

# Comparative Study of Ketone and Surfactant for Enhancement of Water Imbibition in Fractured Porous Media

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**ABSTRACT:** This paper presents a comparative study of two wettability modifiers with different characteristics for enhancing water imbibition from a fracture into the surrounding matrix. One is 3-pentanone, a symmetric short ketone, and the other is 2-ethylhexanol–4 propylene oxide–15 ethylene oxide, a non-ionic surfactant with an ultrashort hydrophobe. They were used as low-concentration additives (approximately 1 wt %) to reservoir brine in this research. The coreflooding experiments using fractured limestone cores showed that the 3-pentanone solution resulted in more rapid oil recovery by water imbibition than the surfactant solution. The difference in oil recovery response between the two chemical solutions was attributed to the main difference between them as wettability modifiers; that is, the 3-pentanone solution keeps the original water/oil interfacial tension, but the surfactant solution lowers it by 2 orders of magnitude.

## 1. INTRODUCTION

Tight oil reservoirs often show a rapid decline in the production rate, indicating a critical need for improved oil recovery methods. For example, a decline of 60–70% in the oil production rate within the first year has been reported for tight formations in the Eagle Ford.<sup>1,2</sup> Therefore, primary recovery factors in tight oil reservoirs are typically smaller than 10%.<sup>2–7</sup>

Several methods of improved oil recovery in shales (or shale IOR) have been proposed and studied in the literature. They are likely affected by the significant heterogeneity typically observed for shales.<sup>8,9</sup> For example, their petrophysical properties are complex because of a variety of minerals and total organic content. As a result, shale IOR methods using aqueous injection fluids will be affected by the heterogeneous wettability in addition to ultralow permeabilities.<sup>10,11</sup> Alvarez and Schechter stated that most tight oil reservoirs are originally intermediate-wet to oil-wet.<sup>11</sup>

Surfactant solutions were studied for shale IOR and/or fracturing fluids by many researchers. Expected mechanisms include wettability alteration and interfacial tension (IFT) reduction between the aqueous and oleic phases.<sup>7,12–21</sup> Different types of surfactants (e.g., anionic, non-ionic, and cationic surfactants) have been tested for their ability to alter rock wettability, reduce the water/oil IFT, and improve oil recovery.<sup>15,17–19,21</sup> Alvarez et al. showed that both anionic and non-ionic surfactants altered the wettability of carbonate shale and siliceous shale from oil-wet to water-wet.<sup>15</sup> Liu et al. tested anionic and non-ionic surfactants with siliceous shale.<sup>21</sup> Their results showed that non-ionic surfactants did not affect the contact angle, while anionic surfactants altered rock wettability.

Alvarez et al. indicated that the IFT reduction was important, but the IFT should not reach an ultralow value ( $10^{-3}$  mN/m) for shale IOR.<sup>17,18,22</sup> Kathel et al. also stated

that an ultralow IFT limited the surfactant imbibition rate and, therefore, oil recovery.<sup>7,14</sup> Adibhatla et al. demonstrated that the oil recovery rate decreased with decreasing IFT when the wettability was altered by a surfactant solution.<sup>23,24</sup> This seems to be a marked difference from the conventional surfactant-enhanced oil recovery, which depends upon achieving ultralow IFT during the oil displacement.<sup>25</sup>

In addition to surfactant, alcohol solution was studied in the literature for wettability alteration. Lu et al. presented a study of 1-pentanol solution for wettability alteration.<sup>26</sup> Their experimental results showed that the contact angle of a petroleum fluid on calcite was significantly decreased in 1 wt % 1-pentanol solution. The effect was more evident with 0.5 wt % 1-pentanol at a high NaCl or MgCl<sub>2</sub> concentrations. They explained that this wettability alteration was because of the accumulation of 1-pentanol in the thin brine film between oil and the rock surface.

Chahardowli et al. investigated solvent-enhanced spontaneous imbibition with dimethyl ether (DME) and diethyl ether (DEE).<sup>27,28</sup> They performed spontaneous imbibition experiments with sandstone and carbonate cores using DME/DEE solution in brine and demonstrated that DME/DEE could improve oil recovery. They attributed the mechanisms of improved oil recovery to oil swelling and oil viscosity reduction. Their research did not study wettability alteration.

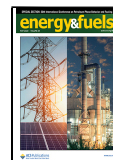
Wang et al. investigated 3-pentanone as an additive to reservoir brine (RB) for improved oil recovery from mixed-wet

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or oil-wet cores.<sup>29</sup> This symmetric ketone is a colorless liquid at standard conditions, nontoxic, widely used in the food industry, and commercially available at a relatively low cost. It was proposed as a novel multifunctional solvent that acts as a wettability modifier without lowering the water/oil IFT and also as a miscible solvent with crude oil at reservoir conditions. Two sets of imbibition experiments using oil-aged limestone cores were performed with RB and 1.1 wt % 3-pentanone solution in RB at 347 K. Results from the spontaneous imbibition experiments showed that the oil recovery factor reached 50.0% with the 3-pentanone solution in RB and 10.0% with RB at day 3. The final oil recovery factor was 51.0% with the 3-pentanone solution in RB and 12.0% with RB. The subsequent forced imbibition determined the Amott index to water to be 0.76 with the 3-pentanone solution and 0.23 with RB. These results indicated a clear, positive impact of a low-concentration 3-pentanone in RB on oil recovery by water imbibition in the cores tested. The improved oil recovery mechanisms include not only wettability alteration but also the miscibility of 3-pentanone with oil that yielded oil swelling and oil viscosity reduction.

