Application of anionic surfactant\engineered water hybrid EOR in carbonate formations: An experimental analysis

Aigerim Sekerbayeva, Peyman Pourafshary [*], Muhammad Rehan Hashmet

Department of Petroleum Engineering, School of Mining and Geosciences, Nazarbayev University, Nur-Sultan, Kazakhstan

ABSTRACT

A hybrid enhanced oil recovery (EOR) method by combining low salinity water (LSW) and low salinity surfactant (LSS) flooding techniques was designed. Different experiments were done to screen the Caspian seawater (SW) with altered ionic composition and surfactant, for the optimized performance in Kazakhstani carbonate oil fields. Changing to a more water-wet state and creating the middle phase were studied as the main criteria to select the best-engineered brine and anionic surfactant. The largest alteration towards the water-wet condition was recorded at 10 times dilution of the SW with 3- and 6- times spiked calcium and sulfate ions, respectively (10xSW-6SO4, Mg, 3Ca). This combination of anionic surfactants with carbonate formations is considered as a new approach in hybrid EOR methods. Among the anionic surfactants screened, Soloterra-113H (Alkyl Benzenesulfonic acid) showed the best solubilization ratio, aqueous stability, and Winsor type 3 microemulsions. The wettability alteration by the combination of optimized brine and screened surfactant was greater compared to the standalone LSW, which was confirmed by the $10°$ difference in contact angle measurement. The microemulsion phase constituted nearly 40% of the total height of the oil/brine column by the hybrid method. The recovery factor after injecting formation water was 52%, and it increased to 61% after optimized LSW injection. After switching to the engineered brine/surfactant, the recovery factor reached 70%, which proves the effectiveness of the hybrid method. The proposed combined method works better than either standalone EOR method due to the higher alteration in capillary number by changing wettability and reducing IFT, which leads to higher oil recovery.

1. Introduction

Conventional oil recovery methods leave roughly two-thirds of the oil originally in place (OOIP) in the reservoir. Thus, there is a need for novel approaches to improve oil recovery. One solution is low salinity water flooding (LSW), where brines with reduced dissolved salt concentration are injected into the reservoir. Interest in this method is increasing due to its simplicity and low cost compared to other enhanced oil recovery (EOR) techniques [1]. Many studies are confirming the efficiency of LSW to improve the oil recovery from carbonate formations [2,3]. There are various governing mechanisms suggested, but most common is wettability alteration by multi-component ionic exchange (MIE). Significant enhancement in the oil recovery process from carbonates is achieved by spikes in active ions, such as Ca^{2+}, Mg^{2+}, and SO_4^{2-}, in the injection brine [4,5]. There are ions, such as Na^+ and Cl^-, that are not active in the MIE process but still limit access of the active ions to the surfaces and, thus, should be reduced to optimize the ion exchange process. Hence, to optimize the oil recovery process with LSW, the composition of ions should be altered to improve the effectiveness of active ions on the complex crude oil/brine/rock (CBR) interactions in the porous media.

Another proven EOR approach is injecting a small amount of surfactant in an aqueous solution into the reservoir. Oil recovery increases due to governing mechanisms, such as a reduction in water/oil interfacial tension (IFT) and alteration in the rock wettability [6]. The positive effects of the increased capillary number and enhanced microscopic sweep efficiency lead to a higher recovery factor. Numerous surfactant flooding projects are reported with promising results on both sandstone and carbonate formations [7,8].

A novel hybrid EOR method, called low salinity surfactant flooding (LSS), can be developed by a combination of a low saline environment and surfactant flooding. It is an attractive hybrid method that comprises several governing mechanisms, such as wettability alteration by LSW and interfacial tension reduction by surfactant [9]. The benefits of the LSW/LSS in terms of higher oil recovery, higher surfactant stability, lower surfactant retention, and lower chemical consumption compared to conventional surfactant flooding have been studied and reported [10–12]. The hybrid method can be used as a tertiary stage after high saline waterflooding (HSW) [13]. For example, in the study conducted by Alagic et al., after tertiary injection of the hybrid LSW/LSS method, oil recovery was in the 92–94% of OOIP range, which was about 45% higher than recovery by standalone LSS flooding [14].

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Table 1
Crude oil composition.

Component	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15+	Other
Wt%	0.8	0.43	1.63	7.36	8.7	17.87	5.09	5.44	8.3	6.15	30.55	7.66
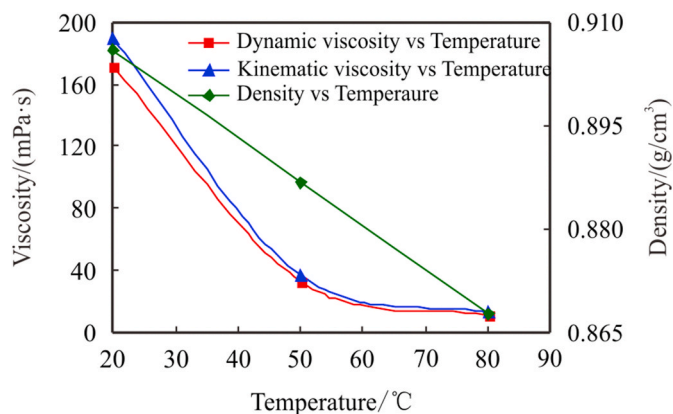
Fig. 1. Oil dynamic, kinematic viscosity and density versus temperature.

Although most research has been done for sandstones, there is an increasing interest in applying a hybrid LSW/LSS method for carbonates and a few promising results are reported [15]. For example, in the study conducted by Alameri et al., the oil recovery factor after the sequential injection of seawater followed by LSW was 57%, an additional 10% was obtained after tertiary injection of LSS [9]. The same observation in improving recovery in carbonates by LSS was reported in Ref. [16]. The instability of oil layers due to the alteration in wettability from oil-wet to more water conditions by LSW makes the performance of LSS better with higher oil recovery, which has been confirmed experimentally [17–20]. Hence, the combined effects of LSW and surfactant in the hybrid method provide lower residual oil saturation than the value predicted by the capillary desaturation curves (CDC).

