone samples were chosen to represent oil-wet carbonate rocks. Static contact angle and spinning drop method were adopted for wettability assessment and IFT measurement, respectively. Spontaneous imbibition was adopted to reflect on the oil recovery mechanisms in different cases. The impact of IFT reduction, WA, and permeability on the coupled effect was discussed by choosing four pairs of comparison tests. Results showed that when the coupled effect took place, both a higher IFT value and a stronger WA performance resulted in faster and higher oil recoveries. The importance of IFT reduction was enhanced in the higher-permeability condition, while the importance of WA was enhanced in the lower-permeability condition.

$$P_c = \gamma \cos\theta \frac{2}{r}$$
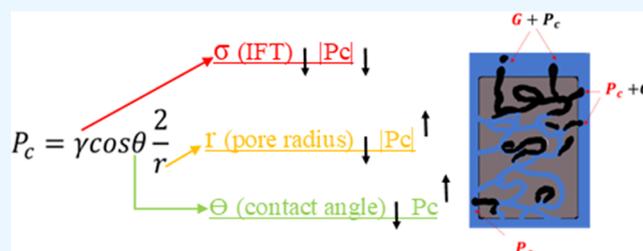
1. INTRODUCTION

Most of the carbonate reservoirs are oil-wet, or strongly oil-wet, and heterogeneous.[1,2] Under such conditions, the injected water during water flooding tends to flow in high permeability channels. There is only a small pressure gradient on the rock matrix.[3] On the other hand, the lower permeability is usually related to a smaller average pore throat radius,[4,5] which in turn relates to stronger capillary pressure according to the Young−Laplace equation.[6,7] In an oil-wet rock matrix, the capillary pressure is negative,[8] which prevents water from entering the rock matrix. The small pressure gradient and the stronger capillary pressure combine to result in a large portion of oil left as residual oil in the rock matrix. The recovery of this residual oil has significant potential for increasing oil production. It has been extensively studied in the enhanced oil recovery (EOR) topic.[2,9,10]

To recover this type of residual oil, either the pressure gradient should be increased or the negative capillary pressure should be reduced. By applying EOR materials with better mobility control, such as polymers,[11] viscoelastic surfactants,[12,13] and foam,[14] the pressure gradient exerted on the rock matrix can be increased, thus increasing the macro sweep efficiency. By applying EOR materials that either reduce interfacial tension (IFT) or induce wettability alteration (WA),[15−18] the capillary pressure is changed to less negative

or even positive conditions,[19] thus releasing the trapped oil in the rock matrix and increasing the micro sweep efficiency.

In the EOR applications, IFT reduction and WA usually happen at the same time. Surfactants are widely used EOR materials for IFT reduction. The WA potential of surfactants has gained a lot of attention. It is observed that cationic surfactants, in general, have strong and irreversible WA performance on oil-wet carbonate rock.[17] Under conditions like this, two mechanisms are combined to form a coupled effect on the oil recovery. However, there is confusion regarding the impact of IFT reduction when WA happens.

Some studies observed a positive impact of IFT reduction alongside WA. Alvarez and Schechter conducted spontaneous imbibition tests on eight Bakken core samples (oil-wet or intermediate-wet, silicious, and carbonate) using different EOR materials. Results showed that a lower IFT led to faster oil recovery.[6] Li et al. conducted water flooding experiments on 2D sand packs (water-wet and oil-wet). They observed that the
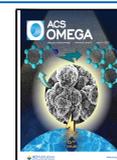
Table 1. Previous Studies Showing Synergic/Opposed Effect between IFT Reduction and WA[a]

no.	rock	EOR material	IFT (mN/m)	CA (deg)	incremental RF (%)	flooding/imbibition	synergic/opposed effect	ref
1	carbonate (3.5−3.9 mD)	deionized water	27	134	NG	flooding	synergic	Nourinia et al.[27]
		surfactant (CP)	9.1	45.8	8.2			
		nanocomposite ZnO/MMT	19	26	6			
		CP + ZnO/MMT	2.4	17.8	13			
2	sandstone (30 mD)	deionized water	35	140	NG	flooding	synergic	Nazarahari et al.[28]
	sandstone (30 mD)	nanocomposite (1000 ppm)	20.15	34	15.79			
	carbonate (8.23 mD)	deionized water	35	150	NG			
	carbonate (8.23 mD)	nanocomposite (250 ppm)	15.42	33	11.72			
3	carbonate (4.8−5.3 mD)	deionized water	>30.367	>148.93	NG	flooding	synergic	Haghighi et al.[29]
	carbonate (4.8−5.3 mD)	nonionic surfactant (843 ppm)	18.087−19.123	118.92−128.87	18.81			
4	sandstone (186 mD)	water	26.3	130	59.33	flooding	synergic, WA seems to have a stronger impact than IFT reduction	Roustaei et al.[30]
		hydrophobic lipo-philic polysilicon nanofluid	1.75	95.44	28.57			
		water	26.3	135.5	64.28			
		neutrally wet poly-silicon nanofluid	2.55	81.88	32.20			
5	limestone (120 mD)	surfactant Alf-35	0.03	70−80	56	imbibition	opposed	Seethepalli et al.[24]
		surfactant Alf-38	0.009	32−60	56			
		surfactant Alf-68	0.0007	90−100	35			
6	dolomite (0.4 mD)	water	17.2	120.6−122.6	8.4	imbibition	opposed	Alvarez and Schechter[31]
		anionic surfactant	0.3	44.5	23.6			
		nonionic-cationic surfactant	4.5	55.1	27.8			
7	carbonate (0.122 mD)	NG	0.0088−0.049	NG	14−40	numerical simulation	opposed, the effect of WA is more important in imbibition than in flooding	Sheng[32]

[a]NG: not given.

applied surfactant solution (NI) could alter the sand pack from oil-wet to water-wet while reducing IFT. Significant oil recovery was obtained.[20] Lu et al. conducted both spontaneous imbibition and coreflooding experiments in oil-wet, fractured carbonate samples. The surfactant mixture was found to almost entirely remove the oil in the contact angle measurement, indicating a strong WA performance. It also implied an ultralow IFT based on a solubility ratio of 16. Results showed a 33.3% imbibition oil recovery and a 65.9% incremental oil recovery by flooding. Sensitivity studies were conducted in numerical simulations using UTCHEM for corefloods. Results showed that combining IFT reduction and WA led to a faster and higher oil recovery than IFT reduction alone or WA alone.[21] Moradi et al. conducted coreflooding experiments in oil-wet carbonate samples. The tested surfactant obtained considerable IFT reduction. The seawater conditioned with sulfate (SW2.5S) obtained auspicious WA performance. The combination of surfactant + SW2.5S achieved higher oil recovery than surfactant alone or SW2.5S alone.[22] Chen and Mohanty conducted spontaneous imbibition experiments on oil-wet Silurian dolomite samples. They observed the oil recovery sequence from high to low: IFT reduction + WA > WA > IFT reduction.[23]

Some other studies suggest a negative effect of IFT reduction alongside WA. Seethepalli et al. conducted spontaneous imbibition experiments on oil-wet carbonate samples (Iceland spar, limestone, marble, and dolomite plates).

