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Design of formulations based on ionic liquids for enhanced oil recovery

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DESIGN OF FORMULATIONS BASED ON IONIC LIQUIDS FOR ENHANCED OIL RECOVERY

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Design of formulations based on ionic liquids for enhanced oil recovery

Dª. Ana María Soto Campos

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In Santiago de Compostela, 2nd of June 2023

Prof. Ana María Soto Campos

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In the words of the writer Ralph Waldo Emerson: “Life is a journey, not a destination”. During these years, I have recognized that the true value of this Thesis lies not only on the final outcomes but also in the process of exploration, personal growth, and discoveries gained along the way. Throughout this research journey, I have embraced the joy of learning, the resilience in overcoming obstacles, and the satisfaction of uncovering new insights.

Thank you all for being a part of this.

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Abstract in English

Crude oil is expected to remain a primary source of energy and materials for the foreseeable future. Given the declining number of new oil field discoveries, it is crucial to maximize oil production from apparently depleted reservoirs. The main objective of this Thesis was the design of formulations based on surface-active ionic liquids to improve current enhanced oil recovery methods. A comprehensive review of the ionic liquids proposed in the literature for surfactant flooding, with a focus on practical approaches, was conducted to establish the basis for the experimental work required. Initially, a preliminary formulation based on 1-decyl-3-methylimidazolium triflate was developed, yielding promising results. However, surface-active ionic liquids were found to be better employed to improve the performance of traditional surfactants, rather than used by themselves. Thus, various formulations were designed to improve the application of lineal alkyl benzene sulfonates in carbonate reservoirs. By incorporating cocosalkylpentaethoximethylammonium methylsulfate, the adsorption of these traditional surfactants was reduced, and their stability in high salinity environments was improved. Furthermore, the addition of N-ethyl-N-bis[poly(ethylene glycol)]-N-tallow ammonium ethylsulfate, an ionic liquid with a higher degree of ethoxylation, enhanced the formulation's performance at high temperatures. Finally, expanding the possible application of surface-active ionic liquids in oil recovery methods, some of these salts were also evaluated for foam generation in CO_2 flooding. They were revealed as promising agents for this application since they improved foam stability and increased the mobility ratio compared to other traditional surfactants. The studies involved in this Thesis provide a solid foundation and open up new possibilities for the utilization of surface-active ionic liquids in enhanced oil recovery.

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1. OBJECTIVES



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Crude oil is ubiquitous as a fossil fuel in the daily lives of global consumers. It is an essential source of energy, but petroleum is also indispensable as a chemical raw material. It is undeniable that a shift away from fossil-based towards renewable sources is crucial to avoid climate-change disaster. However, this transition may take some considerable time. With global energy demand set to increase and the declining number of new oil field discoveries, it is necessary to sustain production from existing reservoirs by application of new recovery technologies.

More than 50% of the crude oil remains trapped by capillary forces in the reservoir after the implementation of conventional recovery methods. In addition, more than 60% of global oil reserves reside in carbonate reservoirs. They are commonly characterized by a complex pore network, low permeability, harsh conditions of temperature and salinity, and unfavorable wettability conditions, making oil extraction very challenging. Enhanced oil recovery (EOR) techniques are being developed to overcome these issues and recover the remaining oil in place. Among EOR methods, surfactant flooding is a well-established technique that has proven to be successful as it increases oil recovery through a combination of mechanisms. However, the intolerance of these chemicals to harsh conditions such as high temperature and salinity limits their application in many reservoirs. In addition, traditional anionic surfactants widely used in sandstone reservoirs cannot be applied to carbonate rocks, due to the high adsorption values expected. Surface-active ionic liquids (SAILs) are emerging as possible candidates to improve EOR processes due to their attractive features such as their functionalization. Therefore, the overall objective of this Thesis is the design of formulations based on SAILs for application in EOR.

To achieve this major objective, some specific goals are established. In this context, an initial objective is to review the ionic liquids (ILs) already proposed in the literature for this application, focusing on practical approaches. Since the number of studies using carbonate rocks is very low, the second objective is the design of a formulation based on a SAIL able to improve the performance of surfactant flooding in carbonate reservoirs. These two objectives are accomplished in the first publication of this Thesis entitled "*Oil recovery tests with ionic liquids: A review and evaluation of 1-decyl-3-methylimidazolium triflate. Petroleum Science 19 (2022) 1877-1887*".

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Lineal alkylbenzene sulfonates (LASs) are inexpensive traditional anionic surfactants, widely used in sandstone reservoirs but not applied in carbonate ones due to their low tolerance to high salinity formation brines, and high adsorption on this type of rock. This being the case, the solution of blending SAILs with these traditional surfactants to improve their features and enable their use in carbonate reservoirs is suggested. A study of this notion is developed in the second paper of this Thesis entitled "*Design and performance analysis of a formulation based on SDBS and ionic liquid for EOR in carbonate reservoirs. Journal of Petroleum Science and Engineering 209 (2022) 109856*" that derives from a patent (*ES2922249 / WO2022184955*). In this work, commercial sodium dodecylbenzene sulfonate (SDBS) is mixed with the ammonium SAIL cocosalkylpentaethoximethylammonium methylsulfate (C1EG). Formulation stability, wettability alteration ability, adsorption and oil recovery capacity of the proposed formulation in carbonate rocks are studied to show the validity of the proposal.

Following this line, the next objective is to investigate the influence of alkyl chain length and isomer distribution of petrochemical LASs on the performance of the blend containing the SAIL C1EG, for application in carbonate reservoirs. In the third paper of this Thesis, entitled "*Experimental evaluation of blends containing lineal alkylbenzene sulfonates for surfactant flooding in carbonate reservoirs. SPE Reservoir Evaluation & Engineering (2023) SPE 215828:1-14*" blends of C1EG and three different LASs are carried out to meet this objective. Phase behavior, aqueous stability and interfacial tension (IFT) tests are performed to assess the structure-performance relationship. Static adsorption, wettability alteration and oil recovery ability from carbonate material are also investigated, to ensure the effectiveness of the formulations.

With the aim of improving LASs performance at high temperatures, the next objective is to develop a formulation based on a SAIL and a traditional LAS surfactant with good performance in those conditions. This objective is achieved in the fourth work of this Thesis entitled: "*A formulation based on a cationic surface-active ionic liquid and an anionic surfactant for enhanced oil recovery at a carbonate reservoir. Fuel 345 (2023) 128363*". A formulation based on a C15-C18 LAS, obtained from the petrochemical industry, and the SAIL N-ethyl-N-bis[poly(ethylene glycol)]-N-tallow ammonium ethylsulfate (T2EG) is designed. The formulation's performance is tested at temperatures between 25°C and 75°C in carbonate rocks.

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Switching the attention to other EOR techniques, gas EOR and more specifically, CO_2 injection is attracting new market interest. This technology can generate a product with high economic value whilst also sequestering CO_2 in underground formations previously occupied by oil. In this context, foam injection has the potential to improve CO_2-EOR processes by increasing sweep efficiency. However, the stability of the foam remains a challenge, especially at harsh conditions of temperature, pressure, and salinity. Therefore, the final objective of this Thesis is to carry out a study on the application of SAILs to stabilize foams in gas EOR processes. This objective is achieved in the fifth paper of this Thesis entitled: "*Experimental evaluation of foams stabilized by ionic liquids for enhanced oil recovery. Journal of CO_2 Utilization 72 (2023) 102507*". The paper is the result of a short stay at the University of Texas at Austin under the direction of Professor Kishore K. Mohanty. Six SAILs with the most common functional groups (imidazolium, pyridinium and ammonium) are evaluated for application at harsh conditions of temperature, salinity and pressure. Air and CO_2 are used as foaming gases for ambient pressure stability studies. High-pressure stability tests and gas-formulation co-injection experiments are performed with the most promising formulations using CO_2.

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2. INTRODUCTION



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The growing evidence of on-going climate change and its severe expected impacts has led governments to adopt energy transition policies. In accordance with these, substantial changes must be made in all sectors of the economy, and a mobilization of a wide range of resources is required. In addition to technological innovation in renewable sources, changes in consumer preferences and choices are also needed to reduce greenhouse gas emissions. According to the Annual Energy Outlook 2022 published by the U.S. Energy Information Administration [1], despite the rapid growth of renewable energies, petroleum and natural gas will remain the most-consumed energy sources in the United States through 2050. In some sectors like transportation, changes are expected to be slow, and gasoline is set to remain the most prevalent transportation fuel for at least the next 20 years. Similar conclusions were reported by the Joint Research Centre of the European Commission in their report "The POTEnCIA Central scenario: An EU energy outlook to 2050" [2]. It is predicted that renewable energies will experience exponential growth in the upcoming years, driven mainly by the steep uptake of solar and wind. As shown in Figure 2.1, according to EU report, the combined share of renewable energies will exceed 30% in 2050 compared to a 13% in 2015. However, liquid fuels will remain the most important fuel source throughout the projection period, with a relative share of 31.3% in 2050.

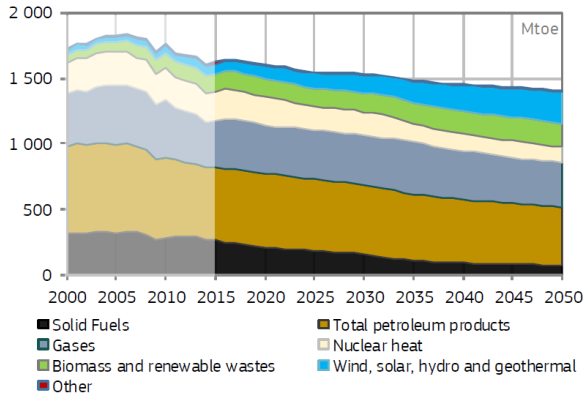


Figure 2.1. Evolution of energy consumption by fuel type in the European Union. Source [2]. Copyright authorization (see Appendix B).

Petroleum is also used by the petrochemical industry as a feedstock to make a great variety of products such as plastics, polyurethane, solvents, and hundreds of other intermediate and end-user goods. Shifting toward renewable feedstocks entails more

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than simply changing raw materials. It involves the development of new growing and harvesting methods, supply and feedstock preparation infrastructures, new chemical pathways and new processing technologies. Compared to crude oil, biomass has a more complex chemical structure, and contains more extraneous components. These factors add considerable complexity to the economical and efficient conversion of biomass into useful chemical building blocks. Comprehensive research and development are necessary in this field [3]. In conclusion, important efforts are required to move towards a deep decarbonization and avoid climate crisis, but there is no doubt that it will take a considerable period of time. While sustainable sources are being developed, it is important to make the most of the available traditional energy and material resources.

2.1 Oil recovery methods

Oil recovery operations can be subdivided into three stages: primary, secondary, and EOR [4].

- **Primary recovery**. During this first extraction, the oil is naturally driven into the wells by the pressure gradient between the bottom of the well and the reservoir. As the fluids in the reservoir expand, the pressure drops until it is too low to produce more oil without an external energy source. The percentage of oil recovery during this stage is on the order of 10-15% of the original oil in place (OOIP) but can be as low as 5% in low permeability reservoirs with high viscosity crude oil.

- **Secondary recovery**. Secondary extraction methods are usually implemented after primary production declines. They consist of injecting a fluid cheaper than crude oil (water, gas, etc.) into injection wells to maintain a certain pressure gradient and displace oil towards production wells. An average 25-30% of the OOIP is usually recovered during this stage.

- **Enhanced oil recovery.** This stage refers to any process undertaken to change the existing rock/oil/brine interactions in the reservoir. It includes thermal recovery, miscible gas (CO_2, nitrogen, hydrocarbon, flue gas) flooding, chemical

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(polymer, surfactant, alkaline, emulsion) flooding, microbial EOR, and combinations thereof.

2.2 Enhanced oil recovery with surfactants

After primary and secondary oil recovery stages, some 60-80% of the OOIP remains trapped in the reservoir due to capillary forces (residual oil) and low permeability areas in which the secondary extraction fluid does not penetrate (bypassed oil). Taking into account the declining number of new oil field discoveries and that they are most likely to lie offshore, deep offshore or in difficult to produce areas, EOR is emerging as an essential technique to sustain production from mature oil fields [5]. Among EOR methods, surfactant EOR has been adjudged as one of the most promising techniques because of its high efficiency, technical and economic feasibility and reasonable capital cost. In addition, it can be applied in a great variety of reservoirs, unlike thermal EOR methods that are unsuitable for reservoirs with great depth and thin pay zone.

2.2.1 Surfactant flooding

Surfactant flooding is a proven EOR technique used for mobilizing residual oil trapped in the reservoir. This chemical method improves pore-scale displacement efficiency through the mechanism of IFT reduction, wettability alteration, or a combination of both [6].

- **Interfacial tension reduction**. After conventional waterflooding, a great amount of oil remains trapped in the pores of the rock due to capillary forces. These forces are measured by the dimensionless capillary number (*Nc*):

$$N_c = \frac{\mu \cdot v}{\sigma} \tag{2.1}$$

where μ and v are the displacing fluid viscosity and velocity respectively and σ is the IFT between displacing (water) and displaced (oil) fluid.

It is known that residual oil recovery in porous media is closely related to the value of *Nc*. For values of *Nc* lower than 10^{-6}, the residual oil recovery is essentially zero and it is considerably improved when values are higher than 10^{-3}. According to the equation, an increase in *Nc* can be achieved in three different ways: increasing displacing fluid velocity, increasing injecting fluid

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viscosity, and reducing IFT. An increase in displacing fluid velocity may give rise to an injection pressure that exceeds the fracture pressure, thus causing the fracturing of the reservoir. Polymer solutions are used to increase displacing fluid viscosity, although higher viscosity results in the need for higher pressure gradients to obtain the same fluid velocity. Thus, increasing *Nc* using this technique is limited to increments of less than 100 times its initial value. In practical applications, the only method that can be used to increase *Nc* by 1000 times is reducing IFT. When surfactant solutions are injected along with brine into oil reservoirs, the hydrophilic head interacts with water while the hydrophobic tail interacts with crude oil components. These interactions lower the IFT at the oil/water interface, resulting in a weakening of the capillary forces and causing oil droplets to flow with ease from the rock pore throats to form an oil bank downstream [6,7].

- **Wettability alteration**. The inclination of a solid surface for a particular type of fluid in the presence of other immiscible fluids is called wettability. The wettability of a reservoir rock determines the distribution and flow of the fluids. Wettability of reservoirs can be categorized into oil-wet, water-wet and mixed-wet. Altering the wettability of a surface from oil-wet to water-wet diminishes the adhesive force of capillarity and increases oil permeability of the reservoir. Thus, wettability alteration targets carbonate reservoirs since they are more likely oil-wet. Cationic surfactants are commonly used for this purpose. They form ion pairs with the adsorbed organic carboxylates of crude oil and stabilize them within the oil, changing the rock surface to water-wet [6,8].

2.2.2 Foam-assisted enhanced oil recovery

Surfactants can be also used in other EOR applications, such as foam-assisted, to improve mobility control during gas flooding. Gas flooding consists of the injection of hydrocarbon or other gases into oil reservoirs that have usually been waterflooded first. CO_2 injection has recently received a great deal of attention. CO_2 emissions caused by human activities grew by 0.9% to over 36.8 Gt in 2022 [9]. The application of CO_2-driven EOR processes benefits human society by providing the capability of boosting

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hydrocarbon production whilst capturing and storing CO_2 in petroleum-bearing underground geological formations. In addition, CO_2 forms a dense or supercritical phase at typical reservoir pressures and temperatures. Supercritical CO_2 has a characteristic of high density and viscosity compared to other gases, which makes the displacement front more stable. However, almost all gas injection processes suffer from early breakthrough and poor sweep efficiency due to the large viscosity contrast between gas and both oil and water. Although these limitations may seem to have less importance for dense or supercritical CO_2 injection, they are still very challenging issues. This process can be significantly improved by injecting the gas in the form of foam.

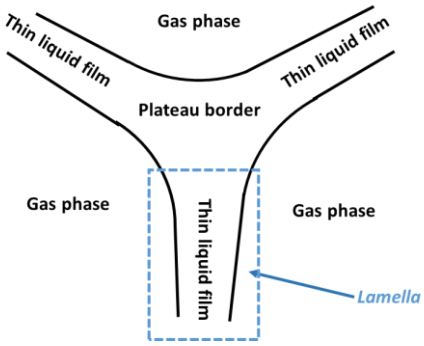


Figure 2.2. Two-dimensional foam system scheme.

Foam is a dispersion of a relatively large volume of gas in a small volume of liquid. A foaming agent (surfactant) is required to generate and stabilize a foam. Figure 2.2 shows a two-dimensional foam system scheme. In this system, the gas phase is separated from a thin liquid film by an interface. The region highlighted by a blue dotted square, composed of the thin liquid film with two interfaces on either side and a junction, is called *lamella*. The thickness of the lamellae is a critical factor in determining its stability. Surfactants reduce the surface tension of the liquid, allowing stable bubbles to form and persist. However, if the *lamellae* are too thick, the surface tension can cause their rupture, leading to foam collapse. On the other hand, if they are too thin, coalescence forces can break them, also causing the foam collapse. Therefore, optimal *lamellae* thickness is important for foam stability [10]. Foams are thermodynamically unstable and eventually collapse. Thus, the development of surfactant formulations able to maintain the appropriate lamellae thickness and improve foam stability is one

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of the major issues in this field. Foams are usually destabilized due to two processes as follows:

- Diffusion. Gas bubbles have a non-uniform size distribution and small bubbles have higher pressure than big bubbles. This pressure difference produces a gas diffusion through the liquid from small to larger bubbles, causing their coalescence. This diffusion effect is also known as Ostwald ripening. Thus, foams are more stable if bubble sizes are more uniformly distributed.

- Liquid drainage. Liquid drainage caused by gravity causes the liquid films to become thinner resulting in bubble coalescence. An increase in fluid viscosity can reduce the drainage rate [11].

The application of conventional surface-active agents in surfactant EOR and foam-assisted EOR methods have some limitations. Most traditional surfactants lose their efficacy under harsh salinity and temperature conditions present in the reservoir. In addition, surfactant losses due to adsorption on reservoir rocks is another major issue that needs to be addressed to implement technically and economically efficient EOR processes based on these chemicals. Moreover, most low-cost traditional surfactants are anionic and cannot be applied in carbonate rocks due to the high adsorption values expected. Due to these reasons, it is necessary to design new surfactants capable of tolerating harsh conditions and reducing adsorption, especially in carbonate rocks [6].

2.3 Ionic liquids

ILs are generally defined as liquid compounds that consist exclusively of ions with melting or glass transition temperatures below 100°C. The scientific potential of ILs is almost unlimited. Their physical, chemical, and biological properties can be easily tuned by switching anions and cations to obtain task specific compounds. The numerous combinations of anions and cations that meet the definition of ILs lead to a diverse suite of behaviors making it difficult to generalize ILs properties. Regardless, ILs usually have negligible vapor pressure, and therefore do not evaporate under normal conditions. Thus, they are called “green” because atmospheric contamination is avoided. These salts are generally non-flammable, and usually remain thermally stable at temperatures higher than conventional solvents. Finally, they present a high solvation capacity, a

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large electrochemical window, and frequently a wide liquid range. Consequently, ILs can potentially be used as solvents and new materials in a wide range of applications such as electrochemistry, biochemistry, material science and pharmaceuticals among many others [12].

The IL cation is typically a large organic structure of low symmetry. The choice of cation can significantly affect solubility, thermal stability, viscosity and reactivity. The cationic center usually includes a positively charged nitrogen or phosphorus. Most common cations used in ILs include imidazolium, pyridinium, pyrrolidinium, ammonium, and usually completely substituted phosphonium. The anion is typically a weakly basic inorganic or organic compound that has a diffuse or protected negative charge. The choice of the anion can significantly impact properties such as polarity, acidity/basicity, ionic conductivity and electrochemical stability of the IL. Common anions used in ILs include chloride, bromide, tetrafluoroborate and hexafluorophosphate (it is currently known that these ions can be hydrolytically unstable in the presence of water), triflate, bis(trifluoromethylsulfonyl)imide, alkyl sulfates, alkyl carbonates, etc. The chemical structures of most common cations and anions are depicted in Figure 2.3 [13].

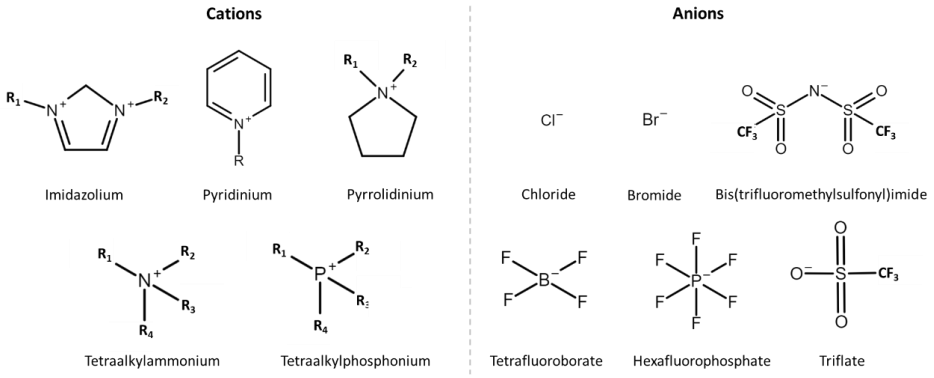


Figure 2.3. Most common cations and anions used in ILs.

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2.4 Surface-active ionic liquids in enhanced oil recovery

The unique properties of ILs make them attractive candidates to improve EOR processes, as they can be tailored to target specific types of oil and reservoir conditions. SAILs are ILs with significant surface activity and have, therefore, the ability to alter the interfacial properties between two immiscible phases such as water and oil. SAILs possess amphiphilic structures: a charged hydrophilic headgroup and a hydrophobic tail, that make them capable of self-aggregate in solution like traditional surfactants [14].

It has been demonstrated in literature that SAILs may exhibit numerous improvements over traditional surfactants for EOR applications. It has been shown that SAILs have low critical micelle concentration (CMC) values compared to traditional surfactants with similar structures, and therefore they perform efficiently even at low concentration. SAILs can also reduce IFT between crude oil and water more efficiently even in high temperature and salinity conditions. As mentioned earlier, most common traditional surfactants possess an anionic nature and thus cannot be applied in carbonate rocks, due to the undesirable adsorption in this material. In addition, divalent ions present in the formation brines of most carbonate reservoirs usually cause their precipitation. In such cases, cationic surfactants serve as potential candidates to overcome these issues. However, the number of conventional cationic surfactants is low and their cost usually high. SAILs are mostly cationic in nature. Thus, they have potential for application in EOR processes in carbonate formations.

Another advantage of the potential application of SAILs in EOR is that they can increase the viscosity of the injected fluid, improving the mobility ratio. Some SAILs have also been reported to alter the wettability of the rock towards water-wet, which is of practical interest for EOR processes.

Some works in the literature [15,16] have shown that SAILs with heterocyclic headgroups exhibit higher interfacial activity compared to aliphatic ones even in high salinity conditions. In addition, those SAILs having aromatic headgroups are more efficient in reducing IFT between oil and water as compared to SAILs with a non-aromatic ring. This is due to the strong interaction between this aromatic headgroup and the aromatics present in crude oil. However, the addition of co-surfactants or alkalis to the SAIL formulation in usually mandatory to enable the achievement of ultra-

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low IFT between oil and water in the reservoir, whilst keeping the formulation stable in reservoir conditions.

It is clear that SAILs are an attractive alternative to conventional surfactants in EOR applications, especially for carbonate formations. At the beginning of this Thesis this research topic was taking off. The main works were collected in the first paper of this Thesis: "*Oil recovery tests with ionic liquids: A review and evaluation of 1-decyl-3-methylimidazolium triflate*". However, very few works addressed the whole problem. Several SAILs were proposed, but formulations were not adequately designed through phase behavior studies to ensure the achievement of ultra-low IFT. Adsorption tests were, on most occasions, neglected. In fact, the proposal of cationic SAILs for EOR in sandstone rocks was the most common in spite of expected adsorption problems. The design of formulations without considering divalent ions is still a serious lack in current publications. This Thesis aims to design formulations based on SAILs for EOR applications ensuring their validity through the required studies: phase behavior, stability in absence of oil and in presence of divalent ions, IFT, wettability, adsorption, and oil recovery.

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3. PUBLICATIONS



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Review Paper

Oil recovery tests with ionic liquids: A review and evaluation of 1-decyl-3-methylimidazolium triflate

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ABSTRACT

The main advantages of the use of ionic liquids in enhanced oil recovery are their tunability and stability in harsh environmental conditions. In this work, a comprehensive review of ionic liquids proposed to improve current chemical oil recovery methods has been presented, focusing on core flooding experiments. With an almost infinite number of possible ionic liquids, the amount of experiments carried out up to now has been very limited. However, results are promising, with additional recovery after secondary flooding of up to 32% of the original oil in place. Most formulations with ionic liquids have been proposed for sandstone reservoirs, the number of studies with carbonate cores being very scarce. The possibilities of a new room temperature surface active ionic liquid, 1-decyl-3-methylimidazolium triflate, for this application were analyzed. It was shown that it is able to drastically reduce the water/oil interfacial tension. An optimized formulation was proposed for carbonate reservoirs. After secondary flooding with brine, an additional recovery of 10.5% of original oil in place was achieved at room conditions. A combination of the proposed method followed by a polymer flooding step with polyacrylamide led to a lesser but still significant recovery, reducing the costs associated to the ionic liquid.
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1. Introduction

Demand for energy is increasing worldwide, and petroleum will be needed not only as a source of energy, but also of materials for many years. Most of the current world oil production comes from mature fields due to the declining number of new oil field discoveries. Therefore, increasing oil recovery from these aging resources is the primary concern for oil companies and authorities globally (Pal et al., 2018; Saxena et al., 2019). After primary and secondary recovery methods, a reservoir still contains two thirds of the original oil in place (OOIP). This is because the efficiency of these methods is limited by capillary forces that retain the residual crude oil in pore structures. Moreover, at the reservoir scale, there are certain areas in which the fluid injected during secondary recovery does not penetrate adequately due to the low permeability of the rocks or because of preferential pathways (Shah and Schechter, 1977). Enhanced oil recovery (EOR) techniques are being developed to overcome these problems. The main EOR techniques include thermal recovery, miscible gas injection and chemical methods (Sheng, 2011).

Among chemical EOR methods, surfactant injection has received in the last decades a great deal of attention because of its ability to reduce water/oil interfacial tension (IFT) to ultra-low values. Toxicity, high cost, and degradation at harsh conditions of temperature and salinity are the main issues that companies face during surfactant flooding process (Bin Dahbag et al., 2019). Surfactant retention also plays a significant role in chemical EOR application because it drastically affects the economics of the process (Ahmadi and Shadizadeh, 2015). In practice, it is very common to implement a tertiary surfactant flooding in combination with other chemicals in so-called alkali-surfactant-polymer (ASP) flooding. Alkalis are deployed to improve the interfacial activity of surfactants through *in situ* saponification by reaction of the alkali with the naphthenic acids (saponifiable components) of crude oil. Moreover, alkalis are cheap, so their application improves project economics. In addition, the employment of polymers aims to increase displacing fluid viscosity and thus to increase sweep efficiency (Sheng, 2011; Tackie-Otoo et al., 2020).

Surface Active Ionic Liquids (SAILs) have been shown to improve

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the features of conventional surfactants (Bera and Belhaj, 2016). Ionic liquids (ILs) are salts with melting or glass transition temperatures below 373.15 K. In many cases these temperatures are low enough that SAILs are liquids at room conditions, thus facilitating their manipulation. Other properties useful for their application in EOR are their negligible vapor pressure and their high thermal stability and solvating capacity. Moreover, in comparison with traditional surfactants SAILs have been found to have advantages regarding stability in harsh environments (high salinity and temperature) (Benzagouta et al., 2013; Hezave et al., 2013). However, their most interesting attribute is likely tunability. Cations and anions can be selected to make task-specific compounds, so they can be designed with respect to the characteristics of each individual reservoir (Pillai et al., 2018; Nandwani et al., 2019a).

In this paper, a comprehensive review of SAILs proposed for EOR is presented focusing on core flooding experiments. Moreover, a new IL, namely 1-decyl-3-methylimidazolium triflate is proposed for chemical EOR. Selection criteria were based on stability in brine solution and IFT reduction performance. Phase behavior of SAIL/brine/oil systems is studied by means of pipette tests. An optimal formulation is defined through the minimization of water/oil IFT by changing salinity, and surfactant and alkali concentrations. Adsorption tests and core flooding experiments in sandstone and carbonate reservoirs are carried out to analyze the capability of the SAIL to extract oil. Furthermore, the performance of alkali-surfactant (AS) and ASP flooding is compared.

2. Review

In the last decade, the number of papers proposing the use of ILs for EOR has increased exponentially. However, the number of core flooding tests carried out up to now is very limited, although this technique is considered the most suitable to determine and evaluate the effect of injecting fluids to enhance oil recovery in crude oil reservoirs. In this current section, the most important work on oil recovery with SAILs are presented. Test conditions may be either ambient temperature and low confining pressure or high temperature and pressure. The core material often comes from an oil reservoir but some tests use sand packs prepared manually with uniform sand grains. In addition, rocks are classified as sandstone or carbonate reservoir rocks.

2.1. Tests using real reservoir rocks

Hezave et al. (2013) tested the SAIL [C_{12}mim]Cl and found out that an increase in the concentration of the surfactant led to a significant decrease in water/oil IFT even at high salinity conditions. The authors also carried out core flooding tests and obtained extractions of about 50% of the OOIP in secondary water flooding, and an additional 8% of OOIP in tertiary flooding with a 4000 ppm SAIL solution in water. Higher recovery was observed using a formation brine-surfactant solution at the same SAIL concentration, obtaining a recovery of 13% of OOIP. It should be noted that the authors report high adsorption values (16 mg of surfactant per gram of rock). Rocks used for the analysis had a porosity between 14 and 23% and a permeability around 8–16 mD. However, no further information was offered about the type of rock.

Bin Dahbag et al. (2015) suggested the use of a tetra-alkyl ammonium sulfate (Ammoeng 102) after screening nine ILs. Solubility in brine solutions, surface activity and solution stability at high temperatures were the selection criteria. Optimization of Ammoeng 102 formulation was done based on IFT reduction. Core flooding experiments were conducted on Berea sandstone samples. The injection of 20 wt% brine solution (83% NaCl and 17% $CaCl_2$) allowed an extraction of about 43% of the OOIP. An additional oil recovery (AOR) of about 5% of the OOIP was achieved in tertiary flooding with the injection of 500 ppm of Ammoeng 102 diluted in the same brine solution. However, Ammoeng 102 was proven to be more effective injected in secondary mode (as a slug followed with brine or as a continuous surfactant injection) than in tertiary mode. Achieved recoveries ranged from 63% to 70% of OOIP. However, a high tendency for the surfactant to be adsorbed on rock surface at reservoir conditions was noticed, which increased at higher salinity conditions.

Deep Eutectic Solvents (DESs) are mixtures generally composed of two components that form an eutectic system with a melting point lower than that of each individual component. This is due to the formation of strong hydrogen bonds between the two components, one being a hydrogen bond donor and the other a hydrogen bond acceptor. DESs are seen as an interesting alternative to ILs in some applications. Mohsenzadeh et al. (2015) used two DESs, Choline Chloride:Glycerol (1:2) and Choline Chloride:Urea (1:2), for oil recovery. Surprisingly, formulations were defined using 50% volume concentration of DES on formation brine, far too high for real applications. Core flooding experiments were carried out in Berea Sandstone core plugs at three different temperatures using formation brine. The results revealed that the injection of Choline Chloride:Glycerol in tertiary recovery mode resulted in AOR of 14.0% at 318.15 K, 22.3% at 333.15 K and 29.8% at 353.15 K based on the OOIP. The injection of the Choline Chloride:Urea DES produced an AOR of 23.2%, 30.8% and 26.3% at 318.15 K, 333.15 K and 353.15 K, respectively. Heavy oil recovery increased by increasing the temperature. IFT between crude oil and formulation with DES ranged from 31 mN/m to 40 mN/m, and little information is given about the possible mechanism of this recovery. Moreover, according to the authors, the emulsions used were not stable.

Gou et al. (2015) used water-soluble complexes containing a hydrophobically associating co-polymer and a series of imidazolium-based ionic liquids including [$C_n$mim]Br (n = 6, 8, 10,12, 14 and 16). The polymer, denoted as PAAD, was prepared with acrylamide, acrylic acid and N,N-diallyl-2-dodecylbenzenesulfonamide. The incorporation of [$C_n$mim]Br (n = 10, 12, 14 and 16) in PAAD led to a white thick gel, while the addition of [C_6mim]Br around critical micelle concentration resulted in a large decrease in the viscosity of the solution. The authors concluded that PAAD/[C_8mim]Br complex was the most effective chemical. Temperature and PAAD, [C_8mim]Br and NaCl concentration in the formulation were optimized via IFT measurements. They performed core flooding tests in Berea sandstones at 343.15 K using brine at a concentration of 20 g/L of NaCl. They tested the optimized combination of copolymer/IL and compared it with the use of the individual chemicals. They found out that the best results were obtained with a combination of 3 g/L of PAAD and 5 g/L of [C_8mim]Br extracting 21.25% of the OOIP.

Jia et al. (2017) examined the use of a blend of a cationic SAIL: N-dodecyl-N-methylpyrrolidinium bromide (L12) with a traditional anionic surfactant: sodium dodecyl sulfate (SDS) for chemical EOR. Cores from sandstone reservoirs were used in flooding experiments at 338.15 K L12/SDS ratio and process temperature were optimized via IFT studies. At the optimal L12/SDS molar ratio of 1:2.5, the blend effectively reduced the IFT of water/oil to an ultralow value (~4×10^{-3} mN/m) using a low surfactant concentration (500 mg/L). An extraction of 25% of OOIP was achieved by adding the surfactant solution mixed with 2000 mg/L of partially hydrolyzed polyacrylamide (HPAM) in tertiary mode.

Manshad et al. (2017) screened four ionic liquids, namely: [C_{12}mim]Cl, [C_{18}mim]Cl, [C_8Py]Cl and [C_{18}Py]Cl. [C_{18}mim]Cl was found to be the best IL based on IFT reduction and wettability alteration towards water-wet. Core flooding with the selected IL at a low concentration of 170 ppm revealed a 13% increase in oil

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recovery compared to flooding with brine. These tests were performed using carbonate core samples. Wettability measurements proved that the effect of the wettability is not particularly significant, the increase in oil production being mainly due to the IFT reduction.

Nabipour et al. (2017) tested two ionic liquids [C_{12}mim]Cl and [C_{18}mim]Cl alongside other conventional surfactants. Emulsification and compatibility tests were performed to study the tolerance of surfactants to harsh conditions of salinity. The IL-based surfactants were compatible with formation brine but [C_{18}mim]Cl was discarded due to its poor dispersion in seawater with a high concentration of divalent ions. [C_{12}mim]Cl was selected due to its capacity to shift the wettability of reservoir rock towards more water-wet whilst reducing crude oil/seawater IFT. Core flooding experiments were carried out using a surfactant solution of 1000 ppm in seawater. The authors showed the IL to be more effective than other conventional surfactants. They carried out the tests in a native core; however, they do not specify if it was made from sandstone or carbonate material. To verify the contribution of wettability alteration to oil recovery, tests adding a soaking step of 21 days (designed to change the wettability of the rock towards water-wet) were performed. With the soaking step, the tertiary oil recovery efficiency was increased from 8% up to 12.7% of the OOIP. The effectiveness of soaking to enhance the wettability alteration mechanism is highlighted in the paper.

Rodríguez-Palmeiro et al. (2017) found that a formulation consisting of 4000 ppm of [P_{44414}]Cl in a solution of 4 wt% NaCl and 5000 ppm NaOH was able to reduce the IFT between water and crude oil from 19.2 mN/m to 0.1 mN/m. They carried out core-flooding experiments at room temperature using Berea Sandstones, and compared extraction using three different processes. Firstly, as a tertiary oil recovery method, the optimized formulation was injected. Secondly, the brine + SAIL solution was injected before the optimized formulation. Finally, brine + NaOH was injected before the formulation. The authors tested adsorption in terms of resistance factor and residual resistance factor and found that there was no significant retention of the SAIL. An AOR of about 8.1% of the OOIP was reached when the optimized formulation was used after secondary recovery with brine (4 wt% NaCl). It was concluded that direct injection of the optimized formulation gave practically the same result as injection of the formulation after the brine + NaOH solution. The injection of SAIL before the optimized formulation led to the worst result.

Liu et al. (2018) studied the ability of 1-butyl-3-methylimidazolium dioctylsulfosuccinate (BMOT) to reduce the IFT between crude oil and water, obtaining an ultra-low value on the order of 10^{-3} mN/m. This was selected as the most promising surfactant by comparison with the traditional anionic surfactant, sodium dioctylsulfosuccinate (AOT) and the anionic SAIL 1-butyl-3-methylimidazolium dodecyl sulfate (BMDS). The effect of BMOT concentration, salts and temperature on IFT was studied. An artificial core from a sandstone reservoir was used in the core flooding tests. The extractions were carried out at 335.15K. 12.5% of the OOIP was obtained using BMOT (1500 mg/L) which clearly improved on results with AOT or BMDS.

Zabihi et al. (2019) studied two different families of surfactants including conventional and IL-based surfactants. From the family of ILs, they tested several imidazolium and pyridinium chlorides varying the length of alkyl chain. To that aim brine/oil formation IFT was measured using a spinning drop tensiometer. The conventional surfactant sodium dodecylbenzenesulfonate (SDBS) was capable of reducing the IFT value even at high salinity, but surfactant concentrations higher than 1600 ppm led to precipitation problems. [C_{12}mim]Cl and [C_{18}mim]Cl showed the best capability for IFT reduction and precipitation problems were not encountered. Further emulsification and Amott wettability tests revealed a greater capability of SDBS for emulsification while the ILs showed higher capability to alter the wettability of the rock surfaces toward mixed wet. Finally, the core flooding tests performed revealed that [C_{12}mim]Cl and [C_{18}mim][Cl] were able to enhance the tertiary oil recovery up to 13% and 16.5%, respectively, while the SDBS increased recovery up to 26%. The difference in performance was justified in terms of the involved mechanisms. While the dominant mechanism in the recovery with ILs was the wettability alteration, the main mechanism for SDBS was the IFT reduction.

Details regarding oil, brine, rock type, and temperature conditions for all the works considered in this section are shown in Table 1.

2.2. Tests using unconsolidated sand packs

Pereira et al. (2014) proposed the use of a non-surfactant IL [C_2mim][OT_S], as an ionic additive to improve oil recovery. The results showed that using a 2 wt% solution of [C_2mim][OT_S] in brine, 20.56% of the OOIP could be recovered in tertiary flooding, almost double the extraction with brine solution alone. A vertically oriented acrylic column uniformly packed with dry sand was used as the core. This increase in oil recovery is believed to have been caused by the aromatic character of the IL that contributes to the increase of the interactions with aromatic oil fractions. This may be an interesting oil recovery mechanism associated with aromatic ILs.

Tunnish et al. (2016) also proposed the use of an IL without a surfactant character: [C_2mim][Ac]. For core flooding experiments, unconsolidated sand packs made from Ottawa sandstones were used at 290.15 K with formation brines of 0.1 and 1 wt% of NaCl (also containing divalent ions). The best result was obtained when a brine solution (0.1 wt% NaCl) containing 3000 ppm [C_2mim][Ac] was injected. A tertiary extraction of 16.68% OOIP was achieved, even though the IFT between the optimized formulation and crude oil was quite high (7.31 mN/m). They also tested the use of formation brine but results showed a better oil recovery for lower salinity ratios in the absence of divalent ions. The authors also point out that the main mechanisms of improvement in oil recovery were wettability alteration and increase of viscous forces. The IL proved to be more effective than traditional surfactants such as SDS.

Sakthivel et al. (2016) also tested SDS and a variety of alkyl ammonium ILs, at several temperatures and salinities, to enhance the recovery of low waxy crude oil. [$OHPrNH_3$][CF_3COO] was noted as the most promising IL, even though its water/oil IFT was 9.38 mN/m. Core flooding experiments were carried out using a horizontal sandpack column, and surfactant flooding with SDS or IL. A second stage of polymer flooding with an aqueous solution of polyacrylamide (PAM) was also tested. The IL + polymer flood showed significant increase in oil recovery as compared to the rest of the flooding schemes. 17–23% of the OOIP was recovered using IL + polymer flood system under low salinity conditions, which further improved to 28% under high saline conditions. It was observed that the ILs possessing longer alkyl chain lengths increased oil recovery more than those with shorter alkyl chain lengths.

Sakthivel et al. (2017) investigated the use of lactam and imidazolium based ionic liquids (ILs) for EOR. SDS was used for comparative purposes. With a similar procedure to the previous paper, it was found that among all the ILs studied, [CP][$C_6H_{13}COO$] led to the best performance. Better results were found for high salinity conditions. It should be noted that the measured IFT between SDS or IL and crude oil were always higher than 8 mN/m. When flooding was carried out with aqueous solution of IL and polymer, the AOR was quantified in the range of 22–25%, whereas in the case of high saline conditions it was enhanced up to 31%.

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Table 1
Core flooding works on Ionics liquids for EOR application using real reservoir rocks.

Author	Ionic Liquid[a]	Temperature	Brine	Crude Oil	Rock type	Rock properties	Secondary Extraction (% OOIP)	Aditional Oil Recovery (%OOIP)
Hezave et al. (2013)	4000 ppm [C_{12}mim]Cl	–	Formation brine	Iranian Crude Oil API 30°	–	ø : 14–23% μ : 8–16 mD	50	13
Bin Dahbag et al. (2015)	500 ppm Ammoeng 102	333.15 K	20 wt% (83%NaCl, 17% $CaCl_2$)	Saudi medium Crude Oil API 28.37°	Berea Sandstone	ø : 20–22% μ : 450-300 mD	43	5
Mohsenzadeh et al. (2015)	1. 50 wt% Choline Chloride:Glycerol (1:2)	1. 353.15 K	Formation brine	Omani Heavy Oil	Berea Sandstone	ø : 18–19%	1. 41.60	1. 29.8
	2. 50 wt% Choline Chloride:Urea (1:2)	2. 333.15 K		API 16°		μ : 12–32 mD	2. 40.60	2. 30.8
Gou et al. (2015)	3000 ppm PAAD + 5000 ppm [C_8mim]Br	343.15 K	2 wt% NaCl	Simulated Crude Oil Bohai Suizhong Crude Oil + Kerosene (2:1)	Berea Sandstone	ø : 30% μ : 1500 −1600 mD	41.25	20.25
Jia et al. (2017)	500 ppm L12:SDS (1:2.5) + 2000 ppm HPAM	338.15 K	Formation brine	Jidong Crude Oil API 15.5°	Sandstone	ø : 36–42% μ : 500 −1000 mD	37.10	25.00
Manshad et al. (2017)	170 ppm [C_{18}mim]Cl	–	Formation brine	Iranian Carbonate Reservoir Crude Oil API 31.65°	Carbonate	ø : 21–22% μ : 15-30 mD	38.00	13.00
Nabipour et al. (2017)	1000 ppm [C_{12}mim]Cl	–	Seawater	Iranian Crude Oil API 26°	–	ø : 19.4% μ : 1.8 mD	60.10	12.70
Rodríguez-Palmeiro et al. (2017)	4000 ppm [$P_{4\,4\,4\,14}$]Cl + 5000 ppm NaOH	Room temperature	4 wt% NaCl	Model Oil WIOLTAN SHH 70 API 30.5°	Berea Sandstone	ø : 21–23% μ : 300 −1600 mD	31.40	8.10
Liu et al. (2018)	1500 ppm BMOT	335.15 K	Formation brine	Shengli Crude Oil API 27.13°	Sandstone	ø : 33–35% μ : 470 −515 mD	33.20	12.50
Zabihi et al. (2019)	3500 ppm [C_{18}mim]Cl	353.15 K	Formation brine	Iranian Crude Oil API 30°	Carbonate	ø : 11–18% μ : 3–8 mD	38.00	16.50

[a] Full names of ILs can be found in Table S1 of Supplementary Information.

