**Introduction**

Low salinity water (LSW) injection has been received more attention as a promising method to increase oil recovery. A close look at the LSW literature shows that comparatively most of the previous studies focused on the relevant rock-fluid interactions, but few studies addressed possible interactions between crude oil and aqueous phase, in particular those aspects relevant to the interaction of salinity with crude polar components (CPCs) (Mahzari & Sohrabi, 2014; Al Shalabi & Sepehrmoori, 2017). These polar components tend to arrange themselves at the oil/water interface and also partition into the aqueous phase (Mokhtari & Ayatollahi, 2018). Such partitioning of CPCs could influence the interfacial property of the oil/water system and also lead to incremental oil recovery. It was stated that manipulation of the injected water salinity affects the amount of partitioning of CPCs (Lashkarbolooki & Ayatollahi, 2016). As to the previous works, reduction of water salinity causes formation of an emulsified phase mainly due to the partitioning of CPCs in the aqueous phase that in turn affects oil distribution through pore spaces (Mandal et al., 2010; Moradi et al., 2013). This study aims to provide new insights into the interaction of an asphaltene crude oil and brine with different salinity by addressing the partitioning of the CPCs. To this end, a series of oil displacement tests by seawater and its dilution was performed in a transparent glass micromodel that enabled us to capture the microscopic interaction between oil and water. Also, the effect of brine salinity on the partitioning of the CPCs was described by performing salinity scan analysis aided by pH and IFT measurements.

**Material and Method**

In this study, synthetic seawater (SW) with a salinity of 40,000 ppm and its different dilutions was used. We also used an asphaltene crude oil with a viscosity of 210 cp and asphaltene content 12wt%. The brine solution of 0.1SW and SW were considered as LSW and high salinity water (HSW) in the micromodel study. Other SW dilutions (ranging from 0.05 SW to 1.5SW) were used in the salinity screening analysis, pH and IFT measurements. A tiny amount of the water soluble dye was added into the brine solutions to track fluid flow through the micromodel. In all figures taken from the micromodel, red, blue and black colours represent the presence of 0.1SW, SW and crude oil, respectively. All micromodel experiments were performed at the ambient conditions. We used a 2-D sinusoidal glass micromodel to observe fluid displacement and also explore the O/W interactions. The aspect ratio and average depth of the micromodel were 2.45 and 200 µm. To perform the micromodel experiments, first it was fully saturated by brine and then crude oil was injected until no water was produced. Then, brine (either SW or 0.1SW) was injected into the micromodel at 0.0004 mL/min using a precise syringe pump. Image processing was performed to obtain the displacement efficiency during brine injection. Also, to gain a better understanding of the salinity effect on the partitioning of CPCs into the aqueous phase, salinity scan analysis was performed by tracking the resulting interface between oil and brine over a period of 20 days. To this end, a series of test tubes consisting of a 1:1 volume ratio of brine and oil was prepared. Also, to support the partitioning phenomena, the pH of the brine solution previously contacted by crude oil (aged water) was measured over 20 days. This was followed by measuring the IFT of the crude oil previously contacted by brine (aged crude oil) and fresh brine using pendant drop method.

**Micromodel experiments**

Figure 1 shows the result of 0.1SW injection into the micromodel after one pore volume (PV). Note that micromodel was placed horizontally and flow direction was from left to right. As can be seen, first brine flow (red color) occurs mainly through the middle section of pore body (see the last pore body at the far right after 1PV). As time passes, brine occupies further volume of the pore body. The latter is evident through the first pore bodies where almost half of the oil is displaced by 0.1SW. As to the image analysis results, the displacement efficiency during 0.1SW was about 53% ±2. As to the case of SW brine, water flow (blue color) occurs mostly through a film-like pattern as shown by the pore body located at far right in Figure 2. For those pore located near the injection point (left side), SW brine only displaced a small volume of oil, which was lower than that of done by 0.1SW. The displacement efficiency during SW injection was about 34% ±2. To a have a close look at oil/brine flow, Figure 3 shows a zoomed-in picture of the last two pore bodies during 0.1SW injection. It can be inferred that crude oil was dispersed into 0.1SW brine in the form of an oil-in-water emulsion, while such effect is not evident for the case of SW brine. This could be attributed to the fact that
reduction of water salinity from SW to 0.1SW may affect oil/water interfacial properties most likely due to the partitioning of the CPCs into the aqueous phase. This observation will be elaborated in the next section.

**Figure 1:** 0.1SW injection into micromodel

**Figure 2:** SW injection into micromodel

**Figure 3** Zoomed-in picture of last two pore bodies during 0.1SW injection

### Salinity scan analysis

Figure 4 shows salinity scan results for the crude oil in the presence of different salinities. At each salinity, the phase behavior of the oil/water system is shown at two times: initial state and after 20 days. In all tests, after 20 days a middle emulsified phase region was formed for all salinities mainly due to the partitioning of the CPCs into the aqueous phase. This region was marked by a pair of white parallel lines in Figure 4. At salinity 0.05SW, (Figure 4-A), the middle emulsified phase is clearly evident as compared to its initial state. For the case of 0.1SW (Figure 4-B), the thickness of the middle phase increases further. But, for the salinity 0.25SW (Figure 4-C), this thickness decreases as compared to 0.1SW. By further increasing of brine salinity to 0.5SW and SW (Figure 4-D and 4-E), the thickness of the middle phase continuously decreases such that for the case of 1.5SW it reaches the minimum thickness (Figure 4-F). As to these results, one can see that there is a critical value for brine salinity to obtain the highest thickness of the middle emulsified phase that corresponds to the largest amount of partitioning of CPCs into the aqueous phase.

