Microemulsion-enhanced displacement of oil in porous media containing carbonate cements

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GRAPHICAL ABSTRACT

ARTICLE INFO

Keywords:
- Microemulsion
- Surfactant
- Oil
- Wettability
- Imbibition
- Carbonate cement

ABSTRACT

Subsurface porous formations containing nonaqueous phase liquids (NAPLs) such as crude oils are often targets for surfactant flooding during enhanced oil recovery (EOR) or aquifer remediation processes designed to mobilize and solubilize oil. Recent studies suggested that putting surfactants into microemulsified state prior to injection might improve their performance. Most of these studies proved that microemulsion (ME) efficiency depends on test conditions and the proper selection of their chemical formulations and brine chemistry. However, the impact of rock characteristics on the complex fluid-rock interactions is still unclear, especially in heterogeneous rocks. The goal of this fundamental study was to examine the effect of MEs on oil displacement in three different aged rocks (Berea, Edwards, and Tensleep) and identify the test conditions in which MEs outperform surfactants. The effectiveness of surfactants and MEs was evaluated at two concentrations from different sets of spontaneous imbibition tests and petrographic analyses. Several mechanisms such as reduction of interfacial tension (IFT), oil emulsification, and wettability alteration were responsible for the improved recovery. Wettability alteration of aged cores by surfactants and MEs led to an early oil removal by spontaneous imbibition while emulsification increased the ultimate amount produced. Both additives lowered the IFT from 12 to less than 1 mN/m. However, high ME concentration was able to decrease the size of oil droplets by one order of magnitude.
1. Introduction

Surfactant flooding or flushing processes hold particular promise for cleaning up or recovering the oil left in subsurface formations after secondary waterflooding or traditional pump and treat methods. The oil phase is usually entrapped in the form of ganglia within the fine pores of reservoir rocks due to large capillary forces [1]. With their amphiphilic structure, surfactants to accumulate at oil/water interfaces and lower the IFT, enhancing the mobilization of small and deformable oil droplets through pores and throats [2]. They may also adsorb on rock surfaces and promote the micellar solubilization of surface-active oil species (such as asphaltene), thereby restoring the wettability of the rock. The extent by which wettability is altered depends on the type of surfactant and the rock properties [3]. Surfactants with an intermediate hydrophilic-lipophilic balance (HLB) number favor the mobilization and, to a lower extent, the solubilization of oil in porous media [4]. Mobilization in this case manifests by the in situ formation of bi-continuous Wirsing Type III microemulsions, consisting of bilayer vesicles in equilibrium with oil and water phases [5].

A major limitation of surfactant flooding is the chemical losses encountered within the first few inches of the formation due to adsorption on minerals. Recent studies suggest that putting surfactants into microemulsified state prior to injection may improve their performance. Because MEs exhibit lower adsorption propensity on mineral rocks [6], better demulsification capacity [7], and higher stability at elevated temperature and brine pH/salinity compared to surfactant solutions [8], they are considered as good carrier systems that can deliver surfactants deeper into the formation [9], and maintain the surfactant concentration in the displacement front [10]. Microemulsions are dynamic systems in which the interface is continuously and spontaneously fluctuating [11]. They can form a wide variety of structures and phases depending upon the proportions of their components and other characteristics [12].

Microemulsions typically consist of thermodynamically stable, isotropic, and macroscopically homogeneous dispersions of two immiscible fluids (hydrocarbon and brine) stabilized by a surfactant and co-surfactant [13–15]. The presence of both surfactant and co-surfactant has a dual effect on lowering the IFT [16,17]. The hydrocarbon phase (also called carrier fluid) could be C₆-C₁₈ alkanes [18], biodiesel [19], or natural oils such as pine oil [20], palm oil [21], and terpenes like d-limonene [22,23], which are usually preferred for their solvent qualities and biodegradability [24]. The surfactant should be able to create stable microemulsions when used in specific proportions. The most commonly used ones are biodegradable nonionic surfactants with an HLB number between 8 and 18. Examples include linear alcohol ethoxylates with various ethylene oxide numbers (EON) [23,25], alkyl polyglucosides [21], as well as those from the tergitol family [18], and polyisobutene (or tween) family [19]. The co-surfactant consists of short or medium chain primary, secondary and tertiary alcohols with 1–20 carbon atoms such as 2-propanol [18,23], isoamyl alcohol [26], and glycerol monooleate [27]. The alcohol serves as a coupling agent between the solvent and the surfactant, thereby stabilizing the microemulsion by increasing the total interfacial area [28], enhancing the surfactant mass transfer to the interface and decreasing the repulsive forces between its hydrophilic groups [9]. Furthermore, the alcohol lowers the freezing point and the viscosity of MEs to prevent the formation of rigid structures like liquid crystals and gels at the interface [18].

