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Effect of Chemical Partition Behavior on Oil Recovery by Wettability Alteration in Fractured Tight Reservoirs

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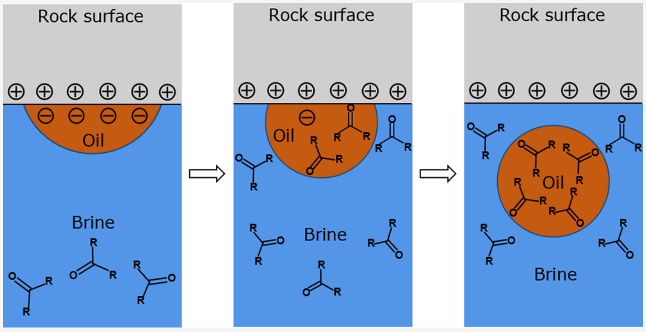

ABSTRACT: Various compounds have been studied as aqueous wettability modifiers that alter the matrix wettability for enhanced oil recovery from shales. This paper compares the oil recovery performance/characteristics using different wettability modifiers that have different partition behaviors into oil and water. We used two types of wettability modifiers: (1) a naturally occurring sulfate-rich injection brine (IB) of 13 500 ppm salinity containing 3900 ppm of sulfate and (2) 1.0 wt % 3-pentanone in IB (3pIB). Sulfate is highly polar, while 3-pentanone is miscible with oil and only slightly soluble in IB. Contact angle experiments using oil-aged calcite surfaces confirmed that IB and 3pIB changed the wettability from 122° to 69° and 72°, respectively, within 3 days. Furthermore, spontaneous imbibition and forced imbibition experiments determined the Amott index to water of 0.68 for IB and 0.67 for 3pIB, indicating similar levels of wettability alteration. This result posed an important question as to how both modifiers would perform in oil recovery from the matrix in huff-n-puff, where the rapid transfer from the fracture to the matrix is an important step. Therefore, we tested IB and 3pIB in huff-n-puff experiments using Wolfcamp shale outcrop cores that were initially saturated with dead oil. Results showed that 3pIB started producing oil from the matrix from the first cycle and continued to produce until the fifth cycle, with a final oil recovery of 57%. IB did not show oil recovery until the second cycle, reaching a final oil recovery of 15% after 5 cycles. IB, however, showed no clear difference in brine composition between the injected and produced water. This is the first comparative study of wettability modifiers with different levels of polarity, which affect the mass transfer between the fracture and the matrix volumes in huff-n-puff.

1. INTRODUCTION

Primary recovery factors in tight oil reservoirs are typically smaller than 10%.[1,2,7,10,12,13] There exists a critical need for enhanced oil recovery (EOR) methods in tight oil reservoirs. Although techniques, such as horizontal drilling and multistage hydraulic fracturing, have made it possible and economically feasible to recover oil from tight formations, tight formations often show a rapid decline in the production rate.[19] A decrease of 60−70% in the oil production rate within the first year has been reported in the Eagle Ford.[11,13]

Contact angle values measured by Alvarez and Schechter on shale samples from tight reservoirs, such as the Bakken, Barnett, Eagle Ford, and Wolfcamp, show that these reservoirs are in an intermediate-wet to oil-wet state.[3] Wettability alteration agents are thus employed to recover oil from tight reservoirs by changing the rock wettability from oil-wet to water-wet to enhance water imbibition and, subsequently, oil recovery. Previously studied methods for recovering oil from reservoirs in intermediate- or oil-wet states by wettability alteration include surfactant solution injection, alcohol solution injection, and low-salinity water injection.[4−6,15,16] During these processes, wettability alteration agents are injected into tight rock matrices to enhance water imbibition.

More recently, Wang et al. investigated 3-pentanone, a symmetric dialkyl ketone, as an additive to reservoir brine for enhanced water imbibition into intermediate- or oil-wet matrices.[19] They performed two sets of imbibition experiments on oil-aged Indiana Limestone cores at 347 K with reservoir brine (RB) and 1.1 wt % 3-pentanone solution in reservoir brine (3pRB). They found 3-pentanone to be a promising wettability modifier for enhancing brine imbibition from a fracture to the surrounding matrix. Using a novel material balance analysis, Wang et al. further compared the wettability

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alteration ability of 3pRB and surfactant solution in enhancing oil recovery through two sets of vertical dynamic imbibition experiments.[21] They observed less efficient wettability alteration and subsequently brine imbibition by the surfactant solution when compared to 3pRB. This led to a lower oil recovery rate for the surfactant likely as a result of the inefficiency of surfactant imbibition and the lowered interfacial tension (IFT) between the aqueous and oleic phases.

