Article

Locally Synthesized Zwitterionic Surfactants as EOR Chemicals in Sandstone and Carbonate

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ABSTRACT: Zwitterionic surfactants are found to be highly effective in reducing the IFT and changing the wettability. This work studied the solubility and wettability alteration performance of locally synthesized zwitterionic surfactants in Berea sandstone and Indiana limestone. Contact angle measurements were conducted to study the wettability under different conditions. SEM images and TGA results were combined to reflect on the wettability alteration mechanism. The zeta potential test was adopted to study the surface charge of the Indian limestone powder. Results showed that five of the six surfactants dissolved in deionized water to form 1.0 wt % solution, indicating efficient solubility for EOR purposes. Although its wettability alteration performance on oil-aged Berea sandstone is weak to moderate, the performance of ZW6 on Indiana limestone is excellent. ZW6 can change the strongly oil-wet (162°) rock back to water-wet (62.9°) conditions. Increasing its concentration from 0.01 to 0.5 wt % continuously enhanced the performance. The addition of NaCl to 150000 ppm did not affect the wettability alteration. However, the addition of $CaCl_2$ largely suppressed the wettability alteration, while Na_2SO_4 and $MgCl_2$ both enhanced the performance. With the same headgroup, a more hydrophobic tail group impairs the wettability alteration. The quite different wettability alteration performance of $MgCl_2$ and $CaCl_2$ cases (which had approximately the same amount of calcite dissolution), and the comparable wettability alteration performance of Na_2SO_4 and $MgCl_2$ (which had very different calcite dissolution amounts) indicate that calcite dissolution is unrelated to wettability alteration.
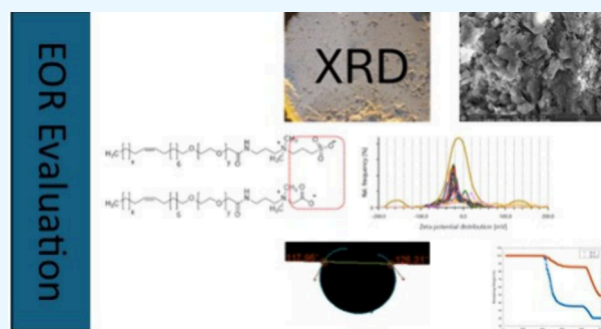
1. INTRODUCTION

In the oil and gas industry, surfactant flooding has been applied in many mature reservoirs for enhanced oil recovery (EOR) purposes.[1−3] New surfactants are developed every day to achieve specific targets including ultralow interfacial tension (IFT),[4,5] microemulsion generation,[6−8] wettability alteration,[9−11] enhanced stability in harsh conditions,[12,13] lower cost,[14,15] etc. Different from other types of surfactants, zwitterionic surfactants have both postively and negatively charged functional groups in the headgroup. A few examples of zwitterionic surfactants are listed in Figure 1. Zwitterionic surfactants are found to have better stability in high-temperature[16] and high-salinity[17,18] conditions. They are very effective in reducing IFT[4,19,20] and changing wettability.[20,21] Popularly adopted zwitterionic surfactants in EOR projects include dimethyl amine oxide (DAO) surfactants,[22,23] cocoamidopropyl betaine (CAPB),[24,25] cocoamidopropyl hydroxysultaine (CAHS),[26,27] lauryl betaine,[28,29] etc. The outstanding properties of zwitterionic surfactants make them promising materials for EOR, while the high cost[21] limits their application.

3-(N-stearamidopropyl-N, N-dimethyl ammonium) propanesulfonate

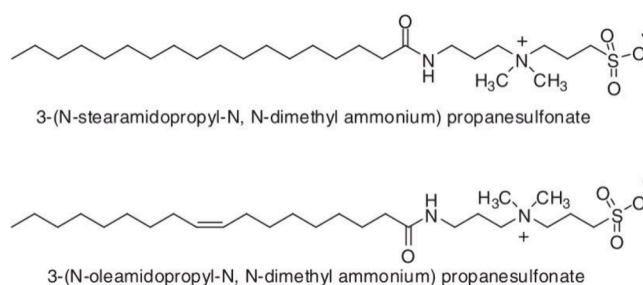3-(N-oleamidopropyl-N, N-dimethyl ammonium) propanesulfonate

Figure 1. Two examples of zwitterionic surfactants. (Adapted with permission from ref 30. Copyright 2018 John Wiley and Sons.)

To evaluate the performance of surfactants in the oil/water/ rock system for EOR purposes, properties including surface

Table 1. Information on the Six Locally Synthesized Zwitterionic Surfactants

Abbreviation	Structure
ZW1	
ZW2	
ZW3	
ZW4	
ZW5	
ZW6	

tension, IFT, viscosity, thermal stability, salinity tolerance, and wettability are usually examined.[31−33] Surface tension measurement is usually applied as an efficient method to decide the critical micellization concentration (CMC) of surfactant.[34,35] IFT measurement obtains the reduction of IFT in the oil/water system. It is usually conducted by either the spinning drop method[36] or the pendant drop method.[37] The spinning drop method applies to relatively lower IFT, while the pendant drop method applies better to relatively high IFT.[38] Thermal stability and salinity tolerance of the surfactant solutions are usually conducted by monitoring the transparency of the liquid and the aggregation or precipitation in the liquid while the liquid is prepared and set at specific salinity and temperature conditions.[39] Wettability measurements vary depending on factors, including the dimensions of the samples, the impact of the measurement on the experiment, etc. For samples in powder form, the flotation test can be used.[40] For surface wettability study, contact angle measurements on rock slices can be used.[41] For an overall wettability assessment of a core plug sample, methods such as the Amott-Harvey test,[42] NMR study,[43] and in situ contact angle by micro-CT,[44] can be used. Zeta potential measurement is used to study the surface charge change of powder samples during a specific treatment.[45] It is often adopted to help understand the wettability change.[46] Thermogravimetric analysis (TGA) monitors the mass loss during heating up.[47] High-performance liquid chromatography (HPLC) monitors the concentration change of a component in the solution.[48] Both methods can be used in studying the adsorption or desorption of materials on the rock surface.[49,50]

Previous studies of zwitterionic surfactants are more focused on the IFT reduction performance. For example, Jia et al. reported ultralow IFT value of 5.7×10^{-4} mN/m,[4] Zhang et al. obtained 4.6×10^{-3} mN/m by mixing erucic acid amido propyl-betaine (EDAB) with sodium dodecyl sulfate (SDS),[51] Kurnia et al. obtained 1×10^{-3} mN/m level IFT by combining zwitterionic surfactants cocamidopropyl hydroxysultaine (CHS) and various anionic surfactants.[26] Recently, interest in their wettability alteration performance has grown rapidly. Chen et al. analyzed the X-ray computed tomography (CT) images and discussed the impact of the mixed-wet condition on oil saturation after flooding with zwitterionic surfactants.[52] Kumar and Mandal studied the wettability alteration by zwitterionic surfactants on quartz surfaces at various salinity conditions.[53]

Recently, several betaine-based zwitterionic surfactants were synthesized with different head groups, unsaturation, and hydrophilicity. They are reported to have outstanding stability and efficiency for carbonate EOR when mixed with seawater.[54] This work aims to reflect on the mechanism of the wettability change induced by these zwitterionic surfactants, discuss the impact of molecular structure on their wettability alteration performance, and evaluate the impact of influencing factors on their wettability alteration performance in both sandstone and carbonate.

