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Amphoteric and Cationic Surfactants for Enhanced Oil Recovery from Carbonate Reservoirs

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Abstract -In recent decades, chemical surfactants have significantly been utilized in enhanced oil recovery (EOR) process and researchers still have a distinctive look to applications of these chemicals. In this study, Hexadecyl-tetra Methyl Ammonium Bromide (henceforth; HTMAB) and Hexadecyl-Amino-Benzene Sulfonic Acid (henceforth; HABSA) were used as surfactants to drive relative permeability curves in carbonate rocks. To this end, the contact angle between different concentrations of two surfactant solutions was measured in the bulk volume of kerosene using a VIT-6000 apparatus. Additionally, the unsteady state core flooding process (JBN method) in three steps (water injection, surfactant HTMAB injection and surfactant HABSA injection) was utilized to analyze the relative permeability measurements and finally oil recovery was evaluated at different conditions. According to the results of this study, HTMAB has the maximum oil

recovery factor of 63.50% among the other scenarios assessed in this work. Hence, it is concluded that in carbonate rocks, HTMAB is more effective than HABSA as it has better efficiency to modify the wettability toward water-wet. Furthermore, for HTMAB flooding, it is indicated that relative permeability curves intersection depicts the water saturation of 0.67 and according to the outcomes; the end-point of water is less than oil in relative permeability curve. Therefore, it can be concluded that HTMAB is more impressive than HABSA in wettability variation of these sorts of rocks.

Keywords -Surfactant; Hexadecyl-tetra Methyl Ammonium Bromide (HTMAB); Hexadecyl-Amino-Benzene Sulfonic Acid (HABSA); Wettability; Contact angle; Relative permeability.

1. Introduction

Nowadays because of the soaring tendency of countries to energy use and the subtractive of the new oil fields (greenfield) discoveries, there is a crucial need of technological methods to re-expand the oil fields to reinforcement at the reservoir condition[1-4]. The rate of exploitation of different trapped sorts of fossil resources affects common energy requisition[5-9]. Although the high amount of oil is exploited daily, approximately thirty percent of the oil reserves have been produced by natural drive mechanisms of oil recovery techniques[10-15]. Thus, enhanced oil recovery (EOR) methods can exploit the extra oil[16-19] because the remaining trapped oil is a huge and charming target for EOR techniques in petroleum industry[20-24].

The two main parameters that have a straight influence on EOR processes are capillary number and mobility ratio and in EOR sector be attempted to improve oil production by changing these two factors. Altering wettability might have a major effect on the capillary force, relative permeability, flooding behavior, residual oil saturation, etc[25-30]. Thus, one of the vital matters that cannot be overlooked is still wettability. Naturally, the reservoir rocks tend to be more intermediate to oil-wet because of the mineral composition of the rock, combination of reservoir fluids, temperature and pressure of the reservoir [31-33]. A significant part of oil reservoirs includes carbonate reservoirs, and most of them are oil-wet. Capillary pressure in this type of reservoirs is normally low and negative; therefore, water cannot spontaneously imbibe into the matrix [34-38]. Some useful methods to enhance the displacement of efficiency carbonate oil reservoirs are to reduce oil viscosity and lessen the interfacial tension to alter rock wettability. The fulfillment of surfactant injection in reservoir has caused to rock wettability alteration, and it leads to favorable exploit of the trapped oil[39, 40]. In surfactant flooding, the surfactant molecules reduce the interfacial tension of very small of oil droplets to enhance its mobility[41-43].