Wettability alteration agents typically have different partition behaviors into the oleic and aqueous phases. Components (e.g., sulfate) in naturally occurring sulfate-rich injection brine (IB) do not partition into the oleic phase. 3-Pentanone as an additive in 1.0 wt % 3-pentanone in IB (3pIB) can transfer from the aqueous phase into the oleic phase, weakening the interactions between a charged rock surface with polar components through both the aqueous and oleic phases. The partition behavior of surfactants between an aqueous surfactant solution and crude oil has been widely studied to determine the performance of surfactants during surfactant flooding chemical EOR.[8,9,18] Different surfactants have different partition coefficients depending upon their solubility in both phases (surfactants can partition into both the aqueous and oleic phases). As wettability modifiers, however, the surfactant solution lowers the water/oil IFT, while the 3-pentanone solution does not.[20]

In this paper, we examine the impact of chemical polarity on water imbibition using a newly designed high-pressure, high-temperature (HPHT) huff-n-puff experiment. In this huff-n-puff experiment, a pressure difference exists between the huff and puff stages. We expected this pressure difference to increase oil recovery through fluid volume expansion. Furthermore, we obtained oil recovery factors after 5 huff-n-puff cycles and determined the efficiency of 3-pentanone in enhancing oil recovery. The chemicals compared were an IB, which was available for injection near a shale oil field in Texas, and 1.0 wt % 3pIB. Although surfactants can partition into both the oleic and aqueous phases, they are unsuitable for the comparison in this experiment primarily because of their reduction of the water/oil IFT and secondarily because of their variability in partition behavior. For each injection fluid, the experiment was performed using Wolfcamp shale outcrop cores with dead oil at 338 K. Sections 2 and 3 present the materials and methods used for this study. Section 4 presents the main experimental results. Section 5 summarizes the results.

2. MATERIALS

The crude oil sample used in this study was obtained from a tight oil reservoir in Texas. The pressure and temperature of the reservoir are 7250 psia and 338 K. Table 1 gives a summary of the properties of the crude oil sample. The oil densities were measured at different pressures at 295 K (room temperature) and 338 K, as shown in Figure 1. The reservoir brine (RB) and IB used in this study were prepared using available field data, and their ionic compositions are shown in Tables 2 and 3, respectively. Wolfcamp shale outcrop cores were used for the huff-n-puff experiments. These shale cores are rich in calcite, and their mineral concentration, measured using X-ray diffraction (XRD) analysis, is shown in Table 4.

3. METHODS

3.1. Contact Angle Experiments. Contact angle experiments were performed on oil-aged calcite surfaces with IB and 3pIB at different concentrations at 338 K. Calcite is one of the major minerals often observed in tight formations, and its surfaces can represent an oil-wet state after being aged in oil. The polished calcite surfaces were cleaned with deionized water and air-dried. Then, the dried calcite pieces were aged in RB for 24 h at 338 K and air-dried. Next, the calcite pieces were aged in crude oil for at least 3 weeks at 338 K and

Table 1. Properties of the Crude Oil Sample Used in This Study

molecular weight (g/mol)		239
density (kg/m^3)		821.3 (at 295 K and 1 atm)
		807.9 (at 338 K and 4100 psi)
viscosity (cP)		1.09 (at 338 K)
SARA (wt %)	saturates	86.1
	aromatics	9.8
	resins	<4.3
	asphaltenes (pentane insoluble)	<0.1
acid number (mg of KOH/g of oil)		0.02

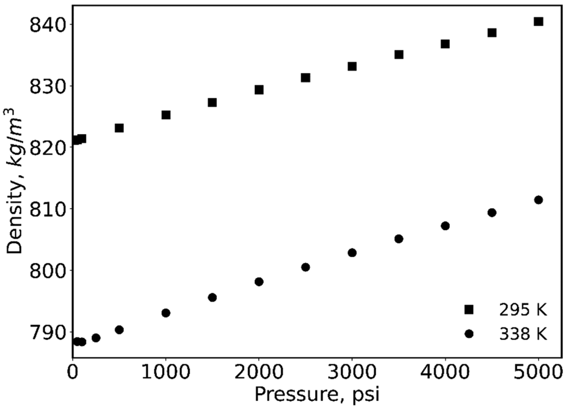


Figure 1. Crude oil densities at room temperature (295 K) and reservoir temperature (338 K).

Table 2. Composition of the RB Used in This Study (65 888 ppm)

cations	ppm	anions	ppm
Na^+	24497	Cl^-	38181
Ca^{2+}	723	SO_4^{2-}	2049
Mg^{2+}	121		
K^+	317		

Table 3. Composition of the IB Used in This Study (13 520 ppm)

cations	ppm	anions	ppm
Na^+	2877	Cl^-	5078
Ca^{2+}	973	SO_4^{2-}	3900
Mg^{2+}	610	HCO_3^-	61
Sr^{2+}	21		

Table 4. Mineral Concentrations of the Calcite-Rich, Wolfcamp Shale Outcrop Cores Used

mineral	concentration (wt %)
quartz	2.3
calcite	96.7
dolomite	0.6
feldspar	<0.5
pyrite	0.0
clays	0.0

then in a heavy oil for at least 4 weeks at 338 K. The heavy oil was used to ensure that the calcite surfaces were oil-wet. After the aging process, the calcite pieces were removed from the oil and any excess oil was carefully removed from the surfaces by gently wiping the surfaces with Kimtech delicate task wipers.

Before the contact angle measurements, IB and 3pIB at different concentrations (0.5, 1.0, 2.0, and 2.66 wt %) were prepared and degasified at 338 K. Then, two glass chambers, each containing one aqueous solution (IB or 3pIB) and one calcite piece, were prepared. A droplet of crude oil was placed on the bottom surface of each calcite piece, and the glass chamber was tightly closed. Photos of each oil droplet were taken to quantify the initial contact angle. The glass chambers were then placed inside an oven at 338 K. Photos of the oil droplets were taken every day for up to 3 days, and the contact angles on both sides of each oil droplet were measured using an on-screen protractor software. The average and standard deviation of the contact angle data were then calculated.