Nandwani et al. (2017) tested three long-chain 1-alkyl-3-methylimidazolium bromides ([C_{12}mim]Br, [C_{14}mim]Br and [C_{16}mim]Br) in terms of aggregation in water and dynamic IFT under high salinity conditions. The most promising was found to be the one with longest chain: [C_{16}mim]Br, providing an IFT value of 3.9 mN/m. The core flooding experiments were performed at room temperature using a vertically placed acrylic sand packed column. 3 wt% NaCl and 0.3 wt% of surfactant concentration were selected for aqueous formulations after optimization via IFT measurements. Greater extraction was obtained with the IL than with the traditional cationic surfactant cetyl trimethyl ammonium bromide (CTAB) at the same composition. It was shown that, unlike other conventional surfactants, [C_{16}mim]Br interfacial activity remains even at high temperature conditions.

Nandwani et al. (2018), in line with previous work, performed flooding experiments using a horizontal sand pack holder. Pure [C_{16}mim]Br and a mixed system containing this IL and the non-ionic surfactant Tergitol 15-S-9, at a molar ratio 4:1, were tested. To that aim, pipette tests were carried out to determine optimal formulations. The mixed surfactant system showed a middle phase microemulsion, related to the drastic reduction of IFT to very low values ($2x10^{-2}$ mN/m). Surfactant flooding, with the IL at the optimal salinity, led to an oil recovery of 3.7% of the OOIP, whereas for the blend the percentage of oil recovered was 9.79% of the OOIP. The optimal salinities found for crude oil and kerosene were 30.1 and 32 wt% respectively. Thus, the proposed formulation is a potential candidate to be used in oil reservoirs with high salinity formation brine.

Pillai et al. (2018) studied three tetrafluoroborate ILs ([C_8mim][BF_4], [C_{10}mim][BF_4], and [C_{12}mim][BF_4]) to reduce IFT and change wettability of reservoirs. Results demonstrated that the ILs remained stable at high temperature and saline conditions, and were able to significantly reduce IFT. They also carried out emulsification tests and static adsorption studies, leading to the conclusion that [C_{12}mim][BF_4] was the most promising SAIL for EOR applications. This IL provided a IFT value of 2.1 mN/m. Thus, sand pack flooding experiments were conducted, with this IL, using crude oil. An organic alkali, triethanolamine (TEA), and the polymer HPAM, were used as chemical additives to improve oil extraction. Initially, the HPAM polymer slug was injected after conventional water flooding which resulted in an AOR of 15.7%. In a second experiment, a slug of [C_{12}mim][BF_4] and polymer was injected achieving 28.17% of AOR after chase water flooding. Finally, the extraction was improved by the injection of a chemical slug containing [C_{12}mim][BF_4], polymer and alkali. AOR of 32.28% was obtained.

Nandwani et al. (2019a) proposed a chemical formulation containing the SAIL [$P_{6\,6\,6\,16}$]Br and a nonionic surfactant (Tergitol 15-S-9). Formulation was optimized via pipette tests, achieving a Winsor type III microemulsion. It was observed that after the water flooding process the individual nonionic surfactant recovered only 7.28% additional oil, whereas the optimized chemical formulation, containing both SAIL and non-ionic surfactant in an equimolar ratio, recovered 16.68% additional oil at the same salinity. They simulated a carbonate reservoir by tightly packing calcite powder. Experiments were carried out at room temperature with 9.25 wt% brine.

Tunish et al. (2019) carried out chemical flooding experiments using alkali and alkali + IL (AIL) mixtures in unconsolidated sand packs. They used Na_2CO_3 as alkali and four different imidazolium-based ILs: [C_2mim][Ac], [C_2mim]Cl, [C_4mim][NTf_2] and [C_{12}mim]Cl, only the latter being a surfactant. Best results were obtained

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with [C_2mim][Tf_2N] (13.47% OOIP) followed by [C_2mim][Ac] (11.47% OOIP) and [C_2mim]Cl (10.40% OOIP). Surprisingly, extraction using [C_{12}mim]Cl led to the worst result even though it was the IL that led to the lowest IFT. The increase of IL concentration (0.7 wt% Na_2CO_3 + 3000 ppm [C_2mim][Tf_2N]) and slug size led to further improvement in tertiary recovery reaching 21.12% of OOIP. The authors found that a viscous effect was not predominant and point to changes in surface wettability and IFT reduction as dominant mechanisms.

It should be mentioned that all these tests were carried out without confining pressure, so the results could be affected by the existence of side flows. Details regarding oil, brine, rock type, and temperature conditions for all the works considered in this section are shown in Table 2.

2.3. Discussion

Despite the huge potential of ILs to improve current EOR methods, the number of flooding experiments carried out up to now is still very limited. Most studies are conducted using unconsolidated sand packs. Porosity and permeability of this kind of systems is much higher than that of real reservoirs. This leads to lower capillary pressures and a consequent easier crude oil extraction. ILs have mostly been proposed as surfactants but also no surface active ILs have been suggested as chemicals in EOR. In the case of SAILs, they drastically reduce the IFT water/oil even in harsh conditions, but ILs can also increase viscosity, change wettability, or in some cases promote solubilization of oil through aromatic interactions. Most of ILs proposed for the application are aprotic, however the use of protic ILs (Sakthivel et al. 2016, 2017) also led to interesting results.

Optimal formulations are mostly defined using IFT as the target property. In very few cases the formulation was obtained by phase equilibria studies. SAILs tested in core-flooding experiments corresponded to a Winsor type I behavior. Blends with traditional surfactants have been proposed to obtain Winsor Type III systems. However, no noticeable increase in the recovery is detected with this behavior.

After secondary recovery (with water or brine), additional oil recoveries of up to 32% of OOIP have been shown in the literature, using ILs or combinations of these salts with other surfactants or polymers. Nonetheless, many of these studies are carried out on unconsolidated sand packs. Thus, the recovery in oil reservoirs could be drastically lower. Regarding experiments with real reservoir rocks, oil recoveries with pure ILs have achieved up to 16.5% of additional recovery, and using combinations with other chemicals values up to 25% have been shown. Surprisingly, up to now only [C_{18}mim]Cl has been proposed for carbonate rocks. Most of the studies propose the use of SAILs in sand pack rocks where a high adsorption would be expected due to the cationic nature of the proposed ILs. The number of adsorption studies found in the literature is very scarce. Oil recovery obtained with DES derived from Choline Chloride is notable. However, the quantity of the chemical used make the proposed formulation unrealistic for real applications. More studies with these kinds of chemicals are required to analyze the possibilities of these chemicals for EOR.

The practically unlimited number of ILs, and in particular SAILs, drastically multiplies the possibilities of surfactant EOR. These salts can be tailor-made to solve the main problems associated with this oil recovery method, such as stability of the surfactant at high temperature and salinity conditions, whilst keeping adsorption at very low values. However, a significant number of papers published to date are incomplete or inconclusive. Both experts on ILs and surfactant EOR must combine their knowledge and resources in order to find a suitable formulation, and carry out adequate tests to prove its efficiency. Once laboratory results are solid and promising, field-scale simulations will be required as a necessary step before carrying out the first pilot tests in the field.

3. EOR using 1-decyl-3-methylimidazolium triflate

3.1. Materials and methods

3.1.1. Materials

In the present work, the room temperature IL 1-decyl-3-methylimidazolium triflate, [C_{10}mim][OTf], was purchased from

Table 2
Core flooding works on Ionics liquids for EOR application using unconsolidated sand packs.

Author	Ionic Liquid[b]	Temperature	Brine	Oil	Sandpack properties	Secondary Extraction (%OOIP)	Additional Oil Recovery (%OOIP)
Pereira et al. (2014)	20000 ppm [C_2mim][OTs]	313.15K	2 wt% NaCl	Brazilian Crude Oil API 27.6°	ø : 36–38% μ : -	68.70	20.56
Tunnish et al. (2016)	3000 ppm [C_2mim] [Ac]	290.15K	0.1 wt% NaCl	Pelican Crude Oil API 14°	ø : 35.2% μ : 3200 mD	54.90	16.68
Sakthivel et al. (2016)	5000 ppm [OHPrNH$_3$][CF_3COO] + 500 ppm of PAM	353.15K	10 wt% NaCl	Low Waxy Crude Oil API 25.6°	ø : 33.6–36.2% μ : 315–542 mD	44.07	27.97
Sakthivel et al. (2017)	5000 ppm [CP][C_6H_{13}COO] + 500 ppm of PAM	353.15K	10 wt% NaCl	Low Waxy Crude Oil API 25.6°	ø : 34–36% μ : 300–550 mD	41.13	31.45
Nandwani et al. (2017)	3000 ppm [C_{16}mim][Br]	Room temperature	3 wt% NaCl	Paraffin liquid light oil _	ø : 40–42% μ : -	63.86	25.95
Nandwani et al. (2018)	6000 ppm [C_{16}mim][Br]+ Tergitol 15-S-9 (1:4)	308.15K	32 wt% NaCl	Kerosene _	ø : 35–39% μ : 190–220 mD	38.75	9.79
Pillai et al. (2018)	2400 ppm [C_{12}mim][BF_4]+ 2000 ppm HPAM + 10000 ppm TEA	–	0 wt% NaCl	Indian Crude Oil API 29.21°	ø : 38–39% μ : 1300–1900 mD	50.58	32.28
Nandwani et al. (2019a)	10000 ppm [P_{66616}]Br + Tergitol 15-S-9 (1:1)	Room temperature	9.25 wt% NaCl	Synthetic Oil Paraffin light oil + benzene + toluene	ø : 35–38%[c] μ : : 670–700 mD[c]	38.24	16.69
Tunish et al. (2019)	3000 ppm [C_2mim][Tf_2N]+ 7000 ppm Na_2CO_3	Room temperature	Formation brine	Pelican Crude Oil API 14°	ø : 37% μ : : 4320 mD	45–47	21.12

[b] Full name of ILs can be found in Table S1 of Supplementary Information.
[c] In this case the sand pack is made from calcite powder to simulate a carbonate reservoir.

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Iolitec (purity >99 wt%). Prior to its characterization, it was purified under high vacuum (<1 Pa) while stirred magnetically and heated at ca. 373–383 K for elimination of water and potential volatile impurities. Brine solutions were prepared by weight dissolving sodium chloride purchased from Panreac (purity >99 wt%) in distilled water. Sodium hydroxide in the shape of anhydrous pellets (purity >99 wt%) and n-octane (purity >99 wt%) were supplied by Sigma-Aldrich. Potassium iodide (purity >99 wt%), used as a tracer for dynamic adsorption tests, was also supplied by Sigma-Aldrich.

Partially hydrolyzed polyacrylamide (HPAM) with a molecular weight of 5–8 million Daltons and a hydrolysis degree of 30% (Flopam 3230S), and polyacrylamide (PAM) without hydrolysis (Flopam FA 920 SH) with the same molecular weight, were kindly provided by SNF Floerger.

Crude oil was kindly supplied by Repsol (refinery of A Coruña, Spain). Its main properties are summarized in Table 3 and ASTM D86 test presented in Table S2 of SI.

Sandstone cores were purchased from Vinci Technologies and used for dynamic adsorption tests. Their mineralogy was analyzed by X-Ray diffraction. Results are shown in Table 4. Low permeability carbonate cores made from limestone and dolomite were used for dynamic adsorption and core flooding tests. These cores were purchased from Kocurek Industries and their mineralogy was also analyzed by X-Ray diffraction. Results are shown in Table 5.

3.1.2. Methods

3.1.2.1. Ionic liquid characterization. [C_{10}mim][OTf] water content was measured using Karl-Fischer titration in a Metrohm 899 coulometer. Density was determined in an Anton Paar DMA 5000M density meter. An Anton Paar LOVIS 2000 ME microviscometer was used to measure IL viscosity. Surface tension in aqueous solutions was measured using the Wilhelmy plate method in a Krüss K11 tensiometer in order to determine the critical micelle concentration (cmc). Experiments were performed at 298.15 K and repeated at least twice to ensure repeatability.

3.1.2.2. Pipette tests. Salinity tests were performed following the encased-glass-pipette method *(Puerto et al., 2012)*. In this test, 1 cm^3 of brine with SAIL and 1 cm^3 of oil were added into individual pipettes sealed at the tip. Thereafter, pipettes were top sealed, mixed in a rotatory mixer at room temperature for 24 h and then put into a test tube filled with silicon oil. Finally, the glass encased pipettes were left to equilibrate in a dry block heater OVAN model BD200-RE at the target temperature until phase volume remained constant. N-octane was chosen as the oil because it is known that optimal salinities of various surfactants using this oil are not greatly different from crude oil *(Puerto et al., 2012)*. Surfactant concentration in the pipette was 2 wt% overall. A salinity range from zero to 15 wt% NaCl was studied at 298.15, 323.15 and 348.15 K.

3.1.2.3. Dynamic interfacial tension. Dynamic IFT between crude oil and surfactant solution were measured using a Krüss SITE100 spinning drop tensiometer. All measurements were carried out at 298.15 K, using circulating oil from a Julabo EH-5 thermostatic bath to keep the temperature constant, and atmospheric pressure. The aqueous solution (dense phase) was used to fill the capillary tube ensuring that there were no air bubbles. A drop of 4 μL of crude oil (light phase) was injected in the middle of the capillary tube, using a Hamilton micro-liter syringe, rotating at slow speed (100 rpm). Rotating velocities between 2000 and 7000 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:

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

where $\Delta\rho$ is the density difference between dense and light phase, ω is the angular velocity and D is the diameter of the oil drop. All the experiments were performed at least twice to ensure repeatability.

3.1.2.4. Adsorption and core flooding. Adsorption and flooding experiments were conducted in a core-flooding system equipped with a Hassler Core Holder H00-021-0, and two floXlab BTSP 500-5 piston pumps equipped with an accurate pressure sensor for brine or surfactant solution and oil. The Core Holder and pumps were purchased from Vinci Technologies (Fig. S1 in Supplementary Information). Experiments were carried out at room temperature and a constant injection rate of 2 mL/min. To prevent hydraulic side flow, a confining pressure was maintained at a value at least 35 bar higher than the flooding pressure using an Enerpac P142 manual hydraulic pump.

Both sandstone and carbonate cores, as described in materials section, were used in experiments. The reservoir plugs were 3.51 cm in diameter and 7.62 cm length. To characterize the rocks, the core was initially vacuumed for 24 h and then saturated with brine (2 wt% NaCl). After 24 h, pore volume (PV) was determined using the dry and wet weights of the core. Absolute permeability (k_w) of the brine was calculated by flooding the core with brine solution at different injection rates. The pressure difference between inlet and outlet (ΔP) was recorded for each injection velocity. Injection flow rate versus pressure drop yields a straight line. The slope of the straight line was used to calculate the absolute permeability of brine using Darcy's law.

Dynamic adsorption tests were carried out to evaluate the retention of the IL in the rocks. Around 60 mL of tracer or IL solution in brine were continuously injected at a rate of 2 mL/min. Effluent fractions were collected for analysis every 4 mL. IL and tracer concentrations were determined by UV absorption using an HP Presario SR1000 UV/Vis spectrophotometer.

In oil recovery tests, after brine saturation the core was flooded

Table 3
Crude oil properties (provided by supplier).

Property	Value
Density at 288.15 K, kg/m^3	811.1
Reid vapor pressure, kPa	44.9
Viscosity at 293.15 K, cSt	4.861
Carbon residue, wt%	1.2522
Asphaltenes, wt%	0.4624
API°	42.9

Table 4
Berea Sandstone mineralogy.

Compound name	Content, %
Quartz	79
Muscovite 2M1	4
Pentahydroborite	13
Albite	4

Table 5
Carbonate core mineralogy.

Compound name	Content, %
Calcite	89
Sodium Calcium Pentafluoroaluminate Fluoride-Beta	2
Diopside	9

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with crude oil by increasing flow rate from 2 mL/min to 10 mL/min until there was no further water coming from the effluent. OOIP was then calculated as the volume of oil retained in the core. Initial oil saturation (S_{oi}) and initial water saturation (S_{wi}) were calculated using Eqs. (2) and (3) respectively:

$$S_{oi}(\%) = OOIP \cdot 100/PV \quad (2)$$

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

The core was allowed to rest for 4–5 days. After this aging step, the plug was ready to initiate the core flood. First, a water flood was done injecting 3–4 PV of brine (2 wt% NaCl) 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 flood (ORWF) was determined and residual oil saturation (S_{or}) was calculated as follows:

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

The core was then subjected to tertiary flooding. For the case of AS flooding, the core was flooded with 3–4 PV of the optimized formulation at a constant flow rate of 2 mL/min. For the ASP flooding, one pore volume (1 PV) of the optimized formulation was flooded through the core at a constant rate of 2 mL/min followed by the injection of 3 PV of solution of polymer in brine increasing its flow rate from 1 mL/min to 2 mL/min to maintain a differential pressure of at least 20 bar. In addition, a third core flooding test was carried out implementing polymer flooding after secondary recovery. In this test 4 PV of polymer solution in brine were injected at 2 mL/min to determine the ability of the polymer to extract oil. Oil fractions collected correspond to the oil recovered after tertiary flooding (ORTF). Thus, additional oil recovery (AOR) was calculated as a function of the OOIP:

$$AOR(\%OOIP) = ORTF \cdot 100 / (OOIP - ORWF) \quad (5)$$

3.2. Results and discussion

3.2.1. Ionic liquid characterization

The main characteristics of [C_{10}mim][OTf] are listed in Table 6. Results of cmc measurements can be seen in Fig. 1. A value of 8.03 mmol/kg was obtained, which corresponds to 3890.84 ppm, with a surface tension at this concentration of 28.86 mN/m.

3.2.2. Pipette tests

Microemulsion systems can be classify as Winsor I, Winsor II or Winsor III (Winsor, 1948). In a Winsor I system there is an equilibrium between an oil-in-water microemulsion and an upper excess oil phase, whereas in the Winsor II system the equilibrium is between a water-in-oil microemulsion and a lower excess water phase. The Winsor III system has a middle microemulsion phase in equilibrium with an upper excess oil phase and a lower excess water phase.

Phase behavior of [C_{10}mim][OTf] was studied with *n*-octane by carrying out pipette tests (Fig. S2 of Supplementary Information).

Table 6
[C_{10}mim][OTf] water content and physical properties at 298.15 K and atmospheric pressure.

Property	Value
Water content, ppm	187
Density, kg/m^3	1149.68
Viscosity, mPa·s	335.67

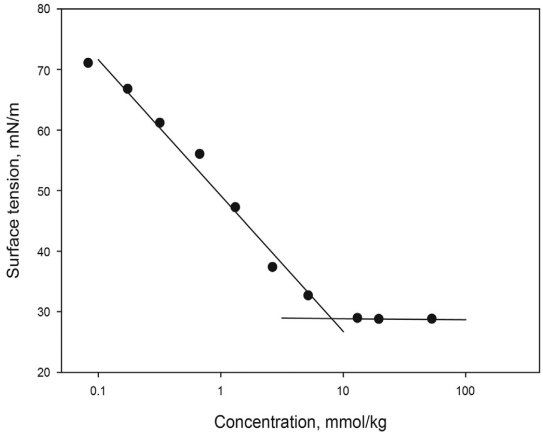


Fig. 1. Surface tension of aqueous solutions of [C_{10}mim][OTf] at 298.15 K.

Winsor type I systems were found for salinities from 0 to 15 wt% NaCl at 298.15, 323.15 and 348.15 K. It is known that Winsor type III microemulsions lead to ultra-low interfacial tensions (10^{-3} mN/m) but they usually experience high adsorption and bad solubility in brine (Spildo et al., 2014). Moreover, surfactant loss through partitioning into the crude oil can be responsible for 30% of surfactant losses. As an advantage, in the case of very hydrophilic surfactants (Winsor type I systems), the surfactant loss is near zero (Salari et al., 2011).

The knowledge of phase behavior is the first and fundamental step to select an adequate surfactant for EOR but required, decisive tests are core flooding experiments using reservoir cores (Sheng, 2011). As the selected IL showed Winsor Type I behavior in all the range of salt concentrations, an optimization of the composition of the formulation was carried out by means of dynamic IFT measurements prior to the core flooding tests.

3.2.3. Dynamic interfacial tension

Four different concentrations of [C_{10}mim][OTf] were prepared in distilled water: 2000 ppm, 3000 ppm, 4000 ppm and 5000 ppm, and IFT with crude oil measured at 298.15 K and atmospheric pressure. As shown in Fig. 2, the dynamic IFT between crude oil and surfactant solution decreases when increasing SAIL concentration. Equilibrium values of 6.70 mN/m, 2.42 mN/m, 0.36 mN/m and 0.41 mN/m were obtained for 2000 ppm, 3000 ppm, 4000 ppm and 5000 ppm respectively. Concentrations of 4000 and 5000 ppm led to similar results, therefore a value of 4000 ppm was selected. This result is in accordance with the value obtained for cmc in section 3.2.1.

The salinity of the aqueous phase has a strong influence on the interfacial tension of crude oil/aqueous systems. For this reason, various experiments were carried out varying sodium chloride concentration from 0 wt% to 4 wt% in the aqueous phase while maintaining a constant concentration of [C_{10}mim][OTf] at 4000 ppm. As seen in Fig. 3, an increase in NaCl concentration from 0.1 wt% to 1 wt% led to an increase in the IFT, providing equilibrium values of 0.57 mN/m and 0.93 mN/m respectively. NaCl concentration in the range of 2 wt%-4 wt% provided similar IFT equilibrium values (1.1 mN/m–1.3 mN/m). As formation water contains salts, a value of 2 wt% NaCl was chosen to avoid high values of the IFT. Furthermore, according to Fig. 3, even if the salinity increased, interfacial tension would not be greatly affected.

Alkalis improve the interfacial activity, generating surfactants *in*

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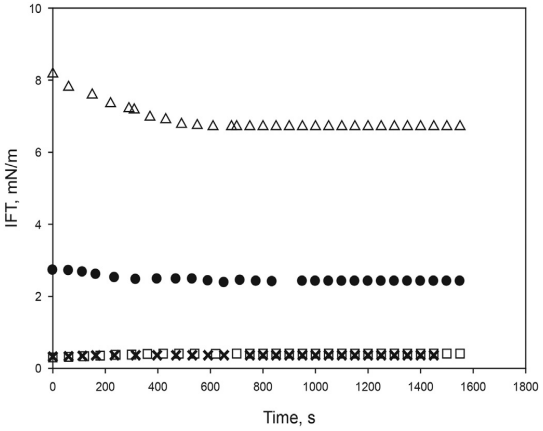


Fig. 2. Effect of [C_{10}mim][OTf] concentration on dynamic interfacial tension between water and crude oil at 298.15 K and atmospheric pressure.
Δ 2000 ppm, ● 3000 ppm, × 4000 ppm, □ 5000 ppm.

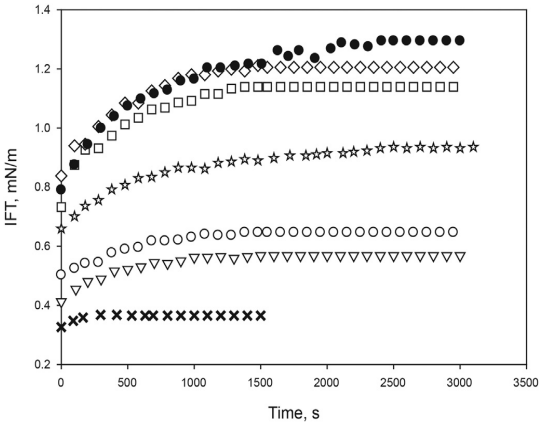


Fig. 3. Effect of NaCl concentration on the dynamic interfacial tension between aqueous solution of [C_{10}mim][OTf] (4000 ppm) and crude oil at 298.15 K and atmospheric pressure. × 0 wt%, ▽ 0.1 wt%, ○ 0.2 wt%, ☆ 1 wt%, □ 2 wt%, ◇ 3 wt%, ● 4 wt %.

situ reacting with the naphthenic acids of crude oil, so they can improve the economy of the process since they reduce the amount of surfactant needed to obtain low IFT (*Tackie-Otoo* et al., *2020)*. For this reason, three different concentrations of an alkali (NaOH) were prepared using a solution of [C_{10}mim][OTf] (4000 ppm) in brine (2 wt% NaCl) and varying concentration of NaOH from 0% to 1.5%. Fig. 4 shows a significant decrease of dynamic IFT from 1.20 mN/m in the absence of NaOH to 0.56 mN/m for 1 wt% NaOH. Higher concentrations of the alkali did not further reduce the IFT, thus a value of 1 wt% NaOH was selected. The optimized formulation is clear and stable with time.

3.2.4. Adsorption

Adsorption of surfactants in porous media is a fundamental issue in EOR. Loss of surfactants owing to their interactions with reservoir rock and fluid affects the effectiveness of the chemical solution injected, and may make the process economically unfeasible (Bera et al., 2013). It is known that surfactant adsorption

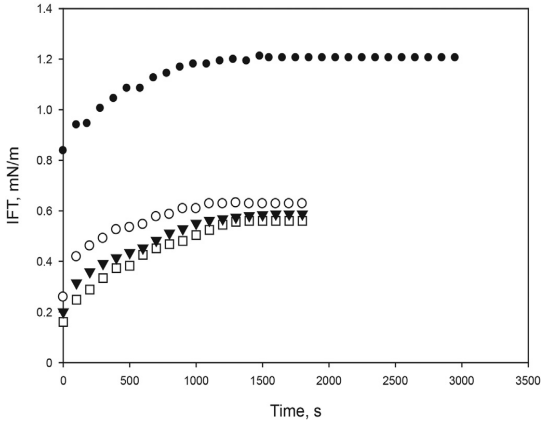


Fig. 4. Effect NaOH concentration on the dynamic interfacial tension between brine solution (2 wt% NaCl) of [C_{10}mim][OTf] (4000 ppm) and crude oil at 298.15 K and atmospheric pressure. ● 0 wt%, ○ 0.5 wt%, □ 1 wt%, ▼ 1.5 wt%.

depends on surfactant, solid surface and aqueous phase, the electrostatic attraction between charged surface of the rock and charged head group of surfactant likely being the most important factor. (Curbelo et al., 2007; Salari et al., 2011; Ma et al., 2013; Hanamertani et al., 2018).

The adsorption of the optimized formulation was studied in Berea sandstone. After 4 PV of injected optimized formulation (4000 ppm IL, 1 wt% NaOH, 2 wt% NaCl), no ionic liquid concentration was detected in the effluent, so the adsorption was very high. This is not surprising. As mentioned above, the adsorption of ionic surfactants is strongly influenced by the composition of the rock that makes the core surface negatively or positively charged. Sandstone cores used in this study contain 4% muscovite and 4% albite (Table 4) which are silicate-like minerals, and the proposed SAIL is a cationic surfactant. So adsorption takes place mainly due to the presence of negatively charged components of sand particles, such as silica, which are negative at neutral pH or in water (Bera et al., 2013).

The adsorption of the optimized formulation in carbonate cores was also studied. Fig. 5 shows the ratio between surfactant concentration of the effluent and injected formulation as a function of injected PV. The SAIL and the tracer potassium iodide were compared. As shown, both tracer and [C_{10}mim][OTf] are detected for the first time in the effluent at approximately 0.5 PV, but the tracer takes longer to reach initial concentration. Therefore, adsorption of the SAIL in carbonate rock can be assumed to be low enough to consider the formulation suitable for the application. For carbonate material, the presence of calcite and other minerals containing Mg^{2+} makes the core surface positively charged (Tagavifar et al., 2017). Thus, the strong repulsion between positively charged rock surface and positively charged surfactant, prevents adsorption from occurring.

This low adsorption is in agreement with previously findings showing that imidazolium-based ILs lead to less adsorption in carbonate rocks than pyrrolidinium or pyridinium or even other conventional cationic surfactants. (Nandwani et al., 2019b).

3.2.5. Core flooding

Three core flooding runs were performed in fresh carbonate cores as reported in Table 7. Test 1 was started with secondary brine flooding until reaching the residual oil saturation (S_{or}) followed by tertiary flooding of 4 PV of optimized formulation containing

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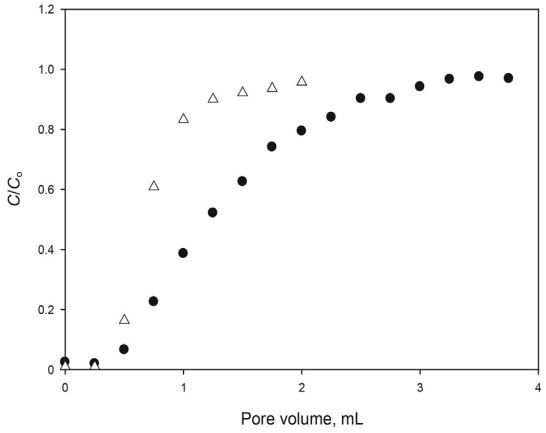


Fig. 5. Dynamic adsorption of the optimized formulation at 25°C in Carbonate rock. ● Tracer Δ Optimized formulation.

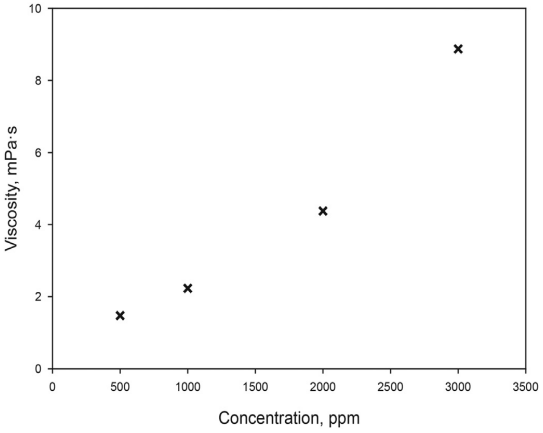


Fig 6. Effect of PAM concentration on viscosity.

4000 ppm of [C_{10}mim][OTf] and 1 wt% NaOH in brine solution. Direct injection of the optimized formulation was preferred to a two-step injection with initially the alkali and then the surfactant because it has been shown that both procedures lead to the same oil extraction (Rodríguez-Palmeiro et al., 2017).

With the aim of saving surfactant, a Test 2 combining surfactant and polymer flooding was carried out. A first attempt using HPAM was performed. However, an uninterrupted increase in pressure was experienced and no additional oil was obtained in the effluent. This is due to the high adsorption of the polymer caused by the electrostatic attraction of the negatively charged HPAM and positively charged carbonate surface. So, the use of this polymer was discarded and the non-ionic polymer (PAM) was selected. Fig. 6 shows viscosity of aqueous solutions of PAM. The mechanism of enhanced recovery involved in polymer flooding is based on decreasing the mobility difference between displacing and displaced fluids. Thus the displacing phase should have lower mobility than the displaced phase. As mobility is inversely proportional to viscosity (Raffa et al., 2016), a concentration of 1000 ppm of PAM was chosen in order to obtain a viscosity of 2.23 mPa s, twice the viscosity of the crude oil. In Test 2, brine was flooded in secondary mode until reaching residual oil saturation, and for the EOR step a slug of 1 PV of optimized formulation was injected into the core, followed by continuous injection of 3 PV of aqueous solution of PAM at the same salinity. To support the idea that combined method is better in terms of oil recovery, a new flooding test (Test 3) was carried out. In this essay, after conventional water flooding, 4 PV of PAM at the same concentration (1000 ppm) in brine were continuously injected.

No stable emulsion was found in the effluent in any of the flooding experiments. The results obtained (Table 7) show that a significant EOR can be achieved using the SAIL [C_{10}mim][OTf]. The results indicate an additional oil recovery of 10.48% and 7.98% of the OOIP for AS and ASP flooding, respectively. In the case of polymer flooding, a very low additional oil recovery was achieved (1.1% of the OOIP). This result indicates that the increase in the viscosity of the injected formulation has little effect on crude oil extraction, the most effective mechanism being the reduction of IFT with the surfactant. This justifies the better results obtained in terms of oil recovery with AS in comparison with ASP methods. However, in terms of potential economic savings, the costs associated to the latter would be significantly lower, making the method more promising.

4. Conclusions

The recent awareness of the possibilities of ILs has led to developed or under development technologies being reviewed

Table 7
Summary of core flooding experiments.

	Test 1	Test 2	Test 3
Porosity of the core, %	18.76	18.60	16.59
Permeability, mD	62.18	51.75	12.83
Pore volume, mL	15.96	15.82	14.25
OOIP, mL	10.5	9.4	9.1
Initial oil saturation, %	65.79	59.42	63.88
Initial water saturation, %	34.21	40.58	36.12
Oil recovered after water flood, %OOIP	62.86	73.40	68.13
Residual oil saturation, %	24.44	15.80	20.36
Surfactant slug injected	4 PV of 4000 ppm [C_{10}mim][OTf] and 1 wt% NaOH in 2 wt% NaCl brine	1 PV of 4000 ppm [C_{10}mim][OTf] and 1 wt% NaOH in 2 wt% NaCl brine	–
Additional Oil Recovered during surfactant flooding, %OOIP	10.48	2.13	–
Polymer slug injected	–	3 PV of 1000 ppm PAM in 2 wt% NaCl brine	4 PV of 1000 ppm PAM in 2 wt% NaCl brine
Additional Oil Recovered during polymer flooding, %OOIP	–	5.85	1.10

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considering the contributions that these salts can provide. This is the case of surfactant EOR. The main advantages highlighted regarding the use of SAILs in EOR are their tunability and stability in harsh environments (high salinity and/or temperature). However, the number of flooding experiments carried out up to now is still very limited and the conclusions obtained must be considered with caution. Despite this, from the literature review and work presented here some tentative conclusions may be established.

- The early results are promising and research on this topic should be encouraged.
- There is a need to uniformize, as far as possible, the experimental methodology used in core flooding experiments to facilitate comparison among ILs.
- There is a lack of adsorption studies that should always be considered prior to flooding experiments.
- Up to now, most ILs have been proposed for sandstone reservoirs. The number of studies with carbonate cores is very scarce.

- The SAIL [C_{10}mim][OTf] is able to drastically reduce the water/oil IFT. The value of this property increases with NaCl and reduces with NaOH concentration.
- A formulation consisting of 4000 ppm of [C_{10}mim][OTf] and 1 wt% NaOH in brine solution (2 wt% NaCl) was proposed for EOR. A high adsorption was detected in sandstone rocks which discounts its use in these kinds of rocks. In the case of carbonate cores, after secondary recovery with brine, an additional 10.5% of OOIP recovery was achieved at room conditions.
- 8% of the OOIP was extracted using just one PV of surfactant followed by an aqueous solution of PAM. Even though a lower recovery was achieved, the low cost of polymer in comparison with the IL could make the process competitive.
- The main mechanism associated with the improvement in the oil recovery for the proposed formulation is IFT reduction. Increasing of viscous forces has a lesser effect.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.petsci.2021.10.025.

References

Ahmadi, M.A., Shadizadeh, S.R., 2015. Experimental investigation of a natural surfactant adsorption on shale-sandstone reservoir rocks: static and dynamic conditions. Fuel 159, 15–26. https://doi.org/10.1016/j.fuel.2015.06.035.

Benzagouta, M.S., AlNashef, M.S., Karnanda, W., Al-Khidir, K., 2013. Ionic liquids as novel surfactants for potential use in enhanced oil recovery. Kor. J. Chem. Eng. 30, 2108–2117. https://doi.org/10.1007/s11814-013-0137-1.

Bera, A., Belhaj, H., 2016. Ionic liquids as alternatives of surfactants in enhanced oil recovery—a state-of-the-art review. J. Mol. Liq. 224, 177–188. https://doi.org/10.1016/j.molliq.2016.09.105.

Bera, A., Kumar, T., Ojha, K., Mandal, A., 2013. Adsorption of surfactants on sand surface in enhanced oil recovery: Isotherms, kinetics and thermodynamic studies. Appl. Surf. Sci. 284, 87–89. https://doi.org/10.1016/j.apsusc.2013.07.029.

Bin Dahbag, M., AlQuraishi, A., Benzagouta, M., 2015. Efficiency of ionic liquids for chemical enhanced oil recovery. J Petrol Explor Prod Technol 5, 353–361. https://doi.org/10.1007/s13202-014-0147-5.

Bin Dahbag, M.S., Hassanzadeh, H., AlQuraishi, A.A., Benzagouta, M., 2019. Suitability of ionic solutions as a chemical substance for chemical enhanced oil recovery–A simulation study. Fuel 242, 368–373. https://doi.org/10.1016/j.fuel.2018.12.125.

Curbelo, F.D.S., Santanna, V.C., Barros Neto, E.L., Dutra Jr., T.V., Castro Dantas, T.N., Dantas Neto, A.A., Garnica, A.I.C., 2007. Adsorption of nonionic surfactants in sandstones. Colloid. Surface. 293, 1–4. https://doi.org/10.1016/j.colsurfa.2006.06.038.

Gou, S., Yin, T., Yan, L., Guo, Q., 2015. Water-soluble complexes of hydrophobically modified polymer and surface active imidazolium-based ionic liquids for enhancing oil recovery. Colloid. Surface. 471, 45–53. https://doi.org/10.1016/j.colsurfa.2015.02.022.

Hanamertani, A.S., Pilus, R.M., Kamal Idris, A., Irawan, S., Tan, I.M., 2018. Ionic liquids as a potential additive for reducing surfactant adsorption onto crushed Berea sandstone. J. Petrol. Sci. Eng. 162, 480–490. https://doi.org/10.1016/j.petrol.2017.09.077.

Hezave, A.Z., Dorostkar, S., Ayatollahi, S., Nabipour, M., Hemmateenejad, B., 2013. Investigating the effect of ionic liquid (1-dodecyl-3-methylimidazolium chloride ([C_{12mim}] [Cl])) on the water/oil interfacial tension as a novel surfactant. Colloid. Surface. 421, 63–71. https://doi.org/10.1016/j.colsurfa.2012.12.008.

Jia, H., Leng, X., Hu, M., Song, Y., Wu, H., Lian, P., et al., 2017. Systematic investigation of the effects of mixed cationic/anionic surfactants on the interfacial tension of a water/model oil system and their application to enhance crude oil recovery. Colloid. Surface. 529, 621–627. https://doi.org/10.1016/j.colsurfa.2017.06.055.

Liu, J., Huang, P., Feng, Q., Lian, P., Liang, Y., Huang, W., et al., 2018. Systematic investigation of the effects of an anionic surface active ionic liquid on the interfacial tension of a water/crude oil system and its application to enhance crude oil recovery. J. Dispersion Sci. Technol. 40, 1657–1663. https://doi.org/10.1080/01932691.2018.1527230.

Ma, K., Cui, L., Dong, Y., Wang, T., Da, C., Hirasaki, G.J., Biswal, S.L., 2013. Adsorption of cationic and anionic surfactants on natural and synthetic carbonate materials. J. Colloid Interface Sci. 408, 164–172. https://doi.org/10.1016/j.jcis.2013.07.006.

Manshad, A.K., Rezaei, M., Moradi, S., Nowrouzi, I., Mohammadi, A.H., 2017. Wettability alteration and interfacial tension (IFT) reduction in enhanced oil recovery (EOR) process by ionic liquid flooding. J. Mol. Liq. 248, 153–162. https://doi.org/10.1016/j.molliq.2017.10.009.

Mohsenzadeh, A., Al-Wahaibi, Y., Jibril, A., Al-Hajri, R., Shuwa, S., 2015. The novel use of Deep Eutectic Solvents for enhancing heavy oil recovery. J. Petrol. Sci. Eng. 130, 6–15. https://doi.org/10.1016/j.petrol.2015.03.018.

Nabipour, M., Ayatollahi, S., Keshavarz, P., 2017. Application of different novel and newly designed commercial ionic liquids and surfactants for more oil recovery from an Iranian oil field. J. Mol. Liq. 230, 579–588. https://doi.org/10.1016/j.molliq.2017.01.062.

Nandwani, S.K., Malek, N.I., Chakraborty, M., Gupta, S., 2017. Study on interfacial properties of Imidazolium ionic liquids as surfactant and their application in enhanced oil recovery. Colloid. Surface. 516, 383–393. https://doi.org/10.1016/j.colsurfa.2016.12.037.

Nandwani, S.K., Chakraborty, M., Bart, H.J., Gupta, S., 2018. Synergism, phase behaviour and characterization of ionic liquid-nonionic surfactant mixture in high salinity environment of oil reservoirs. Fuel 229, 167–179. https://doi.org/10.1016/j.fuel.2018.05.021.

Nandwani, S.K., Malek, N.I., Chakraborty, M., Gupta, S., 2019a. Potential of a novel surfactant slug in recovering additional oil from highly saline calcite cores during the EOR process: synergistic blend of surface active ionic liquid and nonionic surfactant. Energ fuel 33, 541–550. https://doi.org/10.1021/acs.energyfuels.8b03419.

Nandwani, S.K., Chakraborty, M., Gupta, S., 2019b. Adsorption of surface active ionic liquids on different rock types under high salinity conditions. Sci Rep –UK 9, 14760. https://doi.org/10.1038/s41598-019-51318-2.

Pal, S., Mushtaq, M., Banat, F., Sumaiti, A.M.A., 2018. Review of surfactant-assisted chemical enhanced oil recovery for carbonate reservoirs: challenges and future perspectives. Petrol. Sci. 15, 77–102. https://doi.org/10.1007/s12182-017-0198-6.

Pereira, J.F.B., Costa, R., Foios, N., Coutinho, J.A.P., 2014. Ionic liquid enhanced oil recovery in sand-pack columns. Fuel 134, 196–200. https://doi.org/10.1016/j.fuel.2014.05.055.

Pillai, P., Kumar, A., Mandal, A., 2018. Mechanistic studies of al by imidazolium-based ionic liquids as novel surfactants. J. Ind. Eng. Chem. 63, 262–274. https://doi.org/10.1016/j.jiec.2018.02.024.

Puerto, M., Hirasaki, G.J., Miller, C.A., Barnes, J.R., 2012. Surfactant systems for EOR in high- temperature, high-salinity environments. SPE J. 17, 11–19. https://doi.org/10.2118/129675-PA.

Raffa, P., Broekhuis, A.A., Picchioni, F., 2016. Polymeric surfactants for enhanced oil recovery: a review. J. Petrol. Sci. Eng. 145, 723–733. https://doi.org/10.1016/j.petrol.2016.07.007.

Rodríguez-Palmeiro, I., Rodríguez-Escontrela, I., Rodríguez, O., Soto, A., Reichmann, S., Amro, M.M., 2017. Tributyl(tetradecyl)phosphonium chloride ionic liquid for surfactant-enhanced oil recovery. Energ fuel 31, 6758–6765. https://doi.org/10.1021/acs.energyfuels.7b00544.

Sakthivel, S., Gardas, R.L., Sangwai, J.S., 2016. Effect of alkyl ammonium ionic liquids on the interfacial tension of the crude oil–water system and their use for the enhanced oil recovery using ionic liquid-polymer flooding. Energ fuel 30, 2514–2523. https://doi.org/10.1021/acs.energyfuels.5b03014.

Sakthivel, S., Velusamy, S., Nair, V.C., Sharma, T., Sangwai, J.S., 2017. Interfacial tension of crude oil-water system with imidazolium and lactam-based ionic

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liquids and their evaluation for enhanced oil recovery under high saline environment. Fuel 191, 239–250. https://doi.org/10.1016/j.fuel.2016.11.064.
Salari, Z., Ahmadi, M.A., Kharrat, R., Shahri, A.A., 2011. Experimental studies of cationic surfactant adsorption onto carbonate rocks. Aust. J. Appl. Sci. 5, 808–813. ISSN 1991-8178.
Saxena, N., Goswami, A., Dhodapkar, P.K., Nihalani, M.C., Mandal, A., 2019. Bio-based surfactant for enhanced oil recovery: interfacial properties, emulsification and rock-fluid interactions. J. Petrol. Sci. Eng. 176, 299–311. https://doi.org/10.1016/j.petrol.2019.01.052.
Shah, D.O., Schechter, R.S., 1977. Improved Oil Recovery by Surfactant and Polymer Flooding. Academic Press, New York.
Sheng, J.J., 2011. Modern Chemical Enhanced Oil Recovery. Theory and Practice. Elsevier, Amsterdam.
Spildo, K., Sun, L., Djurhuus, K., Skauge, A., 2014. A strategy for low cost, effective surfactant injection. J. Petrol. Sci. Eng. 117, 8–14. https://doi.org/10.1016/j.petrol.2014.03.006.
Tackie-Otoo, B.N., Mohammed, M.A.A., Yekeen, N., Negash, B.M., 2020. Alternative chemical agents for alkalis, surfactants and polymers for enhanced oil recovery: research trend and prospects. J. Petrol. Sci. Eng. 187, 106828. https://doi.org/10.1016/j.petrol.2019.106828.
Tagavifar, M., Jang, S.H., Sharma, H., Wang, D., Chang, L.Y., Mohanty, K., Pope, G.A., 2017. Effect of pH on adsorption of anionic surfactants on limestone: experimental study and surface complexation modeling. Colloid. Surface. 538, 549–558. https://doi.org/10.1016/j.colsurfa.2017.11.050.
Tunish, A., Shirif, E., Henni, A., 2019. Alkaline-ionic liquid slug injection for improved heavy oil recovery. Can. J. Chem. Eng. 97, 1429–1439. https://doi.org/10.1002/cjce.23431.
Tunnish, A., Shirif, E., Henni, A., 2016. Enhanced heavy oil recovery using 1-ethyl-3-methyl-imidazolium acetate. Can. J. Chem. Eng. 95, 871–879. https://doi.org/10.1002/cjce.22733.
Winsor, P.A., 1948. Hydrotropy, solubilisation and related emulsification processes. Part I. Trans. Faraday Soc. 44, 376–398. https://doi.org/10.1039/TF9484400376.
Zabihi, S., Faraji, D., Rahnama, Y., Hezave, A.Z., Ayatollahi, S., 2019. Relative permeability measurement in carbonate rocks, the effects of conventional surfactants vs. Ionic liquid-based surfactants. J. Dispersion Sci. Technol. 41, 1797–1811. https://doi.org/10.1080/01932691.2019.1637262.