Okasha et al. evaluated the wettability of Unayzah reservoir by utilizing USBM, Amott, and the prediction of contact angle in Central Saudi Arabia fields. Due to the USBM and Amott indices, it was deduced that the wettability is not unique and alters from neutral to water-wet. For both oil-brine/rock and oil-brine/quartz systems, there is a disclosed water-wet condition due to the contact angle evaluations[44]. Christina M. assessed the behaviour of wettability differentiations of oil-wet carbonate rocks by the utilization of various ionic concentrations, varying salinities and non-ionic surfactants. The investigation of wettability alteration was conducted by employing the sessile drop contact angle measurement. They suggested that Ca^{2+} ions alone could cause wettability alteration of carbonate rock toward water-wet. Non-ionic surfactants cause a minor alteration in the wettability and thus can be noneconomic to use in field scales[45]. Amirpour and Shadizadeh used three chemical surfactants (CTAB, SDS and Triton X-100) and a natural surfactant (ZizphusSpina Christi) for the determination of wettability alternation in carbonate rocks. They measured contact angle, and their findings show that the natural surfactant flooding provides a profound effect on wettability alteration from oil-wet to mixed-wet or water-wet rock. According to this result, Zizyphus Spina has beneficial effects on oil recovery and wettability alteration[46]. Masoumeh Tajmiri et al. used ZnO nano-particles as an additive in the core flooding process and analyzed relative permeability curves. They concluded that the addition of ZnO nano particles causes the wettability changed to water- wet in the core samples[47]. Safari (2014) investigated the utilization of polysilicon nanoparticles on the oil recovery enhancement as this nanoparticles can alter the rock wettability. It is concluded that increase of nanoparticle concentration caused to decrease the contact angle [48].

The main intention of this research was to use two different surfactants namely Hexadecyl-tetra Methyl Ammonium Bromide (HTMAB) and Hexadecyl-Amino-Benzene Sulfonic Acid

(HABSA) to drive relative permeability curves in carbonate rocks. The unsteady state core flooding process in three different scenarios of water injection, water and HTMAB injection and water and HABSA injection were investigated to analyze the relative permeability measurements and compare the oil recovery factor and contact angle measurements for each of the scenarios. The variety of suitable and comprehensive methods give us a good view and reliable outcomes. It can be concluded that HTMAB, is more impressive than HABSA in wettability variation of these rocks.

2. Materials and Methods

2.1. Materials

2.1.1. Surfactant

In this work, HTMAB and HABSA were used as surfactants. For preparing Hexadecyl Tri Methyl Ammonium Bromide, three chemical solvents were used. 10 mL of Hexadecyl Bromide ($\text{C}_{16}\text{H}_{33}\text{Br}$) ($p \geq 96.5\%$, Sigma-Alorich), 5 mL of Trimethylamine $[(\text{CH}_3)_3\text{N}]$ ($p \geq 99\%$, Sigma-Alorich) and 100 mL of solvent acetonitrile (CH_3CN) ($p \geq 99.9\%$, Merck) were mixed with each other in a container. After heating and stirring the resulted solvent for 24 h, it was cooled down to 25°C . The precipitated white powder was collected and then washed with acetonitrile and finally dried with hot-air[49].

HABSA was prepared by mixing 5 mL of the concentrated hydrochloric acid ($p \geq 30\%$, Merck) and 54 mole of ortho-sulfanilic acid ($p \geq 99\%$, Merck) with 125 mL water. This solvent

was stirred until a homogenous solution was attained. After obtaining a homogenous solution, 6.5 mL of acetic anhydride ($p \geq 98\%$, Sigma-Alorich) was added to this solvent. On the other hand, 5.6 g of sodium acetate ($p \geq 99\%$, Merck) were dissolved in 35 mL of water in another container. The content of both containers was mixed and stirred in an ice bath. The obtained white precipitated powder was collected and then dried in a vacuum oven at $80\text{ }^{\circ}\text{C}$ [50].

2.1.2. Oil Phase

Kerosene was used as a base media for interfacial tension (IFT) measurements, and the crude oil donated from National Iranian South Oil Company, Ahwaz, was utilized as flooding and ageing phase. The viscosity and density of crude oil at ambient temperature that was used in this experiment are 35 cp and 0.8 g/cm^3 , respectively. Moreover, the kerosene density is about 0.84 g/cm^3 (Aging and flooding tests were performed at reservoir temperature, about 60°C).

2.1.3. Core Plug

Primary rock sample, which was used in this study, was prepared from Babakoochi field (Fars state-Iran). The core plug and flat polished pellets were taken from this sample and used for flooding and contact angle measurement tests. **Table 1** presents core sample characterization utilized in this work. The percentage of rock mineral composition is statistically illustrated in **Table 2** according to the XRD method.