In the current research, 3-pentanone and surfactant are compared for the first time as a low-concentration additive to RB, in terms of enhancement of water imbibition from a fracture into the surrounding matrix. They are expected to have different mechanisms as imbibition enhancers because a low concentration of 3-pentanone does not affect the water/oil IFT, unlike surfactant solutions. The surfactant used in this research is a non-ionic surfactant with an ultrashort hydrophobe, 2-ethylhexanol-*x* propylene oxide (PO)-*y* ethylene oxide (EO). Two sets of coreflooding experiments using oil-aged fractured limestone cores were performed with 1.1 wt % 3-pentanone solution in RB and 1.0 wt % surfactant solution in RB at 347 K. In the next section, the materials and methods used for this research are presented. Section 3 presents the main experimental results. Section 4 gives conclusions.

## 2. MATERIALS AND METHODS

This section presents the materials and methods used for the current experimental study. Part of the information regarding 3-pentanone and its mixtures with oil and reservoir brine was presented by Wang et al.<sup>29</sup> Although the important data are duplicated in this paper, more details can be found in their original paper.

**2.1. Reservoir Fluid Properties.** A crude oil sample taken from a tight oil reservoir in Texas was used in this research. Table 1 summarizes properties of this oil sample. The reservoir temperature is 347 K. The reservoir brine (RB) with a salinity of 68 722 ppm was prepared in the lab on the basis of available field data. Table 2 shows the ionic composition of RB. The density of RB was measured to be 1030 kg/m<sup>3</sup> at 347 K and atmospheric pressure. IFT between the crude oil and RB was measured to be 11.44 mN/m at 347 K and

**Table 1. Properties of the Crude Oil Sample Used in This Research<sup>a</sup>**

molecular weight (g/mol)	186
density (kg/m <sup>3</sup> )	823 (at 289 K)
	780 (at 347 K)
SARA (wt %)	
saturates	76.7
aromatics	20.1
resins	3.2
asphaltenes (pentane insoluble)	<0.1

<sup>a</sup>Oil densities and viscosities at high pressures are presented in Figures 1 and 2.

**Table 2. Composition of the RB Used in This Research (68 722 ppm)<sup>a</sup>**

cations	ppm	anions	ppm
Na <sup>+</sup>	25170	Cl <sup>-</sup>	41756
K <sup>+</sup>	210	SO <sub>4</sub> <sup>2-</sup>	108
Ca <sup>2+</sup>	1292		
Mg <sup>2+</sup>	187		

<sup>a</sup>The density of RB was measured to be 1030 kg/m<sup>3</sup> at 347 K and atmospheric pressure.

atmospheric pressure.<sup>29</sup> Figures 1 and 2 show oil viscosities and densities measured at different pressures at 344 K (slightly lower than the reservoir temperature of 347 K).

**2.2. 3-Pentanone Properties.** A sample of 3-pentanone (Sigma-Aldrich) had a purity greater than 99%. The density of 3-pentanone is 760 kg/m<sup>3</sup> at 347 K and atmospheric pressure.<sup>30</sup> The previous research presented the aqueous stability of 3-pentanone in RB at the experimental conditions and investigated wettability alteration and oil dilution (density and viscosity reduction) by 3-pentanone.<sup>29</sup>

Key findings from the previous research are briefly summarized here. It was shown that the average contact angle of oil droplets on oil-aged calcite surfaces in 1.1 wt % 3-pentanone solution in RB rapidly decreased from 95° to 74° within 2 h and then gradually decreased to 26° after 66 h. After 3 days, no oil droplets were observed on the calcite surfaces.

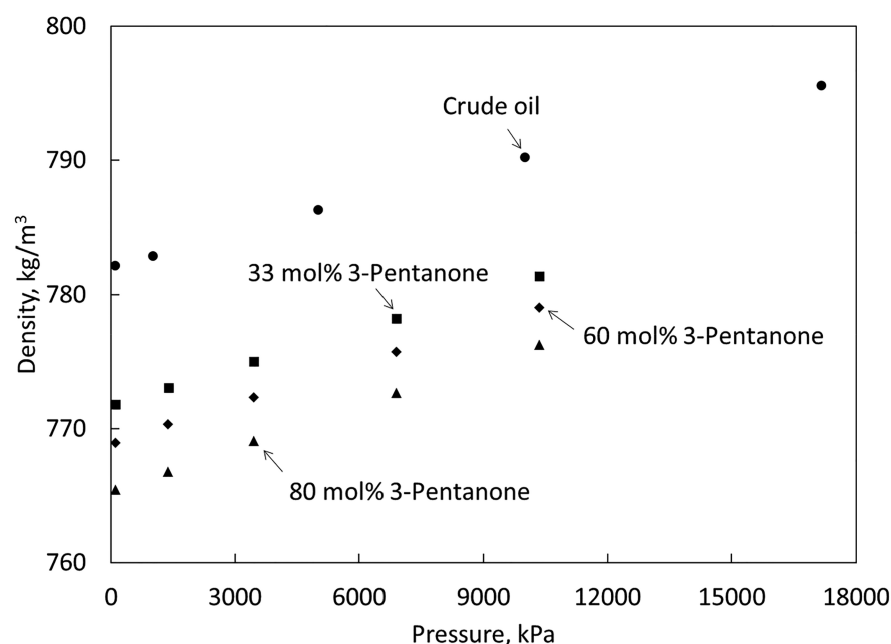
The IFT experiment indicated that the presence of 3-pentanone did not affect the IFT between crude oil and RB (11 mN/m). Density and viscosity experiments for mixtures of crude oil with 3-pentanone showed the capability of oil dilution of 3-pentanone as a solvent (Figures 1 and 2). It is important to reduce oil viscosity even for this light oil in shale IOR.

