A Novel Method with Dilute Surfactant Flooding by Considering the Effect of Time and Temperature on Crude Oil Aging, Experimental Study on Heavy Oil of Bangestan

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Abstract

Wettability alteration has been a sophisticated issue for scientists and reservoir engineers since early 20th century; thus, many investigations have been carried out to determine wettability and enhance it to ideal conditions, which leads to improvement in oil recovery. Dilute surfactant flooding has been ap-proved as one of the noteworthy methods in chemical flooding. Several petroleum reservoirs were rec-ognized as suitable nominees for surfactant/water flooding when screening criteria were established. Surfactant flooding was applied to mobilize the trapped oil in reservoirs. The key mechanism to enhance oil recovery by surfactant flooding was defined as rock wettability alteration. Experimental investigations into the impact of aging and temperature on wettability alteration were performed. Subsequently, core flooding test of surfactant was performed to define the effect of thinned cationic surfactant slug with cyclic 7 days technique (Multi-slug injection) on displacement sweep efficiency in the carbonate core of Bangestan reservoir with its heavy oil reservoir. Moreover, contact angle and interfacial tension (IFT) measurements were made to gain the supplementary information for a surfactant/waterflooding. The best concentration of C19TAB was determined by measuring interfacial tension values of the crude oil in contact with surfactant solutions prepared in synthetic brackish water. Results displayed a decrease in residual oil saturation by changing the contact angle and IFT reduction between oil and water. Moreover, aging was known as a significant constraint to change the wettability index to make similar oil-wet condition. Besides, laboratory experiments verified that the influence of wettability alteration was higher than IFT reduction.

Keywords

Oil aging IFT;
Surfactant flooding;
Time;
Temperature;
RPM.

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1. Introduction

Wettability is a topic of significance for reservoir engineers. Wettability change is one of the important guides to express the capability of oil recovery of reservoir. The main target in oil-wet condition is to alter wettability to water-wet condition to achieve additional recovery. Many classification methods for wettability measurement, such as Contact angle, Amott methods, and USBM, have been suggested by Anderson and others [5]. Some of these methods are more accurate and applicable than others. The most accurate and precise technique among others is contact angle for wettability measurement. Wettability is one of the considerable factors to select the greatest method for effective surfactant flooding in which small change in wettability will cause increase in oil recovery deeply. Contact angles (measured through the water) from 0 to 75° are consider water-wet, from 75° to 105° intermediate wet, and from 105° to 180 oil-wet [16]. Moreover, in recent years, different types of wettability alteration approaches have been proposed and conducted by scientists and experts in lab and reservoir conditions to change the wettability of rock formations, such as surfactant flooding, nanofluid injection, microbial, alkaline flooding, and so on.

Surfactant flooding is applied to mobilize the oil that is trapped in the interstice of reservoir rock. This approach aids to decrease residual oil by depressing IFT between oil – water, which leads to rise in capillary number [15]. Flood of surfactant similarly assists to recover additional oil by varying the reservoir rock wettability (Sheng, 2010) [23]. Babadagli studied the influence of chemicals and hot water on the capillary imbibition [13]. In the case of hot water injection, the maximum oil recovery was attained because of water imbibition. Additionally, he found that adding surfactant to the solution would result in more oil recovery at a higher production rate in comparison with the saline water injection.

Chen et al. in Yates-San Andreas reservoir core examined the impact of dilute surfactant on the oil recovery [17,21]. The results disclosed more oil recovery in dilute surfactant case than in brine injection. The two previous mechanisms for EOR were based surfactant flooding: both mechanisms had major impacts on mobilization of trapped oil wettability alteration versus IFT reduction. Wagner in 1996 found the importance of measurement of IFT in different areas, such as chemistry, chemical engineering, and petroleum engineering. Surfactant provided a low IFT with the oil phase, which could sweep trapped oil in interstice of reservoir rock. Fundamentally, when the surfactant formulation had contact with residual oil, non-aqueous drops under a pressure gradient were deformed as a result of low IFT and displaced through the pore throats. Nowadays, the main goal in IFT investigation is to determine optimum value of surfactant concentration versus cost and the price of oil. As the surfactant cost is comparatively high, in some cases, lower IFT could lead to further oil recovery and minor residual oil; however, it is not reasonable with regards to the cost of production of oil in Iran and economic evaluation indices with today's oil price. Therefore, the main purpose is to gain maximum economic profit.

