

Evaluation of Surface-Active Ionic Liquids in Smart Water for Enhanced Oil Recovery in Carbonate Rocks

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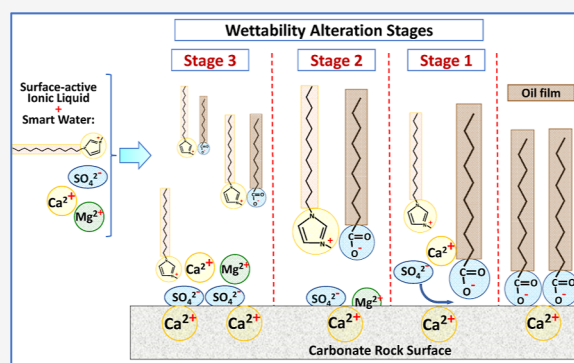
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ABSTRACT: Ionic modification of injected brines (Smart Water EOR) has previously demonstrated great potential for wettability alteration in carbonates from initially mixed-wet toward more water-wet conditions. However, the efficiency of Smart Water application is temperature-dependent, which reduces its ability as a rock wettability modifier at low temperatures (below 100 °C). Moreover, at low temperature conditions, the acid number of crude oils tends to increase in the reservoir, causing a stronger oil wetting character and less water-wet initial conditions. This paper evaluates the wettability alteration potential of surface-active ionic liquids added to Smart Water to obtain a synergistic enhanced oil recovery effect in low-temperature carbonate reservoirs. $[C_{12}mim]Br$, $[C_{12}Py]Cl$, and $[C_{16}Py]Cl$ were formulated in Smart Water (SW0Na) and tested as wettability modifiers in mixed-wet carbonate chalk cores.

Spontaneous imbibition oil recovery tests showed that the addition of $[C_{12}mim]Br$ and $[C_{12}Py]Cl$ can cause wettability changes, resulting in increased oil recovery compared to pure SW0Na brine at 90 °C. The highest incremental oil recovery in tertiary mode of 24.6 % OOIP was obtained using $[C_{12}mim]Br$ in SW0Na, followed by $[C_{12}Py]Cl$ in SW0Na with 22.4 % OOIP, and only 11.5 % OOIP was recovered by pure SW0Na brine. The potential for wettability alteration for carbonate rocks was further evaluated in viscous flooding tests using the best formulation from the results obtained in the spontaneous imbibition experiments ($[C_{12}mim]Br$ in SW0Na). The core flooding results showed an ultimate recovery of 79.3 % OOIP achieved in secondary mode injection. Despite the difference in the head groups of the cationic $[C_{12}mim]Br$ and $[C_{12}Py]Cl$ ionic liquids, both formulations showed abilities to desorb polar organic components of crude oil from the chalk mineral surfaces, thus improving the performance of Smart Water EOR at 90 °C.



1. INTRODUCTION

Around 60% of the discovered oil reserves worldwide are located in carbonate formations, and most of them are mixed to oil-wet, naturally fractured, and low permeability reservoirs.^{1–3} The injection of water as a secondary recovery method in those reservoirs (fractured mixed-wet or oil-wet) shows low recovery efficiency due to the high capillary pressure differences between fractures and matrix pores, making the penetration of water into the matrix difficult. In water-wet reservoirs, injected water can penetrate from fractures to matrix blocks through the spontaneous imbibition process, thus expelling the crude oil and increasing the recovery.^{4–6} However, conventional water injection is normally carried out using the produced water from the reservoir, which is similar in composition to the initial formation water. As a result, the chemical equilibrium between crude oil, brine, and rock (COBR) systems cannot be altered, and wettability modification toward a more water-wet state is hard to achieve.⁷

Carbonate rock surfaces are positively charged below their isoelectric point of pH ~ 9.5 ⁸ and, hence, are sensitive to negatively charged components at reservoir conditions. Accordingly, anionic polar compounds present in crude oil (mainly carboxylates, $R-COO^-$, which are dissociated carboxylic acids) can adsorb onto the carbonate surface, modifying the original water-wet state toward less water-wet conditions.^{9–11} The alteration of rock wettability toward a more water-wet state using surfactants has previously been investigated.^{12,13} Surfactants are amphiphilic molecules, possessing both a hydrophilic polar moiety and a hydrophobic non-polar moiety (generally a hydrocarbon chain), with

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significant surface activity. Conventional surfactants can be classified on the basis of their hydrophilic groups as anionic, cationic, zwitterionic, or non-ionic.^{13,14} Currently, bio-based surfactants (from natural sources)^{15,16} are gaining interest due to their environmental benefits.^{15,16} The potential of different types of surfactants to alter the wettability in oil-wet carbonate rocks has been evaluated through imbibition tests.^{17–19} Spontaneous imbibition with cationic surfactants (primarily from the quaternary ammonium and phosphonium families) showed a clearly higher potential to expel oil compared to anionic surfactants (mainly from the ethoxylated sulfonate and sulfate families). The proposed imbibition mechanism for cationic surfactants suggests that the positive head groups electrostatically interact with the adsorbed negative compounds of the crude oil on the rock surface, forming ion pairs. These ion pairs are stabilized by hydrophobic interactions between their alkyl chains, and the material is desorbed from the carbonate surface.^{17,19} The spontaneous imbibition is driven by capillary forces, turning oil-wet cores more water-wet. As a result, the capillary force increases and overcomes the low capillary force due to the surfactant.^{17,20} The ability of anionic surfactants to displace oil was generally low. Among them, ethoxylated sulfonates showed relatively higher efficiency. For anionic surfactants, the formation of a surfactant layer was suggested, in which the hydrophobic chains were oriented toward the hydrophobic carbonate surface, exposing the hydrophilic part, thereby making the surface double-layer water-wet.^{17,20,21} Moreover, assessments of non-ionic surfactants (specifically ethoxylated alcohol types) showed that they were much less effective than the tested cationic surfactants.^{18,22} Similar to anionic surfactants, the wettability alteration mechanism for non-ionic surfactants was suggested to involve the formation of a bilayer structure.²²

Furthermore, several studies revealed that alteration of carbonate wetting toward water-wet conditions can be achieved by injecting water with a different composition than that originally found in reservoirs (i.e., seawater, SW), thus improving oil recovery.^{5,23,24} The injection of SW, or smart water (SmW), is categorized as an enhanced oil recovery (EOR) method since it can alter the chemical equilibrium of the COBR system, change the wettability state toward more water-wet, and improve the oil recovery. SmW is designed by adjusting the composition of ions present in the injection water to a specific COBR system.

Focusing on chalk rocks, potential determining ions (PDI) Ca^{2+} , Mg^{2+} , and SO_4^{2-} present in SW and SmW can modify the charges on the surface rock and trigger favorable wettability conditions. The suggested mechanism^{24,25} for that process indicates that when SW or SmW is injected in chalk rocks, SO_4^{2-} ions are adsorbed on the positively charged surface due to their high affinity to Ca^{2+} . The positive charge on the surface is reduced, and the electrostatic interaction of surface Ca^{2+} with the carboxylate groups of the crude oil diminishes, and in addition, the repulsion between surface Ca^{2+} and water Ca^{2+} is reduced. Then, the water Ca^{2+} concentration near the surface increases, and Ca^{2+} ions interact electrostatically with carboxylate groups, inducing their desorption from the chalk surface.^{24,25} The Mg^{2+} ion has the ability to replace Ca^{2+} from the carbonate surface; hence, it can also help to remove the carboxylic group- Ca^{2+} complex from the rock surface.²⁶ However, the interaction between PDIs and the carbonate surface is dependent on temperature: the higher the temperature, the higher SO_4^{2-} adsorption on the carbonate surface.

This means a higher affinity for water Ca^{2+} on the surface and higher oil recovery by wettability modification.^{25,27} Mg^{2+} is also more reactive at high temperatures due to dehydration, that is, the breaking of the hydrogen bonds between the water molecules, solvating the Mg^{2+} ions and reducing their reactivity.^{26,28} Hence, SW and SmW have reduced efficiency as wettability modifiers at low temperatures below 100 °C.

