



Design and performance analysis of a formulation based on SDBS and ionic liquid for EOR in carbonate reservoirs

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ARTICLE INFO

Keywords:

Anionic
Cationic
Synergy
Microemulsion

ABSTRACT

A large proportion of extant crude oil is found in carbonate reservoirs worldwide. Alkylbenzene sulfonates are inexpensive anionic surfactants but they cannot be used in these reservoirs due to their incompatibility with divalent ions and high adsorption on the rocks. This paper proposes the solution to that problem by blending this kind of surfactant with surface-active ionic liquids. Namely, a formulation containing sodium dodecylbenzenesulfonate (SDBS) and cocosalkylpentaethoximethylammonium methylsulfate ([C1EG][MeSO₄]) was designed for the application. Two optimal blends, at 40/60 and 73.7/26.3 SDBS/[C1EG][MeSO₄] ratios, were found in synthetic seawater via equilibria and interfacial tension (IFT) studies. Core-flooding tests were carried out to check the performance of both blends. The first blend ratio (40 wt% SDBS) was selected to define an optimal formulation (1 wt% blend in synthetic seawater at 298.15 K) due to its better injectability, higher reduction of the IFT, lower adsorption, and better oil recovery. Attained tertiary oil recovery (18% of the original oil in place), with low blend adsorption (0.37 mg_{blend}/g_{rock}), shows the promising performance of the solution. The main mechanism associated with improved oil recovery is IFT reduction. This work offers a significant advance in the application of natural petroleum sulfonates in carbonate reservoirs.

1. Introduction

Worldwide petroleum consumption is expected to increase at an annual rate of 0.6% between 2021 and 2050 primarily led by China and other emerging economies (U.S. Energy Information Administration, 2019). According to the BP Statistical Review of World Energy 2020 (BP, 2020) around 48% of the world's oil reserves are in the Middle East and approximately 70% of these reserves are in carbonate reservoirs. More than 30% of the daily world oil production comes from these mature reservoirs. Carbonate reservoirs are characterized by their heterogeneity, low permeability, complex pore network, presence of natural fractures, and unfavorable wettability conditions (oil-wet or intermediate-wet). All those factors contribute to poor recovery efficiency (Sheng, 2013a).

Capillary forces, responsible for trapping a large portion of the oil phase within the pores of the rocks, are several orders of magnitude greater than viscous forces after conventional water-flooding (Melrose and Brandner, 1974). It is known that residual oil recovery in a porous media is essentially zero when the capillary number is lower than 10^{-6} and it is considerably improved when values are higher than 10^{-3} (Guo

et al., 2015, 2017; Khosravi, 2010). The two mechanisms that can improve oil recovery are: increasing the displacing phase viscosity and reducing oil/water interfacial tension (IFT). However, the higher the viscosity of the aqueous phase, the greater the pressure gradient required to obtain the same fluid velocity. Therefore, the increase of the capillary number through this method is limited. Thus, to obtain high residual oil recovery, it is necessary to use surfactants to achieve ultra-low water/oil IFT values (Sheng, 2015). Another important mechanism associated with enhanced oil recovery (EOR) is wettability alteration. Oil extraction is facilitated by changing the wetting state of the rock from oil-wet to mixed-wet or water-wet.

The high oil saturation remaining after primary and secondary recovery makes carbonate reservoirs attractive candidates for surfactant EOR. There is a great potential to increase well production. However, the use of surfactants in this type of rock is limited by their tolerance to harsh conditions such as high temperature and salinity (Alammari et al., 2020). Moreover, most traditional surfactants are anionic, thus they are attracted to positively charged carbonate surfaces leading to high adsorption values (Bera et al., 2013). Wettability alteration by surfactant flooding in carbonate rocks has been widely studied by several

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<https://doi.org/10.1016/j.petrol.2021.109856>

Received 15 June 2021; Received in revised form 9 November 2021; Accepted 13 November 2021

Available online 19 November 2021

0920-4105/© 2021 The Authors.

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authors in recent years (Ahmadi et al., 2014; Alammari et al., 2020; Seethepalli et al., 2004; Standnes and Austad, 2003). Cationic surfactants are generally proposed. They form ion pairs with adsorbed negatively charged carboxylates of crude oil and stabilize them within the oil, thereby changing the rock surface towards water-wet (Pal et al., 2018).

Surface-active ionic liquids (SAILs) are emerging as possible candidates for improving surfactant EOR methods (Bera and Belhaj, 2016). SAILs are ionic liquids, salts with melting or glass transition temperature below 373.15 K, that are surface-active agents. Among the promising properties of ionic liquids (negligible vapor pressure, wide liquidus range, high capacity of solvation, etc.), the possibility of their functionalization is the most attractive. They can be designed to be stable in harsh environmental conditions, or even optimized according to the requirements of a specific reservoir (Tackie-Otoo et al., 2020).

The potential of different SAILs for EOR in carbonate reservoirs has been previously investigated (Cao et al., 2016; Joonaki et al., 2016). However, analysis of the real performance of the SAILs proposed through core flooding studies is very scarce. Manshad et al. (2017) proposed the use of the SAIL $[C_{18}mim]Cl$. Core flooding tests using a formulation containing 170 ppm of SAIL in formation brine revealed 13% additional oil recovery after water-flooding in carbonate cores. Further tests proved that the increase in oil production was mainly due to the IFT reduction, and that the effect of wettability alteration was not particularly significant. Zabihi et al. (2019) also proposed formulations consisting of 4000 ppm of $[C_{12}mim]Cl$ or 3500 ppm of $[C_{18}mim]Cl$ in formation brine and compared them with the use of the traditional surfactant sodium dodecylbenzenesulfonate (SDBS). SDBS showed the best capability for IFT reduction while the SAILs showed higher capability to alter the wettability of the rock towards mixed wet. Core flooding tests showed that $[C_{12}mim]Cl$ and $[C_{18}mim]Cl$ were able to enhance oil recovery by 13% and 16.5%, respectively, while an additional oil recovery of 26% was found with SDBS. IFT reduction was found to be more efficient than wettability alteration as the main recovery mechanism. Nandwani et al. (2019) proposed a chemical formulation containing the SAIL $[P_{6,6,6}Br]$ and a nonionic surfactant (Tergitol 15-S-9). The formulation (without divalent ions) was optimized via phase equilibria studies, achieving a Winsor type III microemulsion. For core flooding tests, a carbonate reservoir was simulated by tightly packing calcite powder. An additional oil recovery of 16.68% of the original oil in place (OoIP) was achieved using the optimized formulation.

Alkylbenzene sulfonates are one of the most common surfactants employed in chemical EOR (Negin et al., 2017). Natural petroleum sulfonates are inexpensive anionic surfactants, stable at high temperature but sensitive to divalent ions. Therefore, the biggest impediment to the use of these surfactants in chemical EOR is the very poor solubility and compatibility of these surfactants in water containing divalent cations (Zulkifli et al., 2020). The addition of co-solvents and co-surfactants is needed to prevent precipitation and improve surfactant salt tolerance at reservoir conditions (Montes et al., 2018; Sheng, 2013b). Another significant challenge is that alkylbenzene sulfonates show high adsorption values in carbonate rocks (Hemmati et al., 2017; Montes et al., 2018), so the use of these surfactants in carbonate material has barely been tested. In this paper, derived from a recent patent (Somoza Cerviño and Soto Campos, 2021), the drawbacks of this kind of surfactants are avoided by mixing them with an ammonium-based ionic liquid. The advantages of this proposal lie in the fact that the combination of a traditional anionic surfactant with a cationic IL with different ramified chain lengths obtains alcohol-free microemulsions. Moreover, the ratio of surfactants can be optimized to obtain the desired hydrophilic-lipophilic balance needed to achieve ultra-low IFT, as well as other practical requirements such as low adsorption and stability in harsh conditions. The optimization of the formulation is carried out via phase equilibria studies, injectability tests and IFT measurements. Dynamic adsorption of the optimized formulation in carbonate rocks is investigated. The effectiveness of the newly proposed surfactant mixture

in recovering residual oil is determined via core flooding tests. In addition, wettability alteration using contact angle measurements is analyzed in order to better understand recovery mechanisms.