2. MATERIALS

Six locally synthesized zwitterionic surfactants (information given in Table 1) were tested in this study. Their synthesis procedures are explained in a recent work.[55] These six surfactants can be divided into two groups based on the negatively charged headgroup: sulfonates (ZW1−3) and carboxylates (ZW4−6). ZW2 and ZW4 have a number of -EO- groups in the tail while lacking the double bond when compared to ZW1 and ZW4. ZW3 and ZW6 have both the -EO- groups and a double bond. A double bond in the tail
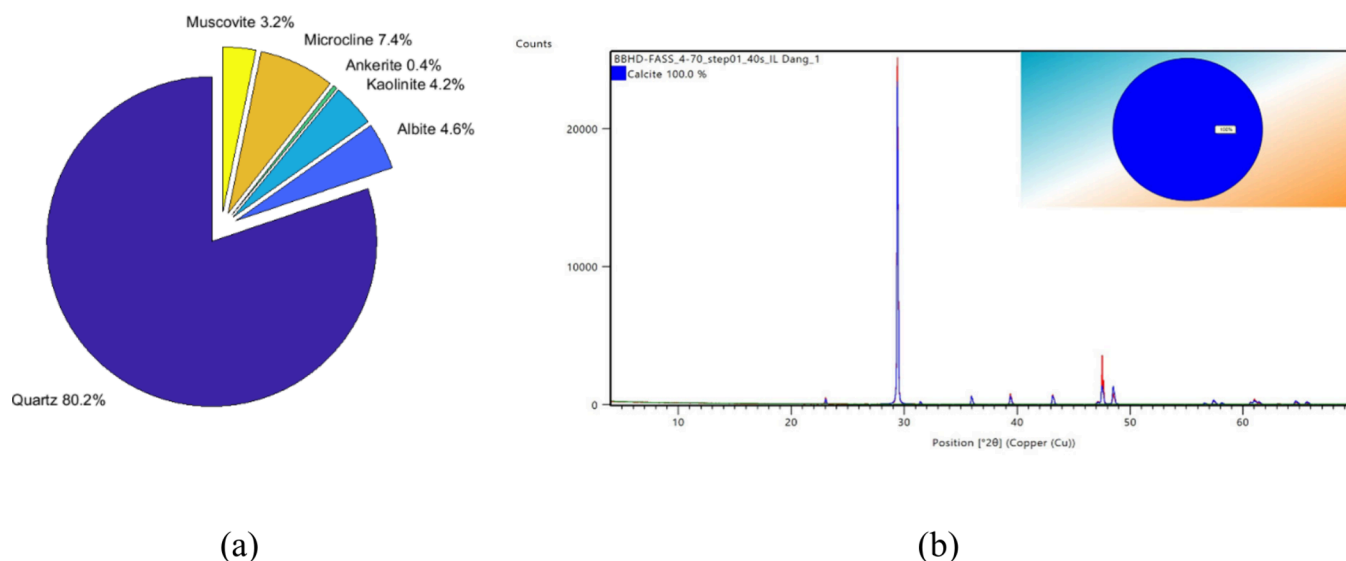
Figure 2. XRD results: mineral composition of (a) Berea sandstone; (b) Indiana limestone.

group adds slightly to the hydrophilicity of the surfactant molecules. The addition of -EO- groups, however, adds a lot to the hydrophilicity. ZW2 and ZW5 are more hydrophilic than ZW1 and ZW4, respectively. ZW3 and ZW6 are more hydrophobic than ZW2 and ZW5, respectively.

Berea sandstone (BS) and Indiana limestone (IL) outcrops were used in this study to represent the sandstone and carbonate. As shown in Figure 2, Berea sandstone contains quartz at a dominant percentage, as well as clay minerals accounting for about 20%. Indiana limestone contains 100% calcite, with a trace amount of other minerals. Rock samples were cut into substrates (diameter 1 in., thickness 3−4 mm), and their surfaces were smoothed using sandpaper of particle size P500. Toluene and methanol were used to soak the rock substrates in the Soxhlet to remove organic and inorganic contaminations.

Salts, including NaCl (≥99%), MgCl$_2$ (98.0−101.0%), CaCl$_2$ (≥99%), and Na$_2$SO$_4$ (≥99%), were purchased from Sigma-Aldrich. They were dissolved in deionized water to form solutions of different concentrations. For MgCl$_2$, CaCl$_2$, and Na$_2$SO$_4$, the concentration of 50000 ppm was adopted to study the impact of different salts. For NaCl, a stepwise concentration sequence (0, 25000, 50000, 100000, 150000 ppm) was adopted to study the impact of salinity.

3. EXPERIMENTS

The following experiments were conducted at room conditions (21.5 °C and 1 atm) to reflect on the wettability alteration performance and the mechanisms of the studied zwitterionic surfactants: pH measurements, zeta potential measurements, contact angle measurements, and thermogravimetric analysis (TGA).

For pH measurements, a liquid sample of no less than 15 mL was prepared. A SevenExcellence pH meter manufactured by METTLER TOLEDO was used. For each liquid, the reported pH value is an average of three measurements.

Contact angle measurements were conducted using a Drop Shape Analyzer 25B manufactured by KRUSS. BS and IL substrates were oil-aged by soaking in crude oil at a lifted temperature of 70 °C (to accelerate the aging process[56]) in the oven for 20 days. After being oil-aged, the substrates were

treated with different surfactant solutions for 2 days. The contact angle values were obtained before and after the treatment to reflect on the wettability change due to the surfactant treatments.