It has also been shown that at lower temperatures, the acid number (AN) of crude oils tends to increase because carboxylic acids suffer from decarboxylation at high temperatures.²⁹ Knowing that crude oils with high AN induce higher oil wetting, carbonate reservoirs will be likely more oil-wet at lower temperatures than at higher temperatures.³⁰

This work aims to assess a new method, based on ionic liquids, to improve the performance of SmW for EOR in carbonate reservoirs at low temperatures. Taking into account that cationic have shown effectiveness over anionic and nonionic surfactants for wettability alteration processes,^{17,31} some cationic ionic liquids were selected as possible alternatives to the widely proposed cationic surfactant C_{12}TAB . Ionic liquids are salts with melting or glass transition temperatures below 100 °C. They are characterized by high thermal stability, a high capacity of solvation, and the possibility of being functionalized. They can be designed to be stable in harsh environmental conditions.^{32,33} Due to their negligible vapor pressure, these salts avoid atmospheric contamination and are cataloged as environmentally friendly.³⁴ Ionic liquids with long alkyl chains (more than six carbon atoms) are surface-active agents (SAILs), self-aggregating in micelles when dissolved in water and being able to decrease the interfacial tension (IFT).^{35–38} In recent years, the potential of SAILs to be used in EOR applications as a surfactant agent has been studied. Analyzing the first publications on this topic, Bera and Belhaj³³ highlighted the SAILs' ability to reduce water-oil IFT and their tolerance at harsh conditions (salinity and temperature). Somoza et al.³⁹ reviewed core-flooding tests conducted with these salts and found that the majority of the studies were carried out in sandstone rocks, despite the expected high adsorption of cationic surfactants in this kind of rock. Additional oil recoveries (AOR) of about 5–12% original oil in place (% OOIP)^{32,40,41} were found. Evaluations of SAILs in carbonate cores achieved AOR values in the range of 8–20 % OOIP.^{39,42–44} Despite these positive results, ultra-low IFT with pure SAILs is not easy to achieve. For this reason, cationic SAILs have also been blended with traditional anionic surfactants to promote the formation of mixed micelles (also named catanionic micelles), thus increasing the surface activity with the oil phase. Core flooding tests injecting these kinds of blends suggested an improvement in performance when the blends were compared to the pure surfactants.^{45,46} According to contact-angle measurements, some SAILs were also able to change wettability toward a more water-wet state.^{42,47,48} However, a few studies^{49,50} conducted imbibition tests with SAILs to evaluate the capability for wettability alteration of these salts. Sakthivel and Elsayed⁴⁹ and Manshad et al.⁵⁰ carried out spontaneous imbibition tests in carbonate cores at 80–100 °C (secondary mode), with SAIL formulations prepared in formation brine or seawater. Spontaneous imbibition values up to 34% AOR were found.

In this study, SAILs are combined with Smart Water for the first time, investigating potential synergistic effects in the wettability alteration process. Three imidazolium and pyridinium SAILs with different alkyl chain lengths

([C₁₂mim]Br, [C₁₂Py]Cl, and [C₁₆Py]Cl) were considered to improve the performance of SmW for EOR in carbonate rocks. SAIL formulations were prepared in SmW, and their wetting alteration capacity was tested on mixed-wet chalk cores by spontaneous imbibition tests at 90 °C in tertiary mode. The efficiency of the best performing formulation was additionally evaluated by means of viscous flooding tests in secondary and tertiary modes.

2. EXPERIMENTAL WORK

2.1. Material. **2.1.1. Ionic Liquids.** Three cationic SAILs were evaluated in this study. 1-dodecyl-3-methylimidazolium bromide ([C₁₂mim]Br) with a purity >98 wt % was purchased from Iolitec. 1-dodecylpyridinium chloride ([C₁₂Py]Cl) and 1-hexadecylpyridinium chloride ([C₁₆Py]Cl) with purity grades of 98 wt % and 99 wt %, respectively, were supplied by Sigma-Aldrich. Figure 1 shows the chemical structures of the evaluated SAILs.

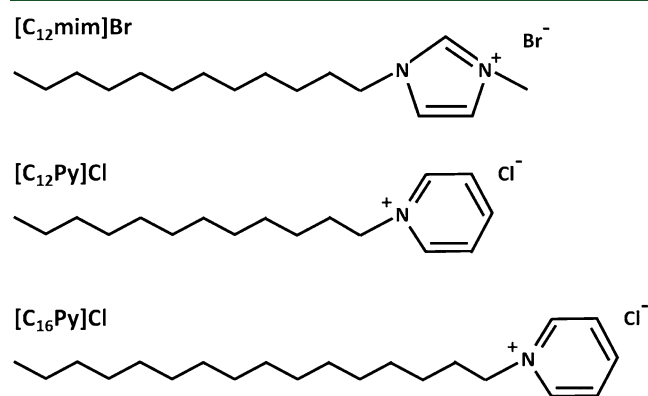


Figure 1. Chemical structures of the used SAILs.

2.1.2. Brines. Synthetic brines were used in the experimental work. The Valhall formation brine (VBOS) was employed to initially saturate the cores and as the first spontaneous imbibition fluid, in secondary mode. The composition of the VBOS brine is similar to that of the reservoir formation water of the Valhall chalk field in the North Sea, but it is depleted in sulfate ions (SO₄²⁻) to not induce initial wettability alteration. Synthetic North Sea SW was only used as make-up water in initial evaluations of the phase behavior and thermal stability of the SAIL formulations. The Smart Water SWONa was used in secondary and tertiary modes in spontaneous imbibition and viscous core flooding tests, as well as make-up water for SAIL formulations. The SWONa composition is similar to that of SW but depleted in NaCl salt. For sulfate influence evaluations, SWOS brine (SWONa without sulfate ions) was also prepared. The brines SW1/2T

and SWOT (with and without tracer ions, SCN⁻), previously tested in chromatographic wettability tests for chalk,²⁵ were used in the adsorption test. All brines were prepared by dissolving reagent-grade salts in deionized water, stirring overnight, and then filtering through a 0.22 μm filter. The brine compositions are listed in Table 1.

2.1.3. Oil. A model crude oil, termed Res40-m, was used for the core preparation process and oil recovery tests. This model oil was obtained by mixing the crude oils Res40 and Res40-0, with ANs of 1.8 and 0.0 mg KOH/g, respectively, in a ratio of 1:2 Res40/Res40-0.^{25,51} The crude oil Res40 was prepared by diluting Heidrun crude oil and *n*-heptane at a 3:2 Heidrun/heptane blend ratio, and no precipitation of asphaltenes was observed. Res40-0 oil was obtained by treating Res40 oil with 10 wt % of silica gel under stirring at room temperature for 3 days to remove the acidic material present in the crude oil.³⁰ After preparation, the oils were centrifuged and filtered through a 5 μm filter. The resulting AN and base number (BN) of Res40-m oil were 0.6 and 0.3 mgKOH/g, respectively, measured with a Mettler Toledo T50 auto-titrator using methods developed by Fan and Buckley,⁵² which are modified versions of ASTM D2896 and D664 for BN and AN titration, respectively. Res40-m oil density was 0.803 g/cm³, measured using an Anton Paar density meter (model DMA 4500).

2.1.4. Core Samples. Ten outcrop chalk cores from the Stevns Klint (SK) quarry in Denmark were used as carbonate rock models in the experimental work. SK cores have often been used to represent North Sea chalk reservoirs.⁵³ This material generally contains around 98% CaCO₃⁵⁴ with most of the pore sizes ranging from 0.1–0.5 μm,⁵⁵ has high porosity (40–50%) and low permeability (1–3 mD), and has shown reproducible results in wettability and recovery tests in previous studies.^{53,55,56}

2.2. Methodology - SAILs Evaluation. To prevent possible interactions between SAILs and divalent salts contained in the SWONa brine, before blending them, stock solutions of the SAILs [C₁₂mim]Br, [C₁₂Py]Cl, and [C₁₆Py]Cl were first prepared individually in deionized water at 8 wt % SAIL concentration. To avoid dilution of the make-up brines, these were prepared at a higher concentration than the original (1.2 times the original concentration of each brine) so that, when they were mixed with the SAIL stock solutions, the formulations reached both the original brine concentration and the desired SAIL concentration. To compare the obtained results with previously performed work with cationic surfactants at 1 wt % concentration,¹⁷ 1 wt % was also selected as the SAIL concentration.

