Dynamic interfacial tension and wettability of shale in the presence of surfactants at reservoir conditions

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Dynamic interfacial tension and wettability of shale in the presence of surfactants at reservoir conditions

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highlights

- IFT/CA measurements were performed on shale systems at reservoir conditions.
- A framework is established to study surfactant concentration/brine chemistry on shales.
- Increase in salinity and anionic surfactant concentration resulted in higher CA.
- Shale remained water–wet due to low adsorption of nonionic surfactant.
- Use of tap water versus reservoir brine resulted in lower IFT and work of adhesion.

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abstract

The production of oil from shale formations often requires the utilization of chemical surfactants as additives in fracturing fluids in order to change the characteristics of oil/brine interfaces and/or induce wettability alteration at the shale surface. Although the effect of some surfactants on the interfacial properties of shale oil systems has been investigated in the past, the limited data available in the literature were mainly obtained at ambient conditions and thus may not be representative of fluid-rock interactions at actual reservoir conditions.

In this study, a new framework is proposed to investigate the effect of surfactants on fundamental parameters governing fluid displacement in two brine/oil/shale systems (A and B) at reservoir conditions. The critical micelle concentration (CMC) of anionic and nonionic surfactants in brine and their adsorption propensity on shale was first determined by ultraviolet–visible spectroscopy and pendant drop method. Rising/captive bubble technique was validated for ultra-low interfacial tension systems then utilized to measure dynamic interfacial tensions and contact angles in the presence of surfactants in Systems A and B at ambient and reservoir conditions. The effects of pressure and temperature, surfactant concentration, and brine chemistry on the above-mentioned parameters were investigated in a systematic manner. The results revealed that nonionic surfactants adsorb much less on shales than anionic surfactants. As a result, shale samples used in this study remained strongly water–wet with the nonionic surfactant regardless of surfactant concentration and brine chemistry. The lowest work of adhesion was obtained right above the CMC, which represents the optimum surfactant concentration. Moreover the use of tap water instead of reservoir brine in System B was preferred due to a further reduction in IFT.

1. Introduction

Unconventional shale oil and gas reservoirs are becoming increasingly important to hydrocarbon supplies across the world. Shale rocks have intricate nano- and micro-scale pore networks and complex matrix mineralogy. They mainly consist of clay minerals, carbonate/quartz grains, and organic matter. Their porosities are typically less than 15% and their permeabilities are in the range of nano- to micro-Darcy [1]. Shale rocks are artificially fractured to improve the poor permeability and pore connectivity in these reservoirs; however, the presence of nano pores, micro pores, and micro fractures in the matrix causes high capillary pressures in the medium. Therefore only a limited portion of the original oil in place is recoverable by primary production. The rationale behind this work is to reduce the capillary pressure of the system using surfactants as additives in fracturing fluids. Hence, more oil can be produced due to further imbibition of brine into these rocks.
Capillary pressure is responsible for holding oil and brine phases during hydraulic fracturing processes and can be, for a circular pore, calculated from Eq. (1), also known as Young–Laplace equation, where $\gamma_{ow}$ is the oil–brine interfacial tension (IFT), $\theta_{ow}$ is the contact angle (CA) at the three-phase contact line, and $r$ is the pore radius.

$$P_{cw} = \frac{2\gamma_{ow}\cos\theta_{ow}}{r} \quad (1)$$

Reducing the capillary pressure by, for instance, using surfactants with hydraulic fracturing fluid, can potentially increase the amount of oil recovery from shale reservoirs. Surfactant molecules tend to accumulate at fluid–fluid and rock–fluid interfaces and hence reduce $P_c$ by lowering $\gamma_{ow}$ and altering $\theta_{ow}$ on shale surfaces.

There are several suitable IFT measurement methods for systems containing surfactants, among which the spinning drop technique can be used to measure extremely low values (0.0001 mN/m) [2]. Yet, this method cannot be used at high pressure and its maximum temperature tolerance is 100 °C. On the contrary, the pendant drop technique is the most suitable IFT measurement tool for high-pressure/high-temperature conditions [3–6]; although it may not be the best for ultra-low IFT systems. Likewise, several methods are available to characterize the relative wetting preference of a reservoir rock using core flooding or centrifugation such as Amott and USBM (U.S. Bureau of Mines) Tests [7,8]. However, these methods are extremely time consuming especially for shale samples and are not sensitive enough at neutral wettability [7]. Pendant/sessile drop technique, on the other hand, can be utilized to measure dynamic IFT and CA at reservoir conditions with a greater accuracy [9]. The results can be used in capillary pressure calculations and pore-scale modeling.