Controlling surfactant retention is another essential benefit of the hybrid method that affects the economic feasibility of the project. The retention was 10 times lower for the case of LSS compared to conventional surfactant flooding due to the lower cation concentration [19]. The effect of dilution and ion adjustment on retention and critical micelle concentration was also observed by Hosseinzade et al. [21]. Applying the hybrid LSW/LSS method improves the performance of both methods due to the favorable environment for surfactant, which is created at the low saline condition [22,23]. The low saline environment provides more flexibility to choose commercial surfactants without the need to tailor to achieve ultralow IFT, which makes the process more convenient and cheaper [24]. Surfactant behavior is also improved by higher solubility and lower loss of chemicals, which results in higher oil recovery even without ultra-low IFT [17,25,26]. Different screening parameters, such as reservoir temperature, oil composition, clay content, and water salinity, should be considered to achieve good performance during surfactant flooding. Laboratory studies, such as aqueous stability analysis, phase behavior, and core flooding, were conducted to study the effect of operational parameters on surfactant flooding [27]. A similar approach shows that criteria such as initial wettability are essential as a prerequisite for successful LSW/LSS technique applications [24]. In-situ and injected brine composition also has a significant effect on the performance of the LSW/LSS method and should be optimized [28].

The adsorption of anionic surfactants on the positively charged carbonate surfaces is higher due to the electrostatic attraction. Hence, non-ionic or cationic surfactants are preferred for application in carbonate formations [16,29]. However, there are some studies confirming a relatively equal amount of adsorption of some cationic and anionic surfactants [30]. Chen and Mohanty investigated the wettability alteration to the water-wet condition by anionic surfactants and they observed better performance at low salinity conditions [31]. Moreover, it is possible to control anionic surfactant adsorption by adding alkalis. Anionic surfactants are more capable of achieving ultralow IFT between oil and water phases and are less expensive [10,31]. Thus, in this study, anionic surfactants were used to design an LSW/LSS hybrid method for carbonate formations as a novel approach to developing cheaper oil

Table 2
Required chemicals for brines preparation.

Chemical formula	Purity	Producers
$NaHCO_3$	≥99.0%	SIGMA-ALDRICH
Na_2SO_4	≥99.0%	
NaCl	≥99.0%	
$CaCl_2 \cdot 2H_2O$	≥96.0%	ACROS ORGANICS
$MgCl_2 \cdot 6H_2O$	≥99.0%	SIGMA-ALDRICH

Table 3
Ionic composition of dilutions and formation water in the field [32].

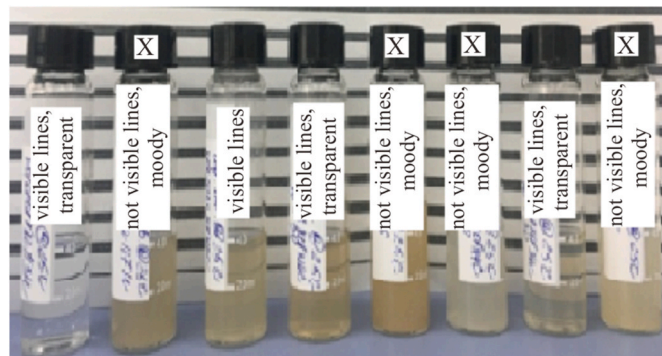| Ion	Formation water, ppm	South Caspian Sea (SW), ppm	2 times dilution, ppm	10 times dilution, ppm	20 times dilution, ppm
Na^+ + K^+	81600	3240	1620	324	162
Ca^{2+}	9540	350	175	35	17,5
Mg^{2+}	1470	740	370	74	37
Cl^-	90370	5440	2720	544	272
SO_4^{2-}	0	3010	1505	301	150,5
HCO_3^-	0	220	110	22	11
Total	181980	13000	6500	1300	650
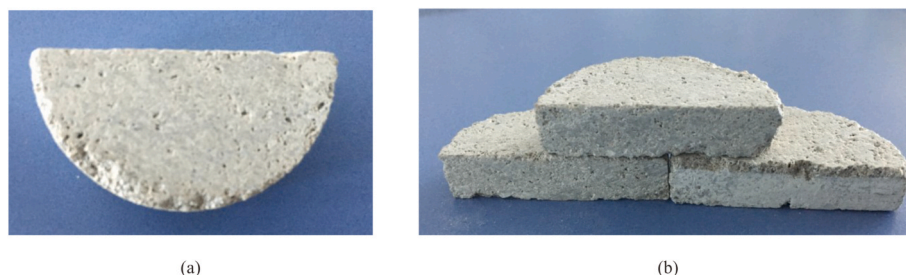
Fig. 2. Core samples.

Table 4
Composition of ions in EW samples.

Ions	10SW-S, Mg, Ca	10SW-0S, Mg, Ca	10SW-4S, 2 Mg, 2Ca	10SW-4S, 2 Mg, Ca	10SW-4S, Mg, 2Ca	10SW-6S, 3 Mg, Ca	10SW-6S, Mg, 3Ca	10SW-8S, 4 Mg, 4Ca
$Na^+ + K^+$	325	325	325	325	325	325	325	325
Ca^{2+}	35	35	35	35	70	35	105	140
Mg^{2+}	74	74	74	148	74	222	74	296
Cl^-	544	544	544	544	544	544	544	544
SO_4^{2-}	301	0	602	1204	1204	1806	1806	2408
HCO_3^-	22	22	22	22	22	22	22	22
Total	1301	1000	1602	2278	2239	2954	2876	3735

Fig. 3. OCA 15 EC measuring unit.

Fig. 4. Core flooding scheme.

recovery techniques. Experiments were conducted to select the optimized ion concentration of diluted water, which is called engineered water (EW) in this paper. The effects of different anionic surfactants and EW samples on the CBR interactions were studied to design the optimum EW/LSS method.

2. Methodology

2.1. Oil, brines, and rock samples

Since the target of this work was an application in carbonate oil fields in Kazakhstan, materials were selected from the target fields in the country. Crude oil from an oil field in West Kazakhstan was used, and its

Fig. 5. Aqueous stability test.

composition is shown in Table 1.

The viscosity and density of the oil sample were recorded at three different temperatures, 20, 50, and 80 °C, using an SVM 3001 Viscometer from Anton Paar, as shown in Fig. 1.
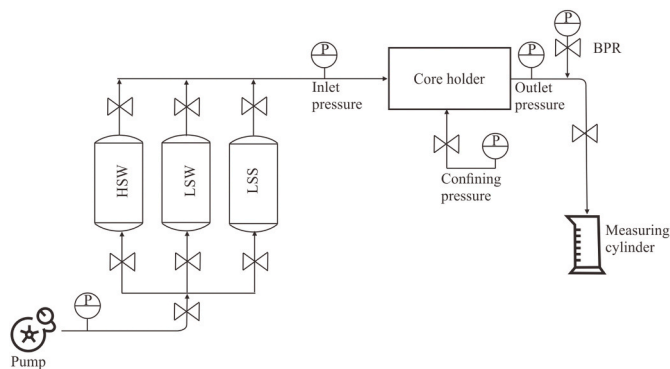
In this study, limestone outcrops were used due to the similarity of the rock composition to our target carbonate fields. X-ray diffraction (XRD) analysis was used to confirm that the material consists of calcite (about 99%). Rock samples were cut into half circle pellets with a 1-inch length and 1.5-inch diameter, as shown in Fig. 2, for further contact angle measurement tests.

