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Graphical Abstract

Figure 1. Microscopy images of THE synthetic oil/different brine interface, (a) captured images using the camera, (b) converted images to grayscale
Effect of Water Salinity on Oil/Brine Interfacial Behavior during Low Salinity Waterflooding: A Mechanistic Study

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Abstract

In recent years, controlling the salinity and composition of the injected water has become an emerging enhanced oil recovery (EOR) technique, often described as low salinity (LS) waterflooding. This work is done with the intention to contribute to the ongoing discussions about LS waterflooding mechanism(s). For this purpose, a series of different experiments were conducted. At first, the effect of salinity on the interfacial tension (IFT) and the contact angle was evaluated with a crude oil sample. Then to achieve more accurate results in observing oil/water interface, similar IFT experiments were also carried out on a synthetic oil containing asphaltenes. Thereafter, microscopic visualization using glass micromodel was performed on the interface of the synthetic oil and brine. Four brine solutions including Sea Water (SW), it’s

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dilutions and formation water (FW) were used for various experiments. Finally, to investigate the presented mechanism by other authors, a series of Environmental Scanning Electron Microscopy (ESEM) analysis on the synthetic oil was carried out to understand better the phase behavior after contacting both synthetic oil and water phases from the micromodel experiment. Based on the existing mechanism, there exists an optimal concentration beyond which dilution is no longer an effective process.

**Keywords:** Water salinity, Wettability, Interfacial tension, Oil/Brine interface, Low salinity waterflooding

### 1. Introduction

Water is often used to pressure maintenance and displacing oil from oil reservoirs, and generally, seawater (SW) is considered for this purpose. In recent years, the water injection process is being rigorously studied experimentally by assessing the impact of water chemical modification on the final oil recovery. However, modification of the water composition has shown to be an excellent way to increase oil recovery from both sandstones and carbonates. Compared to other tertiary methods, low salinity water flooding may be one of the cheapest and environmentally friendly approaches. It has been observed that using a water with lower saline content or specific ions, the performance of the water-flooding would be influenced by increasing the ultimate oil recovery in both sandstone and carbonate oil reservoirs. The low salinity method was first discovered in the late 1950s when fresh water was injected to increase recovery and displace viscous oil (Martin, C., 1959) [1]. Lately, several laboratory studies on LS flooding with both outcrop and reservoir cores have shown increased oil recovery [2-8]. There is another study confirming this theory that using a brine with lower salt content resulted in higher oil recovery compared to higher salinity brines [9]. In a petroleum reservoir, the capillary forces are dependent upon several factors, such
as pore size and geometry, wetting characteristics of the system, surface and IFT of the rock and fluids (Ahmed, 2000) [10]. Several investigations have revealed a lower salinity threshold to observe an increased oil recovery, which is a good degree less than salinity of the formation brine [3, 5, 11, 12].

Asphaltene deposition behaviour in porous media has been highly regarded in recent decades. Telmadarreie and Trivedi analyzed the asphaltene deposition behaviour in fractured porous media during hydrocarbon solvent injection in a heterogeneous-fractured micromodel. They used three types of hydrocarbon solvents (nC5, nC7, and nC12) in their experiments for extra-heavy oil recovery (30 000 cP at 22 °C). They concluded that either diffusion dominant or viscous dominant will affect the shape of deposited asphaltene as the dominant flow mechanism [13]. Kord et al. performed several dynamic and static asphaltene deposition tests on dead and live crude oil and real core samples. They investigated the effect of fluid velocity on formation damage and concluded that the ability of current deposition models is under question [14].

In the last two decades, the oil-brine-rock interaction has been accentuated in determining the underlying mechanism of LSW which remain overlooked.