Despite numerous studies on the impact of surfactants on the surface properties of conventional rocks (i.e., carbonates and sandstones) [10–11], limited studies are available on shale oil rocks especially at reservoir conditions. The majority of existing literature on shale rocks involves spontaneous imbibition tests in the presence of surfactants as a function of several parameters such as pH, salinity, and divalent cations [12–17]. Borysenko and coworkers [18] performed spontaneous and forced imbibition experiments on crushed shale packs, sessile drop tests, and dielectric and NMR spectroscopy to characterize the wetting tendency on three different shale rocks at ambient conditions. They found that different shales have different wetting states depending on their petrophysical properties. For instance, illitic and smectitic shales are more hydrophilic and have higher surface activity whereas kaolinitic shales are preferentially oil–water. Wang and co-workers [14] examined the wettability alteration of Bakken shale in the presence of several surfactants using a modified Amott-Harvey method. Surfactants could alter the wettability of shale cores from originally oil–water or intermediate–water to water–water. In another study, the same group suggested that surfactant concentration, brine salinity, and divalent ion concentration are the major factors affecting oil recovery from shales [12]. Takahashi and Kovscek [19] examined the wettability of low-permeability siliceous shale at different pH values by using zeta potential measurements. They found that shale was more water–water at very high or very low pH and interpreted the results based on surface force calculations. The adsorption tendency of surfactants on shale rocks can adversely affect their efficiency due to chemical losses. This phenomenon may be more significant on shale surfaces considering the higher surface area available for adsorption in these rocks. Zelenev and Champagne [20] measured the adsorption of micromulsions on shale fines through surface tension measurements before and after equilibrium. Muherei and coworkers [21] also examined the adsorption of two surfactants and their mixtures on sandstones and shales using the same method. They concluded that nonionic surfactants tend to adsorb more on shales than on sandstones, possibly due to hydrophobic bonding.

The limited data on shale wettability currently available in the literature were mainly obtained at ambient conditions and thus may not be representative of fluid–fluid and fluid–rock interactions at actual reservoir conditions. The objective of this study is to establish a new framework to investigate the effect of anionic and nonionic surfactants on dynamic interfacial tensions and contact angles of surfactant-in-brine/oil/shale systems at reservoir conditions (3000–7000 psi, 80–116 °C). In other words, the intention was not to focus on identifying the best surfactants from recovery standpoint for shale systems. Instead, we present, for the first time, a detailed methodology for measuring the interfacial properties of these systems, including shale substrate preparation, thin needle utilization, fluid pre-equilibration, in-line density measurements, all of which are critically important due to surfactant partitioning in brine and oil phases. The experimental framework was first validated with simple ultra-low IFT systems using the rising/captive bubble technique, then successfully applied to two shale systems (A and B) at ambient and reservoir conditions. The effect of pressure, temperature, surfactant concentration, and brine chemistry on IFT and CA were investigated in a systematic manner. For both shale systems, the work of adhesion was determined at various experimental conditions and its significance on improved oil recovery was discussed.

2. Materials and methods

2.1. Shales

Two subsurface shale samples from different depths were utilized as substrates: Shale A (non preserved) and Shale B (preserved). Micrographs of the two shale samples were acquired using high-resolution scanning electron microscopy (SEM) in back-scattered electron (BSE) mode, as shown in Fig. 1a and b. The elemental maps of these rocks were also obtained by energy dispersive spectroscopy (EDS) and are presented in Fig. 1c and d. The pore size distribution of these shales is between 10 and 400 nm [22]. The porosity and organic content are also provided in Table 1. Although both shales have similar porosities, their mineralogy is very different. Shale A is a clay-rich rock with pores mainly associated with the organic matter. In contrast, Shale B is a dolomitic siltsstone containing insignificant amounts of organic matter. The zeta potentials of Shale A and B in distilled water were measured with a Zeta Potential Analyzer (Brookhaven Instruments Corporation) and the values are –25.2 and –26.4 mV, respectively.

2.2. Crude oils

Gibbs crude oil from Wyoming (Crude oil A) and reservoir oil from Shale B reservoir (Crude oil B) were employed in this study. The properties of these crude oils are presented in Table 2. Both crude oils were first centrifuged at 6000 rpm for one hour and then filtered with 0.8 and 0.5 μm filters before use. For IFT and CA validations, n-tetradecane (98%, Fisher Scientific) was used as a substitute for oil.