The salts shown in Table 2 were used to prepare different brines.

HSW was prepared for use as the formation brine to achieve the initial condition of the core samples. The composition of HSW was obtained from an oil field in West Kazakhstan, as shown in Table 3, and the salinity was about 182,000 ppm. The water composition of the South Caspian Sea, which has a salinity of 13,000 ppm, was chosen as a base brine for waterflooding. Different samples of diluted brine were prepared, as shown in Table 3. The base water was diluted 2, 10, and 20 times to study the effect of dilution on the performance of waterflooding.

This dilution degree was obtained by taking into consideration optimized dilutions from our previous similar experiments and initial low salinity of the South Caspian Sea. Different levels of dilutions and ion concentrations were examined in our experiments.

Sulfate ions play a catalytic role in displacing the carboxylic group from the carbonate surfaces by divalent ions like magnesium and calcium ions. Injection water containing two times higher concentration of sulfate ions than divalent calcium/magnesium ions could be an excellent wettability alternating reference fluid [33]. To study the effect of EW on wettability alteration, samples were prepared and concentrations of active ions $Mg^{2+}+SO_4^{2-}$, $Ca^{2+}+ SO_4^{2-}$ and $Mg^{2+}+ Ca^{2+}+ SO_4^{2-}$ were spiked. To trace the effect of magnesium/sulfate or calcium/sulfate groups, the concentration of both calcium and magnesium ions was increased two, three, and four times, while the concentration of sulfate ions was spiked twice more than divalent cations. In this paper, a specific format is used to clarify the type of water. For example, 10SW, 4S, 2 Mg, 2Ca shows 10 times diluted Caspian Seawater in which the
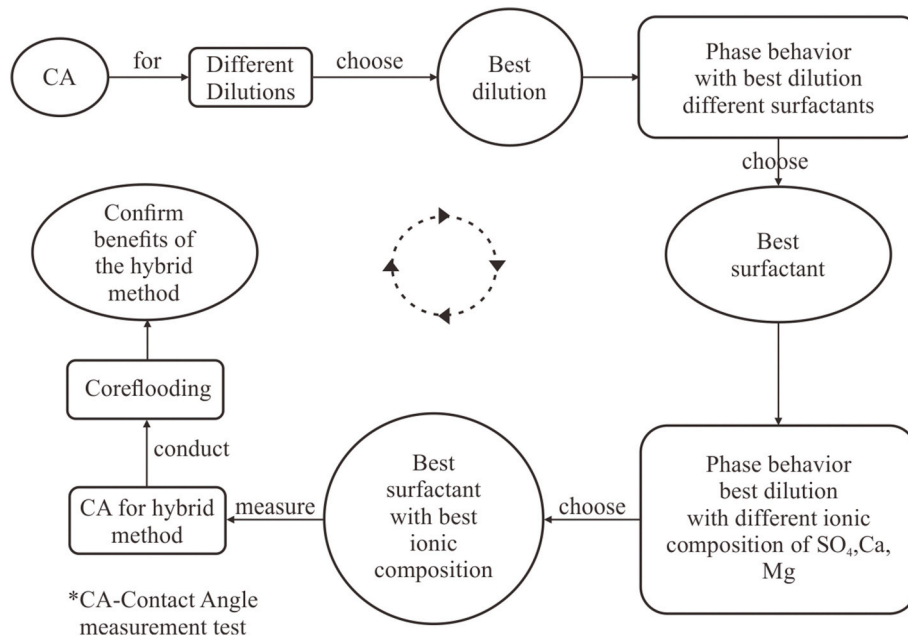
Fig. 6. A general roadmap of experiments.

Table 5
Contact angle measurement at different dilutions.

Brine	Initial contact angle	Final contact angle	Contact angle difference
Base	94	103	9
2X Dilution	94	112	18
10X Dilution	94	115	21
20X Dilution	94	111	17

concentration of sulfate ions is spiked for four times and concentration of calcium and magnesium cations are increased twice. Table 4 shows the composition of the different EW samples prepared for this study.

2.2. Surfactants

Anionic surfactant samples were used to achieve ultralow IFT between oil and water phases more easily and cheaply. Moreover, the challenge related to surfactant adsorption to the carbonate surfaces could be fixed by adding alkali (Na_2CO_3) and changing the surface charge of carbonate to a negative one [31]. In this study, two alkyl aryl sulfonate surfactants of benzenesulfonic acid, dimethyl-, mono-C11-16-alkyl deriv. (XOF-25S) and benzenesulfonic acid, C14-24-branched and linear, alkyl deriv. (XOF-26S) that was supposed to be thermally stable at 80 °C, from Huntsman were used. They interact very well with crude oils with short hydrocarbon lengths. We also used two types of anionic surfactants of benzenesulfonic acid, 4-C15-16-sec- alkyl deriv. (Soloterra 117H) and benzenesulfonic acid, 4-C10-13-sec- alkyl deriv. (Soloterra 113H), that were provided by Sasol Company. They were stable at 80 °C.

A co-surfactant, oxirane, methyl-, polymer with oxirane, mono (2,4-dinonylphenyl) ether (XOF-314C) from Huntsman, was used as well. Producers suggest mixing this co-surfactant with the main surfactant in 50:50 to 30:70 ratios. Also, poly (oxy-1,2-ethanediyl), alpha-butyl-omega-hydroxy (Sulfonic L4-2) co-solvent was used for fixing solution stability to the surfactant formulation and for decreasing the viscosity of the interfacial emulsion. Some additional information about the abovementioned surfactants and co-surfactants are shown in Appendix A.