2.2. Methods

2.2.1. CMC Measurement

CMC (Critical Micelle Concentration) is an essential property of a surfactant. In EOR processes, this property of surfactant is very applicable. Previous researchers recommend different

methods for CMC measurement. These techniques include interfacial tension, electrical conductivity, turbidity and pH measurement. The electrical conductivity technique was used to measure the CMC of surfactants. Therefore, various solutions of the surfactant in distilled water were prepared over the range of 50 to 7000 ppm. If the conductivity of solutions is plotted versus the concentration of surfactant, two distinct trend lines will appear. The intersection of these lines in the unique concentration is called CMC[51].

2.2.2. Contact Angle Measurement

To investigate wettability alteration on a rock surface, contact angle method is used. The angle is assumed as a criterion of rocks surface wettability. In this approach, these species, before ageing at different concentrations of surfactants, at first were cleaned by Soxhlet extractor with toluene as a solvent and then aged with the reservoir crude oil from Asmari formation (Iran) for approximately two weeks (around 60 °C) to become oil-wet ultimately[52]. These measurements were obtained in a three-phase system [35]. One of the polished pellets was aged with distilled water to control the results. This measurement must be fulfilled very masterfully to ensure that the water drop is fixed to the sample surface [53]. All the experiments were conducted at 25°C, and images of the drop shape were captured with a high-quality camera. Kerosene was utilized as a bulk fluid and distilled water as a dropping fluid. A VIT-6000 system was used for this purpose. The water drop was scattered on the rock surface, and the contact angle was evaluated.

2.2.3. Relative Permeability Measurement

Relative permeability curves were used as a qualitative approach for analyzing wettability alteration in carbonate rocks. These curves have two indicators of wettability alteration: the end-

point value and the intersection of two curves. End-point of the non-wetting will be more than the wetting end-point, and the intersection point of two curves, where wetting phase relative permeability (K_{rw}) is equal to non-wetting phase relative permeability (K_{rnw}) can also serve as a wettability index [54].

To measure relative permeability, the unsteady-state technique was applied. In this technique, at first, the core sample is saturated with wetting phase, however, unlike the steady-state method, one phase is only injected into one side of the core and two-phase is left from the other side. Water driving test is quick and very simple by unsteady-state method. To do so, a homogenous core is selected, and its petrophysical properties like gas permeability, helium porosity and bulk volume are determined. The core sample absolute permeability is obtained, and the oil phase is flooded into the core sample at unchanged condition (rate/pressure) to measure the initial water saturation. Finally, the core plug is de-saturated in water saturation processes at one side; both oil and water are attained at the other side.

After that, the oil phase was injected at low rates (0.5 or 1 cc/min) for two pore volumes because it should displace water with a uniform front. Oil was then injected with the flow rate of 2 or 3 cc/min to ensure that no more moveable water existed in cores. At this point, the core was at connate water saturation; therefore, distilled water was not observed in the effluent produced by the 1 or 2 oil pore volume injection. Since then, the water phase was injected at a low rate to obtain the residual oil saturation. At first, water was injected and then when oil had not been observed in the effluent, the produced oil was collected and measured, and hence residual oil saturation was obtained[55].

2.2.4. Core Flooding Procedure

The plug was covered by a sleeve and was embedded in the core holder. The overburden pressure was fixed, and distilled water was allowed to inject to the plug with a steady condition was recorded digitally by the pressure gauge. The oil produced was measured and calculated the total oil recovery. To attain the residual oil saturation, water flooding with distilled water was fulfilled after the oil flooding. By injection approximately three pore volumes of distilled water into the core by a slight steady flow rate (0.2–0.5 cc/min) the natural residual oil saturation was attained after water flooding. For making sure that there is no more moveable oil existed, these different flow rates were applied in the core. After measuring the amount of oil recovery from the primary and secondary recovery process, the core samples were flooded with the surfactant solution with an unchanged rate. Finally, the oil produced was estimated and used to measure the critical oil saturation and oil recovery factor.