Microemulsions have had several applications in the environmental and petroleum industries. Recent investigations have demonstrated that in-situ flushing with surfactant/alcohol mixtures enhances the remediation of NAPL-contaminated aquifers. The best surfactants had HLB numbers between 12 and 14 [29]. Soil core data indicated that approximately 90–95% of the most prevalent NAPL constituents were removed [30]. Dilute concentrations of microemulsions in brine were also found to be effective in remediating damaged wells during drilling and stimulation treatments. The enhanced fluid recovery and relative permeability were the result of IFT and CA alterations [18,31]. Hydraulic fracturing operations, particularly in tight gas reservoirs, have seen a continuous surge of interest in utilizing MEs to reduce flowback pressure and allow piston-like flow during the recovery of injected fluids, resulting in minimal losses [10]. Unlike wellbore remediation methods, microemulsion flooding involves more than one well and can sweep a much larger area of the reservoir. Several microemulsion formulations in tertiary oil recovery experiments were able to recover a significant portion of the residual oil by drastically reducing the IFT to ultra-low values, enhancing the spontaneous emulsification and displacement of the oil in porous media. Early core flooding experiments with Berea sandstone and microemulsion slugs of finite size showed that the residual oil left behind the flood decreased with increased surfactant concentration and flooding rate [27]. Moreover, higher ME viscosity may enhance the flooding efficiency in reservoir sandstones [26]. Other studies with sandpacks indicated that MEs could produce 4.3% more oil than typical polymer flooding due to the ultra-low IFT values [27]. More recent work with aged carbonate rocks examined the influence of wettability alteration on oil recovery using microemulsion solutions (7 wt% in brine) formulated with different types of surfactants [25]. Cationic surfactants had the highest potential for wettability alteration from neutral-wet to water-wet, leading to incremental recoveries over 26% after conventional waterflooding. Exceptionally high oil recovery factors (over 90%) were also obtained with Tensleep rock by spontaneous imbibition of brine containing complex nanofluids [33].

To better understand the wettability alteration of aged calcite surfaces, molecular dynamics (MD) simulations were performed with model oil molecules and a microemulsion based on a linear alcohol ethoxylate [34]. The simulations revealed that polar molecules of oil (such as naphthenic acids) irreversibly adsorbed on calcite and served as a platform upon which further non-polar molecules could accumulate and form a weakly bound adsorbed layer. The hydrocarbon phase of MEs was effective at swelling the adsorbed layer and reducing its interaction with polar components, leading to easier removal when subjected to a water flow. MD flow simulations with MEs were also performed in aged graphite capillaries to represent kerogen pores in shale [35]. The hydrocarbon and surfactant molecules played separate roles that were both essential in solubilizing the adsorbed oil film. The surfactant acted as a linker that diminished slip effects at the oil/water interface, thereby enabling the hydrocarbon solvent to penetrate the oil film and displace its molecules.

Almost all existing laboratory studies indicate that MEs have a superior ability to mobilize and solubilize oil in porous media, compared to surfactants alone. Yet, microemulsion flooding is considered controversial in EOR and has been debated for many years. The use of ME flooding is mainly dependent on fluid-rock interactions, which are complex especially in heterogeneous rocks. Furthermore, the impact of rock petrophysical attributes on these interactions is still unclear. The objective of this study was to examine the effect of MEs on oil recovery or cleanup from different aged rocks and identify the test conditions in which MEs outperform surfactants alone. We used two different outcrops and a heterogenous reservoir rock to demonstrate the magnitude, significantly enhancing oil mobilization in all three rocks. The solubilization capability of MEs was superior in Tensleep due to their unique ability to penetrate dolomite cements and alter their wettability.
dependence of ME performance on surface mineralogy, roughness, and wettability state of oil-bearing rocks. Novel insights are gained on the unique ability of MEs to alter the wettability of carbonate cements often ubiquitous in heterogeneous rocks.