2.3. Brines

Synthetic brine, tap water, and reservoir brine (from Shale B reservoir) were used as aqueous phases. The synthetic brine solutions were prepared with distilled-deionized water (resistivity of 2.75 × 10^6 Ω m) and various NaCl (ACS grade, Fisher Scientific) concentrations. The dominant cations and anions in the reservoir brine were Na⁺, Ca²⁺, Mg²⁺, and Cl⁻, as presented in Table 3. The
pH and resistivity of brine solutions were measured with a pH meter (Phtestr 30, EUTECH). The reservoir brine had total dissolved solids (TDS) of 237,755 ppm, a pH of 4.27, and a resistivity of 0.05 $\Omega$ m at 25 °C. This brine was filtered using a 0.1 μm syringe filter before any measurement. Tap water was used as a model fracturing fluid for Shale B reservoir with a neutral pH and a TDS of 120 ppm, as shown in Table 3.

### Table 1
Physical characteristics of the shale samples.

<table>
<thead>
<tr>
<th>Shale</th>
<th>Porosity, %</th>
<th>Organic content, vol%</th>
<th>Mineralogy (in order of abundance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shale A</td>
<td>1.3</td>
<td>8.3</td>
<td>Illite/smectite clays, feldspar, calcite, quartz, pyrite framboïds, and organic matter</td>
</tr>
<tr>
<td>Shale B</td>
<td>1.5</td>
<td>&lt;1</td>
<td>Dolomite, calcite, quartz, and illite clays</td>
</tr>
</tbody>
</table>

### Table 2
Properties of the crude oils. TAN: Total Acid Number, TBN: Total Base Number.

<table>
<thead>
<tr>
<th></th>
<th>Density, g/cc 20 °C</th>
<th>Viscosity, cp</th>
<th>Asphaltene content, wt%</th>
<th>TAN, mg of KOH/g</th>
<th>TBN, mg of KOH/g</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil A</td>
<td>0.9</td>
<td>11.833</td>
<td>10.23</td>
<td>0.146 $^*$</td>
<td>2.466 $^*$</td>
<td>1.483</td>
</tr>
<tr>
<td>Crude oil B</td>
<td>0.81</td>
<td>2.804</td>
<td>0.45</td>
<td>0.23</td>
<td>0.68</td>
<td>1.46</td>
</tr>
</tbody>
</table>

* Reported from Ref. [50].

### Table 3
Concentrations of dominant ions in tap water and reservoir brine.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Tap water, ppm</th>
<th>Reservoir brine, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>8</td>
<td>78,950</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>47</td>
<td>15,320</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>14</td>
<td>1160</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>7</td>
<td>141,510</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>18</td>
<td>400</td>
</tr>
<tr>
<td>NO$_3$</td>
<td>10</td>
<td>–</td>
</tr>
</tbody>
</table>

#### 2.4. Surfactants

Surfactants include a liquid anionic surfactant (ammonium alkyl ether sulfate) from Stepan Chemical Company and a nonionic surfactant from ChemEOR Company. Phase behavior tests were performed with these surfactants at a brine/oil ratio of one and in the presence of crushed shale particles. Both surfactants were soluble in brine with insignificant turbidity and no visible microemulsion phase between oil and brine within the concentration range used in this study. Sodium dodecane sulfate (SDAS) (99%, Fluka), diethylene glycol monohexyl ether (C$_6$E$_2$) (98%, Aldrich), and dioctyl sodium sulfosuccinates (AOT) (98%, Aldrich) were also used for IFT and CA validations. The adsorption of surfactants on shales was measured using a double-beam ultraviolet-visible (UV–Vis) spectrophotometer (Cary 4000, Varian, Inc.). The mixing of surfactant solutions and shale fines was performed with an incubating mini shaker (VWR International LLC). Based on the HRTEM (High Resolution Transmission Electron Microscopy) images shown in...
The average size of surfactant micelles was about 100 nm. This is within the pore size distribution of shales (see Section 2.1), therefore surfactant micelles can imbibe into micro pores, micro fractures, and the majority of nano pores.

2.5. Experimental setup and procedure

Dynamic interfacial tensions and contact angles of surfactant-in-brine/oil/shale systems were measured by rising/captive bubble tensiometry enhanced by video-image digitization technique. This system is capable of measuring dynamic IFT as well as advancing and receding CA at reservoir conditions (up to 15,000 psi and 200 °C). The experimental setup shown in Fig. 3 includes a Hastelloy measurement cell, a high-resolution camera, a Yamato oven, a Hastelloy equilibrium cell, a dual-cylinder 5000-series Hastelloy Quizix pump to supply stable flow rates and pressures during the measurements, and an in-line density meter (Anton Paar DMA HPM). The IFT analysis is very sensitive to input parameters such as the density difference between fluid phases. This difference must be measured very accurately to reduce the error in IFT analysis especially for ultra-low values; however, it has been very common in the literature to calculate density values numerically [23,24]. In this work, we measured the density of fluids using an in-line density meter at actual experimental conditions in order to obtain more accurate IFT data.

