Experimental investigation of chemical solutions effects on wettability alteration and interfacial tension reduction using nano-alkaline–surfactant fluid: an EOR application in carbonate reservoirs

M. Sadegh Rajabi1,2 · Rasoul Moradi2,3 · Masoud Mehrizadeh1

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Abstract
The wettability preference of carbonate reservoirs is neutral-wet or oil-wet as the prevailing of hydrocarbon reserves that affects approximately half of the total production of hydrocarbons of the world. Therefore, due to surface wettability of carbonate rocks the notable fraction of oil is held inside their pores in comparison with sandstones. Since shifting the wettability preference toward water-wet system is of great interest, numerous components were used for this purpose. In this experimental research, the wettability alteration of dolomite surface by interacting with a novel nano-surfactant–alkaline fluid has been investigated in order to diminish its adhesion to crude oil droplets. The solutions were prepared by homogenous mixing of nanosilica particles with cetyl trimethyl ammonium bromide and sodium carbonate, respectively, as a cationic surfactant and alkaline agent. The maximum wettability alteration from oil-wet to water system was obtained by employing a mixture of nanoparticles in association with surfactant–alkaline. Then, the fluids were employed in core-surface from detached and attached forms to compare their interfacial effects on saturated thin sections by crude oil and to measure the wettability. In addition, the interfacial tension (IFT) between solutions and crude oil was investigated and the maximum IFT reduction was obtained from nano-surfactant. Finally, all chemical solutions were flooded to the dolomite plugs separately after water flooding in order to evaluate the maximum oil recovery factor acquired by nano-surfactant.

Keywords Wettability alteration · Interfacial tension reduction · Enhanced oil recovery · Carbonate rock

Abbreviations
CA Contact angle
CEOR Chemical enhanced oil recovery
CTAB Cetyl trimethyl ammonium bromide
EOR Enhanced oil recovery
IFT Interfacial tension
NPs Nanoparticles
OOIP Original oil in place
Swi Initial water saturation
Soi Initial oil saturation
RF Recovery factor

Introduction
Over the past decades, enhanced oil recovery (EOR) processes have been implemented, particularly in several oil-rich countries, to increase the amount of oil that can be extracted from the oil fields after primary and secondary productions. The significance of EOR arises from several factors such as deficiency of oil resources, depletion of mature fields all around the world as well as the enormous investment of capital for exploring a new oil field. Nonetheless, due to some reasons including dramatic increase in applying renewable energies, oversupply of oil resources, cost of storing oil tanks, lack of demand for purchase and recent
expected price recession, the misconception that the oil reservoirs are coming to the end of their power and shelf life is foregrounded more than ever. However, according to the British Petroleum statistical review of world energy (Petroleum 2019), currently oil is widely used more than one-third of the total energy consumption among all types of energies including petroleum, natural gas, coal, hydroelectric, nuclear and emerging renewable energy sources as shown in Fig. 1. Therefore, there is a strong necessity for overcoming the reservoirs obstacles to attain the highest oil recovery.

Chemical flooding is one of the main EOR methods which involves the injection of water containing various chemical agents. The offered conventional chemical enhanced oil recovery (CEOR) methods are polymer flooding, surfactant and alkaline flooding (Samanta et al. 2012). Meantime, combinations of these flooding types such as alkaline–polymer (AP), alkaline–surfactant (AS) and alkaline–surfactant–polymer (ASP) flooding were generated to assist with their separate unique properties to improve and rectify the shortcoming of the individual component chemical flooding process (Mandal 2015). For example, the presence of alkaline in AS and AP flooding decreases the adsorption of expensive surfactant and polymer while the presence of polymer in AP and SP flooding could control the mobility ratio and prevent the fingering phenomenon (Guo et al. 2017; Gbadamosi et al. 2019; Zhong et al. 2020). Besides, the presence of surfactant leads to IFT reduction and further wettability alteration (Gbadamosi et al. 2019). CEOR techniques have been widely used in sandstone reservoirs compared to carbonate reservoirs (Deng et al. 2020). However, considering great potential of the applications of CEOR methods, recently they have been taking into account for implementation in carbonate reservoirs (Pal et al. 2018). ASP and polymer flooding have been the most widely used among all CEOR technique for field application (Gbadamosi et al. 2019). For instance, Mooney field in Canada and Marmul field in Oman as the sandstone reservoirs were treated by HPAM (Hydrolyzed Polyacrylamide) with 12–25% and 12% incremental oil recovery, respectively (Koning et al. 1988; Watson et al. 2014; Gbadamosi et al. 2019), while Cambridge Minnelusa field in the USA and Shengli field in China as the carbonate reservoirs were fulfilled by ASP technique with 36% and 16–28% oil recovery, respectively (Vargo et al. 2000; Guo et al. 2017; Gbadamosi et al. 2019).

