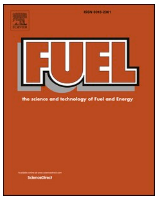
Fuel 346 (2023) 128363

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Full Length Article

A formulation based on a cationic surface-active ionic liquid and an anionic surfactant for enhanced oil recovery at a carbonate reservoir

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ARTICLE INFO

Keywords:
Chemical flooding
Blend
Catanionic surfactant
High temperature
Carbonate rock

ABSTRACT

With the still huge dependence on crude oil, it is crucial to develop enhanced oil recovery techniques to improve reservoir production and lifespan. Carbonate reservoirs constitute over half the world's oil reserves, but they are challenging in terms of recovery due to their complex pore network, oil-wet or mixed-wet rocks, and harsh conditions of temperature and salinity. This work offers a significant contribution to the exploitation of these reservoirs. A new formulation, able to provide very low interfacial tension at high temperatures with reduced adsorption on carbonate rocks, was designed. A low-cost traditional alkyl benzene sulfonate (RECOLAS158) was mixed with the cationic surface active ionic liquid N,N-diethoxylated-N-tallow-N-ethylammonium ethylsulfate. A formulation containing 56.4 wt% RECOLAS158 was selected for its good performance in terms of phase behavior, injectability and interfacial tension at a wide range of temperatures and salinities. A very significant tertiary oil recovery (19.53% of the original oil in place) and low blend adsorption (0.086 mg_{blend}/g_{rock}), demonstrated the promising performance of the formulation. The key mechanism associated to the improvement of oil recovery is interfacial tension reduction.

1. Introduction

A transition from fossil-based fuels to renewable energies must be carried out in the upcoming decades in order to avoid climate change disaster. However, such transition will take a considerable period of time, therefore it is important to make an efficient and sustainable use of currently available resources. The declining number of new oil field discoveries and the increasing energy consumption worldwide have led to the need to redevelop oil reservoirs, through the application of new recovery technologies [1]. Water flooding in conventional reservoirs generally results in the recovery of 35–50% of the oil after reaching the economic limit [2]. Enhanced oil recovery (EOR) techniques must be applied to recover the remaining oil in place. There are different EOR methods such as chemical flooding, thermal recovery and miscible gas injection. Chemical EOR is one of the major EOR techniques and relies on the injection of chemicals (alkali, surfactant and/or polymer) to improve displacing efficiency [3].

It is known that approximately 50% of the world's oil reserves are in the Middle East and around 70% of these reserves are held in carbonate reservoirs [4]. However, most of the documented chemical EOR applications have been conducted in sandstone, so the results cannot be simply extrapolated to carbonates [3,5]. Carbonate reservoirs are usually characterized by low permeability, complex pore networks and high heterogeneity which directly affect well productivity [6]. In addition, unlike sandstone reservoirs, a carbonate surface is positively charged at moderate pH conditions. On this basis, negatively charged carboxylic acids present in crude oil tend to be adsorbed onto the rock surface yielding a more oil-wet state. Accordingly, 80% of carbonate reservoirs are naturally oil-wet [5]. Even though the high residual oil saturation of carbonate reservoirs makes them attractive candidates for chemical EOR, it is a challenge to select chemicals that can be successfully applied in these systems. High temperature coupled with high brine salinity and hardness limits the application of many chemicals due to their intolerance to such harsh conditions [7].

Among chemical EOR methods, surfactant flooding is a well-established technique that can theoretically be applied in a variety of reservoir conditions [8]. Surfactants are amphiphilic molecules that consist of a hydrophobic tail and a hydrophilic head able to reduce water/oil interfacial tension (IFT) and thus increase the capillary number. This mechanism gives rise to a viscous/buoyancy-dominated flow

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https://doi.org/10.1016/j.fuel.2023.128363
Received 3 February 2023; Received in revised form 23 March 2023; Accepted 6 April 2023

allowing oil trapped by capillary forces to be displaced [7]. Another important mechanism associated with surfactant EOR is wettability alteration to a more favorable water-wet state, thus altering the capillary pressure and promoting counter-current water imbibition into oil-bearing pores [9]. Recent research has led to the development of surfactant systems suitable for carbonate environments [10]. Most studies focus on wettability alteration as the main mechanism for extraction. Cationic surfactants are generally proposed [11–14]. However, water/oil IFT and viscosities of the phases also play a crucial role in controlling capillary pressure, therefore it is important to develop formulations that also take these mechanisms into account [15].

The number of works focusing on the design of formulations able to reach ultra-low IFT is very limited [2,16–21] and very few are proposed for high temperature reservoirs. Ahmadi and Shadizadeh (2013) [17] suggested the use of a saponin surfactant derived from *Z. spina christi*, a plant species from Iran. Core flooding experiments were performed in low permeability carbonate cores at 373.15 K and a cumulative oil recovery of 81.08% of OOIP was obtained. However, the high surfactant concentration (8 wt%) and low brine salinity (15000 ppm of total dissolved solids) of the proposed formulation would likely render the method economically and technologically unfeasible. Lu *et al.* (2014) [19] studied a formulation consisting of a large-hydrophobe guerbet alkoxy carboxylate surfactant and an internal olefin sulfonate (IOS) co-surfactant in 1:1 ratio. Oil recovery experiments were conducted in a fractured oil-wet carbonate core at 373.15 K, obtaining a cumulative oil recovery of 65.9% OOIP. Surfactant retention of 0.086 mg/g_{rock} was reported. Further simulation studies showed that both mechanisms, IFT reduction and wettability alteration, were involved in oil recovery. Different blend formulations of various types of traditional surfactants (sulfonates, carboxylates and betaine) and IOS co-surfactants were proposed by this same research group in three subsequent papers [2,16,18]. However, short chain alcohols, phenol based cosolvents or crude oil were required to improve stability and adsorption behavior of formulations. Alkali-surfactant-polymer [16] and surfactant-polymer [2,18] flooding strategies were also assessed for low permeability carbonate reservoirs at temperatures between 353.15 and 373.15 K. Surfactant retentions between 0.08 and 0.4 mg/g_{rock} and cumulative oil recoveries between 77 and 92% OOIP were reported. Traditional anionic surfactants such as alkyl benzene sulfonates, widely used in sandstone reservoirs, are not recommended for use in carbonate rocks due to the high adsorption values expected and poor stability in harsh conditions [20,22]. Blends with other surfactants are proposed to solve these drawbacks. Thus, Montes *et al.* (2018) [20] blended a traditional linear alkyl benzene sulfonate and an alkyl ethoxy carboxylate in a ratio of 40/60. Core flooding experiments were performed in low permeability carbonate cores at 393.15 K and an incremental oil recovery of 32% of OOIP was obtained. However, a very significant adsorption (3.52 g/g_{rock}) was calculated from dynamic experiments. These results show promising potential for surfactant EOR applications in carbonate cores. However, adsorption, stability at high temperature and salinity, and the number of chemicals required are issues that still need to be addressed in order to develop feasible processes.