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Review

Oil recovery tests with ionic liquids: a review and evaluation of 1-decyl-3-methylimidazolium triflate

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SUPPLEMENTARY INFORMATION

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Table S1. Full names of Ionic Liquids

Abbreviation	Name
$[C_{10}mim][BF_4]$	1-decyl-3-methylimidazolium tetrafluoroborate
$[C_{10}mim]Br$	1-decyl-3-methylimidazolium bromide
$[C_{12}mim][BF_4]$	1-dodecyl-3-methylimidazolium tetrafluoroborate
$[C_{12}mim]Br$	1-dodecyl-3-methylimidazolium bromide
$[C_{12}mim]Cl$	1-dodecyl-3-methylimidazolium chloride
$[C_{14}mim]Br$	1-methyl-3-tetradecylimidazolium bromide
$[C_{16}mim]Br$	1-hexadecyl-3-methylimidazolium bromide
$[C_{18}mim]Cl$	1-methyl-3-octadecylimidazolium chloride
$[C_{18}Py]Cl$	1-octadecylpyridinium chloride
$[C_2mim][Ac]$	1-ethyl-3-methylimidazolium acetate
$[C_2mim][OT_s]$	1-ethyl-3-methylimidazolium tosylate
$[C_2mim]Cl$	1-ethyl-3-methyl imidazolium chloride
$[C_4mim][NTf_2]$	1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide
$[C_6mim]Br$	1-hexyl-3-methylimidazolium bromide
$[C_8mim][BF_4]$	1-methyl-3-octyl-imidazolium tetrafluoroborate
$[C_8mim]Br$	1-methyl-3-octyl-imidazolium bromide
$[C_8Py]Cl$	1-octylpyridinium chloride
[CP][C6H13COO]	Caprolactam hexanoate
$[OHPrNH_3][CF_3COO]$	3-hydroxypropylammonium trifluoroacetate
$[P_{44414}]Cl$	tributyl(tetradecyl)phosphonium chloride
$[P_{6\,6\,6\,16}]Br$	tributylhexadecylphosphonium bromide
BMDS	1-butyl-3-methylimidazolium dodecyl sulfate
BMOT	1-butyl-3-methylimidazolium dioctylsulfosuccinate
L12	N-dodecyl-N-methylpyrrolidinium bromide

Table S2. ASTM D86 test for crude oil

Initial	172.4 °C
5%	195.2 °C
10%	207.5 °C
20%	225.4 °C
30%	243.6 °C
40%	260.2 °C
50%	276.0 °C
60%	292.8 °C
70%	310.9 °C
80%	330.2 °C
90%	356.7 °C
95%	378.5 °C
Final	395.0 °C

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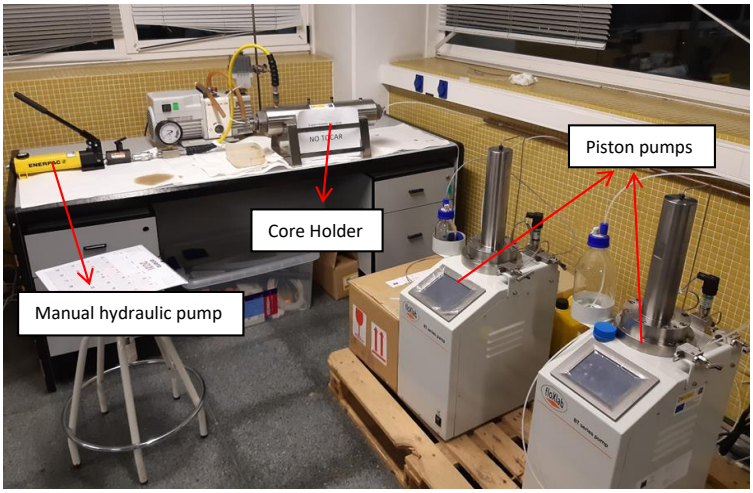


Fig S.1 Core-flooding experimental setup

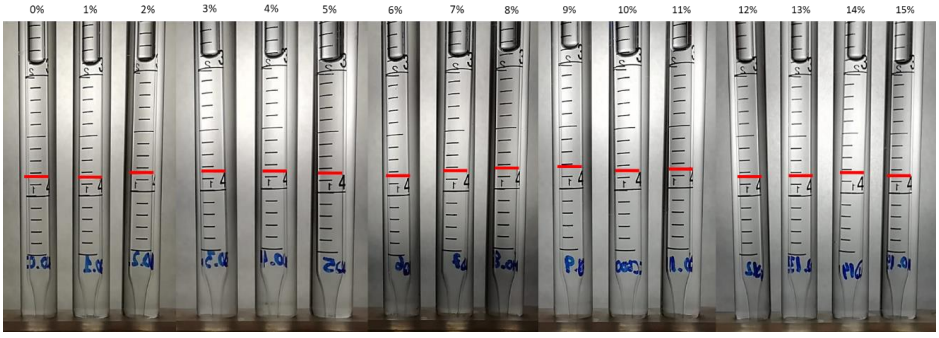


Fig S.2 Pipette tests with [C_{10}mim][OTf]

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

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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][$MeSO_4$]) was designed for the application. Two optimal blends, at 40/60 and 73.7/26.3 SDBS/[C1EG][$MeSO_4$] 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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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 [$P_{6\,6\,6\,16}$]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 cocosalkylpentaethoxymethylammonium 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.

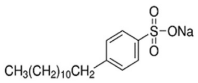
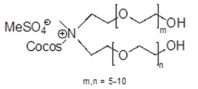
2.2.1. Phase behavior

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 ~0.5 cm^3 of the blend with the required SDBS/[C1EG][$MeSO_4$] mass ratio. Then, ~0.5 cm^3 of a brine solution with a concentration of salts twice that shown in Table 1 was added to obtain ~1 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.

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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_2SO_4	4.84
$CaCl_2{\cdot}2H_2O$	1.89
$MgCl_2{\cdot}6H_2O$	15.06
NaCl	27.94

Table 3
Crude oil properties.

Density at 288.15 K (kg/m^3)	811.1
API°	42.9
Reid vapor pressure (kPa)	44.9
Viscosity at 293.15 K (kg/m·s)	$4.861{\cdot}10^{-3}$
Saturates (wt%)	43.5
Aromatics (wt%)	41.7
Resins (wt%)	11.6
Asphaltenes (wt%)	3.2

Finally, 1 cm^3 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 rotatory 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][$MeSO_4$] 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][$MeSO_4$] ratio, a Mettler Toledo XPE205 analytical balance with a precision of 10^{-4} g was used.

The stock solution of [C1EG][$MeSO_4$] 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][$MeSO_4$] 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/cm^3. 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 floXlab 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

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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 (Alnoush 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 μL 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 Abushaikha, 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][$MeSO_4$] ratio. Fig. 1 shows the phase behavior of a blend scan of different SDBS/[C1EG][$MeSO_4$] 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][$MeSO_4$] and 73.7 wt% SDBS + 26.3 wt% [C1EG][$MeSO_4$]. 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

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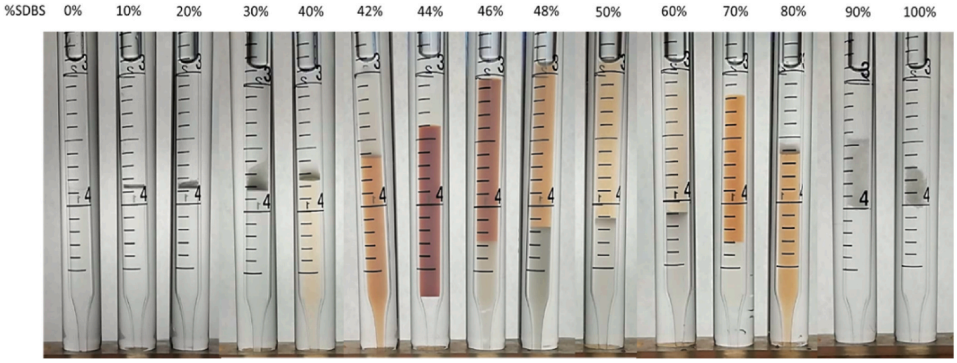


Fig. 1. Blend scan for SDBS/[C1EG][$MeSO_4$] at 298.15 K.

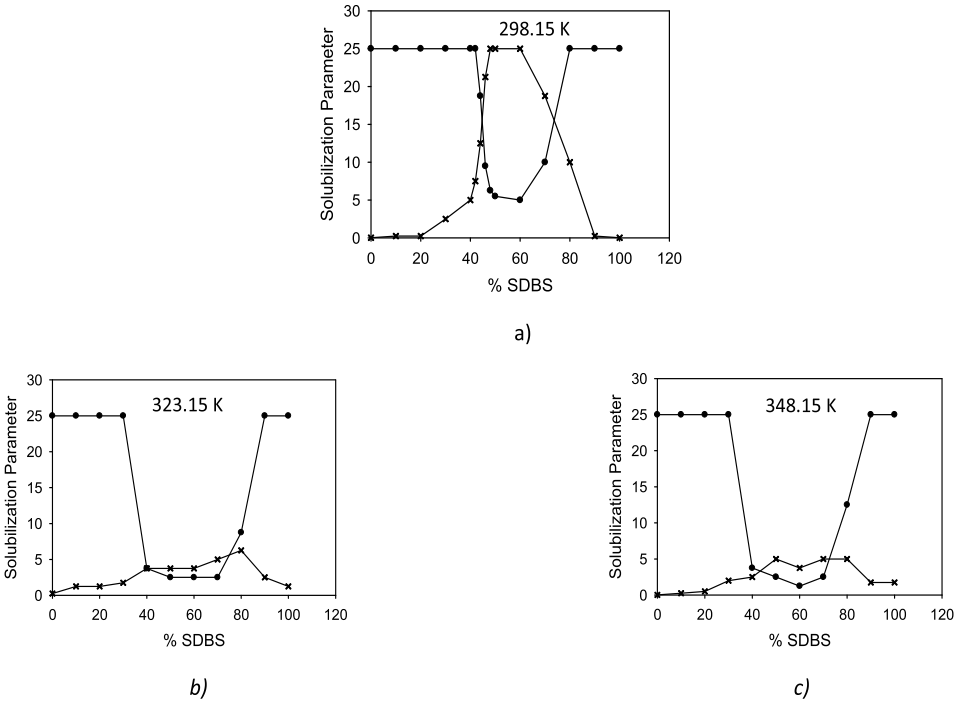


Fig. 2. Solubilization parameters (● Vw/Vs, × Vo/Vs) for different blend ratios at (a) 298.15 K, (b) 323.15 K, (c) 348.15 K.

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][$MeSO_4$] 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

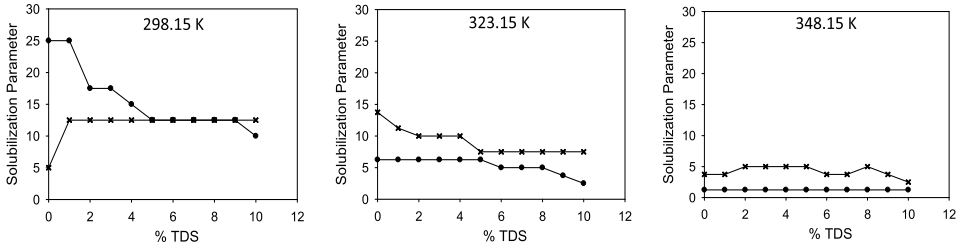


Fig. 3. Solubilization parameters (● Vw/Vs, × Vo/Vs) for 44.7 wt% SDBS blend at different TDS contents and temperatures. (a) 298.15 K, (b) 323.15 K, (c) 348.15 K.

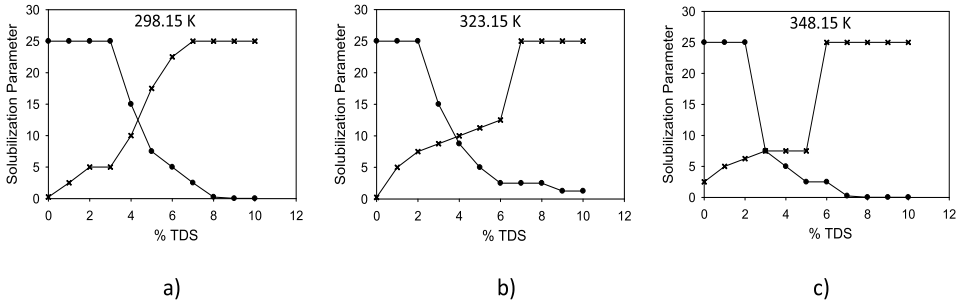


Fig. 4. Solubilization parameters (● Vw/Vs, × Vo/Vs) for 71.7 wt% SDBS blend at different TDS contents and temperatures. (a) 298.15 K, (b) 323.15 K, (c) 348.15 K.

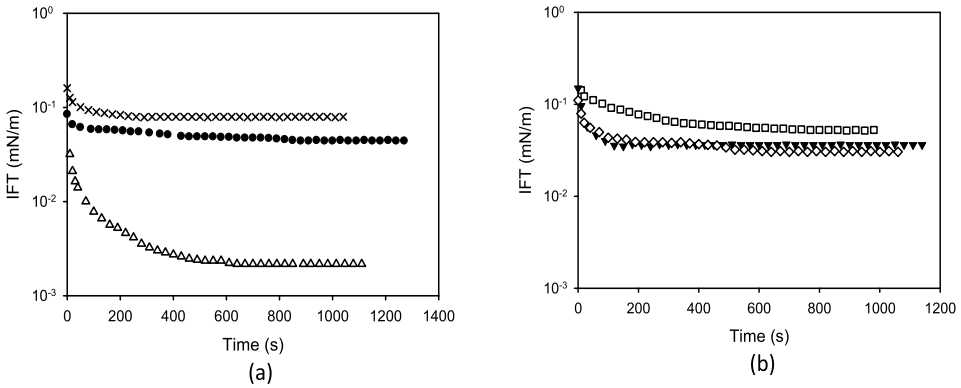


Fig. 5. Dynamic IFT between crude oil and surfactant blend solution in SSW at different SDBS/[C1EG][$MeSO_4$] ratios: (a) First optimum blend (b) Second optimum blend. Δ 40 wt% SDBS, ● 44.7 wt% SDBS, × 50 wt% SDBS, □ 65 wt% SDBS, ▼ 73.7 wt% SDBS, ⋄ 78 wt% SDBS.

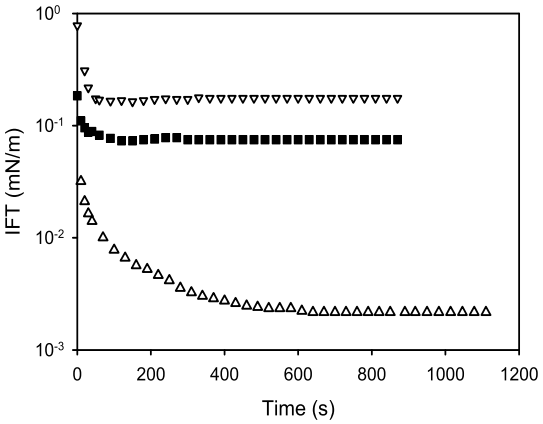


Fig. 6. Dynamic IFT between crude oil and surfactant blend (40 wt% SDBS) solution in SSW at different blend concentrations. Δ 1 wt% ■ 0.25 wt% ▽ 0.1 wt%.

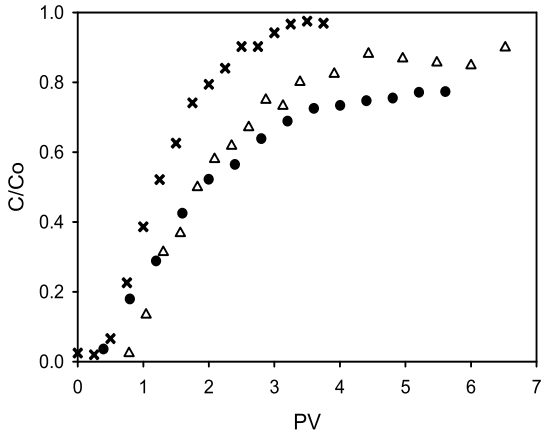


Fig. 7. Dynamic adsorption of the optimized formulation in carbonate rock at 298.15 K × Tracer, △ 40 wt% SDBS, ● 73.7 wt% SDBS.

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 mg_{blend}/g_{rock} for the formulation consisting of 40 wt% SDBS and 0.51 mg_{blend}/g_{rock} for 73.7 wt% SDBS. No preferential adsorption of any of the blend components was detected, the mixture

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behaving as a single component. The combination of SDBS with [C1EG][$MeSO_4$] 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][$MeSO_4$] 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][$MeSO_4$]. 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 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.

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

A similar test (Test 2) was carried out with the second optimal blend (73.7 wt% SDBS + 26.3 wt% [C1EG][$MeSO_4$]). 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 [C_{18}mim]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][$MeSO_4$]). 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

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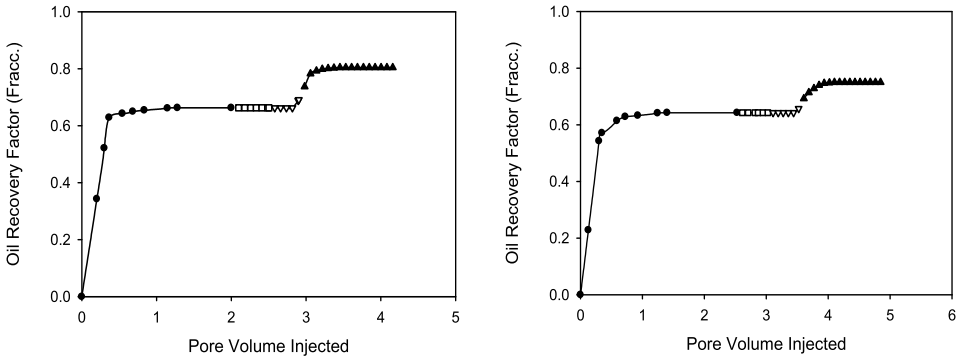


Fig. 8. Core flooding tests: 3 (left) and 4 (right). ● water flooding (0.05 mL/min), □ surfactant flooding (0.025 mL/min), ▽ polymer flooding (0.025 mL/min), ▲ polymer flooding (0.05 mL/min).

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	ø: 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)	ø: 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)	ø: 35–38% μ: 670–700 mD	9.25 wt% NaCl	Room temperature	Not determined	Not determined	16.69
	1000 ppm Platinum Foam Plus Surfactant	ø: 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	ø: 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)	ø: 14% μ: 8.87 mD	4.97 wt% TDS	Room Temperature	0.002	0.37	18.29

[a] Calculated from the Freundlich isotherm figure.

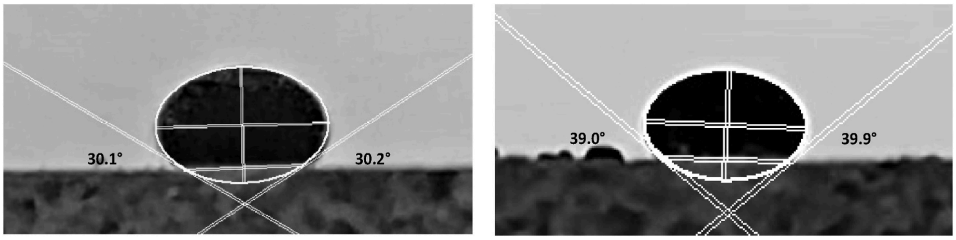


Fig. 9. Contact angle measurements in water-wet rock before (left) and after (right) treatment with the surfactant formulation (room conditions).

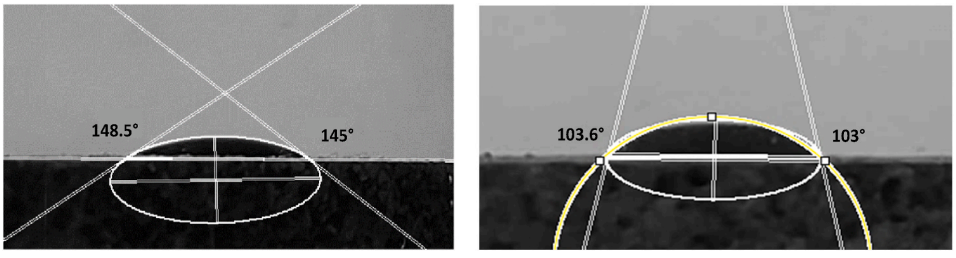


Fig. 10. Contact angle measurements in oil-wet rock before (left) and after (right) treatment with the surfactant formulation (348.15 K).

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][$MeSO_4$] 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][$MeSO_4$] 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][$MeSO_4$] 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][$MeSO_4$] 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][$MeSO_4$]) 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.

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Appendix A. Supplementary data

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

References

Ahmadi, M.A., Galedarzadeh, M., Shadizadeh, S.R., 2014. Wettability alteration in carbonate rocks by implementing new derived natural surfactant: enhanced oil recovery applications. Transport Porous Media 106, 645–667. https://doi.org/10.1007/s11242-014-0418-0.

Alammari, F.G., Miller, C.S., Mohanty, K.K., 2020. Wettability altering surfactants for high temperature tight carbonate reservoirs. In: SPE IOR Conference. https://doi.org/10.2118/200348-ms. Virtual. SPE-200348-MS.

Alnoush, W., Sayed, A., Alyafei, N., 2019. Optimization of contact angle and interfacial tension measurements for fluid/rock systems at ambient conditions. Methods (Orlando) 6, 1706–1715. https://doi.org/10.1016/j.mex.2019.07.009.

Bera, A., Belhaj, H., 2016. Ionic liquids as alternatives of surfactants in enhanced oil recovery. A state-of-the-art review. J. Mol. Liq. 224, 177–188. https://doi.org/10.1016/j.molliq.2016.09.105.

Bera, A., Kumar, T., Ojha, K., Mandal, A., 2013. Adsorption of surfactants on sand surface in enhanced oil recovery: isotherms, kinetics and thermodynamic studies. Appl. Surf. Sci. 284, 87–99. https://doi.org/10.1016/j.apsusc.2013.07.029.

Bin Dahbag, M.S., AlQuraishi, A.A., Benzagouta, M., 2015. Efficiency of ionic liquids for chemical enhanced oil recovery. J Petrol Explor Prod Technol 5, 353–361. https://doi.org/10.1007/s13202-014-0147-5.

Bp, 2020. Statistical Review of World Energy 2020. https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2020-full-report.pdf, 26.09.21.

Cao, N., Mohammed, M.A., Babadagli, T., 2016. Wettability alteration of heavy-oil-bitumen-containing carbonates by use of solvents, high-pH solutions, and nano/ionic liquids. SPE Reservoir Eval. Eng. 20, 363–371. https://doi.org/10.2118/183646-PA.

Cebolla, V.L., Jarne, C., Membrado, L., Vela, J., 2016. Determination of SARA (saturates, aromatics, resins and asphaltenes) in bitumen by HPTLC. CAMAG Application Notes. A-101. 1, 1–4.

Drelich, J., Fang, Ch, White, C.L., 2002. Measurement of interfacial tension in fluid-fluid systems. In: Hubbard, A.T. (Ed.), Encyclopedia of Surface and Colloid Science. Marcel Dekker, New York.

Doan, T., Acosta, E., Scamehorn, J.F., Sabatini, D.A., 2003. Formulating middle-phase microemulsions using mixed anionic and cationic surfactant systems. J. Surfactants Deterg. 6, 215–224. https://doi.org/10.1007/s11743-003-0264-3.

Gao, J., Kwak, H.T., AlSinan, M., 2019. Wettability study of mixed-wet carbonate with multiple pore systems using advanced in-situ MRI technologies. In: SPE/IATMI Asia Pacific Oil & Gas Conference and Exhibition, Bali, Indonesia. https://doi.org/10.2118/196359-ms. SPE-196359-MS.

Guo, H., Dou, M., Hanqing, W., Wang, F., Yuanyuan, G., Yu, Z., Yansheng, W., Li, Y., 2017. Proper use of capillary number in chemical flooding. J. Chem.-NY 4307368. https://doi.org/10.1155/2017/4307368.

Guo, H., Dou, M., Hanqing, W., Wang, F., Yuanyuan, G., Yu, Z., Yansheng, W., Li, Y., 2015. Review of capillary number in chemical enhanced oil recovery. In: SPE Kuwait Oil & Gas Show Conference, Mishref, Kuwait SPE-175172-MS. https://doi.org/10.2118/175172-ms.

Hemmati, N., Tabzar, A., Ghazanfari, M.H., 2017. Adsorption of sodium dodecyl benzene sulfonate onto carbonate rock: kinetics, equilibrium and mechanistic study. J. Dispersion Sci. Technol. 39, 687–699. https://doi.org/10.1080/01932691.2017.1382373.

Jia, H., Leng, X., Hu, M., Song, Y., Wu, H., Lian, P., Liang, Y., Zhu, Y., Liu, J., Zhou, H., 2017. Systematic investigation of the effects of mixed cationic/anionic surfactants on the interfacial tension of a water/model oil system and their application to enhance crude oil recovery. Colloid. Surface. 529, 621–6127. https://doi.org/10.1016/j.colsurfa.2017.06.055.

Joonaki, E., Erfani Gahrooei, H.R., Ghanaatian, S., 2016. Experimental study on adsorption and wettability alteration aspects of a new chemical using for enhanced oil recovery in carbonate oil reservoirs. J. Unconv. Oil Gas Resour. 15, 11–21. https://doi.org/10.1016/j.juogr.2016.05.001.

Khosravi, V., 2010. Developing surfactant to increase the production in heavy oil reservoirs. In: Trinidad and Tobago Energy Resources Conference, Port of Spain, Trinidad. SPE-132575-MS. https://doi.org/10.2118/132575-ms.

Kume, G., Gallotti, M., Nunes, G., 2008. Review on anionic/cationic surfactant mixtures. J. Surfactants Deterg. 11, 1–11. https://doi.org/10.1007/s11743-007-1047-1.

Li, Y., Zhang, W., Kong, B., Puerto, M., Bao, X., Sha, O., Shen, Z., Yhang, Y., Liu, Y., Gu, S., Miller, C., Hirasaki, G.J., 2016. Mixtures of anionic/cationic surfactants: a new approach for enhanced oil recovery in low-salinity, high-temperature sandstone reservoir. SPE J. 21, 1164–1177. https://doi.org/10.2118/169051-pa.

Li, Y., Puerto, M., Bao, X., Zhang, W., Jin, J., Su, Z., Shen, S., Hirasaki, G., Miller, C., 2017. Synergism and performance for systems containing binary mixtures of anionic/cationic surfactants for enhanced oil recovery. J. Surfactants Deterg. 20, 21–34. https://doi.org/10.1007/s11743-016-1892-x.

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

Manshad, A.K., Rezaei, M., Moradi, S., Nowrouzi, I., Mohammadi, A.H., 2017. Wettability alteration and interfacial tension (IFT) reduction in enhanced oil recovery (EOR) process by ionic liquid flooding. J. Mol. Liq. 248, 153–162. https://doi.org/10.1016/j.molliq.2017.10.009.

Massarweh, O., Abushaikha, A.S., 2020. The use of surfactants in enhanced oil recovery: a review of recent advances. Energ. reports 6, 3150–3178. https://doi.org/10.1016/j.egyr.2020.11.009.

Melrose, J.C., Brandner, C.F., 1974. Role of capillary forces in detennining microscopic displacement efficiency for oil recovery by waterflooding. J. Can. Pet. Technol. 13, 54–62. https://doi.org/10.2118/74-04-05.

Mohanty, K.K., Tong, S., Miller, C., Zeng, T., Honarpour, M.M., Turek, E., Peck, D.D., 2017. Improved hydrocarbon recovery using mixtures of energizing chemicals in unconventional reservoirs. SPE Reservoir Eval. Eng. 22, 1436–1448. https://doi.org/10.2118/187240-PA.

Montes, J., Blin, N., Alvarez, A.E., Barrio, I., Panadero, A., Rodriguez, R., Coca, M., Trujillo, F., 2018. Novel anionic surfactant formulation for high temperature carbonate reservoirs. In: SPE EOR Conference at Oil and Gas West Asia. https://doi.org/10.2118/190353-ms. Muscat, Oman. SPE-190353-MS.

Nandwani, S.K., Malek, N.I., Chakraborty, M., Gupta, S., 2019. Potential of a novel surfactant slug in recovering additional oil from highly saline calcite cores during the EOR process: synergistic blend of surface active ionic liquid and nonionic surfactant. Energy Fuel. 33, 541–550. https://doi.org/10.1021/acs.energyfuels.8b03419.

Negin, C., Ali, S., Xie, Q., 2017. Most common surfactants employed in chemical enhanced oil recovery. Petrol. Times 3, 197–211. https://doi.org/10.1016/j.petlm.2016.11.007.

Pal, S., Mushtaq, M., Banat, F., Al Sumaiti, A.M., 2018. Review of surfactant-assisted chemical enhanced oil recovery for carbonate reservoirs: challenges and future perspectives. Petrol. Sci. 15, 77–102. https://doi.org/10.1007/s12182-017-0198-6.

Pillai, P., Mandal, A., 2019. Wettability modification and adsorption characteristics of imidazole-based ionic liquid on carbonate rock: implications for enhanced oil recovery. Energy Fuel. 33, 727–738. https://doi.org/10.1021/acs.energyfuels.8b03376.

Puerto, M., Hirasaki, G.J., Miller, C.A., Barnes, J.R., 2012. Surfactant systems for EOR in high-temperature, high-salinity environments. SPE J. 17, 11–19. https://doi.org/10.2118/129675-PA.

Rodriguez-Escontrela, I., Puerto, M.C., Miller, C.A., Soto, A., 2017. Ionic liquids for low-tension oil recovery processes: phase behavior tests. J. Colloid Interface Sci. 504, 404–416. https://doi.org/10.1016/j.jcis.2017.05.102.

Rodríguez-Palmeiro, I., Rodríguez-Escontrela, I., Rodríguez, O., Soto, A., Reichmann, S., Amro, M.M., 2017. Tributyl(tetradecyl)phosphonium chloride ionic liquid for surfactant-enhanced oil recovery. Energ. fuel 31, 6758–6765. https://doi.org/10.1021/acs.energyfuels.7b00544.

Seethepalli, A., Adibhatla, B., Mohanty, K.K., 2004. Wettability Alteration during Surfactant Flooding of Carbonate Reservoirs. SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma. https://doi.org/10.2118/89423-ms. SPE- 89423-MS.

Sharma, H., Lu, J., Weerasooriya, U.P., Pope, G.A., Mohanty, K.K., 2016. Adsorption in chemical floods with ammonia as the alkali. In: SPE IOR Conference. https://doi.org/10.2118/179682-MS. Tulsa, Oklahoma. SPE-179682-MS.

Sheng, J.J., 2011. Modern Chemical Enhanced Oil Recovery. Elsevier, Amsterdam.

Sheng, J.J., 2013a. Review of surfactant enhanced oil recovery in carbonate reservoirs. Adv. Petrol. Explor. Dev. 6, 1–10. https://doi.org/10.1016/B978-0-12-386545-8.00012-9.

Sheng, J.J., 2013b. Surfactant–polymer flooding. In: Enhanced Oil Recovery Field Case Studies. Elsevier, pp. 117–142.

Sheng, J.J., 2015. Status of surfactant EOR technology. Petrol. Times 1, 97–105. https://doi.org/10.1016/j.petlm.2015.07.003.

Sohrabi, B., Gharibi, H., Tajik, B., Javadian, S., Hashemianzadeh, M., 2008. Molecular interactions of cationic and anionic surfactants in mixed monolayers and aggregates. J. Phys. Chem. B 112, 14869–14876. https://doi.org/10.1021/jp803105n.

Somoza Cerviño, A., Soto Campos, A.M., 2021. Composición para la extracción mejorada de crudo. ES202130177. Priority date: 03/03/2021.

Sotomayor, M., Alshaer, H., Chen, X., Panthi, K., Balhoff, M., Mohanty, K., 2021. Surfactant-polymer formulations for EOR in high temperature high salinity carbonate reservoirs. Dubai, UAE. SPE-206321-MS. In: SPE Annual Technical Conference and Exhibition. https://doi.org/10.2118/206321-MS.

Standnes, D.C., Austad, T., 2003. Wettability alteration in carbonates: interaction between cationic surfactant and carboxylates as a key factor in wettability alteration from oil-wet to water-wet conditions. Colloid. Surface. 216, 243–259. https://doi.org/10.1016/S0927-7757(02)00580-0.

Tackie-Otoo, B.N., Ayoub Mohammed, M.A., Yekeen, N., Negash, B.M., 2020. Alternative chemical agents for alkalis, surfactants and polymers for enhanced oil recovery: Research trend and prospects. J. Petrol. Sci. Eng. 187, 106828. https://doi.org/10.1016/j.petrol.2019.106828.

Tie, H., Morrow, N.R., 2005. Oil recovery by spontaneous imbibition before and after wettability alteration of three carbonate rocks by a moderately asphaltic crude oil. Toronto, Canada, SCA2005–11. In: International Society of Core Analysts Annual Meeting.

U.S. Energy Information Administration, 2019. Internaltional Energy Outlook 2019 with Projections to 2050. https://fossil.energy.gov/app/DocketIndex/docket/DownloadFile/627, 26.09.21.

Vonnegut, B., 1942. Rotating bubble method for the determination of surface and interfacial tensions. Rev. Sci. Instrum. 13, 6–9. https://doi.org/10.1063/1.1769937.

Weiss, E., Groenen-Serrano, K., Savall, A., 2007. Electrochemical mineralization of sodium dodecylbenzenesulfonate at boron doped diamond anodes. J. Appl. Electrochem. 37, 1337–1344. https://doi.org/10.1007/s10800-007-9367-4.

Zabihi, S., Faraji, D., Rahnama, Y., Zeinolabedini Hezave, A., Ayatollahi, S., 2019. Relative permeability measurement in carbonate rocks, the effects of conventional surfactants vs. Ionic liquid-based surfactants. J. Dispersion Sci. Technol. 41, 1797–1811. https://doi.org/10.1080/01932691.2019.1637262.

Zulkifli, N.N., Mahmood, S.M., Akbari, S., Manap, A.A.A., Kechut, N.I., Elrais, K.A., 2020. Evaluation of new surfactants for enhanced oil recovery applications in high-temperature reservoirs. J. Pet. Explor. Prod. Technol. 10, 283–296. https://doi.org/10.1007/s13202-019-0713-y.

Zhu, Y., Lei, M., 2016. Effects of crude oil components on the interfacial tension between oil and surfactant solutions. In: SPE Asia Pacific Enhanced Oil Recovery Conference. Kuala Lumpur, Malaysia. https://doi.org/10.2118/174593-MS. SPE-174593-MS.

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DESIGN AND PERFORMANCE ANALYSIS OF A FORMULATION BASED ON SDBS AND IONIC LIQUID FOR EOR IN CARBONATE RESERVOIRS

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SUPPLEMENTARY INFORMATION

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1.- Critical Micelle Concentration Determinations

Surface tension was measured to determine the critical micelle concentration (cmc) of the surfactants in aqueous solution at 298.15 K. To that aim, a Krüss K11 tensiometer based in the Wilhelmy plate method, with a Julabo F12 cryogenic thermostat for temperature control, was used.

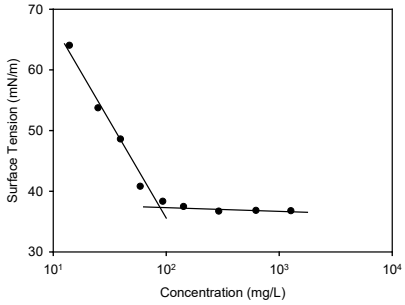


Figure S1. Critical micelle concentration of [C1EG][MeSO4] at 298.15K

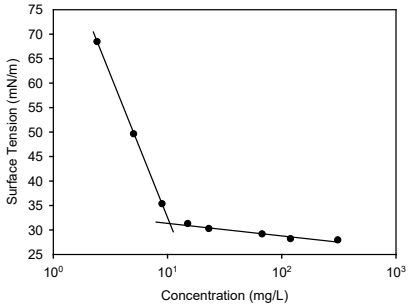


Figure S2. Critical micelle concentration of 44.7 wt% SDBS + 55.3 wt% [C1EG][MeSO4] at 298.15K

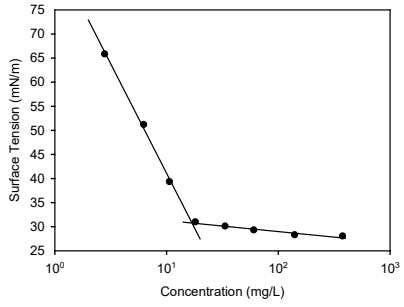


Figure S3. Critical micelle concentration of 73.7% wt% SDBS + 26.3 wt% [C1EG][MeSO4] at 298.15K

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2.- Core flooding experimental setup

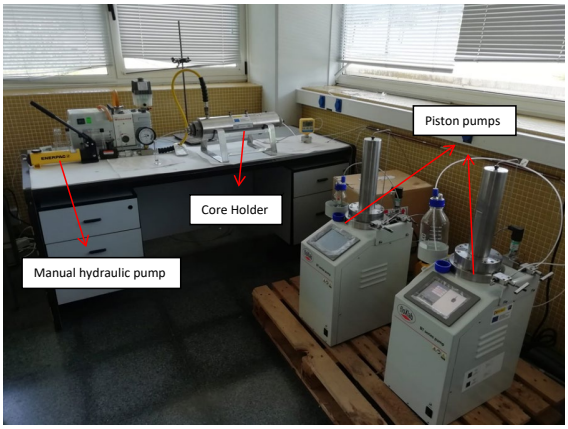


Figure S4. Core flooding experimental setup

3.- Blend scans at 323.15 K and 348.15 K

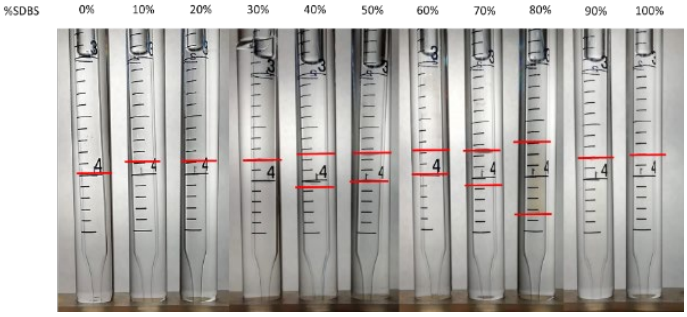


Figure S5. Blend scan for SDBS/[C1EG][MeSO4] at 323.15 K

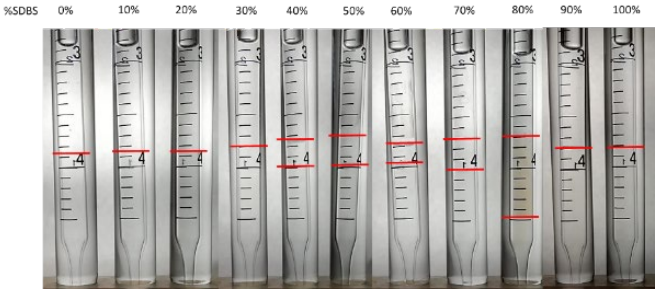


Figure S6. Blend scan for SDBS/[C1EG][MeSO4] at 348.15 K

4.- Blend scans at 298.15 K, 323.15 K and 348.15 K under polarized light

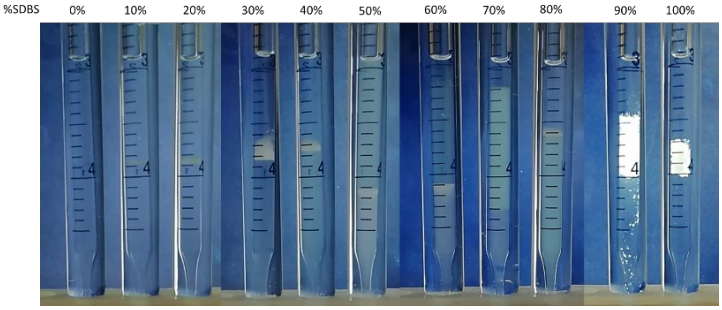


Figure S7. Blend scan for SBDS/[C1EG][MeSO4] at 298.15 K under polarized light

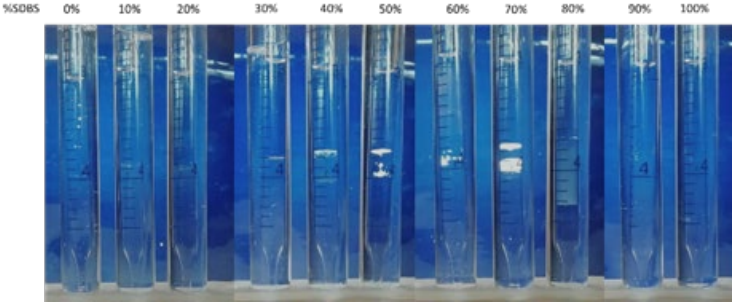


Figure S8. Blend scan for SBDS/[C1EG][MeSO4] at 323.15 K under polarized light

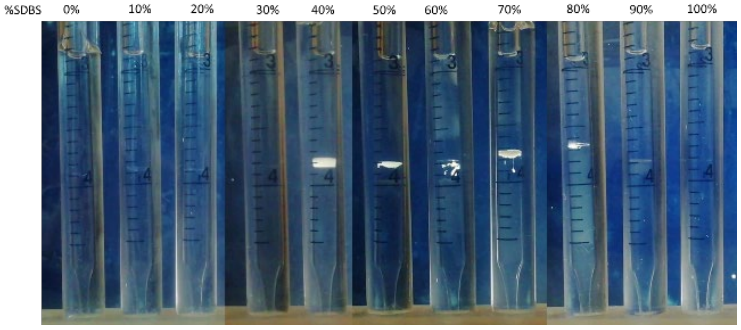


Figure S9. Blend scan for SBDS/[C1EG][MeSO4] at 348.15 K under polarized light

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5.- Salinity scans for the first optimal blend (44.7 wt% SDBS + 55.3 wt% [C1EG][$MeSO_4$]) at 298.15 K, 323.15 K and 348.15 K

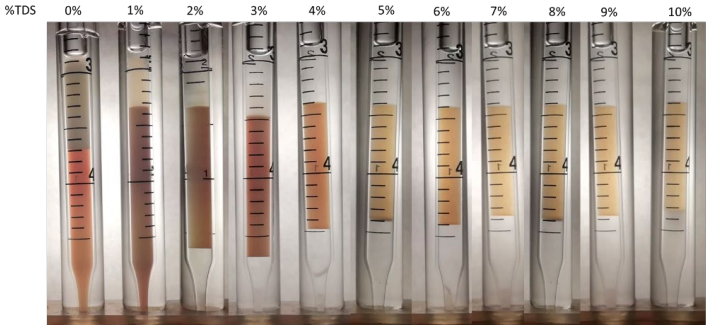


Figure S10. Blend scan for 44.7 wt% SBDS + 55.3 wt% [C1EG][MeSO4] at 298.15 K

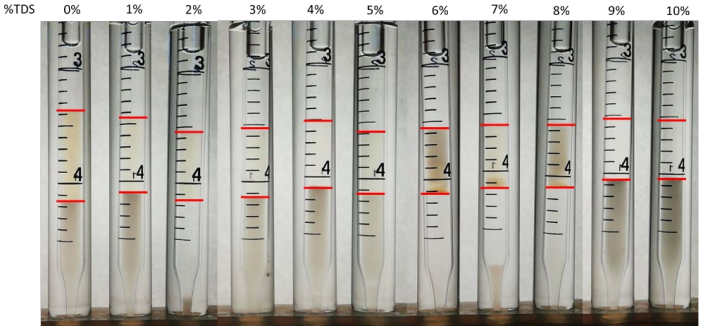


Figure S11. Blend scan for 44.7 wt% SBDS + 55.3 wt% [C1EG][MeSO4] at 323.15 K

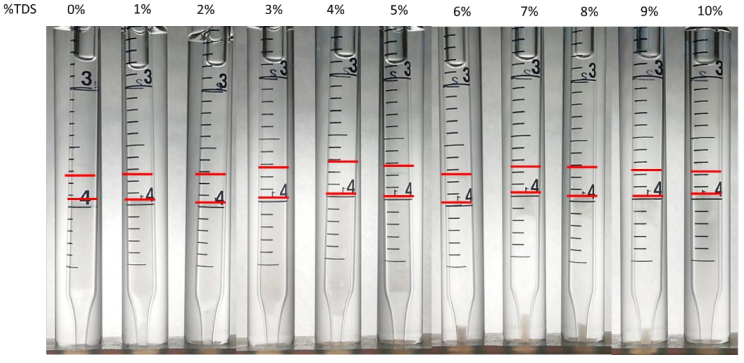


Figure S12. Blend scan for 44.7 wt% SBDS + 55.3 wt% [C1EG][MeSO4] at 348.15 K

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6.- Salinity scans for the second optimal blend (73.7 wt% SDBS + 26.3 wt% [C1EG][$MeSO_4$]) at 298.15 K, 323.15 K and 348.15 K

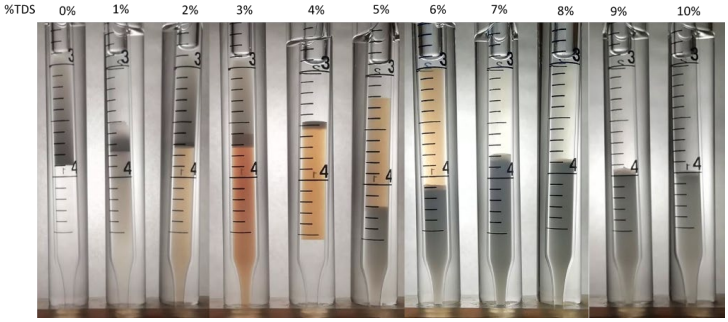


Figure S13. Blend scan for 73.7 wt% SBDS + 26.3 wt% [C1EG][MeSO4] at 298.15 K

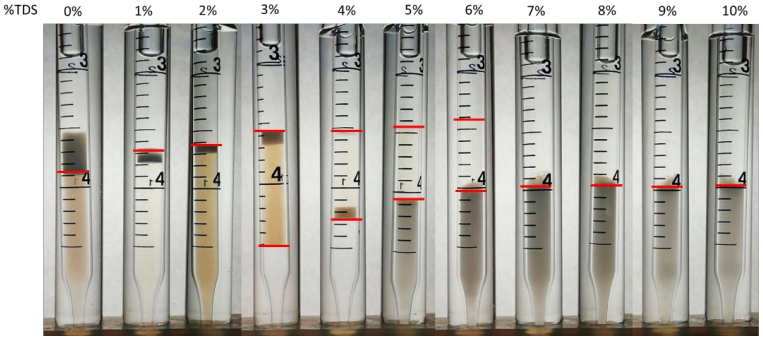


Figure S14. Blend scan for 73.7 wt% SBDS + 26.3 wt% [C1EG][MeSO4] at 323.15 K

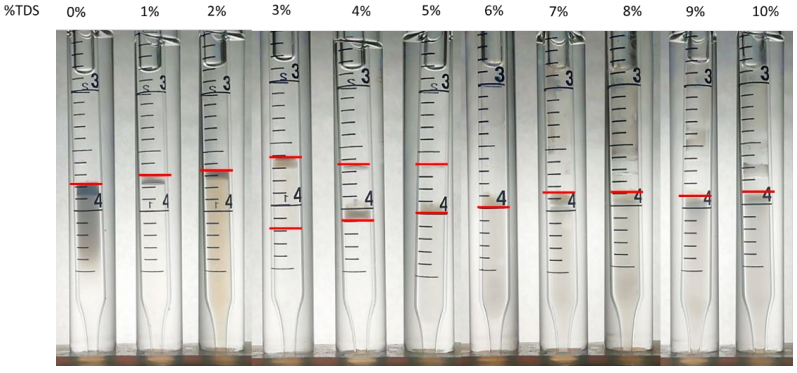


Figure S15. Blend scan for 73.7 wt% SBDS + 26.3 wt% [C1EG][MeSO4] at 348.15 K

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7.- Injectability tests

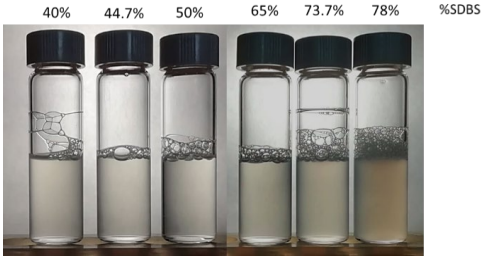


Figure S16. Injectability tests of different SDBS/[C1EG][MeSO4] blends in SSW at 298.15 K (picture taken after one week)

7.1.- Injectability tests of the blend 40 wt% SDBS + 60 wt% [C1EG][MeSO4] at harsh conditions

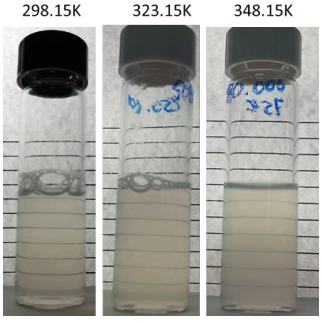


Figure S17. Injectability tests of 40 wt% SDBS + 60 wt% [C1EG][MeSO4] in 250000 ppm TDS brine (17000 ppm hardness) at different temperatures (picture taken after one week)

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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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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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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

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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:

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

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. 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).