However, based on the fact that over than half of the world’s proven hydrocarbon reserves are in the carbonate reservoirs type, developing novel flooding solvents is of great importance EOR. Indeed, carbonate formation are fragile and more likely to be fractured compared to sandstone formations (Deng et al. 2020). Hence, this property leads to technical difficulty associated with applying a large pressure gradient through the matrix to dominate the capillary forces which the oil is preserved (Hirasaki and Zhang 2007). As a result, a massive volume of Original-Oil-in-Place (OOIP) still left in carbonate reservoirs after water flooding (Rostami Ravari et al. 2011; Chen and Mohanty 2013).

The main parameters that control residual oil saturation in porous media are capillary forces, wettability, pore distribution, relative permeability, rock heterogeneity and so forth. Among all these operative parameters, capillary force and wettability are considered as two critical factors which have directly strong effect on fluids flow inside the porous media for improving the production recovery. Moreover, in the reservoir rock system, the wettability of the rock surface controls the settling, distribution and flow of the fluids within the reservoirs (Alhammadi et al. 2017). The wettability of the majority of oil reservoirs is classified into oil-wet, water-wet and mixed-wet system (Christensen and Tanino 2017). Adjusting the wettability of the surface from oil-wet to water-wet changes the adhesive force of capillarity. Hence, it can be deduced that higher oil recovery is more achievable in the water-wet case compared to oil-wet reservoir (Gbadamosi et al. 2019).

Nanotechnology as a multidisciplinary field for unifying the structure on molecular and nano-scales levels could bring a revolutionary transformation in several areas of the oil and gas industries such as EOR (Agista et al. 2018). Nanoparticles (NPs) are new components of novel wettability modifier which are added to any base fluids such as water, brine or other effective liquids to provide homogenous colloidal solutions known as nanofluids.Emerging nanofluids possess great potent to be employed for improving the oil recovery. For instance, nanofluid flooding has been appraised as a chemical EOR operation under field-scale in the Colombian fields (Franco et al. 2017). The EOR mechanisms of nanofluids mainly include disjoining pressure, pore...
channels plugging, viscosity increase of injection fluids, IFT reduction, wettability alteration and preventing asphaltene precipitation (Sun et al. 2017). Size and concentration of NPs, salinity of displacing nanofluids are the main factors that influence the performance and reaction of nano-enabled EOR (Agista et al. 2018). Size of NPs can regulate surface wettability and oil recovery. NPs of smaller size (11–14 nm) lead to smaller water contact angle (CA), i.e., hydrophilicity, and higher recovery compared to larger sizes (30–40 nm) (Gbadamosi et al. 2019). Moreover, increasing the concentration of NPs would enhance the viscosity of the nanofluid and spreading of NPs on the grain surface resulting in higher displacement efficiency (El-Diasty and Aly 2015), dramatic decrease of IFT and a higher wettability alteration effect. However, there is a limitation for increasing the concentration of NPs which beyond that NPs will agglomerate and tend to block the pore throat (Hendraningrat et al. 2013;El-Diasty and Aly 2015). In addition, increasing the nanofluids salinity seems to increase the adsorption of NPs and improve the oil recovery. More salinity could alter the rock wettability to be more water-wet system, but simultaneously the stability of NPs will be reduced in a high salinity environment (Mcelfresh et al. 2012;Hendraningrat et al. 2013). Among all reported NPs, silicon-based NPs, aluminum oxide, iron oxide and titanium oxide are the most common and widely used in EOR approaches.