Surface-active ionic liquids (SAILs) are emerging as possible candidates to improve surfactant EOR processes [23,24]. SAILs have many promising properties such as negligible vapor pressure, high solvation capacity, frequently wide liquid range and thermal stability. However, the most attractive feature is likely their tunability, since they can be designed to be stable in harsh environments and in accord with the requirements of individual reservoirs [25]. Some research has been published on the application of SAILs on carbonate rocks [26–28] showing promising results that encourage this line of research. In our previous work [29], the cationic SAIL cocosalkylpentaethoximethylammonium methylsulfate (C1EG) was used to improve the performance of the traditional anionic surfactant sodium dodecylbenzenesulfonate (SDBS) in carbonate reservoirs. The formulation was found to be stable in brine up to 250000 ppm of total dissolved solids, overcoming one of the main challenges of the application of alkylbenzene sulfonates in carbonate fields. A tertiary oil recovery of 18.29% of the original oil in place (OOIP) was achieved with a low dynamic adsorption (0.37 mg/g rock). However, IFT increased with temperature and the performance of the formulation diminished. Thus, further research was required focusing on high temperature reservoirs. In this paper, the cationic SAIL N,N-diethoxylated-N-tallow-N-ethylammonium ethylsulfate is proposed to improve the performance of a linear alkyl benzene sulfonate in carbonate rocks. Phase behavior studies, stability tests and IFT measurements are carried out to define the optimal formulation. Contact angle measurements are performed to study the wettability alteration ability of the blend as a function of reservoir temperature. Surfactant adsorption in carbonate material is estimated via static and dynamic adsorption tests, and finally the effectiveness of the newly proposed surfactant formulation is evaluated via core flooding tests, to determine tertiary oil recovery potential.

2. Material and methods

2.1. Materials

RECOLAS158, a C15-C18 linear alkylbenzene sulfonate (LAS) with a molecular weight of 412 g/mol and neutralized with sodium hydroxide to pH = 8.8, was supplied by Cepsa. LAS is one of the most commonly used synthetic surfactants in EOR, because of its relatively low cost and good performance in terms of interfacial tension reduction at high temperatures. To prevent anionic surfactant precipitation and reduce adsorption in carbonate reservoirs, a second surfactant was added to the formulation. The cationic room temperature ionic liquid N,N-diethoxylated-N-tallow-N-ethylammonium ethylsulfate (purity >95 wt %), commercially named Iolilyte T2EG (T2EG), was supplied by Iolitec.

Synthetic seawater (SSW) was prepared by dissolving different amounts of salts in distilled water with the composition shown in Table 1. Sodium chloride was purchased from Panreac (purity >99 wt %). Sodium sulphate (purity >99 wt%), magnesium chloride hexahydrate (purity >99 wt%), and calcium chloride dihydrate (purity >99 wt %), were supplied by Sigma-Aldrich.

Potassium iodide (purity >99 wt%), used as a tracer for dynamic adsorption tests, was supplied by Sigma-Aldrich. Crude oil used in this study was supplied by Cepsa and its main properties are summarized in Table 2. *N*-octane (purity >99 wt%) was purchased from Sigma-Aldrich and used as model oil for blend and salinity scan experiments. Polyacrylamide (PAM) with a molecular weight higher than 8.5 million Daltons (Flopam FA 920 VHM) was kindly provided by SNF Floerger and used for core flooding experiments.

Low permeability carbonate cores, purchased from Kocurek Industries, made from limestone and dolomite were used for wettability, adsorption and core flooding tests. Cores used for the experiments were 3.8 cm in diameter and 7.6 cm in length. Their mineralogy was analyzed by X-Ray diffraction and the composition is shown in Table 3.

2.2. Methods

2.2.1. Phase behavior tests

Phase behavior studies were performed following the encased-glass-

Table 1
Synthetic seawater (SSW) composition.

Salt	Concentration (g/kg solution)
Na_2SO_4	4.84
$CaCl_2{\cdot}2H_2O$	1.89
$MgCl_2{\cdot}6H_2O$	15.06
NaCl	27.94
Total dissolved solids (TDS)	49.73

Table 2
Crude oil main properties (provided by supplier).

Property	Value
API	33.0
Density at 288.15 K (g/cm3)	0.8600
Viscosity at 293.15 K (cSt)	10.3
Acidity (mgKOH/g)	0.06
Saturates (%)	61
Aromatics (%)	33
Resins (%)	4.6
Asphaltenes (%)	1.4
Carbon residue (%)	4.53

Table 3
Carbonate core mineralogy.

Compound name	Content (%)
Calcite	89
Sodium Calcium Pentafluoroaluminate Fluoride – Beta	2
Diopside	9

pipette method [30]. Mixtures from 100/0 to 0/100 RECOLAS158/T2EG were evaluated in SSW brine to determine the optimal ratio for best performance. Aqueous formulations were prepared by mixing the required amounts of 8 wt% surfactant stock solutions in distilled water to obtain 0.5 cm^3 of blend with the required mass ratio. Then 0.5 cm^3 of brine solution twice the concentration shown in Table 1 were added to obtain an aqueous solution of 4 wt% surfactant blend in SSW. To carry out pipette tests, 1 cm^3 of 4 wt% surfactant blend in SSW (aqueous phase) was mixed with 1 cm^3 of *n*-octane in 3 cm^3 borosilicate glass pipettes, which were consequently top sealed. A high surfactant concentration was selected to facilitate the visualization of the phases. Pipettes were placed in a rotatory mixer at room temperature for 24 h and then encased in a test tube filled with silicon oil. Encased glass pipettes were left to equilibrate in a dry block heater, OVAN model BD200-RE, at 298.15, 323.15 and 348.15 K until phase volumes remained constant. The existence of liquid crystals in the microemulsions was tested looking for birefringence under polarized light.

Promising formulations selected in blend scan experiments were later studied in a salinity range from 0 to 100000 ppm of total dissolved solids, aiming to determine their performance in different salinity environments. In this case, salinities lower than SSW were prepared by mixing SSW and distilled water. Higher salinities were prepared by increasing sodium chloride concentrations while keeping the divalent ion concentration constant.

2.2.2. *Stability tests*

Aqueous formulations containing 1 wt% blend, at promising ratios, were prepared (following the above protocol) in different brines (5 to 10% TDS) to ensure the stability of the formulations in the absence of oil. Stability was judged by visual inspection after several weeks. Dynamic light scattering (DLS) measurements were carried out using a Malvern Zetasizer Nano-ZS to determine the size of surfactant aggregates.

2.2.3. *Dynamic interfacial tension*

IFT values between surfactant formulation and crude oil were measured using a spinning drop tensiometer (SITE100 from KRÜSS). A capillary tube filled with surfactant solution and a drop of 4 μL of crude oil was spun at rotating velocities between 2000 and 5000 rpm. Spinning continued and IFT values were recorded until an equilibrium condition at the tested temperature was observed. Temperature was controlled using a circulating oil thermostatic bath Julabo EH-5 at 298.15, 323.15 and 348.15 K. IFT was calculated according to the Vonnegut equation:

$$IFT = \Delta\rho \cdot \omega^2 \cdot D^3 / 32 \tag{1}$$

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. All experiments were performed at least twice to ensure repeatability.

2.2.4. *Wettability alteration*

Most carbonate reservoirs are believed to be mixed-wet or oil-wet [6]. Chemical EOR research in this type of rocks has been focused on using surfactants to change wettability from oil-wet to a more favorable water-wet condition. The effect of the proposed formulation on wettability of oil-wet carbonate rocks was evaluated by means of contact angle measurements. The static sessile-drop technique was applied using a home-made glass cell with a holder to fix the rock sample in place. The images of the injected oil drop (6 μL) were recorded by a camera. The contact angles were determined using ImageJ software.

A carbonate core was sliced and polished into discs of 0.4 cm thickness. Three carbonate discs were immersed in SSW for 24 h at ambient temperature. Then the rocks were aged in crude oil at 348.15 K for 10 days. At this point, the initial wettability of the rock was determined by measuring contact angle of rock-crude oil with the disc immersed in SSW. Finally, rocks were immersed in surfactant formulation for 2 weeks at 298.15, 323.15 or 348.15 K. The contact angle was measured every 24 h with the rock immersed in SSW.

2.2.5. *Static adsorption tests*

To study the adsorption of surfactant on carbonate rocks, static adsorption tests were performed based on previous studies [31,32]. Carbonate core was crushed to small pieces and then sieved to achieve a uniform particle size in the range of 0.5–1.0 mm. It is important to note that in this type of experiment, surface area is significantly higher than that corresponding to field rocks, so adsorption values obtained will clearly exceed those expected in real wells.