3.2. Spontaneous Imbibition. Spontaneous imbibition experiments were conducted to quantify the effect of 3-pentanone on oil recovery solely through capillary-induced imbibition. The experiments were performed using oil-aged Texas Cream limestone cores of 4.44 in. in length and 1 in. in diameter and Amott cells at 338 K. The experiments largely followed the procedure described by Wang et al.[19,20] The limestone cores were prepared through core-flooding experiments by first saturating the cores with crude oil and then measuring core properties, such as porosity, permeability, water saturation, and oil saturation.[20] Table 5 summarizes the measured core properties for the core samples used in the imbibition experiment.

Table 5. Properties of the Core Samples Used for the Imbibition Experiments

property	core for the IB case	core for the 3pIB case
porosity	0.2808	0.2808
permeability (mD)	17	17
water saturation	0.286	0.286
oil saturation	0.714	0.714

Aqueous solutions of IB and 1.07 wt % 3pIB were used for the imbibition experiments. The core samples were first placed in the Amott cells. Then, the corresponding aqueous solution was carefully poured into the Amott cell. This transfer was performed inside a heated oven at 338 K to minimize any oil recovery from thermal expansion of fluids. The recovered oil volume was then periodically measured during the experiments at 338 K. For the 3pIB case, the concentrations of 3-pentanone in the recovered oleic phase and the aqueous solution were measured using the proton nuclear magnetic resonance (^{1}H NMR) technique.

3.3. Forced Imbibition. The forced imbibition experiment commenced following the conclusion of the spontaneous imbibition experiment. Figure 2 shows a schematic of the experimental setup for the forced imbibition experiment conducted at 338 K. The setup consists of a pressurization pump, an accumulator for IB/3pIB, a Hassler-type core holder, a hydraulic manual pump to maintain the overburden pressure, a differential pressure gauge, and an oven. For each forced imbibition experiment, the recovered oleic phase from the spontaneous imbibition experiment was transferred to a clean container. Then, the core was removed from the Amott cell and placed inside the core holder. The corresponding aqueous solution was injected into the core at a constant flow rate, with the outlet pressure kept at atmospheric pressure.

The injection rates for the forced imbibition experiments were set for a capillary number limit of 2×10^{-5}.[14] The capillary number, N_{vc}, is defined as

$$N_{vc} = \frac{u\mu_w}{\sigma} \tag{1}$$

where u is the interstitial velocity, μ_w is the viscosity of the aqueous solution, and σ is the oil/water IFT.

The produced oil volume was periodically measured. Once the water cut was greater than 99%, the injection rate was increased to eliminate the effect of capillary holdup. According to Rapoport and Leas, this capillary holdup effect can be neglected when the scaling coefficient is greater than 3.0 cP cm^2 min^{-1}.[14,17] The scaling coefficient, N_{RL}, is defined as

$$N_{RL} = Lu\mu_w \tag{2}$$

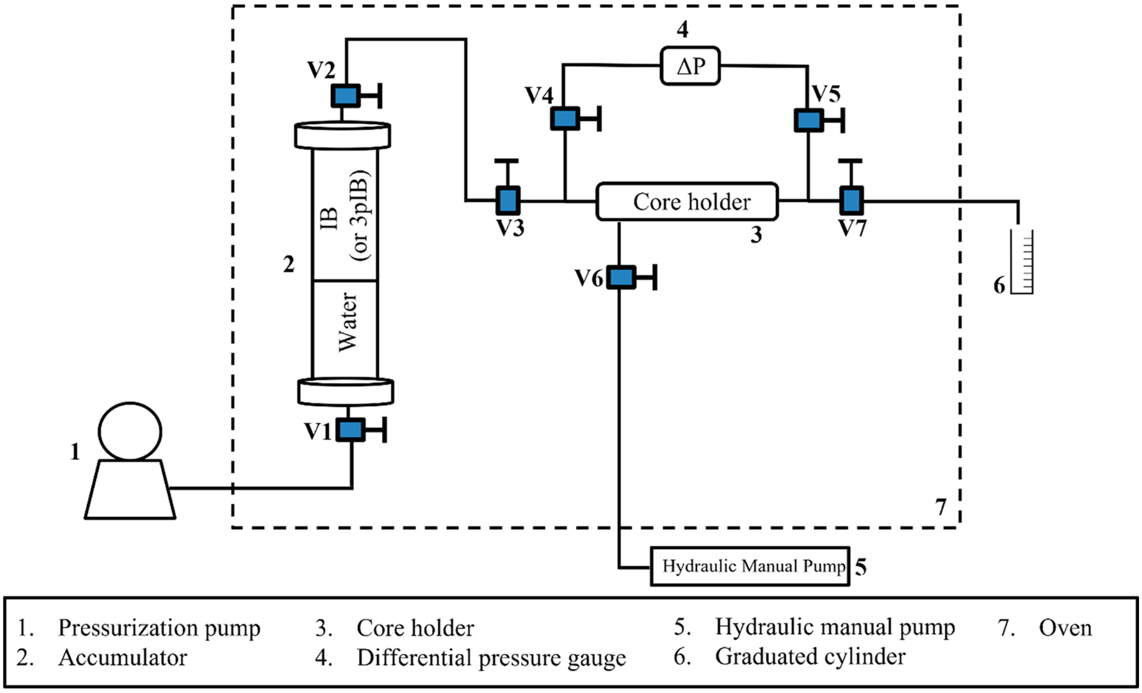


Figure 2. Schematic of the forced imbibition experimental setup.

where L is the length of the core sample, u is the injection rate, and μ_w is the viscosity of the aqueous solution.

