ABSTRACT: The objective of this study is to investigate the intermolecular interactions between the surfactants and the fractions of heavy crude oils. Two possible interactions were considered: polar and ionic interactions for two heavy crude oil–surfactant systems, and 20 surfactant-steam flooding tests were conducted on these crudes by testing nine surfactants (three anionic, three cationic, and three nonionic) with different tail lengths and charged head groups. The performance differences observed in each core flood were discussed through the additional analyses. To explain polar interactions, the pseudo blends of crude oil fractions (fractionation of saturates, aromatics, resins, and asphaltenes) were exposed to the surfactant solutions under vapor and liquid water conditions and their mutual interactions were visualized under an optical microscope. To explain ionic interactions, the charges on asphaltene surfaces were analyzed by zeta potential measurements before and after core flood tests on both the produced and the residual oil asphaltenes. The addition of surfactants improved the oil recovery when compared to steam injection alone. However, different oil recoveries were obtained with different surfactants. Further analyses showed that asphaltenes are key and the interaction of asphaltenes with other crude oil fractions or surfactants determines the success of surfactant-steam processes. The polar interactions favor the emulsion formation more; hence, if the polar interactions are more dominant than the ion interactions in the overall crude oil–surfactant system, the surfactant flooding process into heavy oil reservoir became more successful.

INTRODUCTION

Chemical surfactants are widely used in the oil industry to enhance oil recovery. They have polar head groups and nonpolar tails, and their amphiphilic structure is designed in a way that polar head stays in the water phase and nonpolar tail in the oil phase. Hence, they are able to align themselves at the water–oil interface and reduce the interfacial tension (IFT) between water and oil. There are four types of surfactants whose head groups might be charged after they interact with water. When dissolved in water, anionic surfactants have negative polar head groups, cationic surfactants have positive, nonionic surfactants have no charge, and zwitterionic surfactants’ polar head have both negative and positive ions. All types of surfactants show the greatest performance at their critical micelle concentration (CMC) which is the minimum concentration value giving the greatest IFT reduction. At the CMC, the dissolved surfactants’ monomers aggregate forming micelles. Excessive dose of surfactants over CMC results in no change in the IFT value. Thus, to reduce the cost of surfactant flooding operations, it is important to inject surfactants at their CMC.

The formation of a microemulsion layer which contains at least one immiscible liquid, intimately dispersed within another in the form of droplets, the thickness of the formed layer, surfactant stability, and the reservoir temperature during surfactant flooding are key for effective oil recovery through surfactant flooding. The microemulsion formation in surfactant solutions is favored by mainly the polarity of the molecules present in the water–oil system. Polarity is in general formed either because of imbalance in molecular structure or because of the existence of polar functional groups.
in the molecules.\textsuperscript{14} For instance, while propane (C\textsubscript{3}H\textsubscript{8}) has no polarity (zero Debye), propanol (C\textsubscript{3}H\textsubscript{7}O\textsubscript{1}) has a polarity (1.68 Debye) or while benzene (C\textsubscript{6}H\textsubscript{6}) has no polarity (zero Debye), toluene (C\textsubscript{7}H\textsubscript{8}) has a polarity (0.36 Debye).\textsuperscript{15,16} In other words, the molecular imbalance between benzene and toluene or the impurity content of propanol makes these hydrocarbons polar.\textsuperscript{14,17}

While the polar head group of surfactants is attracted by polar water molecules, it should be noted that hydrocarbons (like propanol or toluene examples above) may also have polar functional groups in their molecular structures.\textsuperscript{18,19} Hydrocarbon molecules like crude oils have both molecular imbalance in their complex molecular structures and nonhydrocarbon components (i.e., heteroatoms other than hydrocarbons) contain several functional groups with polarities.\textsuperscript{17,19,25}

However, the determination of overall polarity in such structures is not easy because of the mutual interaction of polar groups present in crude oils.\textsuperscript{21} For example, while water is a highly polar molecule (1.85 Debye) and benzyl alcohol (C\textsubscript{7}H\textsubscript{8}O) is a polar molecule (1.71 Debye), their blend may not end up having a polarity proportional to their polarity and volume in the mixture.\textsuperscript{15} Thus, while it is important to learn the individual role of each functional group in the overall polarity of the crude oil system, it is still very difficult to estimate the mutual contribution of each functional group with respect to the overall polarity.

The fractionation of saturates, aromatics, resins, and asphaltenes (SARA) is one of the crude oil grouping methods and it is used also in this study to determine the role of polarity on surfactant–crude oil interaction. SARA fractionation groups the crude oil components based on their solubility in different solvents. Saturates are linear, branched, or cyclic alkane chains with no double or triple carbon–carbon bonds, hence, they are known as nonpolar. An aromatic fraction contains one or more aromatic rings of hydrocarbons with a possible trace of nitrogen, sulfur, and oxygen (NSO), which is known as nonpolar.\textsuperscript{17,22,23}

However, because of the molecular imbalance and the impurity content of saturate and aromatic fractions, it has recently been found that they may have also polarity.\textsuperscript{24} Resins are known as polar fraction of the crude oil, which is soluble in lower molecular weight n-alkanes and contains less amount of metals as compared to asphaltenes.\textsuperscript{25,26} Asphaltenes are the most polar and the heaviest fraction of crude oil and are insoluble in lower molecular weight n-alkanes and soluble in aromatic solvents; they contain NSO and heavy metals in their molecular structure.\textsuperscript{27} Because of the high polar fraction content of heavy crude oils, during surfactant flooding, an interaction between the polar head group of the surfactant and polar fractions of crude oil (mainly in resins and asphaltenes) is expected.