Various vials containing approximately 9 g of surfactant formulation along with 1 g of crushed rock were shaken at room temperature in a Selecta Boxcult orbital shaker. Samples were taken from each vial at different times until reaching equilibrium and surfactant concentration remained constant. Samples were centrifuged at 10000 rpm for 5 min using an OrtoAlresa Digicen 21R centrifuge in order to separate solid particles. The supernatant was analyzed using an Agilent UV-Vis 8453 spectrophotometer. Adsorption density was calculated using Eq. (2).

$$q_t = (C_0 - C_e) \cdot V_s / m_{rock} \tag{2}$$

where q_t is the surfactant adsorption density (mg_{surf}/g_{rock}), C_0 is the initial surfactant concentration (mg/L), Ce is the concentration of surfactant in the solution at equilibrium conditions (mg/L), V_s is the initial volume of solution (L), and m_{rock} is the mass of crushed rock (g).

2.2.6. *Dynamic adsorption and core flooding tests*

Dynamic adsorption [20,33] and core flooding experiments [27,29,34] were performed based on previous literature. Experiments were carried out in a core-flooding system equipped with a Hassler Core Holder *H*00-021–0. An overburden pressure of 70 bar was applied using an Enerpac P142 manual hydraulic pump to prevent hydraulic side flow. Two floXlab BTSP 500–5 piston pumps equipped with pressure sensors, purchased from Vinci Technologies, were used for crude oil and aqueous formulation injection. Experiments were performed at ambient conditions.

The core was placed in the core holder, vacuumed for 24 h and saturated with SSW. After 24 h, the pore volume (*PV*) was determined using the dry and wet weights of the core. Darcy's law was used to calculate the absolute permeability (*kw*) of the rock. After flooding the core with SSW, either adsorption or oil extraction tests were performed.

Surfactant blend retention in carbonate rock was determined via dynamic adsorption tests. After water flooding, the potassium iodide tracer or the aqueous blend formulation (1 wt%) were injected at 0.1 mL/min. Injection was continued until concentration in the effluent equaled the value of initial concentration. Samples were collected every 2 mL and tracer or surfactant blend concentrations were determined by UV absorption using an HP Presario SR1000 UV/Vis spectrophotometer. Adsorption was calculated measuring the delay between the tracer and the surfactant exit in the effluent:

$$\tau = \left(PV_{surf,50\%} - PV_{tracer,50\%}\right)\cdot PV\cdot[C]_{surf}/m_{rock} \tag{3}$$

where τ is blend adsorption in mg/g of rock, $PV_{surf,50\backslash\%}$ and $PV_{tracer,50\backslash\%}$ are the pore volumes at which tracer or blend concentration reached 50% of initial concentration, PV is the pore volume in mL, $[C]_{surf}$ initial blend concentration in mg/mL, and $mass_{rock}$ the core dry weight in grams.

To better understand the adsorption mechanism, zeta potential of the surfactant blend in SSW was measured using a Malvern Zetasizer Nano-ZS at 298.15 K.

Blend extraction ability was tested using core flooding experiments. After the core was saturated with SSW, crude oil was used to displace the brine. The oil injection flow rate was increased from 1 mL/min to 10 mL/min until reaching the irreducible water saturation (S_{wi}). As an aging step, the core was allowed to rest for 7 days. Subsequently, to simulate conventional extraction flooding, SSW was injected with velocity of 2 mL/min until no crude oil was found in the effluent and differential pressure remained stable. Then an EOR step was implemented. To that aim, 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. Additional oil recovery (AOR) was calculated as a function of the OOIP. Volumes of oil or brine exiting the core were measured by collecting the produced fluid in 10 mL graduated test tubes.

In order to make a better approximation to real oil field operations, an additional core flooding test was carried out combining surfactant and polymer flooding at low injection velocities. In this case, crude oil and SSW were injected at a velocity of 0.05 mL/min, which is equivalent to 1 ft/day in a large-scale reservoir. Then 0.5 PV of surfactant formulation were injected at 0.025 mL/min (0.5 ft/day). After surfactant flooding, 0.5 PV of solution of 2000 ppm of PAM were injected at the same flow rate to ensure the whole rock PV was swept at the same velocity. This flooding was followed by the injection of 2 PV of polymer PAM at 0.05 mL/min.

3. Results and discussion

3.1. Phase behavior tests

Blend scan experiments were carried out to determine the optimal RECOLAS158/T2EG ratio. Tests were conducted with aqueous

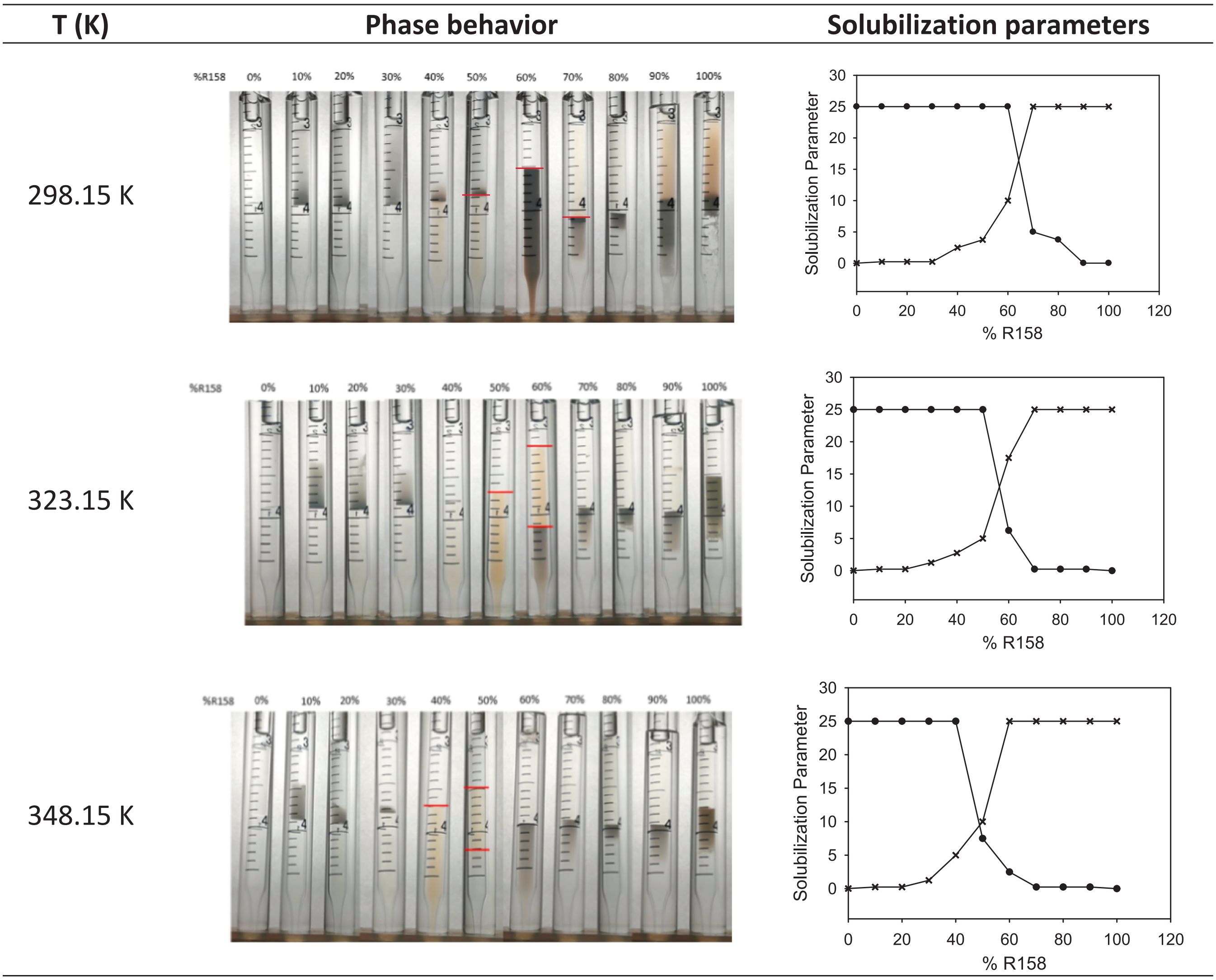

Fig. 1. Blend scans for RECOLAS158/T2EG and solubilization parameters (● Vw/*Vs*, × Vo/*Vs*) at 298.15 K, 323.15 K and 348.15 K.

formulations, in SSW, and *n*-octane at 298.15, 323.15 and 348.15 K. Surfactant concentration was set to 2 wt% overall (4 wt% in the aqueous phase) and water oil ratio (WOR) was 1:1.