2.3. Contact angle measurement

Contact angle measurements were done by the OCA 15 EC system manufactured by DataPhysics Instruments GmbH, Filderstadt (Fig. 3). The captive bubble method was used, where core pellets were placed into the medium of the studied fluid sample, and an oil drop was injected by syringe from the bottom of this core pellet. The oil drop rose and attached to the surface of the core pellet due to the density difference. The contact angle was recorded 3 times from both sides of the core pellets after stabilizing the oil drop. The average value was reported. To restore the initial reservoir rock conditions, for each test, core samples were inserted into the formation water for aging for 3 days at 80 °C.
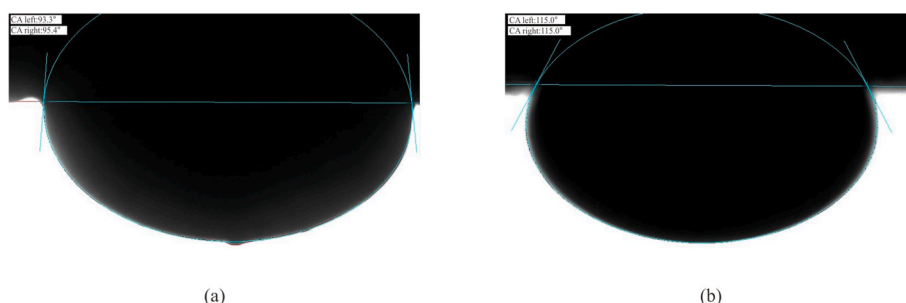

Fig. 7. Oil droplet on the rock surface after aging in oil (left) and aging in 10X dilution aqueous solution (right).

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Table 6
Surfactants screened at 10X diluted SW.

#	Surfactant	Surfactant ratio	Co-surfactant ratio
1	XOF-25S	30	70
2		40	60
3		45	55
4	XOF-26S	30	70
5		40	60
6		45	55
7	XOF-25S	50	50
8		70	30
9		100	0
10	XOF-26S	50	50
11		70	30
12		100	0
13	Soloterra 113H	100	0
14	Soloterra 117H	100	0

Cores were then aged by the crude oil at 80 °C for 30 days. Core samples were then inserted into different EW samples for 5 days to study the most optimized dilutions or the best ionic composition for the wettability alteration to a more water-wet state.

2.4. Aging & core flooding

The preparatory stages to reestablish core wettability were conducted on an aging cell apparatus (ACA 700) by Vinci Technologies. 3-inch plug samples were cleaned with distilled water and dried in the oven for 24 h. Plug porosity was measured by gas porosimeter with nitrogen, and absolute permeability was measured by injecting HSW. Core samples were saturated in the brine for three days and then for five weeks with crude oil at 80 °C to restore the original wettability. Flooding was conducted by the consequent injection of different fluids into the core sample (HSW, EW, and LSS). The whole system is schematically illustrated in Fig. 4. During work with this unit, confining pressure was set to about 1500 psi, back pressure was 500 psi, and the injection flow rate was altered from 0.5 to 10 cc/min to overcome the capillary end effect. All tests were conducted at 80 °C to mimic carbonate reservoir conditions in West Kazakhstan.

2.5. Aqueous stability & phase behavior study

Aqueous stability and phase behavior tests were conducted for different anionic surfactants in prepared EW samples. The surfactant stability, possible precipitation, and microemulsion phase development were studied. Samples with different ratios of XOF-314C co-surfactant to surfactant XOF-25S and XOF-26S were prepared. We selected ratios of 30/70, 40/60, 45/55, 50/50, 70/30, and 100/0. Aqueous solutions were mixed with magnetic stirring for an hour at 800 rpm. For each case, samples were poured into 10 ml glass burettes. Samples were traced after 3 days and 7 days. The stable surfactant formulations were identified visually by the clarity of black lines in the background. The same procedure was applied for surfactants provided by Sasol at 1 wt%

(a)

(c)

(b)

(d)
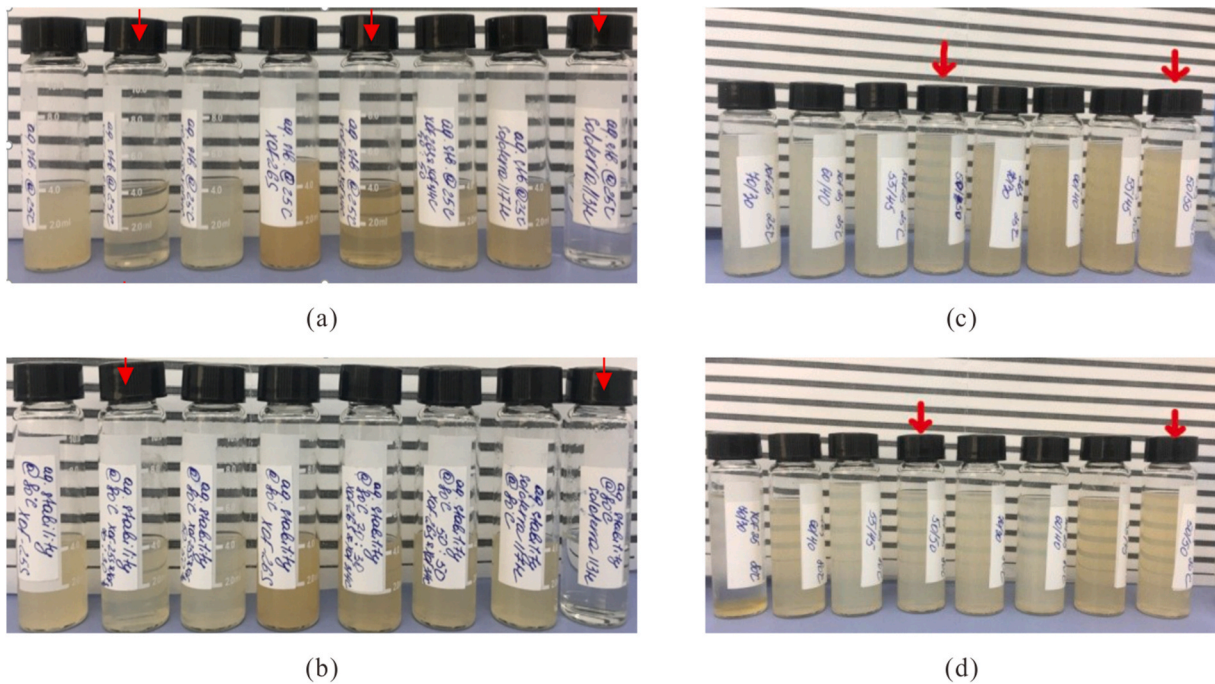
Fig. 8. a. Aqueous stability tests after 3 days at 25 °C (left); b. at 80 °C (right).