BS and IL rock were ground into powders. Considering the difficulty in separating crude oil and oil-aged fine rock powders, a model oil consisting of *n*-decane and stearic acid was prepared to age the rock powders. Aged powders were treated with different surfactant solutions. In the vials, 3 g of powder (BS/IL), model oil, was added to have a total volume (solid + liquid) of 25 mL. They were conditioned at room temperature for 24 h and then put in the VWR shaking bath (18L). Shaken at a speed of 120 strokes per minute and 18 mm per stroke. After 24 h, they were centrifuged using a Z326 K Centrifuge manufactured by HERMLE, at a speed of 3000 rpm for 3 min. About 0.8 mL of liquid sample was taken from the top of each centrifuged mixture and was used to measure the zeta potential. For the rest of the solutions, rock powders were separated from the mixture by filtering and drying. After drying, samples were used for TGA studies by using the PerkinElmer Thermogravimetric Analyzer TGA8000, and underwent a heating process from 30 to 700 or 1000 °C at a rate of 10 °C/min.

To study the changes in the surface charge of rock powder, the particle size analyzer Litesizer 500 provided by Anton Paar was applied to measure the zeta potential. Each measurement had 100 processed runs at an adjusted voltage of 200 V. Measurement on the same sample was repeated three times to obtain an average zeta potential value.

4. RESULTS AND DISCUSSION

4.1. Zwitterionic Surfactants Solution Stability. Surfactants were dissolved in DI water to prepare solutions of 1.0 wt % concentration. Among all six surfactants, ZW1 did not fully dissolve to form a transparent solution, indicating a much weaker stability than the other five surfactants. ZW1 was not tested in the following experiments. The other five surfactants dissolved fully under room conditions.

4.2. The pH Values of the Zwitterionic Surfactant Solutions. The 0.5 wt % solutions of surfactants ZW2−6 were prepared by diluting the 1.0 wt % solutions. Their pH values

under room conditions were measured. After that, surfactant solutions were used to treat the oil-aged BS and IL substrates. After the substrates were soaked for 4 days, the pH values of the solutions were measured. Results are shown in Figure 3. The pH value for DI water under room conditions (20.8 °C, 1 atm) was around 5.4. All zwitterionic solutions are acidic at their initial status.
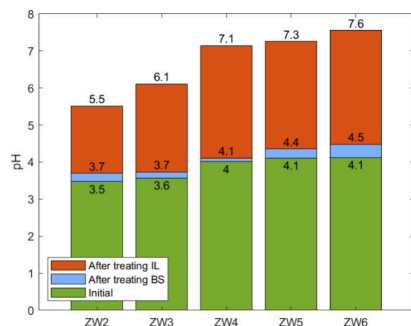

Figure 3. pH values of 0.5 wt % zwitterionic surfactant solutions before and after soaking oil-aged Berea sandstone and Indiana limestone substrates in room conditions for 4 days.

Soaking the BS substrates slightly increased the pH values. Soaking IL substrates had an apparent effect on the pH values of the solutions. All solutions had a pH value increase of 2−3.5. ZW2 and ZW3 were changed to preferentially acidic, while ZW4−6 became neutral. Calcite, the dominant mineral of Indiana limestone, dissolves in water and forms the bicarbonate ions, which consume the hydrogen ions in the water. BS, however, lacks a sufficient amount of minerals that can dissolve in water and induce significant changes in the pH.

The solutions of surfactants ZW2 were prepared. Their pH values in room conditions were measured. After that, they were used to treat oil-aged BS. After 4 days of soaking the substrates, the pH values of the solutions were measured. Results were shown in Figure 4. Results confirmed that soaking oil-aged BS substrates slightly increased the pH value of the solution.

The solutions of surfactant ZW6 were prepared. Their pH values in room conditions were measured. After that, they were used to treat oil-aged IL. After 4 days of soaking the substrates, the pH values of the solutions were measured. Results were shown in Figure 5. Results confirmed that soaking oil-aged IL substrates significantly increases the pH value of the solution,
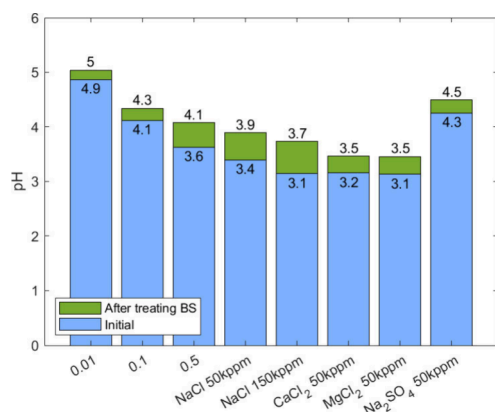

Figure 4. pH values of ZW2 solutions before and after soaking oil-aged Berea sandstone in room conditions for 4 days.
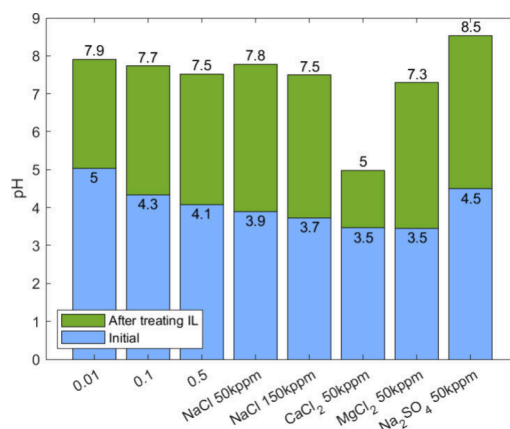

Figure 5. pH values of ZW6 solutions before and after soaking oil-aged Indiana limestone in room conditions for 4 days.

except when 50000 ppm of $CaCl_2$ was dissolved in the water. The direct addition of Ca^{2+} into the solution suppressed further dissolution of calcite, limiting the generation of bicarbonate ions, thus obtaining a much lower pH value (5.0) compared to the $MgCl_2$ case (7.3), which also had an initial pH of 3.5.

The self-ionization of water provides H^+ and OH^- to counter the carboxylic/sulfonate group (which carries a negative charge) and the ammonium group (which carries a positive charge). The attraction between OH^- and the ammonium group is enhanced by the forming of hydrogen bond[57] and thus can be stronger than that between H^+ and the carboxylic/sulfonate group. As a result, the solutions of tested zwitterionic surfactants are acidic and the surfactant molecules exhibit a negative charge more than a positive charge in the solution. The sulfonic group is generally considered more electronegative than the carboxylic group in molecules with similar structures.[58,59] As a result, ZW2 (which contains a sulfonic group) achieved pH values lower than those of ZW6 (which contains a carboxylic group).

Both ZW2 and ZW6 solutions showed the same trend that adding salts altered the pH values. NaCl reduced the pH as its concentration increased. NaCl is usually considered to have no impact on the pH value. It requires further study to reflect on the mechanism. $CaCl_2$ and $MgCl_2$ reduced the pH values, while Na_2SO_4 increased the pH value. The provided multivalent ions (Ca^{2+}, Mg^{2+}, SO_4^{2-}) acted as the stronger counterions (compared to spectacular ions Na^+ and Cl^-) of the zwitterionic acids. As a result, Ca^{2+} and Mg^{2+} enhanced the concentration advantage of H^+ over that of OH^-, giving rise to lower pH values. SO_4^{2-}, on the other hand, diminished the concentration advantage, giving rise to higher pH values. Calcite dissolution (concentration increase) can be estimated roughly based on the concentration change of H^+ according to eq 3.