Fig. 1(left) shows the photographs of the blend scans at different temperatures. Solubilization parameters *Vw/Vs* and *Vo/Vs* were determined as the volume of water (*Vw*) or volume of oil (*Vo*) solubilized per volume of surfactant (*Vs*) in the microemulsion phase. As usual in these tests, it was assumed that the surfactant was entirely retained in the microemulsion phase. Solubilization parameters as a function of RECOLAS158 percentage are also presented in the Fig. 1(right). The cationic SAIL T2EG is very hydrophilic and it shows a Winsor type I behavior at the tested salinity. However, the anionic surfactant RECOLAS158 at the fixed test salinity shows a Winsor II behavior. When mixed, a classical Winsor I-III-II transition occurred at all the temperatures tested. As shown, an increase in RECOLAS158 ratio causes hydrophilicity to decrease and the blend of surfactants becomes more lipophilic, producing a change from an oil-in-water microemulsion (Winsor I) to a middle-phase microemulsion (Winsor III) and finally a water-in-oil microemulsion (Winsor II). An optimal Winsor III condition occurred when *Vw/Vs* = *Vo/Vs*. At 298.15 K, an optimal blend ratio was found with a concentration of 64.29% RECOLAS158. Optimal blends with 56.40% RECOLAS158 and 48.89% RECOLAS158 were found at 323.15 K and 348.15 K, respectively. Solubilization parameters decreased from 16.43 at 298.15 K to 13 and 9.45 at 323.15 K and 348.15 K, respectively. As temperature increases the optimal blend ratio becomes richer in the hydrophilic surfactant (T2EG in this case) and solubilization parameters decrease. This behavior has been previously reported for this kind of blend [29,35,36]. Additionally, pipettes were visually tested under cross-polarized light looking for a birefringence phase. As shown in Fig. S1 – S3 in the supplementary information (SI), birefringence was not observed at any of the three tested temperatures for any blend ratio. Thus, there were no precipitates or liquid crystal phases.

It is known that when anionic and cationic surfactants are mixed, they strongly interact and the two hydrophilic groups merge into a nonionic-like surfactant, usually referred as catanionic species. This ion pairing phenomenon reduces micelle surface charge and therefore the area of the combined surfactant head groups, and imparts much higher surface activity [37]. For that reason, the new species has completely different properties than the parent molecules: it is much more lipophilic, less sensitive to electrolytes, has higher surface/interface activity, and lower critical micelle concentration (cmc) than the individual components [38,39]. Additionally, mixing two oppositely charged surfactants can produce microstructures such as vesicles or rod-like micelles, not formed by the individual molecules.

The three promising blends (64.29, 56.40 and 48.89% RECOLAS158) were further tested in salinity scan experiments, to analyze the effect of salt concentration on performance. To that aim, the surfactant blends were prepared in water at different salinities and new pipette tests were carried out at the three temperatures (see Fig. S4 – S6 in SI). Fig. 2 shows the phase behavior (Winsor I, II or III) as a function of salinity and temperature. Additionally, solubilization parameters are presented in Fig. 3. As expected, an increase in salinity shifts the microemulsion behavior from WI to WIII and to WII, due to the salting-out effect [40]. For the blend under study, and at the optimized ratio for each temperature, a moderate variation of salt concentration (usually found in reservoirs when formation and injection brines are different) keeps the desirable Winsor type III behavior associated to ultra-low IFT values. Regarding the effect of temperature, the system becomes less hydrophilic as temperature increases, a behavior classically found in nonionic surfactants. The hydrophilic groups of this kind of surfactant (generally polyoxyethylene groups) present a coil-shaped structure that is able to envelope water molecules. As temperature increases, the hydrogen-bonds weaken, water molecules start to separate and hydrophilic properties decrease [41]. Moreover, Bhattarai (2015) [42] studied micellization of anionic-cationic surfactant blends and found that temperature increases make the formation of micelles less favorable since interactions of oppositely charge surfactants are highly exothermic, primarily due to tail association. Thus, the degree of dissociation goes up with increases in temperature. A larger fraction of monomers is dissociated at these conditions leading to a decrease in solubilization parameters. Interestingly, the blend with 56.4% RECOLAS158 keeps a promising triphasic behavior with solubilization parameters higher than 10 in the whole range of temperatures studied, with optimal salt concentration decreasing at higher temperatures.

In our previous work [29] the formation of liquid crystals and low solubilization parameters above 323.15 K made the application of an anionic-cationic mixture of sodium dodecylbenzenesulfonate (SDBS) and cocosalkylpentaethoximethylammonium methylsulfate (C1EG) unfavorable at high temperatures. However, in the present study it was found that acceptable solubilization parameters and an absence of liquid crystal could be achieved using T2EG, a cationic surfactant with higher content of polyoxyethylene groups than C1EG. Several authors [9,43–45] studied the influence of polyoxyethylene groups in nonionic surfactant performance and found out that more oxyethylene groups increase the cloud point, and hence enhance the thermal stability of surfactant molecules.

3.2. *Stability tests*

While developing a blend formulation, care must be taken to avoid the formation of precipitates between oppositely charged surfactants. For an economically viable EOR process, the aqueous surfactant solution must be a single phase until it enters the reservoir and makes contact with oil [46]. The stability of several formulations prepared in SSW at 1

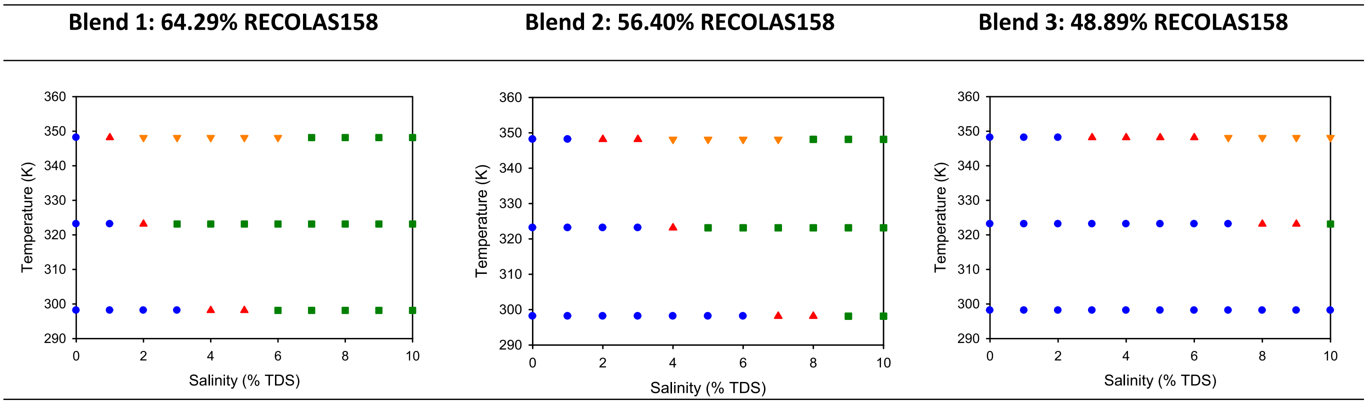

Fig. 2. Phase behavior of the three promising blends as a function of salinity and temperature (● Winsor I ▲Winsor III ▼Winsor III with low solubilization parameters ■Winsor II).