2. Materials and methods

2.1. Rocks

The rocks consist of two outcrops: Berea sandstone and Edwards limestone, and a reservoir rock from Tensleep formation in Wyoming. The rocks were drilled and cut into small cores 1 inch in diameter and 5 cm in length. Their physical properties are provided in Table S1 of the Supporting Information. Berea and Edwards cores were baked at 110 °C for 24 h to remove any water. Tensleep cores were first cleaned by flooding them with a 50/50 vol mixture of toluene/methanol at 1000 psi and 80 °C until the produced solution was colorless, then baked at 120 °C for 24 h in a constant temperature oven (DKN402, Yamato) to remove the solvents. The porosity and Klinkenberg-corrected permeability of these core samples were measured simultaneously by an automated porosimeter and permeameter (AP-608, Coretest system).

2.1.1. Mineralogy and pore size distribution

The mineralogy of core samples was evaluated using a QEMSCAN 650F from FEI. Imaging by this technique was captured at 25 kV and 6.2 nA and the beam was optimized within 0.05 nA of 10.00 nA. X-ray detectors were used to generate 3.0 × 3.0 mm mineralogy maps with an optical resolution of 0.73 μm per pixel. The pore size distributions of these cores with 5 mm diameter and 20 mm length were measured using an FEI HeliScan micro-CT scanner with a resolution of 1.5 μm per pixel at 100 kV and 52 μA. The digital images were analyzed by using

![Fig. 1. Size distribution (left), micro-CT image of core cross-section (center), and mineralogy map (right) of a) Berea, b) Edwards, and c) Tensleep. The two peaks in pore size distributions represent average pore and throat sizes. A large fraction of Tensleep pores contain dolomite microcrystals (or cement) that are not found in Berea or Edwards.](image-url)
Avizo software.

2.1.2. Petrographic thin section analysis

In order to analyze rock wettability after spontaneous imbibition with different solutions, three sets of petrographic thin sections of Edwards, Berea and Tensleep rocks were prepared by Wagner petrographic company. The thin sections of the clean rocks were also provided as a reference. The size of the thin sections was 46 × 24 mm. Blue epoxy impregnation, K-feldspar stain, plagioclase stain and calcite stain were applied on the thin sections. A petrographic microscope (Zeiss AXIO, Scope. A1) was used for visualization of thin sections. AXIO vision software was also selected to analyze the thin section images.

2.2. Fluids

We used a medium gravity crude oil from Tensleep formation in Wyoming as a NAPL phase (Table S2). The oil was first centrifuged at 6000 rpm for one hour and then filtered with 0.5 μm filter. The brine phase consisted of 0.1 M NaCl in distilled water. A linear alcohol ethoxylate, Biosoft N25-9 (Stepan Co.) was used as a nonionic surfactant (Table S2). This surfactant was also used as an emulsifying agent in microemulsions where d-limonene (MP Biomedicals) was the hydrocarbon solvent and 2-propanol (Fisher Scientific) was the co-surfactant. The surfactant was added to brine to prepare solutions at high (3.3 wt %) and low (0.3 wt%) concentrations. Both concentrations were selected above the critical micelle concentration (CMC) of the surfactant to enhance its efficiency. Although not viable, the high concentration was merely used to better understand differences in the fundamental mechanisms of surfactant and ME floodings.

In order to visualize the structures of these MEs, a Tecnai TF-20 S-Twin High Resolution Transmission Electron Microscope (HRTEM) from FEI was used at 220 kV. MEs were carefully transferred on silicon dioxide coated carbon TEM grids (SPI supplies) and dried overnight before the imaging process. ImageJ software was used for image analysis.

2.3. Dynamic interfacial tension and contact angle

The interfacial tension between Tensleep oil and different brine solutions (0.1 M NaCl, 0.3 wt% surfactant, and 0.8 wt% ME containing 0.3 wt% surfactant) were measured by the pendant drop and rising/captive bubble tensiometer, which was described in a previous study [36]. The needle diameter was selected between 0.364 mm to 1.762 mm in order to approach a bond number close to unity. Images were captured every 1 min and analyzed using Axisymmetric Drop Shape Analysis (ADSA). The dynamic IFT of brine solutions with low additive concentration (0.3 wt% surfactant and 0.8 wt% ME containing 0.3 wt% surfactant) was measured at least 3 times and the average values were reported in figures with error bars. The IFT of brine solutions with high additive concentration (3.3 wt% surfactant and 8 wt% ME containing 3.3 wt% surfactant) were also measured by a spinning drop tensiometer (SITE100, Kruss) due to their low values. The rotation speed was set to 3260 rpm and the measurement interval was 30 s.