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2 \qquad (1)$$
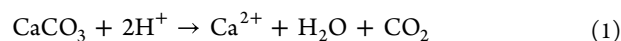
$$p(H^+) = -\lg(\text{concentration}(H^+)) \qquad (2)$$

$$\text{dissolution}(CaCO_3)(\text{mol/L}) \approx \frac{1}{2}(10^{pH_{initial}} - 10^{pH_{final}}) \qquad (3)$$

The estimated dissolution amounts (represented by increases in concentration) are shown in Figure 6. It is apparent that the

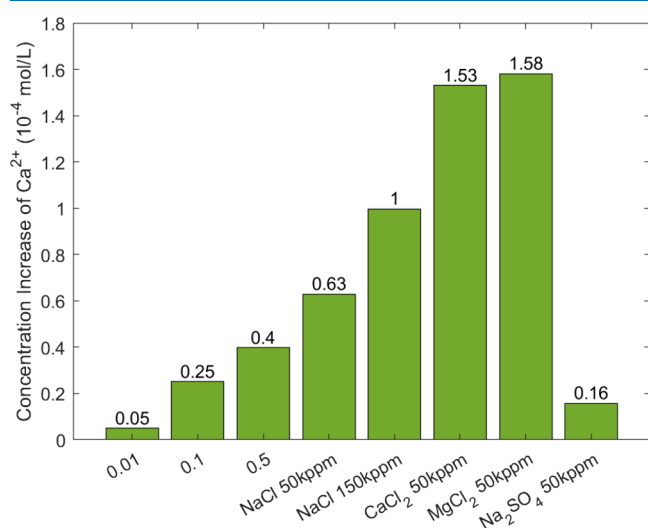dissolution amount is mainly dependent on the initial pH value.

Figure 6. Estimated concentration increases of Ca^{2+} due to calcite dissolution.

4.3. Wettability Alteration on Oil-Aged Sandstone by Zwitterionic Surfactants.

Contact angle values obtained from the Berea sandstone substrate surface before and after soaking in surfactant solutions are shown in Figure 7. Comparing all five surfactants, ZW4 had no impact on oil-aged BS wettability. Compared to the other four surfactants, ZW4 has no -EO- group (which increases the hydrophilicity of the molecule), resulting in a smaller HLB (hydrophilic–lipophilic balance) than ZW5 and ZW6. If we consider materials that changed oil-wet rock to less oil-wet, intermediate-wet, and water-wet conditions, as having weak, moderate, and strong, wettability alteration potential, ZW2, ZW3, ZW5, ZW6 showed comparably moderate wettability alteration performance. For example, ZW2 changed a weakly oil-wet sample (123.2°) to water-wet (63.5°) condition, and also a strongly oil-wet (172.9°) sample to intermediate-wet (133.9°) condition. Based on the molecule structures of the surfactants, ZW2 is more hydrophilic than ZW3. ZW5 is more hydrophilic than ZW6. The observed wettability alteration results showed a good accordance with the HLB of the surfactants that the higher HLB, the better wettability alteration performance on sandstone.

There is a trend of gradual enhancement in wettability alteration by increasing the concentration of ZW2, though increasing the concentration by 50 times (0.01 wt % to 0.5 wt %) did not significantly improve the resulting wettability. Increased salinity impaired the performance of ZW2. The extent of impairment is also dependent on the type of salt. According to Figure 7(d), the extent of impairment can be arranged in a sequence: $CaCl_2$ > $MgCl_2$ > Na_2SO_4 ≈ NaCl.

Overall, the tested zwitterionic surfactants do not have the strong wettability alteration potential in sandstone as in carbonate.[54]

4.4. Wettability Alteration on Oil-Aged Carbonate by Zwitterionic Surfactants.

Contact angle values obtained from the Indiana limestone substrate surface before and after soaking in surfactant solutions are shown in Figure 8. Here, ZW4 was compared with ZW6. ZW6 has a much stronger

performance than ZW4 and most of the surfactants discussed in a previous review work.[60] At the same time, ZW6 has stronger hydrophilicity than ZW4. The accordance between the wettability alteration performance and HLB was observed in both sandstone and carbonate cases.

ZW6 changed the strongly oil-wet substrate to a water-wet status. Concentration increase from 0.01 to 0.5 wt % significantly enhanced the performance, implying an even stronger performance at a concentration higher than 0.5 wt %. At 0.01 wt %, the molar concentration of ZW6 is approximately 1.18×10^{-4} mol/L, lower than its CMC (critical micellization concentration) 3.46×10^{-4} mol/L.[55] CMC was not a deciding factor in the wettability alteration by ZW6, a betaine type polyoxyethylene zwitterionic surfactant containing carboxylic and ammonium head groups.

Increased salinity seemed not to have a major impact. $MgCl_2$ and Na_2SO_4 enhanced the wettability alteration of ZW6. Mg^{2+} and SO_4^{2-} are found to make carbonate rock water-wet in many reports.[46,61] It appeared that ZW6 and these two ions have a synergic effect on wettability alteration. $CaCl_2$, however, largely impaired the wettability change.

Based on the pH results, an increased concentration of ZW6 resulted in more calcite dissolution. Both $MgCl_2$ and $CaCl_2$ cases had the highest estimated dissolution amounts. However, their wettability alteration performances differed significantly. On the other hand, Na_2SO_4 case had a relatively low estimated dissolution amount, while achieving the best wettability alteration performance. Though believed to be helpful in wettability alteration,[62] calcite dissolution seems not to be a main contributing factor in this study, in accordance with some studies.[63,64]

4.5. Carbonate Surface Charge Modification by Zwitterionic Surfactants.

Zeta potential values of IL powder treated with different solutions were measured, and the results are shown in Figure 9. IL powder had a negative value at its initial state. After aging with model oil containing stearic acid, it had a near-neutral value. The resulting zeta potential value increased as the concentration of ZW6 increased from 0.01 wt % to 0.5 wt %. Increased salinity largely impacted the consistency of the measured zeta potential values. $CaCl_2$ and $MgCl_2$ seemed to increase the value more than did NaCl. Na_2SO_4, however, increased the value less than did NaCl.