Several modifiers have been made by different properties and different reactions to inject toward the formation. Modifier for a specific formation should be attentively designated according to the inherent of the formation rock, oil properties and composition, water formation pH, reservoir temperature and salinity. Wettability modifiers in the carbonate rock and corresponding reservoirs are categorized into four main classes including surfactants, salts, alkalines and NPs (Deng et al. 2019). Nowadays, researchers are interested to investigate the new possibilities of the combination these kinds of modifiers and their pros and cons by comparing together such as surfactant–alkaline, nano-surfactant, nano-alkaline and adding NPs to different electrolyte concentrations. It has been proved that nanosilica combination with surfactant has a great potential to oil recovery rather than their sole implementation (Pei et al. 2015; Vatanparast et al. 2017). Furthermore employing the nanosilica in the presence of alkaline reduce the IFT and effectively alter the wettability to water-wet system (Ghalamizade Elyaderani and Jafari 2019). Moreover, addition of alkaline to different types of surfactants could alter the wettability and result in IFT reduction (Hosseini et al. 2019), meanwhile it significantly reduces the surfactant consumption (Kumar and Mandal 2016). Likewise, the combination of these kinds of modifiers have been succeeded considerably in increasing RF.

The scope of the present work is commenced by doing an experiment and analyzing the wettability alteration and IFT reduction with focus on the oil recovery. First, the stability of the nanofluids was studied by the sedimentation photography method regarding to critical salt concentration. In the next step, effects of NPs, surfactant and alkaline on wettability and IFT, their further performance separately and in combination form of nanofluid were investigated. Figure 2 displays the detailed flowchart of experimental procedure of this work.

Materials and methods

Carbonate core plugs and thin sections preparation

In this work, the experiments were implemented in a carbonate outcrop rock. In the first step, nine plugs were prepared from the rock sample by core cutting and precise plugging machine. Then, they were trimmed, polished and heated in the drier apparatus at 100 °C for three hours in order to remove any possible contamination and to have them entirely dry. Thereafter, thin layered cylindrical slice with around 2 mm thickness were cut off from one of the plugs to be employed in water CA measurements, and other plugs were conducted in core flooding measurements.

Thin section properties

In order to investigate the optical properties of the minerals in the rock, a thin section was mounted on a glass slide and then was abraded progressively by using a finer abrasive blade until the sample became very thin. Figure 3 illustrates the microphotographs of thin sections which were taken from the petrographic microscope in order to reveal the origin and evolution of the rock. Figure 3a and b illustrates cross-polarized light (XPL) and plane polarized light (PPL), respectively. The thin section is a clastic carbonate and mainly supported by grain and precipitated by matrix. Hence, the section is a packstone type and deformed bioclasts of dolomite. Moreover, Fig. 4 shows the X-ray diffraction (XRD) of thin section measured at temperature of 25 °C and humidity 25% (BRUKER D4, Germany.) The XRD analysis indicates that thin sections are pure dolomite (CaMg(CO3)2) without observable impurities.

Core plugs properties

Eight dolomite plugs were prepared in the same manner aforementioned, and then, the helium porosimeter was used to determine the porosity of plug samples while liquid method was employed for absolute permeability measurements. Table 1 shows the dimensions and properties of plugs used in this work.
Carbonate Rock

Crude Oil
Core Plugs/Thin Sections

Synthesis & Characterization
NPs SiO₂
Surfactant CTAB
Alkaline Na₂CO₃
Brine NaCl

NP Suspension
Dispersant
Dispersant
Based Fluid

XRD FE-SEM
Photomicrography

Aging

Chemical Solutions

Nanofluids Preparation
Magnetic Stirring
Ultrasonic Vibration

pH Density Viscosity Stability

CA Measurement

IFT Measurement
Core Flooding

Fig. 2 Flowchart of experimental procedure

Fig. 3 Microphotographs of thin section under a cross-polarized light; b plane polarized light
Crude oil

Light crude oil sample was used to conduct measurement of CA of carbonate thin sections and IFT. API (American Petroleum Institute), density, viscosity and other properties of the crude oil are listed in Table 2.