1.1. Effect of LSW on IFT and Wettability Alteration

Extensive researches that have been carried out over the past two decades have clearly demonstrated that low salinity waterflooding can improve oil recovery from reservoirs. Most studies believe that LSW would change wettability toward less oil-wet or more water-wet state [15] contributing to a more favourable condition which resulted in further oil recovery. The recent novel studies conducted by Alvarado et al. [16] and Firoozabadi et al. [9] revealed the paramount importance of Oil/Brine interactions. It has been observed by many researchers that
LSW affects the capillary forces, and this is seen mainly in contact angle (wettability) change rather than IFT change. Different trends have been reported in the literature for the effect of salinity on the IFT of water/oil systems. An increase in IFT with increasing salinity in systems including pure oil presented by several authors, such as Ikeda et al., Cai et al., Badakhsan and Bakes, and Aveyard and Saleem studies [17-20]. Several authors presented a steadily trend in increasing or decreasing IFT by adding salt [20]. By contrast, Alotaibi and Naser-El-Din’s study on N-dodecane indicated that decreasing IFT during salt adding is not always steadily since as it reaches the equilibrium, IFT of the system including 5 wt% NaCl drops compared to the 2 and 10 wt% systems. But, Vijapurapu and Rao [21] observed approximately 10% decrease in IFT (22.1 to 12.4 dyne/cm3) by diluting Yates reservoir brine with deionized water (DW) to a moderate level (60% brine and 40% DW) compared to more dilution (10% brine and 90% DW). In addition, Alotaibi and Naser [22] observed that decreasing the salt concentration increase the IFT and moreover and found a critical salt concentration for lowest IFT to enhance oil recovery. Al-Alatar et al [23] noted that IFT decreases by reducing the \( \text{SO}_4 \) and \( \text{Ca}^{2+} \) concentration in injection water, but they did not find it to be a low salinity effect in their case because maximum recovery was not gained at the minimum concentration of those ions. In another side, Yousef et al [24] reported that SW has a little effect on the IFT of crude oil and brine. Their group [25] also suggested that 10 times diluted SW (10SW) improved the ultimate oil recovery which had an effect in lowering IFT between crude oil and brine. The systematic works carried out by Alvarado’s group showed an increase in interfacial viscoelasticity which caused further oil recovery through LSW injection [26-29]. It is speculated that the existence of polar components in crude oil leads to higher viscoelasticity which is a critical factor for higher oil recovery in each enhanced oil recovery (EOR) process [26, 28, 30]. Furthermore, Spiecker and Kilpatrick
demonstrated that the presence of an elastic film made up from asphaltene aggregates at the Oil/Brine interface [30]. Moreover, for acidic crude oils [31], it has been reported that the impact of \( \text{SO}_4^{2-} \) on IFT depends greatly on the counter ions such as \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \). Sohrabi et al. [32] and Mahzari et al. [33] proposed the crucial role of fluid-fluid interactions during LSW injection and introduced the water micro-dispersion at the Oil/Brine interface as a substantial mechanism. Kazempour et al. [34] believed that additional concentration of \( \text{SO}_4^{2-} \) ion appears to be favorable for each waterflooding stage since it can mitigate the anhydrate dissolution which leads to adjust water hardness. On the contrary, other researchers [35-37] reminded the negative effects of additional \( \text{SO}_4^{2-} \) as it can form hard scales when the water comes into contact with formation brine with strontium and barium ions. Therefore, some consideration must be taken into account to reach the best chemical receipt of water injection. However interfacial properties of oil/brine systems are complex and dependent on various factors, such as experimental conditions, salinity, the quantity of asphaltene, other surface active material present in the system etc. [38] which make it more difficult to identify and distinguish the main mechanism compared to the pure systems [39]. Vijapurapu and Rao investigated the effect of salinity on the IFT between a crude oil and different brines. They used synthetic and reservoir brine as a high salinity water to identify the IFT trend during diluting it with deionized water (DIW). They presented that increasing the dilution to 50% (2 times diluted) lead to a lower IFT whereas any further dilution beyond that would result in higher IFT. Hence they found a critical brine concentration in which the oil/brine system has a minimum IFT [21].

The aforementioned studies in the last two decades show that it has been a growing interest in understanding the low salinity mechanism which may result in additional oil recovery. Many theories on how low salinity water works have been proposed, but the main mechanism is still
debated. Generally, the complex oil/brine/rock interactions are still being debated in the literature. The aim of this study is to clarify the role of fluid-fluid interactions during LSW injection and provide a mechanistic study with novel experiments using study the behaviour of the fluid in a single pore when brine solution comes into contact with crude oil. To identify the IFT reduction mechanism, a glass micromodel was also fabricated and several oil/water interaction tests by monitoring a synthetic oil/water interface under 20x magnification microscope were carried out. This visualize experiment helps to more accurate understanding the mechanism of IFT reduction. The purpose of this experiment is to recognize the existence of asphaltene aggregates at the Oil/Brine interface in different brine solutions and find a reasonable interpretation by regarding IFT results. Finally to investigate the formation of water micro-dispersions in the synthetic oil due to the synthetic oil-brine interaction in our experiments, several IFT tests and ESEM analyzes were also performed on the synthetic oil sample containing asphaltene to investigate a novel concept of formation or absence of water micro-dispersion in oil when low salinity or high salinity water comes into contact with the synthetic oil. It was observed that no water micro-dispersions were formed inside the synthetic oil.