The zeta potential of calcite is observed to be determined by the $p(Ca^{2+})$.[65] More dissolution of calcite leads to an increased concentration of Ca^{2+} and thus a lower $p(Ca^{2+})$. While soaking the rock powder in the model oil, polar components adsorbed on the rock surface. After capturing all the adsorption sites, they acted as adsorption anchors for organic acid and n-decane molecules. The n-decane vaporized during the drying process. However, the organic acid molecules do not vaporize a lot at a drying temperature of 70 °C. After the drying process, the powder was soaked in aqueous solutions. The adsorbed organic acid does not disperse in aqueous solution at a mildly acidic condition, leaving the surface oil-wet. The nonpolar alkyl chain largely prohibited the adsorption of either H^+ or OH^- ions and inhibited calcite dissolution, causing a zeta potential value of −0.8 mV, close to neutral.

Based on the pH results, surfactants with the carboxylic group dissolved calcite until pH was over 7. Carboxylic surfactants have a strong dissolving capacity. As a result, mixtures of rock powder and ZW6 had high zeta potential values. By increasing the concentration of ZW6 (which obtains a lower initial pH), more calcite was dissolved, resulting in an
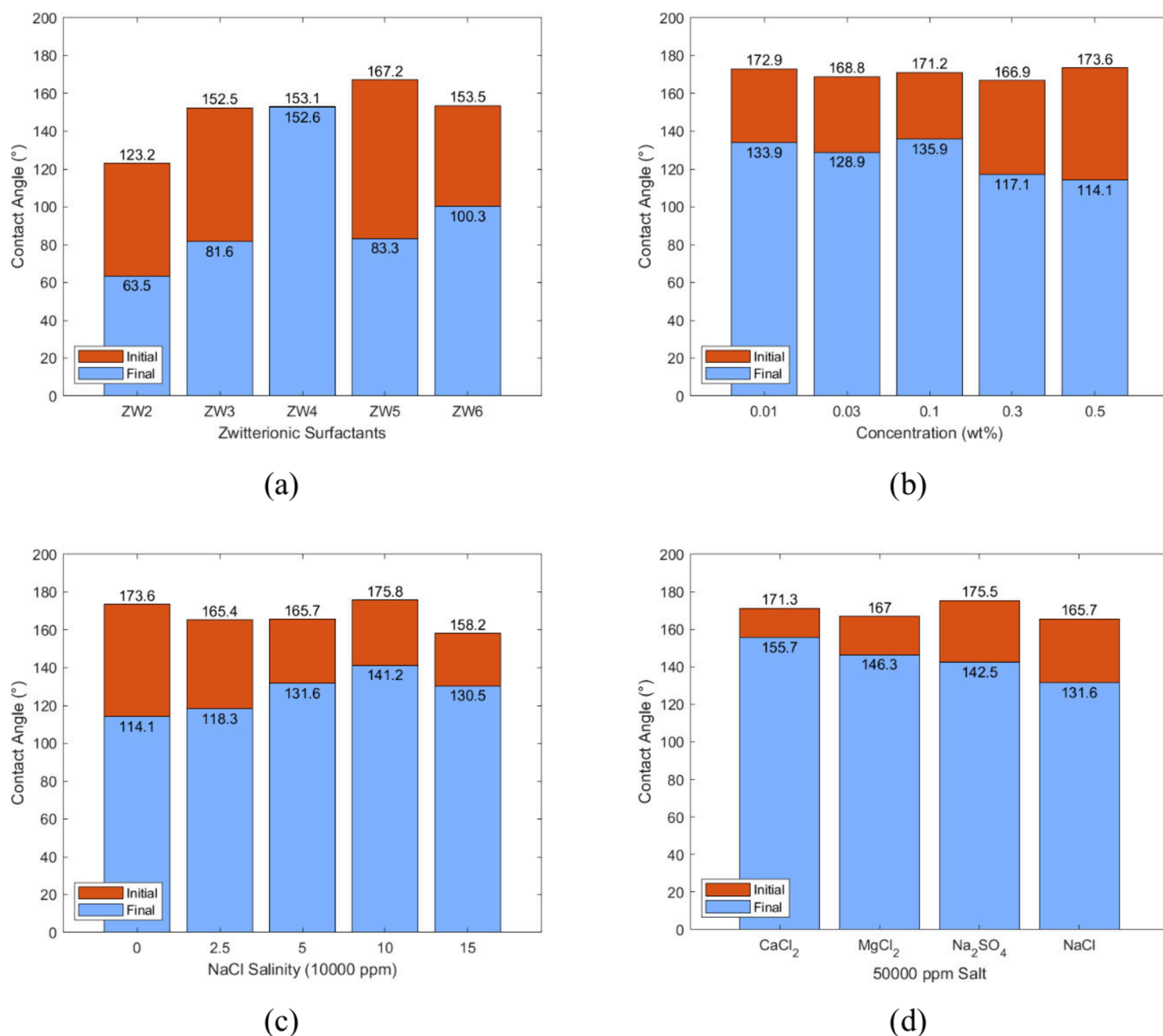
Figure 7. Contact angle values obtained from Berea sandstone substrate surface before and after soaking in surfactant solutions. (a) Impact of different surfactants with a concentration of 0.5 wt %; (b) Impact of ZW2 concentration on rock wettability alteration; (c) Impact of salinity on the wettability alteration by 0.5 wt % ZW2; (d) Impact of salt type on the wettability alteration by 0.5 wt % ZW2.

increasing zeta potential value. A rough accordance between pH results, the estimated calcite dissolution amount, and zeta potential results was observed for Indiana limestone treated with ZW6.

pH results showed that the addition of NaCl did not affect or slightly enhance the calcite dissolution, thus having a limited impact on the p(Ca^{2+}). However, the addition of salts caused larger measurement errors in the zeta potential results, especially in the NaCl 100000 and 1500000 ppm cases. At a high salinity condition, the EDL (electrical double layer) is largely compressed. Added ions can effectively screen the charged surface of the particles, resulting in a small absolute zeta potential value and a larger standard deviation among measurements.

$CaCl_2$ and $MgCl_2$ reduced the initial pH of the solutions to 3.5. The resulting pH caused by $MgCl_2$ was much higher than that of $CaCl_2$, indicating inhibited calcite dissolution when $CaCl_2$ was added. However, added $CaCl_2$ increased the

concentration of Ca^{2+} directly. Ca^{2+} and Mg^{2+} are both PDIs (potential determining ions) for calcite, the increased concentration of Ca^{2+} or Mg^{2+} lifted the zeta potential to positive values. The zeta potential value in the Na_2SO_4 case was higher than that in the 0.5 wt % ZW6 case, though the estimated dissolution amount of calcite in Na_2SO_4 case is lower. The compression of the EDL is a possible explanation.

A more detailed study on the impact of the ZW6 concentration was conducted. The results are shown in Figure 10. The zeta potential of oil-aged IL powder decreased and then increased when the ZW6 concentration increased.