For CA measurements, the shale samples were cut with a precision saw and then polished using a polishing apparatus at 100 rpm for 40 min. Silicon carbide powder (18 mm) and diamond suspension (3 mm) were used during the polishing process in order to generate a smooth shale surface and to remove irregular and uneven areas created during the cutting process. The shale substrate was first mounted on the rock sample holder (Fig. 3v) inside the measurement cell and the cell was subsequently filled with the desired brine solution. After adjusting pressure and temperature to the experimental conditions, the system was left for at least six (6) hours so that the shale surface and brine solution reached equilibrium. Pre-equilibrium of fluids prior to measurement is a critical factor affecting IFT and CA measurements, particularly in systems containing surfactants. Crude oil, pre-equilibrated with brine for several hours (overnight) inside the equilibration cell (Fig. 3d) at the experimental conditions, was then injected into the measurement cell through a needle (0.3–2.1 mm outside diameter) with a very small flow rate (0.001 ml/min) and an overall time of six (6) hours for each measurement. Images of oil bubbles were captured at 5 s intervals while the bubble was slowly growing or shrinking.

Fig. 2. TEM micrographs in BF mode (200 kV voltage, and pixel resolution of 0.24 nm) for micelles of (a) Surfactant A, and (b) Surfactant B.

Fig. 3. Schematic of the experimental setup: (a) nitrogen cylinder, (b) mechanical convection oven, (c) dual-cylinder Quizix pump, (d) equilibration cell, (e) density meter, (f) measurement cell, (g) heating jackets, (h) RTD, (i) light source, (j) apochromatically corrected lenses and CCD camera, (k) adjustable stand, (l) anti-vibration table, (m) Rosemount pressure sensor, (n) current source, (o) temperature control system, (p) data acquisition computer, (q) shelf cart, (r) IFT/CA needle, (s) fluid bubble, (t) solid substrate, (u) movable tray, (v) crystal holder, (w) fluid level observation opening, (x) horizontal drive shaft, and (y) vertical drive shaft.
3. Validation of interfacial tension and contact angle measurement method

3.1. Interfacial tension

In order to validate the pendant drop/rising bubble technique for low interfacial tension systems, two IFT measurements were performed using ultra-thin needles (e.g., 0.3 mm outside diameter) to reach Bond numbers close to unity. In these tests, surfactants, brine, and oil were mixed in a container and left to equilibrate for several days. Each liquid phase was then retrieved from the container for IFT measurements. The results were compared with literature values measured by both spinning drop and pendant drop techniques [25]. The first measurement was conducted on water/n-tetradecane/C6E2 as shown in Table 4. In this table, γ_{oil} is the IFT of liquid α (oil-rich phase) in liquid β (surfactant-rich phase) and γ_{water} is the IFT of liquid α (oil-rich phase) in liquid ω (water-rich phase) at 25°C and atmospheric pressure. For the second measurement, water/AOT/NaCl/heptane were used with the same preparation and measurement procedure as mentioned earlier. The results are given in Table 5 where γ_{water} is the IFT of liquid α (oil-rich phase) in liquid ω (water-rich phase). A comparison between our results and the literature data demonstrates that the pendant drop technique is quite reliable for ultra-low IFT measurements.

3.2. Contact angle

Although this technique was previously validated for contact angle measurements using Decane/Air/Teflon system [26], we further tested its accuracy and reproducibility with ultra-low IFT systems such as water/n-tetradecane/SDAS at ambient conditions. First, a drop of water containing SDS was placed on top of a Teflon-coated solid surface, which was immersed in tetradecane (sessile drop method). Then CA measurement was performed using the same procedure as in Ref. 26. Table 6 indicates that our results are in good agreement with the literature data [27].