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

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

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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:

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

where τ is blend adsorption in mg/g of rock, $PV_{surf,50\%}$ and $PV_{tracer,50\%}$ 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

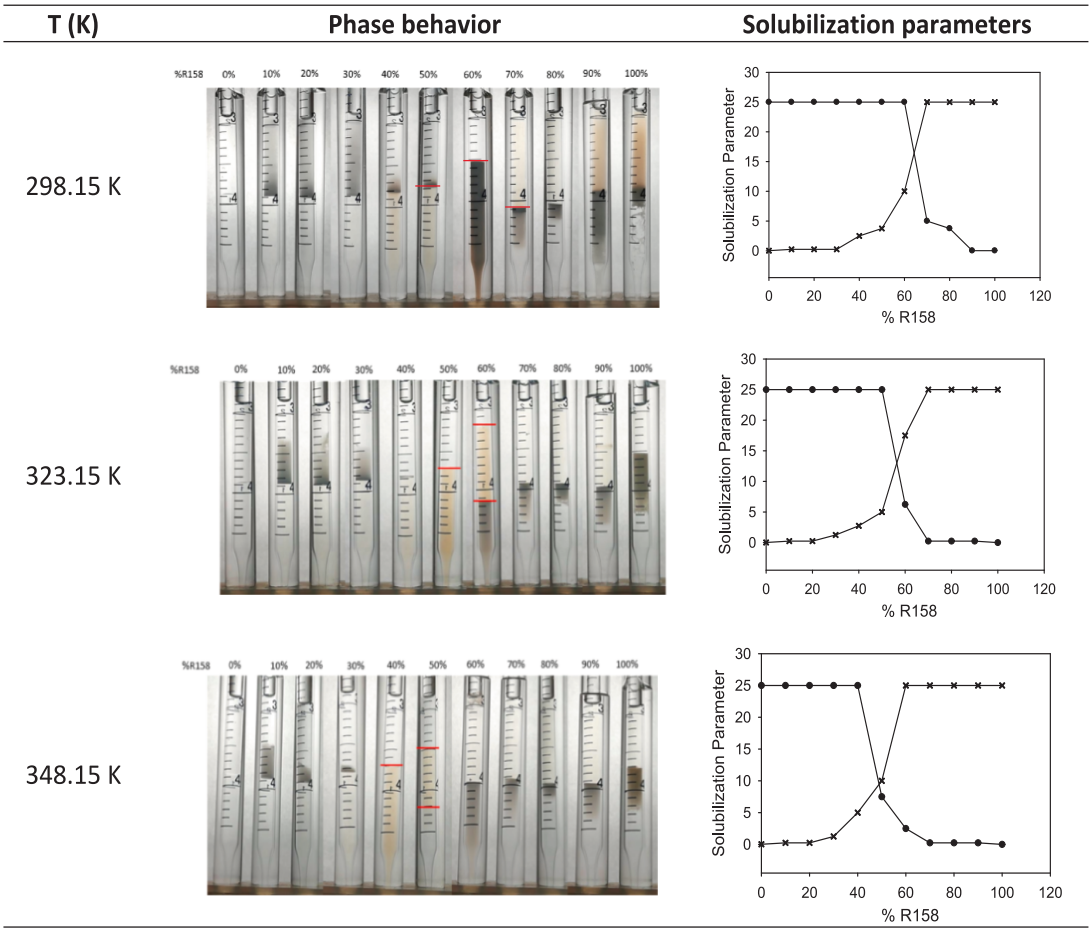


Fig. 1. Blend scans for RECOLAS158/T2EG and solubilization parameters (● Vw/*Vs*, × Vo/*Vs*) at 298.15 K, 323.15 K and 348.15 K.

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 cocosalkylpentaethoxymethylammonium 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

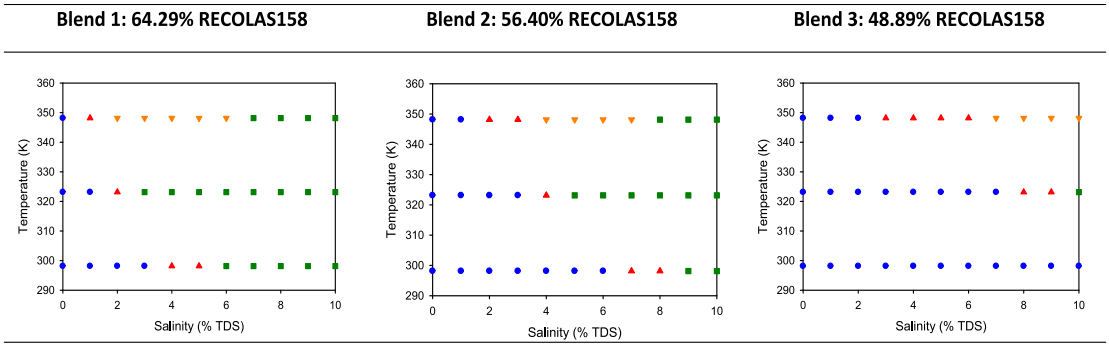


Fig. 2. Phase behavior of the three promising blends as a function of salinity and temperature (● Winsor I ▲Winsor III ▼Winsor III with low solubilization parameters ■Winsor II).

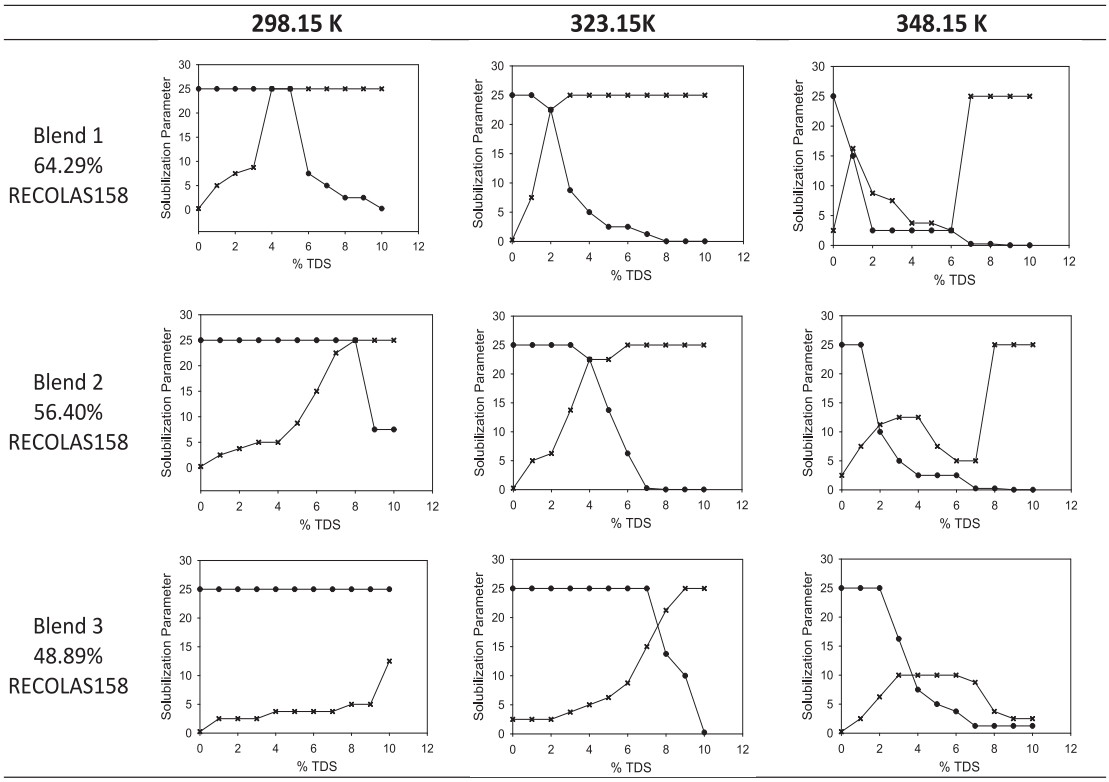


Fig. 3. Solubilization parameters (● Vw/*Vs*, × Vo/*Vs*) as a function of salinity at 298.15 K, 323.15 K and 348.15 K for the three promising blend formulations.

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.

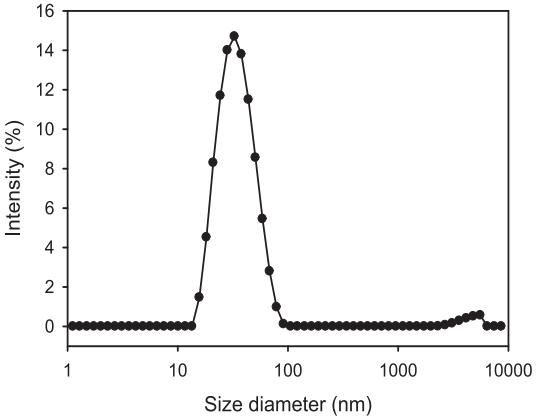


Fig. 4. Size diameter distribution of 56.4% RECOLAS158 formulation on seawater at 298.15 K.

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

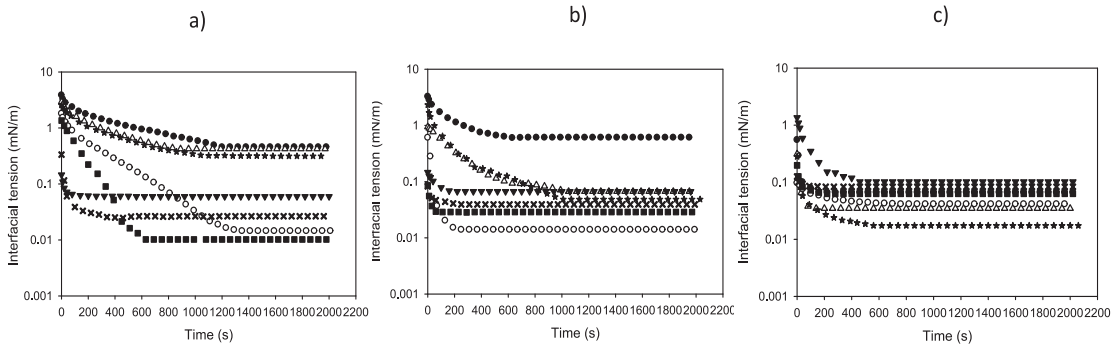


Fig. 5. Dynamic IFT between crude oil and different RECOLAS158/T2EG formulations in SSW at 298.15 K (a), 323.15 K (b) and 348.15 K (c). (● 45% Δ 48.89% ★ 50% ○ 56.4% ■ 60% × 64.29% ▼70% RECOLAS158).

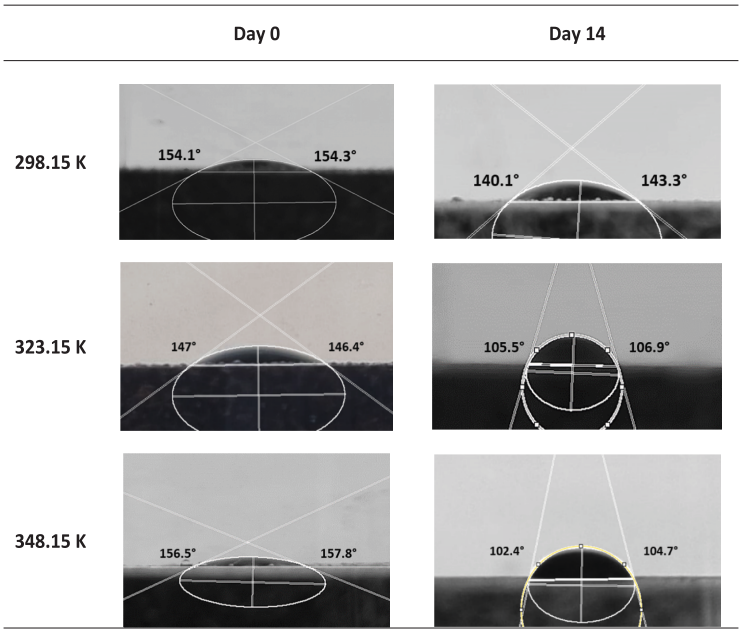


Fig. 6. Contact angle measurements in oil-wet rock before and after treatment with the surfactant formulation at different temperatures.

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 $C_{14}E_6$.

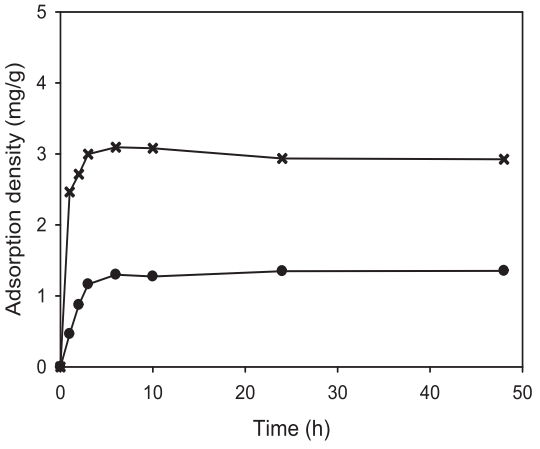


Fig. 7. Static adsorption comparison of two blends containing RECOLAS158 at 298.15 K (● 56.4% RECOLAS158 + 43.6% T2EG; x 36% RECOLAS158 + 64% C1EG).

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

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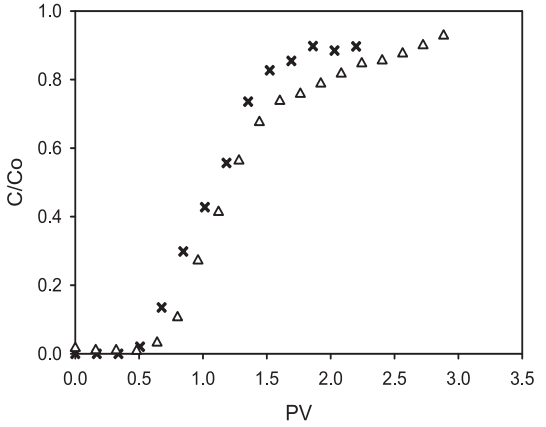


Fig. 8. Dynamic adsorption of the optimized formulation in carbonate rock at room conditions (×Tracer, △ Blend 56.4% RECOLAS158).

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:

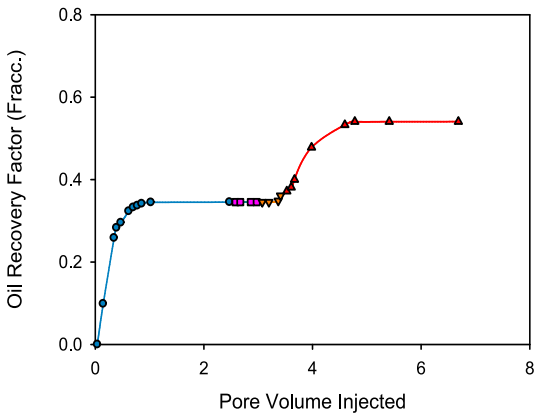


Fig. 9. Core Flooding test 2. ●Water flooding (0.05 mL/min) ■ Surfactant flooding (0.025 mL/min) ▼ Polymer Flooding (0.025 mL/min) ▲ Polymer Flooding (0.05 mL/min).

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- 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 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.

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Appendix A. Supplementary data

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

References

[1] Saxena N, Goswami A, Dhodapkar PK, Nihalani MC, Mandal A. Bio-based surfactant for enhanced oil recovery: Interfacial properties, emulsification and rock-fluid interactions. J Pet Sci Eng 2019;176:299–311. https://doi.org/10.1016/j.petrol.2019.01.052.

[2] Sotomayor, M., Alshaer, H., Chen, X., Panthi, K., Balhoff, M., Mohanty, K. Surfactant-Polymer Formulations for EOR in High Temperature High Salinity Carbonate Reservoirs. Paper presented at the SPE Annual Technical Conference and Exhibition, Dubai, UAE, September 2021. https://doi.org/10.2118/206321-MS.

[3] Sheng JJ. Status of surfactant EOR technology. Petroleum 2015;1(2):97–105. https://doi.org/10.1016/j.petlm.2015.07.003.

[4] Statistical Review of World Energy 2020. BP statistical reviews 69th edition. https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2020-full-report.pdf ; 2022 [accessed 14 June 2022].

[5] Han, M., Alsofi, A., Fuseni, A., Zhou, X., Hassan, S. Development of Chemical EOR Formulations for a High Temperature and High Salinity Carbonate Reservoir. Paper presented at the International Petroleum Technology Conference, Beijing, China, March 2013. https://doi.org/10.2523/IPTC-17084-MS.

[6] Sheng JJ. Review of Surfactant Enhanced Oil Recovery in Carbonate Reservoirs. Advances in Petroleum Exploration and Development 2013;6:1–10. https://doi.org/10.3968/j.aped.1925543820130601.1582.

[7] Alammari, F.G., Miller, C.S., Mohanty, K.K. Wettability Altering Surfactants for High Temperature Tight Carbonate Reservoirs. Paper presented at the SPE Improved Oil Recovery Conference, Virtual, August 2020. https://doi.org/https://doi.org/10.2118/200348-MS.

[8] Massarweh O, Abushaikha AS. The use of surfactants in enhanced oil recovery: A review of recent advances. Energy Rep 2020;6:3150–78. https://doi.org/10.1016/J.EGYR.2020.11.009.

[9] Yao Y, Wei M, Kang W. A review of wettability alteration using surfactants in carbonate reservoirs. Adv Colloid Interface Sci 2021;294:102477. https://doi.org/10.1016/J.CIS.2021.102477.

[10] Pal S, Mushtaq M, Banat F, Al Sumaiti AM. Review of surfactant-assisted chemical enhanced oil recovery for carbonate reservoirs: challenges and future perspectives. Pet Sci 2018;15(1):77–102.

[11] Chen, P., Mohanty, K.K. Wettability alteration in high temperature carbonate reservoirs. Paper presented at the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA, April 2014. https://doi.org/10.2118/169125-ms.

[12] Jarrahian K, Seiedi O, Sheykhan M, Sefti MV, Ayatollahi S. Wettability alteration of carbonate rocks by surfactants: A mechanistic study. Colloids Surf A Physicochem Eng Asp 2012;410:1–10. https://doi.org/10.1016/j.colsurfa.2012.06.007.

[13] Seethepalli A, Adibhatla B, Mohanty KK. Wettability Alteration During Surfactant Flooding of Carbonate Reservoirs. Tulsa, Oklahoma: Paper presented at the SPE/DOE Symposium on Improved Oil Recovery; 2004. https://doi.org/https://doi.org/10.2118/89423-MS.

[14] Standnes DC, Austad T. Wettability alteration in carbonates: Interaction between cationic surfactant and carboxylates as a key factor in wettability alteration from oil-wet to water-wet conditions. Colloids Surf A Physicochem Eng Asp 2003;216:243–59. https://doi.org/10.1016/S0927-7757(02)00580-0.

[15] Joonaki E, Erfani Gahrooei HR, Ghanaatian S. Experimental study on adsorption and wettability alteration aspects of a new chemical using for enhanced oil recovery in carbonate oil reservoirs. Journal of Unconventional Oil and Gas Resources 2016;15:11–21. https://doi.org/10.1016/j.juogr.2016.05.001.

[16] Abalkhail N, Liyanage PJ, Upamali KAN, Pope GA, Mohanty KK. Alkaline-surfactant-polymer formulation development for a HTHS carbonate reservoir. J Pet Sci Eng 2020;191:107236. https://doi.org/10.1016/j.petrol.2020.107236.

[17] Ahmadi MA, Shadizadeh SR. Implementation of a high-performance surfactant for enhanced oil recovery from carbonate reservoirs. J Pet Sci Eng 2013;110:66–73. https://doi.org/10.1016/j.petrol.2013.07.007.

[18] Ghosh P, Mohanty KK. Study of Surfactant-Polymer Flooding in High-Temperature and High-Salinity Carbonate Rocks. Energy Fuel 2019;33:4130–45. https://doi.org/10.1021/acs.energyfuels.9b00407.

[19] Lu J, Goudarzi A, Chen P, Kim DH, Delshad M, Mohanty KK, et al. Enhanced oil recovery from high-temperature, high-salinity naturally fractured carbonate reservoirs by surfactant flood. J Pet Sci Eng 2014;124:122–31. https://doi.org/10.1016/j.petrol.2014.10.016.

[20] Montes, J., Blin, N., Alvarez, A.E., Barrio, I., Panadero, A., Rodriguez, R., Coca, M., Trujillo, F. Novel Anionic Surfactant Formulation for High Temperature Carbonate Reservoirs. Paper presented at the SPE EOR Conference at Oil and Gas West Asia, Muscat, Oman, March 2018. https://doi.org/https://doi.org/10.2118/190353-ms.

[21] Rabbani HS, Osman Y, Almaghrabi I, Rahman MA, Seers T. Dynamics of Surfactant Flooding in Tight Carbonate Rocks. Paper presented at the SPE Kuwait Oil & Gas Show and Conference. October 2019.

[22] Hemmati N, Tabzar A, Ghazanfari MH. Adsorption of sodium dodecyl benzene sulfonate onto carbonate rock: Kinetics, equilibrium and mechanistic study. J Dispers Sci Technol 2018;39:687–99. https://doi.org/10.1080/01932691.2017.1382373.

[23] Bera A, Belhaj H. Ionic liquids as alternatives of surfactants in enhanced oil recovery—A state-of-the-art review. J Mol Liq 2016;224:177–88. https://doi.org/10.1016/J.MOLLIQ.2016.09.105.

[24] Somoza A, Arce A, Soto A. Oil recovery tests with ionic liquids: A review and evaluation of 1-decyl-3-methylimidazolium triflate. Pet Sci 2022;19:1877–87. https://doi.org/10.1016/J.PETSCI.2021.10.025.

[25] Tackie-Otoo BN, Ayoub Mohammed MA, Yekeen N, Negash BM. Alternative chemical agents for alkalis, surfactants and polymers for enhanced oil recovery: Research trend and prospects. J Pet Sci Eng 2020;187(106828). https://doi.org/10.1016/J.PETROL.2019.106828.

[26] Manshad AK, Rezaei M, Moradi S, Nowrouzi I, Mohammadi AH. Wettability alteration and interfacial tension (IFT) reduction in enhanced oil recovery (EOR) process by ionic liquid flooding. J Mol Liq 2017;248:153–62. https://doi.org/10.1016/j.molliq.2017.10.009.

[27] Nandwani SK, Malek NI, Chakraborty M, Gupta S. Potential of a Novel Surfactant Slug in Recovering Additional Oil from Highly Saline Calcite Cores during the EOR Process: Synergistic Blend of Surface Active Ionic Liquid and Nonionic Surfactant. Energy Fuel 2019;33:541–50. https://doi.org/10.1021/acs.energyfuels.8b03419.

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[28] Zabihi S, Faraji D, Rahnama Y, Zeinolabedini Hezave A, Ayatollahi S. Relative permeability measurement in carbonate rocks, the effects of conventional surfactants vs. Ionic liquid-based surfactants. J Dispers Sci Technol 2020;41(12):1797–811.

[29] Somoza A, Tafur N, Arce A, Soto A. Design and performance analysis of a formulation based on SDBS and ionic liquid for EOR in carbonate reservoirs. J Pet Sci Eng 2022;209:109856. https://doi.org/10.1016/j.petrol.2021.109856.

[30] Barnes, J.R., Smit, Johan, Smit, Jasper, Shpakoff, G., Raney, K.H., Puerto, M. Development of surfactants for chemical flooding at difficult reservoir conditions. Paper presented at the SPE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, USA, April 2008. https://doi.org/10.2118/113313-MS.

[31] Ahmadi MA, Shadizadeh SR. Spotlight on the New Natural Surfactant Flooding in Carbonate Rock Samples in Low Salinity Condition. Sci Rep 2018;8:1–16. https://doi.org/10.1038/s41598-018-29321-w.

[32] Hanamertani AS, Pilus RM, Idris AK, Irawan S, Tan IM. Ionic liquids as a potential additive for reducing surfactant adsorption onto crushed Berea sandstone. J Pet Sci Eng 2018;162:480–90. https://doi.org/10.1016/j.petrol.2017.09.077.

[33] Sharma, H., Lu, J., Weerasooriya, U.P., Pope, G.A., Mohanty, K.K., 2016. Adsorption in chemical floods with ammonia as the alkali. Paper presented at the SPE Improved Oil Recovery Conference, Tulsa, Oklahoma, USA, April 2016. https://doi.org/10.2118/179682-MS.

[34] Bin Dahbag M, AlQuraishi A, Benzagouta M. Efficiency of ionic liquids for chemical enhanced oil recovery. J Pet Explor Prod Technol 2015;5:353–61. https://doi.org/10.1007/s13202-014-0147-5.

[35] Li, Y., Zhang, W., Kong, B., Puerto, M., Bao, X., Sha, O., Shen, Z., Yang, Y., Liu, Y., Gu, S., Miller, C., Hirasaki, G.J. Mixtures of Anionic-Cationic Surfactants: A New Approach for Enhanced Oil Recovery in Low-Salinity, High-Temperature Sandstone Reservoir. Paper presented at the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA, April 2014. https://doi.org/10.2118/169051-MS.

[36] Rodriguez-Escontrela I, Puerto MC, Miller CA, Soto A. Ionic liquids for low-tension oil recovery processes: Phase behavior tests. J Colloid Interface Sci 2017;504:404–16. https://doi.org/10.1016/j.jcis.2017.05.102.

[37] Li Y, Puerto M, Bao X, Zhang W, Jin J, Su Z, et al. Synergism and Performance for Systems Containing Binary Mixtures of Anionic/Cationic Surfactants for Enhanced Oil Recovery. J Surfactant Deterg 2017;20:21–34. https://doi.org/10.1007/s11743-016-1892-x.

[38] Antón RE, Andérez JM, Bracho C, Vejar F, Salager JL. Practical surfactant mixing rules based on the attainment of microemulsion-oil-water three-phase behavior systems. Adv Polym Sci 2008;218:83–113. https://doi.org/10.1007/12_2008_163.

[39] Jia H, Leng X, Hu M, Song Y, Wu H, Lian P, et al. Systematic investigation of the effects of mixed cationic/anionic surfactants on the interfacial tension of a water/model oil system and their application to enhance crude oil recovery. Colloids Surf A Physicochem Eng Asp 2017;529:621–7. https://doi.org/10.1016/j.colsurfa.2017.06.055.

[40] Veiskarami S, Jafari A, Soleymanzadeh A. Phase behavior, wettability alteration, and oil recovery of low-salinity surfactant solutions in carbonate reservoirs. SPE J 2020;25:1784–802. https://doi.org/10.2118/200483-PA.

[41] Nakama Y. Surfactants. Cosmetic Science and Technology: Theoretical Principles and Applications 2017:231–44. https://doi.org/10.1016/B978-0-12-802005-0.00015-X.

[42] Bhattarai A. Studies of the Micellization of Cationic-Anionic Surfactant Systems in Water and Methanol-Water Mixed Solvents. J Solution Chem 2015;44:2090–105. https://doi.org/10.1007/s10953-015-0391-4.

[43] Inoue T, Misono T. Cloud point phenomena for POE-type nonionic surfactants in a model room temperature ionic liquid. J Colloid Interface Sci 2008;326:483–9. https://doi.org/10.1016/j.jcis.2008.04.047.

[44] Mirchi V, Saraji S, Akbarabadi M, Goual L, Piri M. A Systematic Study on the Impact of Surfactant Chain Length on Dynamic Interfacial Properties in Porous Media: Implications for Enhanced Oil Recovery. Ind Eng Chem Res 2017;56:13677–95. https://doi.org/10.1021/acs.iecr.7b02623.

[45] Wu J, Xu Y, Dabros T, Hamza H. Effect of EO and PO positions in nonionic surfactants on surfactant properties and demulsification performance. Colloids Surf A Physicochem Eng Asp 2005;252:79–85. https://doi.org/10.1016/j.colsurfa.2004.09.034.

[46] Puerto M, Hirasaki GJ, Miller CA, Barnes JR. Surfactant Systems for EOR in High-Temperature. High-Salinity Environments SPE Journal 2012;17:11–9. https://doi.org/10.2118/129675-PA.

[47] Mahboob A, Kalam S, Kamal MS, Hussain SMS, Solling T. EOR Perspective of microemulsions: A review. J Pet Sci Eng 2022;208:109312. https://doi.org/10.1016/j.petrol.2021.109312.

[48] Kume G, Gallotti M, Nunes G. Review on anionic/cationic surfactant mixtures. J Surfactant Deterg 2008;11:1–11. https://doi.org/10.1007/s11743-007-1047-1.

[49] Doan T, Acosta E, Scamehorn JF, Sabatini DA. Formulating middle-phase microemulsions using mixed anionic and cationic surfactant systems. J Surfactant Deterg 2003;6:215–24. https://doi.org/10.1007/s11743-003-0264-3.

[50] Zulkifli NN, Mahmood SM, Akbari S, Manap AAA, Kechut NI, Elrais KA. Evaluation of new surfactants for enhanced oil recovery applications in high-temperature reservoirs. J Pet Explor Prod Technol 2020;10:283–96. https://doi.org/10.1007/s13202-019-0713-y.

[51] Chang, L.Y., Pope, G.A. Prediction of the aqueous stability limit of surfactant EOR formulations. Paper presented at the Offshore Technology Conference, Houston, Texas, May 2019. https://doi.org/10.4043/29330-ms.

[52] Li W, Mu L, Zhao L, Li J, Wang S, Fan Z, et al. Pore-throat structure characteristics and its impact on the porosity and permeability relationship of Carboniferous carbonate reservoirs in eastern edge of Pre-Caspian Basin. Pet Explor Dev 2020;47:1027–41. https://doi.org/10.1016/S1876-3804(20)60114-8.

[53] Miaomiao L, Benbiao S, Changbing T, Xianyu M. Relationship between pore throat and permeability of porous carbonate reservoir in the Middle East. Arab J Geosci 2022:15. https://doi.org/10.1007/s12517-021-08462-9.

[54] Yang H, Li S, Liu X. Characteristics and resource prospects of tight oil in Ordos Basin. China Petroleum Research 2016;1:27–38. https://doi.org/10.1016/S2096-2495(17)30028-5.

[55] Strand S, Høgnesen EJ, Austad T. Wettability alteration of carbonates - Effects of potential determining ions (Ca^{2+} and SO_4^{2-}) and temperature. Colloids Surf A Physicochem Eng Asp 2006;275:1–10. https://doi.org/10.1016/j.colsurfa.2005.10.061.

[56] Souayeh M, Al-Maamari RS, Aoudia M, Karimi M, Hadji M. Experimental Investigation of Wettability Alteration of Oil-Wet Carbonates by a Non-ionic Surfactant. Energy Fuel 2018;32:11222–33. https://doi.org/10.1021/acs.energyfuels.8b02373.

[57] Somoza, A., Rodríguez-Cabo, B., Barrio, I., García-Mayoral, M.F., Soto. A. Experimental evaluation of blends containing linear alkylbenzene sulfonates for surfactant flooding in carbonate reservoirs. Unpublished results.

[58] Curbelo FDS, Santanna VC, Neto ELB, Dutra TV, Dantas TNC, Neto AAD, et al. Adsorption of nonionic surfactants in sandstones. Colloids Surf A Physicochem Eng Asp 2007;293(1-3):1–4.

[59] Singh SK, Notley SM. Adsorption of Nonionic Surfactants (CnEm) at the Silica - Water and Cellulose - Water Interface. J Phys Chem B 2010;114:14977–82. https://doi.org/10.1021/jp107224r.

[60] Upadhyaya A, Acosta EJ, Scamehorn JF, Sabatini DA. Adsorption of anionic-cationic surfactant mixtures on metal oxide surfaces. J Surfactant Deterg 2007;10:269–77. https://doi.org/10.1007/s11743-007-1045-3.

[61] Kang W-L, Zhou B-B, Issakhov M, Gabdullin M. Advances in enhanced oil recovery technologies for low permeability reservoirs. Pet Sci 2022;19(4):1622–40. https://doi.org/10.1016/j.petsci.2022.06.010.

[62] Ghosh P, Sharma H, Mohanty KK. ASP flooding in tight carbonate rocks. Fuel 2019;241:653–68. https://doi.org/10.1016/j.fuel.2018.12.041.

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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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SUPPLEMENTARY INFORMATION

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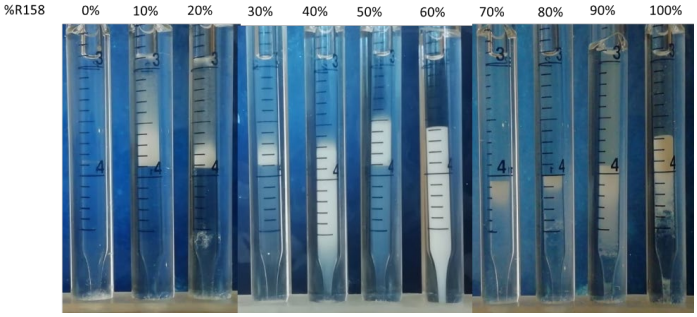


Figure S.1. Blend scan for RECOLAS158/T2EG at 298.15 K under polarized light

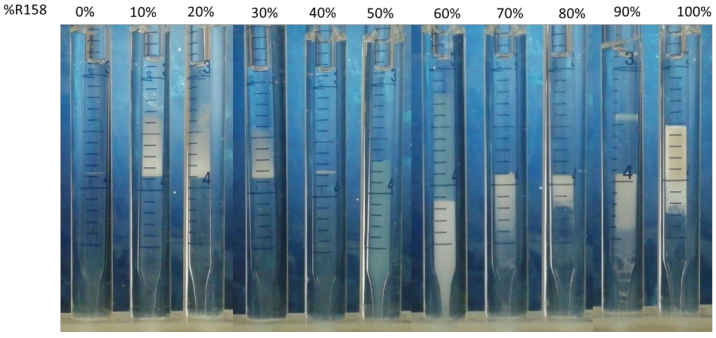


Figure S.2. Blend scan for RECOLAS158/T2EG at 323.15 K under polarized light

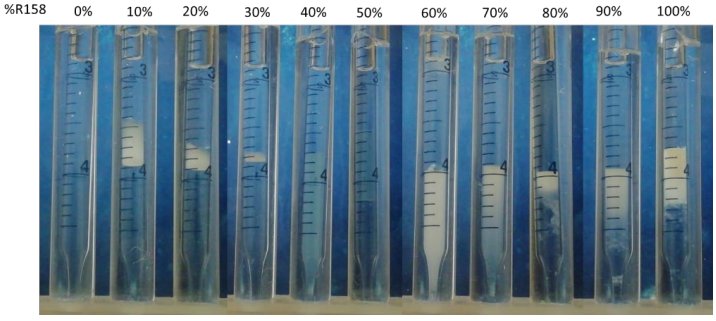


Figure S.3. Blend scan for RECOLAS158/T2EG at 348.15 K under polarized light

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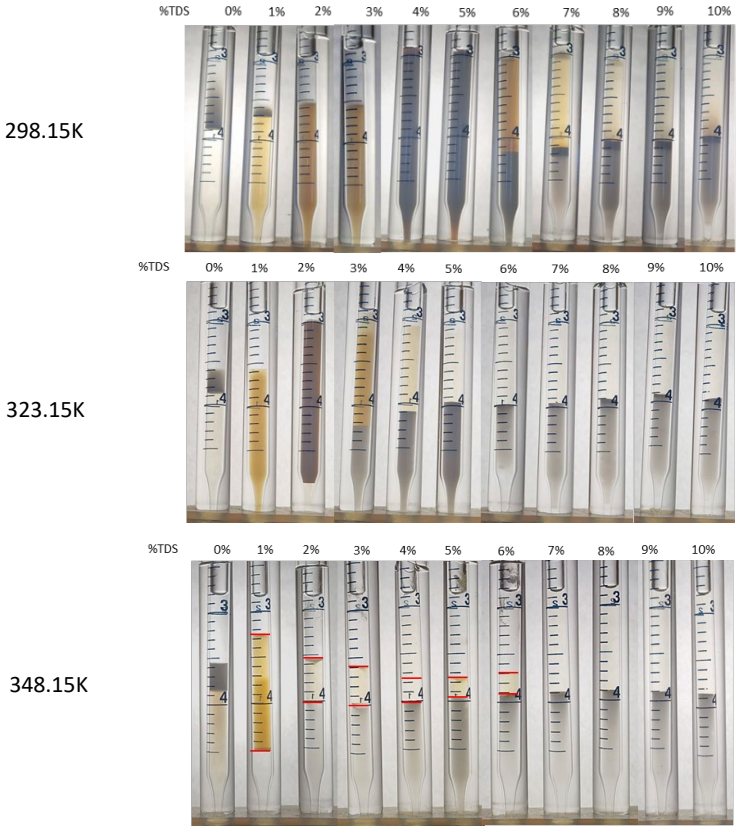
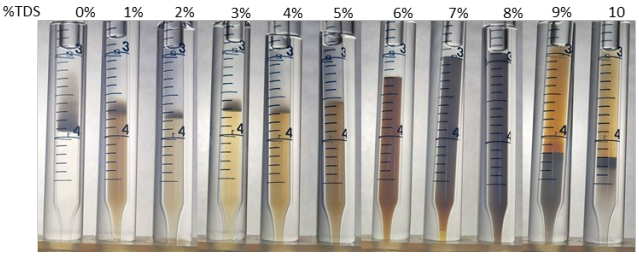


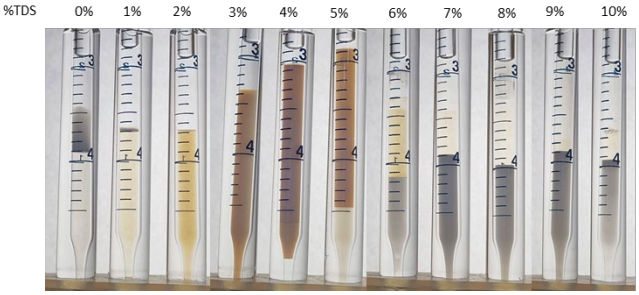
Figure S.4. Salinity scan phase behavior for 64.29% RECOLAS158 + 35.71% T2EG at 298.15 K, 323.15 K and 348.15 K.

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298.15K



323.15K



348.15K

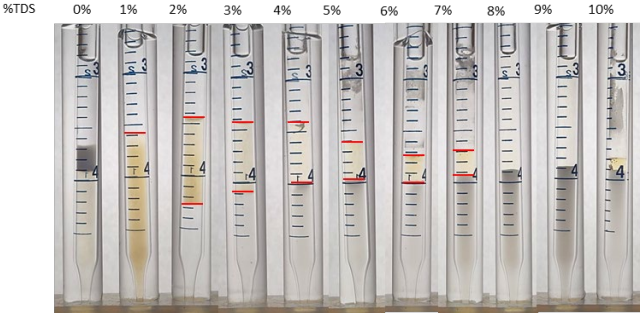


Figure S.5. Salinity scan phase behavior for 56.40% RECOLAS158 + 43.60% T2EG at 298.15 K, 323.15 K and 348.15 K.