For conventional light oil reservoirs in which resin and asphaltene contents are minimal, anionic surfactants are preferred because of low adsorption of these surfactants onto the rock surface.\textsuperscript{1,11} However, for the heavy oil reservoirs, not only reservoir rocks but also asphaltenes are charged because of interactions of asphaltenes with reservoir rock.\textsuperscript{28,30,31} Thus, in heavy oil reservoirs, the reservoir rock particles may physically be attached to asphaltene clusters and make the asphaltene surfaces charged.\textsuperscript{28,32} Although this interaction is physical and not chemical, since this interaction is in micro- and nanoscales, it is irreversible.\textsuperscript{33–35} Therefore, the interaction between the charged polar head of surfactants with charged asphaltene surfaces may be inevitable.

Entrapment of crude oil components within the micellar structure of surfactants is really a complex phenomenon where saline water (reservoir brine), surfactant, presence of polar components (resin and asphaltenes) of crude oil play important roles.

This study investigates the interaction between the polar head group of surfactants with polar functional groups in heavy crudes (namely, resins and asphaltenes) and polar-charged head group of surfactants with charged asphaltene surfaces. Since the point of interest is around heavy fractions of crude oil, heavy crude oils were selected for the study. Because of the mobility (high viscosity) issue of heavy crude oils, to enhance the mobility of crude oils, heat is introduced in the form of steam and the performance of different surfactants was investigated by coinjecting different surfactants with steam through core flood experiments.

\section*{MATERIALS AND METHODS}

\textbf{Crude Oil Characterization}. Two oil samples from Canada and Mexico were used in this study. The samples were characterized based on their viscosity using a Brookfield DV-III Ultra rheometer, and API gravity using an Anton Paar DMA 4100 density meter. The crude oils were divided into their SARA fractions by following the ASTM D2007–11 method based on their solubility in different solvents and adsorption affinity toward the attapulgus clay and silica gel because of polarity.\textsuperscript{36} Characterization of the oil samples is summarized in Table 1.

\begin{table}[h]
\centering
\caption{Crude Oil Properties and SARA Fractions}
\begin{tabular}{lcccccc}
\hline
Sample & Viscosity (cP) at 22.3 °C & Density (API) at standard conditions & SAT & ARO & RES & ASP \\
\hline
Oil 1 & 10,100 & 12.09 & 16.51 & 37.81 & 17.1 & 28.58 \\
Oil 2 & 208,500 & 11.56 & 10.14 & 38.01 & 13.09 & 38.76 \\
\hline
\end{tabular}
\end{table}

\textbf{Surfactant Characterization}. Nine surfactants with the same polar-charged head but different nonpolar hydrocarbon tail lengths were used as steam additives; three anionic sulfates (A1, A2, and A3; A1 has the longest tail length and A3 has the shortest tail length among anionic surfactants), three cationic alkyl-ammoniums (C1, C2, and C3; C1 has the longest tail length and C3 has the shortest tail length among cationic surfactants), and three nonionic phenol ethoxylates (N1, N2, and N3; N1 has the longest tail length and N3 has the shortest tail length among nonionic surfactants). Their specifications are given in Table 2. In this table, CMC and hydrophilic–lipophilic balance (HLB) values were obtained through a literature survey.\textsuperscript{4,37,38}

Generally, as the hydrocarbon tail length of ionic surfactants decreases, their molecules become more hydrophilic and soluble in water. Thus, the surfactants with a high HLB number (10 >) are predominantly hydrophilic, prefer to dissolve in water, and form oil-in-water (O/W) emulsions.\textsuperscript{39} For viscous oils and during surfactant flood, these O/W emulsions are preferred as their viscosity values are significantly less than initial crude oil’s viscosity.\textsuperscript{40,41} However, it has been observed that as the tail length decreases, HLB and CMC values increase for anionic and cationic surfactants (ionic surfactants) and decrease for nonionic surfactants (Table 2). In other words, while anionic and cationic surfactants’ solubility increases in water with a
decrease in tail length, nonionic surfactants solubility in water decreases with the decrease in tail length.

**Core flood Experimental Procedure.** In total, 20 core flood experiments were conducted; either only steam (E1 on Oil 1 and E11 on Oil 2) or surfactant-steam (E2 through E10 on Oil 1 and E12 through E20 on Oil 2) flooding. The core flooding experimental set-up is shown in Figure 1.

Because sand is known to be less reactive, to reduce the complexity associated with the surfactant adsorption, as reservoir rock, Ottawa sand with 20−40 mesh size, 39.1% porosity, and 4−5 Darcy permeability was used in all core flood tests. Another simplification was made for the salt content of the reservoir brine. Because it is a known fact that surfactant performances reduced significantly in the presence of brine.

Thus, in the core flood tests, 40 vol % of the pore volume of the sand pack was filled with distilled water and 60 vol % was saturated with the crude oil samples. Then, mixture was packed into a 20 cm long and 5.36 cm in diameter stainless steel core holder. The inlet of the holder is connected to the steam generator and surfactant container, and the outlet is connected to the backpressure regulator (100 psig) and separator (0 psig). During the core flood tests, 18 mL/min steam was injected with a D-series syringe pump, and 2 mL/min surfactant solution was injected with a Beckman 100A pump. The temperature at the center of the sand pack was monitored continuously with J-type thermocouples. The produced liquids were collected every 20 min and stored in a Thermolyne conventional oven at 60−70 °C for slow separation of water from the collected produced oil samples. During the slow water separation process, the weight of the samples was measured every day until no change was observed in the weight of the samples. The water content in the produced liquids was determined based on the total weight change in collected samples through slow evaporation for around 20 to 40 days. The amount of water trapped in crude oil was also determined through fast heating; 15 mg of produced oil samples were heated up at 10 °C/min heating rate under air injection to 200 °C and analyzed using thermogravimetry (TGA) and differential scanning calorimetry (DSC). The endothermic peaks observed between 100 to 150 °C in DSC curves were used to determine the water evaporation temperatures and the corresponding weight percent obtained through TGA graphs was used to determine the amount of water trapped in produced oil samples. In addition to water content determination, the produced oils were further analyzed by determining asphaltene content using n-pentane washing. At the end of each experiment, spent rock samples were visualized and residual oil saturation at injection and production points were determined through toluene washing.