Aqueous phase and brine

The aqueous phase used in solution preparation was distilled water with density of 0.998 g/mL and viscosity of 1 cp at constant temperature of 25 °C. Specified solutions were prepared by dispersion of exact quantities of materials in aqueous phase. Sodium chloride (Merck) was used in both water formation and dispersed medium of specified fluids. The properties of sodium chloride are tabulated in Table 3.

Surfactant and alkaline

Cetyl trimethyl ammonium bromide (CTAB) as a cationic surfactant and sodium carbonate (Na₂CO₃) as alkaline modifier were purchased from Merck. Table 3 and Fig. 5 display the properties and the molecular structure of CTAB and Na₂CO₃, respectively.
In this study the silica NPs (US Nano Company) are used as modifier. Table 4 indicates the properties of silica NPs and Fig. 6 illustrates the field emission scanning electron microscopy (FE-SEM) images of NPs taken by TESCAN MIRA III apparatus, Czech Republic. For this purpose, the silica NPs were coated with an extremely thin layer of gold as the conductive material to prevent the electron beam deflection. Then, sample was dried and placed in the center of sample vessel under detector apparatus to record the structure of NPs. The FE-SEM images demonstrate the diameter of NPs by software in the range of 20–30 nm and the mean value was 23.61 nm. In addition, the XRD pattern shown in Fig. 7 specifies the crystalline features of the used silica NPs.

**Core plugs and thins sections aging**

In order to imitate the reservoir conditions as close as possible, the core plugs and thin sections were aged in crude oil for appropriate time period. For this purpose, first the clean and dried samples were allowed to achieve ionic equilibrium in the brine 3 wt% NaCl for seven days. The saturated plugs were placed inside the core holder and then crude oil was injected (Eldex pump, USA) until no brine was produced in order to conduct the drainage process. Afterward, initial water saturation ($S_{wi}$) and initial oil saturation ($S_{oi}$) were calculated as shown in Table 5. At the same time, the sections were removed from the brine and submerged in the beaker filled with crude oil for three weeks. The beaker was kept inside the temperature adjusted at 100 °C as closely as possible to alter wettability to oil-wet (Seyyedi et al. 2015). After the aging process, the bulk oil volume was removed from the thin sections surface and eventually the thin sections were used for further investigations for both un-aged and aged sections as shown in Table 6 and Fig. 8. Moreover, the surface morphology of pristine and treated samples is obtained by FE-SEM images as illustrated in Fig. 9.

**Contact angle test**

The CA was measured by sessile drop method (OCA20, Data Physics Company, Germany) using a needle (0.52 mm diameter) loaded with water. Water slowly fell from needle onto the interested points of the surface of the thin section, and images of droplets were taken using a high resolution digital camera. All measurements were repeated 10 times for each sample.
Interfacial tension test

To measure IFT values between oil and the fluids containing brine or alkaline, Du Noüy (ring tensiometer) method, KSV Sigma-701 was employed. In this method, a platinum ring as the probe was submerged inside the fluid container by adjusting the stage. Then, the ring was gradually pulled out through the interface of liquids and IFT was measured by software apparatus based on Young–Laplace model. However, this method is not suitable for low IFT values. Therefore, spinning drop tensiometer (SDT) apparatus was applied for surfactant fluids (Fars Enhanced Oil Recovery Technology Company, Iran). This method has been widely used, especially for ultra-low IFT with accuracy less than ±0.01%. A drop of crude oil was injected to fluid tube with a diameter of 4 mm and a length of 4 cm by a syringe, then the system was rotated horizontally at 4000 rpm and the shape of drop deformation was captured by digital camera of apparatus software. All IFT measurements were taken at room temperature and pressure. The test was repeated at least three times for each fluid type, and the results are reported as the mean value.