Roehl and Choquette published a paper, which showed that more than half of the world's discovered oil reserves were in carbonate reservoirs. Furthermore, they estimated that more than 80% of Iran oil reserves were carbonate reservoirs. Mattax and Holstein found out that surfactants usage in carbonate reservoirs had restricted applications because of some difficulties, including high temperature, fractures, low matrix permeability, dead pore volume, high hardness and excessive salinity, heterogeneity, and adsorption. Thus, over 75% of reservoirs were not appropriate to current surfactant flooding.

Most of carbonate reservoirs are oil-wet or intermediate wet with low or intermediate permeability. The effect of reservoir wettability was a hot topic for reservoir engineers for a long time. Xianmin Zhou et al. in 1996 discussed the significance of creating wettability in the last recovery of oil by water flood. Aging is a procedure that influences the wettability index [19]. Two crucial parameters play important roles in aging: time and temperature. Commonly, geological time in reservoir condition is too long; however, to compensate for the influence of time, temperature is increased for a short time on cores in lab. Yao and Li in 2009 studied the wettability alteration performance of surfactants, which were importantly related to their item, type, and structure; consequently, the mechanism of ion pair formation by C_nTAB with acidic components in crude oil was experimentally confirmed to be prevailing in wettability change of carbonates. The rate of imbibition was amplified with temperature and reduced with saturation of irreducible water. Dodecyl Trimethyl Ammonium Bromide (DTAB), shown by Standnes and Austadin 2000 as a cationic surfactant at concentrations more than CMC, had 70% original oil in place (OOIP) recovery in oil-wet cores [18].

2. Experimental Setup

Core flood experiments were carried out in both water-wet and oil-wet carbonate cores of Bangestan reservoir. Besides, a lime stone core was also used to run in surfactant flooding. Contact angles were measured by a Dinolite digital capture camera microscope type AM413FI2TA Dino-Lite Pro. The stock tank oil used in this investigation had the viscosity of 0. 025Pa.s at reservoirs conditions (105°C, 17.2Mpa), and 0.06091 Pa.s and density 0.9095 gr/cm^3 at 25°C. The oil properties are provided in Table 1. For all steps of experiments, brine water was applied with salinity of 1 weight percent of NaCl and different surfactants, such as octylphenol ethylene oxide condensate (Triton X100) as anionic surfactant, sodium lauryl sulfate (SLS) as anionic surfactant, sodium dodecyl sulfate (SDS) as anionic surfactant, and Hexadecyl trimethyl ammonium bromide (C19TAB) as cationic surfactant, were applied in IFT test.

3. Aging of Core Slice

Two different techniques were applied for oil aging, of which one considered effect of time and the other considered effect of temperature. A core was split to several thin slices almost with the width of 2mm; some of core slices were aged at 25°C and some at 50°C. Saline droplet was utilized at the top face of core slices to measure contact angle. The contact angle was documented every thirty seconds, of which the change was less than 0.2 degree. This experiment was accompanied by waterproof sand paper of silicium carbid sofflex (Germany) to eliminate contamination and surface roughness of the core in advancing (receding) contact angle method. Furthermore, contact angle was measured repeatedly and the arithmetic average of contact angles was recorded for each experiment. All of the recording data had parallel trends in contact angle alteration. However, it was observed that both time and temperature had significant impact on contact angle. The optimum time to reach near (neutral) intermediate wet condition (Bangestan reservoir condition) at 50°C was about 10 days, although it took about 63 days with 25°C. Contact angle data are classified in Figs. 1-4.