Measurements of the static contact angle of oil/water/rock systems were performed using the IFT/CA apparatus [36]. The rocks were cut into small substrates that were vacuumed at 10⁻⁷ psi for 12 h then immersed in oil. After aging in oil for 7 and 14 days at 60 °C, they were gently placed in the IFT/CA cell. Brine (with and without chemical additives) was then transferred to the cell until the substrates were fully immersed. The oil inside the substrates formed several small oil droplets on the surface of the rock, as it was released by spontaneous imbibition of brine. Images of these droplets were taken after 24 h and analyzed by ImageJ software to estimate the contact angles. Fig. S1 illustrates an example of these images with Edwards rock substrates after being aged in oil for 0, 7, and 14 days.

2.4. Droplet size distribution

In order to estimate the oil drop size distributions in brine solutions, oil and brine (50/50 vol ratio) with different additive concentrations were mixed for 5 h at a speed of 500 rpm. The rag layers (or Winsor Type III microemulsions) formed between these phases were diluted 20 times in the same brine solutions to enhance their transparency to light, then immediately transferred into cuvettes. A particle sizer and zeta potential analyzer (Brookhaven Instruments Co.) was used to measure the droplet size of emulsions via dynamic light scattering technique (DLS). Each measurement was conducted for 1 min and repeated at least 5 times to reduce experimental error. ZetaPlus Particle Sizing Software was used to analyze the droplet size distribution of these emulsions.

2.5. Spontaneous imbibition

For the spontaneous imbibition tests, the cores were first vacuumed at 10⁻⁷ psi for 12 h. Oil was then injected into the vacuum cell to saturate the cores for 24 h. The cores were aged in Tensleep oil at 60 °C for 7 and 14 days. After the aging process, the cores were weighed, placed in Amott cells, and then immersed in different brine solutions (0.1 M NaCl, 0.3 wt% surfactant, 3.3 wt% surfactant, 0.3 wt% ME, and 3.3 wt% ME). The produced oil was recorded in time until recovery was complete.

3. Results

3.1. Rock characterization

The mineral map and composition of the three core samples are provided in Fig. 1 and Table S3. They show that Berea consists of 85% quartz and a small fraction of other minerals, such as kaolinite, K-feldspar, illite, albite, etc. Edwards is homogeneous with respect to mineralogy and contains over 99% of calcite. Tensleep consists of 84% quartz and small fractions of other minerals, which are similar to Berea. However, in contrast to Berea, some of the pores in Tensleep are filled with gypsum/anhydrite and most of the pores contain dolomite microcrystals. These microcrystals may have formed during the precipitation of evaporite minerals within Sabkha sediments. Although the percentage of these microcrystals is only about 3.7%, the dolomite coatings can change the mineralogy of the pore surface and increase its roughness, thereby affecting wettability and fluid flow in the porous rock.

Fig. 1 also displays the micro-CT images of the three rocks under study. Berea is a fine-grained, well sorted, and well-rounded sandstone. Its pore size distribution has two peaks, which represent their average pore and throat sizes. The average pore and throat sizes of Berea are about 55 μm and 3 μm, respectively. In contrast, the average pore size of Edwards is about 65 μm, which is higher than Berea. The pore size distribution of Edwards is much wider than Berea, which means that Edwards has a larger number of small and large pores than Berea. Thus, the size distribution of Edwards makes it easier to trap oil inside the pores compared to Berea. Tensleep has fine to medium, subrounded detrital quartz grains that are embedded in a pervasive microcrystalline dolomite cement, seen here as white particles inside the pores [37]. These cements enhance the roughness of grain surfaces, in agreement with the mineralogy map. Abundant gypsum/anhydrite patches or stripes are also distributed in the rock with almost no porosity. This matrix heterogeneity is a result of variation in lithologies, depositional structures, and diagenetic modifications [38]. Tensleep has the widest pore size distribution, which indicates that there is a large amount of big and small pores available in this rock. The average pore size of Tensleep is about 60 μm.
3.2. Microemulsion phase behavior

The pseudo-ternary phase diagram of MEs was prepared by first mixing surfactant and alcohol at a fixed weight ratio of 2.5/1 to form Smix. D-limonene was then added at different weight ratios (1/9, 2/8, 3/7, 4/6, 5/5, 6/4, 7/3, 8/2, 9/1) and the phase diagram was obtained by titrating these mixtures with brine. Fig. 2a presents the phase diagram of this system where the solid arrows indicate the path of microemulsion dilution in brine until the desired surfactant concentrations were reached. We found that mixtures of surfactant, d-limonene, brine, and 2-propanol generated at a specific weight ratio of 2/1/1/0.8 provided stable and transparent microemulsions over a period of 3 months at ambient conditions. When Smix to d-limonene ratio was lower than 4/6 (area below dashed line), oil-in-water (o/w) emulsions formed and extended over a wide area with increasing water content. The size of emulsions was large enough to scatter light and as such they appeared as cloudy milky white colloidal solutions. Conversely, when Smix to d-limonene ratio was higher than 4/6 (area above dashed line), transparent MEs were obtained. The high concentration of Smix contributed to a lower IFT and higher emulsification ability, which could promote the formation of MEs. More details of the preparation procedure are provided elsewhere [39].