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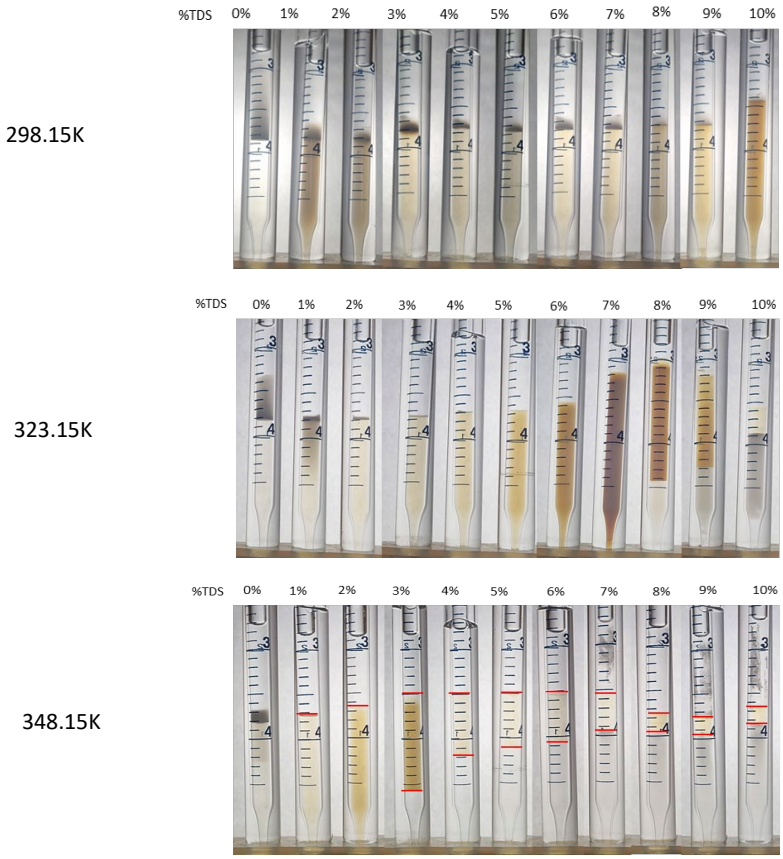


Figure S.6. Salinity scan phase behavior for 48.89% RECOLAS158 + 51.11% T2EG at 298.15 K, 323.15 K and 348.15 K.

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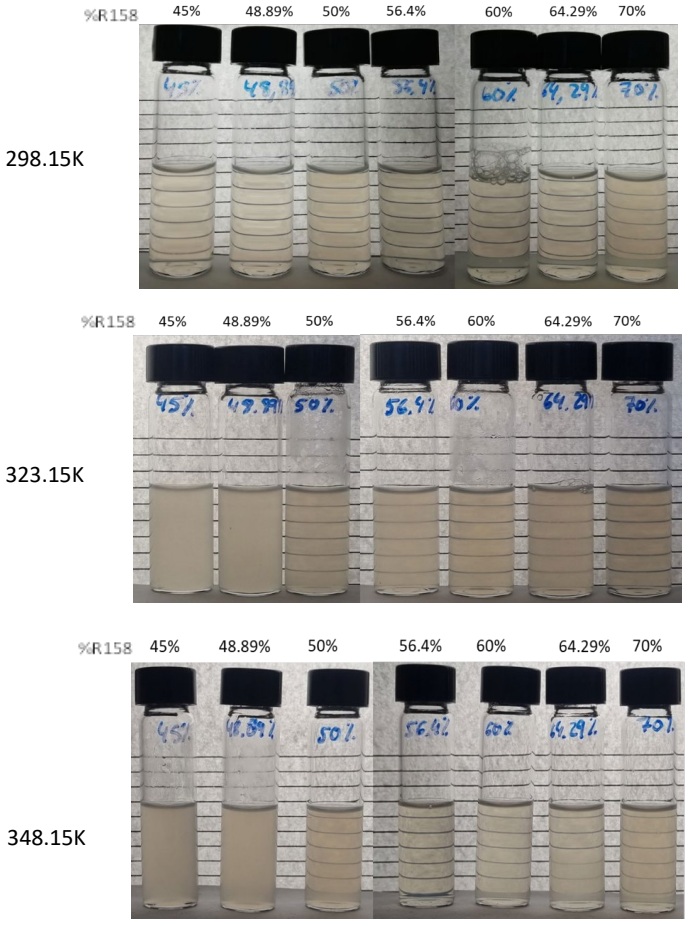


Figure S.7. Solubility of different blend ratios RECOLAS158/T2EG in SSW at 298.15 K, 323.15 K and 348.15 K.

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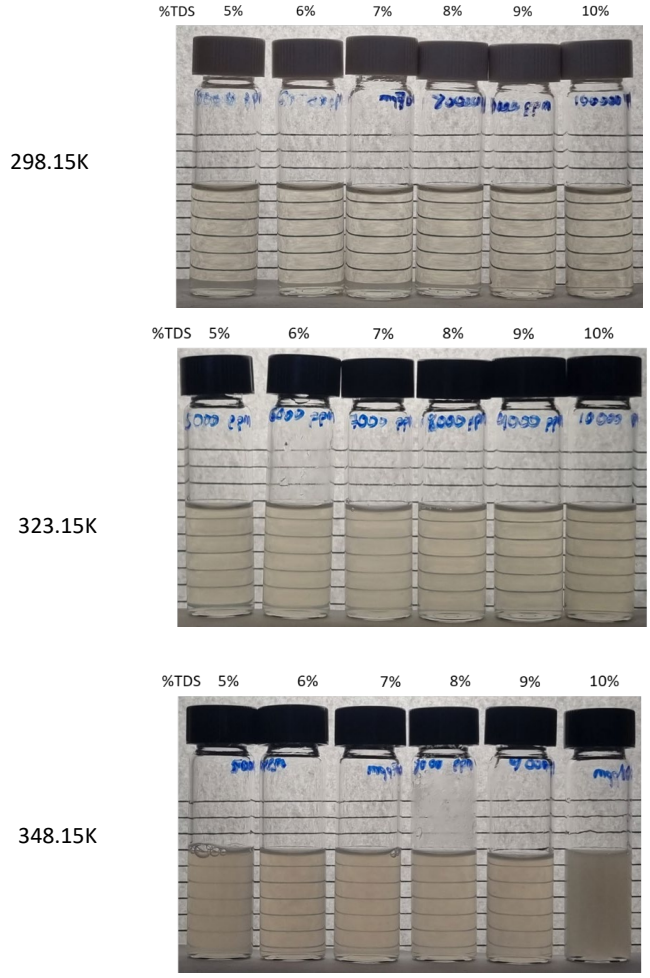


Figure S.8. Solubility of 56.4% RECOLAS158 + 43.6% T2EG in brines with different TDS at 298.15 K, 323.15 K and 348.15 K.

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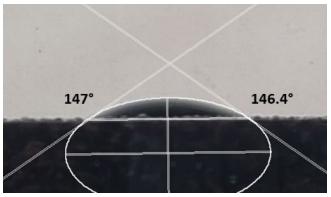
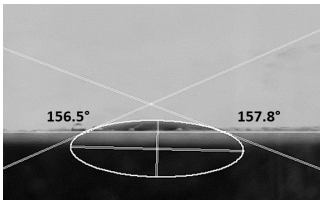
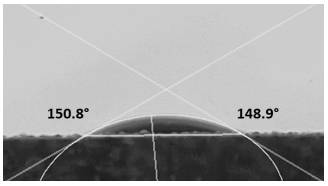
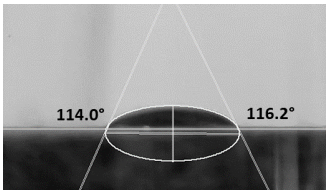
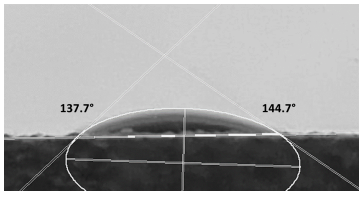
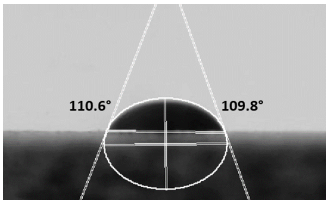
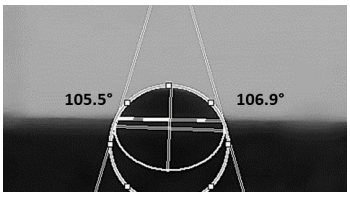
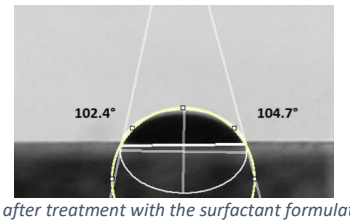
	323.15 K	348.15 K
Day 0		
Day 3		
Day 7		
Day 14		

Figure S.9. Contact angle evolution with time of oil-wet rock after treatment with the surfactant formulation at 323.15 K and 348.15 K.

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Table S1. CMC at 298.15 K and surface tension at CMC of the blend and its constituents 298.15K*

Compound	CMC (mg/L)	Surface tension (mN/m)
RECOLAS158	19.31	42.01
T2EG	36.32	45.34
56.4% RECOLAS158 + 43.6% T2EG	13.99	45.11

*Surface tension was determined using the Wilhelmy plate method in a Krüss K11 tensiometer.

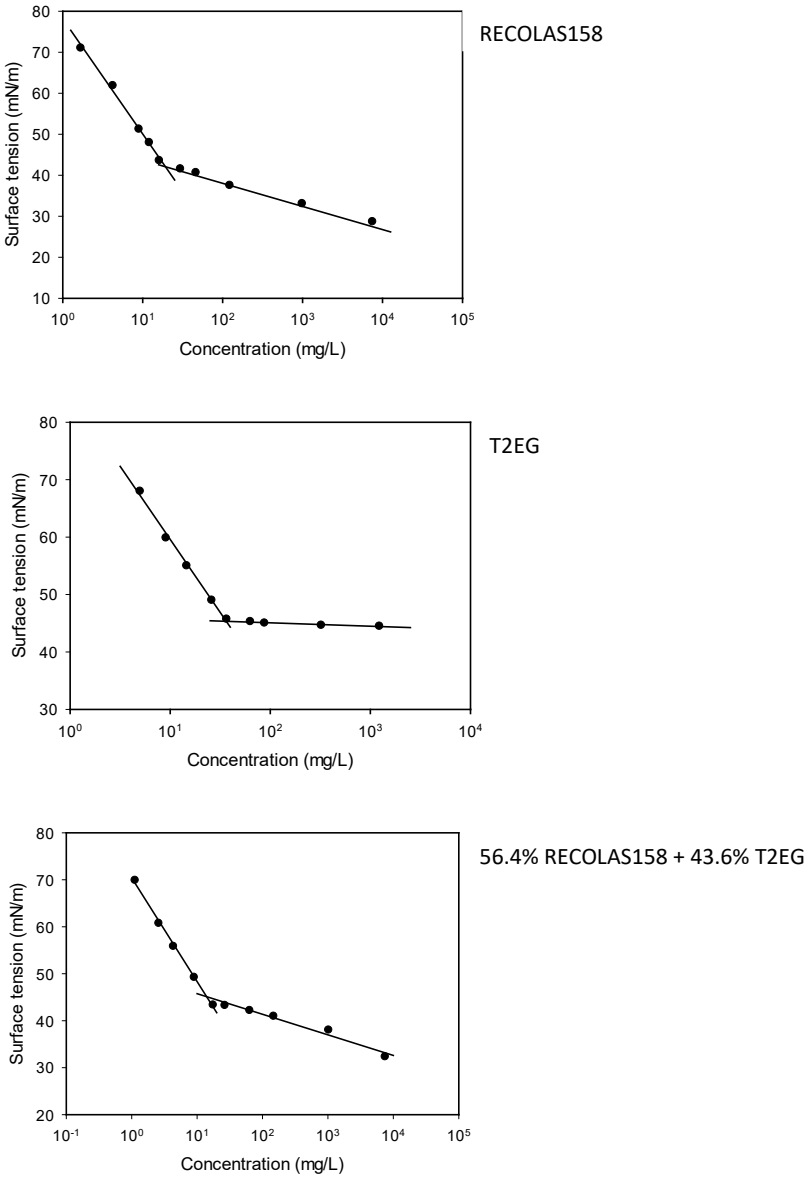


Figure S.10. Critical micelle concentration of the blend and its constituents 298.15K

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Experimental evaluation of foams stabilized by ionic liquids for enhanced oil recovery

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CO_2 sequestration

ABSTRACT

Foam injection has the potential to improve CO_2 enhanced oil recovery (EOR) and simultaneous CO_2 sequestration processes by increasing sweep efficiency. However, the stability of the foam remains a challenge specially at harsh conditions of temperature, pressure, and salinity. Surface-active ionic liquids (SAILs) are promising chemicals that usually exhibit high surface activity, salinity tolerance, and thermal stability. This study investigates the performance of SAILs to produce foam for CO_2 EOR in two high salinity reservoirs (A and B). Both reservoirs are at high salinity conditions with salinities of 125,356 mg/L and 255,470 mg/L. Half-life time and initial foam height were considered to represent foam stability and foaming ability, respectively. An optimal formulation of 0.5 wt% [C_{16}mim]Cl was selected for reservoir A conditions, whereas 0.5 wt% [C_{16}Py]Cl and 0.5 wt% [C_{16}mim]Cl formulations were studied for reservoir B conditions. Foam mobility was measured at a quality of 80% to test the validity of the proposed formulations. A promising half-life of 7.8 days was obtained for [C_{16}mim]Cl at Reservoir A conditions in high-pressure stability tests, several times higher than those reported in literature for traditional surfactants. Mobility reduction factors higher than 300 were reported for all the cases, with the most promising result (1229) achieved for [C_{16}mim]Cl at Reservoir A conditions. These results indicate that strong foams can be generated at high salinity conditions using SAILs. This work shows the promising possibilities of SAILs to improve the sweep efficiency in CO_2-EOR methods and enhance the gas trapping in sequestration processes.

1. Introduction

Primary and secondary stages of oil production from conventional reservoirs produce an average of 30% of original oil in place, leaving a high percentage of oil behind [1]. With the decline in oil production from mature reservoirs and the global oil demand set to increase, improving oil recovery is still a major issue. In this context, tertiary or enhanced oil recovery (EOR) methods are developed to improve oil production. EOR techniques usually involve injection of chemical solutions (surfactant or polymer EOR), gases (miscible or immiscible EOR), or high-temperature fluids such as steam or hot water (thermal EOR) [2]. Gas flooding is a widely used EOR method; oil can be displaced by different gases, such as, carbon dioxide, hydrocarbon gas, nitrogen, or flue gas [3]. In this context, CO_2 injection is attracting new market interests since it is considered a promising way to ensure cost-efficient avoidance of CO_2 emissions to atmosphere. This technology can generate a product with a strong economic value while it can also sequester CO_2 in underground formations previously occupied by oil [4]. However, the large viscosity contrast between gas and both oil and water during CO_2 injection usually results in early gas breakthrough and poor sweep efficiency. Even in CO_2 sequestration in aquifers, viscous fingering phenomenon is also a significant challenge, as it can impact the long-term storage capacity in underground formations. Injection of gas in the form of foam can help to overcome these issues [5].

Foam is a dispersion of gas bubbles in a water phase produced in the presence of a foaming agent (surfactant). Each bubble is separated by thin liquid films called *lamellae* [6]. Foam reduces the mobility of gas by increasing the apparent gas viscosity and reducing gas relative permeability [7]. Several surfactants have been proposed to stabilize foams in field applications [8]. However, stability of the foam at harsh conditions of temperature, pressure and salinity is still a challenge. At these conditions, the rapidly thinning out of the *lamellae* by film drainage and pressure difference between bubbles cause inter-bubble gas diffusion and subsequent bubble rupture (coalescence), thus de-stabilizing the

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foam. A limited number of studies have been conducted on CO_2 foam performance under harsh reservoir conditions. Some authors [9–13] studied the influence of temperature and pressure on CO_2 foams stabilized by surfactants through foam stability and foam mobility tests. As a general conclusion, all the studies agreed that foam lifetime decreases with temperature, but the effect of pressure was complex to evaluate. Wang et al. [9] found out that the influence of this variable greatly depends on the type of surfactant used. In addition, Zhang et al. [10] and Wang et al. [11] claimed that, at the same conditions, foam stability achieved with higher alkyl chain length was better than with shorter alkyl chain length surfactants. The effect of salinity has also been assessed by several authors [8,14,15]. Studies agreed that foam stability is higher at higher salt concentrations due to the reduction of the electrostatic repulsion between surfactant molecules making the *lamellae* rigid. Nevertheless, in all these studies, half-life time of CO_2 foams stabilized with surfactants did not exceed 300 min. Therefore, it is desirable to develop CO_2 aqueous foams with improved stability at high temperature, salinity, and pressure conditions.

Recently, some researchers have investigated the use of ionic liquids (ILs) as alternative chemicals in enhanced oil recovery processes [16–18]. Surface active ionic liquids can reduce the surface tension of water to about 30–40 mN/m [19]. The water-crude oil interfacial tension can be reduced to about 1 mN/m from about 40 mN/m by the addition of ionic liquids [20]. These compounds are salts with melting or glass transition temperatures below 100 °C. Their negligible vapor pressure, high thermal stability and high solvating capacity makes them ideal compounds for the application. In addition, cations and anions of these salts can be selected to design task-specific compounds that meet the requirements of each specific reservoir. In comparison to traditional surfactants, it has been proven that ILs show advantages regarding stability at high salinity and temperature conditions [20,21]. In this context, ILs seem promising candidates to overcome stability problems of CO_2 foams.

Only a few researchers have investigated the use of ILs in EOR foam applications. Hu et al. [22] and Ouyang et al. [23] studied the effect of imidazolium ILs structure on foam features using Density functional theory (DFT) simulations and foam stability experiments. They concluded that the introduction of hydroxyl groups and longer alkyl chain lengths in the imidazolium cation was favorable for foam features. More applied approaches can also be found in the Literature. Sakthivel and Salin [5] studied the use of imidazolium ILs, with varying alkyl chain length, as additives to a non-ionic surfactant to improve foam stability. They performed bulk and porous-scale dynamic foaming experiments at high-pressure (2200 psi) and high-temperature (80 °C). Stability of the foam in the presence of IL increased by more than 50% compared to their neat surfactant solution. They also concluded that, as in the case of traditional surfactants, longer alkyl-chain exhibited higher stability and higher foamability than shorter alkyl-chain ILs. However, even though they tested different gases in bulk foam experiments, they only worked with N_2 in porous media tests. Deep eutectic solvents (DESs), constituted by choline chloride and two short-alkyl chain imidazolium ILs, were employed by Hanamertani et al. [24] as additives to a mixture of anionic and amphoteric surfactants. Bulk foam experiments at ambient and high temperature (80 °C) were performed to study foam stability. Results showed that ILs and DESs were able to improve surfactant foam stability. In their subsequent work [25], the most promising ILs and DESs were tested on dynamic foam mobility test using N_2 as the foaming gas. Unfortunately, permeability of the core, flow rate and temperature and pressure conditions were not reported. All these results provide an indication of the capability of ILs to reduce gas mobility and increase mobility reduction factor during injection processes.

In this paper, six surface-active ILs (SAILs) with the most common functional groups are tested for CO_2 foam EOR. The influence of the alkyl chain length and ethoxylation degree on the SAILs performance is analyzed. Two different reservoir conditions are evaluated: Reservoir A (63 °C, 125,356 mg/L salinity, and 1910 psi) and Reservoir B (40 °C, 255,470 mg/L salinity, and 1000 psi). Aqueous stability and bulk foam stability experiments at ambient pressure are carried out, aiming to test the performance of the different foams and select the most promising SAILs. Finally, the effectiveness of the proposed SAIL formulations is evaluated via high-pressure stability studies and foam mobility tests. Air but also, for the first time, CO_2 is selected as foaming gas in combination with SAILs. Foam apparent viscosity and mobility reduction factor are determined. This work offers a significant advance in the application of SAILs in CO_2 EOR processes.

2. Materials and methods

Six different cationic SAILs with the most common functional groups (ammonium, imidazolium and pyridinium) were selected for this study. Cocosalkylpentaethoxymethylammonium methylsulfate (C1EG) and N, N-diethoxylated-N-tallow-N-ethylammonium ethylsulfate (T2EG) were supplied by Iolitec with a purity > 95 wt%. T2EG has a higher alkyl chain length and ethoxylation degree than C1EG which results in higher hydrophilicity compared to C1EG. Two different alkyl chain lengths (C_{12} and C_{16}) were studied for pyridinium and imidazolium SAILs. N-Dodecylpyridinium chloride (purity ≥ 93 wt%) and hexadecylpyridinium chloride monohydrate (purity ≥ 99 wt%) were purchased from Sigma Aldrich. 1-Hexadecyl-3-methylImidazolium chloride and 1-Dodecyl-3-methylimidazolium bromide both with a purity > 98 wt% were supplied by Iolitec. Their most important characteristics are listed in Table 1. Density and viscosity at 25 °C and atmospheric pressure were determined for liquid compounds using an Anton Paar DMA 5000 M density meter and an Anton Paar LOVIS 2000 ME microviscometer, respectively. Before measuring physical properties, water content of the corresponding SAILs was measured using Karl-Fischer titration in a Metrohm 899 coulometer. Water content values of 896.1 ppm and 723.3 ppm were obtained for C1EG and T2EG, respectively.

The application of these chemicals in the conditions of two different reservoirs was studied in this paper. Reservoir A is in Canada and its conditions are 63 °C and 1910 psi. Reservoir B is located in Michigan (United States) and it is characterized by a temperature of 40 °C and a pressure of 1000 psi. Formation brines of each reservoir were prepared by dissolving different amounts of salts in distilled water with the compositions shown in Table 2. They are both high salinity reservoirs. Sodium chloride, potassium chloride, calcium chloride dihydrate, magnesium chloride hexahydrate, sodium carbonate and sodium bicarbonate were ACS certified and purchased from Fisher Chemicals.

CO_2 with a purity of 99.9 wt% was purchased from Linde Gas & Equipment. Ottawa sand F95 was used in sand-packs; it was obtained from US Silica.

2.1. Compatibility tests

The compatibility of SAILs with Canada and Michigan brines, at both ambient and reservoir temperatures, was evaluated. To that aim, 10 mL of 0.5 wt% SAIL in the corresponding formation brine were prepared in glass vials and visually monitored for 1 week. To check the stability at reservoir conditions, the vials were placed in an oven operating at 40 °C (B) or 63 °C (A). Optically clear samples were considered stable, while cloudy or precipitated samples were considered unstable.

2.2. Static foam experiments

Static foam experiments were performed to compare the foaming ability of the proposed SAILs. These tests are a fast-screening method to evaluate the suitability of the different surfactants for the application. In this study, initial foam height and foam stability were assessed over time. Two foaming gases were screened: air and CO_2. Experiments were performed at 40 °C (B) and 63 °C (A) according to each reservoir temperature.

Foam was prepared according to the methodology developed in

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Table 1
SAILs used in this study.

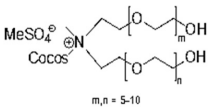
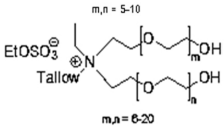
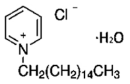
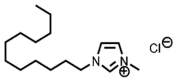
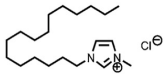
Abbreviature	Compound	Chemical structure	Appearance	Molecular Weight (g/mol)	CMC	Density at 25 °C (g/cm^3)	Viscosity at 25 °C (mPa·s)
C1EG	Cocosalkylpentaethoximethylammonium methylsulfate		Liquid	Not available	88.1 mg/L [26]	1.085466	2477.6
T2EG	N,N-Diethoxylated-N-tallow-N-ethylammonium ethylsulfate		Liquid	Not available	36.32 mg/L [27]	1.077613	609.25
[C_{12}Py]Cl	N-Dodecylpyridinium chloride		Solid	283.88	15.27 mmol/L[28]	-	-
[C_{16}Py] Cl·H_2O	Hexadecylpyridinium chloride monohydrate		Solid	358.00	1.22 mmol/L [29]	-	-
[C_{12}mim]Br	1-Dodecyl-3-methylimidazolium bromide		Solid	331.34	10.6 mmol/kg[30]	-	-
[C_{16}mim]Cl	1-Hexadecyl-3-methylimidazolium chloride		Solid	343.00	0.99 mmol/L [29]	-	-

Table 2
Formation brines composition.

Ion	Reservoir A (Canada)	Reservoir B (Michigan)
Na^+	29,900 mg/L	51,802.3 mg/L
K^+	4210 mg/L	5286.32 mg/L
Ca^{2+}	12,000 mg/L	32,697.7 mg/L
Mg^{2+}	2020 mg/L	5898.2 mg/L
Cl^-	79,000 mg/L	152,318 mg/L
HCO_3	896.7 mg/L	152.5 mg/L
SO_4^{2-}	690 mg/L	4763.505 mg/L
Total salinity	125,356 mg/L	255,470 mg/L

previous studies [31,32]. 2 mL of 0.5 wt% SAIL solution in the corresponding brine were placed in sealed tubes of 15 mL. The tubes were heated in an oven for several hours until reaching the target temperature. Foam was produced by hand shaking the solution for 2 min until foam height was constant. The decay of foam volume was monitored as a function of time until the foam disappeared. The time for which the volume of foam is reduced to half of its original volume is known as the half-life time. Experiments were repeated twice to ensure repeatability and average half-life time and initial foam height were reported.

2.3. Gas-surfactant co-injection experiments

The experimental set-up used for high pressure stability and foam mobility tests is shown in Fig. 1. The equipment contained two ISCO pumps and two accumulators for SAIL solution and CO_2 injection. A sand-pack and a high-pressure view cell were connected in two parallel circuits to work with one of them while keeping the other circuit closed. A back pressure regulator (BPR) was used to maintain the system pressure at either 1000 or 1910 psi. All the equipment was kept inside an oven to perform experiments at the reservoir temperature (40 °C or 63 °C). A pressure transducer was used to monitor pressure drop.

2.3.1. High pressure stability study

Promising SAILs according to static foam experiments were tested by means of high-pressure stability tests. Bulk foam experiments were carried out in a high-pressure view cell to check foam stability at reservoir conditions of pressure and temperature. For these experiments, the system was initially vacuumed for 2 h and then pre-flooded with surfactant solution at a constant injection rate of 5 mL/min. Subsequently, pressure of the system was increased to the target pressure. Surfactant formulation and CO_2 gas were co-injected through a foam generator into the high-pressure view cell. A 7 μm filter was used as foam generator. Flow rates of 0.4 mL/min of surfactant solution and 1.6 mL/min of CO_2 were stablished for a nominal foam quality of 80%. Surfactant concentration was set to 0.5 wt% in the corresponding brine. Pictures of the high-pressure cell were taken inside the oven at different times. The foam height above the liquid was determined using image analysis software. Half-life time was calculated as the time for which the foam is reduced to half of its original volume.

2.3.2. Foam mobility test

Foam-flow experiments were performed in a sand-pack to investigate the ability of the foam created by the most promising SAILs to reduce mobility at reservoir conditions. The primary objective was determining the steady state pressure drop across the sand-pack, to estimate the mobility reduction factor (*MRF*) and apparent foam viscosities (μ_{af}). To that aim, a vertically oriented stainless-steel column, 30.48 cm length and 2.225 cm internal diameter, was uniformly packed with dry sand.

After packing the sand column tightly, pore volume (PV) and permeability of the sand-pack were determined. To this effect, the column was vacuumed for 24 h and flooded with distilled water at constant pressure. *PV* was calculated by measuring the volume of water required to saturate the column. The saturated sand-pack was then flooded with distilled water, at different flow rates, to record the corresponding pressure drops and determine the absolute permeability using Darcy's law. Water was removed by heating and vacuuming the sand-pack.

The sand-pack was then introduced in the equipment, vacuumed for 2 h, and pre-flooded with 2 PV of surfactant solution at a constant

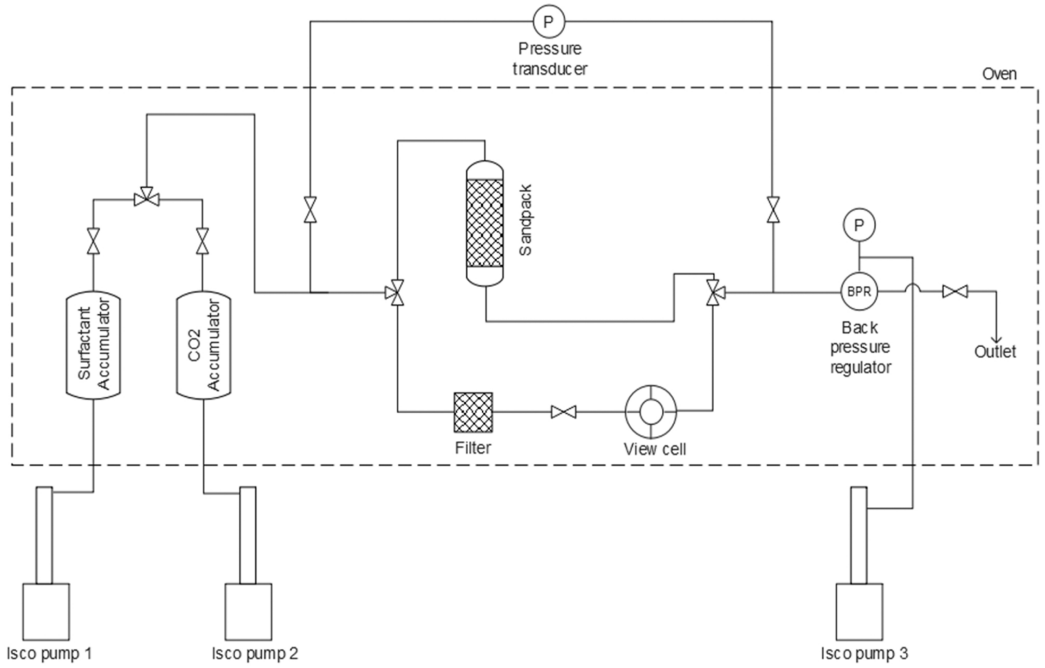


Fig. 1. Experimental set-up for high pressure stability and foam mobility tests.

injection rate of 5 mL/min (to avoid the influence of surfactant adsorption in the subsequent experiments). Surfactant concentration in formation water was 0.5 wt%. Pressure of the system was increased to the target pressure. Subsequently, CO_2 and surfactant formulation were co-injected at 80% foam quality from the top of the sand-pack. Total flow rates of 0.122 mL/min (4 ft/day) and 0.304 mL/min (10 ft/day) were studied. Pressure drop (ΔP) was recorded using a pressure transducer until it remained constant. Distilled water was injected through the sand-pack at a constant pressure after each test to clean it. Permeability was checked to ensure its consistency through the different experiments.

MRF is defined as the ratio of the pressure drop in the presence of foam to the pressure drop during surfactant solution injection [33], i.e.,

$$MRF = \frac{\Delta P_{surf+gas}}{\Delta P_{surf}}. \quad (1)$$

The effective viscosity of the foam, μ_{af} was calculated using (based on Darcy's law):

$$\mu_{af} = \frac{\Delta P_{surf+gas} \cdot k \cdot A}{q \cdot L}, \quad (2)$$

where k is the absolute permeability of the porous medium, A and L are the area and length of the sand-pack and q is the total flow rate of surfactant and gas.

3. Results and discussion

3.1. Compatibility tests

The compatibility of six different SAILs in the formation brines shown in Table 2 was tested at various conditions. As it can be seen in Fig. 2, no precipitation or cloudiness was observed for any SAIL at the

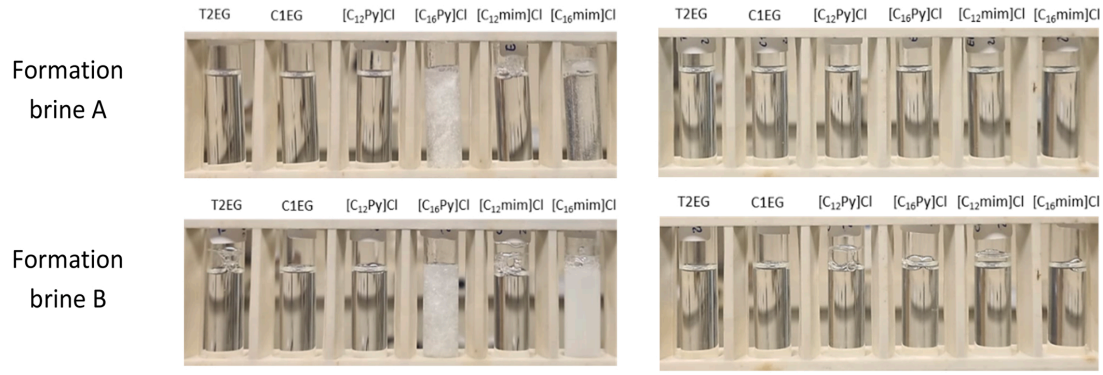


Fig. 2. Stability tests. Pictures taken after 1 week.

reservoir temperature after one week. However, [C_{16}mim]Cl and [C_{16}Py]Cl precipitated after one week at the ambient temperature in both brines. The aqueous solubility of ILs generally increases with temperature [34] and decreases with the alkyl chain length size [35]. Since all the SAILs were stable at reservoir temperature, they were considered for further tests.

3.2. Static foam experiments

Static foam experiments were performed to compare foam ability and bulk foam stability of SAIL formulations. Foams are thermodynamically unstable, and eventually collapse due to gravity drainage of the liquid film and diffusion through gas bubbles, also known as Ostwald ripening. When ionic surfactants like the SAILs tested in this paper are used as surface active agents, the liquid film is charged. Therefore, the overlapping of similarly charged electric double layers opposes film thinning, thus strengthening the stability of foam [36]. Foaming ability was measured by means of the initial foam height (H_0), and half-life time was used to determine foam stability. The study was performed for the two reservoir (A and B) conditions of salinity and temperature. SAIL concentration was fixed at 0.5 wt%, as it is a typical surfactant concentration used in field applications [31]. Two different foaming gases (air and CO_2) were studied. Measurements were repeated twice, and mean deviation was less than 10% for half-life time results and less than 5% for H_0 values.

Table 3 shows H_0 values and half-life times for the different SAILs at reservoir A conditions. Air based foams were found more stable than CO_2 foams, as it was expected due to the higher solubility of CO_2 in the foaming solution [5]. Solubility of gases in water has a negative effect on foam stability because it can accelerate the foam coalescence [9]. The effect of the different SAILs on the analyzed parameters was the same regardless of the foaming gas. Focusing on CO_2 EOR, due to the environmental benefits of the method, the discussion in this section refers to the numerical values of CO_2 foam. A H_0= 5.75 cm and half-life time of 5.27 min were achieved with the SAIL [C_{16}mim]Cl. Half-life time was significantly lower (0.69 min) in the case of [C_{12}mim]Br, but H_0 was remarkably higher (9.95 cm). A similar result was obtained with the SAILs [C_{16}Py]Cl and [C_{12}Py]Cl. Therefore, longer alkyl chain length compounds resulted in a lower foaming ability, but a higher stability. These results are in agreement with other studies previously carried out with different ILs. Hu et al. [22] studied the foaming performances of different alkyl chain length imidazolium ILs. They found that the H_0 was lower for C_8 than for C_6 ILs. They claimed that this reduction is probably caused by the increase of hydrophobic groups, that leads to the decrease of solubility in water, resulting in an inferior foaming performance. They also concluded that the longer the alkyl chain length, the higher the foam stability. Zhang et al. [37] found that the longer the alkyl chain length, the stronger is the interaction between molecules, resulting in greater external forces required for the bursting of foam, and therefore a more stable foam. Comparing SAILs functional groups, pyridinium SAILs showed better foaming ability, but lower stability than imidazolium compounds.

C1EG and T2EG are two quaternary ammonium SAILs. Half-life time (0.34 min) and H_0 (4.35 cm) of T2EG were lower than for C1EG (0.47 min and 11.15 cm). Although T2EG has longer alkyl chain length than C1EG, the higher ethoxylation degree results in higher hydrophilicity. This increase in hydrophilicity, is believed to cause the weakening of the arrangement of surfactant molecules at the interface, due to the strong interactions with water, and thereby weaken the liquid film of the foam [8].

Ideally, a surfactant for EOR should have both, good foamability and foam stability. However, in some cases, it may be necessary to prioritize one property over the other [38]. In general, when dealing with high temperature, pressure or salinity conditions, foam stability may become a more critical factor to consider, as the high temperature and salinity can cause surfactant degradation and lead to foam collapse over time [9]. As a result, selecting a surfactant with good stability properties, can help to improve the longevity and effectiveness of the foam in the reservoir. For this reason, [C_{16}mim]Cl was selected as the most promising SAIL for reservoir A conditions since it showed the highest half-life time and acceptable initial foam height.

In Table 4 results of H_0 and half-life time for the different SAILs at reservoir B conditions are shown. Reservoir B temperature is lower (40 °C) and salinity higher (255,470 mg/L TDS) than reservoir A (63 °C and 125,356 mg/L TDS). As a general remark, the results from these tests indicate that foaming ability decreases and foam stability increases when switching from reservoir conditions A to B. It is known that temperature has little impact on foaming ability, whereas it significantly affects foam stability. Nonetheless, as general rule, the higher the temperature, the less stable is the foam [39]. On the other hand, salinity is a major factor affecting foam ability and stability due to the interaction between electrolytes and surfactant molecules at the interface [8]. Several authors have studied the effect of salinity on foam performance. Kumar and Ghosh [40] have tested several surfactants and reported the existence of an optimum salinity for each compound. They showed that a minimum surface tension of the aqueous solution is the key parameter for good foaming. A little increase in foam height at very low concentrations of NaCl was observed. However, NaCl decreased the foam height at moderate and higher concentrations. Varade and Ghosh [15] and Behera et al. [41] found out that H_0 decreases with the increase of salt concentration. The reason for this reduction in foam volume is proposed to be the fast coalescence rate of bubbles due to the reduction in the electrostatic double layer repulsion. Xu et al. [14] found that stability increases with salt concentration due to the formation of smaller and more stable bubbles. They claimed that high salt concentrations reduce the electrostatic repulsion between surfactant molecules, which facilitates its adsorption on the film, making the lamellae rigid. As a result, the film thinning rate is reduced and stability increased. These findings are in accordance with our results. Foaming ability was found lower and foam stability higher at the lower temperature and higher salinity conditions.

[C_{16}mim]Cl and [C_{16}Py]Cl gave the higher foam stability at reservoir B conditions. However, [C_{16}mim]Cl initial foam height was considered too low. Considering that salinity is the major factor affecting foam ability, a new attempt using half the concentration of the formation brine at the same temperature was made. Table 5 shows the results of

Table 3
Static foam test results for reservoir A.

	[C_{16}mim]Cl	[C_{16}Py]Cl	[C_{12}mim]Br	[C_{12}Py]Cl	C1EG	T2EG
	Air					
H_0 (cm)	6.5	7.25	9.3	10.5	11	4.15
Half-life (min)	21.80	17.20	2.53	1.24	1.99	0.72
	CO_2					
H_0 (cm)	5.75	5.9	9.95	12.05	11.15	4.35
Half-life (min)	5.27	3.58	0.69	0.53	0.47	0.34

Table 4
Static foam test results for reservoir B.

	[C_{16}mim]Cl	[C_{16}Py]Cl	[C_{12}mim]Br	[C_{12}Py]Cl	C1EG	T2EG
	Air					
H_0 (cm)	2.35	4.95	10	10.45	8.35	2.85
Half-life (min)	81.25	54.74	7.81	4.72	6.13	16.64
	CO_2					
H_0 (cm)	2.95	4.6	10.15	11.85	8.65	5.35
Half-life (min)	8.60	3.37	1.94	1.58	0.87	0.67

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Table 5
Static foam test results for reservoir B using half concentration of formation brine.

	$[C_{16}mim]Cl$	
	Air	CO_2
Height (cm)	3.8	3.95
Half-life (min)	19.47	4.36

static foam tests for $[C_{16}mim]Cl$ at these new conditions. The salinity decrease caused a reduction in half-life time from 8.60 min to 4.36 min. However, initial foam height was increased from 2.95 cm to 3.95 cm. For reservoir B, further tests were performed using $[C_{16}Py]Cl$ and $[C_{16}mim]Cl$ with half formation brine salinity.

Although stability tests were not performed in the presence of crude oil, it should be mentioned that crude oil can negatively impact foam stability by reducing surface tension, destabilizing foam lamellae, and coalescing foam bubbles. This can result in a decrease of foam height, shorter foam lifetime, and therefore lower foam stability [42]. Further studies, out of the scope of this paper, are required to determine the compatibility of the foam with crude oil. Regarding adsorption in porous media, Nandwani et al. [43] studied the adsorption mechanism of several SAILs (imidazolium, pyridinium and pyrrolidinium) on different rock types under high salinity conditions. Lower adsorption of SAILs was observed for crushed carbonate than for sandstone samples, reporting lower values than those found for the conventional cationic surfactant CTAB. The imidazolium-based SAIL showed the minimum adsorption among the SAILs studied. They concluded that the increase of temperature and salinity, leads to a decrease of the amount of SAIL adsorbed on both types of rocks. Electrostatic repulsion is the basic mechanism for low adsorption of SAILs in carbonate rocks.

3.3. High pressure stability study

In order to use foams in tertiary oil production, the dispersion of CO_2 bubbles in surfactant solution must be stable at the harsh conditions of the studied reservoirs, including not only high salinity and temperature but also high pressure. For this reason, bulk foam experiments at pressure conditions of each reservoir (1910 psi for A and 1000 psi for B) were performed in a high-pressure cell to determine foam stability. Fig. 3 shows the stability study for $[C_{16}mim]Cl$ at reservoir A conditions. Rate of foam decay was low and half-life time was estimated as 7.8 days, several times higher than those reported in literature for regular surfactants at similar conditions [11]. Figs. 4 and 5 present the high pressure stability study at reservoir B conditions for $[C_{16}Py]Cl$ and $[C_{16}mim]Cl$ (half formation brine salinity), respectively. Half-life time for $[C_{16}Py]Cl$ was estimated as 0.98 h and for $[C_{16}mim]Cl$, 4.5 h. Salinity has a positive effect in foam stability. Although salinity was lower in the case

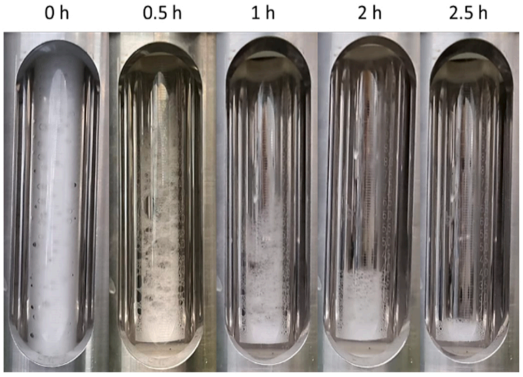


Fig. 4. High pressure stability study of $[C_{16}Py]Cl$ for reservoir B project.

of $[C_{16}mim]Cl$, foam stability was 4 times higher than for the pyridinium IL. Foams produced with the imidazolium SAIL showed smaller bubbles and a more uniform bubble size distribution than in the case of the pyridinium SAIL. Generally, more uniform and smaller bubble sizes lead to high stability of the foam due to reduced Ostwald ripening and coalescence [44].

Foam stability of $[C_{16}mim]Cl$ at reservoir A conditions is considerably higher than for reservoir B conditions. It should be noted that in both cases salinity is ~125,000 ppm of TDS since half concentration of reservoir B formation brine was applied. Reservoir A conditions of pressure and temperature (63 °C and 1910 psi), unlike reservoir B conditions (40 °C and 1000 psi), are above the CO_2 critical point (31.1 °C and 1068.93 psi). When temperature and pressure conditions exceed this critical point, gaseous CO_2 transformed into a liquid-like fluid with a density significantly higher than that of gaseous CO_2, thus reducing the water drainage from *lamellae* [45].