The current study is presented in multiple sections. The materials and methods used in the conducted experiments are presented first. Then, the obtained results are shown. Thereafter, the discussion is taken to explain the mechanism behind the improving oil/water interface. Finally, conclusions are made based on the observed results.

2. Materials and Methods

2.1. Brine
In this study, four samples of synthetic brine (seawater, SW, 2 and 10 times diluted seawater, 2SW and 10SW, and formation water salinity, FW) were used in our experiments. Deionized water was used for the dilution and preparation of the synthetic brines. The formation water and seawater contains dissolved solids. The main dissolved solids are sodium chloride, calcium chloride, magnesium chloride, sodium sulfate, and sodium bicarbonate with the purity of 99 wt%. The density of the different brines is summarized in Table 1. Dissolved salt concentration is expressed in parts per million on a mass basis (ppm). The composition of brine is expressed as the concentration of individual ions and total dissolved solids (TDS) which are reported in table 2.

Table 1. Brines composition

<table>
<thead>
<tr>
<th>Type</th>
<th>Density (gr/cm³) at 28°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>1.0001</td>
</tr>
<tr>
<td>SWS</td>
<td>1.04</td>
</tr>
<tr>
<td>2SWS</td>
<td>1.022</td>
</tr>
<tr>
<td>10SWS</td>
<td>1.006</td>
</tr>
<tr>
<td>FWS</td>
<td>1.06</td>
</tr>
</tbody>
</table>

Table 2. Brines composition

<table>
<thead>
<tr>
<th>Salts (ppm)/Brine</th>
<th>FWS</th>
<th>Salts (ppm)/Brine</th>
<th>SWS</th>
<th>2SWS</th>
<th>10SWS</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>140316</td>
<td>NaCl</td>
<td>28400</td>
<td>14200</td>
<td>2840</td>
</tr>
<tr>
<td>CaCO3</td>
<td>1628</td>
<td>KCl</td>
<td>800</td>
<td>400</td>
<td>80</td>
</tr>
<tr>
<td>MgCl2</td>
<td>2856</td>
<td>MgCl2</td>
<td>6430</td>
<td>3215</td>
<td>643</td>
</tr>
<tr>
<td>CaCl2</td>
<td>40287</td>
<td>CaCl2</td>
<td>1380</td>
<td>690</td>
<td>138</td>
</tr>
<tr>
<td>Na2SO4</td>
<td>2588</td>
<td>Na2SO4</td>
<td>4490</td>
<td>2245</td>
<td>449</td>
</tr>
<tr>
<td>NaHCO3</td>
<td>2016</td>
<td>NaHCO3</td>
<td>100</td>
<td>50</td>
<td>17</td>
</tr>
<tr>
<td>IS* (mole/litre)</td>
<td>4.22</td>
<td>IS (mole/litre)</td>
<td>0.83</td>
<td>0.42</td>
<td>0.08</td>
</tr>
</tbody>
</table>
2.2. Oil Phase

A crude oil sample from an oil reservoir in the southwest of Iran was utilized as an oleic phase in this study. A synthetic oil with asphaltene content of 0.1 wt% was also made to observe fluid-fluid interaction in visualization experiments. The measurement of density and viscosity of the crude oil and the synthetic oil were carried out in the laboratory using Anton Paar 4100 and viscometer respectively. The properties of both oils have been presented in table 3.