2. Materials and methods

2.1. Materials

The anionic surfactant sodium dodecylbenzenesulfonate (SDBS) was purchased from Sigma-Aldrich with technical grade purity. The cationic room temperature ionic liquid cocosalypentaethoximethylammonium methylsulfate (purity >95 wt%), commercially named Iolilyte C1EG ($[C1EG][MeSO_4]$), was supplied by Iolitec. Table 1 shows the chemical formula and critical micelle concentration for the surfactants used in this work. Polyacrylamide (PAM) with a molecular weight of 5–8 million Daltons (Flopam FA 920 SH) was kindly provided by SNF Floerger.

Sodium chloride was purchased from Panreac (purity >99 wt%). Sodium sulfate (purity >99 wt%), magnesium chloride hexahydrate (purity >99 wt%) and calcium chloride dihydrate (purity >99 wt%) were supplied by Sigma-Aldrich. Synthetic seawater (SSW) was simulated with the composition shown in Table 2 (Montes et al., 2018; Puerto et al., 2012; Rodriguez-Escontrela et al., 2017). Potassium iodide (purity >99 wt%), used as a tracer for dynamic adsorption tests, was also supplied by Sigma-Aldrich.

Crude oil used for IFT measurements, wettability and core flooding tests, was kindly supplied by Repsol (refinery of A Coruña, Spain) and its main properties are summarized in Table 3. SARA analysis was carried out using gradient-based high performance thin-layer chromatography (Cebolla et al., 2016) by the Separation and Detection Group at ICB (Zaragoza, Spain). *N*-octane (purity >99 wt%), used as the model oil in pipette tests, was purchased from Sigma-Aldrich.

Low permeability carbonate (limestone and dolomite) cores were purchased from Kocurek Industries. These cores are mineralogically composed of 50–100% calcium carbonate, 0–50% magnesium carbonate and 0–15% crystalline silica (as quartz).

2.2. Methods

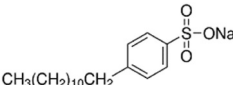
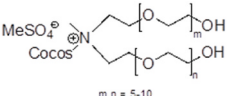
Stock solutions of each surfactant (SDBS and $[C1EG][MeSO_4]$) were prepared at 8 wt% in distilled water.

2.2.1. Phase behavior

Phase behavior studies are useful tools for the search of a chemical formulation able to produce a Winsor Type III microemulsion, with the proper oil solubilization required for attaining ultra-low IFT, and consequently high oil recovery (Sheng, 2011). These tests are conducted in small tubes or pipettes (Puerto et al., 2012). Oil is added to the surfactant solution usually with a water/oil ratio equal to one. In blend scans the temperature, salinity and surfactant concentration are fixed, whereas the surfactant ratio is varied between test tubes. Salinity scans are used to determine the effect of changing salt concentration at fixed surfactant concentration, blend ratio and temperature (Montes et al., 2018; Puerto et al., 2012; Rodriguez-Escontrela et al., 2017).

2.2.1.1. Blend scans. Sulfonate-type surfactants, such as SDBS, precipitate in seawater due to their sensitivity to divalent ions (Zulkifli et al., 2020). For that reason, required amounts of stock solutions were mixed in pipettes of borosilicate glass sealed at the tip, located on an analytical balance, to obtain $\sim 0.5 \text{ cm}^3$ of the blend with the required SDBS/ $[C1EG][MeSO_4]$ mass ratio. Then, $\sim 0.5 \text{ cm}^3$ of a brine solution with a concentration of salts twice that shown in Table 1 was added to obtain $\sim 1 \text{ cm}^3$ of aqueous phase. Thus, the aqueous solution contained 4 wt% of surfactant blend in SSW. This surfactant concentration is higher than that usually injected in reservoirs, but facilitates measurement of the phase volumes to calculate solubilization parameters.

Table 1
Surfactants used in this work.

Compound	Formula	Appearance	CMC (mg/L)
Sodium Dodecylbenzenesulfonate		Solid	157 (Weiss et al., 2007)
[C1EG][MeSO ₄]		Liquid	88.1 ^a

^a Determined in this work (see Supporting Information, SI, for details).

Table 2
Synthetic seawater (SSW) composition.

Salt	Concentration (g/kg solution)
Na ₂ SO ₄	4.84
CaCl ₂ ·2H ₂ O	1.89
MgCl ₂ ·6H ₂ O	15.06
NaCl	27.94

Table 3
Crude oil properties.

Density at 288.15 K (kg/m ³)	811.1
API ^o	42.9
Reid vapor pressure (kPa)	44.9
Viscosity at 293.15 K (kg/m·s)	4.861·10 ⁻³
Saturates (wt%)	43.5
Aromatics (wt%)	41.7
Resins (wt%)	11.6
Asphaltenes (wt%)	3.2

Finally, 1 cm³ of *n*-octane (the hydrocarbon generally used to simulate crude oil) was added as an oil phase and pipettes were top sealed to be mixed in a rotary mixer at room temperature for 24 h. Pipettes were encased inside a test tube filled with silicon oil and left to equilibrate in a dry block heater OVAN model BD200-RE, at the target temperature, until phase volumes remained constant. Three different temperatures were studied: 298.15, 323.15 and 348.15 K. The possible existence of liquid crystals in the microemulsions was tested looking for birefringence under polarized light.

2.2.1.2. Salinity scans. In order to determine the effect of salinity on Winsor type III systems found in blend scans with SSW, further evaluation of these systems was carried out. Pipette tests were prepared, with the optimized SDBS/[C1EG][MeSO₄] mass ratios, varying salinity from 0 wt% to 10 wt% of total dissolved solids. Salinities lower than SSW were prepared by mixing distilled water and SSW. Higher salinities were prepared by increasing sodium chloride concentration while keeping divalent concentration constant. Three different temperatures were studied: 298.15, 323.15 and 348.15 K.

2.2.2. Injectability

Aqueous blend solutions were prepared by weight to ensure the injectability of the formulation, and to be used in dynamic IFT and extraction tests. To accurately prepare the formulations with the corresponding SDBS/[C1EG][MeSO₄] ratio, a Mettler Toledo XPE205 analytical balance with a precision of 10⁻⁴ g was used.

The stock solution of [C1EG][MeSO₄] was first added to water, and then the stock solution of SDBS was added to the mixture. Finally, the same mass of a brine solution with a salt concentration twice that shown in Table 2 was added to obtain an aqueous formulation of 1 wt% of surfactant blend (with the target surfactant mass ratio) in SSW.

The most promising formulation, in terms of interfacial tension

reduction and injectability studies in SSW, was further tested to analyze its injectability in harsh conditions (high salt concentration and temperature). To that aim, a formulation consisting of aqueous solutions at 1 wt% of the optimized SDBS/[C1EG][MeSO₄] mass ratio was prepared in brine with 250000 ppm of TDS (increasing NaCl in SSW shown in Table 2) at several temperatures.

2.2.3. Dynamic interfacial tension

Dynamic IFT between crude oil and surfactant solution at different blend ratios was measured using a Krüss SITE100 spinning drop tensiometer at 298.15 K (Drelich et al., 2002). Temperature was controlled circulating oil from a Julabo EH-5 thermostatic bath. The capillary tube was filled with the aqueous formulation. A drop of 4 μL of crude oil was injected in the middle of the tube at a low rotation speed (500 rpm) using a Hamilton micro-liter syringe. Rotating velocities between 2000 and 4000 rpm were applied in order to obtain a drop length at least 4 times larger than its diameter. The IFT was calculated according to the Vonnegut equation (Vonnegut, 1942):

$$IFT = \Delta\rho \cdot \omega^2 \cdot D^3 / 32 \quad (1)$$

where $\Delta\rho$ is the density difference between the dense and light phases, ω is the angular velocity and D is the diameter of the oil drop. The main sources of error of this technique are uncertainties in measurements of the liquid density (Drelich et al., 2002). These were measured with an Anton Paar vibrating U-tube DMA 5000 density meter with automatic viscosity correction and self-control of the temperature to 0.01 K based on the Peltier effect. The uncertainty in density measurement is 3×10^{-5} g/cm³. All the IFT experiments were performed at least twice to ensure repeatability.