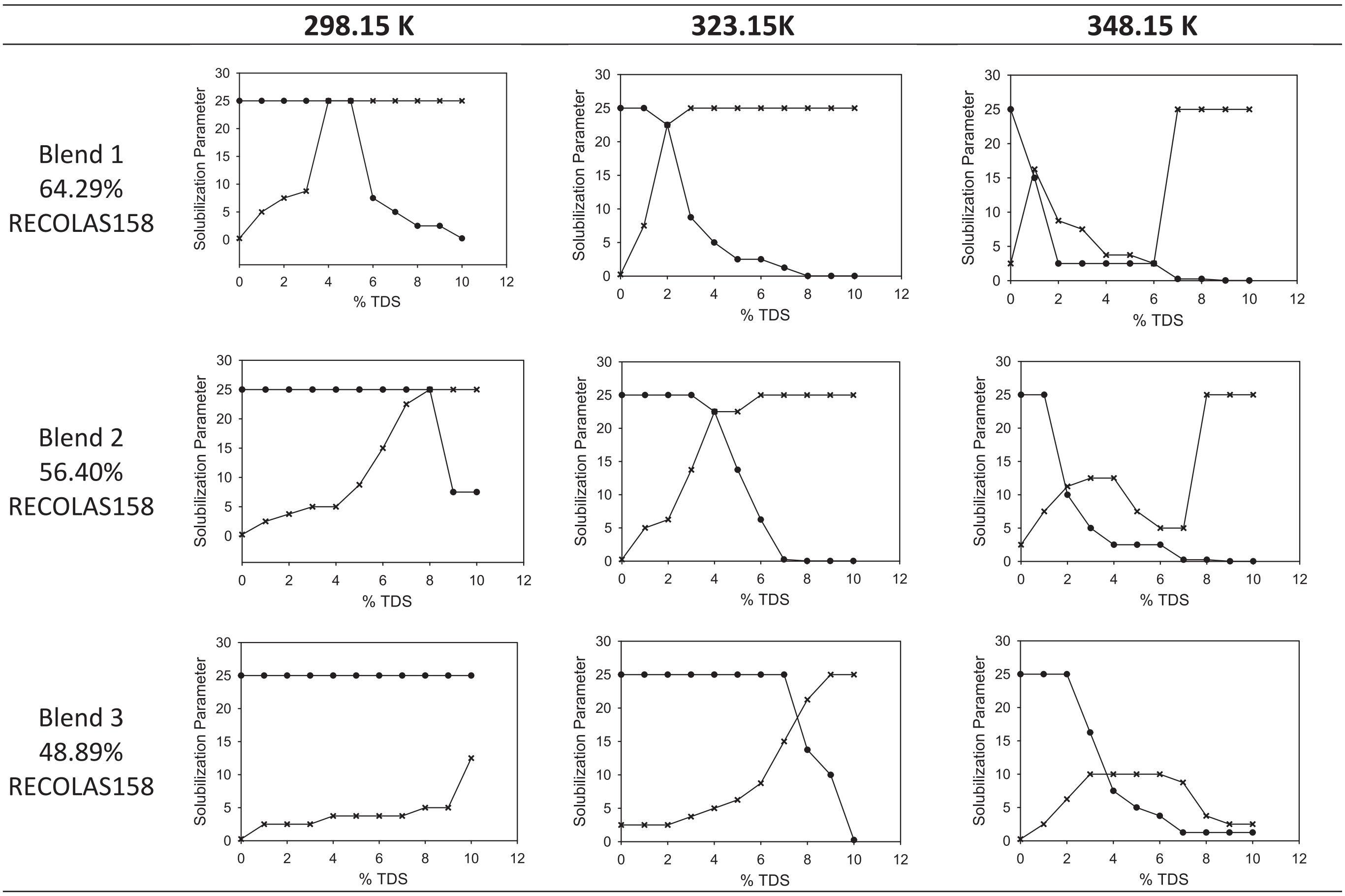

Fig. 3. Solubilization parameters (● Vw/*Vs*, × Vo/*Vs*) as a function of salinity at 298.15 K, 323.15 K and 348.15 K for the three promising blend formulations.

wt% surfactant concentration with different blend ratios (45, 48.89, 50, 56.4, 60, 64.29 and 70 wt% RECOLAS158) was tested at 298.15 K, 323.15 K and 348.15 K for several weeks. No precipitation or cloudiness was observed for any of the formulations at 298.15 K. However, at 323.15 K and 348.15 K formulations containing 45% and 48.89% RECOLAS158 showed cloudiness within 24 h (Fig. S7 in SI). As explained in section 3.1, the mixture becomes more lipophilic as temperature increases, thus solubility in the aqueous phase diminishes. Nonionic surfactants are characterized by a cloud point, defined as the temperature above which a surfactant rich phase separates from an aqueous solution. As temperature increases, oxyethylene groups present in T2EG become dehydrated and, additionally, the degree of dissociation is increased leading to turbidity.

Mixtures of anionic-cationic surfactants have been reported to have a high tendency to precipitate and form gels and liquid crystals, which severely limits their use [47]. However, it is known that when these surfactants are branched the precipitation is reduced [48]. Iolilyte T2EG is a mixture of tail-branched surfactants of varying tail length that fail to fit well into a crystal structure and hence minimize precipitation. The use of this cationic surfactant diminishes hydrophobic Van der Waals interactions by increasing the spacing between surfactant tail groups, thus the number of carbons interacting closely is lower. Van der Waals hydrophobic interactions are the main factor responsible for the formation of insoluble phases [48,49].

It is worth mentioning that sulfonate-type surfactants, such as RECOLAS158, precipitate in brines like seawater due to their high sensitivity to divalent ions [50]. The use of co-surfactants, usually alcohols, is necessary to guarantee a single-phase aqueous solution. Alcohols decrease solubilization of oil and water in microemulsions and cause environmental issues [47]. In the present study, an alcohol-free stable formulation is generated by the addition of a cationic tail-branched surfactant to the sulfonate.

Due to the promising behavior with salinity and temperature of the blend containing 56.4% RECOLAS158 (see section 3.1 and Fig. 3), its stability was further tested at different salinities. It was found to be stable up to 100000 ppm of TDS at 298.15 K and 323.15 K, no precipitation or cloudiness were observed for several days. At 348.15 K, no precipitation was found at salinities up to 90000 ppm TDS, but higher salt concentration led to instability problems within 24 h (see Fig. S8 in SI). It is known that the cloud point decreases with increasing salinity and hardness [9,51].

The size distribution, achieved by DLS, for the formulation containing 56.4% RECOLAS158 in SSW at 298.15 K is shown in Fig. 4. Results show that aggregates in solution have a mean hydrodynamic diameter of 32.30 nm. This diameter is small enough to be injected in most reservoirs [52–54].

3.3. Dynamic interfacial tension

With the aim of analyzing the ability of the surfactant blends to reduce water/oil IFT, dynamic ITF measurements were carried out. As asphaltenes and crude oil resins can significantly influence IFT [34], measurements were carried out at 298.15 K, 323.15 K and 348.15 K with the target crude oil (see Table 2). Promising blend ratios and others close to them (45, 48.89, 50, 56.4, 60, 64.29 and 70 wt% RECOLAS158) were tested in order to select an optimal formulation leading to the lowest IFT.