Surfactants Alf-35, Alf-38, and Alf-68 managed to revert the oil-wetness to water-wetness on the carbonate rock surface. In reducing IFT, Alf-68 was much stronger than Alf-35 and Alf-38. The oil recovery results showed that Alf-35 and Alf-38 recovered an extra 20% residual oil than Alf-68.[24] In Roustaei's study, nanoparticles showed stronger WA and higher IFT than C_{12}TAB. The spontaneous imbibition oil recovery of nanoparticles was faster and higher than C_{12}TAB.[25] Roustaei and Bagherzadeh found that SiO_2 nanofluid increased IFT and induced strong WA. It managed to nearly double the oil recoveries in coreflooding tests.[26] Alvarez and Schechter tested two types of surfactants: anionic surfactants, and nonionic surfactants. They found that the WA performances had no big difference. However, anionic surfactants were much more efficient in reducing IFT. However, the imbibition recoveries by anionic surfactants were lower than by nonionic surfactants.[26] Table 1 summarizes some previous observations about the coupled effect between IFT reduction and WA.

A previous review work has suggested some understanding of this topic.[33] In fact, the coupled effect is also a critical topic in areas such as CO_2 sequestration as well.[34] This work aims at adding some understanding of the coupled effect of IFT reduction and WA through experimental approaches. The influence of permeability is also considered. Inspired by the studies mentioned above, IFT, contact angle, and oil recovery were measured so as to show the main factor in the oil recovery differences. EOR materials of different IFT reduction

Table 2. XRF Results of Low- and High-Permeability Indiana Limestone Samples

mass percentage (%)	Mg	S	Ca	Mn	Fe	Co	Ni	Cu	Zn	Sr	Ru	Rh	Pd	Au
low-k sample 1	0.411	0.057	94.658	0.048	0.326	0.020	0.014	0.007	0.029	0.114	0.613	2.873	0.829	
low-k sample 2	0.462		94.489	0.045	0.273	0.020	0.013			0.110	0.667	2.966	0.932	0.022
low-k sample 3	0.434	0.061	94.567	0.046	0.312	0.022	0.013	0.004	0.028	0.114	0.632	2.907	0.860	
high-k sample 1	0.409	0.038	94.336	0.051	0.572			0.007	0.034	0.113	0.647	2.877	0.916	
high-k sample 2	0.377	0.036	94.454	0.047	0.628			0.005	0.034	0.113	0.624	2.886	0.796	
high-k sample 3	0.390	0.038	94.658	0.048	0.578		0.009		0.033	0.112	0.595	2.807	0.731	

Table 3. Structures of the Studied Chemicals

Short name	Structure
DTPA	
ZS	
GS3	
GS6	
GS-8	
GS-NH	

and WA performances were carefully selected for comparison purposes.

2. MATERIALS

Indiana limestone outcrops are selected to represent carbonate rock. Rock sample substrates (1-in. diameter, 3−4 mm thickness) for static contact angle measurement, and rock sample plugs (1.5-in. diameter, 2-in. height) for spontaneous imbibition tests, are prepared. Rock substrates were prepared by cutting a relatively homogeneous limestone outcrop of

brine permeability around 10 mD. The obtained raw substrates were then smoothened on the surface using P500 sandpaper. The plugs were prepared by cutting limestone outcrops of low (~10 mD) and high permeabilities (~500 mD). Three powder samples were prepared for low-permeability (<100 mD) and high-permeability (>100 mD) conditions each to conduct XRD analysis. Results, as given in Table 2, showed 100% calcite in both low- and high-permeability Indiana limestone outcrops.

Filtered crude oil (API 31.07, viscosity 12.492 cP, density 0.87 g/mL at 25 °C) was used. A zwitterionic surfactant AGA-97 and a chelating agent diethylene triamine penta acetic acid (DTPA) are used as EOR materials. By dissolving KOH in the chelating agent solution, the 3 wt % solution pH was modified to be around 11.

Four types of locally synthesized cationic gemini surfactants are used, including GS3, GS6, GS8, and GS-NH. All have the same tail groups and counterion (Br^-). The only difference lies in the spacer group. GS3 has a saturated straight carbon chain spacer of eight carbon atoms. GS6 has a straight carbon chain spacer of four carbon atoms and a double bond. GS8 has a benzene ring group in the spacer. GS-NH has an amines group in the spacer.

The molecular structures of the studied chemicals are given in Table 3.

Salts provided by Sigma-Aldrich are used to prepare the synthetic seawater (SW) and the synthetic formation brine (FW). Compositions are given in Table 4.

Table 4. Synthetic Seawater and Synthetic Brine Compositions

concentration (g/L)	SW	FW
$NaHCO_3$	0.165	0.487
Na_2SO_4	6.339	0.518
NaCl	41.172	150.446
$CaCl_2 \cdot 2H_2O$	1.802	52.724
$MgCl_2 \cdot 6H_2O$	8.266	9.552
TDS	57.745	213.727

The studied EOR solutions are given in Table 5.

Table 5. Studied EOR Solutions

short name	composition
GS3	GS3 (0.05 wt %) in deionized water
GS6	GS6 (0.05 wt %) in deionized water
GS-NH	GS-NH (0.05 wt %) in deionized water
ZS + DTPA + SW	AGA-97 (0.3 wt %), DTPA (3.0 wt %) in synthetic seawater
GS8 + DTPA + SW	GS8 (0.1 wt %), DTPA (3.0 wt %) in synthetic seawater

3. EXPERIMENTS

3.1. Static Contact Angle. The static contact angle was measured on the Theta Tensiometer produced by Biolin Scientific. All measurements were taken at ambient conditions (~22 °C, 1 atm). The instrument accuracy is ±0.1°. This experiment follows the process below:

(1) Clean the sample with toluene and dry it.
(2) Sample oil aging by dipping the substrates in the crude oil at a lifted temperature (>90 °C) for at least 7 days.
(3) Initial angle measurement: take the sample out from crude oil, clean flowing oil on the surface, and measure the contact angle in the oil/DI water/rock system.
(4) Soak the sample in prepared EOR solution for the required time (1.5 days for GS3, GS6, GS-NH; 4 days for DTPA and AGA-97).
(5) Final angle measurement: take the sample out from the solution, flush the sample with DI water, and measure the contact angle in the oil/DI water/rock system.