(a)

(b)

(c)
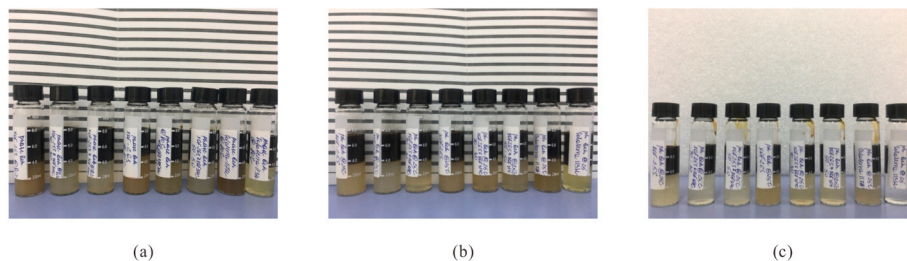
Fig. 9. Change in phase behavior for a few samples: top. Initial condition; middle. after 3 days at 25 °C; bottom. after 3 days at 80 °C.
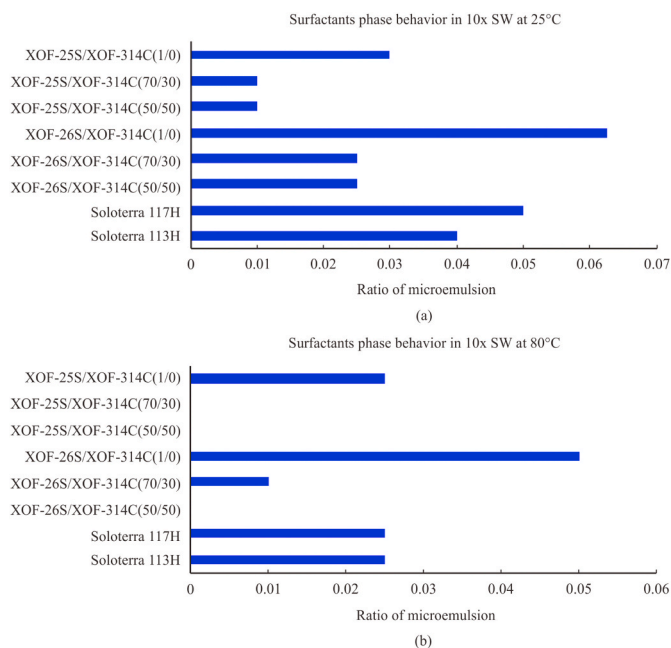
Fig. 10. Surfactant phase behavior in 10x dilution SW after 3 days at 25 °C (left); at 80 °C (right).

Table 7
Samples of chemical/EW for active ions study.

#	Chemical	EW	EW salinity, ppm
15	XOF26S/314C(70/30)	10xSW-S, Mg, Ca	1300
16	XOF26S/314C(70/30)	10xSW-0S, Mg, Ca	1000
17	XOF26S/314C(70/30)	10xSW-4S, 2 Mg, 2Ca	1600
18	XOF26S/314C(70/30)	10xSW-4S, 2 Mg, Ca	2300
19	XOF26S/314C(70/30)	10xSW-4S, Mg, 2Ca	2200
20	XOF26S/314C(70/30)	10xSW-6S, 3 Mg, Ca	3000
21	XOF26S/314C(70/30)	10xSW-6S, Mg, 3Ca	2900
22	XOF26S/314C(70/30)	10xSW-8S, 4 Mg, 4Ca	3700
23	Soloterra 113H	10xSW-S, Mg, Ca	1300
24	Soloterra 113H	10xSW-0S, Mg, Ca	1000
25	Soloterra 113H	10xSW-4S, 2 Mg, 2Ca	1600
26	Soloterra 113H	10xSW-4S, 2 Mg, Ca	2300
27	Soloterra 113H	10xSW-4S, Mg, 2Ca	2200
28	Soloterra 113H	10xSW-6S, 3 Mg, Ca	3000
29	Soloterra 113H	10xSW-6S, Mg, 3Ca	2900
30	Soloterra 113H	10xSW-8S, 4 Mg, 4Ca	3700

concentration and with no co-solvents. The stability of all solutions was analyzed at ambient room temperature, 25 °C, and a reservoir temperature of 80 °C. Unstable samples were screened out at this stage. A sample of the stability test is shown in Fig. 5. 2 ml of crude oil and 2 ml of each stable surfactant solution were added into the 10 ml burette and were shaken for 10 min to analyze the formation of the microemulsion phase. Samples were traced at both temperature ranges after 3 and 7 days to investigate the oil/brine solubility and the appearance of the Winsor type III microemulsion phase.

Contact angle measurements, stability tests, phase behavior studies, and microemulsion analyses were conducted to screen the best EW/LSS scheme. The flowchart in Fig. 6 was followed for the screening phase and oil displacement study. A sequence of experiments was conducted to determine the best dilution of Caspian Seawater. It was followed by aqueous stability and phase behavior tests at a certain dilution of various surfactants to identify the best surfactant formulation. Then, different fluid samples were prepared and their effects on contact angle alteration, aqueous stability, and phase behavior were tested to determine the most optimized ionic composition. The core flooding test was conducted using the proposed hybrid method with the optimized ionic

composition and chosen surfactant to study the oil displacement.

3. Results and discussion

3.1. Screening the best dilution of Caspian sea water

Wettability alteration of the limestone core samples was traced by analyzing the change in contact angle after aging in oil and after aging with different dilutions of the original brine. These readings are shown in Table 5. A sample oil drop attached to the carbonate pellets is illustrated in Fig. 7. The highest alteration in the contact angle occurred after aging in the 10X diluted SW, which was selected for the further stages of the study.

3.2. Aqueous stability & phase behavior

Numerous experimental observations of aqueous and thermal stability were implemented in this study. Sulfonic L4-2 co-solvent was also added in a range from 0.2 wt% to 0.5 wt%. However, there was no significant change in the stability of the samples. Hence, all tests were conducted without the co-solvent. All combinations of surfactant/co-surfactant (XOF314C) that were studied at this phase are shown in Table 6. At this stage, surfactant combinations were screened using 10X diluted SW.

Initially, the aqueous stability of XOF-25S and XOF-26S samples and XOF-314C co-surfactant with a surfactant to co-surfactant ratio varied from 30/70 to 100/0 were analyzed as shown in Fig. 8. Samples were traced after 3 days at the reservoir and ambient temperatures. The ones without precipitations and that were more transparent at both temperature ranges were considered stable, as marked in Fig. 8.