Fig. 5 shows dynamic IFT between crude oil and the aqueous formulations of the selected blends at the three temperatures under study. At 298.15 K, very low IFTs (less than 10^{-2} mN/m) were obtained for blend ratios between 56.4% RECOLAS158 and 70% RECOLAS158.

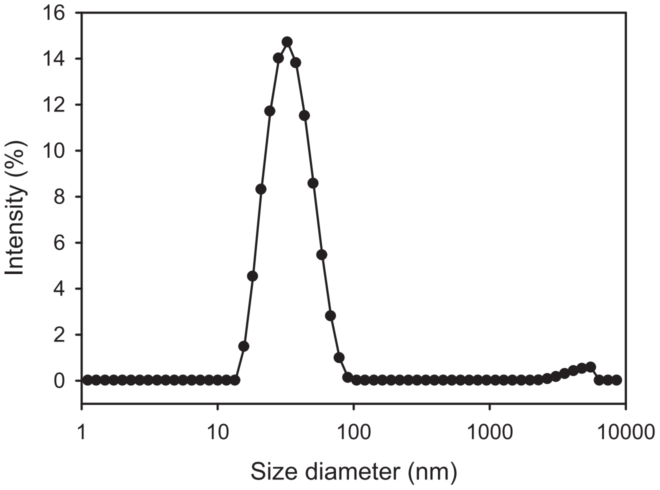

Fig. 4. Size diameter distribution of 56.4% RECOLAS158 formulation on seawater at 298.15 K.

When decreasing the percentage of RECOLAS158 from 64.29% (optimum in the blend scan study) to 60%, IFT is reduced from 2.65x10^{-2} mN/m to 1.02x10^{-2} mN/m (lowest IFT found at this temperature). At 323.15 K, very low IFTs were found for blend ratios higher than 45% RECOLAS158. In this case, the lowest IFT value at this temperature (1.39 x10^{-2} mN/m) was obtained for a blend ratio of 56.4% RECOLAS158, as expected according to blend scan studies. The greater the deviation from this ratio, the higher IFT. Finally, at 348.15 K very low IFTs were found for blend ratios lower than 70% RECOLAS158. When increasing the ratio of RECOLAS158 from 48.89% (optimum in the blend scan) to 50% RECOLAS158, IFT was reduced from 3.47x10^{-2} mN/m to 1.73x10^{-2} mN/m (lowest IFT found at this temperature).

According to phase behavior and IFT studies, a formulation with 1 wt % of 56.4% RECOLAS158 in SSW was considered optimal, since it gives a good performance in terms of stability and IFT reduction at the three tested temperatures, and so was therefore selected for further tests.

3.4. *Wettability alteration*

Carbonate reservoirs are often oil-wet or mixed wet and the surfactant shifting this towards water-wet is desirable. Wettability alteration ability of the optimal formulation (1 wt% of surfactant, 56.4% RECOLAS158, in SSW) was evaluated in oil-wet carbonate rocks at 298.15 K, 323.15 K and 348.15 K. Rock wettability can be classified as a function of contact angle into: water-wet (contact angle <70°), intermediate-wet (contact angle between 70°-110°) and oil-wet (contact angle >110°) [7].

As shown in Fig. 6, contact angles between crude oil and carbonate surface initially ranged from 146.4 to 157.8°, indicating a strong oil-wet character. Treating the rock with the blend solution at 298.15 K hardly changed the wettability of the rock, which was found to be oil-wet after 14 days. A change to intermediate-wet was observed at 323.15 K and 348.15 K achieving contact angles between 102.4° and 106.9° after 14 days. Intermediate results were also taken at 3 and 9 days (see Fig. S9 in SI). Although after 3 days at 348.15 K the wettability already was intermediate-wet, it took 14 days to get a similar change when working at 323.15 K. It is commonly accepted that carbonate reservoirs become more water-wet as temperature increases. Strand *et al.* (2006) [55] studied the influence of temperature on the wettability of oil-wet carbonate cores and found that the imbibition rate increased as the temperature increased. In addition, they reported that no spontaneous imbibition took place at room temperature.

The blend RECOLAS158/T2EG behaves like a catanionic surfactant (Fig. S10 in SI shows a cmc drastically lower for the blend than that corresponding to the individual components), with a benzene ring in the anionic surfactant RECOLAS158 and several ethoxy units provided by the cationic SAIL T2EG. The wettability alteration induced by nonionic surfactants is expected to be weak and reversible. Jarrahian *et al.* (2012) [12] suggested a mechanism for nonionic surfactants with a benzene ring in their structure. Surfactant molecules are adsorbed on the positive rock surface via electrostatic interaction induced by polarization of π electrons in the benzene ring. Thus, surface zeta potential is decreased, and adsorbed carboxylic acids are linked to the adsorbed surfactant molecules through hydrophobic tail-tail interactions. In the case of surfactants containing ethoxy groups, according to Souayeh *et al.* (2018) [56] molecules are adsorbed on the carbonate surface via hydrogen bonding between ethoxy units and hydroxyl or carboxylic groups on the solid surface. Adsorbed organic compounds are replaced and surfactant molecules occupy the active sites of the calcite material. Next, desorbed carboxylic acids form a new layer via hydrophobic interaction with the adsorbed surfactant. Either mechanisms can account for the wettability alteration achieved with the RECOLAS158/T2EG blend.

In our previous work [29] the wettability alteration capacity of the blend SDBS/C1EG was tested. It required 15 days at 348.15 K to switch the wettability of the rock towards a mixed-wet state. The blend RECOLAS158/T2EG only required 3 days at the same temperature to achieve a similar change in contact angle. This confirms that higher ethoxylate content improves the wettability alteration capacity of the surfactant.

3.5. *Static adsorption tests*

Static adsorption tests can be considered a fast-screening method to evaluate and compare the efficiency of different surfactant candidates in terms of adsorption. They should be carried out only with comparative

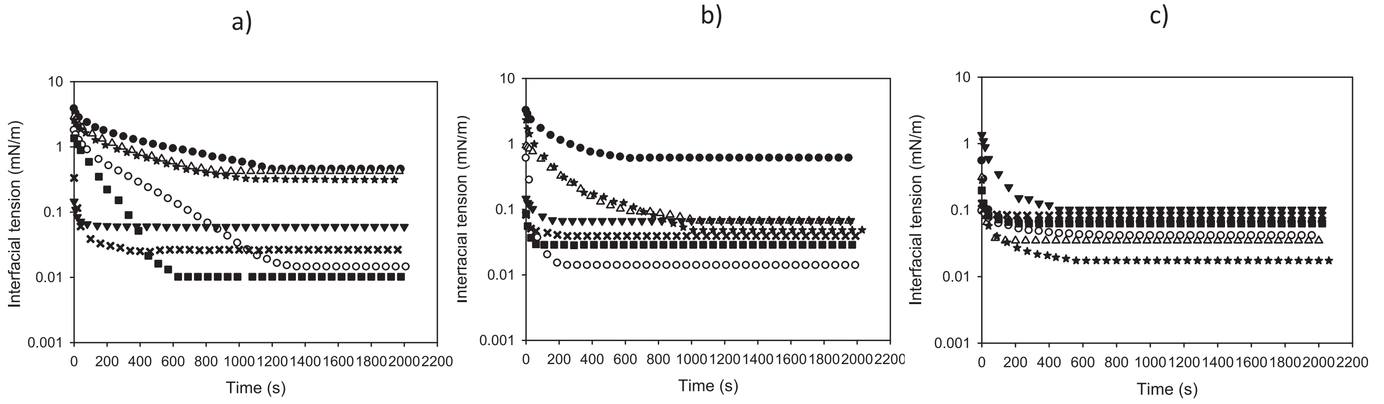

Fig. 5. Dynamic IFT between crude oil and different RECOLAS158/T2EG formulations in SSW at 298.15 K (a), 323.15 K (b) and 348.15 K (c). (● 45% Δ 48.89% ★ 50% ○ 56.4% ■ 60% × 64.29% ▼70% RECOLAS158).