As in the study by Wang et al.,<sup>29</sup> the concentration of 3-pentanone in RB used in this research is 1.1 wt %, the solubility limit of 3-pentanone in RB at 347 K. The density and viscosity of 1.1 wt % 3-pentanone solution in RB were measured to be 1030 kg/m<sup>3</sup> and 0.52 cP, respectively, at 347 K and atmospheric pressure.

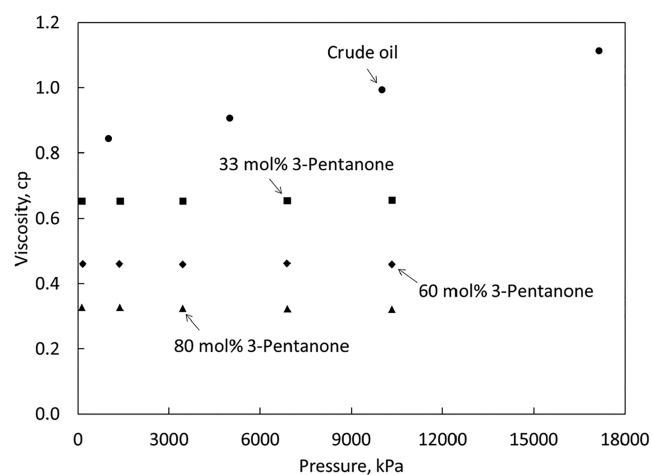
**2.3. Surfactant Formulation.** A non-ionic surfactant was used to make a surfactant solution that lowers the water/oil IFT and changes the wettability to water-wet. The surfactant, 2-ethylhexanol (2-EH)-4PO-15EO, has an ultrashort hydrophobe and was made by alkoxylation of 2-EH with 4 PO and 15 EO groups (Harcros Chemicals). The PO and EO groups affect the hydrophobicity and aqueous stability of the surfactant, respectively. Although other ultrashort hydrophobe surfactants were studied previously for improving polymer flooding by Baek et al., 2-EH-*x*PO-*y*EO surfactants are studied for the first time as a simple surfactant solution for enhancing water imbibition in fractured media in this research.<sup>31</sup>

2-EH-*x*PO-*y*EO was chosen in this research primarily because this cosolvent-based surfactant is simple and abundantly available at a relatively low cost. Several 2-EH-*x*PO-*y*EO surfactants were screened by testing the stability in RB (Table 3). 2-EH-4PO-15EO, 2-EH-4PO-20EO, 2-EH-4PO-25EO, and 2-EH-7PO-20EO in RB showed no salt precipitation, cloudy phase, or phase separation at 347 K. Then, IFTs were measured between the oil (Table 1) and the stable surfactant solutions in RB at 347 K and atmospheric pressure (Table 3). 2-EH-4PO-15EO was selected for this research because it decreases the water/oil IFT and is the shortest among the stable surfactants. The IFT between the oil and the 2-EH-4PO-15EO solution was measured to be 0.21 mN/m at 347 K and atmospheric pressure. The density of the surfactant solution was measured to be 1039 kg/m<sup>3</sup> at 347 K and atmospheric pressure.

Phase behavior was studied with the mixture of oil/2-EH-4PO-15EO/RB at 347 K. Figure 3 shows the sample with a water/oil ratio of 7:3 (i.e., 70 vol % aqueous phase and 30 vol % oil) aged at 347 K for at least 7 days. A small amount of macroemulsion was observed near the interface between the oil and water phases.



**Figure 1.** Densities of crude oil and its mixtures with 3-pentanone. The crude oil densities were measured at 344 K. All other densities were measured at 347 K.



**Figure 2.** Viscosities of crude oil and its mixtures with 3-pentanone. The crude oil viscosities were measured at 344 K, and the other viscosities were measured at 347 K.

**Table 3.** Aqueous Stability of 2-EH-*x*PO-*y*EO Surfactants in RB at 347 K and the IFT Values between the Oil (Table 1) and the Stable Surfactant Solutions at 347 K<sup>a</sup>

surfactant	stability	IFT (mN/m)
2-EH-4PO-15EO	stable	0.21
2-EH-4PO-20EO	stable	0.86
2-EH-4PO-25EO	stable	0.96
2-EH-7PO-10EO	cloudy	
2-EH-7PO-15EO	cloudy	
2-EH-7PO-20EO	stable	0.11

<sup>a</sup>The surfactant concentration is 1 wt %.