HRTEM micrographs of MEs with low surfactant concentration are presented in Fig. 2b. The average size of d-limonene droplets was about 90 nm. The dark layers around these droplets represent surfactant molecules adsorbed at d-limonene/brine interfaces. At these interfaces, the hydrophobic tails of surfactant remain in the d-limonene while the hydrophilic heads of the surfactant stretch toward the aqueous phase. In addition to the adsorbed surfactant molecules on the d-limonene/water interfaces, there was a large fraction of small surfactant micelles in the solution with an average diameter of 3.3 nm. This indicates that free micelles and adsorbed surfactant molecules coexist in microemulsions.

3.3. Dynamic interfacial tension and drop size distribution

The effect of MEs on the dynamic interfacial tension between oil and brine was studied at ambient conditions. Two ME concentrations were used: 8 wt% ME (containing 3.3 wt% of surfactant), and 0.8 wt% ME (containing 0.3 wt% of surfactant). Surfactant solutions in brine (0.3 and 3.3 wt%) were also tested for comparison. Without any additives, the IFT between oil and brine was about 11.8 mN/m after 600 mins. It sharply decreased to 0.8 mN/m and 0.3 mN/m upon introduction of small concentration of surfactant and ME, respectively (Fig. 3a, left). The 2-propanol molecules in ME could partition between the brine and oil phases and behave in many respects as nonionic co-surfactants, further reducing the IFT [40]. At high concentration, IFT reached equilibrium within the first 100 min to stabilize at 0.39 and 0.26 mN/m with surfactant and ME, respectively (Fig. 3a, right). Although the difference between these low IFT values was rather small, it had a large impact on the size of oil droplets. Fig. 3b presents the size distribution of oil droplets measured by DLS at different additive concentrations in
brine. The oil droplets were taken from the diluted rag layer formed between oil and brine phases according to the procedure described in Section 2.3. We found that the average drop sizes generated by low additive concentration were similar and in the 100–200 μm range. However, drops at high ME concentration (D = 9.2 μm) were less polydisperse and more than one order of magnitude smaller than those formed by high surfactant concentration (D = 156 μm). While concentration did not affect drop sizes in surfactant solutions since it was above their CMC, it had a significant impact in MEs. At high concentration, the amount of d-limonene and 2-propanol in ME was large enough to significantly reduce the size of these droplets. This in turn had significant implications for oil mobilization in porous media, as shown in the next sections.

3.4. Wettability alteration

3.4.1. Effect of aging time

The wettability alteration of Berea sandstone, Edwards limestone, and Tensleep sandstone over different aging times with oil was first examined through contact angle measurements with brine alone. The substrates were immersed in oil inside a sealed container for 7 and 14 days at 60 °C. During the aging process, asphaltene molecules adsorbed on the rock surfaces, altering their wettability [4]. Since adsorption is a kinetic process, wettability alteration is a function of aging time. After 7 days of aging, the contact angles became almost constant, indicating that a minimum of one week was needed to alter the wettability of these substrates, as shown in the top curves of Fig. 4. Aging the rocks for 14 days slightly increased the static contact angles, especially for Edwards limestone. Both Tensleep and Edwards exhibited the highest wettability alteration with an increase in CA from 78° to 150° and from 72° to 166°, respectively. This could be explained by the strong adsorption of oil polars onto calcite in Edwards and dolomite in Tensleep [41]. Similar trends were observed with Berea sandstone where wettability was altered from water-wet to weakly oil-wet after 14 days of aging.

The effect of additives on the wettability alteration of Berea,
Fig. 4. Average static contact angles of oil droplets released from aged a) Berea, b) Edwards, and c) Tensleep rocks during imbibition in brine, surfactant and ME. Both surfactant and ME alter the wettability of Berea and Edwards from oil-wet to water-wet, regardless of aging time. With Tensleep however, the surfactant is not as effective as ME in altering wettability, especially at longer aging times.