4. Original shale wettability

Three relatively quick tests were performed to examine the original wettability of Shale A and Shale B surfaces. The wettability of the shale samples was first examined by placing one drop of both crude oil and distilled water on dry shale surfaces without any prior chemical treatment (Fig. 4a and b). The oil drop immediately imbibed into both samples while the water drop remained on the surface with a small constant angle. Note that this behavior may not necessarily represent the wetting state of the shale rocks since the surface tension of oil-air is much smaller than that of water-air system. Thus, the threshold capillary pressures of these two fluid systems are not comparable. The SEM micrographs in Fig. 1 indicate that there are pores in these shales associated with the organic matter. These pores are presumably strongly oil–wet and can spontaneously imbibe crude oil from the shale surface. However, Dehghanpour and coworkers [16] classified their organic shale samples as water–wet, based on imbibition tests. The authors stipulated that both water adsorption and capillary forces should be involved in the determination of shale wettability. Accordingly, contact angle measurements in the presence of both oil and brine phases might offer a better characterization of shale wettability at given P and T conditions.

The second method used to estimate the degree of wetting of shales was a flotation test recommended by API for strongly wetted systems [2]. In this test, distilled water, crude oil, and crushed shale were mixed in a glass bottle and hand-shaken. While, grains of Shale B were settled at the bottom of the bottle, some of them were suspended at the oil–water interface. As depicted in Fig. 4c for Shale A, some shale grains clustered together at the bottom of the bottle forming small oil globules while some of them were suspended at the oil–water interface. While, grains of Shale B were settled at the bottom of the bottle (cf. Fig. 4d). These two configurations are representative rocks with weakly and strongly water–wet behaviors, respectively.

In the third method, the dynamic contact angles of crude oils A and B on polished samples of shales A and B were measured in the presence of distilled water at ambient conditions and are illustrated in Fig. 4e and f. The measured angles were 14.92 ± 1.03° and 14.45 ± 1.46° respectively, which imply strongly water–wet surfaces. These macroscopic angles represent an average wetting behavior of the entire rock surface since shale rocks consist of various minerals and organic matter. Similar contact angle values were obtained when the shale substrates were immersed in crude oil overnight prior to the measurements.

Lastly, the impact of initial exposure of shale samples to crude oil/brine on dynamic contact angle was studied. A shale substrate was equilibrated with reservoir brine for about 12 h,
while the second substrate was initially immersed in the crude oil overnight. Bulk crude oil was gently removed from the surface of the second substrate before immersion in reservoir brine solution. The measured dynamic contact angles of reservoir oil and reservoir brine on shale surfaces (captive bubble configuration) were $17.73 \pm 2.98^\circ$ and $24.67 \pm 0.65^\circ$, on the first and second substrates, respectively. The slight difference between these two values (i.e., $7^\circ$) suggests insensitivity of wettability of the shale substrates to initial exposure of substrates to test fluids.

The representative elementary area (REA) of shale rocks was previously characterized to be less than $300 \times 300 \mu m^2$ [22]. REA is defined as the minimum average area above which the macroscopic characteristics of the porous media remain constant. Here, the area of oil bubbles created on the shale surfaces in all sets of measurements was more than the REA mentioned earlier as the minimum diameter of our needles was 0.3 mm. Therefore, one may consider the measured contact angle values representative of the system at the macro scale.

5. Results and discussion

Two different shale systems were investigated: System A (shale A, crude oil A, anionic surfactant, and synthetic brine with various NaCl concentrations) at ambient and high P–T (3000 psi and 80 °C) and System B (shale B, crude oil B, nonionic surfactant, reservoir brine and tap water) at reservoir conditions (6840 psi and 116 °C). Prior to IFT/CA measurements, the CMC and adsorption propensity of surfactants on shale was measured for Systems A and B using various brines.

5.1. CMC measurements

UV–Vis spectroscopy and pendant drop tests were employed to estimate the CMC of surfactants in Systems A and B. In the UV–Vis spectroscopy method, we measured the light absorbance of brine solutions with various surfactant concentrations at wavelengths of 500 nm (reservoir brine) and 637 nm (5 M synthetic brine). The CMC manifested as a sudden change in the slope of the light absorbance versus concentration line. Such a break occurred between 0.02 and 0.03 wt% for Surfactant A (cf. Fig. 5a) and between 0.005 and 0.01 wt% for Surfactant B (cf. Fig. 5c). In order to verify these values, the interfacial/surface tensions of Systems A and B were measured at different surfactant concentrations using the rising/captive bubble method. A sharp initial decrease in interfacial/surface tension with increasing surfactant concentration was seen up to the CMC for both systems. According to a previous study, surfactants lay flat at the interface when their concentration is much lower than the CMC [28]. However as their concentration increases, they start forming a monolayer at the interface, which leads to an increase in the interfacial pressure and a reduction in both interfacial energy and interfacial tension. Fig. 5b and d reveal that the CMC was reached at 0.03 wt% for System A and 0.01 wt% for System B, in good agreement with the UV–vis measurements. Fig. 5b also indicates a shift in CMC from 0.03 to 0.05 wt% by diluting brine solution from 5 to 0.1 M, which is in accord with previous studies [29,30]. This behavior is known as salting out process which reduces the required surfactant concentration to form micelles [31].