The initial angle shows the initial wettability, which was the wettability right after oil aging; the final angle shows the final wettability, which was the wettability after EOR treatment. By comparing the initial and final angles, the WA performance of the EOR materials can be obtained. Both the initial and final angles were measured in the oil/DI water/rock system to avoid the possible oil spreading problem and avoid the influence of IFT reduction on contact angle results as well.

Table 6 is a classification of rock surface wettability according to the contact angle value. Figure 1 is a schematic of the static contact angle measurement.

Table 6. Wettability and Contact Angle[a]

type	contact angle (deg)
strongly water-wet	0−30
water-wet	30−70
intermediate-wet	70−110
oil-wet	110−150
strongly oil-wet	150−180

[a]Reproduced with permission from ref 35. Copyright 2022 American Chemical Society.
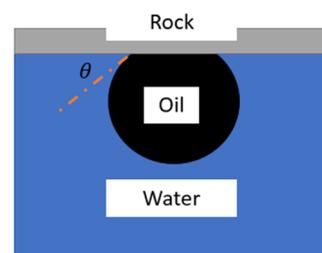
Figure 1. Schematic of the static contact angle measurement.

3.2. Spinning Drop Method. The spinning drop method is widely used in measuring IFT. In our study, the spinning drop tensiometer provided by Kruss was used. The IFT was measured based on the Young−Laplace approach that requires the curvature of the drop shape. Measurements were all conducted at ambient conditions (~22 °C, 1 atm). Figure 2 is a schematic of the spinning drop method.
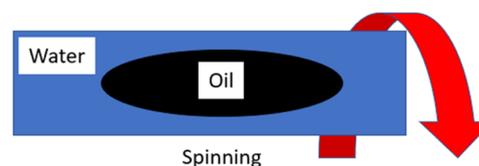
Figure 2. Schematic of the spinning drop method.

3.3. Spontaneous Imbibition. The spontaneous imbibition experiment is a commonly adopted experiment for the EOR potential evaluation in highly heterogenous formations. In the spontaneous imbibition test, no pressure is supplied. The main driving forces include gravity (buoyancy) and capillary pressure. It is a convenient method to relate EOR materials' IFT reduction and WA performance to oil recovery, as well as reflect on the recovery mechanisms. In the study, the spontaneous imbibition experiments were conducted using the Amott cells (suit core diameter, height) provided by Vinci Technologies, at ambient conditions (~22 °C, 1 atm). Figure 3

shows a schematic of the spontaneous imbibition experiment. This experiment follows the process below:
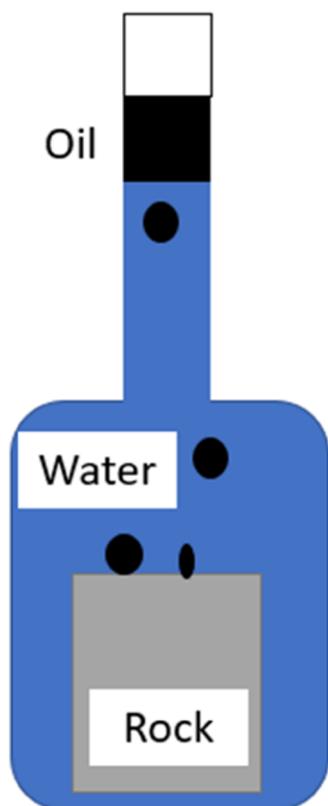
Figure 3. Schematic of the spontaneous imbibition experiment.

(1) Clean the sample with toluene and dry it.

(2) Fully saturated the sample with synthetic brine by vacuuming.

(3) Centrifuge the sample using the URC-628 centrifuge provided by Beckman Coulter with crude oil to establish oil and water saturations.

(4) Dip the sample in crude oil at an elevated temperature (>90 °C) for more than 15 days.

(5) Take out the sample, remove the oil on its surface, and put the sample in the Amott cell.

(6) Fill the Amott cell with the prepared EOR solution.

(7) Record oil production along with time. Calculate the oil recovery.

4. RESULTS AND DISCUSSION

Static contact angle results reflect the wettability alteration performance of the studied EOR materials. Spinning drop results show the IFT reduction performance. Spontaneous imbibition results relate the performance of the EOR materials to oil recovery.

4.1. Static Contact Angle Results: Wettability Alteration. Wettability alteration attracts attention since capillary pressure can improve micro sweep efficiency. Capillary pressure can be expressed according to the Young−Laplace equation, eq 1, as shown below

$$\Delta p = \frac{2\gamma_{ow} \cos \theta}{r_c} \tag{1}$$

In this equation, $\cos \theta$ is the term that relates contact angle to capillary pressure. The changed capillary pressure affects oil recovery in turn. So, wettability alteration performance can be defined using the initial and final angles, as shown by eq 2