The decrease can be a result of surfactant adsorption. After oil-aging, IL powder had an organic layer on its surface formed by stearic acid with its carboxylic group toward rock and its hydrophobic tail toward bulk fluid. The tail group of the surfactant can adhere to the hydrophobic tail of stearic acid. In this way, the head groups of the surfactant are oriented toward the bulk fluid. As discussed in the pH results, the acidic pH
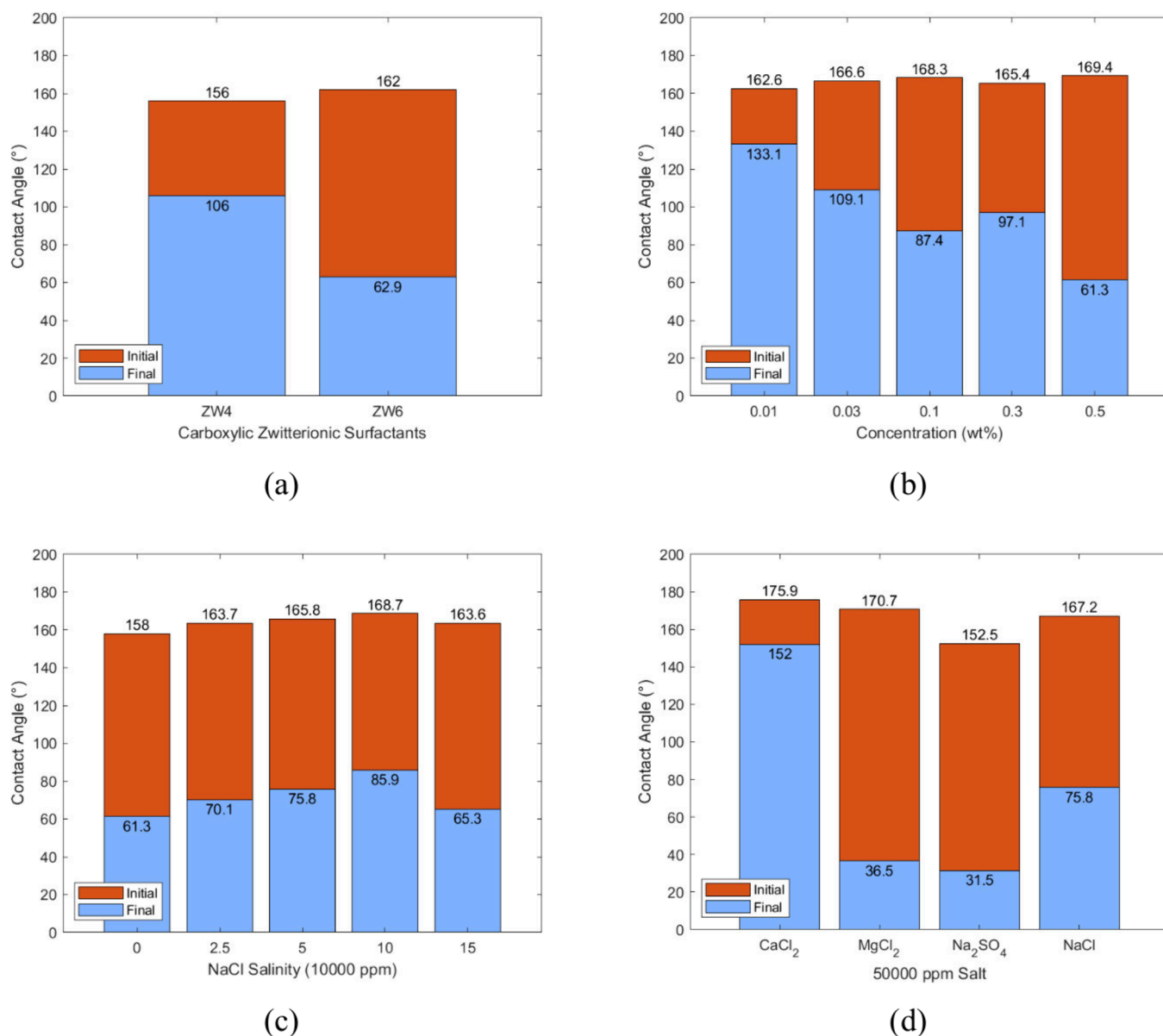
(a)

(b)

(c)

(d)

Figure 8. Contact angle values obtained from Indiana limestone substrate surface before and after soaking in surfactant solutions. (a) Impact of different surfactants with a concentration of 0.5 wt %; (b) Impact of ZW6 concentration on rock wettability alteration; (c) Impact of salinity on the wettability alteration by 0.5 wt % ZW6; (d) Impact of salt type on the wettability alteration by 0.5 wt % ZW6.
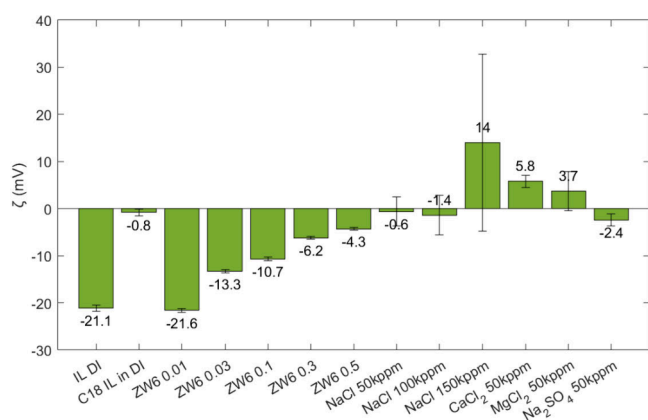

Figure 9. Zeta potential values of the oil-aged Indiana limestone powder mixtures, different ZW6 solutions, or deionized water.

value of the surfactant solutions indicates that the surfactant molecule exhibits the negative charge more than the positive charge in the solution. As a result, the adsorption of surfactant molecules on the organic layer made the zeta potential values of the particles more negative.

The zeta potential increase after 10^{-3} wt % is due to the combined effect of pH and wettability alteration. The pH of ZW6 increased with its concentration, as shown in Figure 5. Increased pH contributed to the calcite dissolution. At a concentration no larger than 10^{-2} wt %, the pH value of the ZW6 solution is higher than 5, and the estimated dissolution amount is minor. When the concentration continued increasing, pH value continued decreasing, and the calcite dissolution was enhanced. Increased Ca^{2+} concentration lifted the zeta potential value.