It is known that as pressure increases, the solubility of CO_2 in brine increases according to Henry's Law, with a negative effect on foam stability. However, at high pressures, the density of CO_2 increases due to the compression of gas [9]. The density increase lowers the liquid drainage and stabilizes foam. We observed that the half-life increases with pressure implying that the density effect was more important than the solubility effect for SAIL foams. However, there is no agreement in the literature about how pressure affects CO_2 foams stability. Some authors concluded that stability increases with pressure [10,46], whereas other authors claimed that it decreases [47,48]. Furthermore, Szabries et al. [44] studied foam stability of Triton X-100, a non-ionic surfactant, at 45 °C and for a pressure range of 0–1233 psi. The authors found that, between 0 and 1087 psi, stability decreased with

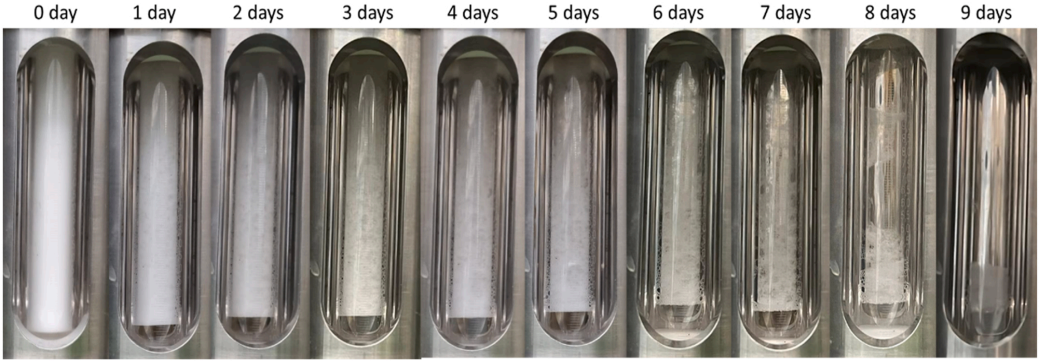


Fig. 3. High pressure stability study of $[C_{16}mim]Cl$ for reservoir A project.

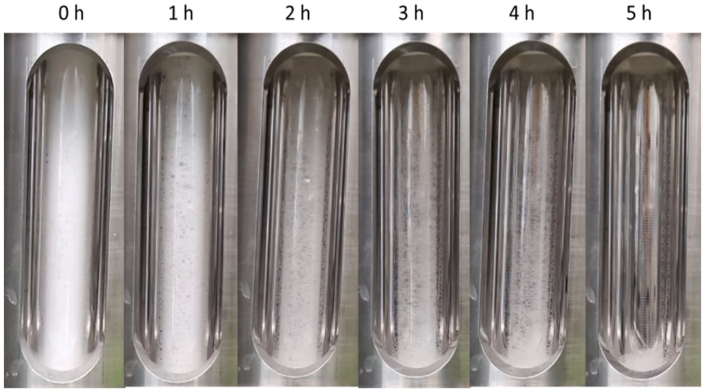


Fig. 5. High pressure stability study of [C_{16}mim]Cl for reservoir B project using half concentration of formation brine.

increasing pressure. However, the contrary behavior was found between 1087 and 1233 psi, and foam stability improved with increasing pressure. In accordance with our results, Zhang et al. [10] found out that foams of tertiary amines were more stable with rising CO_2 density.

The behavior of CO_2 foam stability with pressure is complex, with different classes of surfactants behaving differently with pressure. Wang et al. [9] and Zhang et al. [10] concluded that the effect of pressure on foam stability depends on the hydrophilic-lipophilic balance (HLB) of the surfactant used. The solvation of hydrocarbon tails increases with the density of CO_2, as it becomes more hydrophobic. As a result, strong surfactant hydrophilic heads are needed to balance this interaction. However, if the surfactant is too hydrophilic it can be embedded into the water phase and weaken the liquid film. On the contrary, surfactants with low HLB values can disorder the arrangement of surfactant molecules leading to unstable foams. In conclusion, for surfactants with relatively high HLB values, high pressures can increase the interaction between surfactant molecules and CO_2, making the foam to be at the most stable state. In this state, the arrangement of the molecules at the interface is tightened and foam stability is improved by reducing water drainage and gas diffusion [9]. In this study, [C_{16}mim]Cl and [C_{16}Py]Cl are two hydrophilic surfactants with long carbon chains, therefore the hydrophilicity is not as high as for other surfactants with shorter alkyl chains. For the three cases studied, stability was improved with increasing pressure comparing half-life time at atmospheric (Section 3.2) and reservoir pressure. In addition, the highest stability was reported for the highest reservoir pressure (reservoir A).

3.4. Foam mobility test

Foam-flow experiments in the absence of oil were conducted in a vertically oriented sand-pack column. Pore volume, porosity and permeability of the sand-pack are presented in Table 6. SAIL concentration was kept at 0.5 wt%. Experiments were performed at 80% foam quality for each reservoir conditions of pressure and temperature. Total flow rates of 0.122 mL/min (4 ft/d) and 0.304 mL/min (10 ft/d) were studied, however unstable values of pressure difference were observed for 0.122 mL/min. Several researchers [49–52] have investigated the importance of a critical injection velocity (related to a minimum pressure gradient) in porous media for transition from “coarse” to “strong” foam. Injection rate should be greater than the critical injection velocity to obtain a stable foam. The minimum pressure gradient for mobilization of liquid *lamellae* and foam generation depends on different factors such as permeability of the medium, surfactant type and concentration, gas type and foam quality [3]. The velocity of 4 ft/day is likely below the critical velocity of the system, and therefore results were discarded.

Table 6
Sand-pack properties.

Property	Value
Pore volume (mL)	43.84
Porosity (%)	36.99
Permeability (mD)	6828.04

For tests performed at a total injection rate of 0.304 mL/min, values of differential pressure as a function of pore volume (PV) injected are presented in Fig. 6. A steady-state pressure drop was observed after 1–1.4 PV, indicating the absence of plugging. The average final value was used to calculate *MRF* and μ_{af} according to Eqs. 1 and 2. Values of average steady-state pressure drop, *MRF* and μ_{af} for each case studied are reported in Table 7.

The highest pressure drop recorded was 115.97 psi corresponding to [C_{16}mim]Cl at reservoir A conditions. Regarding reservoir B conditions, a differential pressure of 52.86 and 25.60 were obtained for [C_{16}mim]Cl (using half salinity of formation brine) and [C_{16}Py]Cl, respectively. Mobility reduction factor varied from 300 to 1230. In accordance with results from high pressure stability studies, the higher the half-life time the higher the mobility reduction factor in porous media. Foam apparent viscosity was also calculated to characterize foam flow. It should be noted that apparent viscosity of foam depends on foam velocity. The apparent viscosity decreases as the foam velocity increases [53]. This is probably due to the shear-thinning behavior commonly observed in

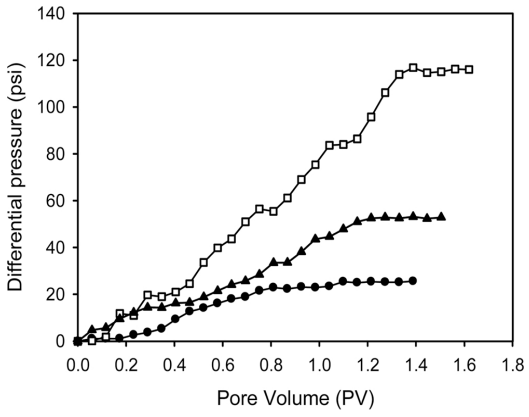


Fig. 6. Foam mobility tests for [C_{16}mim]Cl reservoir A (▫), [C_{16}Py]Cl reservoir B (●) and [C_{16}mim]Cl reservoir B using half concentration of formation brine (▲).

Table 7
Results of sand-pack experiments.

	ΔP (psi)	MRF	μ_{af} (cp)
[C_{16}mim]Cl reservoir A	115.97	1229.01	1356.61
[C_{16}mim]Cl reservoir B (1/2 FB)	52.86	560.19	618.35
[C_{16}Py]Cl reservoir B	25.60	303.46	299.47

foams [54]. Since results from foam mobility tests depends on foam velocity, foam quality, and permeability of the medium, the results should only be compared to works with similar conditions. Gland et al. [55] developed a cationic surfactant formulation and performed sand-pack tests at 80 °C and 1740 psi. Sand-pack permeability was estimated as 13,000 mD. For a foam quality of 80% and an injection velocity of 43 ft/day, an apparent viscosity of ~410 cp was reported. Wang and Mohanty [32] proposed a formulation containing 500 ppm of ethyl cellulose nanoparticles dispersed in brine along with 2.5 wt% non-ionic surfactant. Foam mobility experiments were performed at 100 psi and ambient temperature in a sand-pack with a high permeability (16,000 mD). Foam quality was kept at 80% and a total flow rate of 14 ft/day was applied. A promising pressure gradient larger than 100 psi was reported. However, the high surfactant concentration would likely turn the process economically unfeasible. In a subsequent work, Wang and Mohanty [56] studied the same compounds, but lowered surfactant concentration to 1 wt%. Foam mobility experiments were performed in a 16,000 mD sand-pack applying total flow rates of 8, 12, and 16 ft/day. Experiments were conducted at a pressure of 950 psi and a foam quality to 80%. The highest apparent viscosity was obtained for the lowest velocity and a value of 248.8 cp was reported.

4. Conclusions

Foams have a great potential to improve oil recovery in gas injection processes. However, they are required to be stable enough to overcome the challenging harsh conditions of temperature, salinity, and pressure that characterize a great number of reservoirs. This study investigated the performance of six different SAILs at two reservoir conditions: A (63 °C, 1910 psi and 125,356 mg/L TDS) and B (40 °C, 1000 psi and 255,470 mg/L TDS). The following conclusions can be established:

- At ambient pressure, foams produced with imidazolium SAILs were the most stable, while pyridinium SAILs showed the best foaming ability.
- SAILs with longer alkyl chain length resulted in lower foam ability but higher stability compared to shorter alkyl chain length SAILs.
- SAILs with higher number of ethoxylated groups (higher hydrophilicity) resulted in lower foam performance.
- An optimal formulation of 0.5 wt% [C_{16}mim]Cl was selected for reservoir A conditions. For reservoir B conditions, two optimal formulations of 0.5 wt% [C_{16}Py]Cl and 0.5 wt% [C_{16}mim]Cl with half concentration of formation brine, were identified.
- A half-life time of 7.8 days was achieved with [C_{16}mim]Cl at high pressure reservoir A conditions, several times higher than those reported in literature for foams made with regular surfactants. Lower half-life times up to 4.5 h were obtained for the reservoir B conditions.
- Mobility reduction factors obtained in foam flow experiments were high (more than 300), with the most promising result reported for [C_{16}mim]Cl at reservoir A conditions (1229).
- SAILs have a promising potential for increasing foam apparent viscosity and improving mobility control during EOR and CO_2 sequestration processes in high salinity reservoirs and aquifers.

CRediT authorship contribution statement

Alba Somoza: Conducted experiments, wrote manuscript. **Ana Soto**; Co-directed research and edited manuscript. **Jieqiong Pang**: Conducted experiments, helped with manuscript. **Kishore Mohanty**: Directed research, edited manuscript.

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.

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References

[1] A. Alagorni, Z. Yaacob, A. Nour, An overview of oil production stages: enhanced oil recovery techniques and nitrogen injection, Int. J. Environ. Sci. Dev. 6 (2015) 693–701, https://doi.org/10.7763/IJESD.2015.V6.682.
[2] J.J. Sheng, Chapter 1 – Introduction, in: James J. Sheng (Ed.), Modern Chemical Enhanced Oil Recovery. Theory and Practice, Gulf Professional Publishing, 2011, pp. 1–11. ISBN 9781856177450.
[3] P. Ghosh, K.K. Mohanty, Study of surfactant alternating gas injection (SAG) in gas-flooded oil-wet, low permeability carbonate rocks, Fuel 251 (2019) 260–275, https://doi.org/10.1016/j.fuel.2019.03.119.
[4] S. Roussanaly, A. Grimstad, The economic value of CO_2 for EOR applications, Enrgy Proced. 63 (2014) 7836–7843, https://doi.org/10.1016/j.egypro.2014.11.818.
[5] S. Sakthivel, R.B. Salin, Imidazolium based ionic liquid stabilized foams for conformance control: bulk and porous scale investigation, RSC Adv. 11 (2021) 29711, https://doi.org/10.1039/D1RA04966F.
[6] N. Yekeen, M.A. Manan, A.K. Idris, E. Padmanabhan, R. Junin, A.M. Samin, A. O. Gbadamosi, I. Oguamah, A comprehensive review of experimental studies of nanoparticles-stabilized foam for enhanced oil recovery, J. Pet. Sci. Eng. 164 (2018) 43–74, https://doi.org/10.1016/j.petrol.2018.01.035.
[7] Z. AlYousef, M. Almobarky, D. Schechter, Enhancing the stability of foam by the use of nanoparticles, Energ. Fuel 31 (2017) 10620–10627, https://doi.org/10.1021/acs.energyfuels.7b01697.
[8] T. Majeed, M.S. Kamal, X. Zhou, T. Solling, A review on foam stabilizers for enhanced oil recovery, Energ. Fuel 35 (2021) 5594–5612, https://doi.org/10.1021/acs.energyfuels.1c00035.
[9] Y. Wang, Y. Zhang, Y. Liu, L. Zhang, S. Ren, J. Lu, X. Wang, N. Fan, The stability study of CO_2 foams at high pressure and high temperature, J. Pet. Sci. Eng. 154 (2017) 234–243, https://doi.org/10.1016/j.petrol.2017.04.029.
[10] X. Zhang, W. Zheng, T. Zhang, J. Ge, P. Jiang, G. Zhang, CO_2 in water foam stabilized with CO_2-dissolved surfactant at high pressure and high temperature, J. Pet. Sci. Eng. 178 (2019) 930–936, https://doi.org/10.1016/j.petrol.2019.03.066.
[11] J. Wang, L. Xinjie, S. Rogers, P. Li, Y. Feng, Stabilization of CO_2 aqueous foams at high temperature and high pressure: small-angle neutron scattering and rheological studies, Colloid Surf. A 647 (2022), 129015, https://doi.org/10.1016/j.colsurfa.2022.129015.
[12] W. Li, H. Zeng, Effect of temperature on the stability of supercritical CO_2 foam stabilized with a betaine surfactant at high pressure, Colloid Surf. A 649 (2022), 129362, https://doi.org/10.1016/j.colsurfa.2022.129362.
[13] Z. Xu, L. Zhaomin, S. Cui, B. Li, Q. Zhang, L. Zheng, M.M. Husein, Assessing the performance of foams stabilized by anionic/nonionic surfactant mixture under high temperature and pressure conditions, Colloid Surf. A 651 (2022), 129699, https://doi.org/10.1016/j.colsurfa.2022.129699.
[14] Q. Xu, M. Nakajima, S. Ichikawa, N. Nakamura, P. Roy, H. Okadome, T. Shiina, Effects of surfactant and electrolyte concentrations on bubble formation and stabilization, J. Colloid Inter. Sci. 332 (2009) 208–214, https://doi.org/10.1016/j.jcis.2008.12.044.
[15] S.R. Varade, P. Ghosh, Foaming in aqueous solutions of zwitterionic surfactant: effects of oil and salts, J. Disper Sci. Technol. 38 (2017) 1770–1784, https://doi.org/10.1080/01932691.2017.1283509.
[16] A. Bera, H. Belhaj, Ionic liquids as alternatives of surfactants in enhanced oil recovery: a state-of-the-art review, J. Mol. Liq. 224 (2016) 177–188, https://doi.org/10.1016/j.molliq.2016.09.105.

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[17] P. Pillai, A. Kumar, A. Mandal, Mechanistic studies of enhanced oil recovery by imidazolium-based ionic liquids as novel surfactants, J. Ind. Eng. Chem. 63 (2018) 262–274, https://doi.org/10.1016/j.jiec.2018.02.024.

[18] P. Pillai, M. Maiti, A. Mandal, Mini-review on recent advances in the application of surface-active ionic liquids: petroleum industry perspective, Energy Fuel 36 (2022) 7925–7939, https://doi.org/10.1021/acs.energyfuels.2c00964.

[19] O.A. El Seoud, N. Keppeler, N.I. Malek, P.D. Galgano, Ionic liquid-based surfactants: recent advances in their synthesis solution properties and their applications, Polymers 13 (2021) 1100, https://doi.org/10.3390/polym13071100.

[20] A.Z. Hezave, S. Dorostkar, S. Ayatollahi, M. Nabipour, B. Hemmateenejad, Investigating the effect of ionic liquid (1-dodecyl-3-methylimidazolium chloride ([C_{12}mim][Cl])) on the water/oil interfacial tension as a novel surfactant, Colloid Surf. A 421 (2013) 63–71, https://doi.org/10.1016/j.colsurfa.2012.12.008.

[21] M.S. Benzagouta, M.S. AlNashef, W. Karnanda, K. Al-Khidir, Ionic liquids as novel surfactants for potential use in enhanced oil recovery, Korean J. Chem. Eng. 30 (2013) 2108–2117, https://doi.org/10.1007/s11814-013-0137-1.

[22] K. Hu, H. Zhang, M. Kong, M. Qin, M. Ouyang, Q. Jiang, G. Wang, L. Zhuang, Effect of alkyl chain length of imidazolium cations on foam properties of anionic surface active ionic liquids: experimental and DFT studies, J. Mol. Liq. 340 (2021), 117197, https://doi.org/10.1016/j.molliq.2021.117197.

[23] M. Ouyang, Q. Jiang, K. Hu, Y. Deng, H. Zhang, M. Kong, Y. Shen, F. Li, G. Wang, L. Zhuang, Effect of hydroxyl group on foam features of hydroxyl-based anionic ionic liquid surfactant: experimental and theoretical studies, J. Mol. Liq. 362 (2020), 119416, https://doi.org/10.1016/j.molliq.2022.119416.

[24] A.S. Hanamertani, R.M. Pilus, N.A. Manan, M. Ibrahim, A. Mutalib, The use of ionic liquids as additive to stabilize surfactant foam for mobility control application, J. Pet. Sci. Eng. 167 (2018) 192–201, https://doi.org/10.1016/j.petrol.2018.04.010.

[25] A.S. Hanamertani, R.M. Pilus, N.A. Manan, S. Ahmed, M. Awang, Ionic liquid application in surfactant foam stabilization for gas mobility control, Energ. Fuel 32 (2018) 6545–6556, https://doi.org/10.1021/acs.energyfuels.8b00584.

[26] A. Somoza, N. Tafur, A. Arce, A. Soto, Design and performance analysis of a formulation based on SDBS and ionic liquid for EOR in carbonate reservoirs, J. Pet. Sci. Eng. 209 (2022), 109856, https://doi.org/10.1016/j.petrol.2021.109856.

[27] A. Somoza, M.F. García-Mayoral, A. Soto, A formulation based on a cationic surface-active ionic liquid and an anionic surfactant for enhanced oil recovery at a carbonate reservoir, Fuel 346 (2023), 128363, https://doi.org/10.1016/j.fuel.2023.128363.

[28] L. Tennouga, A. Mansri, K. Medjahed, A. Chetouani, I. Warad, The micelle formation of cationic and anionic surfactants in aqueous medium: determination of CMC and thermodynamic parameters at different temperatures, J. Mater. Environ. Sci. 6 (2015) 2711–2716.

[29] P. Galgano, O. El Seoud, Micellar properties of surface active ionic liquids: a comparison of 1-hexadecyl-3-methylimidazolium chloride with structurally related cationic surfactants, J. Colloid Inter. Sci. 345 (2010) 1–11, https://doi.org/10.1016/j.jcis.2010.01.078.

[30] M. Ao, D. Kim, Aggregation behavior of aqueous solutions of 1–Dodecyl-3-methylimidazolium salts with different halide anions, J. Chem. Eng. Data 58 (2013) 1529–1534, https://doi.org/10.1021/je301147k.

[31] R. Singh, K.K. Mohanty, Study of nanoparticle-stabilized foams in harsh reservoir conditions, Transp. Porous Med. 131 (2020) 135–155, https://doi.org/10.1007/s11242-018-1215-y.

[32] X. Wang, K. Mohanty, Improved oil recovery in fractured reservoirs by strong foams stabilized by nanoparticles, Energ. Fuel 35 (2021) 3857–3866, https://doi.org/10.1021/acs.energyfuels.0c03961.

[33] J. Yang, X. Wang, X. Peng, Z. Du, F. Zeng, Experimental studies on CO_2 foam performance in the tight cores, J. Pet. Sci. Eng. 175 (2019) 1136–1149, https://doi.org/10.1016/j.petrol.2019.01.029.

[34] D. Santos, M. Góes, E. Franceschi, A. Santos, C. Dariva, M. Fortuny, S. Mattedi, Phase equilibria for binary systems containing ionic liquid with water or hydrocarbons, Braz. J. Chem. Eng. 32 (2015), https://doi.org/10.1590/0104-6632.20150324s00003609.

[35] A. Schmitz, M. Bülow, D. Schmidt, D.H. Zaitsau, F. Junglas, T. Knedel, S. Verevkin, C. Held, J. Christoph, Tetrahydrothiophene-based ionic liquids: synthesis and thermodynamic characterizations, ChemistryOpen 10 (2021) 153–163, https://doi.org/10.1002/open.2020.

[36] Chang, Q. Chapter 11 – Emulsion, Foam and Gel. Colloid and Interface Chemistry for Water Quality Control (2016) 227–245. https://doi.org/10.1016/B978–0-12–809315-3.00011–6.

[37] Z. Zhang, M. Qiao, H. Zhao, Q. Ran, S. Yuan, Effect of sodium alkyl sulfate chain length on foam stability: a molecular dynamics study, Colloid Surf. A 656 (2023), 130394, https://doi.org/10.1016/j.colsurfa.2022.130394.

[38] A. Fameau, A. Saint-Jalmes, F. Cousin, B. Houinsou-Houssou, B. Novales, L. Navailles, F. Nallet, C. Gaillard, F. Boué, J. Douliez, Smart foams: switching reversibly between ultrastable and unstable foams, Angew. Chem. Int. Ed. 50 (2011) 8264–8269, https://doi.org/10.1002/anie.201102115.

[39] N.S. Abd Rahim, I.M. Saaid, A.A. Umar, Evaluation of foam performance at different temperature for enhanced oil recovery process, World J. Eng. 6 (2019) 412–418, https://doi.org/10.1108/WJE-06-2018-0210.

[40] S. Kumar, A. Mandal, Investigation on stabilization of CO_2 foam by ionic and nonionic surfactants in presence of different additives for application in enhanced oil recovery, Appl. Surf. Sci. 420 (2017) 9–20, https://doi.org/10.1016/j.apsusc.2017.05.126.

[41] M.R. Behera, S.R. Varade, P. Ghosh, P. Paul, A.S. Negi, Foaming in micellar solutions: effects of surfactant, salt, and oil concentrations, Ind. Eng. Chem. Res 53 (2014) 18497–18507, https://doi.org/10.1021/ie503591v.

[42] AlYousef, Z.; Gizzatov, A.; AlMatouq, H.; Jian, G. Effect of Crude Oil on CO2–Foam Stability. Paper presented at the Offshore Technology Conference Asia, Kuala Lumpur, Malaysia (2020). https://doi.org/10.4043/30210-MS.

[43] S. Nandwani, M. Chakraborty, S. Gupta, Adsorption of surface active ionic liquids on different rock types under high salinity conditions, Sci. Rep. 9 (2019) 14760, https://doi.org/10.1038/s41598-019-51318-2.

[44] M. Szabries, P. Jaeger, M.M. Amro, Foam analysis at elevated pressures for enhanced oil recovery applications, Energ. Fuel 33 (2019) 3743–3752, https://doi.org/10.1021/acs.energyfuels.8b03088.

[45] W. Li, F. Wei, X. Xiong, J. Ouyang, L. Shao, M. Dai, P. Liu, D. Du, A novel supercritical CO_2 foam system stabilized with a mixture of zwitterionic surfactant and silica nanoparticles for enhanced oil recovery, Front Chem. 7 (2019) 718, https://doi.org/10.3389/fchem.2019.00718.

[46] S. Li, Z. Li, P. Wang, Experimental study of the stabilization of CO_2 foam by sodium dodecyl sulfate and hydrophobic nanoparticles, Ind. Eng. Chem. Res 55 (2016) 1243–4253, https://doi.org/10.1021/acs.iecr.5b04443.

[47] Liu, Y.; Grigg, R.B.; Svec, R.K. CO2 Foam Behavior: Influence of Temperature, Pressure, and Concentration of Surfactant. Paper presented at the SPE Production Operations Symposium, Oklahoma City, Oklahoma (2005). https://doi.org/10.2118/94307-MS.

[48] Solbakken, J.S.; Skauge, A.; Aarra, M.G. Supercritical CO2 Foam-The Importance of CO2 Density on Foams Performance. Paper presented at the SPE Enhanced Oil Recovery Conference, Kuala Lumpur, Malaysia (2013). https://doi.org/10.2118/165296-MS.

[49] W.R. Rossen, P.A. Gauglitz, Percolation theory of creation and mobilization of foams in porous media, AIChE J. 36 (1990) 1176–1188, https://doi.org/10.1002/aic.690360807.

[50] Siddiqui, S.; Talabani, S.; Saleh, S.T.; Islam, M.R. A Laboratory Investigation of Foam Flow in Low-Permeability Berea Sandstone Cores. Paper presented at the SPE Production Operations Symposium, Oklahoma City, Oklahoma (1997). https://doi.org/10.2118/37416-MS.

[51] P.A. Gauglitz, F. Friedmann, S.I. Kam, W.R. Rossen, Foam generation in homogeneous porous media, Chem. Eng. Sci. 57 (2002) 4037–4052, https://doi.org/10.1016/S0009-2509(02)00340-8.

[52] A. Skauge, J. Solbakken, P.A. Ormehaug, M.G. Aarra, Foam generation, propagation and stability in porous medium, Transp. Porous Med 131 (2020) 5–21, https://doi.org/10.1007/s11242-019-01250-w.

[53] J.J. Sheng, Chapter 11 - Foams and Their Applications in Enhancing Oil Recovery, in: James J. Sheng (Ed.), Enhanced oil recovery field case studies, Gulf Professional Publishing, Boston, 2013, pp. 251–280. ISBN 9780123865458.

[54] Da, C.; Elhag, A.; Jian, G.; Zhang, L.; Alzobaidi, S.; Zhang, X.; Al Sumaiti, A.; Biswal, S.; Hirasaki, G.; Johnston, K. CO2/Water Foams Stabilized with Cationic or Zwitterionic Surfactants at Temperatures up to 120 °C in High Salinity Brine. Paper presented at the SPE Annual Technical Conference and Exhibition, Dallas, Texas, USA (2018). https://doi.org/10.2118/191479-MS.

[55] Gland, N.; Chevallier, E.; Cuenca, A.; Batot, G. New Developement of Cationic Surfactant Formulations for Foam Assisted CO2-EOR in Carbonates Formations. Paper presented at the Abu Dhabi International Petroleum Exhibition & Conference, Abu Dhabi, UAE (2018). https://doi.org/10.2118/193201-MS.

[56] Wang, X.; Mohanty, K. Nanoparticle Stabilized Strong Foam for EOR in High Salinity Fractured Carbonate Reservoirs. Paper presented at the SPE Improved Oil Recovery Conference, Virtual (2022). https://doi.org/10.2118/209435-MS.

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(54) **Title:** COMPOSITION FOR ENHANCED OIL EXTRACTION

(54) **Título:** COMPOSICIÓN PARA LA EXTRACCIÓN MEJORADA DE PETRÓLEO

(57) **Abstract:** The present invention relates to a composition which comprises an anionic surfactant, specifically an alkylbenzene sulphonate and an ionic liquid. The present invention further relates to the use of said composition in an enhanced crude oil recovery method.

(57) **Resumen:** Se describe una composición que comprende un tensioactivo aniónico, en concreto un sulfonato de alquilbenceno y un líquido iónico. También se describe el uso de dicha composición en un método de recuperación mejorada de crudo.

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COMPOSICIÓN PARA LA EXTRACCIÓN MEJORADA DE PETRÓLEO

CAMPO TÉCNICO DE LA INVENCIÓN

La presente invención se adscribe al campo de la extracción de petróleo y, en concreto, a técnicas de recuperación mejorada de crudo. Así, la presente invención describe una composición que comprende un tensioactivo aniónico y un líquido iónico, así como su uso en un método de recuperación mejorada de crudo.

ESTADO DE LA TÉCNICA

La vida productiva de los yacimientos de petróleo puede ser dividida en varias etapas, dependiendo de la manera y condiciones de recuperación del crudo. En la etapa de extracción primaria la presión del crudo en el yacimiento es suficiente para su extracción a la superficie, por sí solo, o con la ayuda de una bomba adicional. En la etapa de recuperación secundaria, se vuelve a presurizar el yacimiento para empujar la salida del crudo a la superficie, mediante la inyección de agua, gas o de ambos fluidos. La eficiencia de los métodos de extracción primaria y secundaria de crudo está muy limitada por la existencia de fuerzas capilares que retienen el crudo en los poros de las rocas.

Existe una tercera etapa que implica la utilización de métodos de recuperación mejorada (EOR por sus siglas en inglés: Enhanced Oil Recovery) para obtener la recuperación final de hidrocarburos. Dichos métodos suelen estar basados en alguno de los siguientes efectos: la reducción de la tensión interfacial entre el crudo y agua, la mejora en la capacidad de desplazamiento del crudo por parte de los fluidos inyectados o, en la utilización de un disolvente.

A este respecto y, con el objetivo de disminuir la tensión interfacial entre el crudo y el agua, los surfactantes (tensioactivos) más empleados son los sulfonatos de petróleo, alquilbencenosulfonatos y carboxilatos. Se trata de surfactantes aniónicos con alta capacidad de disminuir la tensión interfacial agua/crudo pero que, en cambio, tienen el inconveniente de presentar una baja estabilidad en presencia de iones divalentes.

Se sabe que el mecanismo más importante de adsorción es la atracción electrostática entre la superficie cargada de la roca y la cabeza cargada del surfactante. Así, en los procesos químicos de recuperación mejorada del petróleo (CEOR por sus siglas en inglés: Chemical

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R^1 es un grupo seleccionado de entre cadenas alifáticas saturadas o monoinsaturadas con un número par de entre 8 y 18 átomos de carbono, de manera que al menos 10% de dichas cadenas hidrocarbonadas es un grupo alquilo de 12 átomos de carbono;

R^2 es un grupo C_1-C_3 alquilo; y

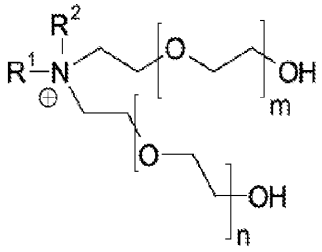
en donde **m** y **n** son dos números enteros tales que **m+n** es un número entero entre 5 y 10; y en un método de recuperación mejorada de petróleo en yacimientos con rocas carbonatadas.

Otra realización de la presente invención se refiere al uso de una formulación que comprende:

- una composición de acuerdo con la presente invención, donde dicha composición comprende:

un sulfonato de un C_8-C_{15}-alquilbenceno, y

un líquido iónico que comprende, a su vez, un catión de fórmula (I)



(I)

en el que:

R^1 es un grupo seleccionado de entre cadenas alifáticas saturadas o monoinsaturadas con un número par de entre 8 y 18 átomos de carbono, de manera que al menos 10% de dichas cadenas hidrocarbonadas es un grupo alquilo de 12 átomos de carbono;

R^2 es un grupo C_1-C_3 alquilo; y

en donde **m** y **n** son dos números enteros tales que **m+n** es un número entero entre 5 y 10; y

- agua o salmuera;

en un método de recuperación mejorada de petróleo en yacimientos con rocas carbonatadas.

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Enhanced Oil Recovery), es inevitable la adsorción de los surfactantes en la superficie de la roca del yacimiento. Esta adsorción provoca la pérdida de surfactante y la reducción de su eficiencia para movilizar el crudo atrapado, lo que puede hacer que el proceso sea económica y tecnológicamente inviable. Por otro lado, es conocido que los tensioactivos aniónicos, cargados negativamente, tienden a adsorberse en superficies con cargas positivas (rocas carbonatadas). (Bera et al, 2013).

En este sentido, los surfactantes aniónicos tradicionales usados en la extracción de crudo presentan una alta adsorción en rocas carbonatadas, lo que limita su aplicación en este tipo de yacimientos. En particular, muchos yacimientos adecuados para extracción mejorada presentan condiciones adversas para la extracción del crudo, como son la existencia de temperaturas y salinidades elevadas (es decir, con una dureza importante que comprenden una cantidad de sólidos disueltos de alrededor de 200.000 mg/L). Además, la dificultad de extracción del crudo en dichos yacimientos se ve acentuada debido a su baja porosidad y permeabilidad y a que, debido a la mojabilidad de sus rocas por crudo o mixta, hacen que el crudo se adhiera fuertemente a la superficie de la roca dificultando su extracción. Además, para la extracción en dichos yacimientos es necesario desarrollar soluciones que proporcionen una tensión interfacial utra-baja con el crudo en dichas condiciones adversas, consiguiendo soluciones acuosas de una sola fase a las temperaturas a las que se inyectan.

En resumen, la extracción de crudo de yacimientos carbonatados maduros supone un reto todavía mayor debido a que presentan condiciones adversas adicionales, tales como altas salinidades, altas concentraciones de iones divalentes, baja permeabilidad, etc. Es por ello que sigue necesitándose métodos más eficaces que permitan una recuperación mejorada del petróleo (EOR) y que permitan obtener mayor cantidad de crudo, en particular en yacimientos maduros, e incluso en rocas carbonatadas donde las condiciones de salinidad y permeabilidad son especialmente adversas.

BREVE DESCRIPCIÓN DE LA INVENCIÓN

La presente invención se refiere a una composición que comprende:

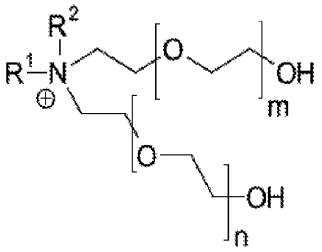
un sulfonato de un C_8-C_{15}-alquilbenceno, y

un líquido iónico que comprende, a su vez, un catión de fórmula (I)

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Otra realización de la invención se refiere a un método de recuperación mejorada de petróleo que comprende:

preparar una formulación de acuerdo con la presente invención, que comprende un sulfonato de un C_8-C_{15}-alquilbenceno, y un líquido iónico que comprende, a su vez, un catión de fórmula (I):



(I)

en el que:

R^1 es un grupo seleccionado de entre cadenas alifáticas saturadas o monoinsaturadas con un número par de entre 8 y 18 átomos de carbono, de manera que al menos 10% de dichas cadenas hidrocarbonadas es un grupo alquilo de 12 átomos de carbono;

R^2 es un grupo C_1-C_3 alquilo; y

en donde **m** y **n** son dos números enteros tales que **m**+**n** es un número entero entre 5 y 10; y agua o salmuera; e

inyectar dicha formulación en un yacimiento de petróleo con rocas carbonatadas.

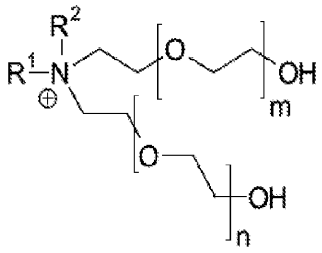
Otra realización de la presente invención se refiere a un método de recuperación mejorada de petróleo comprende inyectar en un yacimiento de petróleo con rocas carbonatadas una formulación que comprende:

- una composición de acuerdo con la presente invención, donde dicha composición comprende:

  un sulfonato de un C_8-C_{15}-alquilbenceno, y

  un líquido iónico que comprende, a su vez, un catión de fórmula (I)

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(I)

en el que:

R^1 es un grupo seleccionado de entre una mezcla de cadenas alifáticas saturadas o monoinsaturadas con un número par de entre 8 y 18 átomos de carbono, de manera que al menos 10% de dichas cadenas hidrocarbonadas es un grupo alquilo de 12 átomos de carbono;

R^2 es un grupo C_1-C_3 alquilo; y

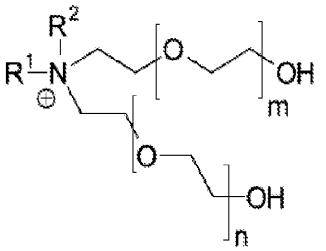
en donde **m** y **n** son dos números enteros tales que **m+n** es un número entero entre 5 y 10.

En particular, la presente invención se refiere a una composición, tal como se describe en el presente documento, en la que el catión de formula (I) es un catión amonio derivado de una amina grasa en la que R^1 es un grupo derivado de una mezcla de ácidos grasos R^1COOH provenientes, preferentemente, del aceite de coco, pero también de otras procedencias, tal como de derivados de petróleo, de derivados lignocelulósicos, o de otras mezclas hidrocarbonadas. Preferentemente R^1 se selecciona de una mezcla de cadenas alifáticas saturadas o monoinsaturadas con un número par de entre 8 y 18 átomos de carbono, de manera que al menos 10% del total de dichas cadenas hidrocarbonadas en la mezcla es un grupo alquilo de 12 átomos de carbono.

Otro aspecto de la invención se refiere a una composición que comprende entre 30% y 75% (m/m) de un sulfonato de un C_8-C_{15}-alquilbenceno y entre 25% y 70% (m/m) de un líquido iónico que comprende, a su vez, un catión cocosalquilpentaetoximetilamonio.

Otro aspecto adicional de la invención se refiere a una composición que comprende entre 55% y 65% (m/m) de metilsulfato de cocosalquilpentaetoximetilamonio y entre 35% y 45% (m/m) de dodecilbenceno sulfonato de sodio.

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(I)

en el que:

R^1 es un grupo seleccionado de entre cadenas alifáticas saturadas o monoinsaturadas con un número par de entre 8 y 18 átomos de carbono, de manera que al menos 10% de dichas cadenas hidrocarbonadas es un grupo alquilo de 12 átomos de carbono;

R^2 es un grupo C_1-C_3 alquilo; y

en donde **m** y **n** son dos números enteros tales que **m+n** es un número entero entre 5 y 10; y

- agua o salmuera.

En particular, dicho método de recuperación mejorada de petróleo comprende preparar una formulación que comprende agua o salmuera y la composición de la presente invención; e inyectar dicha formulación en un yacimiento de petróleo con rocas carbonatadas para la extracción del petróleo.

Preferentemente, la formulación de acuerdo con la presente invención comprende la composición de la presente invención a una concentración en el agua, o en la salmuera, de entre 0,25% y 4% en peso. Es decir, preferentemente la concentración de dicha composición en el agua, o en la salmuera, es de entre 0,25% y 4% en peso. Más preferentemente, la concentración de dicha composición en el agua, o en la salmuera, es de entre 0,5% y 2% en peso, y aún más preferentemente es del 1% en peso.

En una realización particular, el catión de formula (I) es un catión amonio derivado de una amina grasa en la que R^1 es un grupo derivado de una mezcla de ácidos grasos R^1COOH provenientes del aceite de coco o de otra procedencia, tal como de derivados de petróleo, de derivados lignocelulósicos, o de otras mezclas hidrocarbonadas. Así, mayoritariamente, es un grupo seleccionado de entre cadenas alifáticas saturadas o monoinsaturadas con un número

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Otro aspecto adicional de la invención se refiere a una formulación que comprende la composición de acuerdo con la presente invención y agua o salmuera.

La presente invención también se refiere al uso de dicha composición, o de dicha formulación, de acuerdo con la presente invención, en un método de recuperación mejorada de petróleo en yacimientos con rocas carbonatadas.

Finalmente, la presente invención se refiere a un método de recuperación mejorada de petróleo que comprende inyectar en un yacimiento de petróleo con rocas carbonatadas una composición o una formulación de acuerdo con la presente invención.

BREVE DESCRIPCIÓN DE LAS FIGURAS

FIG. 1. Parámetros de solubilización (*(● Vw/Vs, × Vo/Vs)* frente a diferentes % de dodecilbencenosulfonato de sodio (SDBS) a 298,15 K (25 °C). Los parámetros de solubilización (*Vo/Vs* y *Vw/Vs*) indican el volumen de hidrocarburo o agua solubilizada en la microemulsión por volumen de surfactante; en donde *Vo* es el volumen de hidrocarburo, *Vs* es el volumen del tensioactivo o surfactante, y *Vw* es el volumen de agua.

FIG. 2. Parámetros de solubilización frente a diferentes % de SDBS a 323,15 K (**2A**) y 348,15 K (**2B**). (● Vw/Vs, × Vo/Vs)

FIG. 3. Tensión interfacial dinámica (IFT) entre el crudo y la disolución de mezcla de surfactantes a las diferentes proporciones en agua de mar. **3A**: △ 40%m/m SDBS, ● 44.7% m/m SDBS, × 50% m/m SDBS. **3B**: □ 65% m/m SDBS, ▼ 73.7% m/m SDBS, ◇ 78% m/m SDBS

FIG. 4. Adsorción dinámica de la formulación optimizada en roca carbonatada a 298,15 K.

× Trazador (yoduro de potasio), △ 40%m/m SDBS + 60%m/m lolilyte C1EG (metilsulfato de cocosalquilpentaetoximetilamonio), ● 73.7%m/m SDBS + 26.3%m/m lolilyte C1EG.

DESCRIPCIÓN DETALLADA

La presente invención describe una composición que comprende:

un sulfonato de un C_8-C_{15}-alquilbenceno, y

un líquido iónico que comprende, a su vez, un catión de fórmula (I)

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par de entre 8 y 18 átomos de carbono, de manera que al menos 10% de dichas cadenas hidrocarbonadas es un grupo alquilo de 12 átomos de carbono. Preferentemente, R^1 un grupo seleccionado de entre cadenas alifáticas saturadas o monoinsaturadas con un número par de entre 8 y 18 átomos de carbono, de manera que al menos 10%, más preferentemente al menos 25%, y aún más preferentemente al menos 35%, de dichas cadenas hidrocarbonadas es un grupo alquilo de 12 átomos de carbono.

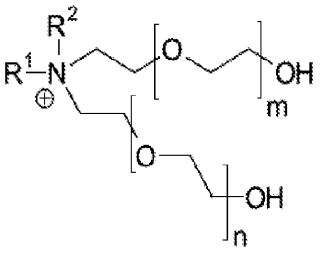
efectos de la presente invención, el término "cadena hidrocarbonada alifática" se refiere a grupos que contienen carbono e hidrógeno y no contienen grupos aromáticos, pudiendo ser saturados, es decir, comprendiendo solamente enlaces sencillos carbono-carbono, o con insaturaciones, es decir, con enlaces dobles o triples, carbono-carbono. Un grupo alquilo, a efectos de la presente invención, es una cadena hidrocarbonada alifática saturada.

En una realización particularmente preferente R^1 es un grupo cocos o un grupo seleccionado de entre cadenas alifáticas saturadas o monoinsaturadas con un número par de entre 8 y 18 átomos de carbono, de manera que comprende: entre 5% y 10% de cadenas alifáticas saturadas de 8 átomos de carbono, entre 5% y 10% de cadenas alifáticas saturadas de 10 átomos de carbono, entre 45% y 50% de cadenas alifáticas saturadas de 12 átomos de carbono, entre 12% y 18% de cadenas alifáticas saturadas de 14 átomos de carbono, entre 7% y 12% de cadenas alifáticas saturadas de 16 átomos de carbono, entre 3% y 8% cadenas alifáticas monoinsaturadas de 18 átomos de carbono y alrededor de 2% a 7% de otras cadenas alifáticas. A efectos de la presente invención, el grupo cocos puede derivar de aceite de coco o de otra procedencia, tal como de derivados de petróleo o de otras mezclas hidrocarbonadas.

Preferentemente, la composición de la presente invención comprende un líquido iónico que comprende, a su vez, un catión de fórmula (I), en el que R^1 un grupo seleccionado de entre una mezcla de cadenas alifáticas saturadas o monoinsaturadas con un número par de entre 8 y 18 átomos de carbono, de manera que al menos 10%, más preferentemente 25%, y aún más preferentemente al menos 35%, de dicha mezcla de cadenas hidrocarbonadas es un grupo alquilo de 12 átomos de carbono; R^2 es un grupo metilo y; en donde **m** y **n** son dos números enteros tales que **m+n** es un número entero entre 5 y 10.