Table 1. Bangestan oil composition

Component	Residual oil (mole %)	Associated gas (mole %)	Reservoir oil (mole %)
H2S	0.00	0.36	0.16
CO2	0.00	1.01	0.45
N2	0.00	3.47	1.55
C1	0.00	51.3	22.90
C2	0.09	17.00	7.64
C3	0.06	11.92	5.35
i C4	0.47	2.02	1.16
n C4	0.19	5.90	2.74
i C5	0.19	1.85	0.93
n C5	0.30	2.13	1.12
C6	6.11	1.99	4.27
C7	7.08	0.82	4.29
C8	6.32	0.22	3.60
C9	5.98	0.01	3.31
C10	5.33	0.00	2.95
C11	4.92	0.00	2.72
C12+	62.96	0.00	34.86
Total	100	100	100
GOR: 338.84 SCF/STB			

Molecular weight of residual oil	274
Molecular weight of C12+ fraction	370
Molecular weight of reservoir oil	165
Sp.Gr. of C12+ Fraction @ 60/60 °F	0.9599

Furthermore, a Dinolite digital capture camera microscope type AM413FI2TA Dino-Lite Pro, with micro touch (touch-sensitive), which was utilized on the microscope for taking pictures of 1.3M pixels (SXGA) and 8 infrared bulbs (940nm) with LED lights and magnification rate of 20x~230x, was used to take snapshots in this experiment (snapshot AM 411T); the results are shown in Fig. 5. Typical images of water droplet are demonstrated in Fig. 6. A typical screenshot of Dino software is shown in Fig. 7.

4. Interfacial Tension Measurement by Spinning Drop Technique

Oil recovery by surfactant flooding significantly depends on interfacial tension (IFT) change in real conditions; thus, analysis of IFT to conduct a good core flooding is indispensable. Surfactants may decrease IFT to 10^{-1}dynes/cm or even less. Four various surfactants were examined, of which three were anionic and one was cationic; octylphenol ethylene oxide condensate (Triton X100), sodium lauryl sulfate (SLS), and sodium dodecyl sulfate (SDS) were anionic surfactants and Hexadecyl trimethyl ammonium bromide (C_{19}TAB) was cationic surfactant. Surfactants concentration range was between 0.01-0.2 weight percent and the tests were piloted at 25°C by use of saline brine solution of Sodium chloride with 1 weight percent as the water phase. The properties of Sodium chloride are shown in Table 2.

Furthermore, IFT measurements were carried out at 2360, 4000, and 6000 Revolutions per Minute (RPM). As the surfactant concentration of C_{19}TAB was amplified, the IFT declined to about 0.05 weight percent and, then, increased. SLS was constant at around 2.5 in 4000RPM. IFT of SDS was gradually reduced with increase in concentration. IFT measurement outcomes indicated that the best surfactant with the lowest IFT was C_{19}TAB in comparison with SDS, SLS, and TRITON X100 for this oil. Thus, C_{19}TAB was chosen for water flooding. The C_{19}TAB was produced by Merck Company with HS NO 29239000 and molecular weight. Critical Micelle Concentration (CMC) of C_{19}TAB was 0.8-1. The spinning drop results disclosed that 0.05 weight percent of C_{19}TAB was the optimum concentration, which well-matched Bangestan oil. IFT increased due to the cavitation phenomenon. Figs. 8-11 demonstrate IFT versus surfactants concentration at various RPMs. PH of surfactant solution was about 8 in all tests. Typical images of IFT software and a drop of oil in surfactant aqueous are shown in Figs. 12-13.