$$WA = \cos \theta_{final} - \cos \theta_{initial} \tag{2}$$
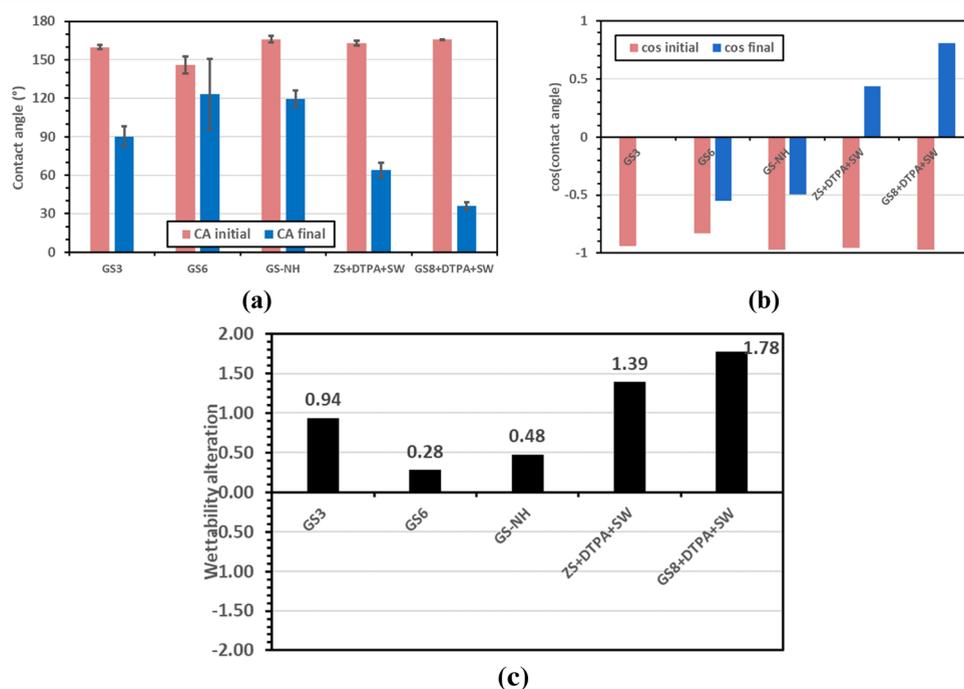
Figure 4. Contact angle results of the EOR solutions. (a) Contact angle before (initial) and after (final) soaking treatment; (b) $\cos \theta$ before and after soaking treatment; and (c) wettability alteration.
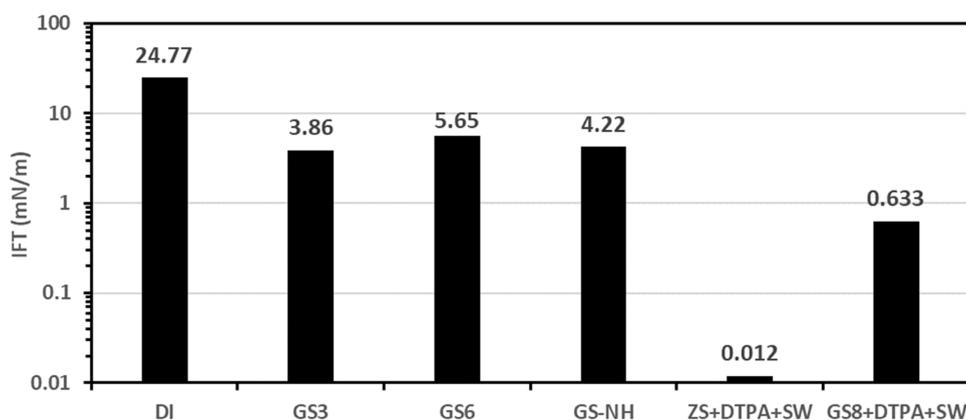
Figure 5. IFT between crude oil and the EOR solutions.
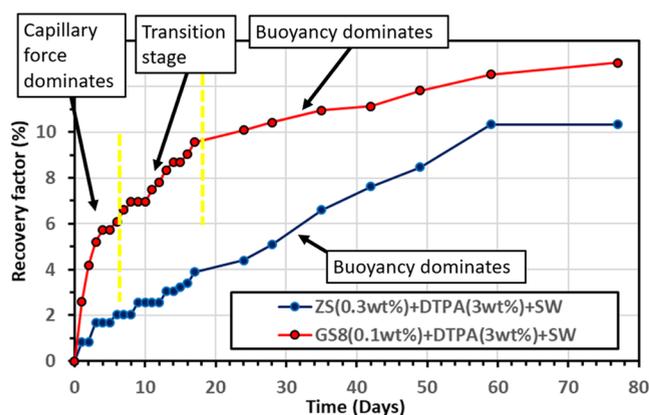
Figure 6. Relationship between driving mechanisms and the recovery curve shape.

In this equation, WA is wettability alteration, $\theta_{initial}$ is the initial contact angle, and θ_{final} is the final contact angle. Since $\cos\theta$ lies in the range $[-1, 1]$, WA lies in the range $[-2, 2]$.

A commonly accepted hypothesis about wettability alteration induced by cationic surfactants is the "ion-pair formation[36]", suggesting that the negatively charged carboxylic groups in the organic molecules adsorb to positively charged carbonate rock surface. By adding cationic surfactants, the positively charged head groups of the surfactant molecules form ion pairs with the negatively charged carboxylic groups, thus desorbing the organic molecules from the rock surface.

The possible reason for the WA induced by chelating agents is the adsorption of the chelating agents on the carbonate rock surface.[37] There are carboxylic groups in the chelating agent molecules. When they adsorb onto the rock surface, the positive charges on the rock surface are neutralized, thus desorbing the organic molecules.

The initial and final contact angles and the WA of the studied chemicals are shown in Figure 4.

The error in contact angle results can come from inherent sources (rock heterogeneity, surface smoothness) and experimental sources (oil drop size, optical angle deviation from horizontal, remaining oil phase on the rock surface, etc.). To obtain reliable evaluations of the WA performance, at least two substrates were treated by each EOR solution. At least two spots on each substrate were selected for measurement. The resulting initial and final angle values are the averages of the measurements. The error bars in Figure 4a show the standard error of all of the measurements for the same solution.

The initial angles are over or close to 150°, indicating that the original wettability of the oil-aged substrates was mostly strongly oil-wet. The final angles varied significantly from close to strongly water-wet condition (GS8 + DTPA + SW, 36.0°) to oil-wet condition (GS6, 123.3°). Among five EOR solutions, GS8 + DTPA + SW has the strongest WA performance. GS6 has the weakest WA performance. The WA caused by GS3 was around 2 times the WA caused by GS-NH. The WA caused by GS8 + DTPA + SW was around 1.28 times the WA caused by ZS + DTPA + SW. All solutions modified oil-wet samples toward the water-wet direction.

4.2. IFT Measurement Results. The IFT measurement results are shown in Figure 5.

Surfactant molecules have hydrophilic groups and lipophilic groups. When added to water/oil system, they distribute on the interface, bringing water and oil molecules together, thus reducing IFT.

Among five EOR solutions, ZS + DTPA + SW reduced the IFT the most. GS6 reduced IFT the least. The IFT values obtained by GS3, GS6, and GS-NH are comparable. The tested zwitterionic surfactant seemed to be very effective in reducing IFT. Regarding the resulting IFT, GS3, GS6, and GS-NH are comparable. GS8 + DTPA + SW is about 52 times higher than ZS + DTPA + SW.

4.3. Spontaneous Imbibition Results. Spontaneous imbibition experiments were conducted on eight Indiana limestone core plugs. The results from four comparison pairs reflect the oil recovery mechanisms.