**2.4. Contact Angle Experiments.** Contact angle experiments were performed with oil-aged calcite pieces at 347 K. Wang et al. reported the results with 1.1 wt % 3-pentanone solution using the same oil and RB as in this research.<sup>29</sup> This paper presents new results

with 1.0 wt % 2-EH-4PO-15EO solution. The procedure largely follows that by Wang et al., but as explained below, a change to the previous procedure was necessary because it was not possible to continuously monitor oil droplets on the calcite surface with the surfactant solution.<sup>29</sup>

Before the contact angle measurement, the chemical solution and RB were separately degasified at elevated temperatures. Then, oil-aged calcite pieces were placed in RB. Oil droplets were placed on the bottom surface of a calcite piece in the RB glass chamber. The glass chamber was then tightly closed and placed in an oven at 347 K, and a photo of the oil droplets was taken after 30 min. Then, the surfactant solution at 347 K was added to the glass chamber to set the overall surfactant concentration to 1.0 wt %. The glass chamber was then tightly closed and placed in an oven at 347 K. It was observed that the oil droplet was slipping away from the calcite surface after 1 h.

The calcite piece was continued to be placed in the surfactant solution and taken out after 1 day. Then, the calcite piece was rinsed with RB and placed in RB with no surfactant. After the RB chamber was heated in the oven at 347 K, a new oil droplet was placed on the bottom surface of the calcite piece. A photo of the oil droplet was taken then. The contact angles of both sides of each oil droplet were measured using onscreen protractor software. An average contact angle and standard deviation were then calculated.

**2.5. Experimental Procedure for Coreflooding.** Coreflooding experiments were performed at 347 K for two limestone cores. The Indiana limestone cores have the common dimensions with a diameter of 0.0254 m and a length of 0.127 m. The cores were saturated with RB first and then oil, during which the core properties were measured, such as porosity, permeability, and water and oil saturations. The cores were then placed in a container filled with oil for at least 4 months at 347 K. The irreducible water saturation can decrease after aging because of wettability alteration; therefore, both cores were flooded by oil one more time after the long aging period.

Figure 4 shows a schematic of the oil-flooding system used. It consists of an accumulator for crude oil, a pump, a Hassler-type core holder, a hydraulic manual pump to maintain the overburden pressure, a differential pressure gauge, cylinders, and an oven. After a core was placed in the core holder, oil was injected into the cores at 100 cm<sup>3</sup>/h and 347 K until no water production was observed.

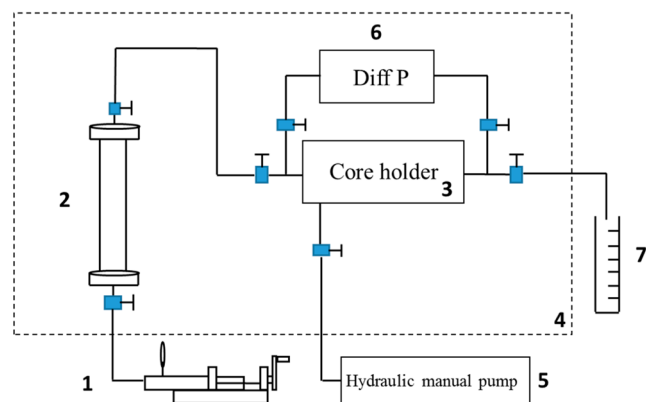
An artificial fracture was created along the longitudinal axis using an electric saw for each core (Figure 5). By following the procedure of



**Figure 3.** Phase behavior test of the mixture of oil/2-EH-4PO-1SEO/RB at 347 K. The surfactant concentration in RB is 1.0 wt %. The water/oil ratio was 7:3 (i.e., 70 vol % aqueous phase and 30 vol % oil).

Mejia, Teflon spacers with 0.001 m in width and 0.127 m in length were placed along two edges of the fracture to maintain a fracture aperture.<sup>32</sup> Then, the core halves were carefully put together with the Teflon spacers in the fracture, wrapped with a Teflon tube, and placed inside a vertically oriented coreholder.

Table 4 summarizes the properties of the cores after the preparation described above. Core 1 was used for the 3-pentanone solution, and core 2 was used for the 2-EH-4PO-1SEO solution.



**Figure 4.** Schematic of the experimental setup for oil flooding (section 2.5).



**Figure 5.** Artificially fractured Indiana limestone core. The diameter is 0.0254 m, and the length is 0.127 m. Table 4 summarizes the properties of fractured cores.

Figure 6 provides a schematic of the experimental setup for coreflooding. It consists of accumulators for crude oil, RB, and chemical solution (3-pentanone or surfactant), a pump, a Hassler-type core holder, a hydraulic manual pump to maintain the overburden pressure, a differential pressure gauge, cylinders, and an oven. As mentioned previously, the oil displacements were gravitationally stable in the vertical direction. After a fractured core was placed in the coreholder, the oven temperature was increased to reservoir temperature (347 K). Then, the core was flooded with crude oil to remove any gas inside the fracture and measure the fracture permeability using the flow rate of 900 cm<sup>3</sup>/h. The overburden pressure was adjusted so that all cores used in this research had similar fracture apertures and fracture permeabilities. Table 4 provides the pressure drops along the cores at 900 cm<sup>3</sup>/h and the overburden pressures used.