Table 5  Core plugs saturation properties

| Plugs Number | Core #1 | Core #2 | Core #3 | Core #4 | Core #5 | Core #6 | Core #7 | Core #8 |
|--------------|---------|---------|---------|---------|---------|---------|---------|---------|
| $S_{wi}$ %   | 18.61   | 12.73   | 12.96   | 19.49   | 16.87   | 13.44   | 13.53   | 11.37   |
| $S_{or}$ %   | 81.39   | 87.27   | 87.04   | 80.51   | 83.13   | 86.56   | 86.47   | 88.63   |

Table 6  Thin sections description

| Thin sections | Description |
|---------------|-------------|
| S1            | Un-aged thin section |
| S2            | Aged thin section by crude oil for 21 D at 100 °C |

Fig. 7  X-ray diffraction of SiO$_2$ NPs

Fig. 8  Thin sections aging, un-aged thin section (S1) and aged thin section by crude oil for 21 D at 100 °C (S2)
Core flooding test

All aged plug samples were individually placed in horizontal core holder to successively apply brine 3 wt% NaCl as a water flooding and prepared solutions flooding tests. Confining pressure was applied by hand pump at 500 psi and injection of water flooding was continued 4–5 pore volume at the rate of 0.15 cc/min until no oil was produced from plug samples. Then, the injected fluid was switched to prepared chemical solutions. Finally, flooding experiment was stopped when no more oil production was observed and the oil RF results were calculated and plotted versus pore volume injected. All the runs were performed at ambient temperature. The schematic of core flooding is illustrated in Fig. 10.

Effect of electrolytes on the stability of chemical solutions

Stability of nanofluids was measured based on sedimentation photograph by settling a certain volume of the prepared nanofluids in a transparent tube and then capturing images of the tube at equal intervals of time using a camera (Wei et al. 2009). The captured images are then compared with each other to inspect the stability of the nanofluid as illustrated in Fig. 11 (Ilyas et al. 2013).

For this purpose, different concentrations of NaCl solutions (0.5, 1, 2 and 3 wt%) were prepared, and 1000 ppm CTAB and Na2O3 were dispersed in each based fluid concentration as a separated and mixed dispersant. By stirring at 1200 rpm for 2 h to make homogeneous solutions. Afterward, 500 ppm nanosilica was added, stirred and sonicated for 2 h at 30 °C and frequency of 37 kHz (Elmasonic ultrasonic bath, Germany).
The effects of different concentrations of NaCl solution on the stability of silica NPs dispersions with CTAB and Na₂CO₃ were investigated. The captured images show that dispersions of higher NaCl concentrations more harshly tend to destabilize the nanofluids. After 1 h silica NPs were thoroughly dispersed in 0.5 and 1 wt% of NaCl solutions, but moderately dispersed in 2 and 3 wt% NaCl solutions concentration (Fig. 12a). Moreover, by addition of Na₂CO₃ no significant enhance in stability of nanofluid was observed (Fig. 12b). On the other hand, the dispersion stability was improved by adding cationic surfactant to each based fluid concentration (Fig. 12c); however, the mixture of surfactant–alkaline also had no potential to make the stable nanofluids in different concentrations of NaCl (Fig. 12d). It was observed from Fig. 12 that NPs homogenous dispersion and stability could not be maintained for a long time above a certain electrolyte concentration. As electrostatic forces extremely depend on electrolyte concentration, by increasing the electrolyte concentration, the thickness of the diffuse electrical layer decreases and NPs are inclined to aggregate. In the other words, at low electrolyte concentration, the electrostatic repulsive forces prevent the aggregation of particles while at high electrolyte concentration, the attractive van der Waals forces dominate and leading to particles aggregation (Esmaeili Azadgoleh et al. 2014; Zhao et al. 2018). Generally, the addition of NaCl up to around 2 and 3 wt% is not good option for dispersion of silica NPs in nanofluids. Clearly visible that the NPs begin to deposit over time; hence, the lastingness of nanofluids after 24 h deduce that the stability of prepared nanofluids is only sustainable in early hours after preparation. Therefore, 1 wt% NaCl was selected as the optimum salt concentration for the stability of NPs in colloid solutions. Table 7 summarizes the stability of the prepared solutions regarding the analysis of the captured images.