5.2. Surfactant adsorption

Using UV–Vis spectroscopy, the adsorption of anionic and non-ionic surfactants on shale fines were measured at ambient conditions by recording the light absorbance for each solution at wavelengths of 276, 500, and 637 nm (depending on the brine concentration) as a function of surfactant concentration before and after equilibrium with shale fines. First, 2 g of shale fines (75 μm < diameter < 150 μm) were equilibrated with 15 g of surfactant solution by constant shaking (300 strokes/minute) overnight. The absorbance of
surfactant solutions equilibrated with shale fines was analyzed and compared to the calibration curve (i.e., surfactant absorbance curve without shale). The amount of surfactant adsorbed per gram of shale was then calculated at different surfactant concentrations and a Langmuir isotherm [31] was used to model the adsorption data. Fig. 6 shows that the maximum adsorption amounts \( C_{\text{max}} \) were about 12 and 3 mg/g for System A (5 M synthetic brine) and System B, respectively. Note that using tap water instead of reservoir brine did not affect the surfactant adsorption in System B. In this system, \( C_{\text{max}} \) was reached after the CMC. The interaction forces between the nonionic surfactant and Shale B are expected to be small. The mechanism of interaction in this case is either through hydrogen bonding, polarization of \( p \) electrons, van der Waals dispersion forces or alternating hydrophobic bonding [32]. Unlike the nonionic surfactant, the adsorption of the anionic surfactant on Shale A is higher and does not reach a plateau even at 0.1 wt%, suggesting multilayer adsorption. This is in agreement with a previous study by Grigg and Bai [33] who found that the adsorption density of an anionic surfactant on negatively charged sandstone increased by increasing NaCl concentration in brine and in the presence of divalent cations.

5.3. Effect of temperature and pressure

5.3.1. Interfacial tension

A series of IFT experiments were performed with System A (5 M synthetic brine) at both ambient (25 °C, 1 atm) and high P–T (80 °C, 3000 psi). Fig. 7a shows that the IFT decreased by increasing temperature and pressure, while the CMC remained unchanged. This decrease in IFT is mostly affected by the increase in temperature [34]. Sharma et al. [35] stated that as temperature rises, the kinetic energy of molecules increases and consequently the attractive forces between them drops leading to a reduction in IFT.

Fig. 5. CMC of anionic surfactant in synthetic brine using (a) UV–Vis spectrometry and (b) pendant drop, and CMC of nonionic surfactant in reservoir brine using (c) UV–Vis spectrometry and (d) pendant drop.

Fig. 6. Adsorption of surfactants on shale fines for Systems A and B. The lines represent the fit with Langmuir isotherm.
between surfactant solution and oil. This is also consistent with results reported by other researchers [2,4,36].

5.3.2. Contact angle

The shale wettability was also examined with System A (5 M synthetic brine) through contact angle measurements at ambient and high P–T conditions. Fig. 7b shows that an increase in temperature and pressure leads to relatively less water–wet conditions on the shale surface, as CA increased. This trend is probably due to a greater adsorption of the anionic surfactant at high P–T in the presence of electrolytes, making the surface less hydrophilic.

5.4. Effect of surfactant concentration

5.4.1. Interfacial tension

The effect of surfactant concentration (up to 0.1 wt%) on IFT was measured for both Systems A and B. For System A (5 M synthetic brine) at high P–T (80 °C and 3000 psi), a sharp decline in IFT with surfactant concentration was observed up to the CMC, as discussed in Section 5.1 and Fig. 5b. However for System B at reservoir conditions (116 °C and 6840 psi), the decline in IFT was not pronounced, as seen in Fig. 8a. An important point here is that using tap water instead of reservoir brine has decreased the IFT by almost 50%, while it has not changed the CMC. This indicates that utilizing municipal water, for example, in fracturing fluids may improve the flow-back of oil after well stimulation by reducing the resistance to flow and mobilizing more oil. Additional tests (e.g., imbibition) are required to assess the performance of these systems as there might be no direct correlation between IFT and oil recovery [37].