Fracture permeabilities were calculated by the method used by Mejia.<sup>32</sup> The equation for flow between parallel plates

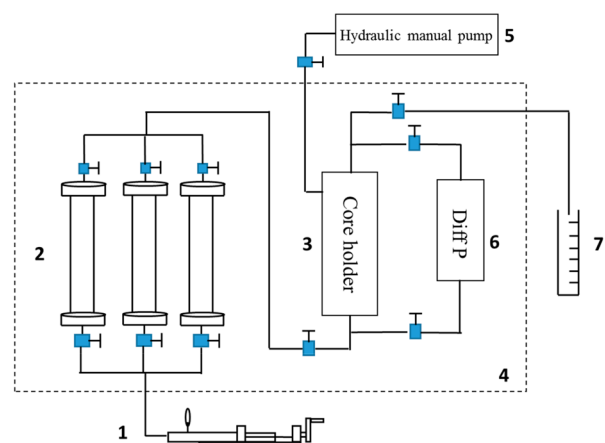
$$b = (3\pi dk_c)^{1/3}$$



**Table 4. Properties of the Cores Used for Coreflooding Experiments<sup>a</sup>**

	core 1	core 2
matrix porosity	0.197	0.203
matrix permeability (mD)	30.8	41.4
matrix water saturation	0.506	0.596
matrix oil saturation	0.494	0.404
flow capacity of the matrix (m <sup>4</sup> )	1.540 × 10 <sup>-17</sup>	2.069 × 10 <sup>-17</sup>
mass of the core before cutting (kg)	0.14847	0.14777
mass of the core after cutting (kg)	0.13691	0.13622
matrix pore volume after cutting (m <sup>3</sup> )	1.166 × 10 <sup>-5</sup>	1.202 × 10 <sup>-5</sup>
pressure drop along with the core at 900 cm <sup>3</sup> /h (kPa)	6.688	6.964
overburden pressure (kPa)	4137	6274
fracture aperture (m)	1.215 × 10 <sup>-4</sup>	1.199 × 10 <sup>-4</sup>
fracture permeability (D)	1246	1214
permeability contrast between fracture and matrix	40455	29324
flow capacity of fracture (m <sup>4</sup> )	3.795 × 10 <sup>-15</sup>	3.649 × 10 <sup>-15</sup>
fracture volume (m <sup>3</sup> )	3.920 × 10 <sup>-7</sup>	3.870 × 10 <sup>-7</sup>
summation of matrix pore volume and fracture volume (m <sup>3</sup> )	1.205 × 10 <sup>-5</sup>	1.241 × 10 <sup>-5</sup>

<sup>a</sup>Core 1 was used for 1.1 wt % 3-pentanone solution in RB. Core 2 was used for 1.0 wt % 2-EH-4PO-15EO solution in RB.



1. Pressurization pump 2. Accumulators 3. Hassler type core-holder 4. Oven 5. Hydraulic manual pump 6. Differential pressure gauge 7. Graduating cylinder

**Figure 6.** Schematic of the experimental setup for coreflooding (section 2.5).

was used to estimate a fracture aperture, where  $b$  is the fracture aperture,  $d$  is the core diameter, and  $k_e$  is the effective oil permeability of the fractured core. The fracture apertures are provided in Table 4. A fracture permeability can be calculated from the fracture aperture by the following equation:

$$k_f = b^2/12$$

Table 4 shows the fracture permeabilities and the permeability contrasts between the fracture and the matrix. The flow capacities of the fracture ( $k_f A_f$ ) and the matrix ( $k_m A_m$ ) are also provided in Table 4.  $A_f$  and  $A_m$  are cross-sectional areas of the fracture and matrix, respectively.  $k_f$  and  $k_m$  are permeabilities of the fracture and matrix, respectively. The flow capacities of the fractures were approximately 200 times greater than those of the matrix.

The corefloods with fractured cores were performed at 347 K in three stages: the first stage with RB, the second stage with a chemical slug (either 3-pentanone or surfactant), and the third stage with "chase" RB. The initial RB stage was at 6 cm<sup>3</sup>/h for 1.5 pore volumes

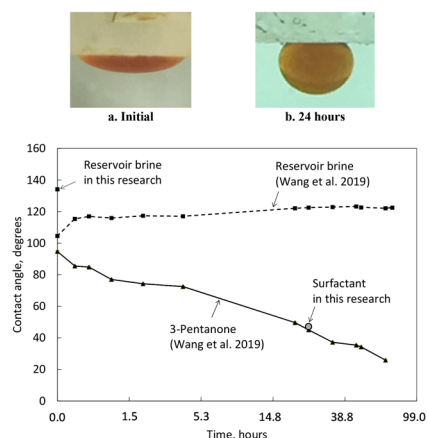
injected (PVI), then at 0.05 cm<sup>3</sup>/h for 0.3–0.4 PVI, and at 6 cm<sup>3</sup>/h until there was no oil production. After that, a chemical slug (3-pentanone or surfactant) was injected at 0.6 cm<sup>3</sup>/h for 1.6 PVI. Finally, the chase RB was injected at 0.6 cm<sup>3</sup>/h. This chase RB flooding was performed until no oil production was observed for core 2 (the surfactant case). However, it was terminated after 1.2 PVI of the chase RB for core 1 because of operational constraints.

The coreflood effluent was collected in plastic graduating cylinders at room temperature. To correct the oil recovery factor for 3-pentanone solubility in oil, the 3-pentanone concentration in recovered oil was measured by the proton nuclear magnetic resonance (<sup>1</sup>H NMR) method for the chemical slug and chase RB flooding periods for core 1.