Fluid preparation

Eight interested fluids were prepared in the same procedure by stirring and sonication in order to measure the CA, IFT, flooding and compare their effect. The concentrations and properties of fluids are presented in Tables 8 and 9, respectively.

Results and discussion

Contact angle measurements

All rocks are mainly considered to be initially water-wet and then moderately shifted to oil-wet in the process of oil migration (Deng et al. 2019). S1 sample surface was clear because of no oil migration inside the section and it was fully discharged from any fluids, so the measured water droplet CA of S1 was reported 39.35° indicating a water-wet preference while for S2, CA was 106.71° showing a moderately oil-wet preference. It should be emphasized that wettability was not changed after three weeks for these examined sections; thereby, it can be stated that the highest wettability preference of sections is moderately oil wet. Figure 13 represents the values of CA test for un-aged and aged thin sections in the bar chart for better comparison. Finally, to investigate the role of all interested fluids on the wettability alteration after aging process, the thin sections were aged for three days in vacuum containers at room temperature, and then, contact angles were measured. Figure 14 illustrates the CA measurement results. However, it should be mentioned that increased contact time inside nanofluids tends to induce more water-wet property on rock surfaces (Aghajanzadeh et al. 2019; Hou et al. 2019). All interested fluids were altered the wettability to water-wet or moderately water-wet system. F1 decreased the CA...
to 96.75° as the less effective fluid for wettability alteration. It is believed that adsorption of Na\(^+\)Cl\(^-\) onto dolomite can change the surface charge and desorb attracted carboxylic crude oil components. F2 decreased the CA to 92.73° which is attributed to the presence of NPs. NPs are able to spread on the dolomite surface and create an imbalance forces between the aqueous and solid surface; hence,

![Fig. 12](image_url)

**Table 7** Stability of NPs on different concentrations of NaCl in the presence of the surfactant and alkaline

| Nanofluids       | wt% NaCl | 1 h       |
|------------------|----------|-----------|
| SiO\(_2\)        | 0.5      | Excellent stability |
|                  | 1        | Excellent stability |
|                  | 2        | Good stability   |
|                  | 3        | Good stability   |
| SiO\(_2\)-Na\(_2\)CO\(_3\) | 0.5 | Excellent stability |
|                  | 1        | Good stability   |
|                  | 2        | Moderate stability |
|                  | 3        | Moderate stability |
| SiO\(_2\)-CTAB   | 0.5      | Excellent stability |
|                  | 1        | Excellent stability |
|                  | 2        | Excellent stability |
|                  | 3        | Good stability   |
| SiO\(_2\)-CTAB-Na\(_2\)CO\(_3\) | 0.5 | Excellent stability |
|                  | 1        | Good stability   |
|                  | 2        | Moderate stability |
|                  | 3        | Weak stability   |

**Table 8** Concentration of nanofluids

| Fluids | NaCl, ppm | Nanosilica, ppm | CTAB, ppm | Na\(_2\)CO\(_3\), ppm |
|--------|-----------|-----------------|-----------|---------------------|
| F1     | 10,000    | –               | –         | –                   |
| F2     | 10,000    | 500             | –         | –                   |
| F3     | 10,000    | –               | 1000      | –                   |
| F4     | 10,000    | –               | –         | 1000                |
| F5     | 10,000    | 500             | 1000      | –                   |
| F6     | 10,000    | 500             | –         | 1000                |
| F7     | 10,000    | –               | 1000      | 1000                |
| F8     | 10,000    | 500             | 1000      | 1000                |