3. Results and discussion

3.1. CMC Measurement by Conductivity Measurement

The conductivity method was employed to determine CMC, as mentioned earlier. Oakton-CON 150 conductivity-meter was used for measuring the electrical conductivity of samples. Concentrations and corresponding conductivity of each surfactant are given in **Tables 3** and **4**. As explained earlier, the CMC point was obtained by plotting the intersection of two lines with different trends in figure. These results for HABSA and HTMAB are shown in **Figures 1** and **2**, respectively. As the results show, HABSA has more CMC than HTMAB. It should be noted that these measurements were accomplished at 25 °C and the atmospheric pressure. The CMC values for HTMAB and HABSA are 814 ppm and 2250 ppm, respectively.

It can be mentioned that, within these measurements some errors might be taken into account. For instance, errors of instruments, environmental conditions (temperature, pressure and etc...), the quality of surfactants or other materials, and human errors may be impressive, but, we tried our best to minimize the mistakes and errors.

3.2. *Contact Angle*

First, the contact angle was measured for a saturated pellet with distilled water employing water drop, indicating the oil-wet condition ($\theta = 147.41$). As can be observed in **Figure 3**, the distilled water drop has not spread on the pellet surface of rock, which depicted that the surface's wettability remained oil-wet. The contact angle was then estimated for all pellets, which were aged at different concentrations of surfactants and all evaluations were performed at ambient condition (P 14.7 psi, T = 25 °C).

Figure 3 depicts the contact angle versus different concentrations of HTMAB surfactant. By raising the concentration of surfactant, the contact angle declines. As approaching the critical micelle concentration, the contact angle declines dramatically to about 64.75. After the CMC point, the contact angle has a steady decrease, and it relatively remained stable. Ultimately, it reaches 62.1° for 3000 ppm of surfactant concentration.

To evaluate the considerable influence of HABSA surfactant on the alteration of wettability, the carbonate pellets were immersed in various surfactant concentrations after being aged them in the crude oil for two weeks. Next, the contact angle of the aged pellets was measured. As can be illustrated in **Figure 4**, the contact angle in 100 ppm of HABSA is 148°. Besides, due to the increase of surfactant concentration, the contact angle diminishes by the concentration of 3000 ppm concentration, and it has reached 83°. Since then, there are no remarkable changes in

the contact angle. Around the CMC amount (2250 ppm) the angle is achieved 87° and the most suitable amount for these experiments is 2250 ppm. Changing in contact angle values after CMC might be related to errors such as error instruments. In addition using surfactant above the CMC level might cause the precipitation of surfactant in porous media and it has a negative impact on permeability and then oil recovery. Finally, it is not important if lower value of contact angle is obtained in higher concentrations **Figure 5** shows the images of water drops on pellets surfaces in different solutions. Furthermore, it can be concluded that the HTMAB is more striking than the HABSA for changing the wettability in these rock pills.

3.3. Relative Permeability

In this work, the oil and water relative permeabilities (K_{ro} & K_{rw}) were obtained by Toth et al. (2006) method. **Figure 6** illustrates these curves during waterflooding. As can be depicted, the intersection point of relative permeability curves was around water saturation of 0.5, and the K_{rw} at the residual oil saturation was 0.25. This is considered as an indication of intermediate to water-wet condition. However, the end-point of K_{ro} at S_{wi} is more than K_{rw} at S_{or} , which is not an indication of oil-wet condition.

Figure 7 illustrates the relative permeability curves of the surfactant (HABSA) flood. As can be observed, the intersection point of two curves was around water saturation of 0.56, and the K_{rw} at the S_{or} was 0.26. As can be seen, the intersection point was shifted slightly to the right and illustrated the water-wet condition. Also, the end-point of K_{ro} at S_{wi} is more than K_{rw} at S_{or} , which is an indication of water-wet condition.

Figure 8 indicates in surfactant HTMAB flooding; the intersecting saturation occurs at $S_w=67\%$, and it displays the water wet system. The end-point of K_{rw} at S_{or} is less than K_{ro} at S_{wi} , which is an indication of water-wet condition. It is indicated in **Figures 6, 7 and 8** that the cationic HTMAB surfactant is more efficient than the HABSA one in wettability alteration.