Table 3. Physical properties of used crude oils

<table>
<thead>
<tr>
<th>Name</th>
<th>Asphaltene Content (%)</th>
<th>Density (gr/cm³) at 28°C</th>
<th>Viscosity (cP) at 28°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude Oil</td>
<td>0.2</td>
<td>0.84</td>
<td>2.35</td>
</tr>
<tr>
<td>S-Oil</td>
<td>0.1</td>
<td>0.78</td>
<td>0.46</td>
</tr>
</tbody>
</table>

2.3. IFT Setup

The low-pressure pendant drop technique (Drop shape analysis, DSA) was used to study the possibility of a fluid-fluid interaction between oil and brine through IFT. The schematic view of the DSA apparatus is shown in Figure 1. The pendant oil drop is formed within the brine phase using a needle installed at the top of the low-pressure cell. A drop shape analysis software (Image-J) is used to measure the equilibrium IFTs of oil/brine systems at laboratory conditions.
To accurately measure the IFT, the equipment (needle, line connections, cell,) were carefully cleaned up with toluene followed by deionized water, finally dried in an oven.

![Figure 1. Schematic of the pendant drop apparatus for IFT measurements](image)

2.4. **Contact Angle Setup**

A few contact angle tests on dolomite rock were performed to determine the effect of different treatments on the wettability. The contact angle measurements were performed at the ambient conditions by using a DSA apparatus. All contact angle tests were performed two times for not only making sure about the accuracy of data but also minimizing the error of measurements. Therefore, the measurement error was pretty lower than ±5% which stem from the low roughness of rock plates and high resolution of taken images of oil droplets. In order to scrutinize the effect of different brines on the wettability state of rock plates accurately, the following procedure was followed:

1- The rock plates were polished to decrease the surface roughness.
2- The Polished dolomite rock slides were first cleaned with alcohol and distilled water, and then placed to a 60 °C oven for drying. The dried rock plates were placed in the ultrasonic bath to eliminate contaminations during preparing rock patches.

3- The cleaned rock patches were soaked in FW for at least 5 days at 90 °C in order to restore initial wettability state.

4- The oil-wet surfaces were created by aging the slides in the crude oil at 90 °C for one week.

5- The contact angles of oil droplets in various brines were determined right after the aging process from 0 to 360 hours.

2.5. Microscopic visualization of Pore-Scale in Micromodel

The setup contains two syringe pumps, a microscope with an attached camera, a waste container and the fabricated glass micromodel. The procedure of this experiments is as follows:

1. The syringes filled with mineral oil and brine were attached to both injection ports of the glass micromodel.

2. Both syringes were placed into separate syringe pumps.

3. The glass micromodel device was placed on the microscope platform.

4. The synthetic oil was injected. If there are pockets of air in the tubing, to make sure that air pockets are removed in the plastic tubes and pore space then begin flowing fluid into the channel.

5. Once the channel was filled with the oil; the brine was injected through the micromodel to remove any air pockets.

6. After the air pockets are removed, begin flowing synthetic oil through the glass micromodel.
7. A microscope was used to observe the oil-water interface inside the pore space, and the phenomena were recorded by a digital camera attached to the microscope.

Schematic of the micromodel setup used for study the oil/water interface is shown in Figure 2. Two pumps were required for the system that has been set up. One pump was used to inject oil, and the other pump injects water or brine.

Figure 2. Schematic of the experimental setup which contains two syringe pumps, a microscope with an attached camera. This view shows how oil and water/brine are injected into the glass micromodel. The yellow arrows show the direction of oil and brine flow in the inlet and the red arrow shows the direction of flow in the outlet.

3. Results
3.1. IFT Measurements (Crude Oil sample)

The main aim of this section is to study the change of IFT using brine solutions with different salinities. The measured IFTs between crude oil and aqueous solutions were used as a screening stage to determine the effective range for salt concentration. IFT measurements were taken for each crude oil/brine system at ambient conditions and were repeated 3 times to ensure repeatability of the results. The obtained results demonstrated that the IFT decreases significantly at the beginning, then increases with the further addition of the salts. There is a critical salt concentration where the IFT between crude oil and brine is minimum. Figure 3 demonstrates that the highest IFT stands for deionized water/oil system, whilst 2SWS-oil holds the lower IFT than the other aqueous solutions. A similar trend was also observed by Vijapurapu and Rao (2004).