**Table 9** Properties of prepared silica nanofluids

| Fluids | Density, g/cm\(^3\) at 25 °C | Viscosity, cP at 25 °C | pH at 25 °C |
|--------|-------------------------------|------------------------|------------|
| F1     | 1.015                         | 1.002 ± 0.01           | 7.4        |
| F2     | 1.020                         | 1.058 ± 0.01           | 7.2        |
| F3     | 1.024                         | 1.122 ± 0.01           | 7.6        |
| F4     | 1.028                         | 1.245 ± 0.01           | 10.1       |
| F5     | 1.030                         | 1.136 ± 0.01           | 7.3        |
| F6     | 1.033                         | 1.258 ± 0.01           | 9.7        |
| F7     | 1.041                         | 1.286 ± 0.01           | 9.9        |
| F8     | 1.035                         | 1.271 ± 0.01           | 9.8        |
a wedged film will be formed at the oil substrate and solid interface due to disjoining pressure structure which finally change the wettability. F3 was able to alter the wettability by shifting the CA to 77.17°, as the dolomite rocks are a type of carbonate reservoirs and contain positively charged mineral surface; hence, negatively charged of crude oil components will be adsorbed. When the surface of dolomite rocks is treated by CTAB as a cationic surfactant, the ion pair formation interaction is happened and as a result CTAB adsorbs the anionic components of crude oil on the rock surface. Desorption of phase from dolomite surface altered the wettability. F4 decreased the CA to 86.49° in the role of alkaline solution. It has been ascertained that alkaline could modify the brine pH and improve wettability alteration as the in situ surfactant. The CA of F5 and F6 was stood at 73.15° and 81.96°, respectively. These results could be attributed that silica NPs/CTAB and silica NPs/Na2CO3 improved wettability alteration in both surfactant and alkaline solutions. F7 also decreased the CA to 72.59° which indicates that the efficiency of surfactant–alkaline solution is higher than individual solution. As earlier stated, alkaline solution reacts with organic acid and acts...
as the surfactant; hence, wettability is altered more to water-wet system. In the last case, CA of F8 was reached to 59.91° as the strongest solution for wettability alteration. It is supposed that the combination of these modifiers could desorb more carboxylic crude oil materials and alter the wettability intensively. The lowest and highest water CA measurement values as well as the images of all samples are tabulated in Table 10.

IFT measurements

Table 11 and Fig. 15 illustrate the results of IFT measurements. In general, brine as the dispersed medium decreases the IFT but in the presence of silica NPs this reduction has a greater value. As it can be seen in Table 11, IFT value of brine was measured 13.960 mN/m while in the presence of SiO₂ it decreased to 6.647 mN/m. It can be deduced that silica NPs are able to decrease frictional forces with crude oil higher than brine. In addition, the IFT value of caustic solution-oil was 2.981 mN/m which indicates a high value reduction in a mixture of brine and sodium carbonate. The reaction between acidic component of the crude oil and alkaline solution generates an organic acid which acts as an in situ surfactant and emulsifies the crude oil and consequently lowers IFT. However, IFT of this solution in the presence of silica NPs was obtained by a greater value to 4.318 mN/m. To clarify this consequence, according to Table 9 adding silica NPs decreases the pH value of all solutions and because the pH of alkaline solutions is an imperative parameter for IFT, reduction of pH in the presence of silica NPs could increase the IFT value for caustic solution. On the contrary, surfactant solutions decrease the IFT in the absence and presence of silica NPs to 0.987 mN/m and 0.180 mN/m, respectively. Since NPs convey the surfactant molecules, they play as a surface-active agent and the IFT is reduced more. This result could be attributed that the hydrophilic head of CTAB reacts with water while the hydrophobic tail of this type of surfactant interacts with the crude oil components. Therefore, an adsorption film is created by interaction of crude oil and tail of surfactant and lowering the IFT at oil–water interface. The mixture of surfactant–alkaline also remarkably decreases the IFT to 0.250 mN/m but it is not as effective as nano-surfactant. In the last case, nano-surfactant–alkaline also decreases IFT value but also it could not have influences as much as nano-surfactant fluid and indicating that adding sodium carbonate to silica NPs has not valuable reduction on IFT. In conclusion, in alkaline solutions pH play a key role on IFT in which by decreasing pH value, IFT increases but this term is not true for surfactant solutions. However, this mechanism needs more investigation to fully understand the behavior of caustic solutions in the presence of NPs and surfactants by various concentrations and different types of chemical solutions.