As a result of qualitative visual tests on these samples, the most aqueous stable surfactant formulations of XOF-25S & XOF-314C in the ratio of 70/30 and 50/50 and Soloterra 113H were identified. They were transparent solutions with visible black lines in the background. The next stage of the surfactant screening procedure was an analysis of the phase behavior, which is shown in Fig. 9. From these tests, the development of microemulsion phases was identified at 25 °C and 80 °C after 3 days. The height of the microemulsion phase for all stable samples in 10X dilution brine is plotted in Fig. 10. The most efficient surfactant/co-surfactant combinations were selected after analyzing stability tests and phase behavior results. Soloterra 113H and XOF-26S/XOF-314C (in the ratio of 70 to 30) surfactants were screened for further experiments.

3.3. Effect of active ions on phase behavior and contact angle

The selected surfactants were used to study the effect of active ions in the hybrid solution on CBR interactions, such as wettability, stability, and phase behavior. It was identified that the presence of Mg^{2+} and Ca^{2+} cations and SO_4^{-} is crucial to activating the multi-ion-exchange mechanism. Hence, the influence of groups of ions, $Mg^{2+}+SO_4^{2-}$, $Ca^{2+}+ SO_4^{2-}$ and $Mg^{2+}+ Ca^{2+}+ SO_4^{2-}$, were studied. Table 7 shows the sample number and the surfactant/brine type for each test. The effect of active ions on altering the contact angle was studied as the first criteria. The initial contact angle before aging in EW was in the 90–95° range, which shows a neutral wettability condition. After aging in EWs spiked by active ions, contact angles were changed to more water-wet conditions, as shown in Fig. 11.

The number of positive ions, such as magnesium and calcium, that are essential in detaching carboxylic groups of oil particles was crucial. The low concentration was not enough to initiate the multi-ion exchange process to detach the oil from the rock surface, while at very high concentrations, cations are repulsed by positively charged carbonate surfaces and are not effective anymore. Another important wettability influencer is a sulfate ion. It reduces the positive charge of the carbonate surface and catalyzes detaching oil particles using cations. Our studies showed that there is an optimum concentration of active ions that
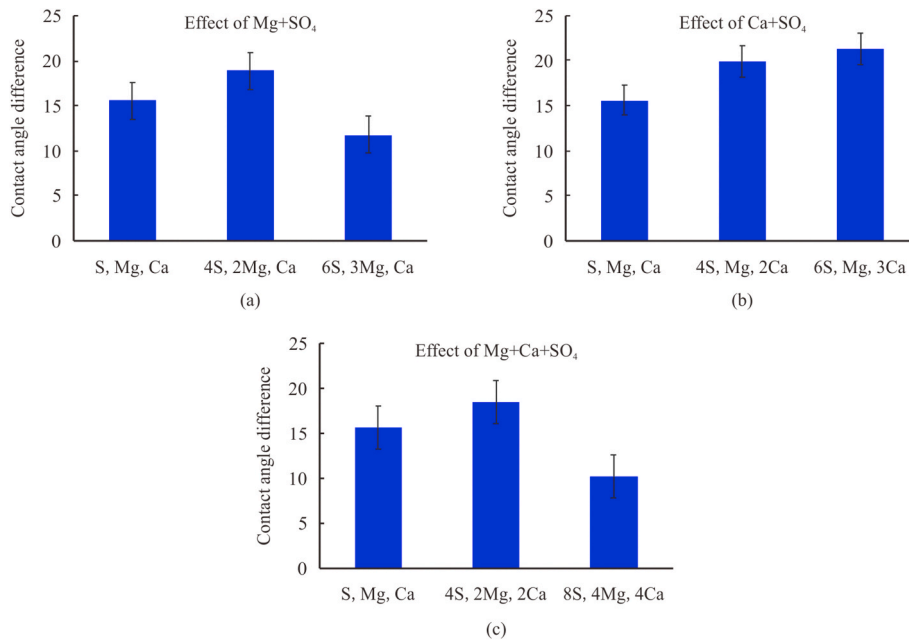
Fig. 11. The effect of various ionic groups on altering contact angle.
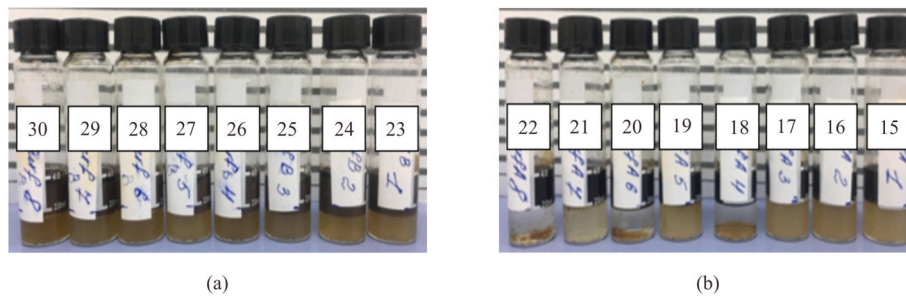

Fig. 12. Phase behavior after 3 days at 80 °C for samples 15–30.

changed the wettability of the limestone cores the most. The most optimal ion composition was identified at 10xSW_6S, Mg, 3Ca, which altered the contact angle to 21.3°, as shown in Fig. 11B. Spikes in the concentration of calcium ions were more effective in changing the wettability compared to magnesium ions due to higher contact angle difference at the test temperature. At elevated temperature magnesium activity is more. For magnesium ions, two times spiked concentration is an optimized amount while the increasing concentration of calcium ions is better for wettability alteration. Hence, 10xSW_6S, Mg, 3Ca and 10xSW_4S, Mg, 2Ca were screened as the most effective EWs at this stage of tests.

As the second criterion, the best performance of each surfactant at certain ionic compositions was studied and identified by stability and phase behavior tests, as shown in Fig. 12. All samples showed acceptable stability at this stage. For both XOF-26S/314C (70/30) and Soloterra 113H surfactants, phase behavior was investigated in the SW brine as the base case. No microemulsion phase was formed at these base cases, which shows the importance of applying EW for this EOR approach.

For all chemical/EW combinations the portion of the microemulsion phase was measured as an indicator of higher solubilization values. Fig. 13 shows the microemulsion ratio for all 16 samples. For Soloterra 113H, the ratio is similar for all EW samples. 10xSW_6S, Mg, 3Ca was selected due to providing the best performance to alter wettability and high microemulsion ratio. For XOF26S/314C (70/30), the size of the microemulsion formed was small and zero in many cases. 10xSW_4S, Mg, 2Ca was chosen due to the best performance in changing contact

angle and development of the microemulsion phase.