2.2.1. Phase Behavior Evaluation. The phase behavior of crude oil and SAILs prepared in VBOS, SW, and SWONa brines was visually evaluated following the so-called encased-glass-pipette method.^{57,58} Borosilicate glass pipettes were heat-sealed at the tip, and SAIL formulations, prepared in the different brines, were placed into the pipettes at a 1:1 aqueous phase/oil phase ratio. Initial interfaces were recorded to easily identify the type of microemulsion. Thereafter, each pipette was heat-sealed at the top and gently mixed for 24 h in a rotary mixer at room temperature. They were enclosed in a 10 cm³

Table 1. Brine Properties and Compositions

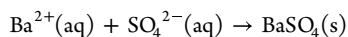
ions	VBOS (mM)	SW (mM)	SWONa (mM)	SWOS (mM)	SWOT (mM)	SW1/2T (mM)
Na ⁺	996.6	450.1	50.0	60.0	460.0	427.0
K ⁺	5.3	10.1	10.1	10.1	10.0	22.0
Li ⁺	0.0	0.0	0.0	0.0	0.0	12.0
Ca ²⁺	28.9	13.0	13.0	13.0	13.0	13.0
Mg ²⁺	7.8	44.5	44.5	44.5	44.5	44.5
Cl ⁻	1066.0	525.1	125.1	126.0	583.0	538.0
HCO ₃ ⁻	9.3	2.0	2.0	2.0	2.0	2.0
SO ₄ ²⁻	0.0	24.0	24.0	0.0	0.0	12.0
SCN ⁻	0.0	0.0	0.0	0.0	0.0	12.0
TDS (g/L)	62.83	33.39	10.01	10.01	33.39	33.39
density (g/cm ³)	1.039	1.023	1.01	1.01	1.022	1.022
ionic strength	1.112	0.657	0.257	0.657	0.643	0.644

Pyrex test tube filled with silicone oil to ensure temperature control and then introduced into an OVAN dry-block heater (model BD200-RE). Phase behavior was monitored at different temperatures, from 50 °C to 130 °C, increasing temperature by 20 °C every 72 h. In this kind of study, the SAIL concentration in the aqueous phase is normally high (4 wt % SAIL) just to easily visualize oil in the aqueous phase^{58,59} and determine the type of microemulsion, Winsor type I, II, or III, according to the Winsor classification.⁶⁰

2.2.2. Thermal Stability Test. The possible precipitation of components in SAIL formulations was visually evaluated by preparing 1 wt % SAIL concentration in different brines (VBOS, SW, and SWONa), aiming to use those formulations in spontaneous imbibition and viscous flooding tests. As in the phase behavior evaluation, the formulations were placed into sealed pipettes in the absence of crude oil and monitored when increasing the temperature from 50 to 130 °C using the OVAN dry-block heater. The evaluation was done based on the translucence of the solutions.^{45,61}

2.2.3. Dynamic Interfacial Tension. The interfacial tension (IFT) between the SAIL formulations (at 1 wt % SAIL concentration) and crude oil was measured using a Krüss spinning drop tensiometer (model SITE100) at 50 °C. For each formulation, a 4 μL crude oil sample was injected into the capillary tube, which was filled with the SAIL formulation. The rotation speed was set at 5000 rpm to guarantee an oil droplet length at least four times larger than its diameter, according to Vonnegut's theory.^{62,63} SAIL formulation densities were obtained using an Anton Paar density meter (model DMA 5000 M).

2.3. Methodology—Core Preparation. **2.3.1. Core Cleaning.** The cores were drilled in the same direction from the same outcrop chalk block. The core cleaning procedure followed the methodology suggested by Puntervold et al.⁵⁶ By using Hassler core holder equipment and a compressed nitrogen piston cell to support a confining pressure of 10 bar, each core was flooded with 5 pore volumes (PV) of deionized water at 0.1 cm³/min at room temperature. The objective was to remove any easily dissolvable salts, especially those containing SO₄²⁻ ions, which might influence the initial wettability behavior of the cores.⁵⁶ The absence of sulfates in the effluent was checked by the addition of Ba²⁺ ions, which will react with available sulfate ions to form BaSO₄ (s), according to the following reaction equation



When no more precipitation of BaSO₄ was observed, each core was dried in an oven at 90 °C until a constant weight was reached (after about 3 days) and thereafter kept in a sealed container.

2.3.2. Initial Water Saturation (*S_{wi}*). The initial water saturation of the cores was established at around 10% by using the desiccator method.⁶⁴ This method is fast compared to desaturation by, e.g., porous plates, and it results in evenly distributed and reproducible *S_{wi}*. The dried cores were first evacuated to be 100% vacuum-saturated with ten times diluted VBOS brine at room temperature. Thereafter, the saturated cores were placed in a desiccator with silica gel until reaching the desired *S_{wi}* of ~10%, obtained by water evaporation from the cores, controlled by weight. Each core was stored in a sealed container and left to equilibrate for 3 days.

2.3.3. Initial Core Wettability. After equilibrating the *S_{wi}* established by the desiccator, reproducible initial oil saturation and initial core wettability were established by introducing a controlled, equal amount of crude oil into each core.⁶⁵ Using a Hassler core holder in horizontal position at a confining pressure of 20 bar, each core was first vacuum-saturated with 1 PV of Res40-m oil and then flooded with 4 PV Res40-m oil at 0.2 cm³/min (injecting 2 PV in each direction). The whole process was performed at 50 °C. Then, the cores were wrapped in Teflon tape to avoid unrepresentative adsorption of active polar organic components on the outer core surface during the aging stage. Each core was placed on marble balls in sealed stainless-steel aging cells surrounded by the effluent Res40-m oil and aged in an oven at 90 °C for 2 weeks.

2.4. Methodology—Oil Recovery Tests. **2.4.1. Spontaneous Imbibition (SI) Tests.** Seven spontaneous imbibition (SI) tests were

conducted. Each aged core was unwrapped and placed vertically on marble balls submerged in VBOS imbibition brine into steel HPHT (high pressure–high temperature) SI cells. The SI cells were connected to compressed nitrogen piston cells, supplying the VBOS brine and keeping the system pressurized at 10 bar. The SI test temperature was kept at 90 °C. VBOS was used as the first imbibition fluid in secondary mode to avoid changes in wettability at this stage and be able to infer the initial wetting state of the chalk cores more accurately. The cumulative oil produced was measured in a graded glass burette and reported as the percentage of OOIP versus time. Once oil recovery reached the plateau, the VBOS imbibition brine was replaced by another imbibition fluid to perform tertiary-mode spontaneous imbibition. This last imbibition brine varied depending on the SI test performed (SWONa or SAIL-SWONa formulation at 1 wt % SAIL).

2.4.2. Viscous Flooding Tests. To validate the efficiency of the best-performing SAIL-SWONa formulation (1 wt % SAIL), two viscous flooding (VF) experiments were conducted at 90 °C. The aged core was placed in the Hassler core holder, positioned horizontally, with confining and back pressure established at 20 and 10 bar, respectively. Each core was flooded at an injection rate of ~1 PV/D with the desired brine or formulation. Volumes of produced oil as a percentage of OOIP were measured, and differential pressures were recorded during the tests until the oil production plateau was reached.