On the other hand, at a concentration of 0.01 wt %, ZW6 is proven to alter rock wettability though at a limited extent (29.5°). In the following section, the desorption of stearic acid
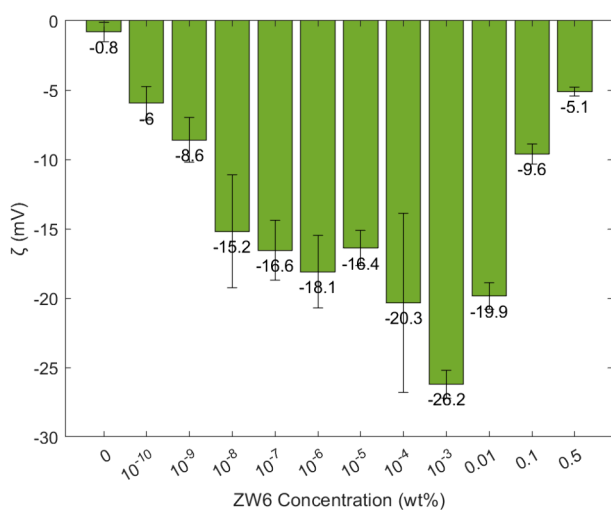
Figure 10. Zeta potential values of the oil-aged Indiana limestone powder soaked by ZW6 solutions of different concentrations.

is suggested to be one of the contributing factors (if not the only) to wettability alteration. When adsorbed stearic acid is removed, less surfactant adsorption on the organic layer would happen. As a result, the zeta potential value would be lifted.

4.6. Desorption of Organic Matters by Zwitterionic Surfactant: Thermogravimetric Analysis. Figure 11 shows
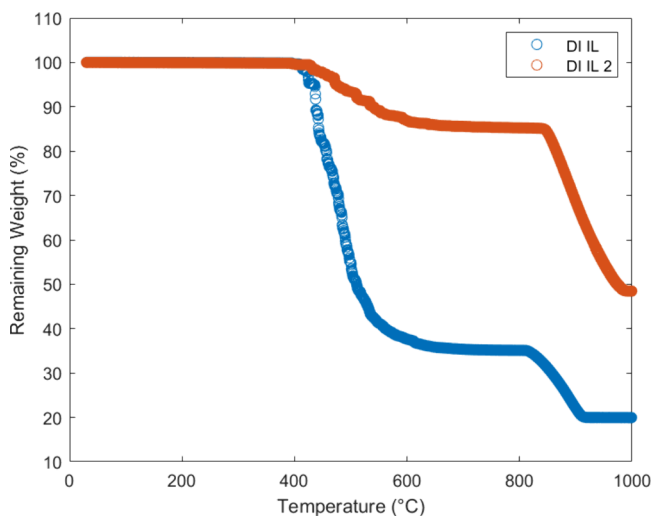

Figure 11. Thermogravimetric analysis results of two unaged Indiana limestones in deionized water suspensions.

the mass decrease curves of two suspensions consisting of deionized water (DI) and unaged Indiana limestone (IL) powder. The significance of the mass reductions indicates that they are mainly due to decomposition. There are two decomposition temperatures: about 420 and about 820 °C. XRD results (obtained with the EMPYREAN diffractometer system with 40 mA, 45 kV as the generator settings) given in the "Materials" section (Figure 2) show that the Indiana limestone is almost pure calcite. The two decompositions should both be calcite decompositions. The usually reported decomposition temperature is above 600 °C.[66,67] The lower decomposition temperature of 420 °C might be due to the small particle size, the plat sheet-like particle shape (shown in

the SEM image Figure 12), and the porous structure. The exact reason for the two-step decomposition requires further study.
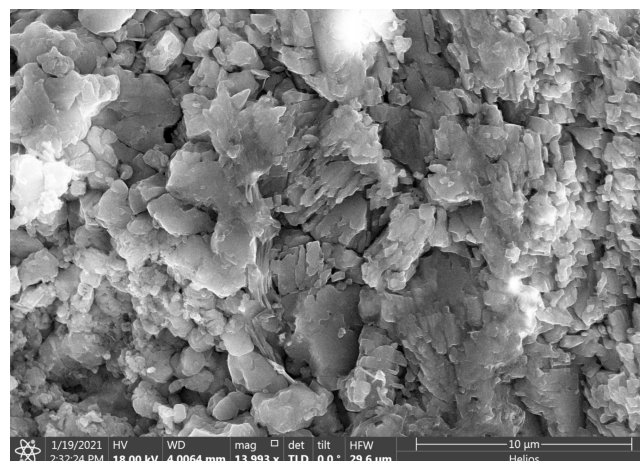

Figure 12. Scanning electron microscopy image of the Indiana limestone surface.

In this study, TGA was conducted to study the difference in the adsorption. Mass loss until 350 °C was compared. The case "ZW6MgCl$_2$" showed a much faster mass decrease than other cases, as shown in Figure 13. This is probably because MgCl$_2$ has the highest hydration energy than other tested salts, thus forming hydrate much more than CaCl$_2$ and Na$_2$SO$_4$, and its dehydration starts at a low temperature,[57] as shown in Figure 13.

The case of the "C18 IL" experienced a rapid mass reduction at a temperature close to 200 °C. This was due to the decomposition of stearic acid, as shown in Figure 14. This confirmed the adsorption of stearic acid molecules on the surface of Indiana limestone powder. This phenomenon was not observed in the case "C18 BS", which indicates that the organic acid adsorption on sandstone is significantly lower than on carbonate.

To avoid disturbance of mass loss from dehydration and calcite decomposition, the mass reduction when the temperature was increased from 200 to 350 °C was compared, as shown in Figure 15. The data can be categorized into two groups. One group, including "DI BS", "DI IL", "DI IL2", and "C18 BS", have a mass reduction of around 0.1% of the initial total mass. The other group contains the rest of the cases and has a mass reduction of around 0.2−0.3% of the initial total mass.

Though there was no stearic acid in "DI BS", "DI IL", and "DI IL2" cases, the mass reduction was still observed, indicating the impact of other factors apart from stearic acid decomposition. In the second group, the mass loss follows a sequence of: "ZW6" < "ZW6 Na$_2$SO$_4$" < "ZW6 CaCl$_2$" < "ZW6 50K" < "ZW6 150 K" < "C18 IL" < "ZW6MgCl$_2$". "ZW6" < "C18 IL" indicates the reduced organic adsorption when surfactant was applied, which supports the idea of wettability alteration by removal of adsorbed organic materials. The amount of remaining stearic acid molecules is reflected by the mass reduction.