Más preferentemente, la composición de la presente invención comprende un líquido iónico que comprende, a su vez, un catión de fórmula (I), en el que R^1 es un grupo cocos o un grupo seleccionado de entre una mezcla de cadenas alifáticas saturadas o monoinsaturadas con un número par de entre 8 y 18 átomos de carbono, de manera que dicha mezcla comprende:

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(I)

en el que:

R^1 es un grupo seleccionado de entre cadenas alifáticas saturadas o monoinsaturadas con un número par de entre 8 y 18 átomos de carbono, de manera que al menos 10% de dichas cadenas hidrocarbonadas es un grupo alquilo de 12 átomos de carbono;

R^2 es un grupo C_1-C_3 alquilo; y

en donde **m** y **n** son dos números enteros tales que **m+n** es un número entero entre 5 y 10.

Preferentemente dicha composición comprende entre 25% y 70% (m/m) de líquido iónico y entre 30% y 75% (m/m) de sulfonato de un C_8-C_{15}-alquilbenceno. Más preferentemente dicha composición comprende entre 55% y 65% (m/m) de líquido iónico y entre 35% y 45% (m/m) de sulfonato de un C_8-C_{15}-alquilbenceno.

Las composiciones descritas en la presente invención son útiles en métodos de recuperación mejorada de petróleo. La recuperación mejorada de petróleo, también denominada recuperación terciaria, se refiere a la extracción de petróleo de un yacimiento (subterráneo) que se lleva a cabo una vez que ya no es posible la recuperación primaria (cuando la presión en el yacimiento es suficiente para hacer aflorar el crudo), ni tampoco es posible la extracción secundaria que utiliza energía externa (inyección de un fluido, por ejemplo) para incrementar la presión en el yacimiento y hacer que el crudo aflore. Tal como se ha comentado, de manera general, los métodos de recuperación mejorada de petróleo suelen estar basados en alguno de los siguientes efectos: la reducción de la tensión interfacial entre el crudo y agua, la mejora en la capacidad de desplazamiento o arrastre del crudo gracias a los fluidos inyectados o, por la utilización de un disolvente. De manera habitual, la recuperación mejorada de petróleo (EOR por sus siglas en inglés) hace uso de tensioactivos tradicionales, que son en muchos casos tensioactivos aniónicos que se inyectan mezclados con agua o salmuera en dichos yacimientos, arrastrando el crudo presente en estos.

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entre 5% y 10% de cadenas alifáticas saturadas de 8 átomos de carbono, entre 5% y 10% de cadenas alifáticas saturadas de 10 átomos de carbono, entre 45% y 50% de cadenas alifáticas saturadas de 12 átomos de carbono, entre 12% y 18% de cadenas alifáticas saturadas de 14 átomos de carbono, entre 7% y 12% de cadenas alifáticas saturadas de 16 átomos de carbono, entre 3% y 8% cadenas alifáticas monoinsaturadas de 18 átomos de carbono y alrededor de 2% a 7% de otras cadenas alifáticas; R^2 es un grupo metilo y; en donde **m** y **n** son dos números enteros tales que **m+n** es un número entero entre 5 y 10.

Por otro lado, de manera ventajosa, el líquido iónico de la composición de acuerdo con la presente invención comprende un anión seleccionado de entre el grupo que consiste en un C_1-C_{15}-alquilsulfato, C_1-C_{15}-alquilbencenosulfonato, C_1-C_{15}-haloalquilbencenosulfonato, haloalquilcarboxilato, haluro, sulfato y nitrato.

De manera preferente el líquido iónico de la composición de acuerdo con la presente invención comprende un anión seleccionado de entre el grupo que consiste en: fluoruro, cloruro, bromuro, ioduro, sulfato, metilsulfato, etilsulfato, dodecilbenceno sulfonato, nitrato, tosilato, metanosulfonato, trifluorometanosulfonato, trifluoroacetato y tetracloroaluminato. De manera también preferente, el anión es un sulfonato de C_8-C_{15}-alquilbenceno o un sulfato de C_1-C_6-alquilo. Más preferentemente el anión es metilsulfato etilsulfato o dodecilbenceno sulfonato.

Más preferentemente, el líquido iónico de la composición de acuerdo con la presente invención comprende un catión de fórmula (I) que es cocosalquilpentaetoximetilamonio.

Aún más preferentemente, el líquido iónico es metilsulfato de cocosalquilpentaetoximetilamonio y el sulfonato de un C_8-C_{15}-alquilbenceno es dodecilbenceno sulfonato de sodio.

En una realización particularmente preferente de la invención, la composición de la presente invención comprende dodecilbenceno sulfonato de sodio y metilsulfato de cocosalquilpentaetoximetilamonio.

Los métodos de EOR que hacen uso de tensioactivos, como los descritos en la presente invención, se basan principalmente en la reducción de la tensión interfacial entre el crudo (petróleo, hidrocarburo) y el agua o la salmuera que se inyecta en los yacimientos.

A efectos de la presente invención, se denomina tensión interfacial a la existente entre el aceite o crudo (petróleo) y agua/salmuera. Por otro lado, se denominan tensiones interfaciales ultra-bajas, a efectos de la presente invención, a aquellas que son menores a 0,05 mN/m y

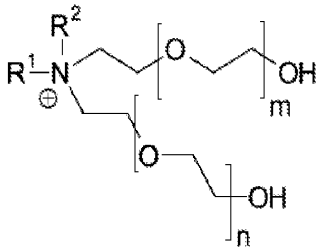
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Así, la presente invención también se refiere a una formulación que comprende:

- una composición de acuerdo con la presente invención, donde dicha composición comprende:

  un sulfonato de un C_8-C_{15}-alquilbenceno, y

  un líquido iónico que comprende, a su vez, un catión de fórmula (I)



(I)

en el que:

R^1 es un grupo seleccionado de entre cadenas alifáticas saturadas o monoinsaturadas con un número par de entre 8 y 18 átomos de carbono, de manera que al menos 10% de dichas cadenas hidrocarbonadas es un grupo alquilo de 12 átomos de carbono;

R^2 es un grupo C_1-C_3 alquilo; y

en donde **m** y **n** son dos números enteros tales que **m**+**n** es un número entero entre 5 y 10; y

- agua o salmuera.

A efectos de la presente invención el término salmuera se refiere a una disolución acuosa con un contenido total en sales de hasta 250000 ppm, y que, preferentemente, tiene un contenido en sales similar al del agua de mar. Por tanto, de acuerdo con la presente invención, la formulación comprende una composición de acuerdo con la presente invención y agua, en donde dicha agua presenta un contenido de entre 0 ppm a 250000 ppm de sales totales disueltas. Preferentemente, el agua presenta un contenido en sales de 50.000 ppm, de los cuales 17000 ppm son iones divalentes (dureza del agua).

Así, a efectos de la presente invención, el término “agua o salmuera” utilizado en las formulaciones, métodos y usos de acuerdo con la presente invención se refiere a agua con

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más preferentemente, menores a 0,01 mN/m, y aún más preferentemente menores a 0,001 mN/m (10^{-3} mN/m).

Las composiciones de la presente invención comprenden un tensioactivo aniónico de tipo sulfonato de alquilarilo, en particular un sulfonato de un C_8-C_{15}-alquilbenceno, junto con un líquido iónico. Así, la presente invención describe como, de manera sorprendente, el empleo de un líquido iónico surfactante concreto que comprende un catión de fórmula (I), permite mejorar las propiedades de un surfactante aniónico concreto en la recuperación mejorada de petróleo y permite obtener un mayor porcentaje de crudo extraído, gracias a que proporciona una tensión interfacial ultra-baja con el crudo de petróleo. En particular, las características proporcionadas por el catión de fórmula (I) son resultado de un equilibrio entre las características del grupo R^1 y del grado de étoxilación de dicho catión. Así, las propiedades ventajosas de dicho catión de fórmula (I) son resultado de las características de sus grupos R^1, provenientes de una mezcla de cadenas de ácidos grasos con una longitud de cadena alifática concreta (tanto en relación a la longitud o tamaño de dicha cadena, como en relación a los porcentajes de grupos R^1 de diferente longitud o tamaño en dicha mezcla), comprendiendo una cantidad ventajosa de grupos alquilo con 12 átomos de carbono igual o superior al 10% del total de grupos R^1 comprendido en dicha mezcla, y además, del grado de etoxilación particular (***m+n***=5-10). Así, dichos cationes de fórmula (I) proporcionan líquidos iónicos, que, en combinación con tensioactivos aniónicos del tipo sulfonato de C_8-C_{15}-alquilbenceno, permiten obtener composiciones y formulaciones, de acuerdo con la presente invención, que proporcionan altos porcentajes de recuperación de crudo, tal como se ilustra en los ejemplos de la presente invención.

En particular, tal como se describe en los ejemplos de la presente invención, en los ensayos de fase se pudo identificar que las composiciones de la presente invención presentan un comportamiento Winsor tipo III, que se relaciona con tensiones interfaciales ultra-bajas. Dichas microemulsiones se forman generalmente mezclando aceite y agua, o aceite y salmuera, en presencia de surfactantes. En condiciones de equilibrio, los sistemas con microemulsiones se pueden clasificar como Winsor I, Winsor II o Winsor III. En los sistemas Winsor tipo I, el surfactante forma una microemulsión de aceite en agua (o/w) en la fase inferior en equilibrio con el exceso de aceite en una fase separada. En los sistemas Winsor tipo II, se forma una fase superior que consiste en una microemulsión de agua en aceite (w/o) en equilibrio con un exceso de salmuera o agua. El sistema Winsor III se caracteriza por tener una fase de microemulsión, o fase intermedia, en equilibrio con una fase superior de exceso

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un contenido de entre 0 ppm a 250000 ppm de sales totales disueltas, y preferentemente un contenido en sales de 50.000 ppm, de los cuales 17000 ppm son iones divalentes.

Además, la extracción de crudo de yacimientos carbonatados maduros supone un reto todavía mayor debido a las condiciones adversas que presentan (altas salinidades, altas concentraciones de iones divalentes, baja permeabilidad, etc.). A este respecto, la composición de la presente invención permite obtener una buena estabilidad (sin turbidez, ni precipitados) a altas temperaturas y altas salinidades y, permite obtener un alto porcentaje de extracción del crudo retenido en yacimientos carbonatados, en los que la extracción de dicho crudo es compleja debido a su baja permeabilidad y a la mojabilidad de sus rocas por crudo o mixta (es decir, por crudo y agua), dado que su adsorción en rocas carbonatadas es muy baja.

A efectos de la presente invención se denominan "yacimientos carbonatados" aquellos que comprenden rocas calizas. De manera general contienen importantes cantidades de dolomita y calcita. Debido a su composición, dichos yacimientos, en contacto con agua o salmuera, inyectada en los métodos de EOR, generan efluyentes de alta dureza (básicos y con alto contenido en sales) que afectan significativamente al comportamiento y eficacia de los tensioactivos inyectados tradicionalmente. Además, dichos yacimientos son muy heterogéneos, y suelen tener porosidades y permeabilidades menores que los areniscos, lo que hace que las presiones capilares generadas durante la extracción del crudo sean altas y, por lo tanto, sea más costoso recuperar el petróleo en ellos. Por otro lado, las rocas de dichos yacimientos tienden a estar mojadas por crudo o bien tener una mojabilidad mixta (por crudo y por agua), que hace que el crudo se adhiera fuertemente a la superficie de la roca dificultando su extracción.

Por otro lado, un yacimiento denominado "maduro", a efectos de la presente invención, es aquel que ya ha sufrido procesos de recuperación de crudo primario y secundarios y requiere técnicas de recuperación de crudo terciarias o mejoradas (EOR) para la extracción de dicho crudo.

A efectos de la presente invención, el término "comprende" indica que incluye un grupo de características, pero no excluye la presencia de otras características, siempre y cuando la presencia de las otras características no haga la invención impracticable. Además, los términos "consta de", "contiene", "incluye", "tiene", "abarca" y sinónimos de dichos términos, deben ser interpretados de la misma manera que el término "comprende". Adicionalmente, a efectos de la presente invención, el término "comprende" puede ser reemplazado por

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de aceite y una fase inferior de exceso de agua. Al estar dichas microemulsiones relacionadas con tensiones interfaciales agua/crudo, ultra-bajas, permiten obtener altas recuperaciones de petróleo.

Para obtener altas recuperaciones de petróleo se estudian los parámetros de solubilización *Vo/Vs* y *Vw/Vs,* que indican el volumen de hidrocarburo (petróleo), o de agua, solubilizada en la microemulsión por volumen de surfactante. Estos parámetros de solubilización representan el volumen de hidrocarburo (V_o) y de agua (V_W) dividido por el volumen de surfactante (V_s) en la fase de la microemulsión.

Para alcanzar una tensión interfacial ultra-baja, los parámetros de solubilización deben ser iguales y deben tener, además, un valor numérico superior a 10. Es decir, en una formulación óptima para la recuperación de petróleo, la microemulsión solubiliza cantidades iguales de hidrocarburo y agua, lo que significa que *Vo/Vs* es igual a *Vw/Vs*. Esta relación óptima se calcula como la intersección entre las líneas de representación de ambos parámetros de solubilización.

Tal como se observa en los ejemplos de la presente invención, y en la figura 1, la composición de la presente invención proporciona dos puntos en los que *Vo/Vs* es igual a *Vw/Vs* y que corresponden a una relación de mezcla de 44,7% dodecilbenceno sulfonato de sodio (SDBS) + 55,3 % metilsulfato de cocosalquilpentaetoximetilamonio; y 73,7 % SDBS + 26,3% metilsulfato de cocosalquilpentaetoximetilamonio. Para ambas concentraciones óptimas, el parámetro de solubilización tiene un valor de 15,5 a 298,15 K (es decir, 25 °C).

Además, la figura 3 muestra una significativa disminución de la tensión interfacial (IFT) desde $4{,}4 \cdot 10^{-2}$ mN/m hasta $2{,}2 \cdot 10^{-3}$ mN/m cuando se reduce la proporción de SDBS desde 44,7 % m/m hasta un 40 % m/m de SDBS, en una composición de acuerdo con la presente invención. Por otro lado, cuando se utiliza una composición de acuerdo con la presente invención con 71,7 % m/m de SDBS, la tensión interfacial aumenta al disminuir la proporción de SDBS en la composición y, prácticamente, no se ve afectada por un incremento de contenido de este surfactante.

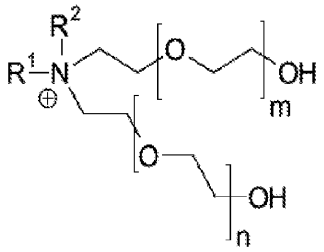
En vista a todo ello, y de manera preferente, la composición de la presente invención comprende entre 25% y 70% (m/m) de metilsulfato de cocosalquilpentaetoximetilamonio y entre 30% y 75% (m/m) de dodecilbenceno sulfonato de sodio. Más preferentemente, la composición de la presente invención comprende entre 55% y 65% (m/m) de metilsulfato de cocosalquilpentaetoximetilamonio y entre 35% y 45% (m/m) de dodecilbenceno sulfonato de

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cualquiera de los términos "consiste en" o "consisten sustancialmente en". Así, cuando el término "comprende" se refiere a un grupo de características técnicas A, B y C, debe interpretarse que puede incluir adicionalmente otras características técnicas además de las características técnicas A, B y C, siempre y cuando la presencia de las otras características no haga la invención impracticable, pero también puede interpretarse como que solamente comprende dichas características A, B y C o, sustancialmente dichas características A, B y C y, por tanto, el término "comprende" referido a un grupo que comprende las características A, B y C debe interpretarse que incluye un grupo que consiste en las características A, B y C, o que consiste sustancialmente en las características A, B y C.

Los líquidos iónicos son sales iónicas que se caracterizan por ser líquidas a temperaturas por debajo de 100 °C. Una de las características estructurales de los líquidos iónicos es que tienen una simetría menor que las sales convencionales y porque la carga de catión y anión se encuentra distribuida en un mayor volumen de la molécula, mediante resonancia, por ejemplo. Como consecuencia, la solidificación de dichas sales ocurre a temperaturas más bajas que en el caso de sales iónicas convencionales, en especial en los casos en los que catión o anión incluyen grupos funcionales de alto peso molecular o de cadena hidrocarbonada larga. De manera general, los líquidos iónicos, se puede mencionar que son alternativas más ecológicas (presentan una presión de vapor casi nula) que los surfactantes tradicionales.

Así, una realización de la invención se refiere al uso de una composición de acuerdo con la presente invención, que comprende un sulfonato de un C_8-C_{15}-alquilbenceno y un líquido iónico que comprende, a su vez, un catión de fórmula (I):



(I)

en el que:

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sodio. Aún más preferentemente, la composición de la presente invención comprende 60% (m/m) de metilsulfato de cocosalquilpentaetoximetilamonio y 40% (m/m) de dodecilbenceno sulfonato de sodio. A efectos de la presente invención los porcentajes indicados como (m/m) son porcentajes en peso (masa/masa).

Una realización particularmente preferente de la presente invención se refiere a una composición que comprende 60% (m/m) de metilsulfato de cocosalquilpentaetoximetilamonio y 40% (m/m) de dodecilbenceno sulfonato de sodio, dado que dicha relación entre líquido iónico y tensioactivo permite obtener una relación optima de solubilización en la que *Vo/Vs* es igual a *Vw/Vs*.

Por otro lado, las formulaciones de la invención tienen ventajosamente una buena inyectabilidad durante los usos y métodos de recuperación mejorada de petróleo descritos. Es decir, las formulaciones de la invención, al ser inyectadas, con agua o salmuera en el yacimiento, se mantienen estables sin precipitación durante un periodo de tiempo adecuado. Así, los ejemplos muestran como para una formulación de acuerdo con la presente invención, que comprende una composición que, a su vez, comprende muy preferentemente entre 40 % m/m de SDBS y 65 % m/m de SDBS (y respectivamente entre 60% y 35% m/m de metilsulfato de cocosalquilpentaetoximetilamonio), no se observó precipitación ni turbidez.

Por otro lado, los ejemplos muestran ensayos de solubilización a 323,15 K (50 °C) y 348,15 K (75 °C), tal como se puede ver en las figuras 2A y 2B respectivamente, el parámetro de solubilización a la relación óptima entre líquido iónico y SDBS disminuyó de 15,5 a 5,6 y 5 respectivamente. Por tanto, la capacidad de las composiciones de la invención para disminuir la tensión interfacial agua/crudo es dependiente de la temperatura.

Así, preferentemente, la recuperación de petróleo se lleva a cabo a una temperatura de entre 15 y 80°C. Más preferentemente, se lleva a cabo a una temperatura de entre 15 y 60°C, aún más preferentemente a una temperatura de entre 20 y 30°C.

Además, los ejemplos incluidos en la presente descripción muestran que las formulaciones de acuerdo con la presente invención que comprenden las composiciones descritas en la presente invención con agua o con salmuera, en las concentraciones utilizadas en los usos y métodos de recuperación mejorada de crudo de la presente invención no dan lugar a cristales líquidos a una temperatura de entre 20 y 30°C, evitando una distribución no uniforme en la roca.

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Por otro lado, las composiciones de acuerdo con la presente invención son especialmente indicadas para su uso en yacimientos carbonatados debido a su baja adsorción en dicho tipo de rocas, evitando la menor pérdida posible de la composición inyectada al quedar esta retenida en la roca. Se sabe que el mecanismo más importante de adsorción es la atracción electrostática entre la superficie cargada de la roca y la cabeza cargada del surfactante. Los surfactantes catiónicos, cargados positivamente, tienden a adsorberse en superficies cargadas negativamente (rocas silíceas), mientras que los tensioactivos aniónicos, cargados negativamente, tienden a adsorberse en superficies con cargas positivas (rocas carbonatadas). (Bera et al, 2013). Las pruebas de adsorción dinámica permiten evaluar la retención de surfactantes en las rocas.

En este sentido, los ejemplos de la presente invención muestran los resultados de adsorción de composiciones de acuerdo con la presente invención con 40 %m/m de SDBS y 60% (m/m) de metilsulfato de cocosalquilpentaetoximetilamonio y, con 73,7%m/m de SDBS y 26,3% (m/m) de metilsulfato de cocosalquilpentaetoximetilamonio, en este tipo de rocas. En la figura 4 se muestran los resultados obtenidos en ensayos de adsorción efectuados con una composición de acuerdo con la presente invención, medidos a 298,15 K (25 °C), en los que se obtuvieron valores muy bajos de 0,37 mg_{mezcla}/g_{roca} para una composición de acuerdo con la invención con un 40 % m/m de SDBS y 60% (m/m) de metilsulfato de cocosalquilpentaetoximetilamonio y de, 0,51 mg_{mezcla}/g_{roca} para una composición de acuerdo con la invención con 73,7 % m/m de SDBS y 26,3% (m/m) de metilsulfato de cocosalquilpentaetoximetilamonio.

Finalmente, los ejemplos de la invención también muestran los resultados obtenidos con las composiciones de acuerdo a la presente invención en una simulación de extracción de crudo en una roca carbonatada. Dichos resultados muestran hasta una extracción terciaria o extracción adicional de 18,2% del crudo original de la roca para una composición preferente de acuerdo con la presente invención con 60% (m/m) de metilsulfato de cocosalquilpentaetoximetilamonio y 40% de SDBS (m/m). Además, los mismos ensayos para una composición de acuerdo con la presente invención que comprende 73,7% m/m de SDBS y 26,3% de metilsulfato de cocosalquilpentaetoximetilamonio proporcionaron valores de tensión interfacial dinámica de $3.6 \cdot 10^{-2}$ mN/m, un valor de adsorción dinámica de 0,51 mg_{surf}/g_{roca} y una extracción adicional del 14,9% del crudo original de la roca. Esto asegura que, aunque la mezcla de la composición con agua o salmuera dentro del yacimiento sufra

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variaciones de concentración en el interior del pozo, las condiciones de extracción siguen siendo favorables.

Así, la presente invención permite obtener formulaciones, con una buena estabilidad a altas temperaturas y altas salinidades, que consiguen, además, extraer un alto porcentaje del crudo retenido en rocas carbonatadas, dado que su adsorción en las mismas muy baja.

Por otro lado, al inyectar agua en un yacimiento (que es una zona rocosa heterogénea per se), se produce un fenómeno de distribución del agua de manera ramificada y que, además, se mueve más rápidamente que el petróleo (aceite) a través de las rocas, que son sólidos porosos, por lo que al final del proceso quedan zonas amplias del yacimiento que no han sido contactadas por el agua, y en las cuales no se ha producido el arrastre del petróleo.

Con el fin de mejorar la eficacia del arrastre del petróleo, en los usos y métodos de la presente invención, durante la inyección con agua o salmuera, la composición de la presente invención o la mezcla de acuerdo con la presente invención, comprenden, además, un polímero. Una realización preferente de la presente invención se refiere a una formulación que comprende agua o salmuera, la composición de la presente invención y un polímero.

También, preferentemente, el método de recuperación mejorada de petróleo de la presente invención comprende preparar una formulación que comprende agua o salmuera, la composición de la presente invención y un polímero; e inyectar dicha formulación en un yacimiento de petróleo con rocas carbonatadas para la extracción del petróleo. En otra realización preferente, el método de recuperación mejorada de petróleo de la presente invención comprende: preparar una formulación que comprende agua o salmuera y la composición de acuerdo con la presente invención; preparar una mezcla de agua o salmuera con un polímero; inyectar dicha formulación en un yacimiento de petróleo con rocas carbonatadas y subsecuentemente inyectar la mezcla de agua o salmuera con un polímero previamente preparada.

En una realización de la invención dicho polímero se selecciona de entre el grupo que consiste en una poliacrilamida, una poliacrilamida parcialmente hidrolizada, poliacrilato, carboximetilcelulosa, polivinilalcohol, sulfonato de poliestireno, polivinilpirrolidona, un copolímero de acrilamida y ácido 2-acrilamido-2-metilpropansulfónico (ABTS), un terpolímero de ABTS, ácido acrílico y acrilamida, un copolimero de estireno y acrilato, copolímeros de acrilamida, ácido acrílico, ABTS y N-vinilpirrolidona, goma de xantana, sizofiran y combinaciones de los mismos. Preferentemente dicho polímero no tiene carga (es decir, es

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de carga neutra) y se selecciona de entre el grupo que consiste en una poliacrilamida y polivinilpirrolidona.

Más preferentemente, la concentración de dicho polímero en la mezcla se selecciona de manera que la mezcla resultante tenga una viscosidad que sea igual o mayor y hasta el doble del valor mayor de entre las viscosidades de, bien el crudo extraído, o de la formulación de acuerdo con la presente invención inyectada en el yacimiento (medida en ambos casos por el mismo método y usando el mismo aparato) que la que se obtendría sin la adición de dicho polímero. Aún más preferentemente, el polímero se selecciona de entre el grupo que consiste en una poliacrilamida y polivinilpirrolidona y la concentración de dicho polímero en la mezcla es de entre 500 a 2000 ppm.

La composición y formulación de acuerdo con la presente invención, que comprenden un sulfonato de un C_8-C_{15}-alquilbenceno, y un líquido iónico que comprende, a su vez, un catión de fórmula (I), o cualquiera de sus realizaciones más preferentes descritas en el presente documento, puede ser utilizada en métodos de extracción mejorada de petróleo, sin la adición de otros componentes durante la inyección en el yacimiento con agua o salmuera y, preferentemente con un polímero, tal como se ha descrito anteriormente, sin necesidad de añadir otros ingredientes, obteniéndose así, elevados porcentajes de extracción de petróleo en yacimientos carbonatados.

Sin embargo, la composición de acuerdo con la presente invención también puede ser utilizada en formulaciones con salmuera y agua de acuerdo con la presente invención, mezcladas con, o con la inyección subsecuente de otros componentes adicionales seleccionados de entre disolventes, pasivadores, inhibidores de parafinas e inhibidores de escamas.

Disolventes adecuados de acuerdo con la presente invención comprenden, pero no se limitan a, alcoholes, tales como alcoholes de cadena carbonada corta como etanol, isopropil alcohol, n-propil alcohol, n-butil alcohol, sec-butil alcohol, n-hexil alcohol sec-hexil alcohol y similares; éteres de alcohol, éteres de alcohol de polialquileno, polialquilen glicoles, poli(oxialquilen)glicoles; éteres de poli(oxialquilen)glicoles u otros disolventes orgánicos, o una combinación de los mismos.

A efectos de la presente invención, el pasivador es una sal de un metal alcalino tal como un hidróxido, un carbonato o un bicarbonato de un metal alcalino, incluyendo, pero sin limitarse

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a carbonato de sodio, bicarbonato de sodio, hidróxido de sodio, hidróxido de potasio, hidróxido de litio, o similares.

De acuerdo con la presente invención, el término inhibidor de parafina se refiere a compuestos que pueden ser añadidos junto con las composición de la presente invención, para inhibir la formación de emulsiones viscosas causadas por aglomeraciones de parafinas en el crudo recuperado. De entre dichos inhibidores de parafina se incluyen, sin limitación, copolímeros de alquil acrilatos, copolímeros de alquil metacrilato, copolímeros de vinilpiridina y alquil acrilato, copolímeros de etileno y vinilacetato, polietilenos ramificados y combinaciones de éstos, entre otros.

Los inhibidores de escamas reducen la deposición de materiales (escamas) durante la extracción e incluyen compuestos tales como polímeros de ácido acrílico, polímeros de ácido maleico, fosfonatos, fosfatos inorgánicos, agentes quelantes como ácidos aminopolicarboxílicos, ácidos policarboxílicos o carbohidratos, entre otros.

EJEMPLOS

Los ejemplos descritos a continuación tienen carácter ilustrativo y no pretenden limitar el ámbito de la presente invención.

1. Materiales y métodos

1.1. Materiales

El surfactante aniónico dodecilbencenosulfonato de sodio (SDBS) se adquirió de Sigma-Aldrich con pureza de grado técnico. El metilsulfato de cocosalquilpentaetoximetilamonio, líquido iónico catiónico comercialmente conocido como Iolilyte C1EG, fue suministrado por Iolitec (pureza>99%). Se simuló agua de mar sintética con la composición indicada en la Tabla 1.

Sal	Concentración (g/kg disolución)
Na_2SO_4	4,84
$CaCl_2 \cdot 2H_2O$	1,89
$MgCl_2 \cdot 6H_2O$	15,06
NaCl	27,94

***Tabla 1**. Composición de la salmuera*

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El cloruro sódico se adquirió de Panreac (pureza> 99% en peso). El sulfato de sodio (pureza> 99% en peso), cloruro de magnesio hexahidratado (pureza> 99% en peso) y cloruro de calcio dihidratado (pureza> 99% en peso) fueron suministrados por Sigma-Aldrich. El yoduro de potasio (pureza> 99% en peso), utilizado como trazador en las pruebas de adsorción dinámica, también fue adquirido de Sigma-Aldrich.

Repsol (refinería de A Coruña, España) suministró el crudo utilizado para las mediciones de tensión interfacial y las pruebas de extracción de crudo. Sus principales propiedades se resumen en la Tabla 2. El *n*-octano (pureza> 99% en peso), utilizado como hidrocarburo en los ensayos de pipetas, se compró a Sigma-Aldrich.

Densidad a 288,15 K (kg/m^3)	811,1
Presión de vapor reid (kPa)	44,9
Viscosidad a 293,15 K (cSt)	4,861
Residuo de carbono (wt%)	1,2522
Asfaltenos (wt%)	0,4624
API°	42,9

Tabla 2. *Propiedades del crudo empleado (proporcionadas por el proveedor)*

Piedras carbonatadas de baja permeabilidad, hechas de piedra caliza y dolomita, se adquirieron de Kocurek Industries. La composición de estas piedras es 50-100% de carbonato de calcio, 0-50% de carbonato de magnesio y 0-15% de sílice cristalina (tipo cuarzo).

1.2. Métodos

Se prepararon disoluciones *stock* de cada surfactante (SDBS y Iolilyte C1EG) al 8% en peso en agua destilada. Para ello se utilizó una balanza Mettler-Toledo AT261 DeltaRange de precisión 10^{-5} g.

1.2.1. Comportamiento de mezclas

El comportamiento de fase de las mezclas de surfactantes se determinó utilizando la metodología de pipeta de vidrio encapsulada (Puerto *et al.*, 2012). Para ello, se introdujo en pipetas de vidrio de borosilicato selladas en la punta, la cantidad necesaria de disoluciones stock para obtener ~0,5 cm^3 de formulación acuosa con la relación SDBS/C1EG requerida. A continuación, se añadieron ~0,5 cm^3 de una disolución con una concentración de sal el doble

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de la indicada en la Tabla 1. Por lo tanto, la disolución acuosa final contenía aproximadamente un 4% en peso de mezcla de surfactantes en salmuera. Esta concentración es más alta que la que se inyecta habitualmente en los pozos, pero facilita la medición de los volúmenes de cada fase para calcular los parámetros de solubilización. Finalmente, se añadió 1 cm^3 de *n*-octano (hidrocarburo generalmente utilizado para simular el crudo de petróleo) y las pipetas se sellaron en la parte superior, se homogeneizaron en un mezclador rotatorio a temperatura ambiente durante 24 h, y luego se introdujeron en un tubo lleno de aceite de silicona.

Las pipetas de vidrio encapsuladas se dejaron llegar a equilibrio en un baño termostático de bloque seco OVAN modelo BD200-RE a la temperatura deseada hasta que los volúmenes de cada fase permanecieron constantes. Se estudiaron tres temperaturas diferentes: 298,15; 323,15 y 348,15 K. A partir de los volúmenes medidos de forma visual, se determinaron los parámetros de solubilización. Estos parámetros representan el volumen de hidrocarburo (V_o) y agua (V_W) dividido por el volumen de surfactante (V_s) en la fase de la microemulsión. Para alcanzar una tensión interfacial ultra-baja, los parámetros de solubilización deben ser iguales y con un valor numérico superior a 10.

Se analizó la posible existencia de cristales líquidos en las microemulsiones buscando birrefringencia bajo luz polarizada.

1.2.2. Inyectabilidad

Se prepararon disoluciones acuosas de la mezcla de ambos surfactantes (en diferentes proporciones), para asegurar la inyectabilidad de la formulación de acuerdo con la presente invención, para su uso en estudios de tensión interfacial dinámica y en los ensayos de extracción. Para ello se utilizó una balanza A&D FA-2000 con una precisión de 10^{-2} g.

Para la preparación, se añadió primero la disolución *stock* de C1EG al agua y posteriormente a esta mezcla se le añadió la disolución *stock* de SDBS. Finalmente, se añadió la misma masa de una disolución con una concentración de sal el doble de la mostrada en la Tabla 1, para obtener una formulación acuosa al 1% en peso de mezcla de surfactantes en la proporción deseada en salmuera.

1.2.3. Tensión interfacial dinámica

La tensión interfacial dinámica (IFT) entre el crudo y la disolución de mezcla de surfactantes en la proporción deseada se midió usando un tensiómetro de gota giratoria Krüss SITE100 a 298,15 K. Para controlar la temperatura se usó aceite proveniente de un baño termostático Julabo EH-5. Se llenó el capilar con la formulación acuosa y se inyectó, mediante una jeringa

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Hamilton, una gota de 4 µL de crudo en el medio del tubo capilar mientras giraba a una velocidad de rotación baja (500 rpm). Se aplicaron velocidades de rotación de entre 2000 y 4000 rpm para obtener una longitud de gota al menos 4 veces mayor que su diámetro. La IFT se calculó según la ecuación de Vonnegut:

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

en donde:

Δρ es la diferencia de densidades entre la fase densa y la fase ligera,

ω es la velocidad angular, y

D es el diámetro de la gota de crudo.

Todos los experimentos se repitieron al menos dos veces para asegurar la repetibilidad.

1.2.4. Ensayos de adsorción y extracción

Los experimentos de adsorción y extracción se llevaron a cabo en un sistema constituido por un recipiente a presión Hassler H00-021-0 y dos bombas de pistón floXlab BTSP 500-5 (equipadas con sensores de presión), equipos suministrados por Vinci Technologies. Para evitar posible flujo hidráulico lateral, en los ensayos se utilizó una bomba hidráulica manual Enerpac P142 para mantener una presión de confinamiento en un valor de al menos 35 bar por encima de la presión de inundación. Los experimentos se llevaron a cabo a temperatura ambiente.

Las rocas utilizadas en los experimentos tenían 3,8 cm de diámetro y 7,6 cm de longitud. Para caracterizarlas, se aplicó vacío durante unas 24 h y se saturaron con salmuera (Tabla 1) a una velocidad de inyección constante de 2 mL/min. Después de 24 h, se determinó el volumen de poro (PV) empleando el peso seco y húmedo de la roca. La permeabilidad absoluta (k_w) se calculó anotando la diferencia de presión entre la entrada y la salida (ΔP) para diferentes caudales de inyección de salmuera. La permeabilidad absoluta se calculó mediante la Ley de Darcy. Tras la inundación de la roca con salmuera, se procedió a la realización de los ensayos de adsorción o de extracción de crudo.

Las pruebas de adsorción dinámica permiten evaluar la retención de surfactantes en las rocas. Para realizar estos ensayos, tras la inundación con salmuera, se inyectó la disolución de trazador (yoduro de potasio) o de formulación acuosa, de la invención, con la mezcla de surfactantes, de forma continua a una velocidad de 2 mL/min, hasta que la concentración en el efluente alcanzó el valor de concentración inicial. Cada 4 mL se recogieron fracciones del

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efluente para ser analizadas. Las concentraciones del trazador y mezcla de surfactantes se determinaron mediante absorción UV usando un espectrofotómetro HP Presario SR1000 UV/Vis. La adsorción se calculó midiendo el retraso entre el trazador y la salida de surfactante en el efluente (Ec. 2),

$$\tau = \frac{(PV_{surf,50\%} - PV_{traz,50\%}) \cdot PV \cdot [C]_{surf}}{masa_{roca}} \qquad (2)$$

en donde:

τ representa la adsorción de surfactante en mg/g de roca,

$PV_{surf,50\%}$ y $PV_{traz,50\%}$ es el volumen de poro para el cual la concentración de surfactante o trazador alcanza el 50% de la concentración inicial,

PV es el volumen de poro en mL,

$[C]_{surf}$ es la concentración inicial de surfactante en mg/mL, y

$masa_{roca}$ se introduce en gramos.

En las pruebas de extracción de crudo, después de la saturación con salmuera, la roca se inundó con petróleo crudo aumentando el caudal de inyección de 1 mL/min a 10 mL/min, con el fin de aumentar la presión de inundación, hasta que no se obtuvo más agua en el efluente. Luego se calculó el crudo inicial de la roca (OOIP) como la diferencia entre el crudo introducido y el crudo extraído.

La saturación de crudo inicial (S_{oi}) y la saturación de agua inicial (S_{wi}) se calcularon usando las Ecuaciones (3) y (4) respectivamente:

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

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

A continuación, como paso de envejecimiento, se dejó reposar la roca durante 5-6 días. Posteriormente, para simular la recuperación secundaria, se realizó una inundación con agua inyectando 3-4 *PV* de salmuera (composición en Tabla 1), a un caudal constante de 2 mL/min, hasta que dejó de salir crudo en el efluente y la presión diferencial se mantuvo constante. La cantidad de crudo recogida mediante la inundación con agua (*ORWF*) permite calcular la saturación de crudo residual (S_{or}):

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

Posteriormente se llevó a cabo una recuperación mejorada de crudo. Para esta etapa de inundación terciaria, la roca se inundó con la formulación de acuerdo a la presente invención, ejemplificada por la combinación de IoLiLyte C1EG y de SDBS, a un caudal constante de 2 mL/min hasta que dejó de obtenerse crudo en el efluente. El petróleo recuperado después de la inundación terciaria (ORTF) permitió el cálculo de la recuperación de petróleo adicional (AOR) en función del OOIP:

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

2. Resultados y discusión

2.1. Comportamiento de mezclas

Las microemulsiones se forman generalmente mezclando aceite y agua o aceite y salmuera en presencia de surfactantes. En condiciones de equilibrio, los sistemas con microemulsiones se pueden clasificar como Winsor I, Winsor II o Winsor III. En los sistemas Winsor tipo I, el surfactante forma una microemulsión de aceite en agua (o/w) en la fase inferior en equilibrio con el exceso de aceite en una fase separada. En los sistemas Winsor tipo II, hay una fase superior que consiste en una microemulsión de agua en aceite (w/o) en equilibrio con un exceso de salmuera o agua. El sistema Winsor III se caracteriza por tener una fase de microemulsión intermedia en equilibrio con una fase superior de exceso de aceite y una inferior de exceso de agua. Este tipo de microemulsiones (sistemas Windsor III) están relacionados con tensiones interfaciales agua/crudo ultra-bajas (10^{-3} mN/m), por lo tanto, pueden conseguir altas recuperaciones de petróleo.

Se utilizó la metodología de pipeta de vidrio encapsulada para determinar la relación óptima SDBS/Iolilyte C1EG, y se analizó mediante escaneo a 298,15 K el comportamiento de fase para diferentes proporciones SDBS/Iolilyte C1EG en la formulación de la presente invención. En esta prueba, la relación agua-hidrocarburo (WOR) fue 1:1 y la concentración de surfactantes total fue aproximadamente del 2% en peso (4% en la fase acuosa).

Se observó una transición de un sistema Winsor I a Winsor III y a Winsor II al aumentar la proporción de SDBS del 0% al 50% en la mezcla. Al aumentar del 50% al 100% de SDBS se observa una segunda transición de un sistema Winsor II a Winsor III y a Winsor I. Los

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parámetros de solubilización a 298,15 K en función de la proporción de SDBS en la formulación se muestran en la Figura 1.

Los parámetros de solubilización (*Vo/Vs* y *Vw/Vs*) indican el volumen de hidrocarburo o agua solubilizada en la microemulsión por volumen de surfactante. En una formulación óptima, la microemulsión solubiliza cantidades iguales de hidrocarburo y agua, lo que significa que *Vo/Vs* es igual a *Vw/Vs*. Esta relación óptima se calcula como la intersección entre las líneas de representación de ambos parámetros de solubilización. Los dos puntos de intersección corresponden a una relación de 44,7% SDBS + 55,3 % Iolilyte C1EG y 73,7 % SDBS + 26,3% Iolilyte C1EG. Para ambas formulaciones óptimas, el parámetro de solubilización tiene un valor de 15,5.

Cuando se repitió el escaneo a 323,15 K y 348,15 K, el parámetro de solubilización a la relación óptima de formulación disminuyó de 15,5 a 5,6 y 5 respectivamente, como se puede ver en la Figura 2. Por tanto, la capacidad de las formulaciones de la presente invención para disminuir la tensión interfacial agua/crudo disminuye cuando se aumenta la temperatura. La temperatura de 298,15 K se selecciona como óptima.

Se estudió la posible existencia de cristales líquidos a la temperatura óptima buscando birrefringencia bajo luz polarizada. Los cristales líquidos en la microemulsión pueden dar lugar a una distribución no uniforme en la roca debido al atrapamiento de fases, por lo que deben evitarse. Las muestras no mostraron birrefringencia bajo luz polarizada hasta una proporción de 80% SDBS + 20% Iolilyte C1EG. Por tanto, no hay cristales líquidos a las proporciones óptimas de la formulación de la presente invención.

2.2. Inyectabilidad

Se estudió la inyectabilidad de las dos formulaciones óptimas, de acuerdo con la presente invención, en agua de mar sintética con una concentración de surfactantes del 1% en peso. También se probaron otras dos proporciones de IoLiLyte C1EG y SDBS ligeramente por encima y por debajo de cada óptimo. Las seis disoluciones acuosas así preparadas se mantuvieron en condiciones ambientales durante varias semanas. Para las proporciones entre 40 % m/m de SDBS y 65 % m/m de SDBS, no se observó precipitación ni turbidez.

En la Figura 3 se muestra una significativa disminución de la IFT dinámica desde $4{,}4 \cdot 10^{-2}$ mN/m hasta $2{,}2 \cdot 10^{-3}$ mN/m cuando se reduce la proporción de SDBS desde 44,7 % m/m (óptimo encontrado en el estudio del comportamiento de mezclas) hasta un 40 % m/m de SDBS. En el caso del segundo óptimo (71,7 % m/m de SDBS), la tensión interfacial aumenta

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al disminuir la proporción de SDBS en la mezcla, y prácticamente no se ve afectada por un incremento de contenido de este surfactante. Los valores de IFT de equilibrio obtenidos fueron de $3{,}6x10^{-2}$ mN/m y $3{,}0x10^{-2}$ mN/m para el 73,7 % m/m y el 78 % m/m de SDBS, respectivamente. Para los ensayos de extracción se seleccionaron las formulaciones de acuerdo con la presente invención, con 40 % m/m y 73,7 % m/m de SDBS, por conducir a valores de IFT muy bajos.

2.4. Adsorción

La formulación propuesta comprende una mezcla de un surfactante aniónico y un líquido iónico catiónico, y se propone para su uso en yacimientos carbonatados. Por ello, se estudió la adsorción de ambas formulaciones óptimas (40 %m/m de SDBS y 73,7%m/m de SDBS) en este tipo de rocas. La concentración inicial de trazador (yoduro de potasio) y surfactante se estableció en el 1% m/m.

En la Figura 4 se representan los valores de adsorción medidos a 298,15 K. La concentración de trazador en el efluente alcanzó el 50% de su valor inicial (*C/Co* = 0.5) tras inyectar 1,2 PV de disolución de trazador. Para SDBS al 40 % m/m y SDBS al 73,7 % m/m, fue necesario inyectar 1,8 PV y 2,0 PV de formulación, respectivamente, para alcanzar el valor de *C/Co* = 0.5. La adsorción se calculó usando la Ec. 2 obteniendo un valor de 0,37 mg_{mezcla}/g_{roca} para la formulación con un 40 % m/m de SDBS y 0,51 mg_{mezcla}/g_{roca} para 73,7 % m/m de SDBS.

2.5. Ensayos de extracción de crudo

Se realizaron dos experimentos de extracción de crudo en rocas carbonatadas cuya caracterización se presenta en la Tabla 3.

El primer ensayo se realizó para estudiar el rendimiento de la formulación optimizada que comprende un 40 %m/m de SDBS y un 60 % m/m lolilyte C1EG. En este ensayo, después de una inundación secundaria con 6.1 PV de salmuera (Tabla 1), sólo se recuperó el 63.43% del OOIP. En el siguiente paso, se inyectaron 5,5 PV de la formulación de surfactante al 1 % m/m hasta que no se extrajo más crudo en el efluente. La cantidad total de crudo recuperado durante el proceso EOR con dicha formulación fue del 18,29% del OOIP.