Spontaneous imbibition reflects oil recovery mechanisms by the oil recovery curves and oil production on the plug surfaces. For imbibition driven mainly by buoyancy, the oil production comes mainly from the top surface of the core. For imbibition driven mainly by capillary force, the oil production comes from

Table 7. Spontaneous Imbibition Details of GS3 vs GS-NH

test	diameter (mm)	height (mm)	ϕ	k (mD)	SOI	EOR	IFT (mN/m)	WA	oil recovery (%)
1	37.87	49.36	0.13	8.95	0.52	GS3	3.86	0.94	24.49
2	37.87	48.03	0.12	8.81	0.57	GS-NH	4.22	0.48	19.55

(a)   (b)

(c)
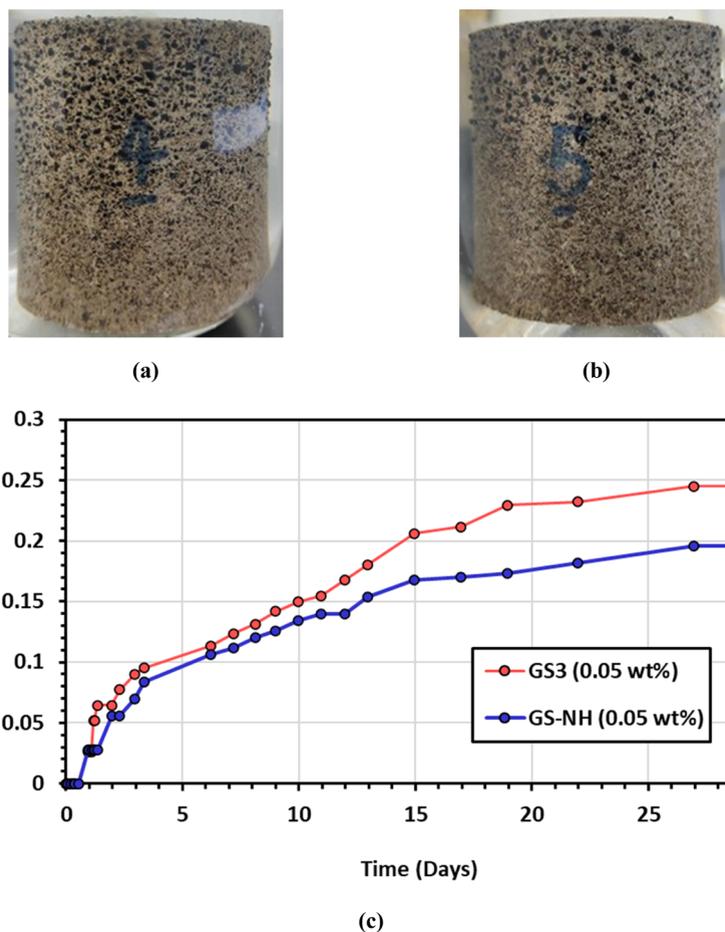
Figure 7. Spontaneous imbibition GS3 vs GS-NH. (a) GS3 sample after 30 days; (b) GS-NH sample after 30 days; (c) oil recovery curves.

Table 8. Spontaneous Imbibition Details of GS8 + DTPA + SW vs ZS + DTPA + SW

test	diameter (mm)	height (mm)	ϕ	k (mD)	SOI	EOR	IFT (mN/m)	WA	oil recovery (%)
3	38.08	50.86	0.15	7.44	0.66	GS8 + DTPA + SW	0.633	1.78	13.04
4	38.08	51.90	0.15	6.72	0.68	ZS + DTPA + SW	0.012	1.39	10.34
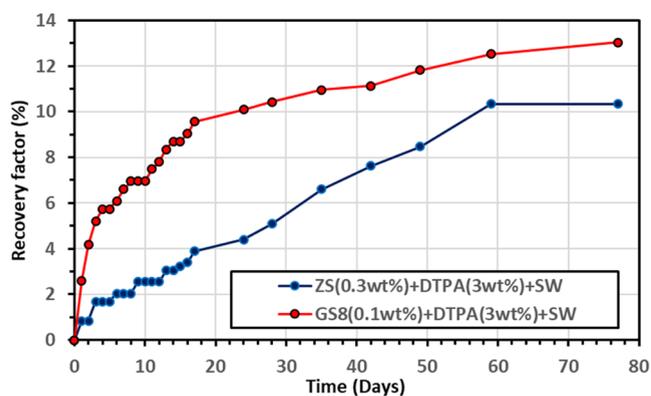
Figure 8. Spontaneous imbibition GS8 + DTPA + SW vs ZS + DTPA + SW.

both top and side surfaces due to the counter-current flow of water and oil.[38,39] Buoyancy contributes to oil recovery at a relatively steady and slow rate, resulting in a nearly linear recovery curve. The oil recovery contribution of capillary force mainly comes at the beginning, resulting in a staged recovery curve.[40] Figure 6 is an illustration of the staged (capillary force dominant) imbibition recovery curve and the linear (buoyancy dominant) imbibition recovery curve.

4.3.1. Comparison 1: Oil Recovery Contribution of Wettability Alteration. To study the contribution of WA, WA between two cases should be different, while IFT values should be comparable. The pair GS3 vs GS-NH satisfies this criterion. The IFT of the GS3/oil system is 0.91 times that of the GS-NH/oil system. The WA of GS3 is about 2 times that of GS-NH. The main difference between GS3 and GS-NH is in

Table 9. Spontaneous Imbibition Details of GS6 in Different Permeability Plugs

test	diameter (mm)	height (mm)	ϕ	k (mD)	SOI	EOR	IFT (mN/m)	WA	oil recovery (%)
5	37.87	50.10	0.15	7.56	0.73	GS6	5.65	0.28	17.66
6	37.87	51.84	0.17	922	0.66				47.16
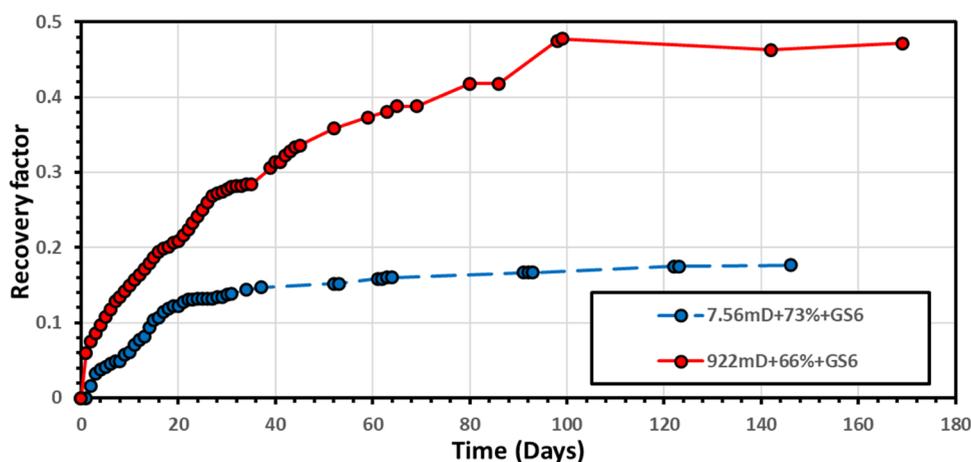
Figure 9. Impact of permeability on the spontaneous imbibition by GS6.