### Table 2. Chemical and Physical Properties of Surfactants Used in this Study

| Surfactant Name (Given Name in this Study) | Structural Molecular Formula | HLB | MW*, g/mole | CMC* Value, mM |
|-------------------------------------------|-----------------------------|-----|-------------|----------------|
| Sodium Dodecyl Sulfate (A1)               |                             | 40  | 288         | 8.39           |
| Sodium Decyl Sulfate (A2)                 |                             | 41  | 260         | 33.2           |
| Sodium Octyl Sulfate (A3)                 |                             | 41.9| 232         | 130            |
| Triton™ X-100 (N1)                        |                             | 13.5| 625         | 0.9            |
| Triton™ X-114 (N2)                        |                             | 12.4| 537         | 0.2            |
| Triton™ X-45 (N3)                         |                             | 10.4| 427         | 0.1            |
| Hexadecyltrimethylammonium Bromide (C1)   |                             | 10.3| 365         | 0.92           |
| Myristyltrimethylammonium Bromide (C2)    |                             | 11.25| 336       | 5              |
| Dodecyltrimethylammonium Bromide (C3)     |                             | 12.2| 308         | 15.6           |

*MW: Molecular weight, CMC: Critical micelle concentration; A: Anionic, N: Nonionic, and C: Cationic Surfactants.

Figure 1. Schematic of the experimental setup for steam and surfactant-steam flooding experiments (Schematic was drawn by the authors).
The amount of each fraction is used. When preparing the pseudo blends of SARA fractions, an equal visualized under a ProRes CT5 Camera attached to an optical crude oil and crude oil components with surfactants were glass under atmospheric conditions. The interactions between at liquid and vapor (steam) water conditions on a microscope asphaltene surfaces were investigated. As it was mentioned in the last paragraph of the Introduction section, this study focuses on developing an understanding toward intermolecular interactions of crude oil components with surfactants. For this purpose, the interaction between the polar head group of surfactants with polar functional groups (namely, resins and asphaltenes) and the interaction between the polar-charged head group of surfactants and charged-asphaltene surfaces were investigated.

a) First, the intermolecular interaction between the polar head group of surfactants and polar functional groups was determined through optical microscopy analysis. Initial oil samples were first separated into their SARA fractions by following an ASTM method, accordingly, first, n-pentane is used, to separate asphaltenes from other crude oil fractions (i.e., known as deasphalted oil (DAO)). DAO, then, is charged through a double column glass percolation in which attapulgus clay is at the top section and silica gel plus clay is at the bottom section. The saturate fraction which is known as the nonpolar fraction of crude oil is collected at the bottom of the assembly without getting adsorbed. On the other hand, the aromatic fraction gets partially adsorbed onto attapulgus clay because of its partial polarity (i.e., contain some heteroatoms), and the rest is adsorbed to the silica gel. The aromatic fractions are collected through n-pentane washing and resins through the mixture of acetone and toluene (1:1 volume ratio).36

Then, bulk crude oils, each SARA fraction, and pseudo blends of SARA fractions were exposed to different surfactant solutions at liquid and vapor (steam) water conditions on a microscope glass under atmospheric conditions. The interactions between crude oil and crude oil components with surfactants were visualized under a ProRes CT5 Camera attached to an optical microscope (Meiji Techno MT9000) at 100X magnification. When preparing the pseudo blends of SARA fractions, an equal amount of each fraction is used.

b) Then, the intermolecular interaction between the polar-charged head group of surfactants and the charged surface of the asphaltenes were investigated through zeta potential measurement using a Brookhaven Instrument, 90Plus ZETA PALS. The zeta potential is defined as the electric potential in the interfacial double layer of a liquid droplet or solid versus a point in the continuous phase far from the interface.10 Thus, the zeta potential provides information about the magnitude and sign of the electrical charges on the particles in a solution. Zeta potential measurements were conducted on the asphaltene samples from initial oil, produced oil, and residual oil samples; 50 mg of asphaltenes were dispersed into 15 mL of ethanol using ultrasound tub for 20 min. Then, 1.5 mL volume of this solution was added to 100 mL of 1 mM potassium chloride solution of 6 ± 1 pH value.42,44 Furthermore, the particle size of these asphaltene solutions was measured using a Brookhaven Instrument, 90Plus PALS.

c) In addition, the polarity of the bulk crude oils and their SARA fractions were estimated indirectly through dielectric constant measurements using a vector network analyzer, FieldFox Handheld at frequency between 500 MHz and 4 GHz. Also, the carbon, hydrogen, and nitrogen content of asphaltenes was determined by the standard combustion method and applying the Leco CHN analyzer Carlo Erba model. The trace elements were deducted using Thermo Intrepid inductively coupled plasma.