Edwards, and Tensleep substrates was also investigated at high concentration. Fig. 4a shows that both surfactant and ME restored the wettability of aged Berea substrates from weakly oil-wet to water-wet, with a contact angle of 66° and 49°, respectively. Surfactant molecules adsorbed with their hydrophobic tails on the mineral surface and created a hydrophilic layer with their polar heads [3], enhancing the momentum transfer efficiency across the oil/water interface and promoting the solubilization of the adsorbed oil layers [35,42]. The high performance of MEs was likely due to the ability of d-limonene to penetrate and swell the adsorbed oil layers, also enhancing the amount of d-limonene solvent and therefore the emulsions. By increasing surfactant concentration in MEs, we are promoting the solubilization of the adsorbed oil layers.

3.4.2. Effect of additive concentration

To further understand the effect of ME on wettability alteration, the contact angles of oil droplets released from 14 day-aged rocks during imbibition in brine, surfactant and ME with different surfactant concentrations (i.e., 0.3 and 3.3 wt%) were measured, as shown in Fig. 5b. Concentration had little effect on the wettability of Berea, indeed both low and high surfactant and ME concentrations altered the wettability of Berea from oil-wet to water-wet. The impact of concentration was more prominent on Edwards rock, with a 40° decrease in CA at high surfactant and ME concentrations. This implies that surfactant molecules interacted similarly with calcite whether they were alone or within microemulsions. In contrast, increasing concentration in surfactant solutions did not affect the neutral wettability of Tensleep, since the contact angles on dolomite cement could only be altered by microemulsions. By increasing surfactant concentration in MEs, we are also enhancing the amount of d-limonene solvent and therefore the ability of this phase to penetrate and swell the adsorbed oil layers, further altering rock wettability from 96° to 57°.

3.5. Spontaneous imbibition

3.5.1. At high additive concentration

Spontaneous imbibition tests with brine, microemulsions, and surfactant solutions with a surfactant concentration of 3.3 wt% were first conducted on Berea, Edwards and Tensleep rocks at different aging times to investigate the performance of MEs. This high concentration was chosen to significantly enhance the differences between surfactant and ME. The volume of oil produced from the cores during spontaneous imbibition was recorded for at least 30 days until no more oil was produced.

3.5.1.1. Berea sandstone. Fig. 6 shows the effect of high surfactant and ME concentration on oil recovery from Berea at different aging times prior to imbibition. Earlier production was recorded with surfactant compared to brine due to wettability alteration towards more water-wet conditions, although the final amount produced was very similar (i.e., about 55%). This is because Berea is a well-sorted sandstone rock with relatively homogeneous pore sizes (Fig. 1a). Brine and surfactant solution could invade into most of the pores, leaving some oil behind due to unfavorable threshold capillary pressures of altered surfaces and bypassing of oil caused by pore-scale displacement mechanisms, which is more prone in water-wet surfaces. The addition of ME to brine could significantly enhance oil removal from Berea and produce 86% of oil, which was 35% more than surfactant and brine. This increase in the amount of oil recovery was independent of aging time, suggesting that emulsification was the driving force and not wettability alteration. The sharp decline of IFT from 11.8 to 0.26 mN/m promoted the formation of very small oil droplets (Fig. 3, right) that were easier to mobilize through the porous rock because their sizes were smaller than the pores and throats of Berea.

Fig. 5a reveals that the contact angle distribution of oil droplets on the substrates immersed in surfactant solutions spans over a wide range of values (i.e., from 70° to 140°). In other words, a small fraction of the substrate surface became water-wet while a larger fraction remained neutral-wet or oil-wet. By comparison, the contact angle distribution with ME was narrower and ranged from 50° to 80°, indicating that the wettability of a large fraction of the rock has been restored to its water-wet condition. The main difference between Tensleep and the other rocks is the presence of dolomite microcrystals throughout the pores (Fig. 1). These rough microcrystalline cements may make it harder for surfactant alone to solubilize oil from their surfaces.
layers adsorbed on grain surfaces that brine alone could not remove. Imbibition with surfactant and ME restored wettability to a great extent by solubilizing most of the adsorbed oil, in agreement with Figs. 4 a and 5 b.