![Figure 3. IFT of the crude oil/water with different salinities](image)

As it can be seen, low salinity water has a positive effect on IFT reduction. IFT decreases with increasing salts concentration until 2SW and beyond this value, IFT increases with increasing salinity.
3.2. Contact Angle Measurements

In this section of the study, the effect of salinity on wettability was also investigated by conducting a series of experiments on the oil-wet rock surface. The surface turned into the neutral-wet state after being contacted with the sea water solution for 360 hours. The surfaces were also turned into the more water-wet state after being contacted with 2 and 10 times diluted sea water. Whilst small change in wettability was observed by formation water. Figure 4 shows the contact angle measurements achieved on the rock surface after its contact with the different brines during 360 hours.

![Contact Angle Measurements](image)

Figure 4. The contact angle of crude oil droplets on oil-wet rock versus time under different solution conditions

These experiments show when brine was diluted to 10 times lower salinity, a following large change in contact angle was observed, believed to be related to the expansion of the electrical double layer (EDL) and multicomponent ion exchange (MIE).

3.3. IFT Measurements (Synthetic Oil sample)
The equilibrium IFT was measurements for the synthetic oil-DI water/brine interfaces. Each test was repeated at environment conditions for at least three times to examine the repeatability of the results. Figure 2 (below) shown the average value of IFT from three runs vs. brine salinity (DI water, SWS, 2 SWS, 10 SWS and FWS).

As shown in Figure 5, the synthetic oil has a similar trend which IFT in oil/2 SWS interface is smaller than that measurement in other interfaces.

![Figure 5. IFT of the synthetic oil/water with different salinities](image)

3.4. **Micromodel-Microscopic Visualization**

Low salinity effects are complex and not easily predicted, due to the number of parameters and the complexity behind oil/brine/rock interactions, which the scope of this research work clearly shows.

In this section of the study, to further investigate the fluid-fluid interaction as a recovery mechanism and observe the salinity level at which fluid-fluid interaction become significant,
several water injection tests were performed in a glass micromodel system with a single pore. The visual evidence in this work is based on microscopic studying of the oil/water interface. The oil and brine were injected into the micromodel, simultaneously. The main aim of these experiments was to investigate the effect of salinity on the presence of asphaltene particles in the interface between the two phases. For this purpose, brine solutions with different salinity including SW, 2 SW, 10 SW, and FW were injected in the micromodel. Deionized water was also injected to better understanding the effect of the salinity. A microscope was used to visualize the behaviour of asphaltene particles at the interface of two phases in the presence of different salinities. The results of this section show a good matched with IFT measurements for both crude oil and synthetic oil conducted in this work.

Figure 6 shows the effect of different salinities on the oil-water interaction mechanism at the interface between the two phases. These experiments evident that in the case of water without salinity, the presence of asphaltene particles at the interface between oil and water is very low and is insignificant which increases the IFT. For 2 SWS, the presence of asphaltene particles at the interface between oil and water is maximized, which reduces IFT. Subsequently, the SWS, FWS and 10 SWS have high levels of asphaltene particles in the interface, respectively, and these results have a good matched with the IFT experiments. These visualize evidence show highest asphaltene adsorption in the interface occurs when oil was contacted with 2 SWS. With these analyses, the fluid-fluid interaction at the interface of the two phases leading to IFT reduction followed by adsorption of the asphaltene in the interface which leads to a better mobility control and hence a better sweep efficiency.
Figure 6. Microscopy images of synthetic oil/different brine interface, (a) captured images using the camera, (b) converted images to grayscale.
3.5. ESEM imaging (Qualitative Observation)

In order to investigate the mechanisms available in the wettability alteration and IFT reduction, good visual images were taken from the synthetic oil contacted with different brines to visually observe any changes into the oil phase in contact with brine using the ESEM analysis. ESEM image of the synthetic oil sample with no brine contacted to it was used as a control system to observe any change in the oil sample contacted with different brines for comparative and qualitative analysis.

For contacting the synthetic oil to brine, both phases were injected into the glass micromodel system from two injection ports, simultaneously and wasted fluids were collected into a test tube from the output port. The test tube was shaken during a mixing period of 1 hour. The schematic of the preparing the synthetic oil after being contacted with brine is shown in figure 7.
Figure 7. Schematic of the preparing the synthetic oil comes into contact with brine to ESEM analysis

The visual experiments approved there is no water micro-dispersion in the oil phase. In these experiments, ESEM images of the synthetic oil prior to being contacted with brine and after being contacted with brine at different salinity were taken. Figure 8 shows ESEM images of control sample compared to the synthetic oil after being contacted with different brines.
Figure 8. ESEM image of the synthetic oil. The picture (1) shows the ESEM of the synthetic oil prior to contacting with brine. Picture (2), (3) and (4) show the same synthetic oil after being contacted with SWS, 10 SWS and FWS sample, respectively.