2.2.4. Adsorption and core flooding

Adsorption and flooding experiments were conducted in a core-flooding system with a Hassler Core Holder H00-021-0 and two floX-lab BTSP 500-5 piston pumps (equipped with pressure sensors), purchased from Vinci Technologies (see Fig. S3 in SI). To prevent hydraulic side flow, a common source of error in these studies, a confining pressure was maintained at least 35 bar higher than the flooding pressure using an Enerpac P142 manual hydraulic pump. Experiments were carried out at room temperature.

The cores used for the experiments were 3.8 cm in diameter and 7.6 cm in length. The core was initially vacuumed for 24 h, thus avoiding errors associated with air trapped inside the rock, then saturated with SSW at a constant injection rate of 2 mL/min. After 24 h, pore volume (PV) was determined using the dry and wet weights of the core. Absolute permeability (k_w) was calculated using Darcy's law, by recording the pressure difference between the inlet and outlet (ΔP) at different injection flow rates of SSW. After flooding the core with SSW, either adsorption or oil extraction tests were performed.

Dynamic adsorption tests were carried out to evaluate the retention of the surfactant blend in the rocks. After water flooding, tracer or aqueous blend formulation were continuously injected at a rate of 2 mL/min until concentration in the effluent equaled the value of initial

concentration injected. Effluent fractions were collected for analysis every 4 mL. Tracer and surfactant blend concentrations were determined by UV absorption using an HP Presario SR1000 UV/Vis spectrophotometer. Adsorption was calculated by measuring the delay between the tracer and the surfactant exit in the effluent (Montes et al., 2018; Sharma et al., 2016),

$$\tau = \frac{(PV_{surf,50\%} - PV_{tracer,50\%}) \cdot PV \cdot [C]_{surf}}{mass_{rock}} \quad (2)$$

where τ is the blend adsorption in mg/g of rock, $PV_{surf,50\%}$ and $PV_{tracer,50\%}$ are the pore volume in which blend or tracer concentration reached 50% of initial concentration, PV is the pore volume in mL, $[C]_{surf}$ is the initial blend concentration in mg/mL, and $mass_{rock}$ is the core dry weight in grams. In addition, zeta potentials of the surfactant blends in SSW were obtained using a Malvern Zetasizer Nano-ZS. This property is useful to understand interactions with surfaces, so the adsorption mechanism can be better understood.

In oil recovery tests (Bin Dahbag et al., 2015; Nandwani et al., 2019; Rodríguez-Palmeiro et al., 2017; Sheng, 2011), after SSW saturation, the core was flooded with crude oil by increasing injection flow rate from 1 mL/min to 10 mL/min, to increase flooding pressure, until there was no further water coming from the effluent. OOIP was then calculated with the total SSW displaced by the oil. Initial oil saturation (S_{oi}) and initial water saturation (S_{wi}) were calculated using Eqs. (3) and (4) respectively:

$$S_{oi}(\%) = OOIP \cdot 100 / PV \quad (3)$$

$$S_{wi}(\%) = (PV - OOIP) \cdot 100 / PV \quad (4)$$

As an aging step, the core was allowed to rest for 7 days. To simulate conventional oil recovery, a water-flooding step was conducted injecting 3–4 PV of SSW, at a constant flow rate of 2 mL/min, until oil was no longer produced and the differential pressure remained stable. Oil recovered after water flooding (ORWF) allowed the determination of the residual oil saturation (S_{or}),

$$S_{or}(\%) = (OOIP - ORWF) \cdot 100 / PV \quad (5)$$

The core was then subjected to EOR. For this tertiary flooding step, the core was flooded with the optimized formulation at a constant flow rate of 2 mL/min until oil was no longer produced in the effluent. The oil recovered after tertiary flooding (ORTF) was then determined. Finally, the additional oil recovery (AOR) was calculated as a function of the OOIP:

$$AOR(\%OOIP) = ORTF \cdot 100 / (OOIP - ORWF) \quad (6)$$

In order to further approximate operation in real oil fields, two core flooding tests were carried out at low injection rates combining surfactant and polymer flooding. Initial water and oil flooding, and secondary recovery with SSW, were carried out at a velocity of 0.05 mL/min, which is equivalent to 1 ft/day in a large scale reservoir. For the surfactant flooding, 0.5 PV of surfactant formulation were injected at 0.025 mL/min (0.5 ft/day) to promote contact between phases. This flooding was followed by the injection of 2.5 PV of polyacrylamide (PAM). The first 0.5 PV of polymer were injected at the same low rate of 0.025 mL/min to ensure the whole rock PV was swept by surfactant at the same velocity.

Volumes of oil or brine exiting the core were measured by collecting the produced fluid in a 10 mL graduated test tube. The estimated measurement uncertainty is 0.1 mL.

2.2.5. Wettability tests

Wettability was evaluated by measuring rock-oil contact angles (Alnough et al., 2019) under SSW. The main objective of this study was to determine the wettability of the rock during the core flooding process to better interpret the results. To that aim, a 3.8 cm diameter carbonate core was sliced and polished into discs of 0.4 cm thickness. A

home-made glass cell with a support for fixing the sliced rock was used for contact angle measurements. The cell was equipped with a septum in its lowest part to inject a 6 μ L crude oil drop.

The polished discs were equilibrated in SSW for 24 h at ambient temperature. Then, the rock was immersed in crude oil and left to equilibrate for 1 week at ambient temperature to simulate core holder conditions. Excess oil was carefully removed from the rock surface using non-absorbent paper. The initial wettability state of the rock was measured by determining the contact angle of crude oil with the disc immersed in SSW. The process was continued by immersing the rock in the surfactant formulation for 10 days, and contact angle was measured again.

Most carbonate reservoirs are oil-wet. Heavier fractions of crude oil, mainly asphaltenes (3.2 wt% in this case) and resins (11.6 wt%), contain carboxylic groups that strongly bond with positively charged mineral surfaces (Massarweh and Abushaikh, 2020; Pillai and Mandal, 2019). For this reason, it was needed to carry out an aging process to alter the original rock wettability towards oil-wet. To that aim, after equilibration in SSW (24 h, ambient temperature) polished discs were immersed in crude oil at 348.15 K for 10 days. These aging conditions are enough to obtain a homogeneous wetting state (Gao et al., 2019; Mohanty et al., 2017; Tie and Morrow, 2005). The oil-wet character of the rock was confirmed by determining the contact angle of crude oil with the disc immersed in SSW. The rock was then introduced in the surfactant formulation at 348.15 K and the contact angle was measured every 24 h.

3. Results and discussion

3.1. Phase behavior

3.1.1. Blend scans

The mixture of surfactants was evaluated in blend scan experiments to determine the optimal SDBS/[C1EG][MeSO₄] ratio. Fig. 1 shows the phase behavior of a blend scan of different SDBS/[C1EG][MeSO₄] ratios at 298.15 K. In this test, the water oil ratio (WOR) was 1:1 and the concentration of surfactants was 2 wt% overall (4 wt% in the aqueous phase).

Transition from Winsor I (oil in water lower-phase microemulsion) to Winsor III (middle microemulsion associated with ultra-low IFT) and to Winsor II (water in oil upper-phase microemulsion) was observed by increasing the proportion of SDBS in the blend from 0 wt% to 50 wt%. Increasing from 50 wt% to 100 wt% SBDS led to a second transition from Winsor II to Winsor III and to Winsor I. Similar behavior was found at 323.15 and 348.15 K. Figures at those temperatures can be seen in SI.