However, the mass reduction results showed no relationship when salts were added. This is a result of the dehydration of salt hydrates. Nevertheless, most of the solutions with salts
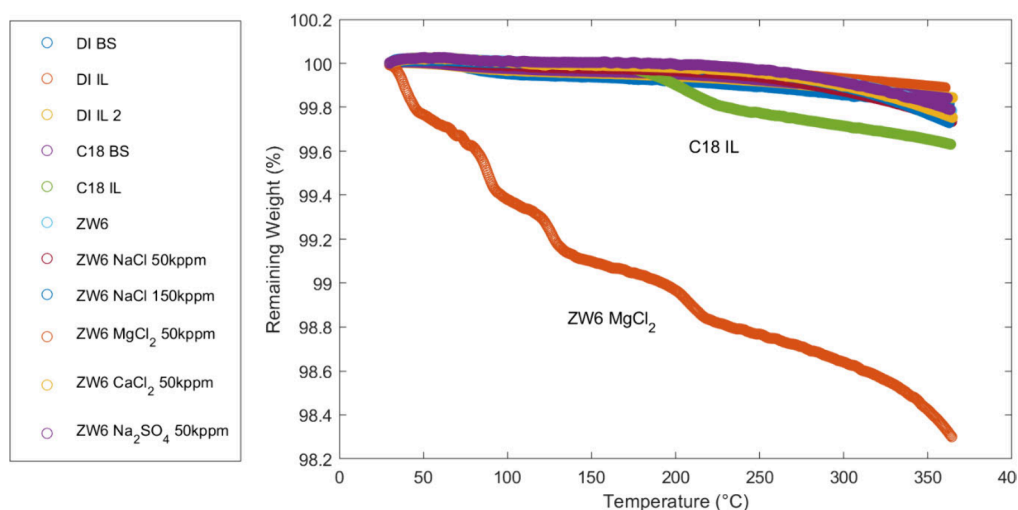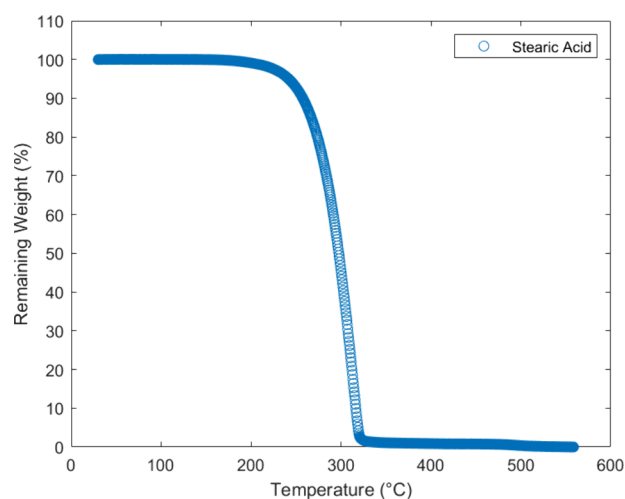
Figure 13. Thermogravimetric analysis results.

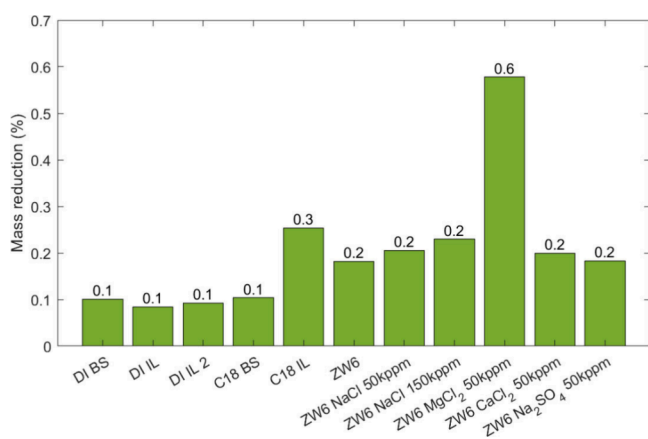**Figure 14.** Decomposition of stearic acid particles.

Figure 15. Mass reduction by heating from 200 to 350 °C.

obtained a smaller mass reduction than the "C18 IL" case, indicating the removal of organic materials during the soakage.

TGA results support the idea that the model oil made Indiana limestone oil-wet by the adsorption of stearic acid. Besides, it supports the idea that the desorption of stearic acid

contributed to the wettability alteration caused by ZW6 on Indiana limestone.

5. CONCLUSIONS

This work studied the solubility and wettability alteration performance of locally synthesized zwitterionic surfactants in Berea sandstone and Indiana limestone. Conclusions are drawn from this study:

1. 5 of the 6 surfactants dissolved in deionized water to form 1.0 wt % solution, indicating efficient solubility for EOR purposes;

2. Although their wettability alteration performance on oil-aged Berea sandstone is weak to moderate, a previous study[54] and this work both showed the promising performance of ZW5 and ZW6 on Indiana limestone;

3. Contact angle results showed that bearing the same headgroup, a more hydrophobic tail group impairs the wettability alteration of surfactants;

4. TGA results confirmed that stearic acid makes Indiana limestone oil-wet by adsorption. The same adsorption is not observed on Berea sandstone. ZW6 can change the rock back to water-wet conditions by desorbing the organic adsorbate. Contact angle results showed that increasing its concentration from 0.01 wt % to 0.5 wt % continuously enhanced the water-wetness of the rock. Altering the salinity by adding NaCl to 150000 ppm did not induce tangible changes. However, when other types of salts were added, the performance was largely influenced. The addition of $CaCl_2$ largely suppressed the wettability alteration, while Na_2SO_4 and $MgCl_2$ both enhanced the performance;

5. Comparing the pH results and contact angle results, calcite dissolution seems unrelated to wettability alteration.

This work proposes ZW6 as a potentially efficient EOR chemical for oil-wet carbonate reservoirs. However, additional tests, including compatibility tests with the formation water, oil recovery tests by coreflooding experiments, and dynamic adsorption tests for cost assessment, are required to justify the applicability of the surfactant. Besides, in-depth studies on the relationship between surfactant structure, its HLB value, and

its wettability alteration performance are helpful for a better understanding.

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Notes

The authors declare no competing financial interest.

ABBREVIATIONS

BS	Berea sandstone
CAHS	Cocamidopropyl hydroxysultaine
CAPB	Cocoamidopropyl betaine
CHS	Cocamidopropyl Hydroxysultaine
CMC	Critical micellization concentration
CT	Computed tomography
DAO	Dimethyl amine oxide
DI	Deionized water
EDAB	Erucic acid amido propyl-betaine
EDL	Electrical double layer
EOR	Enhanced oil recovery
HPLC	High-performance liquid chromatography
IFT	Interfacial tension
IL	Indiana limestone
NMR	Nuclear magnetic resonance
PDI	Potential determining ion
SDS	Sodium alkyl sulfate
SEM	Scanning electron microscope
TGA	Thermogravimetric analysis
ZW	Zwitterionic surfactant

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