ESEM analysis shows similar states when the synthetic oil was contacted with different brines in micromodel as no water micro-dispersion is formed when it was contacted with different salinity brines. Whilst several authors (Emadi and Sohrabi, 2013, Mahzari and Sohrabi, 2014) presented that low salinity injection causes the formation of water micro-dispersions in crude oil due to crude oil-brine interaction [33, 40]. Hence, it can be concluded that the formation of water micro-dispersions depends upon many factors including the properties of oil and experimental conditions.

4. Discussion

The main aim of this work is to investigate the low salinity effect on the fluid-fluid and rock-fluid interactions and examine visually how the oil/water interface would be affected by asphaltene concentration through changing brine salinity. To illustrate how low salinity water
affects oil recovery, IFT and contact angle of crude oil/brine systems were carried out and a glass
micromodel test was also conducted to get a knowledge on the mechanism behind alteration of
IFT by low salinity water injection. ESEM analysis was also performed using a wide range of
brine salinity so as to test out the salinity range at which these changes can be observed.

4.1. LS Effect in Change of IFT

The main difference between current work and surfactant models presented by other authors is
that the surface active agents’ particles in surfactant models is surfactant and moves from the
aqueous phase toward the interface, whereas in the current study the surface active agents’
particles, i.e. asphaltene moves from the oil phase toward the interface. However, the mechanism
behind both model might be similar. In the water/pure hydrocarbon systems, when inorganic
salts are added into the aqueous phase, water molecules form a cage-like structure around the salt
ions. At the interface of hydrocarbon/water system, where water molecules are in contact with
hydrocarbon and disruption of hydrogen bonding, causes higher energy medium for the ions and
due to higher salt concentration in the bulk phase than at the interface, the salt ions migrate to the
bulk of the fluid and depleted at the interface. Therefore, the Gibbs surface excess of salts
becomes negative, resulting in higher IFT.

In the heavy crude oil/brine systems, due to the presence of high content of asphaltene, resins
and waxes in the oil phase, the IFT is much lower than in a pure system without these agents. At
high salt concentration, the oil-soluble asphaltenes are less ionized and become more oil soluble
and hence their tendency to move into the interface reduces. Hence increase the IFT. To identify
the exact underlying mechanism of how salinity can change the IFT, it should be stated that
when salt is added into the bulk phase, the activity coefficient of it in aqueous salt solution
increases as its concentration rises, and the salt molecules transfer to the oil phase [35]. The
cations near the surface tend to interact with the polar asphaltenes leading to a high level of solubility in both oleic and aqueous phases. With the cations present at the interface, negative surface excess concentration for salt turns to be positive, which consequently lowers the IFT according to Gibbs adsorption isotherm. The obtained results in this study represent the accuracy of this phenomena.

By adding more salt, an increasing trend in IFT takes place leaving an optimum salinity behind. The dominant mechanism beyond optimum salinity is suggested to be the “salting-out effect”, i.e., when cations concentration near the interface increases, the water molecules which interact with both ions and organic compounds, are no longer able to support the charges and polarity of both ions and asphaltenes. Thus, the surface active asphaltenes are transferred back to the oil phase and depleted near the interface (negative adsorption) and more and more cations are hydrated. Also, the presence of divalent cations like calcium and magnesium (“hardness” ions) in high salinity systems will deplete the interface from the surface-active agents due to this effect and hence resulting in higher IFT and lower oil recovery [5]. Therefore the observed trend might show different effects from the system including monovalent cation in the system. In addition, Chan and Shah [41] reported that increasing in salt concentration would increases the concentration of surface-active agents in the oleic phase far from the interface due to surrounding the cations by water molecules and consequently, the interface will be totally depleted and both surface excess concentrations of asphaltene and salt become negative which leading to higher IFT at high levels of salinity. Also, it is generally accepted that increasing salt concentration in the aqueous phase increases the density of the aqueous phase, and therefore density differences between the oleic and aqueous phases increases which lead to higher the IFT. This macroscopic
scales does not take place in all cases since there exist other controlling mechanisms in the microscopic scales as some of them were already described.