By comprising all the relative permeability curves on a unique graph, it is observed that the intersection point of the curves moved to the right (**Figure 9**). A numbered arrow (1, 2 and 3) shows the intersections point of the relative permeability curves in water, HABSA and HTMAB injections, respectively. Furthermore, **Figure 9** indicates the combination of all plots for a proper comparison of the cross-points and saturation relative permeability where the residual oil saturation (S_{or}) decreases to 28% by HABSA and 29% by HTMAB injection.

3.4. Pressure Drop

Figure 10 depicts the pressure drop between two sides of the sample versus injected pore volume. Obviously, the pressure drop rose noticeably as the HABSA surfactant and HTMAB surfactant were injected as compared to water injection.

3.5. Oil Recovery

Figure 11 presents the oil recovery factor during flooding. The oil recovery factor rose from 44.4% to 56.25% as HABSA was added and then to 63.5% when HTMAB was injected. When the core is in initial condition (initial water saturation without surfactant), it is oil-wet but after surfactant injection, the molecules of the surfactant are adsorb on the rock-water interface, and the water film becomes unstable and as a result, the core plug becomes water-wet, and the oil movement becomes more favorable. Performing these tests proved that, S_{or} decreased from 32% to 20% and 13%, during water, HABSA and HTMAB flooding, respectively.

4. Conclusions

The main results of this study are as below:

- 1- The analysis of results of quantitative measurement (the contact angle method) indicates that the surfactant, HTMAB, has more ability for the wettability alteration from oil-wet to water-wet as compared to the surfactant, HABSA.
- 2- Each of the aforementioned surfactants in a particular concentration has the most impact on wettability alteration. This concentration is named as CMC. This parameter was measured by the conductivity measurement method. The surfactant, HTMAB, has CMC of 814 ppm, and the surfactant, HABSA, has CMC of 2250 ppm. For core flooding process, these optimum concentrations of solutions were used.
- 3- The results of qualitative measurement (relative permeability method) show in the water injection process, the intersection point of the curves was around water saturation of 0.5. This is considered as an intermediate wettability condition.
- 4- In surfactant HABSA injections, the intersection point of the curves shifts slightly to the right and is around water saturation of 0.56. Also, the end-point of the wetting phase curve (K_{rw}) at S_{or} is less than the non-wetting phase end-point at S_{wi} . These conditions indicate the wettability alteration from oil-wet to water-wet.
- 5- In surfactant HTMAB injections, the results show that the intersection point is around the water saturation of 0.67 and the end-point of K_{rw} is less than the K_{ro} . Therefore, it can be concluded that the surfactant, HTMAB, is more impressive than HABSA in wettability variation of carbonate rocks.

6- In this study, the oil recovery by water, anionic surfactant, HASBA, and cationic surfactant, HTMAB, are 44.40%, 56.25% and 63.50%, respectively. Therefore, it is concluded that in carbonate reservoirs, the effectiveness of surfactant, HTMAB could be more than the anionic surfactant, HASBA.