Table 10. Spontaneous Imbibition Details of GS3 in Different Permeability Plugs

test	diameter (mm)	height (mm)	ϕ	k (mD)	SOI	EOR	IFT (mN/m)	WA	oil recovery (%)
1	37.87	49.36	0.13	8.95	0.52	GS3	3.86	0.94	24.49
7	37.97	52.77	0.17	515	0.66				26.00
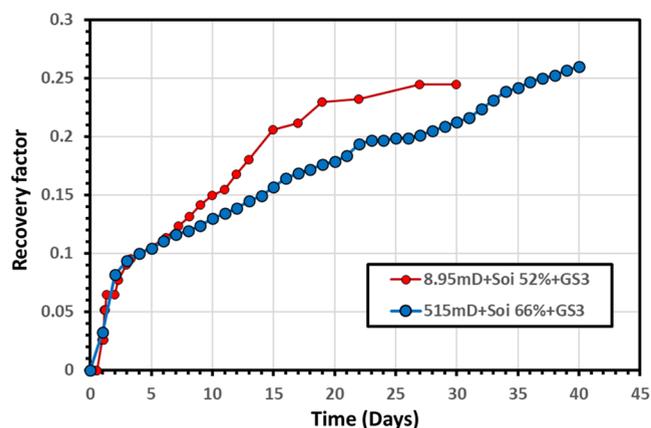
Figure 10. Impact of permeability on the spontaneous imbibition by GS3.

WA. Detailed information on this comparison test is given in Table 7.

Table 5 shows that the two plugs used had similar properties and were centrifuged to comparable initial oil saturations. After treating them with GS3 and GS-NH in the Amott cells, the oil recovery curves were obtained and are shown in Figure 7.

Both the staged shape of the recovery curves and the oil drops from the side surface on both plugs (Figure 7a,b) relate to counter current, indicating the important role of capillary force. In the condition that capillary force was the dominant driving force, GS3 obtained a higher and faster recovery than GS-NH, which corresponds to the fact that GS3 had stronger WA than GS-NH. This accordance supports the idea that when IFT values are comparable, stronger wettability alteration leads to faster and higher oil recovery in the spontaneous imbibition test.

4.3.2. Comparison 2: Oil Recovery Contribution of IFT Reduction. To study the contribution of IFT reduction, IFT between two cases should be different, while WA values should be comparable. The pair GS8 + DTPA + SW vs ZS + DTPA + SW satisfies this criterion. The IFT of the

GS8 + DTPA + SW/oil system is 53 times that of the ZS + DTPA + SW/oil system. The WA of GS8 + DTPA + SW is about 1.28 times that of ZS + DTPA + SW. The main difference is in IFT. Detailed information is given in Table 8, and recovery plots are given in Figure 8.

The staged shape of the GS8 + DTPA + SW recovery curve indicates the important role of capillary force. The nearly linear shape of the ZS + DTPA + SW recovery curve indicates the negligible role of capillary force. Though ZS + DTPA + SW had a comparable WA with GS8 + DTPA + SW, the role of capillary force in oil recovery differed significantly.

According to eq 1, IFT affects the magnitude of capillary force, while wettability affects the magnitude and direction of capillary force. In this comparison pair, both had positive capillary pressure. However, due to the much lower IFT of ZS + DTPA + SW, the magnitude of capillary pressure was reduced to a very low value. ZS + DTPA + SW had an IFT value of 0.012 mN/m that significantly enhanced the role of buoyancy while diminishing the oil contribution from the capillary force. As a result, capillary pressure was the dominant driving force in the GS8 + DTPA + SW case, while buoyancy was the dominant driving force in the ZS + DTPA + SW case. This comparison test supports the idea that when wettability alteration happens, a higher IFT is favored to maintain the magnitude of capillary pressure, increasing both the oil recovery and oil recovery rate.

4.3.3. Comparison 3: Permeability's Impact on Buoyancy's Recovery Contribution. To study the impact of permeability on buoyancy's recovery contribution, an EOR solution that reduces the IFT but has negligible WA performance is required. GS6 satisfies this criterion. Detailed information is given in Table 9.

GS6 had negligible WA, the weakest among all five EOR solutions, as shown in Figure 4c. The rock substrates treated by GS6 were still oil-wet. IFT reduction was the main oil recovery mechanism in the GS6 case. Buoyancy was the main driving force, which is also indicated by the nearly linear shape of the recovery curves (during the oil production period).

On the condition when IFT reduction was the main oil recovery mechanism, a higher permeability resulted in much higher and faster oil recovery (Figure 9). This observation can be explained by Darcy's equation and the relation between permeability with pore throat radius. Increased permeability led to a faster flow rate of oil inside the plug, resulting in a higher oil recovery rate. A higher permeability is usually related to a larger average pore throat radius. A larger pore throat radius, according to eq 1, leads to a smaller magnitude of capillary pressure. Since substrates remained oil-wet after GS6 treatment, the capillary pressure was negative. The reduced magnitude of the negative capillary pressure led to less oil trapped by the capillary pressure, thus increasing the ultimate oil recovery. This comparison test supports the idea that when wettability alteration is negligible, a higher permeability increases the oil recovery rate and the ultimate oil recovery.

4.3.4. Comparison 4: Permeability's Impact on the Coupled Effect. To study the impact of permeability on the coupled effect, an EOR solution that reduces IFT and changes wettability at the same time is required. GS3 satisfies this criterion. Detailed information is given in Table 10, and oil recovery plots are shown in Figure 10.

GS3 showed moderate IFT reduction and WA. The strongly oil-wet substrates were changed to intermediate-wet by GS3 treatment. In such conditions, a higher permeability resulted in higher ultimate oil recovery and a lower recovery rate in the beginning. This observation can be explained the relation between permeability with pore throat radius. As has been iterated in the previous comparison, a higher permeability diminishes the role of capillary pressure, thus reducing the oil recovery contribution from WA. As a result, in stages where capillary pressure was the or one of the main driving force(s), the lower permeability sample had faster oil recovery than the higher permeability sample. On the other hand, when buoyancy played the dominant role, oil recovery was faster in the higher permeability sample than in the lower one, resulting in a further increase in oil recovery and a higher continuing oil recovery.

This comparison test supports the idea that when wettability alteration happens, a higher permeability leads to a slower recovery rate in the beginning, but a faster recovery rate after that, and a higher ultimate oil recovery.

5. CONCLUSIONS

Although the oil recovery contribution of IFT reduction or wettability alteration alone has already been well understood, the coupled effect between these two mechanisms still arises confusion in understanding. This work conducted spontaneous imbibition experiments to show the oil recoveries of the studied EOR solutions. Static contact angle and IFT results were compared to understand the implications of the coupled effect on oil recovery.