3.5.1.2. Edwards limestone. Fig. 7 shows oil recovery from spontaneous imbibition tests conducted on aged and non-aged Edwards cores using brine and high concentration of surfactant and ME. The strong wettability alteration of carbonates from 72° to 166° upon contact with oil (Fig. 4b) is an important parameter that controls fluid displacement in this type of rocks. As the rock becomes strongly oil-wet after 14 days, brine alone is not able to invade the pores resulting in a one order of magnitude drop in oil removal with aging time, from 40% to 4%. Surfactant on the other hand could produce more oil than brine. In non-aged rocks for example, the slight increase in recovery with surfactant compared to brine was mainly attributed to a decrease in IFT. As a result, surfactant could invade some of the larger pores of Edwards that brine alone could not. The oil removal with surfactant was almost independent of aging time, in agreement with Fig. 4b. MEs exhibited the same wettability behavior as surfactants, according to Figs. 4b and 5b. Therefore the constant 25–30% additional oil removal with MEs compared to surfactant in Fig. 7 was mainly due to the increased emulsification of oil droplets (Fig. 3b, right), thereby enhancing their mobilization in Edwards limestone, similar to Berea sandstone. Note that during the imbibition of non-aged Edwards with high ME concentration, the volume of produced oil was 3.68 ml, which indicates that 3.68 ml of the brine phase (containing 0.07 ml of d-limonene) has invaded into the pores to displace this oil. If limonene was produced with the oil, it will constitute only 2% of the oil recovery.

The thin section analysis of Edwards cores used in the spontaneous imbibition tests indicates that the thickness of adsorbed oil layers on grain surfaces has been reduced by high concentration surfactant and ME (Supporting Information, Fig. S3). Due to the strong interactions between oil polar molecules and carbonate, surfactant and ME could solubilize some adsorbed layers but not to the same extent as Berea.

3.5.1.3. Tensleep sandstone. Fig. 8 shows the effect of high concentration additives on oil recovery from aged and non-aged Tensleep cores, and their comparison with brine. Aging this rock in oil delayed and curbed oil production by spontaneous imbibition in brine due to wettability alteration from water-wet to oil-wet (Fig. 4c). A thin section of this core is shown in the Supporting Information (Fig. S4) where wettability alteration was intermediate between those of Berea and Edwards, in agreement with Fig. 4. This explained why brine could displace less than 20% of oil from Tensleep. The behavior of high concentration surfactant solutions was very peculiar in this rock. While
initially larger than 20%, oil removal with surfactant decreased with aging time until it became zero with 14 day-aged cores. This gradual decrease was consistent with the systematic increase in contact angle with aging time, as shown in Fig. 4c with surfactant. Examination of the thin section in Fig. S4c revealed that the surfactant formed large bi-continuous phases at the surface of dolomite cements that could not detach within the time scale of the experiment. At such a high concentration, surfactant micelles were able to penetrate the microporous structure of dolomite cement, due to the low IFT, and trap oil in the form Winsor type I microemulsions. The small oil droplets further clustered and percolated into larger bi-continuous phases that continuously grew and diffused through the porous cement. [43] These phases extended deeper into the oil adsorbed on dolomite surface and did not detach from it because the surfactant could not alter its wettability. The accumulation of these phases on dolomite eventually blocked the water channels within the first day, significantly impeding oil recovery or cleanup. This behavior was not observed with microemulsions. Indeed, MEs were very effective at cleaning up the surface of sand grains including dolomite cements. Due to its lower viscosity, the d-limonene solvent present in MEs could penetrate and swell the oil trapped in dolomite cements, leading to more effective desorption [34,35,44]. A schematic explaining this mechanism is illustrated in Fig. S5 of the Supporting Information.

3.5.2. At low additive concentration
Another set of spontaneous imbibition tests were undertaken to investigate the impact of more economically viable additive concentration (i.e., 0.3 wt%) on oil recovery from 14 day-aged rocks. The results displayed in Fig. 9 indicate that the performance of surfactant and ME was very similar in Berea and Edwards but differed in Tensleep. At low concentration, the oil/brine IFT dropped from 12 mN/m to 0.8 mN/m and 0.3 mN/m with surfactant and ME, respectively. However, the amount of limonene and 2-propanol in ME was not large enough to reduce the size of oil droplets compared to the surfactant alone (Fig. 3b, left). As a result, the amount of oil mobilized by surfactant and ME was comparable and equal to 62% in Berea and 50% in Edwards (Fig. 9a,b). The variations seen in Tensleep were mainly attributed to the unique ability of MEs to solubilize oil from carbonate cements, as detailed in the previous section, although their cleaning power was reduced at low concentration (Fig. 9c). Overall, ME could recover 28% of oil from...
Tensleep, which was 7% higher than surfactant alone and 16% higher than brine. These recoveries were lower than those in Berea and Edwards due to the presence of anhydrite beddings with almost no porosity in Tensleep. In all the rocks examined here, oil recoveries at low additive concentration were lower than those at high concentration, except for surfactant imbibition in Tensleep. In this case, low surfactant concentration produced 20% of oil, compared to none at high concentration. This is because surfactant micelles could not penetrate dolomite cement and formed large bi-continuous phases that restricted oil displacement in this rock.