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References

1. Davarpanah, A., *A feasible visual investigation for associative foam > polymer injectivity performances in the oil recovery enhancement*. European Polymer Journal, 2018. **105**: p. 405-411.
2. Davarpanah, A. and B. Mirshekari, *Experimental Investigation and Mathematical Modeling of Gas Diffusivity by Carbon Dioxide and Methane Kinetic Adsorption*. Industrial & Engineering Chemistry Research, 2019. **58**(27): p. 12392-12400.
3. Hu, X., et al., *Thermodynamic effects of cycling carbon dioxide injectivity in shale reservoirs*. Journal of Petroleum Science and Engineering, 2020. **195**: p. 107717.
4. Zhu, M., et al., *Application of implicit pressure-explicit saturation method to predict filtrated mud saturation impact on the hydrocarbon reservoirs formation damage*. Mathematics, 2020. **8**(7): p. 1057.
5. Pal, N., et al., *Interfacial behaviour, wettability alteration and emulsification characteristics of a novel surfactant: Implications for enhanced oil recovery*. Chemical Engineering Science, 2018. **187**: p. 200-212.
6. Foley, P., E.S. Beach, and J.B. Zimmerman, *Derivation and synthesis of renewable surfactants*. Chemical Society Reviews, 2012. **41**(4): p. 1499-1518.
7. Han, F., et al., *Synthesis and characterization of glucosamide surfactant*. Journal of Surfactants and Detergents, 2013. **16**(2): p. 155-159.
8. Salimon, J., et al., *Synthesis, reactivity and application studies for different biolubricants*. Chemistry Central Journal, 2014. **8**(1): p. 1-11.
9. Pal, N., N. Saxena, and A. Mandal, *Synthesis, characterization, and physicochemical properties of a series of quaternary gemini surfactants with different spacer lengths*. Colloid and Polymer Science, 2017. **295**(12): p. 2261-2277.
10. Rosestolato, J.C., et al., *Lipid nanostructures as surfactant carriers for enhanced oil recovery*. Fuel, 2019. **239**: p. 403-412.
11. Saxena, N., A. Saxena, and A. Mandal, *Synthesis, characterization and enhanced oil recovery potential analysis through simulation of a natural anionic surfactant*. Journal of Molecular Liquids, 2019. **282**: p. 545-556.
12. Davarpanah, A. and B. Mirshekari, *A mathematical model to evaluate the polymer flooding performances*. Energy Reports, 2019.
13. Davarpanah, A. and B. Mirshekari, *Numerical simulation and laboratory evaluation of alkali-surfactant-polymer and foam flooding*. International Journal of Environmental Science and Technology, 2020. **17**(2): p. 1123-1136.
14. Hu, X., et al., *Hybrid Thermal-Chemical Enhanced Oil Recovery Methods; An Experimental Study for Tight Reservoirs*. Symmetry, 2020. **12**(6): p. 947.
15. Nesic, S., et al., *An Analytical Model to Predict the Effects of Suspended Solids in Injected Water on the Oil Displacement Efficiency during Waterflooding*. Processes, 2020. **8**(6): p. 659.
16. Alzahid, Y.A., et al., *Flow regimes during surfactant flooding: The influence of phase behaviour*. Fuel, 2019. **236**: p. 851-860.
17. Alvarado, V. and E. Manrique, *Enhanced oil recovery: an update review*. Energies, 2010. **3**(9): p. 1529-1575.
18. Sheng, J.J., *Foams and their applications in enhancing oil recovery*, in *Enhanced Oil Recovery Field Case Studies*. 2013, Elsevier. p. 251-280.
19. Shabaninejad, M., et al., *Pore-scale analysis of residual oil in a reservoir sandstone and its dependence on water flood salinity, oil composition, and local mineralogy*. Energy & fuels, 2017. **31**(12): p. 13221-13232.