5.4.2. Contact angle

The impact of surfactant concentration (up to 0.1 wt%) on the wettability of Shales A and B was also assessed through dynamic contact angle measurements. Fig. 8b displays the dynamic CA of System A (5 M synthetic brine) at high P–T (80 °C and 3000 psi). The contact angle in this case increased from ~47° (without surfactant) to ~70° at high surfactant concentration. The most significant wettability alteration (to less water–wet) occurred at concentrations above the CMC, possibly due to the increased surfactant adsorption on shale. Based on a previous study by Chaudhuri and Paria [38], it is likely that surfactant molecules primarily adsorb via their tails onto the negatively charged shale surface at low salinity due to Van der Walls attraction between the surfactant tail groups and the negatively charged surface (cf. Fig. 9a). At high salinity, the interaction between cations in brine and the surfactant head groups lowers their electrostatic repulsion. Hence, it is possible that another layer of surfactants adsorbs on the surface with their tails facing outward, which makes the surface more hydrophobic (cf. Fig. 9b). This is in agreement with the adsorption results in Section 5.2.

For System B at reservoir conditions (116 °C and 6840 psi), there is no significant change in shale wettability using the nonionic surfactant, as shown in Fig. 8b. In other words, the shale surface remains strongly water–wet regardless of surfactant concentration. Moreover, CA data with reservoir brine and tap water are analogous, within the experimental errors. This is in agreement with the negligible surfactant adsorption on shale measured by UV–Vis spectroscopy (cf. Fig. 6). Therefore, we expect low surfactant losses due to adsorption on shale during hydraulic fracturing with this surfactant. There are a number of experimental studies that report a reduction in contact angle when using nonionic surfactants with negatively charged surfaces such as quartz and shale [20,39,40]. The reduction in CA was attributed to (i) stronger interactions between water molecules and quartz than those between surfactant molecules and quartz, and (ii) adsorption of surfactant molecules with their hydrophobic tails facing the shale surface. The different trend observed in our study might be due to a lower surfactant adsorption (~3 mg/g compared to 10 mg/g in [20]), which is three to four times smaller than the adsorption of nonionic surfactant in these studies. A study on the wettability of Bakken shale using both anionic and nonionic surfactant solutions found that the wettability of the upper Bakken shifted from oil–wet to neutral–wet and the wettability of the middle Bakken changed from weakly oil–wet to neutral–wet [14]. The discrepancy between these studies and our work might be due to differences in the mineralogy, pore types, composition of crude oil, surfactant structure, and measurement techniques.

It could be argued that the decline in IFT of System B for instance from 27 to 15 mN/m is expected to alter the contact angle. To answer this question, we refer to Young’s equation (cf. Fig. 10), in which the forces along the triple contact line are in thermodynamic equilibrium and are balanced according to:

$$\gamma_{w} = \gamma_{ow} \cos \theta_{w} + \gamma_{os}$$

This study shows that the nonionic surfactant reduced oil–brine IFT, while contact angle was not notably altered. Since the surfactant was more soluble in brine than in oil, \(\gamma_{w}\) was likely to decrease while \(\gamma_{os}\) remained unchanged to satisfy the force balance at the triple contact point. Therefore, the two sides of Eq. (2) can be adjusted without changing the contact angle.

5.4.3. Contact angle hysteresis

During the dynamic contact angle measurements, the angle obtained when oil displaced brine on shale was smaller than the one observed when brine displaced oil (cf. Fig. 11a). The difference between the two angles is called contact angle hysteresis and is mainly due to surface roughness, wettability alteration, and
heterogeneity of solid surface [9]. Contact angle hysteresis directly impacts pore-level displacement mechanisms and the resulting macroscopic multiphase flow functions.

The addition of surfactant into the system significantly reduced the contact angle hysteresis from 10.06° (cf. Fig. 11a) to 0.42° (cf. Fig. 11b). A lower contact angle hysteresis implies that the energy required to overcome the local resistance to flow is lower and therefore, an oil drop shrinks with essentially the same contact angle as it swells. This can have important implications for oil trapping in porous media and therefore for improved oil recovery.

5.5. Effect of brine chemistry

5.5.1. Interfacial tension

In order to investigate the impact of brine chemistry on IFT of Systems A and B, NaCl concentration in synthetic brines were varied from 0.1 to 5 M in System A, while for System B, the pH and salinity of tap water were adjusted using HCl, KOH, NaCl, and CaCl₂. The surfactant concentration in brine was 0.1 wt% in both systems.