The solubilization parameters - volume of oil (V_o) and water (V_w) divided by volume of surfactant (V_s) in the microemulsion phase - were calculated. As usual in these tests, it was assumed that the volume of surfactant was equal to its mass, and that it was entirely retained in the microemulsion phase. Results are shown in Fig. 2. At the optimal blend ratio, the microemulsion phase contains equal amounts of oil and water, which means that $V_o/V_s = V_w/V_s$. This was calculated as the intersection between representation lines of both solubilization parameters. Fig. 2a shows two intersection points at 298.15 K, which correspond to a blend ratio of 44.7 wt% SDBS + 55.3 wt% [C1EG][MeSO₄] and 73.7 wt% SDBS + 26.3 wt% [C1EG][MeSO₄]. For both optimal blend ratios, a solubilization parameter of 15.5 was found. The same samples were tested at 323.15 K and 348.15 K (Fig. 2b and c, respectively). The solubilization parameter at the optimal blend ratio decreased from 15.5 to 3.7 and 3.3, respectively, for the first optimum and from 15.5 to 5.6 and 5, respectively, for the second optimum. Thus, the ability of the blend to decrease water/oil IFT decreases when temperature increases. Higher temperatures would yield lower oil recovery, for that reason 298.15 K was selected as the optimal temperature.

Both individual components show Winsor type I behavior at the given salinity conditions. However, when blended they are able to generate two optimal blends in Winsor III region. This phenomenon has

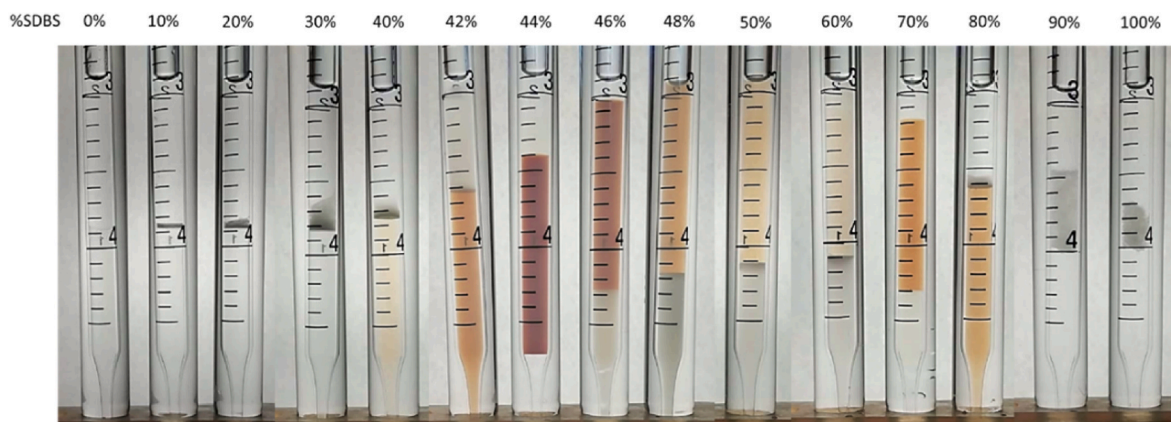


Fig. 1. Blend scan for SDBS/[C1EG][MeSO₄] at 298.15 K.

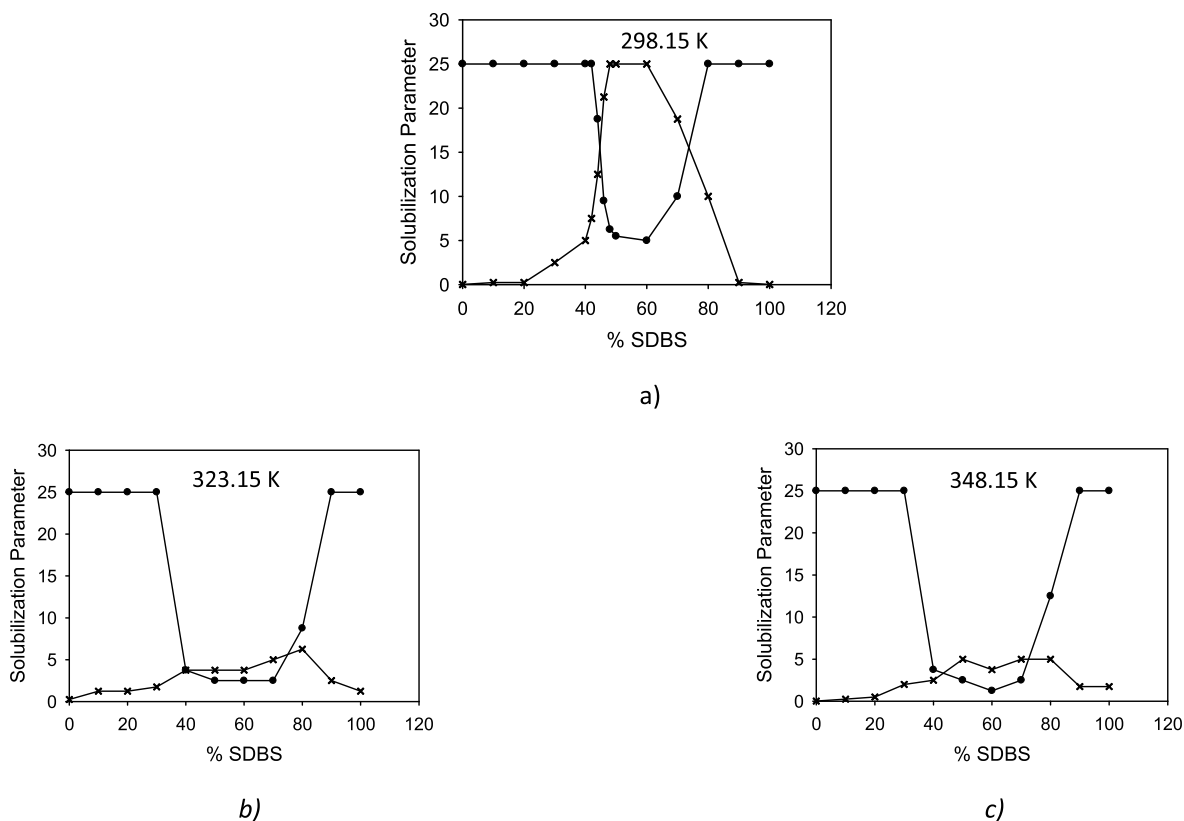


Fig. 2. Solubilization parameters (● Vw/Vs, × Vo/Vs) for different blend ratios at (a) 298.15 K, (b) 323.15 K, (c) 348.15 K.

been reported previously for anionic/cationic surfactant mixtures (Doan et al., 2003; Li et al., 2017; Rodriguez-Escontrela et al., 2017). It is known that mixtures of an anionic and a cationic surfactant tend to form ion pairs or more generally, electrostatically neutral complexes. This is due to electrostatic attraction between the oppositely charged surfactant head groups and intermolecular attraction between the hydrophobic hydrocarbon chains. These ion pairs exhibit many unique properties (Jia et al., 2017; Li et al., 2017) such as higher surface/interface activity, and lower cmc than the individual components. Cmc obtained for the blend with 44.7 wt% SDBS was 10.5 mg/L and for the blend with 73.7 wt% was 16.9 mg/L (see SI for experimental details). Both values are drastically lower than those corresponding to the pure surfactants (see Table 1). The high surface activity caused by the electrostatic interactions leads to an effective reduction of the area of surfactant head groups. Moreover, the formation of new microstructures (rod-like

micelles and/or vesicles) able to increase oil solubilization is also favored in these kinds of systems (Kume et al., 2008).