20. Barati-Harooni, A., et al., *Experimental and modeling studies on adsorption of a nonionic surfactant on sandstone minerals in enhanced oil recovery process with surfactant flooding*. Journal of Molecular Liquids, 2016. **220**: p. 1022-1032.
21. Davarpanah, A., R. Shirmohammadi, and B. Mirshekari, *Experimental evaluation of polymer-enhanced foam transportation on the foam stabilization in the porous media*. International Journal of Environmental Science and Technology, 2019.
22. Hu, Y., et al., *A Laboratory Approach on the Hybrid-Enhanced Oil Recovery Techniques with Different Saline Brines in Sandstone Reservoirs*. Processes, 2020. **8**(9): p. 1051.
23. Pan, F., et al., *Impact of anionic and cationic surfactants interfacial tension on the oil recovery enhancement*. Powder Technology, 2020. **373**: p. 93-98.
24. Haiyan, Z. and A. Davarpanah, *Hybrid chemical enhanced oil recovery techniques: A simulation study*. Symmetry, 2020. **12**(7): p. 1086.
25. Han, Y., et al., *Experimental investigation on the effect of wettability on rock-electricity response in sandstone reservoirs*. Fuel, 2019. **239**: p. 1246-1257.
26. Anderson, W.G., *Wettability literature survey-part 1: rock/oil/brine interactions and the effects of core handling on wettability*. Journal of petroleum technology, 1986. **38**(10): p. 1,125-1,144.
27. Anderson, W.G., *Wettability literature survey part 5: the effects of wettability on relative permeability*. Journal of Petroleum Technology, 1987. **39**(11): p. 1,453-1,468.
28. Anderson, W.G., *Wettability literature survey-part 6: the effects of wettability on waterflooding*. Journal of Petroleum Technology, 1987. **39**(12): p. 1,605-1,622.
29. Jadhunandan, P. and N.R. Morrow, *Effect of wettability on waterflood recovery for crude-oil/brine/rock systems*. SPE reservoir engineering, 1995. **10**(01): p. 40-46.
30. Esfandyari, H., et al., *Implications of anionic and natural surfactants to measure wettability alteration in EOR processes*. Fuel, 2020. **278**: p. 118392.
31. Sohal, M.A., G. Thyne, and E.G. Søgaaard, *Review of recovery mechanisms of ionically modified waterflood in carbonate reservoirs*. Energy & Fuels, 2016. **30**(3): p. 1904-1914.
32. Saxena, N., A. Kumar, and A. Mandal, *Adsorption analysis of natural anionic surfactant for enhanced oil recovery: The role of mineralogy, salinity, alkalinity and nanoparticles*. Journal of Petroleum Science and Engineering, 2019. **173**: p. 1264-1283.
33. Honarvar, B., et al., *Smart water effects on a crude oil-brine-carbonate rock (CBR) system: Further suggestions on mechanisms and conditions*. Journal of Molecular Liquids, 2020. **299**: p. 112173.
34. Morrow, N.R. and G. Mason, *Recovery of oil by spontaneous imbibition*. Current Opinion in Colloid & Interface Science, 2001. **6**(4): p. 321-337.
35. Buckley, J. and Y. Liu, *Some mechanisms of crude oil/brine/solid interactions*. Journal of Petroleum Science and Engineering, 1998. **20**(3-4): p. 155-160.
36. Liu, Y., et al., *Enhanced nitrogen foams injection for improved oil recovery: from laboratory to field implementation in viscous oil reservoirs offshore Bohai Bay China*. International Journal of Oil, Gas and Coal Technology, 2019. **21**(4): p. 463-481.
37. Rahimi, A., B. Honarvar, and M. Safari, *The role of salinity and aging time on carbonate reservoir in low salinity seawater and smart seawater flooding*. Journal of Petroleum Science and Engineering, 2020. **187**: p. 106739.
38. Honarvar, B., et al., *Favorable attributes of low salinity water aided alkaline on crude oil-brine-carbonate rock system*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2020. **585**: p. 124144.
39. Qi, Z., et al., *Wettability alteration of the quartz surface in the presence of metal cations*. Energy & fuels, 2013. **27**(12): p. 7354-7359.