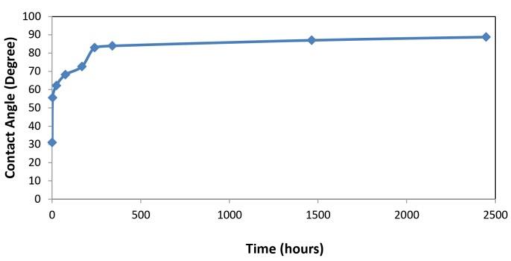

Figure 1. Contact angle measurements without sandpaper in a core slice at 25°C

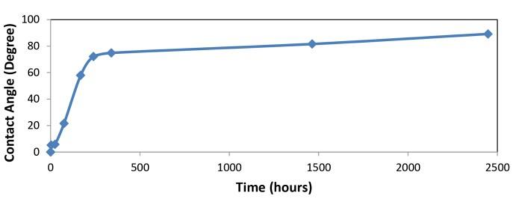

Figure 2. Contact angle measurements with sandpaper in a core slice at 25°C

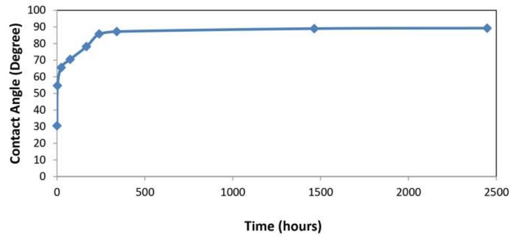

Figure 3. Contact angle measurements without sandpaper in a core slice at 50°C

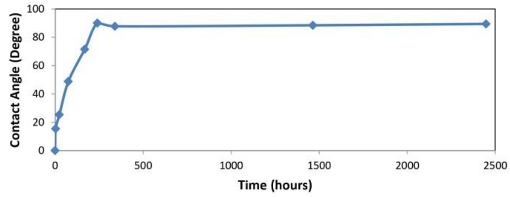

Figure 4. Contact angle measurements with sandpaper in a core slice at 50°C

Table 2. Nacl (Sodium chloride) properties

Assay	>99.5%
PH(5% water)	5-7.5
Br	<.005%
I	<.001%
Po4	<.0025%
So4(sulfate)	<.0005%
As	<.0001%
Loss on drying(130°C)	<.5%

Molecular weight: 58.44 gr/mole, Batch No: 112011219

Figure 5. Schematic view of Dino-Lite Pro Microscope with 10cm (H) x 3.2cm (D) and 100g weight