4.2. LS Effect in Altering wettability

There are several mechanisms involved in oil recovery by brine injection that have been proposed in the literature e.g. fine migration, PH variation, double layer expansion and multi ionic exchange. Several mechanisms descriptions have been presented in the literature which proposed for pure hydrocarbon/surfactant/brine systems and none of them can exactly determine the behaviour of the oil/brine system including the surface activity of asphaltene. Tang and Morrow [42] studied how low salinity waterflooding impacted the oil recovery. They reported an increase in oil recovery by diluting the ionic strength of invading brine. They also reported wettability alteration toward more water-wet conditions as the salinity of injected brine decreased. However, the mechanisms behind each system different with minerals composition, oil properties, water composition, temperature and pressure.

With an overview of oil-brine-rock interactions, we can have a better understanding of the wettability alteration of rock surfaces. Usually, crude oil and carbonates are oppositely charged. Thus electrical double layer (EDL) attraction occurs in carbonate reservoirs and makes them more oil-wet. MIE is also proposed to explain the wettability alteration by brine in carbonates. The dissolution of CaSO$_4$ during LS waterflooding can release more SO$_4^{2-}$ to the brine, which can enhance MIE and alter the rock surface wettability to more water-wet [35]. SO$_4^{2-}$ is a strong potential determining ion that can make carbonates negatively charged. Then Ca$^{+2}$ and Mg$^{+2}$ are able to approach carbonate surface and substitute the absorbed carboxylic group or Ca$^{+2}$-carboxylic complex, and thus make carbonates more water-wet [33].
5. Conclusions

This study was done with the intention to discuss different salinity mechanisms.

Several observations were made for supporting the proposed mechanism. IFT, Contact angle, microscopic visualization of the oil/water interface and ESEM analysis were conducted. Based on the observed results the following conclusions can be made:

1) The effect of low salinity water (2 and 10 times diluted sea water, 2SW and 10SW) on wettability alteration is more significant as compared to high salinity water (formation water, FW and sea water, SW). The change of wettability from oil-wet to water-wet and to strongly water-wet were observed as a result of aging the solid surface with the 2 times and 10 times dilutes seawater, respectively.

2) IFT measurements showed reduced IFT values for 2 times diluted seawater as compared to other brines for both crude oil and synthetic oil.

3) Microscopic visualizations of brine injection demonstrated that the presence of asphaltene particles in the interface between the synthetic oil and brine is maximized when 2SW was injected into the micromodel. Because the presence of the cations at the interface causes negative surface excess concentration for salt turns to be positive and IFT decreases. When cations concentration near the interface increases (in the cases of SW and FW injection), the water molecules, are not able to support the charges and polarity of both ions and asphaltenes for long time. Thus, the surface active asphaltenes are transferred back to the oil phase and depleted near the interface and caused high IFT value. Whilst in the cases which deionized water and 10SW were injected, adsorption of the asphaltene into the interface was very low.
4) The fluid-fluid characterization tests using ESEM image indicated no change in the synthetic oil composition and no water micro-dispersion was observed while several researchers concluded that low salinity injection causes the formation of water micro-dispersions in crude oil. So it can be concluded that the formation of water micro-dispersion within the oil phase depends on several factors, including oil properties, experiment condition (temperature and pressure) etc.

References


[15] (!!! INVALID CITATION !!! {Lager, 2008 #17; Morrow, 2011 #2; Nasralla, 2011 #6; Omekhe, 2012 #7; Sorbie, 2010 #5; Tang, 1997 #14; Tang, 1999 #3; Zahid, 2012 #8; Al Harrasi, 2012 #9; Sorbie, 2010 #4}).


[38] J.S. Buckley, T. Fan, Crude oil/brine interfacial tensions1, Petrophysics, 48 (2007).


Highlights

• Effect of water salinity on properties of oil/brine interface is studied.

• Experimental results show that interfacial tension is reduced during low salinity water.

• Microscopic visualization is performed to better understand mechanisms of reducing interfacial tension.

• 2 and 10 times diluted sea water cause a greater change in oil/water interfacial tension.

• 2 times diluted sea water has a significant on interfacial tension reduction.
Conflict of Interest

The authors declare that there is no conflict of interest.