### 3. RESULTS AND DISCUSSION

This section presents the main results of the contact angle and coreflooding experiments with the 3-pentanone and 2-EH-4PO-15EO solutions. Then, the improved oil recovery mechanisms by 3-pentanone and the surfactant are discussed using the experimental results.

**3.1. Contact Angle Experiments.** As described in section 2.4, the contact angle experiment was performed with 1.0 wt % 2-EH-4PO-15EO solution at 347 K. Figure 7 and Table 5



c. Average contact angles of oil droplets on oil-aged calcite surfaces for three solutions: RB, 1.1 wt% 3-pentanone in RB, and 1.0 wt% 2-EH-4PO-15EO in RB.

**Figure 7.** Contact angles at (a) the initialization of the experiment and (b) 24 h after the calcite piece was immersed in 2-EH-4PO-15EO solution at 347 K and atmospheric pressure. (c) Comparison of the contact angle results for three cases.**Table 5. Contact Angles at the Initialization of the Experiment and at 24 h after the Calcite Piece Was Immersed in 2-EH-4PO-15EO Surfactant Solution at 347 K and Atmospheric Pressure**

droplet	contact angle (deg)		average contact angle (deg)
	left side	right side	
at the initialization	133.2	135.1	134.1
at 24 h	47.5	46.8	47.1

show the contact angles measured at the initialization of the experiment and at 24 h after the oil-aged calcite piece was immersed in the 2-EH-4PO-15EO solution at 347 K and atmospheric pressure. The average contact angle was initially 134.1° but substantially reduced to 47.1° after 24 h. This experiment demonstrated that this ultrashort hydrophobe surfactant can effectively alter the wettability of oil-aged calcite from oil-wet to water-wet within 1 day at 347 K.

Figure 7 also shows the results of the contact angle experiments for 1.1 wt % 3-pentanone solution in RB and RB alone at the same experimental conditions.<sup>29</sup> It appears that 3-pentanone and 2-EH-4PO-1SEO are comparable as wettability modifiers.

**3.2. Coreflooding Experiments.** Coreflooding experiments in this research are concentrated on the water imbibition from a fracture into the surrounding matrix through buoyant and capillary forces. These two forces are considered to be present in tight oil recovery by aqueous injection fluid, but their relative magnitude is uncertain. The buoyant force depends upon the distribution of fluids and fracture dimensions, among many other factors, and these two factors likely become more important when the buoyant force has to overcome a large capillary force at the matrix/fracture interfaces in oil-wet tight reservoirs.

We consider two scenarios for enhancing the water imbibition in shale IOR. One scenario is where a wettability modifier makes the rock surfaces more water-wet without lowering the IFT, which makes the capillary force dominate over the buoyant force. The other is where a surfactant solution makes the water/oil IFT lower and the rock surfaces more water-wet. Both scenarios commonly make the imbibition process less sensitive to the uncertain factors affecting the *in situ* buoyant force, such as fracture properties, petrophysical heterogeneities, and distribution of fluids. The results presented in section 3.1 and those by Wang et al. indicate that we can conveniently use two aqueous injectants, 3-pentanone and 2-EH-4PO-1SEO solutions in RB, for comparing the two scenarios.<sup>29</sup>

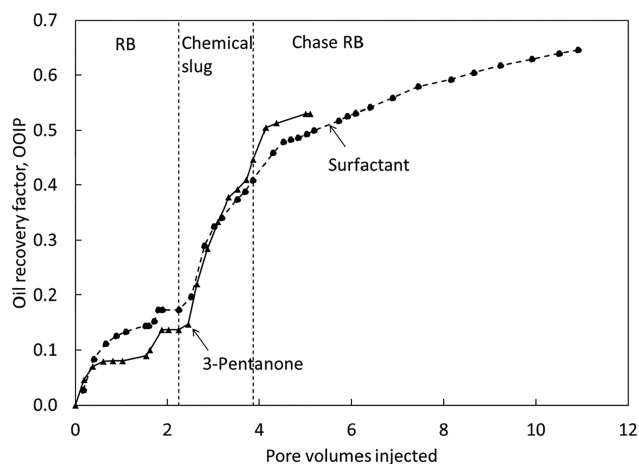
Note that the current experimental study uses non-shale cores. That is, the experiment was designed to compare the two scenarios described above and not to quantify the oil recovery from tight shale cores. How deep the injection fluid will be imbibed into tight shale matrices with available/enhanced imbibition forces is a separate question to be addressed in future research.

Figure 8 presents the oil recovery factors for the two cases: 1.1 wt % 3-pentanone solution in RB with core 1 and 1.0 wt % 2-EH-4PO-1SEO solution in RB with core 2. As indicated in this figure and section 2, each core was first flooded with RB until it reached a residual oil saturation to RB (100% watercut). Then, it was flooded by the respective chemical solution that improved oil recovery through different mechanisms. After 1.6 PVI of a chemical slug, the cores were flooded with the chase RB. The chase RB injection had to be terminated after 1.2 PVI only for core 1 because of operational constraints.