Like the spontaneous imbibition case, the concentration of 3-pentanone in the recovered oleic phase was measured using the ^1H NMR technique. The results of the forced imbibition experiments were used to calculate the Amott index to water as

$$\text{Amott index to water} = \frac{\text{spontaneous imbibition oil recovery factor}}{\text{total oil recovery factor}} \quad (3)$$

where the total oil recovery factor is the sum of the spontaneous and forced imbibition oil recovery factors.

3.4. Core Preparation. The shale cores used in the experiments were 1.5 in. in diameter and 1.5 in. in length. We saturated the cores with crude oil at room temperature. First, we placed the dried cores in an accumulator and evacuated the accumulator for at least 24 h. Then, we injected oil into the accumulator and set the pressure to 9600 psi for 1 week to saturate the cores. Finally, we aged the cores in crude oil for approximately 4 months at reservoir temperature. The pore volume of each core was quantified by a mass balance; we measured the mass of each core piece before and after the saturation. This volume was assumed to be the accessible pore volume (APV). To accurately measure the mass of oil inside the cores, we removed any excess oil from the surface of the cores by gently wiping the surface with Kimtech nitrile exam gloves. The cores were weighed at least 3 times on an analytical balance. The analytical balance has a capacity of 120 g and an accuracy of 0.0001 g. Table 6 presents the properties of the cores.

Table 6. Properties of the Core Pieces Used in This Study[a]

core piece number	length (in.)	accessible pore volume (mL)
1	1.5354	0.07817
2	1.4961	0.06275
3	1.4764	0.14855
4	1.4173	0.17306
5	1.4764	0.20127
6	1.5157	0.03490
7	1.5551	0.04428
8	1.3976	0.13357

[a] Cores 1−4 were used for the IB huff-n-puff, while cores 5−8 were used for the 3pIB huff-n-puff.

3.5. Experimental Setup. Figure 3 presents a schematic of the experimental setup for the huff-n-puff experiments. The setup consists of accumulators for nitrogen, RB, IB/3pIB, and crude oil, an in-house fabricated HPHT huff-n-puff cell to house the cores, two pressurization pumps, a pressure gauge, a back-pressure regulator (BPR), graduated cylinders, and an oven. Produced fluids from the top of the huff-n-puff cell were collected into the graduated cylinders. Because the fluids were produced at reservoir pressure, we placed a BPR at the outlet of the tubing system to allow us to maintain upstream pressure at reservoir temperature while we collected the produced fluids at atmospheric pressure and room temperature. The upstream pressure was regulated using nitrogen. One pump was used to maintain the pressure in the nitrogen accumulator, while the other was used to maintain the pressure in the other three accumulators. The accumulators were used to inject fluids into the huff-n-puff cell. The oven was used to maintain the reservoir temperature.

In this experiment, no artificial fracture was created for each core sample. Instead, the annular space between the core body and the huff-n-puff cell acted as the fracture volume.

3.6. Experimental Procedure. Two sets of huff-n-puff experiments were performed at 338 K: one with IB and the other with 3pIB. In the huff-n-puff experiment, fluid was injected into the cell (huff) and shut-in for some time and the fluid was then produced (puff). Our experiments consisted of a brine flooding stage and 5 cycles of huff and puff with either IB or 3pIB. The pressure difference between the huff and puff was 2000 psi.

During the brine flooding stage, RB was injected at 6 mL/h and 4100 psi for 6 h. Then, the RB was shut in at 6100 psi for at least 12 h. After the shut-in period, RB was injected at 6 mL/h to produce the fluid at 4100 psi until there was no oil production (water-cut was higher than 0.99). Likewise, for the IB (or 3pIB) cycles, IB (or 3pIB) was injected at 6 mL/h to fill the fracture. Then, the system was shut-in at 6100 psi for at least 12 h. After this shut-in period, RB was injected at 6 mL/h until there was no oil production.

The concentrations of 3-pentanone in the produced oleic and aqueous phases were measured using the ^1H NMR technique for each 3pIB cycle. We used these concentration data to correct the oil recovery results for 3-pentanone solubility and to analyze the material balance for each cycle. To quantify the oil recovery, we first measured the total mass of the oleic and aqueous phases in each graduated cylinder. Then, we carefully transferred the aqueous phase from each cylinder containing both phases to a new cylinder. The mass of the recovered oleic phase is the difference between the mass of the graduated cylinder with (M_{oil}) and without ($M_{w/oil}$) the oleic phase. The recovered oil volume was then calculated using the mass of the