2.4.3. Dynamic Adsorption Test. SAIL adsorption on chalk rock was estimated using the best-performing formulation in a single-phase dynamic adsorption test based on the breakthrough difference between the SAIL and tracer fronts. Similar to the chromatographic wettability method used for chalk,²⁵ the first part of the test allowed the determination of the flow behavior of the non-adsorbing tracer thiocyanate (SCN⁻). Also, the SO₄²⁻ profile from the same effluent samples was tracked for comparative purposes. A cleaned, not exposed to oil, chalk core was 100% vacuum-saturated with SWOT brine (without SCN⁻) and placed horizontally in the Hassler core holder. Once the confining and back pressure were established at 20 and 10 bar, respectively, and the temperature reached 90 °C, the core was first flooded at ~1 PV/D by the same brine, SWOT, until the differential pressure stabilized, after which it was flooded by the SW1/2T brine. The effluent was sampled with an autosampler and analyzed using an ion chromatographer for tracer concentration estimation. Thereafter, the core was cleaned by injecting SWONa for 24 h at the same injection rate to finally be flooded by the best-performing SAIL-SWONa formulation (1 wt % SAIL). Effluent samples were collected until the SAIL concentration achieved the value of the injected formulation. The SAIL concentration in the samples was determined by using an HP UV/vis-spectrophotometer (model Presario SR1000). Normalized concentrations (*C/C₀*) of SAIL and tracer profiles were obtained. Then, SAIL adsorption was estimated using the theory of diffuse percolation, that means, the difference in pore volumes corresponding to 0.5 normalized concentration between SCN⁻ and SAIL profiles (eq 1).^{45,59,66} The theory of diffuse percolation suggests that when a solution is flooding a water-saturated core at an injection velocity of *V*, the front at *C/C₀* = 0.5 also moves at that velocity, indicating breakthrough of the fronts when the effluents reach that normalized concentration.⁶⁷

$$\tau = \frac{(\text{PV}_{\text{SAIL},50\%} - \text{PV}_{\text{tracer},50\%}) \times \text{PV} \times [\text{C}_0]_{\text{SAIL}}}{\text{Mass}_{\text{rock}}} \quad (1)$$

where τ is the SAIL adsorption on the chalk rock surface in mg/g, $[\text{C}_0]_{\text{SAIL}}$ is the initial SAIL concentration in mg/cm³, PV is the core pore volume in cm³, $\text{PV}_{\text{SAIL},50\%}$ and $\text{PV}_{\text{tracer},50\%}$ are the pore volumes at 50% injection concentration of SAIL and tracer, respectively, in the effluent, and $\text{Mass}_{\text{rock}}$ is the dry core weight in grams. As an alternative, the adsorption was also estimated using the area between the SCN⁻ and [C₁₂mim]Br curves.

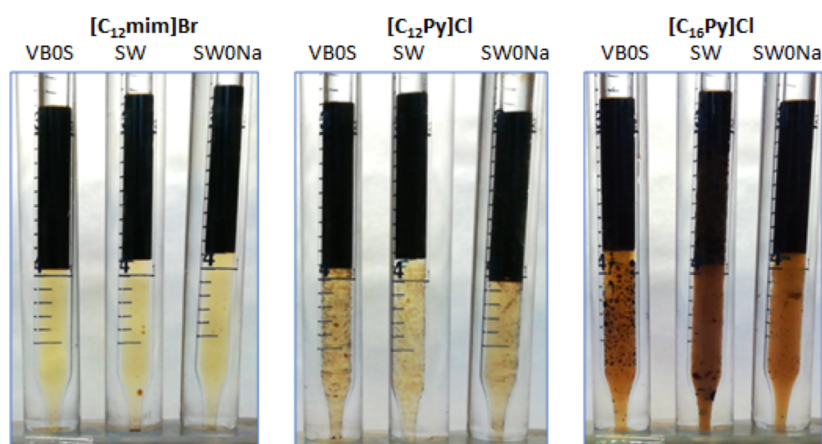


Figure 2. Phase behavior evaluation at 130 °C of the $[C_{12}mim]Br$, $[C_{12}Py]Cl$, and $[C_{16}Py]Cl$ SAIL formulations prepared at 4 wt % SAIL concentration in VBOS, SW, and SWONa brines in contact with crude oil.

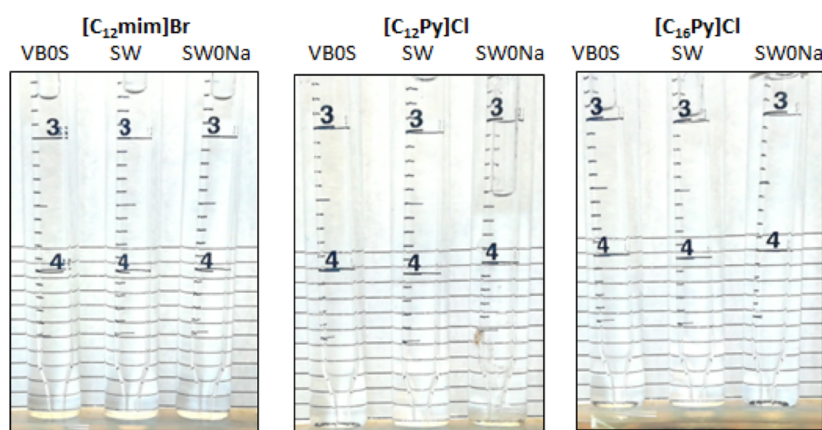


Figure 3. Thermal stability test at 130 °C for the $[C_{12}mim]Br$, $[C_{12}Py]Cl$, and $[C_{16}Py]Cl$ SAIL formulations prepared in VBOS, SW, and SWONa brines at 1 wt % SAIL concentration in the absence of an oil phase.

Table 2. Properties of Outcrop Chalk Cores

property/core ID	C#1	C#2	C#3	C#4	C#5	C#6	C#7	C#8	C#9	C#10
length, cm	7.2	7.3	6.6	6.4	7.0	6.7	6.9	7.3	7.5	6.9
diameter, cm	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
bulk volume, cm ³	81.7	82.7	74.3	72.5	79.2	75.5	77.7	83.7	86.0	78.8
dry weight, g	109.6	111.4	101.6	101.6	106.8	100.7	106.7	114.7	116.9	107.6
pore volume, cm ³	40.3	41.3	36.1	34.6	39.2	38.1	38.1	40.9	42.4	39.2
porosity, %	49.3	49.9	48.6	47.7	49.5	50.4	49.1	48.8	49.3	49.8
K_{abs} , mD	3.7	3.1	4.2	3.8	3.4	4.2	3.9	3.2	3.9	3.0
S_{wi} , %	10.1	10.0	11.3	10.0	10.1	9.9	10.0	10.0	10.2	100.0
OOIP, cm ³	37.4	35.7	30.6	32.1	33.5	34.2	36.6	36.6	38.5	0.0

3. RESULTS AND DISCUSSION

3.1. SAILs Evaluation. 3.1.1. Phase Behavior Evaluation.

The hydrophilicity of the $[C_{12}mim]Br$, $[C_{12}Py]Cl$, and $[C_{16}Py]Cl$ SAILs, each one prepared in three brines (VBOS, SW, and SWONa), was evaluated through phase behavior studies with crude oil. The purpose was to ensure that microemulsion Winsor type I (oil in water) was kept when the temperature increased from 50 to 130 °C. Since polar interactions between water molecules and ionic surfactant head groups can be reduced by the aqueous phase salinity, the partition of surfactant to the oil phase can be induced, and a shift of microemulsion from Winsor I to Winsor II could take place.^{14,68–71} Winsor II, water in oil emulsion, means loss of

formulation efficiency due to the increase of both SAIL retention and oil viscosity.^{72–74} On the other hand, rising temperatures provoke stronger interactions between ionic surfactant head groups and water molecules, making them more hydrophilic as the temperature increases.^{70,75–77} Figure 2 presents the results of the phase behavior study of the SAIL formulations at 130 °C. The evaluated SAILs behaved highly hydrophilic during the test, showing microemulsion Winsor type I in the tested temperature interval and at the highest evaluated salinity (VBOS).

3.1.2. Thermal Stability Test. The thermal stability of the SAIL formulations presented in the previous section was evaluated from 50 to 130 °C. The SAIL formulations were prepared at a 1 wt % SAIL concentration using brines VBOS,

Table 3. Summary of Spontaneous Imbibition Tests Performed at 90 °C

test ID	SI-1	SI-2	SI-3	SI-4	SI-5	SI-6	SI-7
core ID	C#1	C#2	C#3	C#4	C#5	C#6	C#7
OOIP, cm ³	37.4	35.7	30.6	32.1	33.5	34.2	36.6
secondary mode fluid	VBOS	VBOS	VBOS	VBOS	VBOS	VBOS	VBOS
oil recovery, (% OOIP)	27.0	23.0	19.0	38.7	35.8	28.1	26.2
tertiary mode fluid	SW0Na	[C ₁₂ Py]Cl SW0Na	[C ₁₆ Py]Cl SW0Na	[C ₁₂ mim]Br SW0Na	[C ₁₂ Py]Cl SW0Na	SW0S	[C ₁₂ mim]Br SW0S
AOR, (% OOIP)	11.5	22.7	4.9	24.6	22.4	1.2	5.2