The best chemical/EW samples were used to study the wettability alteration and compare the hybrid method to standalone EW. Table 8 shows different combinations of brine and chemicals at this stage. Fig. 14 shows the measured change in contact angle after aging in different samples. The hybrid combination is more effective in terms of wettability alteration towards the water-wet condition. For example, the contact angle difference of the hybrid method was 10° more than standalone EW and 15° more than the conventional surfactant in SW. Figs. 13 and 14 show that hybrid EW/Soloterra 113H was significantly better than EW/XOF-26S/314C due to the higher microemulsion ratio, better aqueous stability, and more alteration in wettability toward the water-wet condition. Hence, Soloterra 113H/10SW_6S, Mg, 3Ca was selected as the best combination for the further oil displacement study. Moreover, for the best combination, IFTs of oil/surfactant and water/surfactant were calculated from the solubilization ratio using the Chun-Huh equation and were equal to 0.007 mN/m and 0.002 mN/m, respectively. The ultralow IFT values generated by the Soloterra 113H with 10SW_6S, Mg, 3Ca increases the capillary number and oil recovery.

3.4. Core flooding test

Our screening studies show that applying the optimized EW/surfactant affects the capillary number by changing IFT and wettability, which reduces the residual oil saturation during oil displacement. A core flooding test was conducted to examine this theory. The properties of the
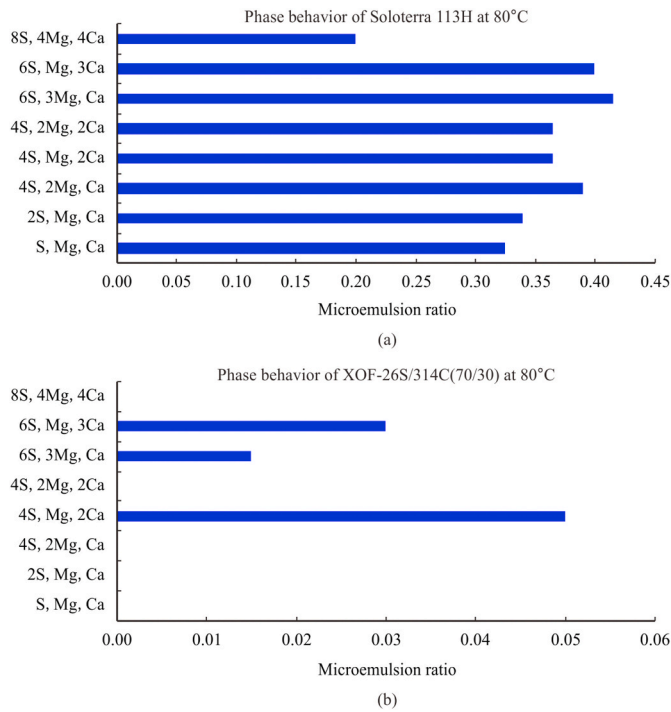
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Fig. 13. Microemulsion ratio of a. Soloterra 113H/EW samples b. XOF-26S/314C (70/30)/EW samples.

Fig. 14. Final contact angle measurement of the hybrid method.

Table 8
Chemical/EW samples to study the contact angle alteration by the best cases.

#	Chemical	Brine
31	Soloterra 113H	Caspian Sea
32	Soloterra 113H	10xSW-6S, Mg, 3Ca
33	–	10xSW-6S, Mg, 3Ca
34	XOF 26S/314C	Caspian Sea
35	XOF 26S/314C	10xSW-4S, Mg, 2Ca
36	–	10xSW-4S, Mg, 2Ca

Table 9
Properties of the core sample used in the oil displacement test.

L, mm	D, mm	Porosity %	Pore volume, ml	Absolute Permeability (mD)
71.45	38.27	19.41	15.95	16

Fig. 15. Pressure difference at various PV injected.

core used in this experiment are shown in Table 9.

The absolute permeability to water was measured by injecting HSW, recording the pressure drop at different injection rates, and applying the Darcy equation. The same procedure was then used by injecting oil. The oil permeability at residual water saturation was measured as 10.59 mD. During the oil injection, the volume of brine produced was measured and the Swi was calculated to be 37%. The core sample was then placed into the oven for 5 weeks at 80 °C and flooded with crude oil again to produce extra water and obtain higher initial oil saturation (Soi) before core flooding. However, no more water was produced and Swi remained 37%.

The core flooding test justified the benefits of the suggested hybrid method. Production enhancement due to the proposed hybrid method was observed from the consequent injection of HSW, EW (low saline smart water of 10xSW_6S, Mg, 3Ca), and hybrid low saline surfactant (10xSW_6S, Mg, 3Ca with Soloterra 113H) flooding. Figs. 15 and 16 show pressure drop and oil recovery, respectively, at different injection sequences. No more oil production and stable pressure drop were achieved at the end of each stage of injection and switching to the next sequence. It was decided to set the injection rate to 0.5 cc/min to have a recordable pressure difference, and then, the flow rate was increased to 5 cc/min to overcome the capillary end effect. As shown in Fig. 15, the initial pressure difference after HSW at 5 cc/min was 58 psi, which was reduced to 9 psi at the end of hybrid injection due to differences in mobility between oil and EW. With a reduction in the amount of oil in
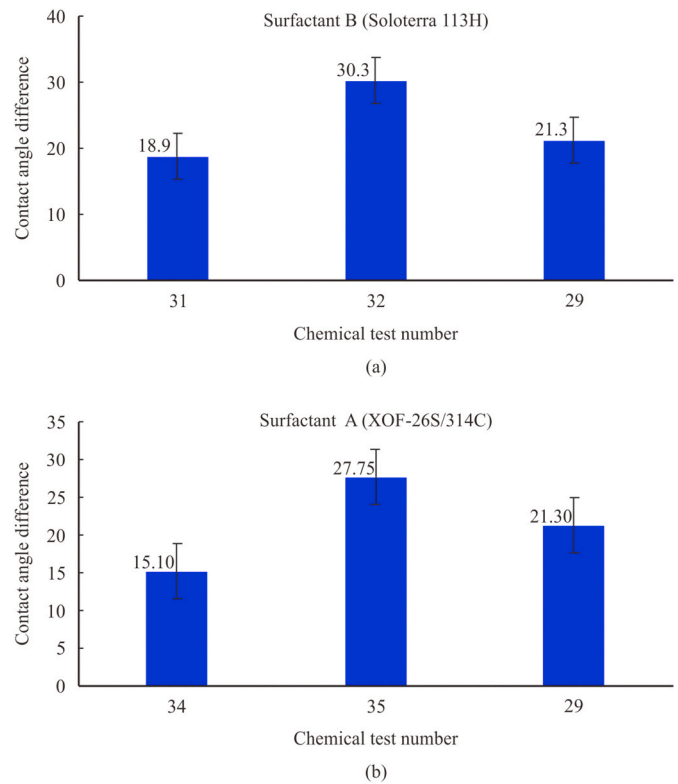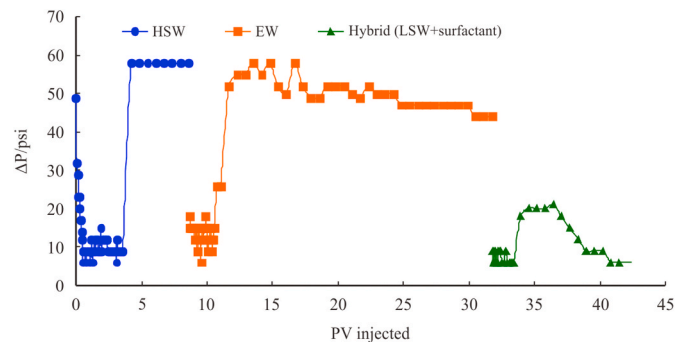
the system pressure drop becomes lower in the low salinity surfactant flooding due to reduced relative permeability to water and change in mobility.