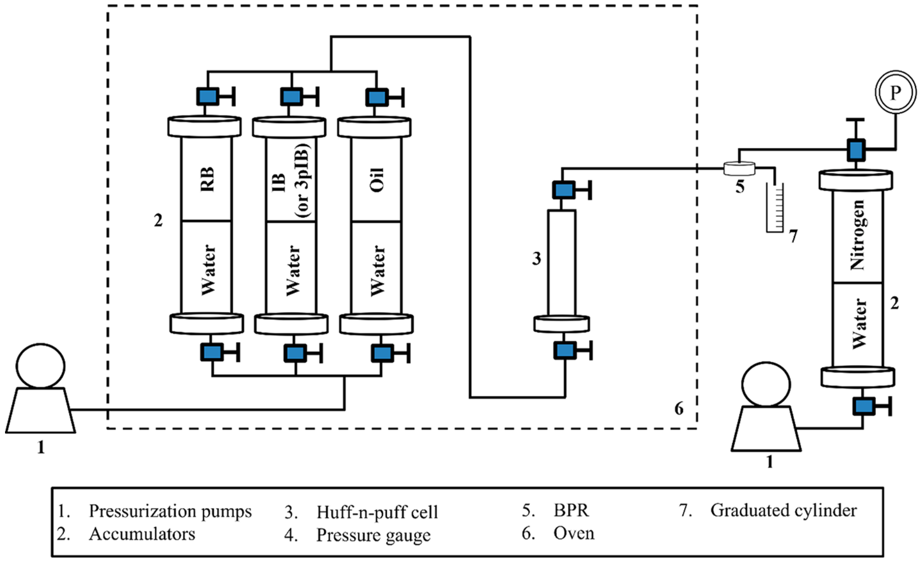
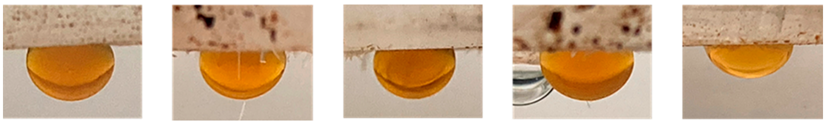


Figure 3. Schematic of the huff-n-puff experimental setup.



(a) 0-wt% (b) 0.44-wt% (c) 0.78-wt% (d) 1.54-wt% (e) 2.46-wt%

Figure 4. Photos of the oil droplets 3 days after the oil-aged calcite pieces were immersed in the solutions at 338 K and atmospheric pressure. (a) IB by itself made the rock surface water-wet. (b−e) The calcite surface became more oil-wet as the 3-pentanone concentration increased.

recovered oleic phase, the concentration of 3-pentanone in the oleic phase, and the density of crude oil at room temperature and atmospheric pressure (ρ_{oil}) as follows:

$$\text{oil recovery factor} = \frac{\left(\frac{M_{oil} - M_{w/oil}}{\rho_{oil}}\right)}{\text{APV}} \times 100\% \tag{4}$$

The efficiency of 3-pentanone in enhancing oil recovery was quantified by the ratio M_{P2}/M_{I3}, where M_{P2} is the mass of the produced oil and M_{I3} is the mass of injected 3-pentanone. The greater the ratio, the higher the efficiency of 3-pentanone in enhancing oil recovery.

4. RESULTS AND DISCUSSION

4.1. Contact Angle Experiments. Contact angles were measured in IB and 3pIB at 0.44, 0.78, 1.54, and 2.46 wt % at 338 K. Figure 4 shows photos of oil droplets 3 days after the oil-aged calcite pieces were immersed in the solutions at 338 K and atmospheric pressure. The oil-aged calcite surface was initially oil-wet. The initial average contact angle in IB was 122°. After 3 days, the average contact angle in IB was 69.06°; that is, IB by itself was able to make the calcite surface water-wet. This is likely because this low-salinity water is rich in sulfate, which reduced the interaction between oil components and rock surfaces.

The contact angle increased as the 3-pentanone concentration increased from 0.78 to 2.46 wt % in Figure 4. Such an increase in the contact angle with the 3-pentanone concentration was not observed previously by Wang et al., and it is not entirely clear why the increase in the contact angle occurred in this research.[17,18] A possible reason is related to the potential association between 3-pentanone and polar oil components, such as resin, increasing the oil-wetness of the calcite surface in the presence of 3-pentanone.

4.2. Spontaneous and Forced Imbibition Experiments. Figure 5 compares the oil recovery from the spontaneous imbibition with IB and 1.07 wt % 3pIB at 338 K. The 3pIB case showed faster and higher oil recovery than the IB case. The 3pIB case reached a final oil recovery of 52.1% after 115 days, while the IB case reached a final oil recovery of 48.7% within the same period. Figures 6 and 7 show the oil recovery from the cores in the Amott cell throughout the spontaneous imbibition experiment for the IB and 3pIB cases, respectively. Oil was recovered not only from the top but also from the side surface of the cores. This indicates increased oil recovery as a result of wettability alteration from both IB and 3pIB.

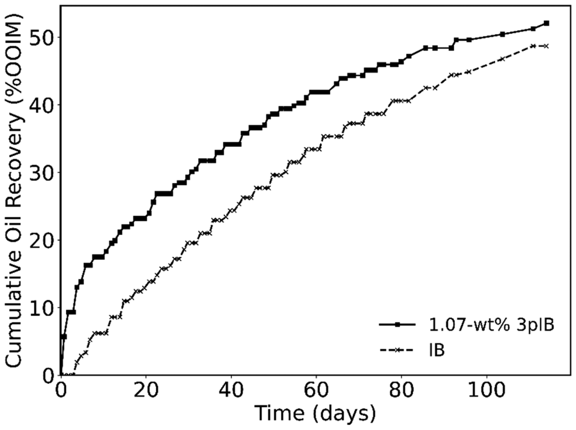


Figure 5. Cumulative oil recovery during the spontaneous imbibition with IB and 1.07 wt % 3pIB at 338 K.