The following conclusions are drawn:

(1) When IFT values are comparable, stronger wettability alteration leads to faster and higher oil recovery in spontaneous imbibition.

(2) When wettability alteration happens, a higher IFT is favored to maintain the magnitude of capillary pressure, increasing both the oil recovery and oil recovery rate.

(3) High permeability enhances the oil recovery by IFT reduction. Low permeability enhances the oil recovery by wettability alteration.

AUTHOR INFORMATION

Corresponding Authors

Muhammad Shahzad Kamal − *Center for Integrative Petroleum Research, King Fahd University of Petroleum & Minerals, 31261 Dhahran, Saudi Arabia;* ⓞ orcid.org/0000-0003-2359-836X; Email: shahzadmalik@kfupm.edu.sa

Shirish Patil − *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, 31261 Dhahran, Saudi Arabia;* ⓞ orcid.org/0000-0002-0131-4912; Email: Patil@kfupm.edu.sa

Authors

Xiao Deng − *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, 31261 Dhahran, Saudi Arabia;* ⓞ orcid.org/0000-0002-8851-5804

Syed Muhammad Shakil Hussain − *Center for Integrative Petroleum Research, King Fahd University of Petroleum & Minerals, 31261 Dhahran, Saudi Arabia;* ⓞ orcid.org/0000-0002-6806-2326

Mohamed Mahmoud − *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, 31261 Dhahran, Saudi Arabia;* ⓞ orcid.org/0000-0002-4395-9567

Dhafer Al-Shehri − *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, 31261 Dhahran, Saudi Arabia;* ⓞ orcid.org/0000-0002-7032-5199

Emad W. Al-Shalabi − *Petroleum Engineering Department, Khalifa University of Science and Technology, P.O. Box 127788 Abu Dhabi, United Arab Emirates;* ⓞ orcid.org/0000-0003-2055-1398

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c07906

Notes

The authors declare no competing financial interest.

ABBREVIATIONS

API American Petroleum Institute
DTPA diethylene triamine penta acetic acid
EOR enhanced oil recovery
GS gemini surfactant
IFT interfacial tension
WA wettability alteration
ZS zwitterionic surfactant

REFERENCES

(1) Kamal, M. S. A Review of Gemini Surfactants: Potential Application in Enhanced Oil Recovery. *J. Surfactants Deterg.* **2016**, *19*, 223−236.

(2) Gupta, R.; Mohanty, K. K. Wettability Alteration Mechanism for Oil Recovery from Fractured Carbonate Rocks. *Transp. Porous Media* **2011**, *87*, 635−652.

(3) Hirasaki, G.; Zhang, D. L. Surface Chemistry of Oil Recovery From Fractured, Oil-Wet, Carbonate Formations. *SPE J.* **2004**, *9*, 151−162.

(4) Gao, Z.; Hu, Q. Estimating Permeability Using Median Pore-Throat Radius Obtained from Mercury Intrusion Porosimetry. *J. Geophys. Eng.* **2013**, *10*, No. 025014.

(5) Lala, A. M. S.; El-Sayed, N. A. A. Controls of Pore Throat Radius Distribution on Permeability. *J. Pet. Sci. Eng.* **2017**, *157*, 941−950.

(6) Alvarez, J. O.; Schechter, D. S. In *Altering Wettability in Bakken Shale by Surfactant Additives and Potential of Improving Oil Recovery during Injection of Completion Fluids*, SPE Improved Oil Recovery Conference, Tulsa, OK, 2016.

(7) Armstrong, R. T.; Porter, M. L.; Wildenschild, D. Linking Pore-Scale Interfacial Curvature to Column-Scale Capillary Pressure. *Adv. Water Resour.* **2012**, *46*, 55−62.

(8) Kumar, K.; Dao, E. K.; Mohanty, K. K. In *Atomic Force Microscopy Study of Wettability Alteration*, SPE International Symposium on Oilfield Chemistry Proceedings, Woodlands, TX, 2005.

(9) Andersen, P.; Evje, S.; Kleppe, H. A Model for Spontaneous Imbibition as a Mechanism for Oil Recovery in Fractured Reservoirs. *Transp. Porous Media* **2014**, *101*, 299−331.

(10) Salehi, M.; Johnson, S. J.; Liang, J. T. Mechanistic Study of Wettability Alteration Using Surfactants with Applications in Naturally Fractured Reservoirs. *Langmuir* **2008**, *24*, 14099−14107.

(11) Kamal, M. S.; Hussein, I. A.; Sultan, A. S. Review on Surfactant Flooding: Phase Behavior, Retention, IFT, and Field Applications. *Energy Fuels* **2017**, *31*, 7701−7720.

(12) Zhang, L.; Yue, X.; Guo, F. Micro-Mechanisms of Residual Oil Mobilization by Viscoelastic Fluids. *Pet. Sci.* **2008**, *5*, 56−61.

(13) Ahmed, M. E.; Hassan, A. M.; Sultan, A. S.; Mahmoud, M. Enhancing the Oil Recovery from Naturally Fractured Reservoirs Using Viscoelastic Surfactant (VES) Flooding: A Field-Scale Simulation. *ACS Omega* **2022**, *7*, 504−517.

(14) Hirasaki, G. J.; Miller, C. A.; Puerto, M. Recent Advances in Surfactant EOR. *SPE J.* **2011**, *16*, 889−907.

(15) Ali, M.; Al-Anssari, S.; Shakeel, M.; Arif, M.; Hussain Dahraj, N. U.; Iglauer, S. In *Influence of Miscible CO_2 Flooding on Wettability and Asphaltene Precipitation in Indiana Lime Stone*, SPE/IATMI Asia Pacific Oil and Gas Conference and Exhibition, 2017; pp 17−19.

(16) Strand, S.; Standnes, D. C.; Austad, T. New Wettability Test for Chalk Based on Chromatographic Separation of SCN- and SO42-. *J. Pet. Sci. Eng.* **2006**, *52*, 187−197.

(17) Standnes, D. C.; Austad, T. Wettability Alteration in Chalk 2. Mechanism for Wettability Alteration from Oil-Wet to Water-Wet Using Surfactants. *J. Pet. Sci. Eng.* **2000**, *28*, 123−143.

(18) Al-Anssari, S.; Arain, Z. U. A.; Barifcani, A.; Keshavarz, A.; Ali, M.; Iglauer, S. In *Influence of Pressure and Temperature on CO_2-Nanofluid Interfacial Tension: Implication for Enhanced Oil Recovery and Carbon Geosequestration*, Abu Dhabi International Petroleum Exhibition and Conference, ADIPEC 2018, 2019.

(19) Gupta, R.; Mohanty, K. Temperature Effects on Surfactant-Aided Imbibition Into Fractured Carbonates. *SPE J.* **2010**, *15*, 588−597.