40. Saxena, N., et al., *Bio-based surfactant for enhanced oil recovery: Interfacial properties, emulsification and rock-fluid interactions*. Journal of Petroleum Science and Engineering, 2019. **176**: p. 299-311.
41. Babu, K., et al., *Studies on interfacial tension and contact angle of synthesized surfactant and polymeric from castor oil for enhanced oil recovery*. Applied Surface Science, 2015. **353**: p. 1126-1136.
42. Arabloo, M., M.H. Ghazanfari, and D. Rashtchian, *Wettability modification, interfacial tension and adsorption characteristics of a new surfactant: Implications for enhanced oil recovery*. Fuel, 2016. **185**: p. 199-210.
43. Golabi, E., et al. *Experimental study of wettability alteration of limestone rock from oil wet to water wet by applying various surfactants*. in *SPE Heavy Oil Conference Canada*. 2012. Society of Petroleum Engineers.
44. Okasha, T.M., J.J. Funk, and H.N. Rashidi, *Fifty Years of Wettability Measurements in the Arab-D Carbonate Reservoir*, in *SPE Middle East Oil and Gas Show and Conference*. 2007, Society of Petroleum Engineers: Manama, Bahrain. p. 10.
45. Shubham, A., et al. *Wettability alteration of carbonates by optimizing the brine and surfactant composition*. in *SPE Kuwait International Petroleum Conference and Exhibition*. 2012. Society of Petroleum Engineers.
46. Amirpour, M., *Experimental Investigation of Wettability Alteration on Residual Oil Saturation Using Capillary Pressure Measurement*. 2013, Petroleum University of Technology.
47. Tajmiri, M., et al., *Wettability alteration of sandstone and carbonate rocks by using zno nanoparticles in heavy oil reservoirs*. Iranian Journal of Oil & Gas Science and Technology, 2015. **4**(4): p. 50-66.
48. Safari, M., *Variations in Wettability Caused by Nanoparticles*. Petroleum Science and Technology, 2014. **32**(12): p. 1505-1511.
49. Campanelli, A. and L. Scaramuzza, *Hexadecyltrimethylammonium bromide*. Acta Crystallographica Section C: Crystal Structure Communications, 1986. **42**(10): p. 1380-1383.
50. Takassi, M.A., et al., *Highly stable polyimide composite films based on 1, 2, 4-triazole ring reinforced with multi-walled carbon nanotubes: study on thermal, mechanical, and morphological properties*. Progress in Organic Coatings, 2015. **80**: p. 142-149.
51. Patist, A., et al., *On the measurement of critical micelle concentrations of pure and technical-grade nonionic surfactants*. Journal of Surfactants and Detergents, 2000. **3**(1): p. 53-58.
52. Anabtawi, M.Z., *Comparison between continuous stirred tank reactor extractor and soxhlet extractor for extraction of El-Lajjun oil shale*. Separation science and technology, 1996. **31**(3): p. 413-422.
53. Zhang, R., et al., *Wettability alteration by trimeric cationic surfactant at water-wet/oil-wet mica mineral surfaces*. Applied Surface Science, 2012. **258**(20): p. 7943-7949.
54. Nazari Moghaddam, R., et al., *Comparative study of using nanoparticles for enhanced oil recovery: wettability alteration of carbonate rocks*. Energy & Fuels, 2015. **29**(4): p. 2111-2119.
55. Sharma, A., et al., *Life cycle assessment of buildings: a review*. Renewable and Sustainable Energy Reviews, 2011. **15**(1): p. 871-875.

Table 1. Core characterization.

Diameter,cm	Length,cm	Bulk	Dry	Wet	Pore	Porosity,	Permeability,m
		volume,cm³	weight,gr	weight,gr	volume,cm³	%	d
3.70	7.30	78.49	175.2	186.7	11.50	14.60	5.30

Table 2. The obtained mineralogical composition of the core plug by XRD method (wt. %).

Compound Name	Formula	wt. %
Calcite	CaCO_3	72.35
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	21.65
Orthoclase	KAlSi_3O_8	3.80
Illite	$(\text{K},\text{H}_3\text{O})\text{Al}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$	2.20

Table 3. HABSA solution conductivity at different concentrations.

Concentration (ppm)	HABSA solution conductivity ($\mu\text{S}/\text{cm}$)	Concentration (ppm)	HABSA solution conductivity ($\mu\text{S}/\text{cm}$)
7000	1662	1000	632
6000	1551	900	554
5000	1462	700	475
4000	1307	500	389
3000	1197	300	283
2000	992	200	216
1500	771	100	122

Table 4. HTMAB solution conductivity at different concentrations.

Concentration (ppm)	HTMAB	Concentration (ppm)	HTMAB
25	14.64	350	86.9
50	19.37	400	81.1
75	21.40	450	104.5
100	28.30	500	181.1
150	42.60	750	196.6
200	52.80	1000	246.0
250	66.60	2000	351.0
300	69.00	3000	437.0

Figure 1. Surfactant solution conductivity versus HTMAB surfactant concentration.

Figure 2. Surfactant solution conductivity versusHABSA surfactant concentration.

Figure 3. Contact angle versus HTMAB solution concentration.

Figure 4. Contact angle versus HABSA solution concentration.

Figure 5. Contact angle measurement at A) distilled water, B)3000 ppm of HTMAB surfactant, C) 3000 ppm of HABSA surfactant.

Figure 6. Relative permeability curves of water flooding by using unsteady state method (JBN method).

Figure 7. Relative permeability curves of surfactant (HABSA) flooding by using unsteady state method (JBN method).

Figure 8. Relative permeability curves of surfactant (HTMAB) flooding by using unsteady state method (JBN method).

Figure 9. Comparison of relative permeability curves.

Figure 10. Pressure drop curves of water, HABSA and HTMAB flooding.

Figure 11. Oil recovery by injection flooding.