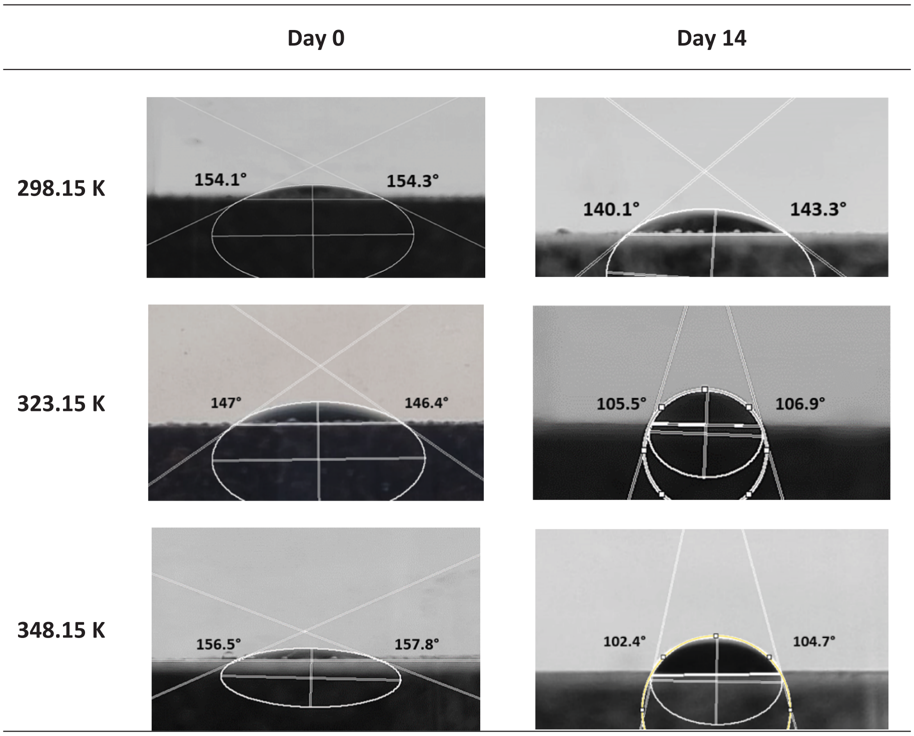

Fig. 6. Contact angle measurements in oil-wet rock before and after treatment with the surfactant formulation at different temperatures.

purposes, since experimental conditions are far from those found in a real reservoir (absence of crude oil, high specific surface, etc.). Adsorption values are usually overestimated in these tests, and values between 0 and 10 mg/g_{rock} are commonly obtained [32].

Fig. 7 shows surfactant adsorption density evolution with time for the blend formulation proposed in this paper. For comparison purposes, adsorption kinetics of a blend consisting of 36% RECOLAS158 + 64% C1EG [57] is also shown. The adsorption density equilibrium value was found as 1.35 mg_{blend}/g_{rock} for the RECOLAS158/T2EG mixture, whereas for the blend containing RECOLAS158/C1EG the value was 2.93 mg_{blend}/g_{rock}. The use of T2EG instead of C1EG (a cationic SAIL with lower alkyl chain length and ethoxylation degree) led to a decrease in adsorption of 54%. These results are in agreement with previous studies. Curbelo *et al.* (2007) [58] investigated the dynamic adsorption of two different nonionic surfactants with an ethoxylation degree of 9.5 and 15.0 on sandstone, which resulted in adsorption values of 13.15 and 8.47 mg/g_{rock}, respectively. They concluded that adsorption decreases with the increase in the ethoxylation degree, due to a higher surface area. For these systems, the amount of surfactant required to cover the internal surface of the rock is lower than for systems employing surfactants with low ethoxylation degrees. Similar results were reported by Singh and Notley (2010) [59]. They reported that $C_{14}E_6$ adsorbed more than $C_{16}E_8$ on silica surfaces based on the smaller effective head size of $C_{14}E_6$.

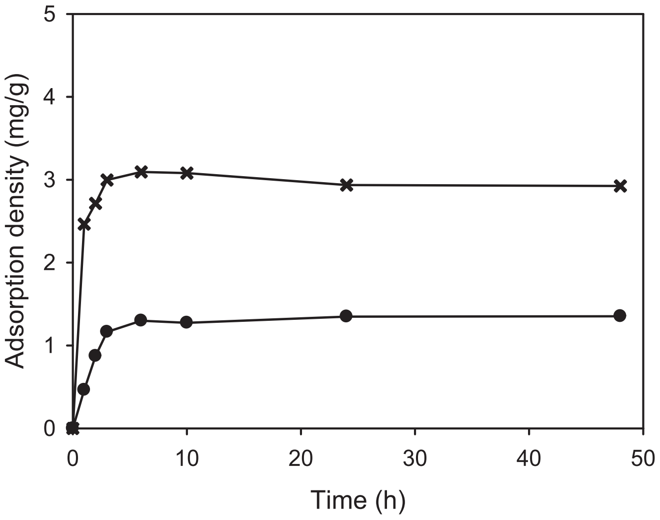

Fig. 7. Static adsorption comparison of two blends containing RECOLAS158 at 298.15 K (● 56.4% RECOLAS158 + 43.6% T2EG; x 36% RECOLAS158 + 64% C1EG).

3.6. Dynamic adsorption tests

LAS surfactants, such as RECOLAS158, show high retention values in carbonate rocks (>2 mg_{blend}/g_{rock}) which is one of the main drawbacks of their application in this type of reservoir [20,22]. Dynamic adsorption tests were carried out, since they provide more realistic results compared to static adsorption experiments that show the improvement in adsorption values when combining the LAS with the SAIL.

Single phase dynamic adsorption experiments without oil were performed by injecting continuous slugs of 1 wt% of either tracer or surfactant formulation in carbonate cores at room temperature. As shown in Fig. 8, the surfactant front is retarded compared to the tracer front, indicating that surfactant is being adsorbed on the rock matrix. Surfactant adsorption was calculated using Eq. (2) and a value of 0.086 mg_{blend}/g_{rock} was obtained. No preferential adsorption of any blend component was detected; thus, the mixture behaves as a single component.

It is believed that the anionic surfactant monomers are being "sequestered" in catanionic micelles [35,60]. Catanionic micelles are electrostatically neutral complexes, therefore adsorption in positively charged carbonate material is lower than for negatively charged LAS surfactants. To test this hypothesis, the zeta potential of 1 wt% surfactant blend in SSW was measured at 298.15 K. It is known that zeta potential is neutral near equimolar compositions that correspond to the

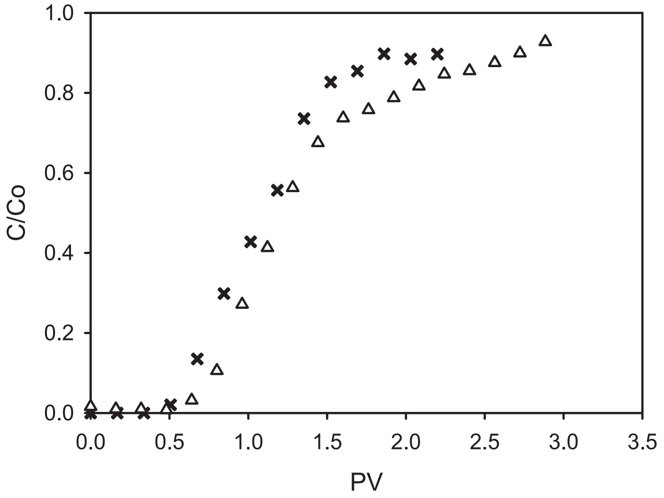

Fig. 8. Dynamic adsorption of the optimized formulation in carbonate rock at room conditions (×Tracer, △ Blend 56.4% RECOLAS158).

formation of catanionic micelles. Values of zeta potentials within ±30 mV are generally regarded as neutral [37]. A value of −1.78 mV was obtained which confirms that blending leads to electrostatically neutral complexes, reducing the adsorption of traditional anionic surfactants in carbonate material. These results are in agreement with our previous work [29]. However, in the present research, adsorption is further reduced to 0.086 mg_{blend}/g_{rock} using a mixture of RECOLAS158/T2EG compared to values between 0.37 and 0.51 mg_{blend}/g_{rock} obtained in our previous paper for blends of SDBS and C1EG. The mechanism associated with this improvement was discussed in section 3.5.