RESULTS AND DISCUSSION

Core flood Experimental Results. Twenty steam and surfactant-steam core flooding tests were conducted to determine the role of intermolecular forces on surfactant-steam performances.

Figure 2 shows the experimental results in terms of cumulative oil recovery and the total emulsified water content of each produced oil sample. The amount of water is determined through a fast heating method by TGA/DSC described in the Materials and Methods section.

The cumulative oil recovery results of steam and surfactant-steam injection tests show that surfactant additives were successful in increasing oil recovery for both crude oils. However, the cumulative oil production of the Oil 2 steam injection experiment was considerably lower than Oil 1’s results (E1 and E11). The performance of the anionic surfactant additives varied for both crude oils and while the anionic

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c00193)

ACS Omega 2020, 5, 27383–27392
surfactant with the longest tail length performed better for Oil 1 (i.e., higher oil recovery), it performed poorly for Oil 2. It has been observed with anionic surfactants that as the tail length increases the oil production increases for Oil 1 and decreases for Oil 2. In other words, it is observed that with the increase in solubility of anionic surfactants in water (as the tail length decreases), the oil recovery for Oil 2 increased and Oil 1 decreased. However, no trend was observed between the tail length of cationic and nonionic surfactants and oil recovery for both oils.

The produced oil from the steam injection core flood experiment (E1 and E11) has high water-in-oil emulsion content (blue bars in Figure 2) for both oil types. Thus, in general (except E12 and E13), surfactant addition to steam stream not only increased the oil recovery but also reduced the water-in-oil emulsion content of the produced oil samples. For almost all surfactant types, less water-in-oil emulsion content was observed in produced oil samples as the tail length of surfactants decreases.

At the end of each experiment, visual inspection on postmortem samples was achieved. Figure 3 shows the pictures of the postmortem samples collected by the end of each core flood test.

For both crude oils, the images show steam injection experiments yielded the darkest spent rock sample among all spent rocks. For Oil 1, spent rock’s lightest color was observed for surfactant-steam experiments with all three nonionic surfactants (N1, N2, and N3) and for Oil 2, surfactant-steam experiments with A3, C1, and C2 have the lightest spent rock color.

Residual oil saturation of spent rock samples (from inlet and outlet of the core flood tests) was determined by toluene wash. The average (average of inlet and outlet residual oil saturations) residual oil saturations for all core flood experiments are shown in Figure 4.

Figure 4 indicates the surfactant-steam injection test result in lower residual oil than steam injection alone. Like in cumulative oil recovery results, the response of Oil 1 to steam and surfactant-steam flooding tests is better than Oil 2.

The asphaltene content of residual oil samples and produced oil samples were determined through n-pentane washing. Table 3 presents those results.

### Table 3. Weight Percent of the Produced and Residual Oil Asphaltenes Based on the Initial Asphaltene Content of Oil 1 and Oil 2

| oil type | experiment no. | surfactant type | surfactant name | produced oil’s asphaltenes, wt % | residual oil’s asphaltenes, wt % |
|----------|----------------|-----------------|-----------------|---------------------------------|---------------------------------|
| Oil 1    | E1 steam -     | -               | -               | 38.5                            | 61.5                            |
|          | E2 steam +     | anionic         | A1              | 59.1                            | 40.9                            |
|          | E3 steam +     | anionic         | A2              | 65.1                            | 34.9                            |
|          | E4 steam +     | anionic         | A3              | 78.4                            | 21.8                            |
|          | E5 steam +     | cationic        | C1              | 68.9                            | 31.1                            |
|          | E6 steam +     | cationic        | C2              | 62.6                            | 37.4                            |
|          | E7 steam +     | cationic        | C3              | 67.5                            | 32.6                            |
|          | E8 steam +     | nonionic        | N1              | 57.0                            | 43.0                            |
|          | E9 steam +     | nonionic        | N2              | 62.6                            | 37.4                            |
|          | E10 steam +    | nonionic        | N3              | 79.4                            | 20.6                            |
| Oil 2    | E11 steam -    | -               | -               | 42.6                            | 57.4                            |
|          | E12 steam +    | anionic         | A1              | 44.6                            | 55.3                            |
|          | E13 steam +    | anionic         | A2              | 40.5                            | 59.5                            |
|          | E14 steam +    | anionic         | A3              | 75.3                            | 24.6                            |
|          | E15 steam +    | cationic        | C1              | 61.4                            | 38.5                            |
|          | E16 steam +    | cationic        | C2              | 67.1                            | 33.0                            |
|          | E17 steam +    | cationic        | C3              | 68.4                            | 31.8                            |
|          | E18 steam +    | nonionic        | N1              | 70.9                            | 29.1                            |
|          | E19 steam +    | nonionic        | N2              | 66.3                            | 33.7                            |
|          | E20 steam +    | nonionic        | N3              | 62.7                            | 37.4                            |

Note that the initial oil asphaltenes are 28.6 wt % for Oil 1 and 38.8 wt % for Oil 2. The results in Table 3 show that during core flood tests with surfactant addition, the asphaltene deposition has been decreased on the rock surface when compared to steam flooding tests alone, which explains more consolidation observed in Figure 3 for E1 and E11.

![Figure 3. Postmortem images at the end of each core flood test. The injection point is at the top (inlet) and the production is at the bottom (outlet) for each picture. (Pictures were taken by the authors)](image)

![Figure 4. Residual oil saturation results for all core flood tests.](image)
Thus, produced oil samples from surfactant-steam flooding tests have higher asphaltene content than steam flooding tests, which is an indication that surfactants are interacting more with the asphaltenes in produced oil, not with the deposited asphaltenes. The possible interaction between surfactants and asphaltenes will be discussed in the next sections.