(20) Li, R. F.; Hirasaki, G. J.; Miller, C. A.; Masalmeh, S. K. Wettability Alteration and Foam Mobility Control in a Layered, 2D Heterogeneous Sandpack. *SPE J.* **2012**, *17*, 1207−1220.

(21) Lu, J.; Goudarzi, A.; Chen, P.; Kim, D. H.; Delshad, M.; Mohanty, K. K.; Sepehrnoori, K.; Weerasooriya, U. P.; Pope, G. A. Enhanced Oil Recovery from High-Temperature, High-Salinity Naturally Fractured Carbonate Reservoirs by Surfactant Flood. *J. Pet. Sci. Eng.* **2014**, *124*, 122−131.

(22) Moradi, S.; Isari, A. A.; Bachari, Z.; Mahmoodi, H. Combination of a New Natural Surfactant and Smart Water Injection for Enhanced Oil Recovery in Carbonate Rock: Synergic Impacts of Active Ions and Natural Surfactant Concentration. *J. Pet. Sci. Eng.* **2019**, *176*, 1−10.

(23) Chen, P.; Mohanty, K. K. In *Surfactant-Enhanced Oil Recovery from Fractured Oil-Wet Carbonates: Effects of Low IFT and Wettability Alteration*, SPE International Symposium on Oilfield Chemistry, Woodlands, TX, 2015; pp 1225−1248.

(24) Seethepalli, A.; Adibhatla, B.; Mohanty, K. K. Physicochemical Interactions during Surfactant Flooding of Fractured Carbonate Reservoirs. *SPE J.* **2004**, *9*, 411−418.

(25) Roustaei, A. An Evaluation of Spontaneous Imbibition of Water into Oil-Wet Carbonate Reservoir Cores Using Nanofluid. *Petrophysics* **2014**, *55*, 31−37.

(26) Roustaei, A.; Bagherzadeh, H. Experimental Investigation of SiO2 Nanoparticles on Enhanced Oil Recovery of Carbonate Reservoirs. *J. Pet. Explor. Prod. Technol.* **2015**, *5*, 27−33.

(27) Nourinia, A.; Manshad, A. K.; Shadizadeh, S. R.; Ali, J. A.; Iglauer, S.; Keshavarz, A.; Mohammadi, A. H.; Ali, M. Synergistic Efficiency of Zinc Oxide/Montmorillonite Nanocomposites and a New Derived Saponin in Liquid/Liquid/Solid Interface-Included Systems: Application in Nanotechnology-Assisted Enhanced Oil Recovery. *ACS Omega* **2022**, *7*, 24951−24972.

(28) Nazarahari, M. J.; Manshad, A. K.; Ali, M.; Ali, J. A.; Shafiei, A.; Sajadi, S. M.; Moradi, S.; Iglauer, S.; Keshavarz, A. Impact of a Novel Biosynthesized Nanocomposite (SiO2@Montmorilant@Xanthan) on Wettability Shift and Interfacial Tension: Applications for Enhanced Oil Recovery. *Fuel* **2021**, *298*, No. 120773.

(29) Haghighi, O. M.; Zargar, G.; Manshad, A. K.; Ali, M.; Takassi, M. A.; Ali, J. A.; Keshavarz, A. Effect of Environment-Friendly Non-Ionic Surfactant on Interfacial Tension Reduction and Wettability Alteration; Implications for Enhanced Oil Recovery. *Energies* **2020**, *13*, 3988.

(30) Roustaei, A.; Moghadasi, J.; Bagherzadeh, H.; Shahrabadi, A. In *An Experimental Investigation of Polysilicon Nanoparticles' Recovery Efficiencies through Changes in Interfacial Tension and Wettability Alteration*, SPE International Oilfield Nanotechnology Conference, 2012; pp 200−206.

(31) Alvarez, J. O.; Schechter, D. S. In *Altering Wettability in Bakken Shale by Surfactant Additives and Potential of Improving Oil Recovery during Injection of Completion Fluids*, Proceedings − SPE Symposium on Improved Oil Recovery, 2016.

(32) Sheng, J. J. Comparison of the Effects of Wettability Alteration and IFT Reduction on Oil Recovery in Carbonate Reservoirs. *Asia-Pac. J. Chem. Eng.* **2013**, *8*, 154−161.

(33) Deng, X.; Tariq, Z.; Murtaza, M.; Patil, S.; Mahmoud, M.; Kamal, M. S. Relative Contribution of Wettability Alteration and Interfacial Tension Reduction in EOR: A Critical Review. *J. Mol. Liq.* **2021**, *325*, No. 115175.

(34) Yekeen, N.; Khan, J. A.; Ali, M.; Elraies, K. A.; Okunade, O. A.; Ridha, S.; Al-Yaseri, A. Impact of Nanoparticles−Surfactant Solutions on Carbon Dioxide and Methane Wettabilities of Organic-Rich Shale and CO2/Brine Interfacial Tension: Implication for Carbon Geo-sequestration. *Energy Rep.* **2022**, *8*, 15669−15685.

(35) Deng, X.; Patil, S.; Kamal, M. S.; Mahmoud, M.; Sultan, A.; Saikia, T. Wettability Alteration of Carbonate Rock by Chelating Agents and Viscoelastic Surfactants: Synergetic Impact. *Energy Fuels* **2022**, *36*, 7391−7401.

(36) Standnes, D. C.; Austad, T. Wettability Alteration in Carbonates: Interaction between Cationic Surfactant and Carboxylates as a Key Factor in Wettability Alteration from Oil-Wet to Water-Wet Conditions. *Colloids Surf., A* **2003**, *216*, 243−259.

(37) Hassan, A.; Mahmoud, M.; Patil, S. Impact of Chelating Agent Salt Type on the Enhanced Oil Recovery from Carbonate and Sandstone Reservoirs. *Appl. Sci.* **2021**, *11*, 7109.

(38) Reis, J. C.; Cil, M. A Model for Oil Expulsion by Counter-Current Water Imbibition in Rocks: One-Dimensional Geometry. *J. Pet. Sci. Eng.* **1993**, *10*, 97−107.

(39) Gautam, P. S.; Mohanty, K. K. Matrix-Fracture Transfer through Countercurrent Imbibition in Presence of Fracture Fluid Flow. *Transp. Porous Media* **2004**, *55*, 309−337.

(40) Ravari, R. R.; Strand, S.; Austad, T. Combined Surfactant-Enhanced Gravity Drainage (SEGD) of Oil and the Wettability Alteration in Carbonates: The Effect of Rock Permeability and Interfacial Tension (IFT). *Energy Fuels* **2011**, *25*, 2083−2088.