The reduction in micelle surface charge due to formation of ion pairs makes the mixture less hydrophilic than the individual components (Li et al., 2017; Sohrabi et al., 2008). In this study, as the proportion of SDBS increases, catanionic micelles are generated and the formulation becomes more lipophilic, switching from a Winsor I to Winsor II system. At higher SDBS concentrations (>60 wt%), the behavior reverses and the blend becomes more hydrophilic again because of the excess of SDBS hydrophilic monomers in solution. The competitive relationship between interfacial adsorption and dissolution into the bulk phase is affected by temperature. The strong electrostatic interactions may retard their interfacial desorption, resulting in lower solubilization parameters and higher IFT, when the temperature increases (Jia et al., 2017).

As liquid crystals in the microemulsion can lead to non-uniform

distribution in the reservoir due to phase trapping, their existence was tested at the optimal temperature looking for birefringence under polarized light. As shown in Figs. S7–S9 (SI), this birefringence was not observed at 298.15 K for samples with a SDBS proportion lower than 80 wt%. Thus, there is absence of liquid crystals at both optimal blend ratios. When the temperature was increased to 323.15 K and 348.15 K, a limited amount of liquid crystals was observed for blend ratios between 40 and 80 wt% SDBS.

3.1.2. Salinity scans

Salinity scans were carried out, for the two optimal blends found, varying total dissolved solids from 0 wt% (pure water) to 10 wt%. Fig. 3 shows the corresponding solubilization parameters at the three studied temperatures (pipette images are presented in SI) for the first blend (44.7 wt% SDBS). Winsor Type III behavior was found for salinities between 2 wt% and 10 wt% of TDS at 298.15 K, and in all the range of salinities at higher temperatures. The system shows high solubilization parameters and is almost insensitive to salinity changes. The mixture behaves as a nonionic surfactant, which is not very sensitive to salinity changes. This behavior was previously found for mixtures of anionic and cationic surfactants (Li et al., 2016). Solubilization parameters decrease with temperature.

Fig. 4 shows the results of the salinity scan for the blend containing 71.7% SDBS. Transitions from Winsor I to Winsor III and Winsor II were found at all the studied temperatures. The second optimum blend, with an excess of the anionic surfactant, is more sensitive to changes in salinity. Low IFT is only achieved with salt concentrations close to that corresponding to SSW. Solubilization parameters and optimal salinity decrease with temperature.

3.2. Injectability

Injectability of both optimal blend ratios was tested in SSW at 1 wt% blend concentration. Two ratios slightly above and below optimal were also tested. The formulations at the six different ratios (40, 44.7, 50, 65, 73.7 and 78 wt% SDBS) were maintained at room conditions for several weeks. No precipitation or cloudiness was observed for the ratios between 40 wt% SDBS and 65 wt% SDBS (Fig. S16 in SI). For 73.7 wt% SDBS, the solution was slightly cloudy after mixing and precipitated within 3 days. Finally, for 78 wt% SDBS the solution was not stable and precipitated after 24 h.

A blend with 40 wt% SDBS was further tested and found stable even at salt concentrations of 250000 ppm of total dissolved solids and temperatures from 298.15 K to 348.15 K. No precipitation or cloudiness was observed for several weeks (see Fig. S17 in SI). Two types of molecular interactions lead to the formation of insoluble phases: electrostatic attraction between the anionic and cationic surfactant head group and Van der Waals hydrophobic interactions between the surfactant tail groups. Van der Waals hydrophobic interactions have a greater impact on the formation of insoluble phases and are inversely proportional to

the distance between tails (Doan et al., 2003). [C1EG][MeSO₄] is a mixture of tail-branched surfactants of different lengths. Branching the tails increase the spacing between them and the number of carbons interacting closely is lower, thus avoiding precipitation.

3.3. Dynamic interfacial tension

Surfactant EOR methods are mainly based on the reduction of IFT between crude oil and water. Crude oil components, especially resins and asphaltenes have significant influence on the IFT (Zhu and Lei, 2016). To improve accuracy in selecting an optimal formulation for this specific oil (see Table 3), measurements of IFT between the above mentioned formulations and crude-oil were carried out. Results are shown in Fig. 5.

Fig. 5 shows a significant decrease of dynamic IFT, from $4.4 \cdot 10^{-2}$ mN/m to $2.2 \cdot 10^{-3}$ mN/m, when decreasing the ratio of SDBS from 44.7 wt% (optimum in the blend scan) to 40 wt% SDBS. For the second optimum obtained in the blend scan (71.7 wt% SDBS), IFT increases with a slight decrease in the proportion of SDBS. Increasing SDBS ratio to 78 wt% did not further reduce the IFT. Equilibrium values of $3.6 \cdot 10^{-2}$ mN/m and $3.0 \cdot 10^{-2}$ mN/m were achieved for 73.7 wt% SDBS and 78 wt% SDBS, respectively. The formulations containing 40 wt% SDBS and 73.7 wt% SDBS were selected for subsequent tests.

Selecting the blend with 40 wt% SDBS, a sensitivity analysis was carried out regarding its concentration in SSW. The main objective of this study was to find the minimal concentration of blend able to maintain adequate performance of the formulation (ultra-low IFT). To that aim, blend formulations in SSW were prepared at 1, 0.25 and 0.1 wt% concentrations and water/oil IFT were measured. Fig. 6 shows that the reduction of the blend concentration from 1 to 0.25 wt%, increased IFT from $2.2 \cdot 10^{-3}$ to $7.5 \cdot 10^{-2}$ mN/m. A further reduction of the concentration down to 0.1 wt%, drastically increased IFT up to 0.17 mN/m.

3.4. Adsorption

In chemical flooding, surfactants are inevitably adsorbed on the reservoir rock surface. Adsorption causes loss of surfactant and reduction of its efficiency to mobilize trapped oil, which may make the process economically and technologically unfeasible. It is known that electrostatic attraction between the charged rock surface and that of the head surfactant group is the most important mechanism of adsorption. Positively charged cationic surfactants tend to adsorb in negatively charged surfaces (sandstone rocks), while negatively charged anionic surfactants tend to adsorb in positively charged surfaces (carbonate rocks) (Bera et al., 2013). Lineal alkylbenzene sulfonates such as SDBS show significant surfactant retention in carbonate rocks. Adsorption mechanisms of SDBS in carbonate rocks have previously been studied. A very high surfactant adsorption on this type of surface was found, with adsorption values higher than 2 mg/g_{rock} (Hemmati et al., 2017; Montes et al., 2018). Such a high value discounts the use of this surfactant by itself in

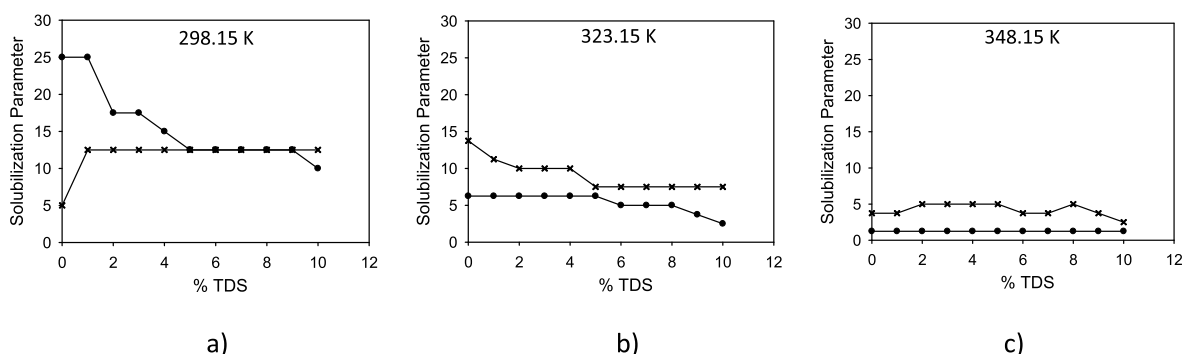


Fig. 3. Solubilization parameters (● Vw/Vs, × Vo/Vs) for 44.7 wt% SDBS blend at different TDS contents and temperatures. (a) 298.15 K, (b) 323.15 K, (c) 348.15 K.