3.7. Core flooding

An aqueous formulation consisting of 1 wt% surfactant blend (containing 56.4% RECOLAS 158 and 43.6% T2G) in SSW was used to perform oil recovery experiments in fresh carbonate cores at room conditions. Two different tests were carried out using different EOR strategies. Before the EOR process, both oil extraction tests were started by injecting SSW in secondary mode, until reaching the residual oil saturation. A summary of core flood parameters as well as results of oil recovery experiments is presented in Table 4.

Test 1 was a quick test to get an idea of the ability of the formulation to extract oil. Injection rates of 2 mL/min were applied both at secondary and tertiary extraction steps. In this test, after secondary recovery with 5.9 PV of SSW, 59.79% of the OOIP was recovered. Subsequently, 4.73 PV of 1 wt% surfactant formulation were injected until no more oil was present in the effluent. 17.28% of the OOIP was recovered during this EOR process.

Test 2 was conducted at low injection rates to offer a more realistic approximation to oil field operations. As a secondary recovery step, 2.47 PV of SSW were injected at 0.05 mL/min. Subsequently, in order to reduce surfactant costs and improve the efficiency, an EOR step was carried out combining the injection of 0.5 PV of surfactant slug followed by the injection of 3.7 PV of PAM polymer. PAM concentration was set to 2000 ppm in SSW in order to obtain a viscosity equal to that of crude oil. The surfactant slug was injected at 0.025 mL/min, and the first 0.5 PV of PAM solution were injected at this same velocity to ensure that the whole PV of the core was swept by the surfactant at the same rate. An additional oil recovery of 19.53% of the OOIP was obtained during this EOR step. Fig. 9 shows the relationship between the oil recovery factor and injected pore volume. The oil recovery factor was calculated as the cumulative oil recovery divided by the OOIP.

It should be noted that the rock permeability in Test 2 (5.33 mD) was lower than in Test 1 (12.94 mD). Low permeability reservoirs have small pores and throats, poor connectivity and a thick boundary layer between the crude oil and the rock [61]. These characteristics increase capillary forces that retain the oil within the pores and seriously affect crude oil production. The higher residual oil saturation obtained in Test 2 might be related to the lower permeability of the rock. In addition, polymer transport in low permeability carbonate cores presents several challenges. There is a limit in the molecular weight of the polymer that can be successfully transported through porous media without plugging. Also, low molecular weight polymers require significantly higher concentrations to generate the same viscosity [62]. The optimization of the polymer formulation is out of the scope of the present paper.

Table 4
Summary of core flooding experiments.

	Test 1	Test 2
Porosity of the core (%)	14.75	14.54
Permeability (mD)	12.94	5.33
Pore volume (mL)	12.66	12.48
OOIP (mL)	8.1	6.4
Initial oil saturation (%)	63.98	51.26
Irreducible water saturation (%)	36.02	48.74
Oil recovered after water flood (% OOIP)	56.79	34.53
Residual oil saturation (%)	27.65	33.56
Surfactant slug injected	4.73 PV of 1 wt% blend solution (56.4% RECOLAS158 + 43.6% T2EG) in SSW	0.5 PV of 1 wt% blend solution (56.4% RECOLAS158 + 43.6% T2EG) in SSW
Polymer slug injected	–	3.71 PV of 2000 ppm PAM in SSW
Additional Oil Recovered (% OOIP)	17.28	19.53

4. Conclusions

Traditional anionic LAS are not suitable for EOR in carbonate rocks when employed alone, due to poor stability and high adsorption. In this study, a new formulation based on RECOLAS 158, a C_{15}-C_{18} LAS obtained from the petrochemical industry, and a T2EG SAIL, has been designed for chemical EOR in carbonate reservoirs. From the studies presented here, some conclusions may be established:

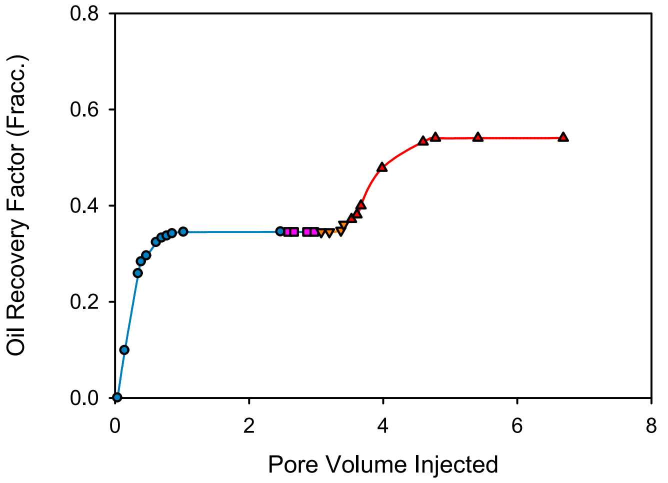

Fig. 9. Core Flooding test 2. ●Water flooding (0.05 mL/min) ■ Surfactant flooding (0.025 mL/min) ▼ Polymer Flooding (0.025 mL/min) ▲ Polymer Flooding (0.05 mL/min).

- The addition of the ionic liquid T2EG to RECOLAS158 improves the properties of the traditional surfactant, and allows the design of a temperature stable alcohol-free formulation for carbonate reservoirs.
- An optimal formulation consisting of 1 wt% of surfactant blend (56.4/43.6 RECOLAS158/T2EG mass ratio) in SSW was successfully designed through stability studies, phase behavior tests, and IFT measurements.
- The formulation was demonstrated to offer a good performance (very low IFT and good stability) at temperatures between 298.15 K and 348.15 K.
- In comparison to a similar blend consisting of a LAS with the SAIL C1EG, also considered promising for carbonate reservoirs, the present formulation clearly renders better performance at high temperature.
- The optimized formulation was found to be stable at high salinity environments, up to 100000 ppm of TDS at 323.15 K and 90000 ppm of TDS at 348.15 K.
- This blend can only change the wettability of oil-wet carbonate rocks towards intermediate-wet.
- The adsorption of the formulation was found to be low enough (0.086 $\mathrm{mg_{blend}/g_{rock}}$) to be economically feasible. Adsorption decreases with the increase of the ethoxylation degree of the surfactant.
- Additional oil recoveries obtained in core-flooding experiments are promising, IFT reduction being the main mechanism of recovery from water-wet carbonate rocks. Wettability alteration should also be considered in the case of oil-wet rocks.
- The combination of surfactant flooding with polymer flooding slightly improves additional oil recovery, so its optimization is required for practical applications.

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.

Data availability

No data was used for the research described in the article.

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 and CEPSA and CEPSA-Química (Madrid) for providing the crude oil and sulfonate surfactant used for the experiments.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2023.128363.

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