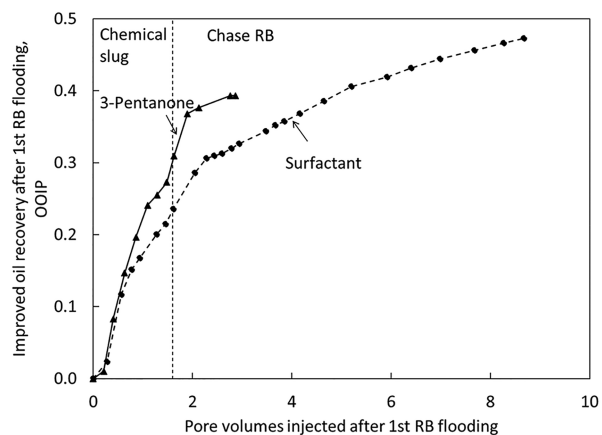
The first RB flooding stage showed that two cores were noticeably different from each other, as expected for Indiana limestone cores because of the heterogeneity. The oil recovery factor for core 1 reached a plateau at 13.7% after 1.89 PVI of RB, but that for core 2 reached 17.3% after 1.81 PVI. As shown in Table 4, core 2 had a higher permeability and lower residual oil saturation to RB than core 1.

The oil recovery factors after the first RB flooding (i.e., incremental oil recovery) are presented in Figure 9. Because of the significant differences between the two cores, the incremental oil recovery factors were corrected using the Leverett factor,  $(k/\phi)^{0.5}$ , for a better comparison.<sup>33,34</sup>

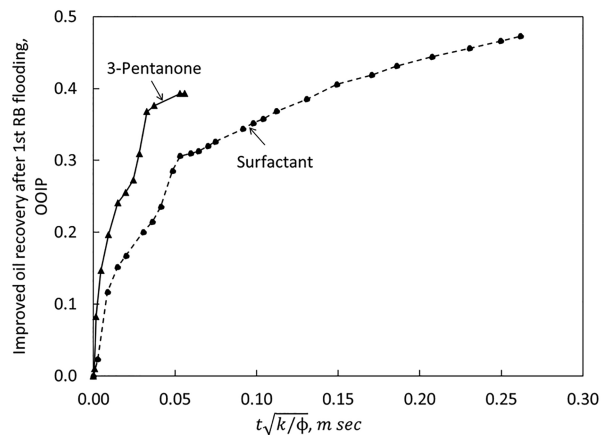
During the chemical flooding stage and the chase RB flooding stage, the oil recovery factor of the 3-pentanone case was systematically higher than that of the surfactant case. The



**Figure 8.** Oil recovery factors during the coreflooding experiments at 347 K. Two cores were first flooded with RB until there was no oil production. Then, they were flooded with a surfactant slug (3-pentanone or 2-EH-4PO-1SEO solution). After 1.6 PVI of the chemical slug, the cores were flooded with the chase RB. The chase RB injection had to be terminated after 1.2 PVI only for core 1 because of operational constraints.



**(a) Improved oil recovery factors with respect to PVI after the 1<sup>st</sup> RB flooding.**



**(b) Improved oil recovery factors with respect to the Leverett factor**

**Figure 9.** Improved oil recovery factors for the 3-pentanone and surfactant cases after the first RB flooding. “Improved oil recovery” represents the amount of oil recovered after the end of the first RB flooding. Note that the oil recovery factor for the 3-pentanone case has been corrected for the 3-pentanone solubility in oil.

oil recovery curves in Figure 9 indicate that the 3-pentanone case resulted in more rapid oil recovery by imbibition than the surfactant case.

The incremental oil recovery factor for the 3-pentanone case was 30.9% for the chemical slug stage (1.6 PVI) and 8.4% for the chase RB flooding stage (1.2 PVI); that is, the total improved oil recovery was 39.3% for the 3-pentanone case. The incremental oil recovery factor for the surfactant case was 23.6% for the chemical slug stage (1.6 PVI) and 23.7% for the chase RB flooding stage (7.0 PVI); that is, the total improved oil recovery was 47.3% for the surfactant case. As mentioned previously, the ultimate improved oil recoveries were not compared because the chase RB was terminated for the 3-pentanone case; however, the ultimate oil recovery factor during the chase RB flooding stage might have been smaller for the 3-pentanone case than for the surfactant case because the water/oil IFT was not lowered by 1.1 wt % 3-pentanone. The slow but steady increase in oil recovery by the chase RB after the surfactant solution injection may also be related to the increase in water/oil IFT after switching to the chase RB injection, during which the surfactant concentration near the matrix/fracture interface was likely reduced.

Note that the oil recovery factor for the 3-pentanone case in Figure 9 has been corrected for the solubility of 3-pentanone in oil (i.e., the mass transfer of 3-pentanone from the brine to the oil during the flooding). The concentration of 3-pentanone in the recovered oil was measured by the  $^1\text{H}$  NMR method, as presented in Table 6. It demonstrated the transient mass

**Table 6. Concentration of 3-Pentanone in Recovered Oil during the Coreflooding Experiment<sup>a</sup>**

time interval (PVI)	3-pentanone concentration in recovered oil (wt %)
2.58–2.77	1.388
2.77–3.01	1.623
3.01–3.24	1.958
3.24–3.47	3.841
3.85–4.00	2.320
4.00–4.27	3.092

<sup>a</sup>The  $^1\text{H}$  NMR method was used for the measurement.

transfer of 3-pentanone from the aqueous phase to the oleic phase, causing the reduction of oil density and viscosity by 3-pentanone (Figures 1 and 2).