3.5.3. Effect of rock type on oil removal

Berea is a well-sorted, relatively homogeneous rock that mainly consists of quartz and a small fraction of other minerals. Because of its relatively uniform pore size distribution and water-wetness, brine, surfactant and ME floodings exhibited the highest ultimate oil recovery with Berea among all three rocks. Edwards is homogenous with respect to mineralogy (over 99% of calcite) but heterogeneous with respect to pore size distribution. Therefore, Edwards tend to trap more oil inside the pores and can easily be altered to oil-wet during the aging process. MEs and surfactant recovered less oil from non-aged Edwards compared to Berea. After 14 days of aging in oil, the ultimate oil recovery with brine from Edwards was significantly lower than that from 14 days aged Berea due to the oil-wet state of Edwards rock. Tensleep consists of 84% of quartz and small fractions of other minerals, which are similar to Berea. However, in contrast to Berea, some of the pores in Tensleep are filled with gypsum/anhydrate. This resulted in a poor connectivity between the capillary elements of this rock and consequently led to more trapped oil. Therefore, brine, surfactant and MEs exhibited the lowest ultimate oil recovery from Tensleep among all three rocks. The existence of pervasive dolomite microcrystals inside Tensleep affected the performance of surfactant significantly. In contrast to Edwards and Berea, high concentration of surfactant could not recover any oil from this rock within the time scale of the experiment due to the existence of dolomite cement while MEs exhibited exceptional performance in oil removal. The results of this study indicate that ME flooding is an attractive remediation or EOR process in oil-wet heterogeneous formations containing microcrystalline carbonate cements.

4. Conclusions

The impact of an environmentally friendly ME formulation on the cleanup or recovery of oil was examined using spontaneous imbibition.
tests and petrographic analyses. Two different outcrops, Berea sandstone and Edwards limestone, and a heterogeneous reservoir rock, Tensleep sandstone, were used to demonstrate the dependence of ME performance on mineral texture and wettability state. The fluids consisted of 1 M NaCl brine, two ME solutions in brine containing 0.3 wt% and 3.3 wt% of a linear alcohol ethoxylate surfactant, and two surfactant solutions at the same concentrations. Rock substrates and cores were aged with crude oil for 7 and 14 days to establish a wide range of wettability states. The cores were then subjected to imbibition tests to investigate the effectiveness of surfactants and MEs in enhancing oil recovery or removal. A systematic analysis of IFT values, drop size distributions, thin sections, and CA data at different aging times was used to explain the fluid displacement mechanism observed during the imbibition process. Below are the main conclusions summarized for each rock:

1. In Berea and Edwards, the ultimate recovery with high ME concentration constantly outperformed that of surfactant and brine in all wettability states due to the emulsification of oil into very small droplets. The amount of d-limonene solvent and 2-propanol cosurfactant in ME was large enough to reduce the size of oil droplets by more than one order of magnitude, resulting in 25–35% additional oil removal over surfactant solutions. On the other hand, the performance of low surfactant and ME concentration was alike due to comparable effects on IFT, emulsification, and wettability alteration. Therefore, the use of ME over surfactant alone was not justified at low concentration.

2. Solubilization of adsorbed oil by surfactant and ME was comparable in Berea and Edwards but very different in Tensleep due to the presence of dolomite cement. The solubilization of oil by high surfactant concentration led to the formation of bi-continuous phases at cement surfaces that blocked water channels, significantly impeding oil removal. Microemulsions outperformed surfactants in Tensleep rock even at low concentrations due to the unique ability of d-limonene solvent to penetrate microcrystalline dolomite cements of Tensleep and alter their wettability.

Acknowledgments

The authors would like to thank Newfield Exploration and the National Science Foundation (Career Award #1351296) for financial support. The authors are also grateful to Elizabeth Barsotti for QEMSCAN analysis, Wendi Kuang for microCT imaging, and Dr. Joshua Stecher for HRTEM imaging.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.colsurfa.2017.07.017.

References