![Figure 4 Salinity scan results over time](image)

**Figure 4** Salinity scan results over time

### IFT measurement

To get an insight about the partitioning of CPCs into the aqueous phase, Figure 5 shows the equilibrium IFT of the aged crude oil and fresh brine of 0.1SW and SW. Note that to perform this test, first crude oil samples were contacted by brine in a test tube for different time to see that how much
oleic polar components could be depleted from the crude oil (or equally partitioned into the brine). As to the results, the IFT value for the case of crude oil aged by 0.1SW is higher than that of aged by SW. This shows a larger amount of the polar components of the aged crude oil has been already partitioned into 0.1SW brine. Therefore, the IFT of the aged crude oil/fresh 0.1SW exhibits a higher value as compared to the case of SW brine with a lower amount of partitioned CPCs. Also, a close look at the IFT profile of 0.1SW shows that the partitioning of CPCs into the aqueous phase occurs over time. That was the reason the IFT value also gradually increases from 35.8 mN/m to 40.3 mN/m ± 0.1 while such effect is not that much pronounced in the case of SW in which IFT only goes up from 30.5 mN/m to 31.4 mN/m ± 0.1.

\[
\text{RCOOH}_{aq} \leftrightarrow \text{RCOO}^{-} + \text{H}^+ \quad \text{(eq 1)} \\
\text{RCOO}^{-}_{aq} + \text{H}^+ + \text{Na}^+ \leftrightarrow \text{H}_2\text{COO}^{-}_{aq} + \text{Na}_2\text{CO}_3 \quad \text{(eq 2)} \\
\text{Na}^+ + 2\text{RCOO}^{-}_{aq} \leftrightarrow \text{RCOO}_2\text{Na}_{aq} \quad \text{(eq 3)}
\]

Accordingly, the CPCs could separate into \(\text{RCOO}^{-}_{aq}\) and \(\text{H}^+\) groups, which are in an equilibrium condition as to Eq. 2. Then, the \(\text{RCOO}^{-}_{aq}\) group could form ionic bonds with those cations being present on the oil/water interface by one of its oxygen atoms as to Eq.3. \(\text{RCOO}^{-}_{aq}\) group could then be solvated in water by forming hydrogen bond between its other oxygen atom and water molecules, which causes formation of a middle emulsified phase as shown schematically by Figure 7. As to the brine salinity effect, increase of cations in the aqueous phase up to a certain value (critical value) along with the formation of hydrogen bond cause the middle emulsified phase becomes thicker (Figure 8) (Taylor, 2019). However, the presence of the inorganic compounds in the brine such as \(\text{Ca}^{2+}\), \(\text{Mg}^{2+}\) could destroy hydrogen bonds (Lee & Lee, 2019). Therefore, if the number of cations exceeds a critical value, they do not allow the CPCs to form hydrogen bonds with water molecules, therefore, the solubility of the CPCs in brine decreases. The latter means the middle emulsified phase becomes thinner as already shown in salinity scan analysis (Figure 4-F). Figure 9 also schematically shows the emulsified phase region above the critical salinity. This phenomenon is known as the salting-out effect (Endo et al., 2012), through which the middle emulsified phase almost disappears at high salinity condition due to the lack of hydrogen bond formation (Figure 10).
Conclusions
This study aimed to provide new insights into the interaction of asphaltenic crude oil/brine with different salinity by addressing the partitioning of the crude polar components (CPCs) into the aqueous phase. This was done by micromodel study using a sinusoidal pattern with several dead-ends. To gain further insight into the interfacial phenomena between crude oil and brine, salinity scan analysis aided by pH and IFT measurements was performed. Micromodel results showed that with the decease of water salinity from seawater (SW) to its 10 times dilution (0.1SW), the partitioning of the CPCs increases in the aqueous phase followed by a formation of an oil-in-water emulsion. It was found that such a partitioning leads to a meaningful reduction in the pH of the aqueous phase. This observation was further supported by an increase in the IFT of crude oil previously contacted by 0.1SW as compared to the crude oil contacted by SW. As to the salinity scan analysis, when brine salinity decreased from 1.5SW to 0.1SW, middle emulsified region was formed between crude oil and brine with a maximum thickness for the case of 0.1SW salinity. However, it was found that below this salinity the thickness of the middle emulsified region diminishes. These results are reminiscent of a critical salinity state above which the partitioning of the oleic polar components into the aqueous phase could be suppressed due to the salting-out effect.

References
Taylor, S. (2019). Colloids and Interfaces in Oil Recovery; MDPI.