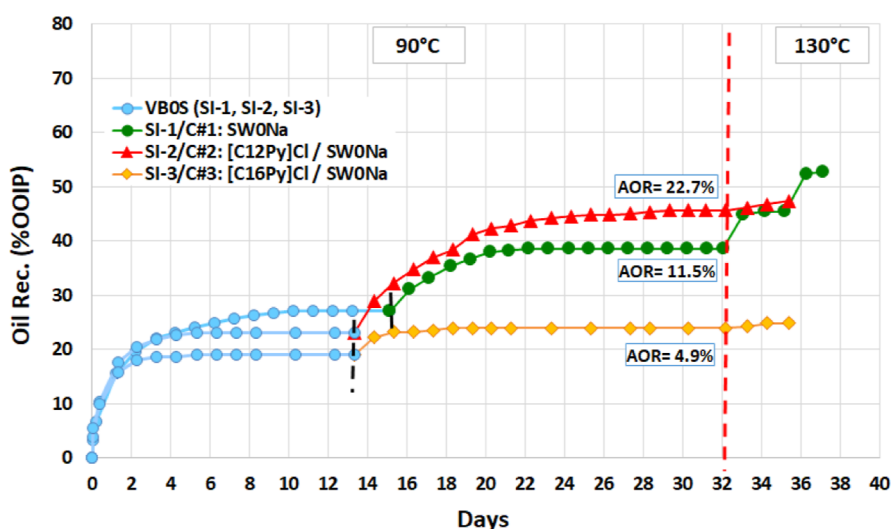


Figure 4. Effect of the SAIL alkyl chain length on spontaneous imbibition at 90 °C, SI-1 (SW0Na), SI-2 ([C₁₂Py]Cl-SW0Na), and SI-3 ([C₁₆Py]Cl-SW0Na). VBOS was used as the first imbibition brine in all three tests.

SW, and SW0Na as make-up water. During the evaluation, no precipitation was observed in the pipettes, and the formulations remained translucent until the end of the test, after 2 weeks. Figure 3 shows the results of this evaluation at 130 °C.

3.1.3. Dynamic Interfacial Tension. As seen in Figure 2, a dark aqueous phase was noticed for all [C₁₆Py]Cl formulations, meaning a higher capacity to solubilize the oil phase inside the aqueous phase and therefore lower expected IFT with crude oil than that corresponding to the other SAIL formulations. That expectation was confirmed through the dynamic IFT measurements performed at 50 °C with the SAIL formulations prepared at a 1 wt % SAIL concentration in SW0Na. The IFT between crude oil and [C₁₂mim]Br was 1.2 mN/m; for [C₁₂Py]Cl, it resulted in 1.7 mN/m, while for the [C₁₆Py]Cl formulation, it was 0.4 mN/m.

3.2. Core Characterization. The characterization of the cores was performed during the core preparation stage. Dimensions, porosity, absolute permeability (K_{abs}), pore volume, initial water saturation (S_{wi}), and OOIP are shown in Table 2 for the 10 used outcrop SK chalk cores.

The physical properties of the outcrop chalk cores were similar to those in previously published research.^{78,79}

3.3. Oil Recovery Tests. Several oil recovery tests were performed to evaluate the ability of the three cationic SAILs to increase oil recovery from outcrop chalk cores when they are formulated in SW0Na brine as make-up water. The evaluation involved seven spontaneous imbibition tests and two additional viscous flooding tests with the best-performing formulation.

3.3.1. Spontaneous Imbibition Tests. The purpose of the SI tests was to determine the efficiency of the SAILs, formulated

in smart water (SW0Na), to induce wettability alteration of chalk cores from mixed-wet to more water-wet at 90 °C. For efficient oil displacement by SI of water in mixed-wet to more oil-wet cores, the capillary forces acting against water intrusion into oil-wet pores must be overcome. As suggested in previous studies,^{17,20,80} SI driven by capillary forces can occur in oil-wet rocks with cationic surfactant formulations, despite their low capillary pressure (low IFT). Cationic elements present in surfactant solutions have the ability to desorb anionic polar compounds of the crude oil from the rock surface and modify the wetting state toward a more water-wet state. However, it has been shown^{17,20} that in addition to the capacity to desorb polar compounds from the rock surface, the cationic surface-active formulations must have a moderate IFT with the oil to promote the penetration of the aqueous phase into the core by capillary forces during the wettability alteration process. On the other hand, anionic surfactants were not able to desorb polar organic compounds from the chalk surface, but could, due to a low to ultra-low IFT, imbibe water and produce oil because of weak capillary forces and sufficient gravity forces.^{17,81} Seven SI tests (SI-1 to SI-7) were carried out at 90 °C using cores C#1 to C#7 (core properties in Table 2). All SI tests were performed with VBOS as the first imbibition fluid (in secondary mode) until the oil recovery plateau was reached. Oil recovery is reported in % OOIP. The moderate oil recoveries obtained after this first imbibition stage showed that the cores were mixed-wet at initial conditions¹² (Table 3). Previously, it has been shown that a very water-wet SK chalk core spontaneously imbibed VBOS, producing 75 % OOIP of the *n*-heptane saturated core in the presence of $S_{wi} = 10\%$ VBOS.⁸² After treating the same core material with 15 PV crude oil, the core spontaneously imbibed a limited volume of

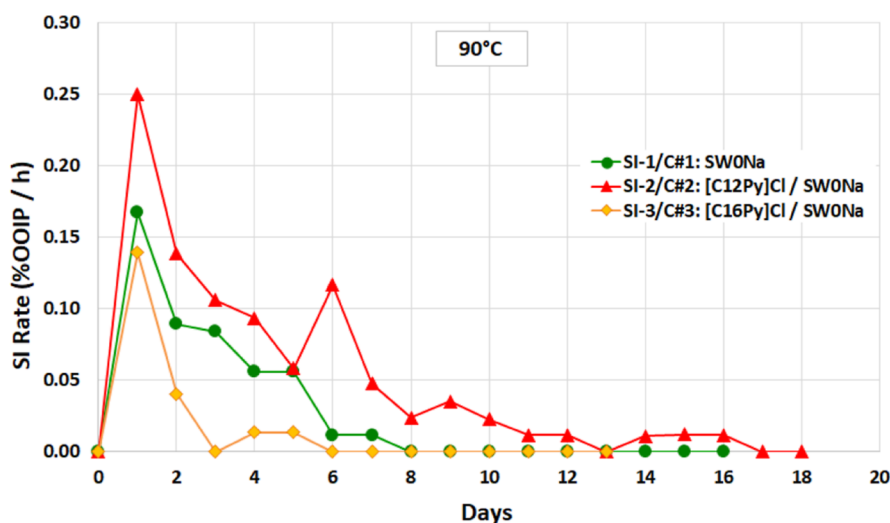


Figure 5. Effect of the SAIL alkyl chain length on spontaneous imbibition rates at 90 °C during tertiary imbibition of SI-1 (SWONa), SI-2 ($[C_{12}Py]Cl$ -SWONa), and SI-3 ($[C_{16}Py]Cl$ -SWONa) tests.

VBOS, producing only 6 % OOIP crude oil at 50 °C, confirming mixed-wet conditions after crude oil exposure. In the SI-1 test (core C#1), the tertiary mode imbibition was carried out with SWONa as the base case. In the SI-2 to SI-7 tests, VBOS brine was replaced by a SAIL formulation (1 wt % SAIL) in the tertiary mode, according to the designed assessment plan with three objectives: (1) evaluation of the effect of two different alkyl chain length SAILS with the same head group (pyridinium ring), (2) evaluation of the effect of different head groups (pyridinium and imidazolium rings) having the same hydrophobic tail length, and (3) evaluation of the effect of sulfate ions on the wettability alteration behavior of the best-performing SAIL formulation.