Fig. 12a reveals that the addition of salt to System A reduced the IFT between oil and brine. Similar behavior has been previously reported by other investigators [41–43] and attributed to a change in surfactant distribution at the oil/brine interface. Increasing salt concentration makes the anionic surfactant less ionized and consequently less soluble in water, promoting more adsorption of surfactant at the oil–brine interface [44].

For System B, we found that the IFT of crude oil and tap water (104 ppm TDS, pH 8) is lower than that of crude oil and reservoir brine (237,340 ppm TDS, pH 4) (cf. Fig. 12a). This decline in IFT could be explained by either the lower salinity or higher pH of tap water. In order to identify the dominant parameter in IFT reduction, the IFT between crude oil and tap water was measured while independently varying its pH and salinity at ambient conditions (cf. Fig. 13). The results illustrated in Fig. 13a and b show that both salt addition and pH increase reduce the IFT, in agreement with previous studies [44–46]. Thus, the lower IFT of tap water compared to reservoir brine in Fig. 12a is likely due to the higher pH of tap water rather than its lower salinity.

5.5.2. Contact angle

A series of dynamic contact angle measurements were performed using the same systems as in Section 5.5.1. Fig. 12b shows that CA in System A increased from 27.04° at 0.1 M to 69.94° at 5 M, leading to a less water–wet shale surface. This trend could be correlated to the adsorption propensity of surfactant on shale, in accord with Sections 5.2 and 5.4.2 and other studies [33,47]. Blunt [48] stated that for weakly water–wet systems with a contact angle lower than 90°, pore-body filling is the dominant displacement mechanism and the residual oil saturation decreases with increase in contact angle. Therefore, an increase in salinity can potentially improve oil recovery from System A. The contact angles of System B did not change using either tap water or reservoir brine (cf. Fig. 12b). This result is consistent with the low adsorption tendency of nonionic surfactant observed in System B (Section 5.2) and suggests that the wettability of Shale B would not be affected using tap water as injection fluid.

5.6. Work of adhesion

A better analysis of the experimental data can be achieved by combining the IFT and CA results through the work of adhesion.

\[ W_a = \gamma_{sv} + \gamma_{sw} - \gamma_{wl} \]

The Young-Dupré equation (cf. Eq. (3)) relates the work of adhesion \( W_a \) to the surface tension between the fluids (\( \gamma \)) and contact angle at the solid surface (\( \theta \)) [49].
This equation presents the work required to separate a drop of liquid from a solid surface in the presence of another fluid. The calculated values of $W_a$ in Systems A and B are listed in Table 7 for different surfactant and salt concentrations. In System A, the lowest work of adhesion was achieved upon the addition of anionic surfactant (above CMC) in high salinity brine (5 M), which resulted in low IFT and high CA. Whereas in System B, the lowest $W_a$ was achieved upon the addition of nonionic surfactant (above CMC) in tap water, which resulted in a further IFT reduction.
6. Conclusions

A new framework was proposed to investigate the effect of pressure, temperature, surfactant concentration, and brine chemistry on fundamental parameters governing fluid displacement (i.e., interfacial tension and contact angle) in brine/oil/shale systems at reservoir conditions. The rising/captive bubble technique was first validated with simple surfactant systems by using very thin needles (i.e., 0.3 mm outside diameter) to reach Bond numbers close to unity. The ultra-low interfacial tensions obtained by this method were comparable to those generated using the Spinning Drop technique. The method was further applied to two shale systems (A and B) and IFT values as low as 0.3 mN/m were measured at reservoir conditions. The main conclusions drawn from this study are summarized below:

1. Brine chemistry did not have any significant effect on the CMC of the nonionic surfactant used in this study. However, increasing brine salinity from 0.1 to 5 M decreased the CMC of anionic surfactant from 0.05 to 0.03 wt% due to salting out effect.
2. The interfacial tension between oil and brine in System A reduced considerably (i.e., 23–0.3 mN/m) by introduction of 0.03 wt% of anionic surfactant. On the other hand, the IFT values for System B reduced only modestly (i.e., 27–15 mN/m) when a nonionic surfactant was used at reservoir conditions.
3. The contact angle on Shale A samples increased by increasing brine salinity and surfactant concentration particularly at high P–T as a result of high surfactant adsorption.
4. The nonionic surfactant showed a low propensity to adsorb on shale B samples. As a result, the shale surfaces remained strongly water–wet with the nonionic surfactant regardless of surfactant concentration and brine chemistry.
5. The lowest work of adhesion was achieved right above the CMC indicating that higher surfactant concentrations may not be required.
6. The use of tap water instead of reservoir brine reduced IFT and work of adhesion considerably.

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