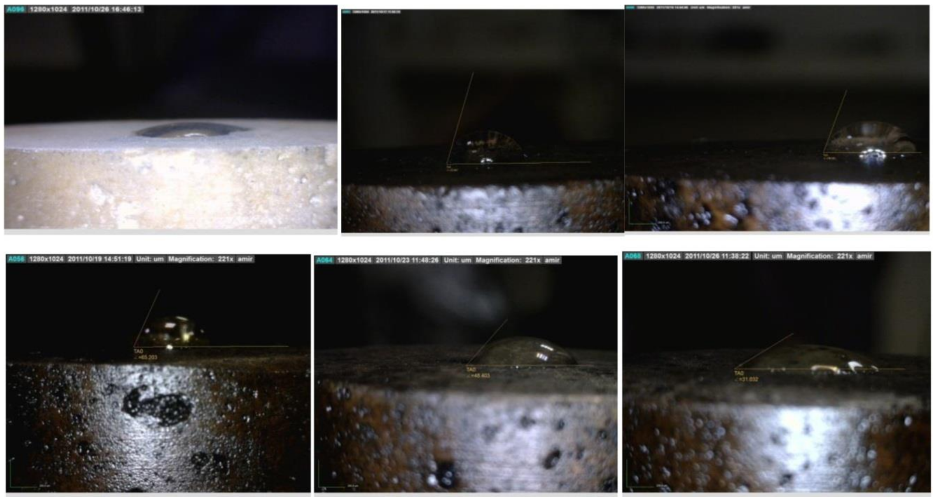

Figure 6. Contact angle measurements during oil aging

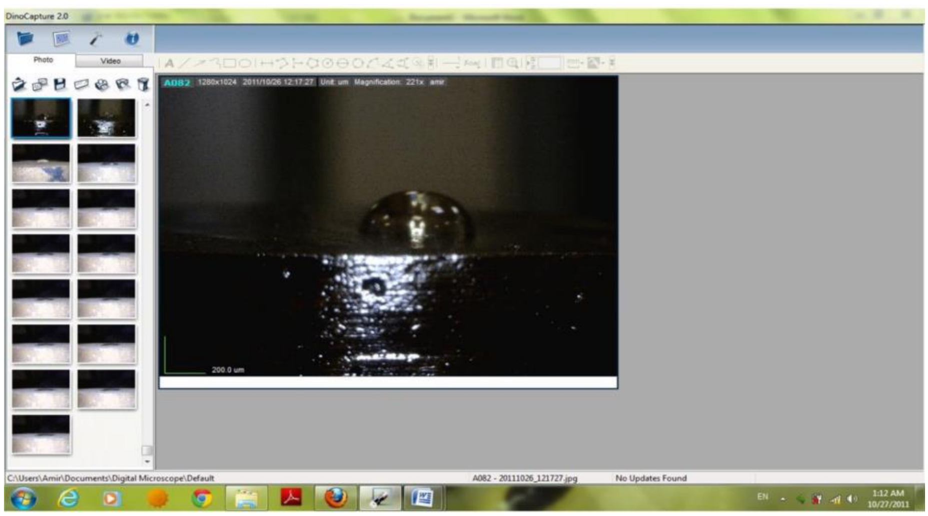

Figure 7. A typical screenshot of Dino software

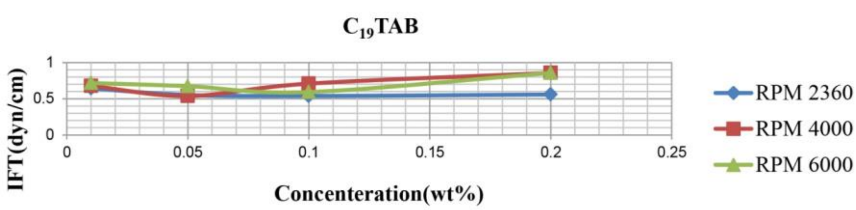

Figure 8. IFT vs. surfactant concentrations at different RPMs for C19TAB

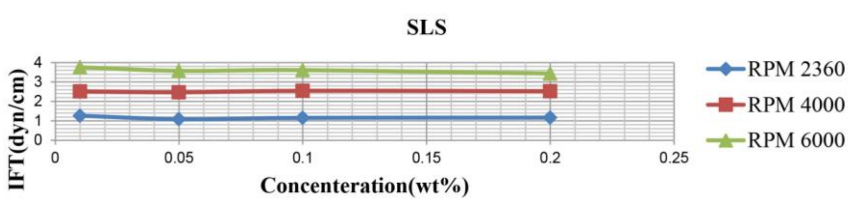

Figure 9. IFT vs. surfactant concentrations at different RPMs for SLS

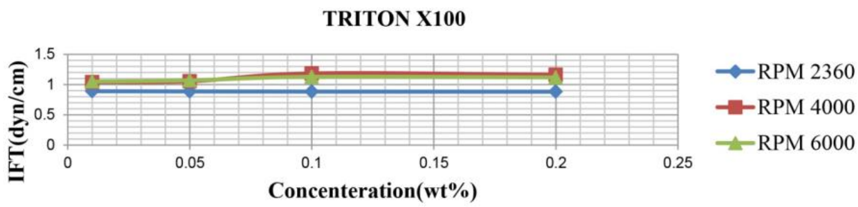

Figure 10. IFT vs. surfactant concentration at different RPMs for TRITON X100

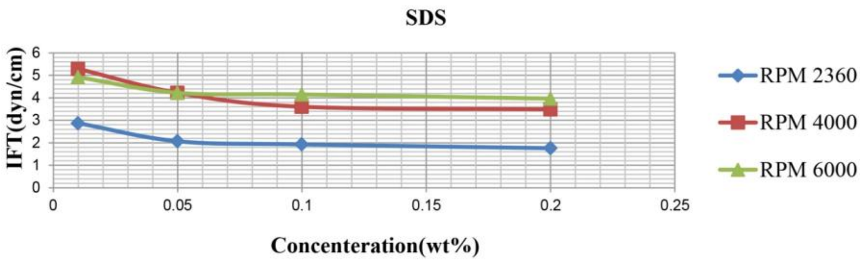

Figure 11. IFT vs. surfactant concentrations at different RPMs for SDS

Figure12. A screenshot of IFT software measurement

Figure 13. Drop of oil in surfactant aqueous

5. Effect of Time on Recovery by Synthetic Brine Soaking

At the first step, cores were aged for 10 days at 50°C. Then, each core was soaked in 1000PPM saline water in different time intervals of 3, 7, and 14 days (time interval was the only variable). Afterwards, experiments were continued step by step by the specific procedure in Table 3. As the results show in the 2nd and 6th