**DISCUSSION ON INTERMOLECULAR INTERACTIONS BETWEEN CRUDE OILS AND SURFACTANTS**

**Polar Interaction.** During surfactant flooding an interaction between polar fractions of heavy crude oils and the polar head group of the surfactant is expected which results in emulsification. It should be noted that oil emulsification is a key mechanism for the success of surfactant flooding processes. In this study, the contribution of each fraction and/or contribution of the mutual interaction of fractions on surfactant-steam flooding performance was investigated. The crude oil emulsification mechanism in the presence of different surfactants was visualized under an optical microscope at 100X magnification. Initial crude oils and their pseudo blends of SARA fractions were exposed to different surfactant solutions at liquid and vapor (steam) water conditions. Figures 5 and 6 show these interactions for Oil 1 and Oil 2, respectively.

For Oil 1, the medium tail length cationic surfactant (C2) resulted in more emulsion formation and the shortest tail length

---

**Figure 5.** Optical microscopy images of intermolecular interactions between crude oil 1, crude oil pseudo SARA fractions, and surfactant blends before and after steam exposure at 100x magnification (scale is shown in the first image). Oil samples were exposed to steam at 150 °C for 10 min at atmospheric pressure. While before images show the interactions with liquid water, after images show the interactions with vapor water (images were taken by the authors).
nonionic (N3) gives smaller and more dispersed emulsions. The resin fractions alone resulted in forming emulsions in different sizes and shapes while the most polar fraction, asphaltenes, did not cause any emulsion formation before or after steam exposure as shown in Figure 5. The pseudo blends of resin and asphaltene fractions did not show any emulsion formation either. However, the addition of aromatic fraction increases emulsion presence and the addition of saturates made the emulsions smaller and more dispersed after surfactant and steam addition in general. The results on the blends prepared with DAO fractions (saturates, aromatics, and resins) show that overall the emulsion formation becomes more visible, dispersed, and smaller in the absence of asphaltenes for Oil 1. When the core flood test results (Figure 2 and Table 3) were examined along with the microscopic images, the following findings were obtained.

For Oil 1, the longest tail length anionic surfactant (A1) resulted in the greatest asphaltene precipitation and at the same time the oil recovery was the greatest among all anionic surfactants (Figure 2). Similarly, the greatest asphaltene precipitation was observed for the medium tail length cationic surfactant (C2), which when used as the steam additive resulted in the greatest oil recovery among all cationic surfactants. In addition, these surfactants additives (A1 and C2) also resulted in the lowest asphaltene content in the produced oil samples (Table 3). On the other hand, the greatest asphaltene content in produced oils is observed using surfactants additives (A3 and

| Sample            | Steam Exposure | None | Anionic Surfactants | Cationic Surfactants | Non-ionic Surfactants |
|-------------------|----------------|------|---------------------|----------------------|-----------------------|
| Bulk Oil          | Before         |      | A1                  | C1                   | N1                    |
|                   | After          |      | A2                  | C2                   | N2                    |
|                   |                |      | A3                  | C3                   | N3                    |
| Resins            | Before         |      |                     |                      |                       |
|                   | After          |      |                     |                      |                       |
| Asphaltenes       | Before         |      |                     |                      |                       |
|                   | After          |      |                     |                      |                       |
| Resins + Asphaltenes | Before   |      |                     |                      |                       |
|                   | After          |      |                     |                      |                       |
| Aromatics + Resins + Asphaltenes | Before |      |                     |                      |                       |
|                   | After          |      |                     |                      |                       |
| Aromatics + Resins | Before |      |                     |                      |                       |
|                   | After          |      |                     |                      |                       |
| Saturates + Aromatics + Resins + Asphaltenes | Before |      |                     |                      |                       |
|                   | After          |      |                     |                      |                       |
| Aromatics + Resins | Before |      |                     |                      |                       |
|                   | After          |      |                     |                      |                       |
| Saturates + Aromatics + Resins | Before |      |                     |                      |                       |
|                   | After          |      |                     |                      |                       |

Figure 6. Optical microscopy images of intermolecular interactions between crude oil 2, crude oil pseudo SARA fractions, and surfactant blends before and after steam exposure at 100x magnification (scale is shown in the first image). Oil samples were exposed to steam at 150 °C for 10 min at atmospheric pressure. While before images show the interactions with liquid water, after images show the interactions with vapor water (images were taken by the authors).
C1) which resulted in the lowest oil recoveries. While our microscopy images prove that the presence of asphaltenes inhibit the emulsion formations, our core flood test results also support this finding. Thus, it can be concluded that asphaltene removal in displaceable oil (asphaltene precipitation) favors the surfactant–steam flooding process more for Oil 1 because of effective emulsion formation. In other words, for Oil 1, the surfactant efficiency is enhanced once the interaction between DAO and asphaltenes is decreased. Thus, it is recommended for Oil 1 that the precipitation of asphaltenes is performed through asphaltene insoluble solvents, first, followed by surfactant injection.

The results for Oil 2 are shown in Figure 6. For Oil 2, the observed interactions are different than Oil 1 and less emulsion formation was observed for Oil 2 than Oil 1. In bulk oil, A3, cationic and nonionic surfactants result in emulsions. Microscopy images revealed that mainly interactions among DAO fractions are responsible from emulsion formation.

Similar to Oil 1, the microscopy images are discussed in the light of the core flood test results (Figure 2 and Table 3). It is observed that A3 had the greatest asphaltene content in the produced oil sample among all anionic surfactants and C3 had the greatest asphaltene content in produced oil samples among all cationic surfactants and resulted in the greatest oil recoveries.