The oil recovery trend can be traced in Fig. 16. Initially, oil recovery after HSW was about 52%. Then, oil recovery increased by 9% after injecting nearly 20 PV of the optimized EW (10xSW_6S, Mg, 3Ca). Switching to the optimized hybrid chemical/EW provides more than 10% increased oil recovery, which is noticeable and proves the good performance of the developed approach. Thus, 70% of oil originally in place was recovered after the tertiary injection of the hybrid method. As a result, of the successful surfactant formulation and study of the stability of emulsions, additional oil recovery after conventional oil
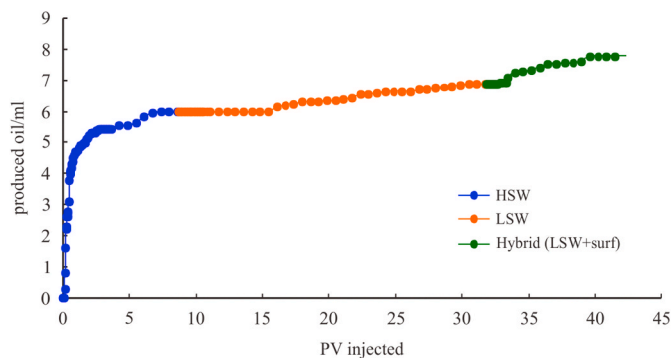
Fig. 16. Oil recovery at various PV injected.

recovery occurs that shows recovery from the trapped pores [34]. Reducing IFT and altering the wettability from the intermediate-wet to the water-wet state affected capillary forces and improved microscopic sweep efficiency [35,36]. These mechanisms are enhanced by applying the hybrid method. Hence, this approach can be used to improve the performance of anionic surfactant flooding in carbonate formations.

4. Conclusions

- The main objective of the study was to screen and design the hybrid EW/LSS method. To fulfill the designated goals of the study, numerous experiments were conducted. These tests mimic Kazakhstani oil fields with carbonate core samples, local crude oil, and brine samples. Wettability alteration, aqueous stability, the solubility of the oil/water interfaces, and oil recovery efficiencies were analyzed via contact angle measurements, phase behavior, and core flooding tests, respectively.
- Soloterra 113H (Alkyl Benzenesulfonic acid) was identified as the most suitable surfactant, which showed the best solubilization ratio, aqueous stability, and Winsor type III.
- The proposed hybrid engineered brine/surfactant combination was 10xSW-6SO$_4$, Mg, 3Ca with Soloterra 113H, which was chosen according to optimized wettability alteration, aqueous stability, and high solubility of oil/water interfaces. It shifted the contact angle 10° more to the water-wet state compared to the standalone optimized brine. The microemulsion phase volume was also increased by 40% compared to surfactant only.
- From the core flooding test, a total of 70% of the oil originally in place was recovered after tertiary injection of the hybrid method, while incremental oil recovery provided by the hybrid EW/LSS was almost 10%. Promising results obtained in this study make the proposed hybrid method relevant and attractive for further investigations and applications.
- Wettability alteration towards water-wet condition and reduction of IFT were effective mechanism to enhance oil recovery by the proposed hybrid method.

Acknowledgments

Appendix A

Name	Type of Chemical	Chemical formulation	Physical state	pH	Boiling/Cond. Point @25 °C	Flash point	Chemical stability at normal cond.
XOF-25S	Surfactant/ Huntsman Activity: 25 %w/w	Benzenesulfonic acid, dimethyl-, mono-C11-16- alkyl deriv., sodium salts	Liquid	7	100 °C	>100 °C	Stable
XOF-26S	Surfactant/ Huntsman Activity: 25 %w/w	Benzenesulfonic acid, C14-24- branched and linear, alkyl deriv., sodium salts	Liquid	7	100 °C	>100 °C	Stable
XOF-314C	Co- surfactant/ Huntsman Activity: 25 %w/w	Oxirane, methyl-, polymer with oxirane, mono(2,4-dinonylphenyl)ether Sodium chloride	Liquid, color white, odour like soup	10.66	Water solubility <500 mg/L, density 1.0126 g/cm3, kinetic viscosity 2034 mm2/s	Method closed cup	Stable
Sulfonic L4-2	co-solvent/ Huntsman Activity: 100 %w/w	Poly(oxy-1,2-ethanediyl), alpha-butyl-omega-hydroxy	Liquid	7.2	120 °C; density– 0,9622, viscosity kinematic– 7.54 cSt;	Method closed cup 64.2 °C	Stable
Soloterra/ 117H	Surfactant/ Sasol Activity: 92.3%w/w	Benzenesulfonic acid, 4-C15-16- sec- alkyl deriv.,	Dark viscous liquid	<2	density– 1.002 g/cm3, viscosity kinematic– 779.2 mm2/s	206.9 °C	Stable
Soloterra/ 113H	Surfactant/ Sasol Activity: 96.5%w/w	Benzenesulfonic acid, 4-C10-13- sec- alkyl deriv.,	Brownviscous liquid	<2	density– 1.06 g/cm3, viscosity dynamic– 2400 mPas	210 °C	Stable

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