columns of Table 3 for the static condition, unlike C_{19}TAB, synthetic brine had small influence on the wettability alteration and recovery. The results for C_{19}TAB soaking are provided in the next section. Recovery by spontaneous imbibition (water) was almost the same and around 3 percent. Besides the effect of time, it is negligible in static condition, because it leads to almost 1.2 percent more recovery.

Table 3. Effect of time on recovery by synthetic brine soaking

Core (1)	Oil recovery (%) (2)	Drying time at 50°C (days) (3)	Vacuum time at 25°C (4)	Soaking time in surfactant (days) (5)	Oil recovery (%) (6)	Drying time at 5°C (days) (7)	Vacuum time at 25°C (8)	Soaking time at 1000PPM synthetic brine (9)
1	3.11	3	8	3	1.24	3	8	3
2	3.09	3	8	3	1.20	3	8	7
3	3.16	3	8	3	1.22	3	8	14

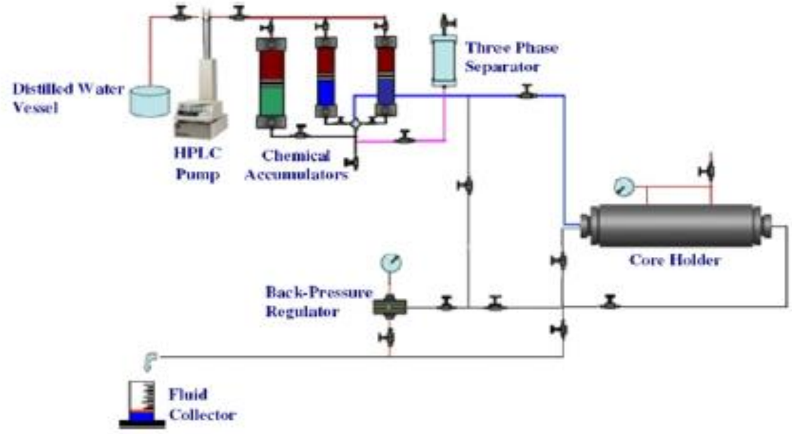

Figure 14. Schematic diagram of core flood device; (1) distilled water container, (2) positive displacement pump, (3) surfactant accumulator, (4) oil accumulator, (5) low saline water accumulator, (6) three-phase separator, (7) core holder, (8) back pressure regulation system, (9) fluid collector