In other words, while the presence of asphaltenes in displaced oil disfavors surfactant effectiveness in Oil 1, it favors for Oil 2. It should be noted that Oil 1 (28.6 wt %) has less initial asphaltenes than Oil 2 (38.8 wt %) and the amount of asphaltenes is not directly related to the intermolecular interactions between the polar groups of surfactant and oil blends.

Because the dielectric constant values of a material correlate with its dipole moment, thus the polarity can be estimated,48,49 the indirect measurement of polarity through dielectric constant measurements was achieved at frequency between 500 MHz and 4 GHz by a vector network analyzer. Further, elemental analysis on initial crude oil’s asphaltenes was achieved through the standard combustion method and by applying the Leco CHN analyzer Carlo Erba model. The presence of heteroatoms with different electronegativity can cause imbalance in distribution of electrons generating dipoles with partial negative (−) and partial positive (+) charges.15,50,51 The results are given in Table 4.

Table 4. Polarity Estimation for Crude Oils and their SARA Fractions and Elemental Analysis of Asphaltenes

| dielectric constant (ε') | elemental analysis, wt % |
|--------------------------|-------------------------|
| fractions                | crude oil 1 | crude oil 2 | elements | oil 1' asphaltenes | oil 2' asphaltenes |
| bulk oil                 | 2.89        | 2.51        | carbon   | 80.3            | 80.4            |
| saturates                | 2.42        | 2.39        | hydrogen | 8.19            | 8.21            |
| aromatics                | 3.45        | 3.34        | nitrogen | 1.43            | 1.38            |
| resins                   | 4.22        | 3.33        | oxygen   | 6.52            | 1.79            |
| asphaltenes              | 4.90        | 3.40        | heteroatoms* | 11.51          | 11.39          |

*Heteroatom wt % is the sum of every element (in wt %) except for C and H.

Table 5. Zeta Potential Values and Cluster Size of Initial Oil Asphaltenes, Produced Oil Asphaltenes, and Residual Oil Asphaltenes

| oil type | exp. no. | surfactant name | produced oil asphaltene | residual oil asphaltene |
|----------|----------|-----------------|-------------------------|-------------------------|
|          | zeta potential, mV | cluster size, nm | cluster size, nm | zeta potential, mV | cluster size, nm |
| Oil 1    | initial  | -25.7          | 12.401                  | -20.5                   | 14.430                  |
| E1       | -42.3    | 2278            | -3.1                    | 26.985                  |
| E2       | -46.8    | 1856            | -3.5                    | 26.974                  |
| E3       | -60.1    | 1087            | -5.0                    | 26.147                  |
| E4       | -60.2    | 1085            | -7.3                    | 25.014                  |
| E5       | -49.3    | 1138            | -6.3                    | 25.354                  |
| E6       | -50.4    | 1126            | -6.2                    | 25.475                  |
| E7       | -53.8    | 1101            | -15.5                   | 19.504                  |
| E8       | -53.1    | 1114            | -18.2                   | 15.845                  |
| E9       | -62.4    | 870             | -23.7                   | 11.541                  |
| E10      | -51.0    | 1115            | -16.0                   | 22.547                  |
| E11      | -18.5    | 16,200          | -3.6                    | 22.874                  |
| E12      | -35.6    | 3214            | -3.8                    | 26.874                  |
| E13      | -36.7    | 3051            | -4.1                    | 26.541                  |
| E14      | -51.2    | 1115            | -4.9                    | 26.150                  |
| E15      | -43.0    | 2250            | -6.6                    | 25.411                  |
| E16      | -32.1    | 4187            | -13.3                   | 22.984                  |
| E17      | -37.6    | 2804            | -16.2                   | 17.451                  |
| E18      | -42.6    | 2260            | -13.7                   | 22.101                  |
| E19      | -40.7    | 2560            | -15.3                   | 19.545                  |
| E20      | -34.6    | 3844            | -18.6                   | 15.821                  |

Zeta potential values may vary between 0 to 100 mV and the sign of the zeta potential value gives the charges of the particles in solution.52 All zeta potential values reported in Table 5 are negatively charged which indicates that surfaces of the asphaltene clusters are negatively charged. As the absolute value of the zeta potential values of asphaltenes approaches 0 mV, those asphaltenes show higher tendency to come together and precipitate, if the cluster size of the asphaltenes is also bigger, asphaltene precipitation will occur quickly. Therefore, the
residual oil asphaltenes give greater particle size with lower zeta potential values. The reverse is also valid; if the absolute value of the zeta potential values of asphaltenes approaches to 100 mV, those asphaltenes show higher stability to stay apart from each other and if the cluster size of the asphaltenes measured with a particle size analyzer is small, then, these asphaltenes will show extreme stability and it will be very difficult to make them precipitate.\textsuperscript{27} This behavior is observed in produced oil asphaltenes.

The zeta potential values of initial asphaltenes suggest that Oil 1’s asphaltenes have more surface charges than Oil 2, hence, asphaltene particles of Oil 1 should be more stable than Oil 2’s asphaltenes. In addition, the results show a good correlation between absolute zeta potential value and cluster size among each oil. Steam injection alone results in more charges on asphaltene surfaces for Oil 1 (compare initial oil 1 asphaltene zeta potential value to E2). The overall results in Table 5 suggest that surfactants can modify and alter the asphaltenes’ charges, hence, the stability of these oil dispersions can be controlled and because the surface charges of the two oil’s asphaltenes are different, their interactions were varied.