3.3.2. Effect of the SAIL Alkyl Chain Length. The influence of the alkyl chain length of SAILS on the wettability alteration process was evaluated using the pyridinium SAILS $[C_{12}Py]Cl$ and $[C_{16}Py]Cl$. In the experiment SI-2 and SI-3, $[C_{12}Py]Cl$ and $[C_{16}Py]Cl$ formulations were used as tertiary mode imbibition fluids using the cores C#2 and C#3. The potential of the formulations was inferred by the recovered oil during the tertiary mode (named additional oil recovery, AOR) and by the imbibition rates. The produced aqueous phase from the SI-2 and SI-3 tests contained a fraction of oil in the form of an emulsion, but this was not taken into account for the AOR results. The results of these tests are shown in Figure 4, which also includes the base case (SI-1 test). As it can be seen, the $[C_{12}Py]Cl$ formulation reached a final AOR almost twice that obtained with SWONa, 22.7 % OOIP and 11.5 % OOIP at 90 °C, respectively. In the case of the $[C_{16}Py]Cl$ formulation, AOR was only 4.9 % OOIP, resulting in poorer imbibition performance than the other tests. Imbibition rates corresponding to these tests are shown in Figure 5. The figure shows that the rate of oil expulsion with the $[C_{12}Py]Cl$ formulation was clearly higher than that corresponding to SWONa during the whole imbibition process. The oil production with the $[C_{12}Py]Cl$ formulation stopped after 17 days, whereas the oil production with SWONa was only maintained for 8 days. The $[C_{16}Py]Cl$ formulation presented the lowest imbibition rates, with oil production ceasing after 6 days.

The imbibition mechanism for the $[C_{12}Py]Cl$ formulation may be analogous to that suggested for the $C_{12}TAB$ surfactant.^{17–19} At first imbibition flood with VBOS in mixed-

wet cores, when no change of wettability state has taken place, the capillary forces are unfavorable for the water to imbibe into the cores and expel the oil. Once VBOS brine has been switched to the $[C_{12}Py]Cl$ formulation, which has even lower IFT (lower capillary pressure) than the VBOS brine, cationic monomers interact with the adsorbed anionic polar components of the oil, desorbing them from the rock surface. The aqueous phase continues to imbibe into the core and expel oil, making the chalk rock more and more water-wet as the process continues. At this point, the capillary pressure between the aqueous and oil phases is now high enough (because water has now become the wetting phase), and the imbibition is driven by capillary forces. Desorbed anionic polar components are solubilized into the oil phase but are also produced through micelles in the aqueous phase.

Regarding the clearly different performance between $[C_{12}Py]Cl$ and $[C_{16}Py]Cl$, similar behavior between the cationic surfactants $C_{12}TAB$ and $C_{16}TAB$ was observed in previous work, where $C_{12}TAB$ obtained a higher imbibition rate and oil recovery than $C_{16}TAB$.¹⁷ In that study, the authors suggested that in the wettability alteration process, only cationic monomers of the surfactants have an active role in the polar component desorption. As explained above, it was also shown that a moderate IFT between the aqueous and oil phases was required to facilitate the imbibition process in which cationic surfactants desorb carboxylates from the chalk surface, improving spontaneous imbibition of water because of sufficient capillary forces present at a moderate IFT.⁸⁰ The capability of the $[C_{16}Py]Cl$ for wettability alteration should be similar to SWONa and $[C_{12}Py]Cl$ since all the formulations have the same Ca^{2+} concentration. However, the water-oil IFT generated by the $[C_{16}Py]Cl$ SAIL could be too low to overcome the capillary forces of the core to invade it and trigger the wettability alteration. To evaluate the influence of high temperatures on the formulation's performance, the temperature was increased to 130 °C. It is known that the efficiency of SmW increases with temperature.^{25–27,83} As expected, the raised temperature from 90 °C to 130 °C reactivated the oil production for the SI-1 test with SWONa brine (Figure 4). Surprisingly, this behavior was not repeated in the SI-2 and SI-3 tests performed with the SAIL formulations. After 5 days, it was clear that SWONa greatly

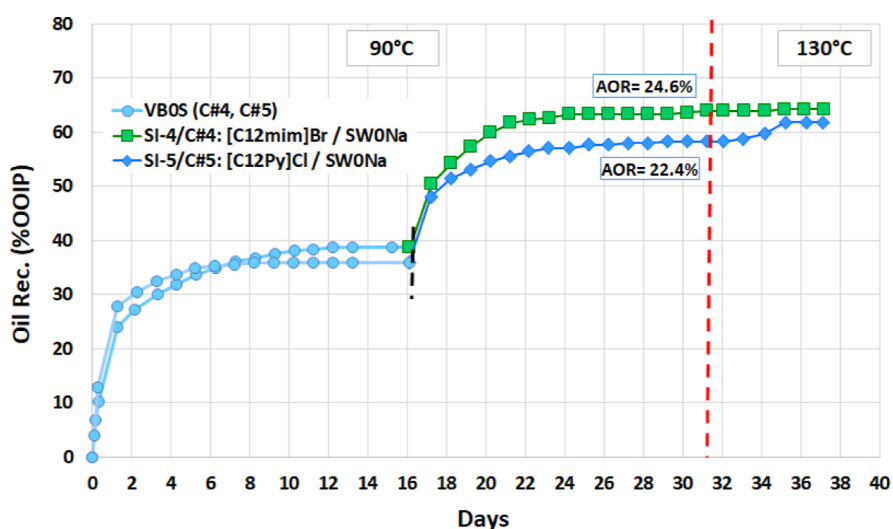


Figure 6. Effect of the SAIL head group on spontaneous imbibition at 90 °C, SI-4 ([C₁₂Py]Cl-SW0Na) and SI-5 ([C₁₂mim]Br-SW0Na). VBOS was used as the first imbibition brine in both tests.

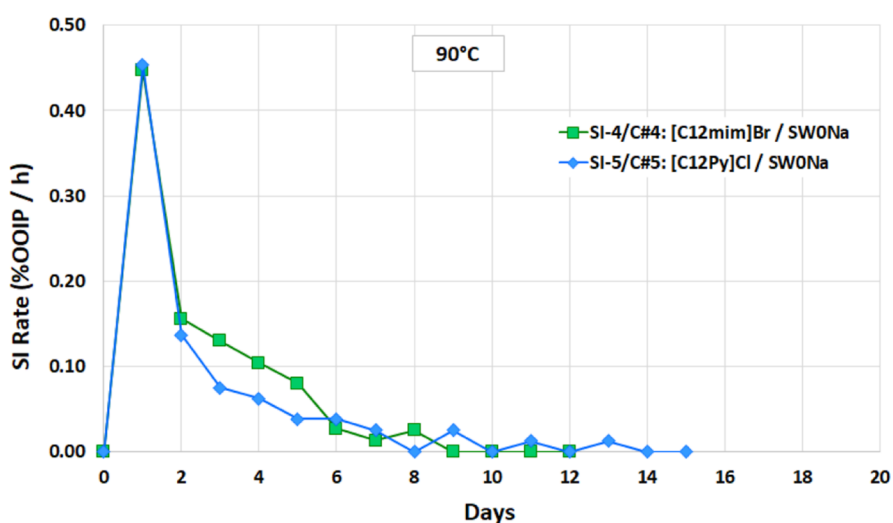


Figure 7. Effect of the SAIL head group on spontaneous imbibition rates at 90 °C during tertiary imbibition of SI-4 ([C₁₂Py]Cl-SW0Na) and SI-5 ([C₁₂mim]Br-SW0Na).

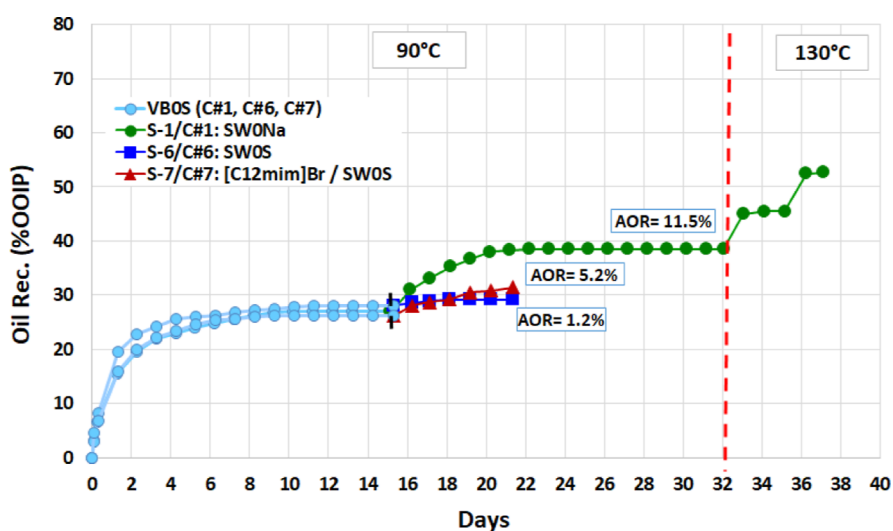


Figure 8. Influence of sulfate on the efficiency of the [C₁₂mim]Br formulation in chalk wettability alteration at 90 °C through spontaneous imbibition tests.