The spontaneous imbibition experiment was followed by the forced imbibition experiment. Figure 8 shows the oil recovery as percentages of the original oil in place (OOIP) by the forced imbibition of IB and 1.07 wt % 3pIB. In Figure 8, the oil recovery at 0 pore volume injected (PVI) is the final oil recovery from the spontaneous imbibition. For the IB case, the oil recovery from the forced imbibition was 21.5% after 18 PVI at the flow rate of 35 cm^3/h. An additional oil recovery of 1.2% was obtained after increasing the injection rate to 150 cm^3/h for 6 PVI to eliminate the effect of the capillary holdup. The total oil recovery for the IB case was thus 71.4%: 48.7% from the spontaneous imbibition and 22.7% from the forced imbibition. The Amott index to water for this core was calculated to be 0.68.

For the 1.07 wt % 3pIB case, the oil recovery from the forced imbibition was 23% after 21 PVI at the flow rate of 35 cm^3/h. An additional oil recovery of 2.4% was obtained after increasing the injection rate to 150 cm^3/h for 9 PVI. The total oil recovery for the 3pIB case was thus 77.5%: 52.1% from the spontaneous imbibition and 25.4% from the forced imbibition. The oil recovery percentages were corrected to account for the concentration of 3-pentanone in the produced oil. The 3-pentanone concentration was measured to be 3.81% using ^{1}H NMR. The Amott index to water for this core was calculated to be 0.67.

The Amott indices show a similar impact of IB and 3pIB on oil recovery by water imbibition in the cores tested. However, the case with 3pIB showed an overall higher oil recovery than the case with IB. It is conceivable that this increased oil recovery was caused by the presence of 3-pentanone.

4.3. Huff-n-Puff Experiments. Table 7 presents the results of the huff-n-puff experiment with IB. Oil recovery was observed only from the second through the fourth cycle of IB injection, with a cumulative oil recovery of 14.6% of the original oil in the matrix (OOIM). The first IB cycle yielded no oil recovery. The second cycle yielded 8.86% oil recovery, followed by 3.98% oil recovery from the third cycle and 1.75% oil recovery from the fourth cycle. The fifth cycle yielded no further oil recovery. The second cycle yielded the largest oil recovery, and the incremental oil recovery decreased for each subsequent IB cycle.

Table 8 presents the results of the huff-n-puff experiment with 1.0 wt % 3pIB. Oil recovery was observed through all 5

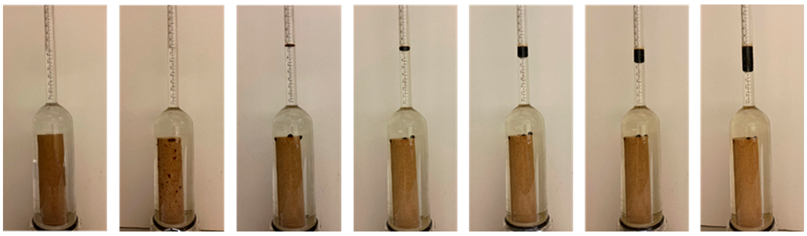


Figure 6. Spontaneous imbibition experiment with IB at 338 K.

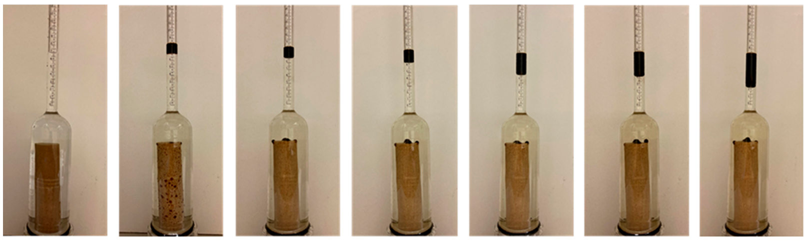


Figure 7. Spontaneous imbibition experiment with 1.07 wt % 3pIB at 338 K.

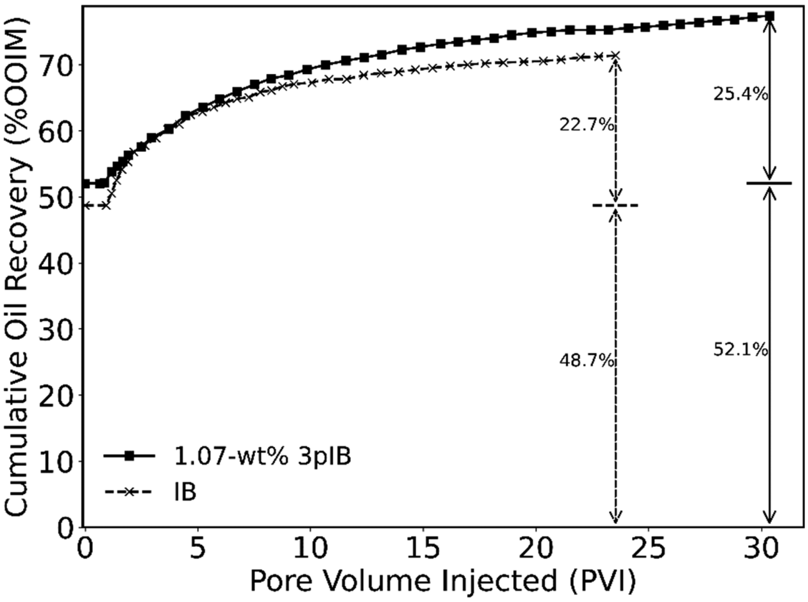


Figure 8. Cumulative oil recovery during the forced imbibition with IB and 1.07 wt % 3pIB at 338 K. The oil recovery at 0 PVI is from the preceding spontaneous imbibition. The Amott indices to water are 0.68 for IB and 0.67 for 3pIB.