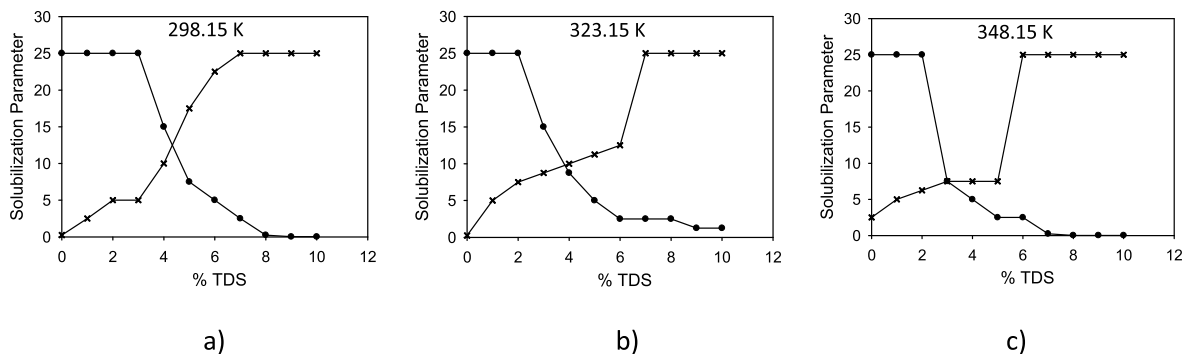


Fig. 4. Solubilization parameters (● V_w/V_s , × V_o/V_s) for 71.7 wt% SDBS blend at different TDS contents and temperatures. (a) 298.15 K, (b) 323.15 K, (c) 348.15 K.

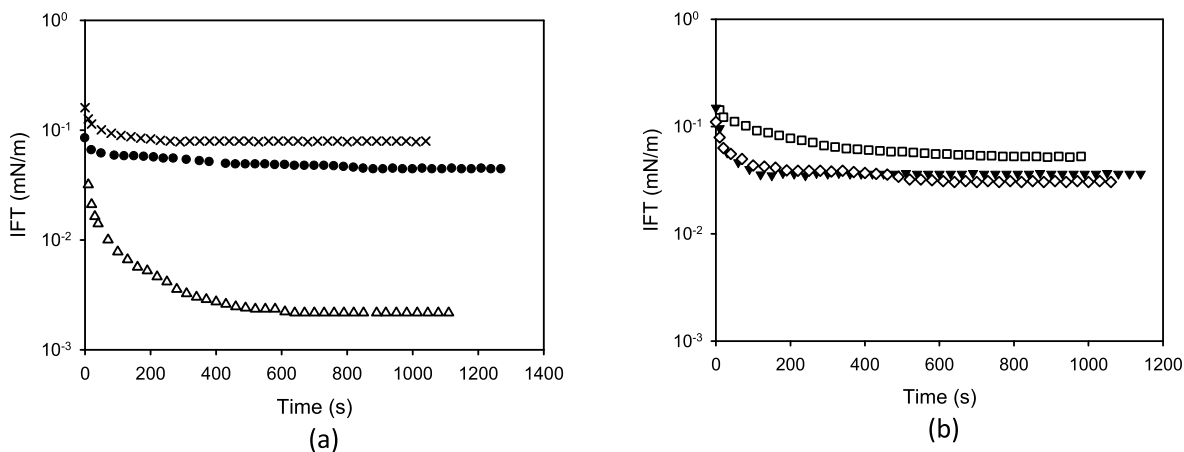


Fig. 5. Dynamic IFT between crude oil and surfactant blend solution in SSW at different SDBS/[C1EG][MeSO₄] ratios: (a) First optimum blend (b) Second optimum blend. Δ 40 wt% SDBS, ● 44.7 wt% SDBS, × 50 wt% SDBS, □ 65 wt% SDBS, ▼ 73.7 wt% SDBS, ◇ 78 wt% SDBS.

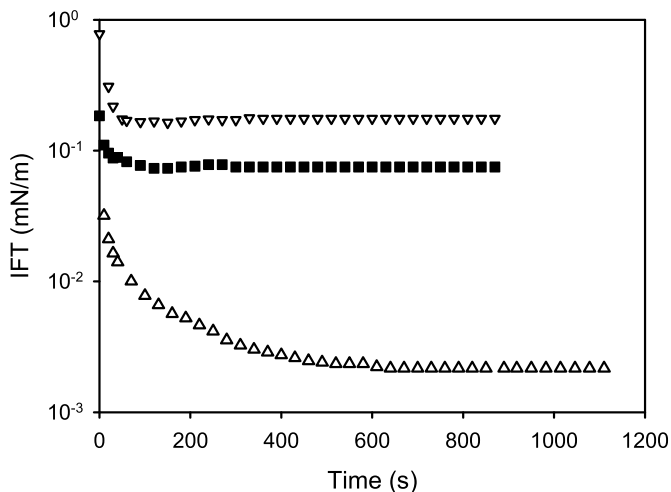


Fig. 6. Dynamic IFT between crude oil and surfactant blend (40 wt% SDBS) solution in SSW at different blend concentrations. Δ 1 wt% ■ 0.25 wt% ▽ 0.1 wt%.

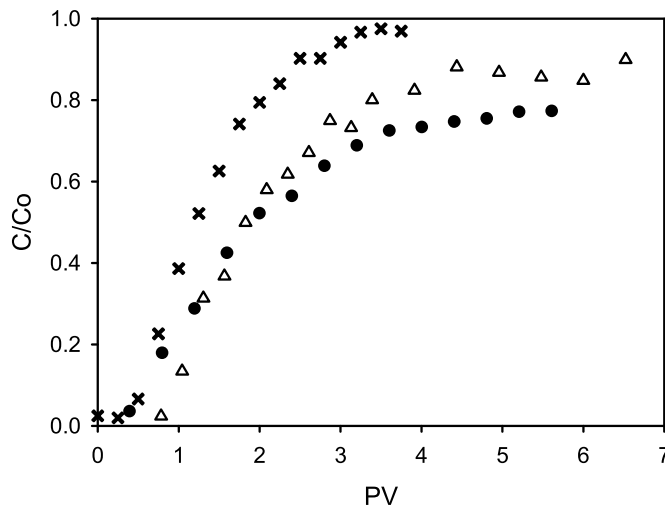


Fig. 7. Dynamic adsorption of the optimized formulation in carbonate rock at 298.15 K × Tracer, Δ 40 wt% SDBS, ● 73.7 wt% SDBS.

carbonate rocks.

The proposed chemical is a mixture of an anionic surfactant and a cationic SAIL. Thus adsorption of both optimal blends (40 wt% SDBS and 73.7 wt% SDBS) was studied in carbonate rocks. Tracer and blend initial concentrations were set to 1 wt%. Fig. 7 represents concentration/initial concentration ratio for tracer and blends as a function of PV injected in carbonate rock at 298.15 K. After 1.2 PV of tracer solution

was injected, tracer concentration in the effluent reached 50% of its initial value ($C/C_o = 0.5$). For 40 wt% SDBS and 73.7 wt% SDBS, the injection of 1.8 PV and 2.0 PV of solution, respectively, was necessary to reach the value of $C/C_o = 0.5$. Adsorption was calculated using Eq. (2) obtaining a value of $0.37 \text{ mg}_{\text{blend}}/\text{g}_{\text{rock}}$ for the formulation consisting of 40 wt% SDBS and $0.51 \text{ mg}_{\text{blend}}/\text{g}_{\text{rock}}$ for 73.7 wt% SDBS. No preferential adsorption of any of the blend components was detected, the mixture

behaving as a single component. The combination of SDBS with [C1EG][MeSO₄] drastically reduces the adsorption of the traditional surfactant in carbonate material.