Oil recovery factors measurements

Figures 16 and 17 present the effect of all fluids on oil RF and the comparison of each fluid, respectively. Injection of 1 wt% NaCl increased RF to 51.72% while in the presence of silica NPs, RF reached to 61.27%. Injection of surfactant and alkaline solely increased RF to 68.81% and 63.21%, respectively, while RF value is stood at 76.75% for nano-surfactant fluid and 64.12% for nano-alkaline fluid. Silica NPs could enhance oil recovery effectively in the presence of surfactant but has not lucrative merit with suspension in alkaline. RF of surfactant–alkaline solution was also obtained 71.93%. It is well known that RF increases by shifting the wettability to water-wet system and reduction in IFT value. Accordingly, nano-surfactant with the highest IFT reduction and decreasing CA showed the maximum RF at 76.75%, and the next ranking was nano-surfactant–alkaline with RF at 73.19%. On the other hand, that the presence of alkaline and NPs was not able to reduce the IFT but improved the wettability which further enhanced RF. Among all modifier used in this study, surfactant showed the highest impact on RF in comparison with others.

Conclusion and recommendation

Based on this experimental study, the following results can be concluded:

- Increasing the concentration of NaCl induces destabilization of nanofluids. Silica NPs has excellent stability in the presence of cationic surfactant at the first hour of preparation while in the presence of alkaline and the mixture of surfactant–alkaline nothing can be observed. Therefore, the appropriate salinity is an important aspect to be considered in order to avoid the agglomeration of NPs.
- During the early first hour after nanofluids preparation, 1 wt% NaCl acts as a good candidate in terms of stability to be used in CA and IFT measurements. Beyond this salt concentration the stability of nanofluids is too poor which results in their sedimentation over time.
- Among all wettability modifiers including electrolytes, surfactant, alkaline and nanoparticles, surfactants are the most effective on dolomite rock. However, all of them have influences on wettability alteration.
- Silica NPs addition into brine also shifts wettability preference to water wet, apart from, in the attendance of CTAB as a cationic surfactant this alteration is performed better than Na₂CO₃ in the role of alkaline.
Table 10  CA values of sections and fluids

| Samples | Minimum value | Maximum value | Mean value of theta | Image |
|---------|---------------|---------------|---------------------|-------|
| S1      | 28.07         | 46.59         | 39.35               | ![Image](image1) |
| S2      | 99.06         | 110.51        | 106.71              | ![Image](image2) |
| F1      | 94.73         | 104.21        | 96.75               | ![Image](image3) |
| F2      | 88.31         | 97.14         | 92.73               | ![Image](image4) |
| F3      | 51.32         | 88.64         | 77.17               | ![Image](image5) |
### Table 10 (continued)

| Samples | Minimum value | Maximum value | Mean value of theta | Image |
|---------|---------------|---------------|---------------------|-------|
| F4      | 62.35         | 92.39         | 86.49               |       |
| F5      | 51.59         | 95.02         | 73.15               |       |
| F6      | 62.38         | 86.28         | 81.96               |       |
| F7      | 69.91         | 91.10         | 72.59               |       |
| F8      | 53.04         | 82.71         | 59.91               |       |

### Table 11 IFT between crude oil and chemical solutions

| Fluids | F1  | F2  | F3  | F4  | F5  | F6  | F7  | F8  |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|
| IFT, mN/m | 13.960 | 6.647 | 0.987 | 2.981 | 0.180 | 4.318 | 0.250 | 2.852 |
The maximum wettability alteration from oil-wet to water-wet system is obtained by employing a mixture of silica NPs in association with surfactant–alkaline.

All specified solutions decrease IFT, but in the combination of sodium carbonate and silica NPs, this value is increased in comparison with sodium carbonate only which indicates sodium carbonate has no lucrative effect on IFT in the presence of silica NPs. Surfactant has more influences than silica NPs for IFT reduction. However, the highest value was recorded by nano-surfactant.

It could be deduced from flooding tests that although all solutions increased RF, surfactant was the most effective
modifier among them; however, all were RF. Surfactant in the presence of silica NPs increased RF rather than in the presence of alkaline.

- The maximum oil recovery is attained by nano-surfactant and adding alkaline did not cause any valuable recovery.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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