Table 7. Results of the Huff-n-Puff Experiment with IB

cycle	oil recovery factor (% OOIM)	cumulative oil recovery factor (% OOIM)
1	0.00	0.00
2	8.86	8.86
3	3.98	12.84
4	1.75	14.59
5	0.00	14.59

3pIB cycles. The oil recovery calculated accounts for the solubility of 3-pentanone in the oleic phase. The concentration of 3-pentanone in the oleic phase was determined to be 1.10 wt % through the ^{1}H NMR technique. The final cumulative oil recovery was 56.6% OOIM. The first 3pIB cycle yielded 18.87% oil recovery, followed by 6.21% oil recovery from the second cycle, 8.30% oil recovery from the third cycle, 19.50% oil recovery from the fourth cycle, and 3.71% oil recovery from the fifth cycle. Overall, the first and fourth cycles yielded the largest oil recovery. Table 8 also includes the efficiency of 3-pentanone in enhancing oil recovery for each cycle.

Figure 9 shows the cumulative oil recovery (% OOIM) for the IB and 1.0 wt % 3pIB huff-n-puff cycles. The experiment with 1.0 wt % 3pIB yielded higher cumulative oil recovery than the experiment with IB. The zeroth cycle represents the oil recovery from the RB flooding stage. For the IB huff-n-puff cycles, there was no oil recovery in the first cycle and a plateau was reached at the fourth cycle, leading to no additional cumulative oil recovery during the fifth cycle. For the 1.0 wt % IB huff-n-puff cycles, however, oil recovery was observed from the first cycle and there exists a 58% increase in the cumulative oil recovery between the third and fourth cycles. This greatly deviates from the 33% increase in the cumulative oil recovery between the first and second cycles and between the second and third cycles. A possible explanation for this deviation is that not all of the oil that was recovered in the matrix was

Table 8. Results of the Huff-n-Puff Experiment with 1.0 wt % 3pIB

cycle	oil recovery factor (% OOIM)	cumulative oil recovery factor (% OOIM)	mass of injected 3-pentanone, M_{I3} (g)	mass of recovered oil, M_{P2} (g)	3-pentanone efficiency, M_{P2}/M_{I3}
1	18.87	18.87	0.1707	0.06416	0.37586
2	6.21	25.08	0.1713	0.02112	0.12329
3	8.30	33.38	0.1731	0.02822	0.16303
4	19.50	52.88	0.1715	0.06630	0.38659
5	3.71	56.59	0.1725	0.01263	0.07322

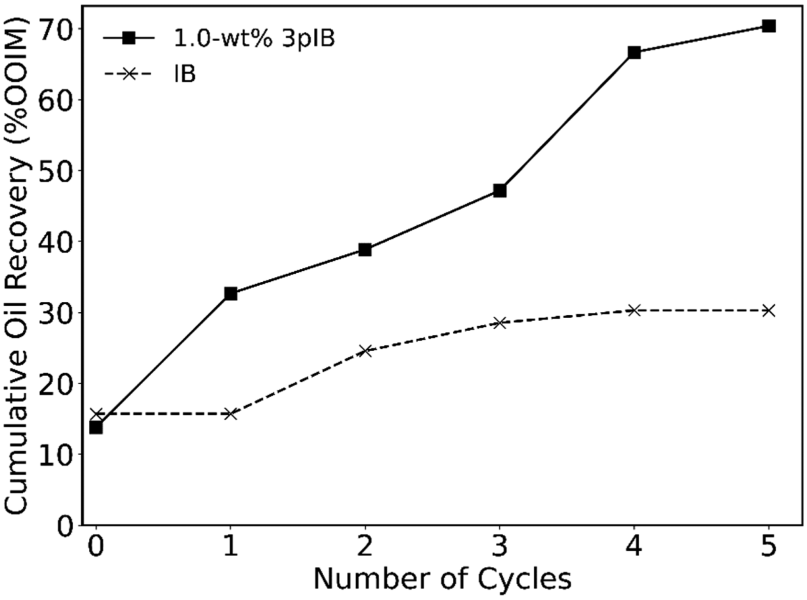


Figure 9. Cumulative oil recovery for both huff-n-puff experiments. Cycle 0 represents the RB flooding stage, and cycles 1−5 represent the IB/3pIB huff-n-puff.

produced during the second and third huff-n-puff cycles. The fourth cycle then recovered some of the remaining oil from the second and third cycles that was not initially produced. There was a 7% increase in the cumulative oil recovery between the fourth and fifth cycles. A plateau was not reached after the fifth cycle for the 1.0 wt % 3pIB huff-n-puff; additional cycles would likely have led to an increase in the cumulative oil recovery.