Carbonate reservoirs have substantial concentrations of divalent cations such as calcium and magnesium. Carbonate surfaces will typically have a positive zeta potential which will increase the adsorption of anionic surfactants with opposite charges (Seethepalli et al., 2004; Sotomayor et al., 2021). For this reason SDBS shows a high adsorption in carbonate rocks. In order to justify the low adsorption obtained with the proposed blends, zeta potentials of 1 wt% SDBS/[C1EG][MeSO₄] optimal blends in SSW were measured at 298.15 K. It is known that zeta potential is neutral near equimolar content and shifts to negative or positive values at anionic-rich or cationic-rich surfactant blends, respectively. Absolute values of zeta potentials within ± 30 mV are generally regarded as neutral (Li et al., 2017). A value of -17.87 mV was obtained for the blend containing 73.7 wt% SDBS and -1.49 mV for the blend consisting of 40 wt% SDBS. This confirms that blending leads to electrostatically neutral complexes (catanionic micelles), reducing the adsorption of the traditional SDBS in carbonate material.

3.5. Core flooding

Four core flooding experiments were performed in fresh carbonate cores, whose details are summarized in Table 4. Test 1 was conducted to study the performance of the first optimal blend consisting of 40 wt% SDBS and 60 wt% [C1EG][MeSO₄]. In this test, after secondary flooding with 6.1 PV of SSW, 63.43% of OOIP was recovered. In the next step, a surfactant slug containing 1 wt% of blend solution was injected until no

Table 4
Summary of core flooding experiments.

	Test 1	Test 2
Porosity of the core (%)	14.33	15.12
Permeability (mD)	8.87	20.70
Pore volume (mL)	12.17	13.22
OOIP (mL)	8.75	8.70
Initial oil saturation (%)	71.87	65.80
Initial water saturation (%)	28.13	34.20
Oil recovered after water flood (%OOIP)	63.43	67.82
Residual oil saturation (%)	26.28	21.18
Surfactant slug injected	5.5 PV of 1 wt% blend solution (40 wt% SDBS + 60 wt% [C1EG][MeSO ₄])	3.7 PV of 1 wt% blend solution (73.7 wt% SDBS + 26.3 wt% [C1EG][MeSO ₄])
Additional Oil Recovered during surfactant flooding (%OOIP)	18.29	14.94
	Test 3	Test 4
Porosity of the core (%)	14.64	14.50
Permeability (mD)	19.79	18.98
Pore volume (mL)	14.64	12.09
OOIP (mL)	7.00	7.00
Initial oil saturation (%)	54.97	57.87
Initial water saturation (%)	45.03	42.13
Oil recovered after water flood (%OOIP)	66.28	64.29
Residual oil saturation (%)	18.53	20.67
Surfactant slug injected	0.5 PV of 1 wt% blend solution (40 wt% SDBS + 60 wt% [C1EG][MeSO ₄])	0.5 PV of 1 wt% blend solution (73.7 wt% SDBS + 26.3 wt% [C1EG][MeSO ₄])
Polymer slug injected	1.66 PV of 1000 ppm PAM solution	1.74 PV of 1000 ppm PAM solution
Additional Oil Recovered (%OOIP)	14.29	10.71

oil was produced in the effluent (5.5 PV). The total amount of oil recovered during the surfactant EOR process was 18.29% of the OOIP.

A similar test (Test 2) was carried out with the second optimal blend (73.7 wt% SDBS + 26.3 wt% [C1EG][MeSO₄]). Secondary flooding required 5.6 PV of SSW until reaching the residual oil saturation (S_{or}). The oil recovered in this step represented 65.80% of the OOIP. Consecutively, a tertiary flooding with 1 wt% blend solution was simulated by injecting the formulation until oil was no longer produced (3.7 PV). An additional oil recovery of 14.94% of the OOIP was achieved during this EOR step.

Tests 3 and 4 were conducted at low injection rates in order to mimic oil field operations. Moreover, considering the economy of the process and to reduce the cost of surfactant, EOR was carried out combining surfactant and polymer flooding. The flooding procedure was as follows: (1) injection of about 2.5 PV of SSW at 0.05 mL/min; (2) injection of 0.5 PV of surfactant slug at 0.025 mL/min; (3) injection of 0.5 PV of polymer slug at 0.025 mL/min; (4) injection of about 1.2 PV of polymer slug at 0.05 mL/min. Polymer concentration was set to 1000 ppm in order to obtain a viscosity twice that of crude oil. Fig. 8 represents the oil recovery factor (cumulative oil recovery divided by OOIP) as a function of the pore volume injected during conventional and tertiary flooding. Additional oil recoveries (Fig. 8 and Table 4) of 14.29 and 10.71 %OOIP were found with the first (40 wt% SDBS) and second (73.7 wt% SDBS) formulation, respectively.

Table 4 shows that in both cases, at high and low injection rates, the formulation containing 40 wt% SDBS is more effective in increasing oil recovery. This trend could be directly related to the effect of IFT reduction, increasing the capillary number and consequently justifying the mobilization of the trapped oil. IFT is reduced to values on the order of 10^{-3} mN/m using the first formulation, while only to 10^{-2} mN/m using the second formulation.

According to the results obtained, the first blend ratio (40 wt% SDBS + 60 wt% [C1EG][MeSO₄]) was selected to define an optimal formulation (1 wt% blend in SSW at 298.15 K) due to its better injectability, higher reduction of the IFT, lower adsorption, and better oil recovery. The importance of designing new formulations based on surfactants for carbonate reservoirs is high due to their abundance and the challenges to make up depleted reserves. The number of works analyzing oil extraction with surfactants in this kind of rocks is very limited, as seen in Table 5 where our results are compared with previous proposals. Studies from Nandwani et al. (2019) and Rabbani et al. (2019) are of limited interest because the formulations were not tested in the presence of divalent ions (the main challenge in this kind of reservoirs). The [C₁₈mim]Cl SAIL seems to be an interesting alternative. A significant tertiary oil recovery was achieved by Zabihi et al. (2019) but no information was given regarding adsorption. Manshad et al. (2017) proposed the use of the same SAIL at a lower concentration, leading to a higher IFT and lower recovery. A rather high adsorption takes place according to the presented Freundlich isotherm. The only paper presenting higher oil recoveries than our study is that of Montes et al. (2018). This study proposes the use of a blend of alkyl benzene sulfonate + alkyl ethoxy carboxylate (40/60). However, the high adsorption of the blend (3.51 mg/g rock) would likely render the method economically unfeasible.

3.6. Wettability tests

With the aim of shedding light on the oil recovery mechanism, wettability alteration tests were carried out in carbonate rock using the most promising blend formulation (40 wt% SDBS + 60 wt% [C1EG][MeSO₄]). Fig. 9 shows that contact angles on carbonate surface were initially 30.1° and 30.2°. After treating the surface with the blend solution, contact angles were 39.0° and 39.9°. The use of the surfactant solution slightly increased the contact angle. However, the formulation did not change the wettability of the rock, which was found to be water-wet in both cases.