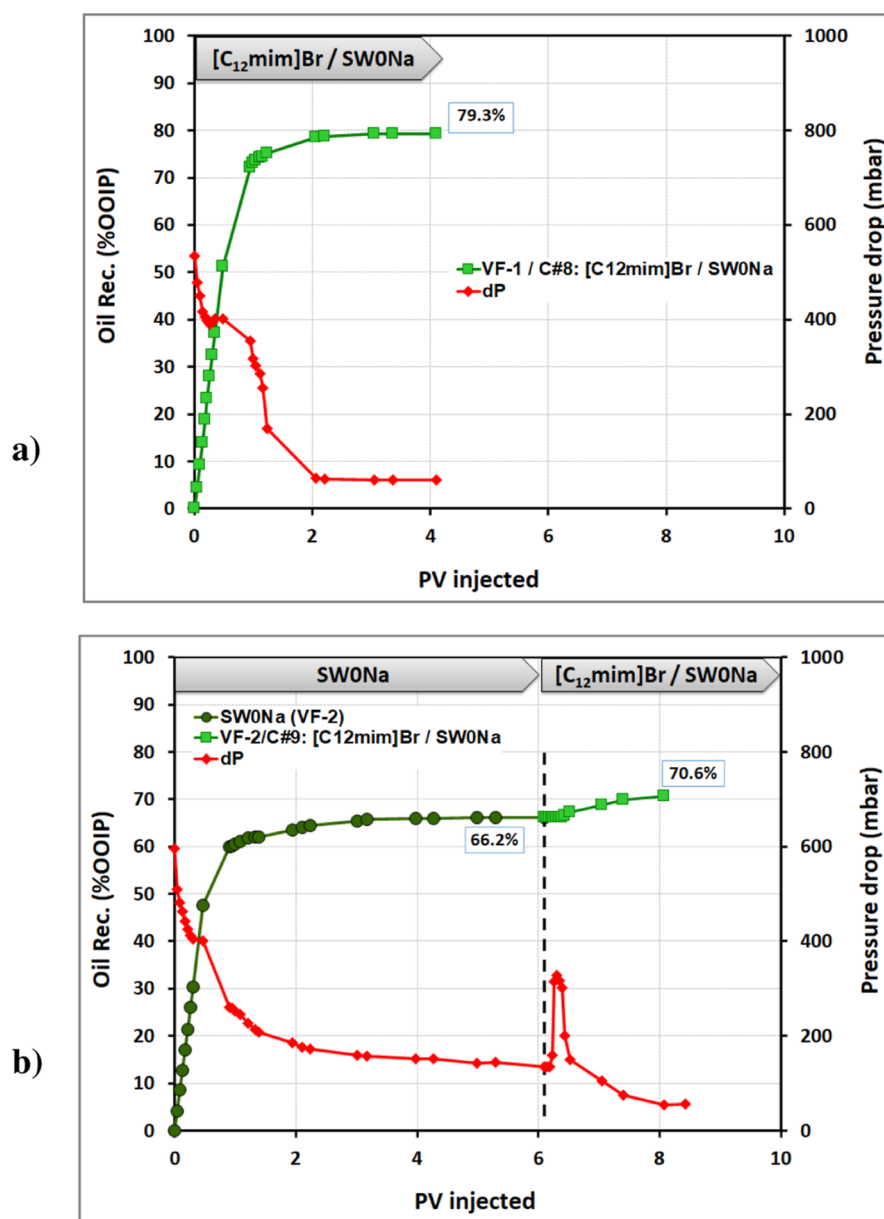


Figure 9. Oil recovery by viscous flooding tests (a) VF-1 using [C₁₂mim]Br formulation in secondary mode; and (b) VF-2 using SW0Na brine in the secondary mode and [C₁₂mim]Br formulation in the tertiary mode. Injection rate: 0.03 cm³/min, test temperature: 90 °C.

improved its efficiency, reaching an AOR of 25.7 % OOIP with the temperature increase. This might be due to the cationic head group of the ionic liquids deactivating the interactions of the temperature-sensitive PDIs with the rock surface during the imbibition process.

3.3.3. Effect of the SAIL Head Group. In order to determine the influence of SAIL head groups on wettability changes, the SI tests SI-4 (using C#4) and SI-5 (using C#5) were carried out with [C₁₂mim]Br and [C₁₂Py]Cl. These SAILs have the same hydrophobic chain length but different rings (imidazolium and pyridinium). The result of this evaluation is shown in Figure 6. As seen, the AOR for the [C₁₂mim]Br formulation was around 24.6 % OOIP, while the [C₁₂Py]Cl formulation achieved an AOR of 22.4 % OOIP. Figure 7 shows that [C₁₂mim]Br kept a slightly higher imbibition rate than [C₁₂Py]Cl for a few days, which resulted in a somewhat higher oil recovery obtained with [C₁₂mim]Br. This outcome could indicate that neither the ring type nor the contra-ion had great

influence on the final AOR (Figure 6) or imbibition rates (Figure 7). The aqueous phase produced in the SI-4 and SI-5 tests had oil in the form of an oil-in-water emulsion, but it was not considered for final oil recoveries. The test temperature was raised from 90 to 130 °C, and in this case, a slight increase in AOR was noticed only with [C₁₂Py]Cl (Figure 6). The [C₁₂mim]Br formulation was selected for further assessments at 90 °C.

3.3.4. Effect of Sulfate. The sulfate ion is one of the three PDIs involved in the wettability alteration of chalk rocks. As discussed above, when SW or SmW are injected, SO₄²⁻ is adsorbed onto the chalk surface, and divalent Ca²⁺ and Mg²⁺ favor the desorption process of the carboxylate from the rock.^{84–86} Removal of SO₄²⁻ from the imbibition fluids has a negative impact on oil recovery.^{5,26,87,88} To evaluate if the sulfate ion has a significant influence on the wettability alteration capacity of the best-performing SAIL formulation, SO₄²⁻ was removed from the SW0Na brine. The new brine

SW0S (SW0Na without SO_4^{2-}) was then used as make-up brine for a new $[\text{C}_{12}\text{mim}]\text{Br}$ formulation (termed $[\text{C}_{12}\text{mim}]\text{Br-SW0S}$). Both imbibition fluids, SW0S and $[\text{C}_{12}\text{mim}]\text{Br-SW0S}$, were evaluated at $90\text{ }^\circ\text{C}$ in the tertiary imbibition mode in the SI-6 and SI-7 tests using cores C#6 and C#7. Figure 8 presents the results of this evaluation together with the base-case SI-1 test. According to these results, the presence of sulfate in the $[\text{C}_{12}\text{mim}]\text{Br}$ formulation was crucial to maintaining the efficiency of the formulation for oil recovery, with a similar role as that observed in SW0Na imbibition tests.

Table 3 shows a summary of the main outcomes obtained for the seven spontaneous imbibition tests.

3.3.5. Viscous Flooding Tests. The best performing SAIL formulation (1 wt % $[\text{C}_{12}\text{mim}]\text{Br}$ in SW0Na) was additionally evaluated at $90\text{ }^\circ\text{C}$ through two viscous flooding tests, VF-1 and VF-2, in the secondary mode and tertiary mode after SW0Na flooding, respectively. In the VF-1 test, 4.11 PV of the $[\text{C}_{12}\text{mim}]\text{Br}$ formulation was injected through the chalk core C#8 at an injection rate of $0.03\text{ cm}^3/\text{min}$ ($\sim 1\text{ PV/D}$) until the oil production ceased. The oil recovery was 79.3 % OOIP (Figure 9a). In the VF-2 test, core C#9 was first flooded by 6.1 PV of SW0Na brine at $0.03\text{ cm}^3/\text{min}$ until no more oil production was observed, reaching an oil recovery of 66.2 % OOIP. Then, the core was flooded by 1.97 PV of the $[\text{C}_{12}\text{mim}]\text{Br}$ formulation at the same injection rate, obtaining a final oil recovery of 70.6 % OOIP (AOR in the tertiary mode was 4.4 % OOIP) (Figure 9b).