\section*{CONCLUSIONS}

The purpose of the current study was to investigate the interaction between the polar head group of surfactants with the polar functional groups in heavy crudes (resins and asphaltenes) and the polar-charged head group of surfactants with charged asphaltene surfaces.

The investigation of polar interaction has shown that asphaltene precipitation favors the surfactant-steam flooding process more for crude oil with high polar asphaltenes and a high oxygen content. An implication of this is surfactant efficiency is enhanced once the interaction between DAO and asphaltenes is decreased allowing oil emulsification via surfactant interaction with DAO. Within DAO, resins are more prompt to form emulsion, thus, in favor of interacting with surfactants.

In contrast, in crude oil with less polar asphaltenes, however, a higher asphaltene content disfavors asphaltenes precipitation during the surfactant-steam flooding process. The analysis of residual and produced oil’s asphaltenes shows ionic interaction between the charged asphaltenes and surfactant head. The produced asphaltene surface charge increased after interacting with steam and surfactants, increasing their stability. In contrast, the surface charge of precipitated asphaltenes has been lowered.

\section*{AUTHOR INFORMATION}

Corresponding Author

Berna Hascakir — Texas A&M University, College Station, Texas 77843, United States; orcid.org/0000-0001-6190-903X; Email: hascakir@tamu.edu

Authors

Lee Yeh Seng — Texas A&M University, College Station, Texas 77843, United States; University Technology PETRONAS, Perak 32610, Malaysia

Murtadha Al-Shaikh — Texas A&M University, College Station, Texas 77843, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00193

Notes

The authors declare no competing financial interest.

\section*{ACKNOWLEDGMENTS}

We acknowledge the financial support and opportunity provided by the Heavy Oil, Oil Shales, Oil Sands, Carbonate Analysis, and Recovery Methods (HOCAM) research team at Texas A&M University in the Petroleum Engineering department.

\section*{NOMENCLATURE}

ASTM tabAmerican Society for Testing and Materials
CMC tabCritical Micelle Concentration
DSC tabDifferential Scanning Calorimetry
DAO tabDe-Asphaltenes Oil
IFT tabInterfacial Tension
SAR tabSaturates, Aromatics, Resins, and Asphaltenes
A1 tabSodium Dodecyl Sulfate
A2 tabSodium Decyl Sulfate
A3 tabSodium Octyl Sulfate
C1 tabHexadecyltrimethylammonium Bromide
C2 tabMyristyltrimethylammonium Bromide
C3 tabDodecyltrimethylammonium Bromide
N1 tabTriton X-100
N2 tabTriton X-114
N3 tabTriton X-45

\section*{REFERENCES}

(1) Green, D.W.; Willhite, P.G. \textit{Enhanced Oil Recovery}, First Edition. Richardson, TX: Henry L. Doherty Memorial Fund of AIME 1998; pp. 239–287.

(2) Henderson, J.H.; Taber, J.J. \textit{Residual Oil Recovery Process Using Water Containing a Surfactant}. In: Google Patents US3,199,586A 1965.

(3) Uren, L. C.; Fahmy, E. Factors Influencing the Recovery of Petroleum from Unconsolidated Sands by Waterflooding. \textit{Trans. Am. Inst. Min., Metall., Pet. Eng., Soc. Min. Eng. AIME} 1927, 77, 318–335.

(4) Egan, R. W. Hydrophile-Lipophile Balance and Critical Micelle Concentration as Key Factors Influencing Surfactant Disruption of Mitochondrial Membranes. \textit{J. Biol. Chem.} 1976, 280, 442–4264.

(5) Myers, D. \textit{Surfactant Science and Technology}, Third edition John Wiley & Sons 2005; pp. 3–55.

(6) Rosen, M.J.; Kunjappu, J.T., \textit{Surfactants and Interfacial Phenomena}, Fourth edition. Hoboken, New Jersey: John Wiley & Sons; 2012; pp. 1–38.

(7) Wagner, O.; Leach, R. O. Effect of Interfacial Tension on Displacement Efficiency. \textit{Soc. Pet. Eng. J.} 1966, 4, 335–344.

(8) Rosen, M., \textit{Surfactants and Interfacial Phenomena}. In: New York: John Wiley & Sons Inc. 1978.

(9) Becher, P., \textit{Emulsions: Theory and Practice}, Second edition. USA: Reinhold Publishing Corporation. 1965; pp. 1–49.

(10) Schramm, L.L., \textit{Fundamentals and Applications in the Petroleum Industry}. Washington, DC: American Chemical Society. 1992; pp. 79–136.

(11) Hirasaki, G.; Miller, C. A.; Puerto, M. Recent Advances in Surfactant Eor. \textit{Soc. Pet. Eng. J.} 2011, 16, 889.

(12) Sheng, J. J. A Comprehensive Review of Alkaline–Surfactant–Polymer (ASP) Flooding. \textit{Asia-Pac. J. Chem. Eng.} 2014, 9, 471–489.

(13) Tadros, T.F., \textit{Emulsions: Formation, Stability, Industrial Applications}, First edition. Germany: Walter de Gruyter GmbH & Co KG. 2016; pp. 20–48.

(14) Dickerson, R.E.; Gray, H.B.; Haight, G.P., \textit{Chemical Principles}, First edition. California: The Benjamin/Cummings Publishing Company, Inc. 1979; pp. 2–33.

(15) Nelson, Jr. R.D.; Lide, Jr. D.R.; Maryott, A.A., Selected Values of Electric Dipole Moments for Molecules in the Gas Phase. National Standard Reference Data System. 1967.