Rock wettability was changed to oil-wet by aging polished discs in

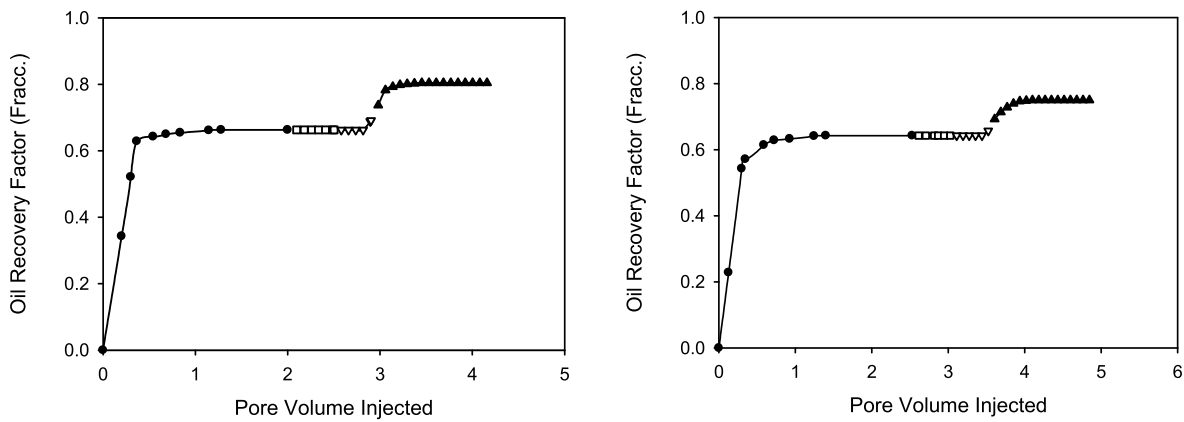


Fig. 8. Core flooding tests: 3 (left) and 4 (right). ● water flooding (0.05 mL/min), □ surfactant flooding (0.025 mL/min), ▽ polymer flooding (0.025 mL/min), ▲ polymer flooding (0.05 mL/min).

Table 5
Comparison with previous studies with surfactants in carbonate rocks.

Author	Chemical Slug	Rock properties	Brine Composition	Temperature	IFT (mN/m)	Adsorption (mg/g rock)	AOR (% OOIP)
Manshad et al. (2017)	170 ppm [C ₁₈ mim]Cl	ϕ: 21–22% μ: 15–30 mD	6.2 wt% TDS	Not specified	0.65	1.25 ^a	13
Montes et al. (2018)	10000 ppm linear alkyl benzene sulfonate + alkyl ethoxy carboxylate (40/60)	ϕ: 21–23%	4.27 wt% TDS	393.15 K	0.005	3.51	32
Nandwani et al. (2019)	10000 ppm [P ₆₆₆₁₆]Br + Tergitol 15-S-9 (1:1)	ϕ: 35–38% μ: 670–700 mD	9.25 wt% NaCl	Room temperature	Not determined	Not determined	16.69
	1000 ppm Platinum Foam Plus Surfactant	ϕ: 21% μ: 0.7 mD	2 wt% NaCl	Room temperature	Not determined	Not determined	2.64
Zabihi et al. (2019)	3500 ppm [C ₁₈ mim]Cl	ϕ: 15.7% μ: 3.1 mD	13.73 wt% TDS	353.15 K	Not determined	Not determined	16.5
Present study	10000 ppm sodium dodecyl benzene sultonate + Iolilyte C1EG (40/60)	ϕ: 14% μ: 8.87 mD	4.97 wt% TDS	Room Temperature	0.002	0.37	18.29

^a Calculated from the Freundlich isotherm figure.

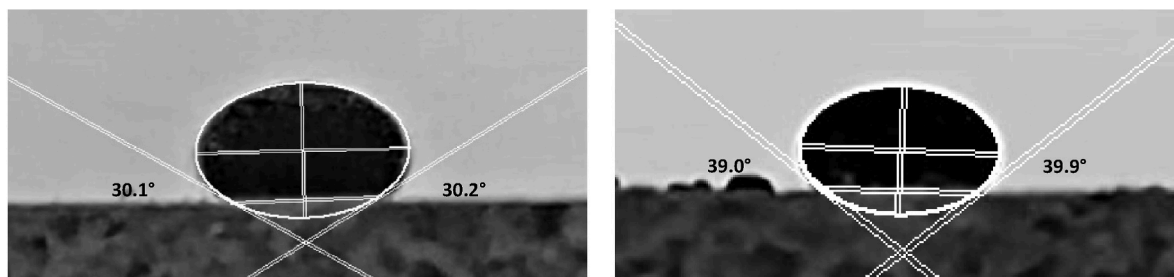


Fig. 9. Contact angle measurements in water-wet rock before (left) and after (right) treatment with the surfactant formulation (room conditions).

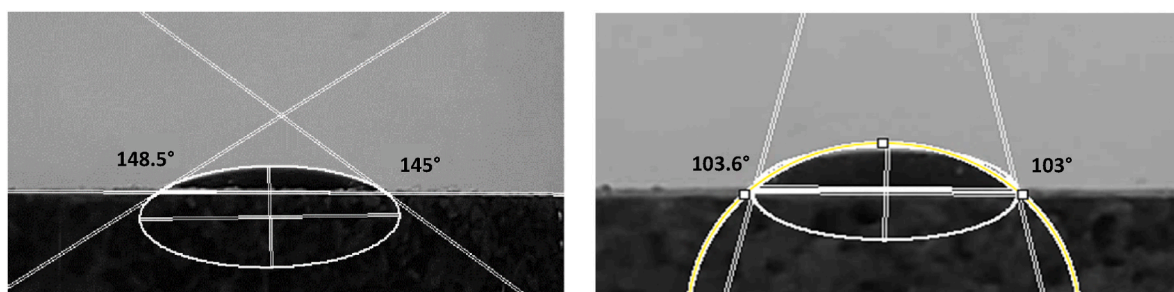


Fig. 10. Contact angle measurements in oil-wet rock before (left) and after (right) treatment with the surfactant formulation (348.15 K).

crude oil at 348.15 K (see section 2.2.5). In this case, contact angles on carbonate surface were initially 148.5° and 148° (Fig. 10). Treating the rock with the blend solution at 348.15 K, a change to intermediate-wet was observed, being contact angles 103.6° and 103° after 15 days.

4. Conclusions

A new formulation, based on the traditional and inexpensive SDBS surfactant and [C1EG][MeSO₄] SAIL, has been designed for chemical EOR. From the studies presented here, some conclusions may be established:

- The combination of SDBS with the ionic liquid [C1EG][MeSO₄] improves the characteristics of the traditional surfactant and allows its use for EOR in carbonate reservoirs.
- IFT measurements and injectability studies resulted in two optimal blends, at 40/60 and 73.7/26.3 SDBS/[C1EG][MeSO₄] mass ratios, in SSW at 298.15 K.
- The adsorption of both blends in carbonate rocks is low enough to allow their use in EOR.
- Both blends are promising for EOR in carbonate reservoirs, according to additional recoveries obtained in core-flooding experiments. The combination of surfactant flooding with polymer flooding slightly reduces additional oil recovery but improves the economy of the process.
- An optimal formulation consisting of 1 wt% blend solution, with a 40/60 SDBS/[C1EG][MeSO₄] mass ratio, in SSW is proposed for its use around room temperatures due to its better injectability, lower IFT and adsorption, and better recovery.
- The robustness of the optimized formulation was tested. The existence of a second optimal blend (73.7/26.3 SDBS/[C1EG][MeSO₄]) ensures that changes in composition produced inside the reservoir would still maintain a very low IFT. Moreover, it was also shown that a significant reduction in blend concentration does not significantly increase IFT.
- The formulation was found to be stable in the absence of oil at very high salinities (250000 ppm) in presence of divalent ions and high temperatures.
- The key mechanism associated with the improvement of oil recovery is IFT reduction. The increase of viscous forces or wettability alteration have a lesser effect.
- The main limitation of the proposed formulation lies in the fact that oil recovery is expected to decrease with temperature due to an increase of IFT. However, high temperatures favor a wettability change to intermediate-wet.

Author contributions

A. Somoza: experimental, analysis, writing. N. Tafur: core tests conceptualization, editing. A. Arce: core tests experimentation, editing. A. Soto: conceptualization, supervision, writing, funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors acknowledge the Ministry of Science and Innovation and State Research Agency for financial support throughout project PGC2018-097342-B-I00, including European Regional Development Fund). A. Somoza also acknowledges predoctoral financial support (grant ref. PRE2019-089101). We would also like to thank SNF Floerger for supplying polymer samples, Repsol (A Coruña) for providing the

crude oil used for the experiments, and L. Membrado (Separation and Detection Group, Instituto Carboquímico de Zaragoza) for the realization of the SARA analysis of the crude oil.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.petrol.2021.109856>.

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