4.4. Effect of Compressibility on Oil Production. As discussed in the Experimental Procedure, the huff-n-puff experiments were conducted with a 2000 psi pressure difference between the huff and puff stages. This pressure difference contributed to oil recovery through a fluid volume expansion, as estimated in this section. For both cases, we assumed that the volume of oil in the pore was 100% oil. Using the densities of oil at 4100 and 6100 psi, we determined the contribution of compressibility to oil production as a percentage of the total produced oil. Table 9 shows the mass of oil produced as a result of compressibility for the IB and 1.0 wt % 3pIB huff-n-puff cycles. Using the density of oil at room temperature and atmospheric pressure, we calculated the volume of oil recovered through fluid volume expansion. Figure 10 shows the cumulative oil recovery (% OOIM) from fluid volume expansion for the IB and 1.0 wt % 3pIB huff-n-puff cycles. In total, 3.87 and 4.68% OOIM were recovered from fluid volume expansion for the IB and 1.0 wt % 3pIB cases, respectively. These results show that 3-pentanone did not significantly contribute to fluid volume expansion; therefore, the wettability alteration by 3-pentanone was the main mechanism for the EOR. Similarly, the results for the IB case show that wettability alteration by sulfate was the main mechanism for the EOR.

Table 9. Mass of Produced Oil through Compressibility for Both Huff-n-Puff Experiments[a]

	mass of oil produced through compressibility (g)	
cycle	IB	1.0 wt % 3pIB
0	0.00444	0.00398
1	0.00000	0.00343
2	0.00374	0.00268
3	0.00335	0.00243
4	0.00317	0.00210
5	0.00000	0.00132

[a] Cycle 0 represents the RB flooding stage, and cycles 1−5 represent the IB/3pIB huff-n-puff.

5. CONCLUSION

In this paper, we studied the impact of the chemical partition behavior or polarity on water imbibition for huff-n-puff oil recovery from shales. We investigated the performance of a naturally sulfate-rich IB and 1.0 wt % 3pIB. We presented a novel experimental setup and procedure for a HPHT huff-n-puff experiment with dead oil using the fracture and matrix volumes. The main conclusions are as follows: (1) Contact angle experiments showed that, at 338 K, the sulfate-rich IB altered the wettability of an oil-aged calcite surface from an oil-wet state to a water-wet state. The contact angle increased at high concentrations of 3-pentanone. The average contact angle

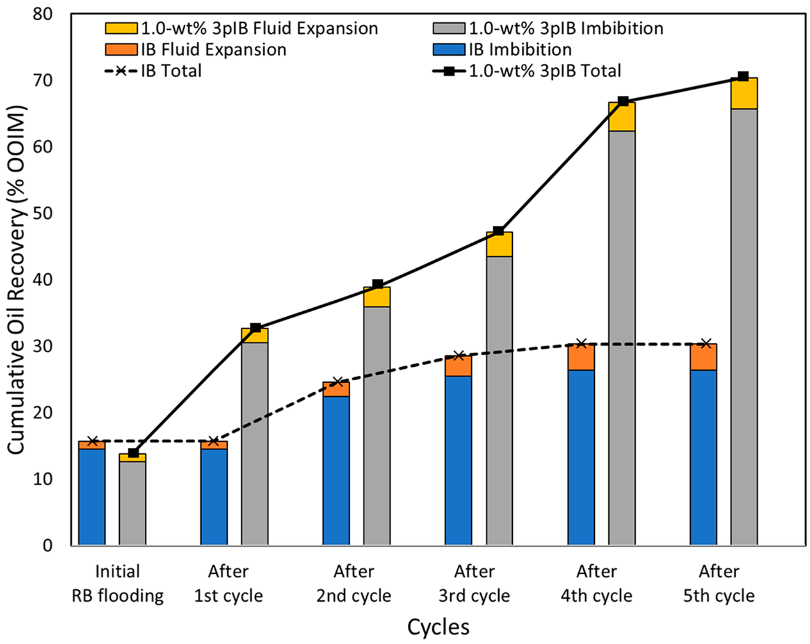


Figure 10. Cumulative oil recovery for both huff-n-puff experiments showing the respective contribution of wettability alteration and fluid volume expansion to oil recovery.

observed after 3 days was 69° for IB, 72° for 0.78 wt % 3pIB, 87° for 1.54 wt % 3pIB, and 104° for 2.46 wt % 3pIB. (2) Results from the spontaneous imbibition showed more rapid oil recovery with 3pIB than with IB, with a total oil recovery of 52.1% for 3pIB and 48.7% for IB. The subsequent forced imbibition yielded a final oil recovery of 77.5% with 3pIB and 71.4% with IB. The Amott indices to water were 0.67 for 3pIB and 0.68 for IB. These results indicated similar levels of wettability alteration for IB and 3pIB. (3) Results from 5 cycles of the HPHT huff-n-puff experiments with dead oil showed higher oil recovery from the shale matrix through the addition of 3-pentanone to the IB than with the IB itself. Although the IB made the calcite surface water-wet, the oil recovery was less and slower than with 3pIB; hence, the wettability alteration is necessary but not sufficient for a wettability modifier to enhance oil recovery from shale rock matrices. This represents the importance of the chemical partition behavior or polarity in this research. Sulfate was unlikely imbibed into the shale matrix as rapidly and efficiently as 3-pentanone. The affinity of 3-pentanone for oil enabled the rapid mass transfer from the fracture to the matrix and the interaction with the rock surface, thus allowing for rapid oil recovery through the enhanced water imbibition. (4) Compressibility calculations showed that the pressure drop between the huff and puff stages of the huff-n-puff experiments contributed to increased oil recovery through fluid volume expansion. 3-Pentanone did not significantly contribute to fluid volume expansion; that is, the wettability alteration by 3-pentanone was the main mechanism for the EOR.

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Notes

The authors declare no competing financial interest.

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