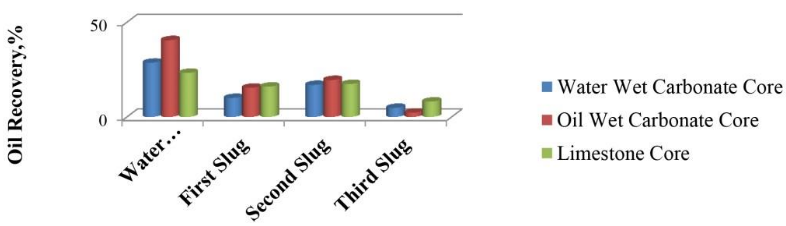

Figure 15. Total oil recovery

6. Dynamic Surfactant Flooding by Core Flooding System

Multi-slug injection of surfactant has higher oil recovery, since it can extend displacement time of surfactant and decrease ineffective flow in the reservoir. However, it has a complex operating process, which increases the operational cost. C_{19}TAB was injected into the carbonate core of Bangestan reservoir with approximate permeability of 19md at 50°C. Surfactant was injected into the cores in water-wet and oil-wet conditions. Furthermore, 2 extra experiments were performed with carbonate core of Bangestan reservoir with typical permeability of 12md to prove the trend of the results in the previous experiment. Similarly, in the similar experimental conditions, an experiment was carried on the limestone core to compare the results of the recovery in limestone and carbonate core. The schematic of core flooding setup is demonstrated in the Fig. 14. Flow rate of injection was set at constant rate of 1cc/min. Moreover, overburden pressure and back pressure regulators was fixed at about 1500Psi and 1000Psi, respectively, to stop formation of gas by light ends in crude oil and continuous fluid production. The concentration of surfactant C_{19}TAB in all tests was precisely 0.05 weight percent.

After measurement of porosity and permeability of samples, the core was saturated with the Bangestan oil from Ilam formation. The test had 4 steps: in the first step, recovery was measured by low saline water injection. In the second step, 0.05 weight percent of $C_{19}TAB$ was injected and recovery was calculated. In this step, since water cut reached 99%, the outlet valve of core holder was closed and 1 pore volume of $C_{19}TAB$ was injected. Then, valve was shut and core was soaked for 7 days in $C_{19}TAB$ solution. In the third step, after 7 days of soaking, again, $C_{19}TAB$ was injected up to 0.99% water cut and the produced oil was measured. Again, in this step, after closing the outlet valve, 1 pore volume of surfactant was injected into the core. Finally, in the last step, the inlet valve was closed and the core was soaked for 7 days in $C_{19}TAB$ solution.

In water wet-condition, for 19md core, water flooding recovery was around 28.64 %. In the first, second, and third steps, $C_{19}TAB$ injection was about 10.02, 16.9, and 4.8 percent, respectively. Furthermore, a test carried out in oil-wet condition showed a significant increase in recovery in each step. In oil-wet condition, water flooding recovery was 40.54% and in 3 steps of surfactant injection, recovery was about 15.42, 19.51, and 2.25 percent, respectively.

In the limestone core with average permeability of 2md, a similar technique was utilized. In the water-wet condition recovery by water flooding was 23.25% and by surfactant injection was about 16.02, 17.39, and 8.12 percent in order. Total recovery is shown in Fig. 15.

7. Conclusion

In this paper, at first, the impact of time and temperature on core oil aging by contact angle was investigated. Then, spinning drop experiments were used to investigate the surfactant type effect on IFT in different RPMs. Furthermore, impact of time on recovery by synthetic brine soaking was considered. At last, surfactant core flooding test was done to investigate the effect of dilute $C_{19}TAB$ on sweep efficiency. The final results could be seen through 1 to 10 as follows:

1. Comparison of recovery in 3 steps of surfactants injection shows that in the second step, (due to wettability alteration) maximum recovery is obtained, followed by that in the in the first step (due to surface tension) and the last step (second wettability alteration), because of high production in the previous 2 steps.
2. The oil impurities do not have any significant effect on the oil aging trend.
3. Wettability alteration is the dominant mechanism in the surfactant flooding recovery in comparison with IFT reduction.
4. Contact angle is mostly affected by temperature, rather than time, in core oil aging in lab. With 25°C, it takes about 63 days to reach reservoir condition; but, in 50°C it takes almost 10 days.
5. The behavior of the IFT vs. surfactant concentration shows more acceptable results for cationic surfactants.
6. In static mode, there is core soaked with salt water at different times, indicating that unlike surfactants, it has negligible effect on the wettability alteration and recovery.
7. Surfactant core flooding shows more recovery in oil-wet case.
8. By increasing RPM in constant surfactant concentration, IFT could increase due to cavitation; therefore, any surfactant has an optimum RPM.
9. The optimum $C_{19}TAB$ concentration is 0.05 weight percent.
10. The total recovery increases step by step.

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