The viscous flooding tests show a beneficial effect of flooding the SAIL formulation (1 wt % $[\text{C}_{12}\text{mim}]\text{Br}$ in SW0Na) compared to flooding pure SW0Na, both in secondary and tertiary injection modes. This is believed to be because of the improved wettability alteration taking place with $[\text{C}_{12}\text{mim}]\text{Br}$ present in SW0Na, as observed in Figures 4 and 6, with values summarized in Table 3.

Moreover, the differential pressure behavior between VF-1 and VF-2 tests after $\sim 0.48\text{ PV}$ was injected was not similar. As observed for VF-1 (Figure 9a), at 0.48 PV , the pressure started to decline slower than for VF-2 (Figure 9b). Then, the pressure in VF-1 dropped sharply to 65 mbar after 2 PV injection. In comparison, the pressure in VF-2 declined smoothly from 0.48 PV to 6.1 PV , ending at 135 mbar. That dissimilar performance may indicate the creation of an oil bank in VF-1, resulting from both the wettability alteration process and the promotion of Winsor type I emulsion (oil in water) due to the IFT between the SAIL formulation and the oil phase. In VF-2, the increase in pressure during the SAIL formulation injection (from 6.1 PV injection) can also be attributed to the formation of a smaller oil bank. After its production, the pressure declined abruptly to 56 mbar. A small fraction of oil was observed in the aqueous phase collected in the burettes during the SAIL formulation core floods; however, it was not considered in the total recovered oil.

The lower tertiary recovery efficiency of the SAIL formulation seen in VF-2 compared to that obtained in VF-1 might be due to the reduced potential of wettability alteration and emulsion formation after the SW0Na flooding in core C#9 due to its already low residual oil saturation (S_{or}).

3.3.6. Dynamic Adsorption. The adsorption of SAIL $[\text{C}_{12}\text{mim}]\text{Br}$ on chalk core at $90\text{ }^\circ\text{C}$ was estimated using the core C#10 and the best-performing formulation (1 wt % $[\text{C}_{12}\text{mim}]\text{Br}$ in SW0Na) in the dynamic adsorption single-phase test. Figure 10 presents the results of this evaluation, showing normalized concentration (C/C_0) profiles of tracer

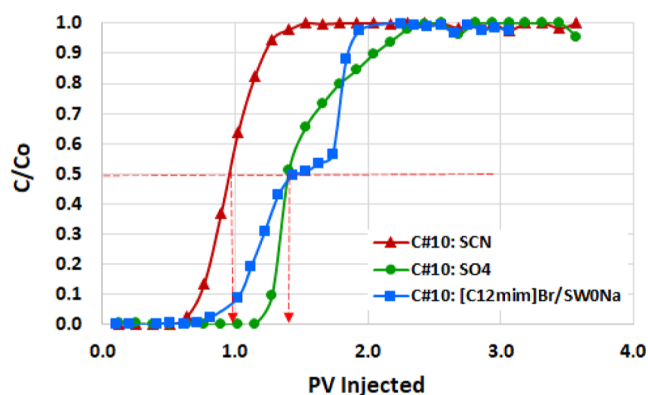


Figure 10. Dynamic adsorption of $[\text{C}_{12}\text{mim}]\text{Br}$ prepared in SW0Na brine on chalk. Single-phase condition. Water-wet chalk core C#10. Injection rate of $0.1\text{ cm}^3/\text{min}$, test temperature of $90\text{ }^\circ\text{C}$.

and SAIL formulations as a function of injected PV. According to diffuse percolation methodology, the fronts ($C/C_0 = 0.5$) for the tracer SCN^- and $[\text{C}_{12}\text{mim}]\text{Br}$ injection were detected at 0.96 and 1.48 PV injected, respectively (Figure 10). The SO_4^{2-} profile was also included in the figure for comparative purposes.

With the use of eq 1, $[\text{C}_{12}\text{mim}]\text{Br}$ adsorption was estimated to be 1.91 mg/g of rock. Using the area between curves SCN^- and $[\text{C}_{12}\text{mim}]\text{Br}$ (around 0.51), a similar value was achieved (1.85 mg/g). This output seems quite high since recent work⁴⁴ with this SAIL prepared in a synthetic SW showed very low dynamic adsorption on Indiana limestone cores of around 0.08 mg/g (at $100\text{ }^\circ\text{C}$ and an injection rate of $0.5\text{ cm}^3/\text{min}$). It was found that increasing the SAIL concentration slightly increased the adsorption until the CMC (250 ppm), where the adsorption increments were not significant.

However, the SK chalk, a biogenic CaCO_3 material, has a much larger surface area than the Indiana limestone. Khan et al.⁷⁸ measured a SK BET surface area of $2.0\text{ m}^2/\text{g}$, which is 3–4 times higher than the BET values in the range of 0.49 to $0.71\text{ m}^2/\text{g}$ reported for Indiana limestone by Churcher et al.⁸⁹ Thus, in SK chalk, there is a much larger surface area available for the adsorption of SAIL; therefore, more adsorption should be expected. In addition, the biogenic chalk surface has previously been found to be more reactive than the recrystallized outcrop limestone surface. The surface reactivity of two outcrop limestones toward the PDIs, Ca^{2+} , Mg^{2+} , and SO_4^{2-} , was tested by Ravari et al.⁹⁰ and was found to be much lower than that observed for SK chalk or reservoir limestone.⁹¹

Nonetheless, a suggested explanation for this high adsorption of cationic ions onto the positively charged chalk surface is a possible binding between surface Ca^{2+} , SO_4^{2-} , and $[\text{C}_{12}\text{mim}]^+$ ions, which should become more prominent in the absence of NaCl salts. It is known that SO_4^{2-} adsorbs onto the chalk surface, which then can aid additional adsorption of $[\text{C}_{12}\text{mim}]^+$ ions.

4. CONCLUSIONS

The potential of three cationic SAILs, $[\text{C}_{12}\text{mim}]\text{Br}$, $[\text{C}_{12}\text{Py}]\text{Cl}$, and $[\text{C}_{16}\text{Py}]\text{Cl}$, prepared in Smart Water (SW0Na), to trigger wettability alteration of chalk cores from mixed-wet toward more water-wet conditions, was evaluated by means of spontaneous imbibition and viscous flooding tests. Some conclusions can be drawn:

- The $[C_{12}mim]Br$ and $[C_{12}Py]Cl$ formulations showed higher potential to alter wetting state of the mixed-wet chalk cores toward more water-wet at 90 °C compared to pure SW0Na brine, as confirmed by a more efficient spontaneous imbibition process using SAIL formulations.
- Although it was observed that the efficiency of the $[C_{12}mim]Br$ formulation was slightly higher than that of the $[C_{12}Py]Cl$ formulation in spontaneous imbibition evaluations, the rings of $[C_{12}mim]Br$ and $[C_{12}Py]Cl$ SAIL did not show a significant effect on additional oil recovered or imbibition rates at 90 °C.
- Solutions formulated with $[C_{12}Py]Cl$ and $[C_{16}Py]Cl$ in SW0Na had a very different performance in imbibition tests. The potential of the $[C_{16}Py]Cl$ formulation to induce changes in rock wetting state was quite low in comparison to $[C_{12}Py]Cl$ and SW0Na due to differences in formulation-oil IFT.
- Contrary to SmW SW0Na brine, an increase of temperature from 90 to 130 °C did not improve the efficacy of the SAIL formulations.
- The evaluation of the effect of sulfate demonstrated that this ion remains key for the chalk wettability alteration by $[C_{12}mim]Br$ formulation, a behavior previously observed with Smart Water, also using the cationic surfactant $C_{12}TAB$.
- The evaluation of the $[C_{12}mim]Br$ formulation with two viscous core floodings showed that the formulation was more efficient than pure Smart Water, injected both in the secondary and tertiary modes.

This work is a preliminary study about the influence of cationic SAIL parameters, such as type of ring and alkyl chain length, on the performance of SmW as an EOR method. Significant further assessments need to be done to have a full understanding of the SAIL behavior in the wettability alteration processes.

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Notes

The authors declare no competing financial interest.

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