Qualitative analysis is presented using the coreflooding results, although we realize that local force balances are transient and coupled with many factors, such as compositional details and heterogeneous petrophysical properties. The capillary force is estimated as

$$P_c = 2\sigma \cos \theta / r$$

where  $\sigma$  is the water/oil IFT,  $\theta$  is the contact angle, and  $r$  is the pore radius. The average pore radius is calculated from

$$r = (8k/\phi)^{0.5}$$

where  $k$  and  $\phi$  are the permeability and porosity of the core, respectively. The buoyant force is calculated as

$$\Phi_g = \Delta\rho gh$$

where  $\Delta\rho$  is the density difference between the aqueous phase and the oleic phase,  $g$  is gravitational acceleration, and  $h$  is the height of the core.

The 3-pentanone case results in the capillary pressure of 18.0 kPa and the buoyant force of 0.3 kPa using the following:  $\sigma = 11$  mN/m,  $\theta = 26^\circ$ , and  $r = 1.1 \times 10^{-6}$  m. The  $\theta$  value was taken from the data after 66 h of observation of oil droplets on an oil-aged calcite surface (as reproduced in Figure 7). This indicates that the oil recovery process in the 3-pentanone case was dominated by the capillary force.

The surfactant case results in the capillary pressure of 0.2 kPa and the buoyant force of 0.3 kPa using the following:  $\sigma = 0.21$  mN/m,  $\theta = 47^\circ$ , and  $r = 1.3 \times 10^{-6}$  m. The  $\theta$  value was taken from Table 5. This indicates that the two forces were comparable in magnitude in the surfactant case.

These conclusions can be obviously drawn using the Bond number and its variants but in an even more qualitative manner. Also, use of typical parameter values for fractured tight formations gives the same qualitative result. The main difference is that the 3-pentanone case would be much more dominated by the capillary force because the water/oil IFT becomes more influential in a medium of ultralow permeability.

To recap on the main differences between the 3-pentanone and surfactant cases, the more rapid imbibition observed for the 3-pentanone case was caused by a greater capillary pressure, for which the 3-pentanone solution rapidly changed the rock wettability to strongly water-wet without lowering the water/oil IFT. Also, the miscibility of 3-pentanone with oil caused the reduction in oil viscosity and density once the mass transfer of 3-pentanone from the aqueous phase to the oleic phase took place. In contrast, the 2-EH-4PO-1SEO solution reduced the water/oil IFT while also changing the rock wettability to water-wet. Although this resulted in a slower imbibition process, the surfactant case showed a very slow but steady increase in oil recovery during the subsequent chase RB injection. This may be because the water/oil IFT gradually increased with the chase RB lowering the surfactant concentration.

#### 4. CONCLUSION

This paper compared two wettability modifiers with different characteristics for enhancing water imbibition from a fracture into the surrounding matrix. One is 3-pentanone, a symmetric short ketone, and the other is 2-EH-4PO-1SEO, a non-ionic surfactant with an ultrashort hydrophobe. They were used as low-concentration additives (approximately 1 wt %) to RB in this research. Results from the contact angle and coreflooding experiments give the following conclusions: (a) The contact angle experiments showed that the two chemicals were comparable as wettability modifiers (Figure 7). For example, the surfactant solution was able to change the contact angle of oil droplets on oil-wet calcite surfaces from  $134^\circ$  to  $47^\circ$  within a day. (b) The coreflooding experiments using fractured limestone cores showed that the 3-pentanone solution resulted in more rapid oil recovery by water imbibition than the surfactant solution (Figure 9). The increase in the oil recovery factor (with the initial RB flood as the baseline) was 30.9% for 1.6 PVI of the 3-pentanone solution and 8.4% for 1.2 PVI of the chase RB. For the surfactant case, it was 23.6% for 1.6 PVI of the surfactant solution and 23.7% for 7.0 PVI of the chase RB. (c) The difference in oil recovery response between the two chemical solutions was attributed to the main difference between them as wettability modifiers; that is, the surfactant solution lowers the water/oil IFT, but the 3-pentanone solution does not. The water/oil IFT was measured to be



lowered from 11 to 0.21 mN/m with the surfactant solution at 347 K. (d) The oil recovery was increasing even after 7.0 PVI of the chase brine after the surfactant slug (Figure 9). This might be related to the water/oil IFT that had been lowered by the surfactant solution slug and then increased during the chase RB injection.

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## NOMENCLATURE

### Roman Symbols

$A$  = cross-sectional area  
 $b$  = fracture aperture  
 $d$  = core diameter  
 $g$  = gravitational acceleration  
 $h$  = height of the core  
 $k$  = permeability  
 $N_B$  = Bond number  
 $P_C$  = capillary pressure  
 $r$  = pore radius

### Greek Symbols

$\phi$  = porosity  
 $\Phi$  = buoyant force  
 $\sigma$  = interfacial tension  
 $\theta$  = contact angle  
 $\rho$  = density

### Subscripts

$e$  = effective  
 $f$  = fracture  
 $m$  = matrix

### Abbreviations

2-EH = 2-ethylhexanol  
 EO = ethylene oxide  
 IFT = interfacial tension  
 PO = propylene oxide  
 PVI = pore volume(s) injected  
 RB = reservoir brine

<sup>1</sup>H NMR = proton nuclear magnetic resonance

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