(16) Schechter, I.; Ben-Chorin, M.; Kux, A. Gas Sensing Properties of Porous Silicon. \textit{Anal. Chem.} 1995, 67, 3727–3732.

(17) Oxtoby, D.W.; Gillis, H.P.; Butler, L.J., \textit{Principles of Modern Chemistry}, 8th edition. Boston, MA: Cengage learning. 2015; pp. 111.
(18) Crocker, M.; Marchin, L. Wettability and Adsorption Characteristics of Crude-Oil Asphaltene and Polar Fractions. *J. Pet. Technol.* 1988, 40, 470–474.

(19) Kar, T.; Hascakir, B. The Role of Resin, Asphaltene, and Water in Water—Oil Emulsion Breaking with Microwave Heating. *Energy Fuels* 2015, 29, 3684–3690.

(20) Punase, A.; Hascakir, B., Demir, A., Bilge, H., and Diederichs, H. Inorganic Content of Asphaltene Impacts Asphaltene Stability. Paper presented at the SPE Latin America and Caribbean Petroleum Engineering Conference, Buenos Aires, Argentina, 17–19 2017. DOI: 10.2118/185543-MS.

(21) Punase, A.; Hascakir, B. Stability Determination of Asphaltene through Dielectric Constant Measurements of Polar Oil Fractions. *Energy Fuels* 2017, 31, 65–72.

(22) Austad, T.; Matre, B.; Milter, J.; Saavareid, A.; Øyno, L. Chemical Flooding of Oil Reservoirs: Spontaneous Oil Expulsion from Oil-and-Water-Wet Low Permeable Chalk Material by Imbibition of Aqueous Surfactant Solutions. *Colloids Surf. A* 1998, 137, 117–129.

(23) Falls, A. H.; Thigpen, D.; Nelson, R. C.; Cisatton, J.; Lawson, J.; Good, P.; Ueber, R.; Shahin, G. Field Test of Cosurfactant-Enhanced Alkaline Flooding. *SPE Reserv Eng* 1994, 9, 217–223.

(24) Prakoso, A.; Punase, A.; Rogel, E.; Ovales, C.; Hascakir, B. Effect of Asphaltene Characteristics on Its Solubility and Overall Stability. *Energy Fuels* 2018, 32, 6482–6487.

(25) Akbarzadeh, K.; Hammani, A.; Kharrat, A.; Zhang, D.; Allenson, S.; Creek, J.; Kabir, S.; Jamaludin, A.; Marshall, A. G.; Rodgers, R. P. Asphaltene—Problematic but Rich in Potential. *Schlumberger Oilfield Rev.* 2007, 19, 22–43.

(26) Fan, T.; Wang, J.; Buckley, J. S., Evaluating Crude Oils by Sara Analysis. Paper presented at the SPE/DOE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA, 13–17 April 2002. *SPE-75228-MS*. DOI: 10.2118/75228-MS. McLean, J. D.; Kilpatrick, P. K. Effects of Asphaltene Aggregation in Model Heptane–Toluene Mixtures on Stability of Water-in-Oil Emulsions. *J. Colloid Interface Sci.* 1997, 196, 23–34.

(27) Mullins, O. C. The Modified Yen Model. *Energy Fuels* 2010, 24, 2179–2207.

(28) Mullins, O. C. The Asphaltene. *Annu. Rev. Anal. Chem.* 2011, 4, 393.

(29) Mullins, O. C.; Sabbah, H.; Eysaoutier, J.L.; Pomerantz, A. E.; Barr, L.; Andrews, A. B.; Ruiz-Morales, Y.; Mostowski, F.; McFarlane, R.; Goul, L. Advances in Asphaltene Science and the Yen–Mullins Model. *Energy Fuels* 2012, 26, 3986.

(30) Coelho, R.; Ovales, C.; Benson, I. P.; Hascakir, B. Effect of Clay Presence and Solvent Dose on Hybrid Solvent–Steam Performance. *J. Pet. Sci. Eng.* 2017, 150, 203–207.

(31) Kar, T.; Ovales, C.; Rogel, E.; Vien, J.; Hascakir, B. The Residual Oil Saturation Determination for Steam Assisted Gravity Drainage (SAGD) and Solvent-Sage. *Fuel* 2016, 172, 187–195.

(32) Demir, A. B., Bilge, H., Hascakir, B., 2016. The Effect of Brine Concentration on Asphaltene Stability. Paper presented at the SPE Annual Technical Conference and Exhibition, Dubai, UAE, 26–28 September. DOI: 10.2118/181706-MS.

(33) Chen, Q.; Gray, M. R.; Liu, Q. Irreversible Adsorption of Asphaltene on Kaulinite: Influence of Dehydroxylation. *Energy Fuels* 2017, 31, 9328–9336.

(34) Blui, U. K.; Sanyal, S.; Saha, R.; Rakshit, S.; Pal, S. K. Steady-state and time-resolved fluorescence spectroscopic study of petroleum crudes in aqueous-surfactant solutions: Its implications for enhanced oil recovery (EOR) during surfactant flooding. *Fuel* 2018, 234, 1081–1088.

(35) Mikami, Y.; Liang, Y.; Matsuoka, T.; Boek, E. S. Molecular Dynamics Simulations of Asphaltene at the Oil–Water Interface: From Nannoggregation to Thin-Film Formation. *Energy Fuels* 2013, 27, 1838–1845.

(36) ASTM International. (2011). ASTM D2007–11, “Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay– Gel Absorption Chromatographic Method”. West Conshohocken, PA, DOI: 10.1520/D2007-11