El segundo ensayo se inició con una extracción secundaria utilizando agua de mar sintética, se requirieron 5,6 PV hasta alcanzar la saturación de crudo residual (S_{or}). En este paso se recuperó el 65,80% del OOIP. Consecutivamente, para la extracción terciaria, se inyectaron 3,7 PV de la formulación de surfactantes en disolución (73,7 % m/m de SDBS + 26,3 % m/m

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de Iolilyte C1EG) al 1% m/m, hasta que dejó de obtenerse crudo en el efluente. Se obtuvo una recuperación adicional de crudo del 14,94% del OOIP (Tabla 3).

	Ensayo 1	**Ensayo 2**
Porosidad de la roca (%)	14.33	15.12
Permeabilidad (mD)	8.87	20.70
Volumen de poro (mL)	12.17	13.22
OOIP (mL)	8.75	8.70
Saturación de crudo inicial, S_{oi} (%)	71.87	65.80
Saturación de agua inicial, S_{Wi} (%)	28.13	34.20
Crudo recuperado tras inundación con agua (%OOIP)	63.43	67.82
Saturación de crudo residual, S_{or} (%)	26.28	21.18
Disolución de surfactante inyectada	5.5 PV de formulación al 1%m/m (40%m/m SDBS + 60%m/m Iolilyte C1EG)	3.7 PV de formulación al 1%m/m (73.7%m/m SDBS + 26.3%m/m Iolilyte C1EG)
Recuperación adicional de crudo con surfactante (%OOIP)	18.29	14.94

Tabla 3. Resumen de los ensayos de extracción de crudo.

REFERENCIAS

Bera, A., Kumar, T., Ojha, K., Mandal, A., 2013. Adsorption of surfactants on sand surface in enhanced oil recovery: Isotherms, kinetics and thermodynamic studies. Applied Surface Science 284, 87-99. http://dx.doi.org/10.1016/j.apsusc.2013.07.029

Puerto, M., Hirasaki, G.J., Miller, C.A., Barnes, J.R., 2012. Surfactant Systems for EOR in High- Temperature, High-Salinity Environments. SPE journal. 17, 11-19. https://doi.org/10.2118/129675-PA

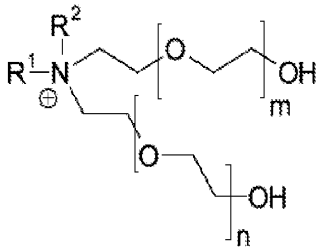
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REIVINDICACIONES

1. Composición que comprende:

un sulfonato de un C_8-C_{15}-alquilbenceno, y

un líquido iónico que comprende, a su vez, un catión de fórmula (I)



(I)

en el que:

R^1 es un grupo seleccionado de entre cadenas alifáticas saturadas o monoinsaturadas con un número par de entre 8 y 18 átomos de carbono, de manera que al menos 10% de dichas cadenas hidrocarbonadas es un grupo alquilo de 12 átomos de carbono;

R^2 es un grupo C_1-C_3 alquilo; y

en donde **m** y **n** son dos números enteros tales que **m+n** es un número entero entre 5 y 10.

2. Composición de acuerdo con la reivindicación 1, en el que el catión de fórmula (I) es cocosalquilpentaetoximetilamonio.

3. Composición de acuerdo con cualquiera de las reivindicaciones 1 o 2, en el que el líquido iónico comprende un anión seleccionado de entre el grupo que consiste en: fluoruro, cloruro, bromuro, ioduro, sulfato, metilsulfato, etilsulfato, dodecilbenceno sulfonato, nitrato, tosilato, metanosulfonato, trifluorometanosulfonato, trifluoroacetato y tetracloroaluminato.

4. Composición de acuerdo con cualquiera de las reivindicaciones 1 a 3, en el que el sulfonato de un C_8-C_{15}-alquilbenceno es dodecilbenceno sulfonato de sodio.

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5. Composición de acuerdo con cualquiera de las reivindicaciones 1 a 4 que comprende dodecilbenceno sulfonato de sodio y metilsulfato de cocosalquilpentaetoximetilamonio.

6. Composición de acuerdo con la reivindicación 5 que comprende entre 25% y 70% (m/m) de metilsulfato de cocosalquilpentaetoximetilamonio y entre 30% y 75% (m/m) de dodecilbenceno sulfonato de sodio.

7. Composición de acuerdo con la reivindicación 6 que comprende entre 55% y 65% (m/m) de metilsulfato de cocosalquilpentaetoximetilamonio y entre 35% y 45% (m/m) de dodecilbenceno sulfonato de sodio.

8. Composición de acuerdo con cualquiera de las reivindicaciones 6 o 7 que comprende 60% (m/m) de metilsulfato de cocosalquilpentaetoximetilamonio y 40% (m/m) de dodecilbenceno sulfonato de sodio.

9. Composición de acuerdo con cualquiera de las reivindicaciones 1 a 8, que comprende, además, un polímero seleccionado de entre el grupo que consiste en: una poliacrilamida y polivinilpirrolidona.

10. Formulación que comprende:

- una composición de acuerdo con cualquiera de las reivindicaciones 1 a 9; y
- agua o salmuera.

11. Uso de una composición según cualquiera de las reivindicaciones 1 a 9 o de una formulación de acuerdo con la reivindicación 10, en un método de recuperación mejorada de petróleo en yacimientos con rocas carbonatadas.

12. Uso de acuerdo con la reivindicación 11, en donde la concentración de dicha composición en agua o salmuera es de entre 0,25% y 4% en peso.

13. Método de recuperación mejorada de petróleo que comprende inyectar en un yacimiento de petróleo con rocas carbonatadas una formulación de acuerdo con la reivindicación 10.

14. Método de acuerdo con la reivindicación 13, en donde la formulación comprende la composición a una concentración en el agua o salmuera de entre 0,25% y 4% en peso.

15. Método de acuerdo con cualquiera de las reivindicaciones 13 o 14, en donde la formulación comprende, además, un polímero seleccionado de entre el grupo que consiste en: una poliacrilamida y polivinilpirrolidona.

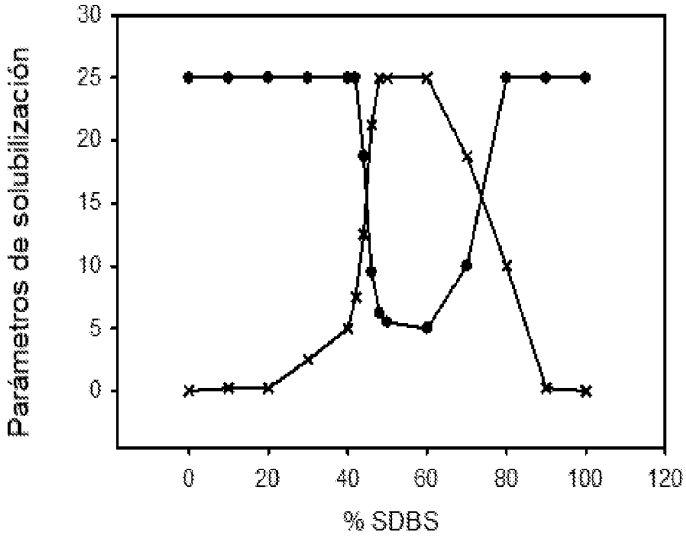
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16. Método de acuerdo con cualquiera de las reivindicaciones 13 o 14, en donde dicho método comprende, además, inyectar un polímero seleccionado de entre el grupo que consiste en: una poliacrilamida y polivinilpirrolidona, mezclado con agua o salmuera.

17. Método de acuerdo con cualquiera de las reivindicaciones 15 o 16, en el que la concentración de dicho polímero es de entre 500 a 2000 ppm.

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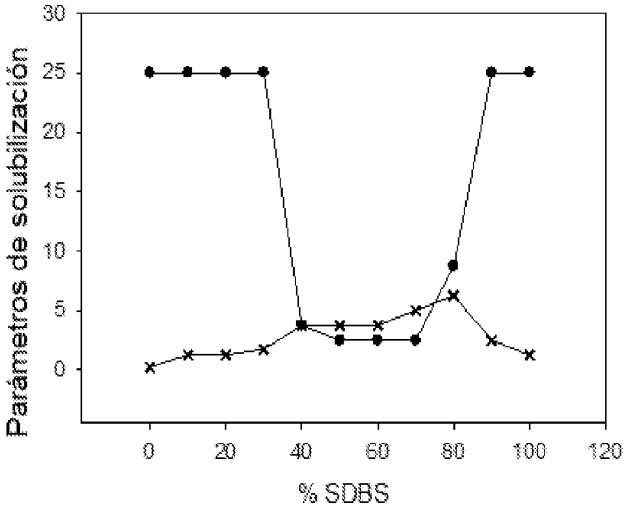
FIGURA 1



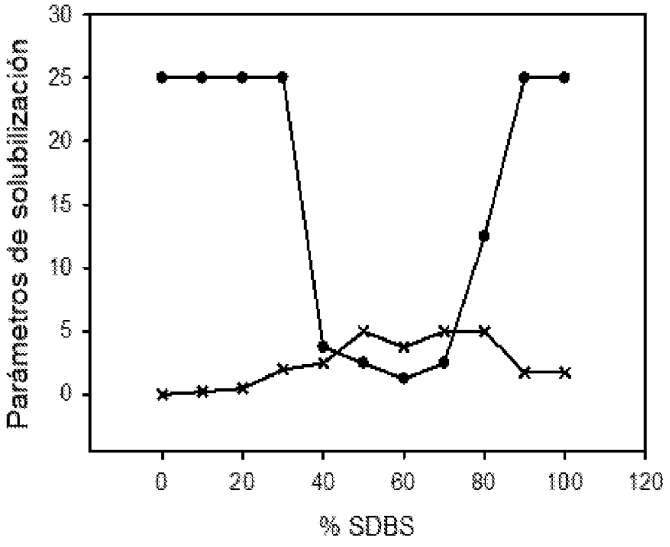
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FIGURA 2

A



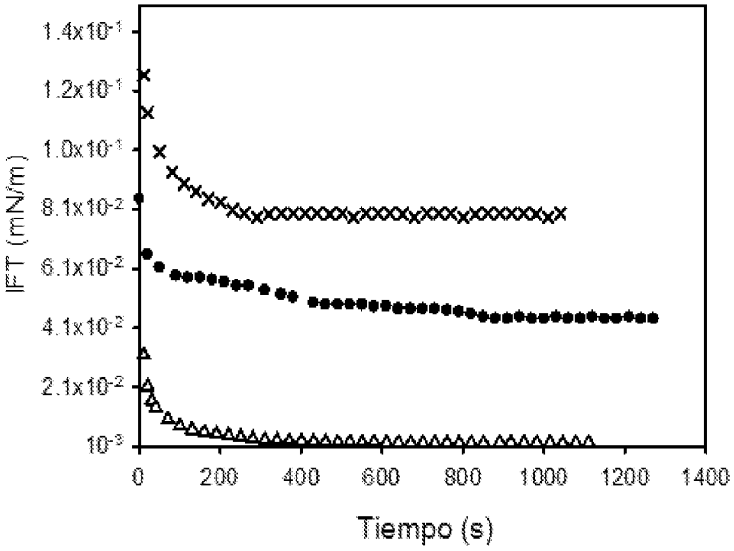
B



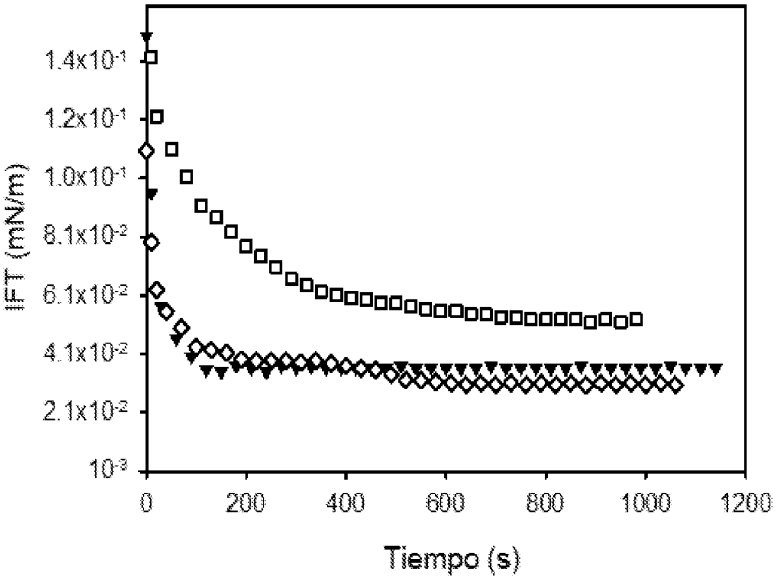
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FIGURA 3

A

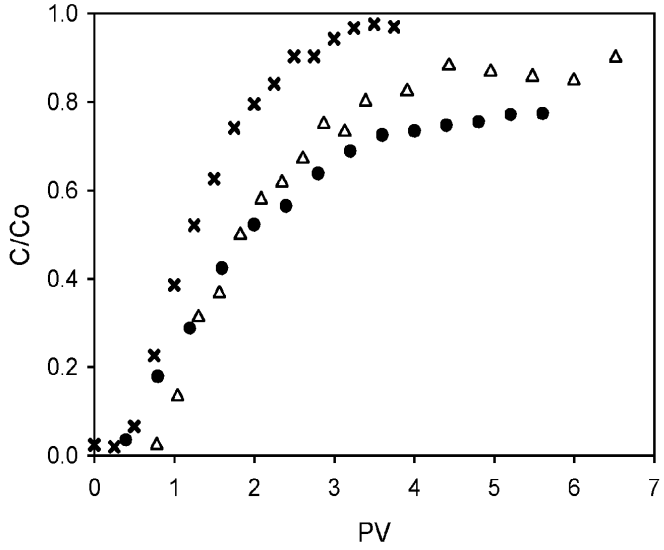


B



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FIGURA 4



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INTERNATIONAL SEARCH REPORT

International application No.
PCT/ES2022/070111

A. CLASSIFICATION OF SUBJECT MATTER

E21B43/22 (2006.01)
C09K8/584 (2006.01)
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
E21B, C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

INVENES, EPODOC, WPI, TXTE, REGISTRY, CAPLUS, EMBASE, XPESP, NPL, GOOGLE SCHOLAR

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHAOS CARBALLO, M.Z. "Modificación de la solubilidad aparente del hexaclorociclohexano (HCH) mediante la aplicación de líquidos iónicos y surfactantes para su potencial aplicación en remediación de suelos". Universidad de Santiago de Compostela. Escuela Técnica Superior de Ingeniería. Máster en Ingeniería Ambiental. July 2020. [Retrieved 24.02.2022]. Retrieved from: <http://hdl.handle.net/10347/2656>.	1-8, 10
Y	See page 29, table 2; page 30, paragraph 1 and part 2.2.	9, 11-17
Y	SAKTHIVEL, S. et al. "Effect of Alkyl Ammonium Ionic Liquids on the Interfacial Tension of a Crude Oil-Water System and Their Use for the Enhanced Oil Recovery Using Ionic Liquid Polymer Flooding". Energy and Fuels 2016, Volume 30, pages 2514-2523. [Available online 15.02.2016]. DOI: 10.1021/acs.energyfuels.5b03014. ISSN: 0877-0624. See page 2514, abstract; page 2520, table 2.	9, 11-17

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance.
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure use, exhibition, or other means.
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27/05/2022	**(30/05/2022)**
Name and mailing address of the ISA/ OFICINA ESPAÑOLA DE PATENTES Y MARCAS Paseo de la Castellana, 75 - 28071 Madrid (España) Facsimile No.: 91 349 53 04	Authorized officer G. Esteban García Telephone No. 91 3495425

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/ES2022/070111

C (continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of documents, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 2792305 A1 (BASF SE, DE) 15.09.2011, page 5, line 34-page 6, line 13; page 8, lines 11-13; 23-25; page 10, lines 30-34; page 15, lines 2-8.	1, 3, 10-14
X	WO 93/04265 A1 (CHEVRON RESEARCH AND TECHNOLOGY COMPANY) 04.03.1993, page 1, lines 9-14; page 4, lines 12-15, 28-31; page 4, line 32- page 5, line 4; page 5, lines 9-28; page 6, line 4-13.	1, 3, 10-14
P,X	SOMOZA, A. et al. "Design and performance analysis of a formulation based on SDBS and ionic liquid for EOR in carbonate reservoirs". Journal of Petroleum Science and Engineering 2022, Volume 209, page 109856. [Available online 19.11.2021]. DOI: 10.1016/j.petrol.2021.109856. ISSN: 0920-4105; 1873-4715 (online). [Retrieved 02.03.2022]. Retrieved from: <https://www.sciencedirect.com/science/article/pii/S0920410521014753>. See page 1, abstract; page 3, table 1; page 10, conclusions.	1-17
A	BENZAGOUTA, M.S. et al. "Ionic liquids as novel surfactants for potential use in enhanced oil recovery". Korean Journal of Chemical Engineering 2013, Volume 30, Number 11, pages 2108-2117. [Available online 06.09.2013]. DOI: 10.1007/s11814-013-0137-1. ISSN: 0256-1115; 1975-7220 (online). [Retrieved 01.03.2022]. Retrieved from: <https://www.cheric.org/PDF/KJChE/KC30/KC30-11-2108.pdf>. See page 2108, abstract; page 2113, scheme 1 and table 1.	1-17
A	US 4434062 A (OSWALD, A.A. et al.) 28.02.1984, column 2, lines 21-35; column 8, line 59-column 9, line 47.	1-17
A	JIA, H. "Systematic investigation of the effects of mixed cationic/anionic surfactants on the interfacial tension of a water/model oil system and their application to enhance crude oil recovery". Colloids and Surfaces A; Physicochemical and Engineering Aspects 2017, Volume 529, pages 621-627. [Available online 22.06.2017]. DOI: 10.1016/j.colsurfa.2017.06.055. ISSN: 0927-7757. [Retrieved 01.03.2022]. Retrieved from: <https://www.sciencedirect.com/science/article/pii/S0927775717306179>. See page 621, abstract; page 622, part 2.1; page 625, part 3.4 and conclusions.	1-17
A	ZABIHI, S. et al. "Relative permeabilty measurements in carbonate rocks, the effects of conventional surfactants vs. Ionic liquid-based surfactants". Journal of Dispersion Science and Technology 2019, Volume 41, Number 12, pages 1797-1811. [Available online 15.07.2019]. DOI: 10.1080/01932691.2019.1637262. ISSN: 0193-2691; 1532-2351 (online). [Retrieved 01.03.2022]. Retrieved from: <https://www.researchgate.net/publication/334473786_Relative_permeability_measurement_in_carbonate_rocks_the_effects_of_conventional_surfactants_vs_Ionic_liquid-based_surfactants>. See page 1797, abstract; page 1809-1810, conclusions.	1-17

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/ES2022/070111

Patent document cited in the search report	Publication date	Patent family member(s)	Publication date
CA 292305 A	20.08.1929	NONE	
WO 9304265 A1	04.03.1993	US5246072 A	21.09.1993
		NO934587L L	01.02.1994
		GB2274128 A	13.07.1994
		GB2274128 B	28.06.1995
		CA2110918 A1	04.03.1993
US 4434062 A	28.02.1984	GB2057533 A	01.04.1981
		GB2057533 B	07.04.1983
		FR2458671 A1	02.01.1981
		FR2458671 B1	14.01.1983
		DE3022336 A1	18.12.1980
		CA1136839 A	07.12.1982

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INFORME DE BÚSQUEDA INTERNACIONAL

Solicitud internacional nº
PCT/ES2022/070111

A. CLASIFICACIÓN DEL OBJETO DE LA SOLICITUD
E21B43/22 (2006.01)
C09K8/584 (2006.01)
De acuerdo con la Clasificación Internacional de Patentes (CIP) o según la clasificación nacional y CIP.

B. SECTORES COMPRENDIDOS POR LA BÚSQUEDA

Documentación mínima buscada (sistema de clasificación seguido de los símbolos de clasificación)
E21B, C09K

Otra documentación consultada, además de la documentación mínima, en la medida en que tales documentos formen parte de los sectores comprendidos por la búsqueda

Bases de datos electrónicas consultadas durante la búsqueda internacional (nombre de la base de datos y, si es posible, términos de búsqueda utilizados)
INVENES, EPODOC, WPI, TXTE, REGISTRY, CAPLUS, EMBASE, XPESP, NPL, GOOGLE SCHOLAR

C. DOCUMENTOS CONSIDERADOS RELEVANTES

Categoría*	Documentos citados, con indicación, si procede, de las partes relevantes	Relevante para las reivindicaciones nº
X	CHAOS CARBALLO, M.Z. "Modificación de la solubilidad aparente del hexaclorociclohexano (HCH) mediante la aplicación de líquidos iónicos y surfactantes para su potencial aplicación en remediación de suelos". Universidad de Santiago de Compostela. Escuela Técnica Superior de Ingeniería. Máster en Ingeniería Ambiental. Julio de 2020. [Recuperado el 24.02.2022]. Recuperado de: <http://hdl.handle.net/10347/2656>.	1-8, 10
Y	Ver página 29, tabla 2; página 30, párrafo 1 y apartado 2.2.	9, 11-17
Y	SAKTHIVEL, S. et al. "Effect of Alkyl Ammonium Ionic Liquids on the Interfacial Tension of a Crude Oil-Water System and Their Use for the Enhanced Oil Recovery Using Ionic Liquid Polymer Flooding". Energy and Fuels 2016, Volumen 30, páginas 2514-2523. [Disponible en línea el 15.02.2016]. DOI: 10.1021/acs.energyfuels.5b03014. ISSN: 0877-0624. Ver página 2514, resumen; página 2520, tabla 2.	9, 11-17

☒ En la continuación del recuadro C se relacionan otros documentos ☒ Los documentos de familias de patentes se indican en el Anexo

* Categorías especiales de documentos citados:
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"L" documento que puede plantear dudas sobre una reivindicación de prioridad o que se cita para determinar la fecha de publicación de otra cita o por una razón especial (como la indicada).
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Fecha en que se ha concluido efectivamente la búsqueda internacional.	Fecha de expedición del informe de búsqueda internacional.
27/05/2022	**30 de mayo de 2022 (30/05/2022)**
Nombre y dirección postal de la Administración encargada de la búsqueda internacional OFICINA ESPAÑOLA DE PATENTES Y MARCAS Paseo de la Castellana, 75 - 28071 Madrid (España) Nº de fax: 91 349 53 04	Funcionario autorizado G. Esteban García Nº de teléfono 91 3495425

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INFORME DE BÚSQUEDA INTERNACIONAL

Solicitud internacional nº
PCT/ES2022/070111

C (Continuación). DOCUMENTOS CONSIDERADOS RELEVANTES

Categoría *	Documentos citados, con indicación, si procede, de las partes relevantes	Relevante para las reivindicaciones nº
X	CA 2792305 A1 (BASF SE, DE) 15.09.2011, página 5, línea 34-página 6, línea 13; página 8, líneas 11-13; 23-25; página 10, líneas 30-34; página 15, líneas 2-8.	1, 3, 10-14
X	WO 93/04265 A1 (CHEVRON RESEARCH AND TECHNOLOGY COMPANY) 04.03.1993, página 1, líneas 9-14; página 4, líneas 12-15, 28-31; página 4, línea 32- página 5, línea 4; página 5, líneas 9-28; página 6, línea 4-13.	1, 3, 10-14
P,X	SOMOZA, A. et al. "Design and performance analysis of a formulation based on SDBS and ionic liquid for EOR in carbonate reservoirs". Journal of Petroleum Science and Engineering 2022, Volumen 209, página 109856. [Disponible en línea el 19.11.2021]. DOI: 10.1016/j.petrol.2021.109856. ISSN: 0920-4105; 1873-4715 (en línea). [Recuperado el 02.03.2022]. Recuperado de: <https://www.sciencedirect.com/science/article/pii/S0920410521014753>. Ver página 1, resumen; página 3, tabla 1; página 10, conclusiones.	1-17
A	BENZAGOUTA, M.S. et al. "Ionic liquids as novel surfactants for potential use in enhanced oil recovery". Korean Journal of Chemical Engineering 2013, Volumen 30, Número 11, páginas 2108-2117. [Disponible en línea el 06.09.2013]. DOI: 10.1007/s11814-013-0137-1. ISSN: 0256-1115; 1975-7220 (en línea). [Recuperado el 01.03.2022]. Recuperado de: <https://www.cheric.org/PDF/KJChE/KC30/KC30-11-2108.pdf>. Ver página 2108, resumen; página 2113, esquema 1 y tabla 1.	1-17
A	US 4434062 A (OSWALD, A.A. et al.) 28.02.1984, columna 2, líneas 21-35; columna 8, línea 59-columna 9, línea 47.	1-17
A	JIA, H. "Systematic investigation of the effects of mixed cationic/anionic surfactants on the interfacial tension of a water/model oil system and their application to enhance crude oil recovery". Colloids and Surfaces A; Physicochemical and Engineering Aspects 2017, Volumen 529, páginas 621-627. [Disponible en línea el 22.06.2017]. DOI: 10.1016/j.colsurfa.2017.06.055. ISSN: 0927-7757. [Recuperado el 01.03.2022]. Recuperado de: <https://www.sciencedirect.com/science/article/pii/S0927775717306179>. Ver página 621, resumen; página 622, apartado 2.1; página 625, apartado 3.4 y conclusiones.	1-17
A	ZABIHI, S. et al. "Relative permeabilty measurements in carbonate rocks, the effects of conventional surfactants vs. Ionic liquid-based surfactants". Journal of Dispersion Science and Technology 2019, Volumen 41, Número 12, páginas 1797-1811. [Disponible en línea el 15.07.2019]. DOI: 10.1080/01932691.2019.1637262. ISSN: 0193-2691; 1532-2351 (en línea). [Recuperado el 01.03.2022]. Recuperado de: <https://www.researchgate.net/publication/334473786_Relative_permeability_measurement_in_carbonate_rocks_the_effects_of_conventional_surfactants_vs_Ionic_liquid-based_surfactants>. Ver página 1797, resumen; página 1809-1810, conclusiones.	1-17

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INFORME DE BÚSQUEDA INTERNACIONAL

Informaciones relativas a los miembros de familias de patentes

Solicitud internacional nº

PCT/ES2022/070111

Documento de patente citado en el informe de búsqueda	Fecha de Publicación	Miembro(s) de la familia de patentes	Fecha de Publicación
CA 292305 A	20.08.1929	NINGUNO	
WO 9304265 A1	04.03.1993	US5246072 A	21.09.1993
		NO934587L L	01.02.1994
		GB2274128 A	13.07.1994
		GB2274128 B	28.06.1995
		CA2110918 A1	04.03.1993
US 4434062 A	28.02.1984	GB2057533 A	01.04.1981
		GB2057533 B	07.04.1983
		FR2458671 A1	02.01.1981
		FR2458671 B1	14.01.1983
		DE3022336 A1	18.12.1980
		CA1136839 A	07.12.1982

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5.GENERAL DISCUSSION



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The unique properties of ILs have led to the exploration of their use in many different industries, such as chemical, pharmaceutical, energy storage, and agriculture [17]. The ability of ILs to act as efficient solvents, surfactants, and catalysts for various reactions and processes makes them a versatile and promising class of compounds. The utilization of ILs in the petrochemical industry is a rapidly progressing field that shows great potential for the future. ILs possess interesting properties such as negligible vapor pressure, tunability, high solvation capacity and good thermal stability, making them highly versatile in refinery-related applications. Thus, they have been proposed to improve both upstream and downstream processes [18,19]. Their ability to dissolve and stabilize complex and challenging components, including heavy hydrocarbons and polar compounds, makes them ideal candidates for efficient extraction and purification processes. Additionally, ILs can serve as effective catalysts or co-catalysts, accelerating reaction rates and enhancing selectivity in complex petrochemical transformations.

EOR methods have become increasingly important as the demand for oil and gas continues to rise. Surfactants are amphiphilic molecules widely used in EOR applications like surfactant flooding processes and foam generation for CO_2-EOR extraction. However, traditional surfactants such as alkyl sulfates, alkyl ether sulfates and alkylbenzene sulfonates (ABSs), can face several problems that limit their effectiveness. These drawbacks include:

- Salinity sensitivity: One of the biggest impediments to the use of these surfactants is their poor solubility and compatibility in water containing divalent cations. The effectiveness of traditional surfactants can be greatly reduced in the presence of high salinity brines present in many petroleum reservoirs.

- Stability: EOR processes often involve high-temperature reservoir conditions causing many traditional surfactants to degrade or lose their effectiveness. The stability of these surfactants in such harsh conditions is a major issue in EOR applications.

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- Adsorption: Surfactants can be adsorbed onto the rock surface, reducing their concentration in the solution thus limiting their effectiveness. Traditional surfactants are generally anionic, and tend to adsorb in positively charged surfaces (carbonate rocks) due to electrostatic interactions. The high adsorption values expected usually rule out the use of these chemicals alone in carbonate reservoirs.

- Environmental impact: Some traditional surfactants can have a negative impact on the environment due to their high toxicity and low biodegradability.

The addition of co-solvents and co-surfactants is usually mandatory to prevent precipitation, reduce adsorption or improve surfactant stability and salt tolerance at reservoir conditions. However, it is crucial to also focus on minimizing the number of chemicals employed to develop feasible processes. These challenges have led to the exploration of new chemicals such as ILs. The papers presented in this Thesis aim to make a contribution to the application of SAILs in chemical EOR processes and address the shortcomings of current methods.

The literature review carried out showed that the main advantages of the use of ILs in EOR are likely their tunability and stability in harsh environmental conditions. However, despite the almost unlimited possibilities of ILs, the number of studies providing a practical approach to their application is still very scarce. Many authors performed oil extraction tests using unconsolidated sand-packs characterized by high permeability and porosity. Thus, results from these experiments should be considered with caution. Crude oil extraction might be overestimated compared to real reservoir rocks due to the lower capillary forces retaining oil within the pores. Additional oil recoveries of up to 32% of the OOIP were reported in the literature in sand-pack extractions tests. Regarding experiments using real reservoir rocks, additional oil recoveries with pure ILs up to 16.5% of the OOIP were reported. Furthermore, when ILs are applied in combination with other chemicals such as polymers or alkalis, values up to 25% of the OOIP were obtained. However, the number of adsorption studies found in the literature is surprisingly scarce and, in some cases, the high concentration of chemicals employed makes the proposed formulations impractical for real applications. Generally, wettability alteration and IFT reduction were the main mechanisms

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associated with the additional oil recovery. It is also worth mentioning that most formulations were defined using IFT reduction as a target property, and there is a limited number of studies analyzing phase behavior. In addition, most ILs were proposed for sandstones. Until recently, only the IL 1-octadecyl-3-methylimidazolium chloride ([C_{18}mim]Cl) had been proposed for carbonate reservoirs [20]. Manshad et al. [20] developed a formulation containing 170 ppm of this IL and performed core flooding tests on real carbonate rocks reporting an additional oil recovery of 13% of the OOIP. A need to research the possibilities of SAILs in EOR processes, especially in carbonate reservoirs, was detected.

In this context, the objective of developing surfactant formulations based on SAILs for EOR in carbonate rocks was set. To achieve this goal, and focusing on the experimental work of this Thesis, the following procedure was established to develop and optimize suitable formulations:

1. IL characterization. It is important to study the characteristics of the surfactant intended for practical application. One of the most important properties is the CMC, the concentration at which surfactant molecules self-assemble to form micelles. At concentrations above the CMC, the surface tension remains relatively constant or changes with a lower slope [21]. Knowing the CMC and the surface tension at that point is crucial to optimize the surfactant concentration. The CMC was determined by measuring the surface tension of IL solutions with varying concentrations using a force tensiometer.

2. Phase behavior studies. The knowledge of phase behavior is the first and fundamental step when selecting an adequate surfactant formulation for EOR. When oil and water or brine are mixed together in the presence of a surfactant, a microemulsion system is usually formed. Microemulsion systems can be classified as Winsor I, Winsor II or Winsor III [22]. In Winsor I systems there is an equilibrium between an oil-in-water microemulsion and an upper excess oil phase. Low IFTs with almost negligible surfactant loss through partitioning into the crude oil can be achieved using these systems. However, they are not the most favorable ones to achieve ultralow IFT between crude oil and water. In Winsor II systems a lower excess water phase is in equilibrium with a water-

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in-oil microemulsion. Winsor II behavior is not favorable for EOR since it leads to a high surfactant retention in the oil phase. Finally, in Winsor III systems a middle phase bicontinuous microemulsion is in equilibrium with both an upper excess oil phase and a lower excess water phase. It is known that Winsor type III microemulsions lead to ultra-low IFT (10^{-3} mN/m) but, the application of these systems can be challenging since they usually experience high adsorption and poor solubility in brine [23]. Surfactants showing Winsor type I or type III behavior are usually considered for EOR applications. Phase behavior of the system can change varying parameters like salinity, temperature or blend ratio. Information obtained from these experiments can help to optimize the surfactant formulation for the specific reservoir conditions. Pipette tests are a practical method to study phase behavior and determine solubilization parameters. Solubilization parameters are defined as the volume of oil or water solubilized per volume of surfactant in the microemulsion phase. Formulations with equal solubilization parameters exceeding 10 are considered optimal for achieving minimum IFT [24].

3. IFT measurements. IFT reduction is a key mechanism by which surfactants improve oil recovery. Measuring IFT at various concentrations and conditions can help to determine the optimum surfactant formulation to enhance oil mobilization. Dynamic IFT between crude oil and surfactant solution were measured using a spinning drop tensiometer. This device employs the principle of rotation to generate a droplet that is suspended and spins in a liquid medium. The Vonnegut equation is used to calculate the IFT between the two non-miscible liquid phases. The Vonnegut equation is a mathematical relationship that takes into account the centrifugal force on the droplet's shape and relates it to the IFT [25]. The equation is given by:

$$IFT = \Delta\rho \cdot \omega^2 \cdot D^3/32 \qquad \text{Eq. (5.1)}$$

where $\Delta\rho$ is the density difference between dense and light phase, ω is the angular velocity and D is the diameter of the oil drop.

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4. Adsorption studies. Adsorption of the surfactant onto the rock surface can affect the performance of the formulation, reducing surfactant availability in the water phase. The study of surfactant retention by means of adsorption experiments is an essential step in designing efficient surfactant EOR strategies. Static and dynamic adsorption studies are two methods used to investigate the interaction between surfactants and reservoir rock surfaces.

   - Static adsorption studies. These tests measure the amount of surfactant adsorbed onto crushed reservoir rocks when they are in contact with no flow or movement. In this method, a known amount of surfactant is mixed with a fixed quantity of crushed rock sample and mixed for a specified period of time. The concentration of the surfactant in the solution is measured with time. The difference between final and initial concentration is used to determine the amount of surfactant adsorbed onto the rock surface. Static adsorption studies provide information about the equilibrium adsorption capacity and adsorption kinetics, which help in understanding the surfactant-rock interactions. It should be noted that results from these tests usually lead to higher adsorption values than those expected in reservoirs, due to the larger surface area used. However, they can be helpful offering a fast-screening method to compare adsorption levels for different surfactant formulations in the same conditions.

   - Dynamic Adsorption Studies. In these tests, adsorption of surfactants onto the rock surface is measured under conditions that mimic the flow of fluids in a reservoir. To that aim, a solution containing a known concentration of surfactant is passed through a rock sample at a specific flow rate. The effluent solution is collected at various time intervals, and the concentration of surfactant in the effluent is measured. By monitoring the concentration of surfactant in the effluent over time, dynamic adsorption studies provide information about surfactant retention during flow. Results obtained from dynamic tests provide more realistic adsorption values than those obtained in static studies.

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5. Wettability measurements. Apart from IFT reduction, wettability alteration is another important mechanism associated with surfactant EOR. Contact angle experiments were implemented to estimate the ability of the surfactant formulation to alter the wettability of carbonate rocks from oil-wet to intermediate-wet or water-wet conditions. Contact angle measurements are performed by placing a droplet of crude oil on the rock surface and measuring the angle formed between them. The effectiveness of the formulation in altering the wettability of the surface is assessed by comparing contact angles before and after surfactant treatment.

6. Core flooding tests. Core flooding tests serve as an important tool for evaluating the effectiveness of surfactant formulations in enhancing oil recovery from reservoir rocks. These tests involve placing a reservoir rock sample inside a core holder and saturating it with seawater and crude oil to mimic real conditions. The subsequent step entails conducting a conventional water flooding process to extract the crude oil until reaching residual oil saturation. Finally, the EOR step is initiated, during which the surfactant formulation is injected into the core to measure the incremental oil recovery achieved. In certain cases, the EOR step combines both surfactant and polymer flooding techniques.

Once the experimental procedure was set, fifteen SAILs with the most common functional groups (imidazolium, pyridinium, ammonium, and phosphonium) were screened to study their viability for the intended application. To select the most promising SAIL, aqueous solubility was checked by preparing a solution of SAIL in distilled water (1 wt%). Subsequently, brine stability of water soluble SAILs was assessed. In these tests, brine concentration was set to 5 wt% NaCl and SAIL concentration to 1 wt%. Solutions showing cloudiness or precipitation were considered unstable and discounted for the application. Finally, IFT between a solution of 1 wt% SAIL in water and crude oil was measured. Results are shown in Table 5.1. The lowest IFT (0.40 mN/m) was found for the SAIL 1-decyl-3-methylimidazolium triflate. Since the literature review revealed IFT reduction to be one of the most important mechanisms for crude oil extraction, 1-decyl-3-methylimidazolium triflate was selected

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as an interesting SAIL to develop a surfactant formulation for EOR in carbonate reservoirs.

Table 5.1. IL screening for surfactant EOR.

Compound	Water solubility	Brine stability	IFT (mN/m)
1,3-Didecyl-2-methylimidazolium chloride	Yes	No	-
1-decyl-3-methylimidazolium triflate	Yes	Yes	0.40
1-methyl-3-octadecylimidazolium choride	No	-	
1-methyl-3-octylimidazolium chloride	No	-	
1-methyl-3-octylimidazolium triflate	Yes	Yes	8.1
1-hexadecylpyridinium chloride	Yes	No	
1-dodecylpyridinium chloride	Yes	Yes	2.5
Methyltrioctylammonium chloride	No	-	
Methyltrioctylammonium triflate	No	-	
Hexadecyltrimethylammonium bromide	No	-	
Benzyldimethyldodecylammonium chloride	Yes	Yes	0.76
IoLiLyte 221PG (quaternary ammonium salt)	Yes	Yes	22
1-hexadecyl triphenylphosphonium bromide	Yes	No	
Sodium 1-decanesulfonate	Yes	No	
Glycolic acid ethoxylate lauryl ether	No	-	

The above mentioned experimental procedure was applied to the development of a formulation based on the SAIL 1-decyl-3-methylimidazolium triflate. It showed a Winsor type I behavior in the salinity range studied (0 -15 wt% NaCl). Subsequently, the optimization of the formulation was carried out via IFT measurements. It was found out that IFT increased with the addition of NaCl and reduced with the addition of NaOH. Alkalis, like NaOH, improve the interfacial activity of surfactants through in situ saponification by reaction of the alkali with the naphthenic acids of crude oil. Taking into account this behavior, a formulation consisting of 4000 ppm of SAIL, 2 wt% NaCl and 1 wt% NaOH (IFT=0.58 mN/m) was proposed. Dynamic adsorption studies revealed that the adsorption of the SAIL in carbonate rock could be assumed to be low enough to consider the formulation suitable for the application. An additional oil recovery of 10.5% of OOIP was obtained injecting 4 PV of surfactant formulation. When the tertiary recovery step was performed combining surfactant (1 PV) and polymer (3 PV) flooding, the additional oil recovered was reduced to 8% of the OOIP. The main mechanism associated with the improvement in the oil recovery for the proposed

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formulation was IFT reduction. Increasing viscous forces has a lesser effect and wettability alteration mechanisms were not studied.

Even though a high oil recovery was found, the IFT between crude oil and the proposed formulation (0.58 mN/m) was far from the ultralow IFT values (0.001 mN/m) required to increase Nc several orders of magnitude. To address these issues, the SAIL 1-decyl-3-methylimidazolium triflate was blended with 6 SAILs and 4 traditional surfactants, aiming for a Winsor III system that generally leads to ultralow IFT values. A fastscreening test was carried out in vials employing 3 different blend mass ratios (30/70, 50/50 and 70/30) looking for Winsor III behavior, or a transition from Winsor I to Winsor II. Results obtained from this fast-screening phase behavior blend tests are shown in Table 5.2.

Table 5.2. Phase behavior of blends of 1-decyl-3methylimidazolium triflate and different compounds.

Compound	Phase behavior
Brij C10	Winsor type I
Brij L4	Winsor type I
Ethylenediamine tetrakis(ethoxylate-block-propoxylate)tetrol	Winsor type I
Glycolic acid ethoxylate lauryl ether	Winsor type I
Poly(ethylene glycol) 4-nonylphenyl 3-sulfopropyl ether potassium salt	Winsor type I
Sodium 1-decanesulfonate	Winsor type I
Sodium dioctyl sulfosuccinate	Winsor type I
Sodium dodecylbenzene sulfonate	**Transition Winsor I –III-II**
Sodium dodecyl sulfate	**Transition Winsor I –III-II**
Igepal CO-520	Winsor type I

Two promising blends with 1-decyl-3methylimidazolium triflate and the traditional anionic SDBS or sodium dodecyl sulfate (SDS) surfactants were found. Pipette tests were carried out with these two blends to obtain more accurate information about phase behavior of the systems (Figure 5.1). In addition, optimum blend ratios were tested in stability tests to check the solubility of the chemicals in brine without oil. The traditional surfactant SDS forms a Winsor Type I system in the presence of oil and brine. When mixed with the proposed imidazolium SAIL, a Winsor type III system was formed at an optimum ratio of approximately 30% SDS (70% SAIL). At this ratio the solubilization parameters were high, but the formulation was not stable and

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precipitated. In the case of SDBS, this surfactant precipitated when employed alone at the tested conditions. When it was mixed with the imidazolium SAIL, a Winsor type III system was again obtained at an optimum blend ratio of 20-30% SDBS (80-70% SAIL). However, in this case, the solubilization parameters were too low, which meant that the desired ultralow values of IFT could not be achieved.



Figure 5.1. Pipette tests for the blend 1-decyl-3methylimidazolium triflate and SDS (up) or SDBS (down) at 25°C

At this point, it was clear that it would not be easy to find a formulation that presented Winsor III behavior with high solubilization parameters, whilst also being stable in brine without oil. Taking into account that the combination of these two traditional surfactants with a SAIL resulted in Winsor III behavior, further research was proposed to explore mixtures of traditional surfactants with new SAILs.

It is known that SDS undergo through hydrolysis at high temperatures, and this can be a significant drawback when considering its suitability for some EOR projects [26]. In contrast, SDBS is generally more stable at high temperatures compared to SDS, as it contains a benzene ring structure that confers higher thermal stability. This makes SDBS potentially more suitable for EOR applications than SDS [27]. However, SDBS like most ABSs, cannot be employed alone in carbonate reservoirs due to its incompatibility

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with divalent ions and high adsorption on the rocks. For this reason, SDBS was chosen as a potential traditional surfactant to be mixed with SAILs aiming to solve these problems, looking for Winsor Type III behavior with high solubilization parameters. To achieve this, a fast-screening of various mixtures of SAIL/SDBS was again conducted in vials to check phase behavior. In addition, brine stability of the promising blends in the absence of oil was checked. Results are shown in Table 5.3.

Table 5.2. Phase behavior of blends of SDBS and different SAILs.

Compound	Phase behavior	Brine stability
1,3-Didecyl-2-methylimidazolium chloride	Winsor type II	-
1-dodecyl-3-methylimidazolium bromide	Transition Winsor I-II	No
1-decyl-3-methylimidazolium chloride	Transition Winsor I-II	No
Iolilyte 221 PG	Winsor type I	-
Iolilyte T2EG	Winsor type I	-
Iolilyte C1EG	**Transition Winsor I-III-II**	**Yes**
Tetradecyltrimethylammonium chloride	Transition Winsor I-II	No
Benzyldimethyldodecylammonium chloride	Winsor type II	-

The blend containing SDBS and Iolilyte C1EG showed promising phase behavior in the screening test and it was also stable in synthetic seawater (SSW). SSW contains 49700 ppm of total dissolved solids (TDS) including divalent ions. Iolilyte C1EG is the commercial name of the ammonium IL cocosalkylpentaethoximethylammonium methylsulphate. In addition, despite the potential high cost associated to ILs, Iolilyte C1EG stands out as an economical choice among ILs currently available on the market, as it competes well in terms of price with conventional surfactants used for EOR. Moreover, Iolilyte C1EG is derived from coconut oil-based fatty acids, making it an environmentally friendly option. For these reasons, the blend SDBS/C1EG was selected as an interesting option to develop a surfactant formulation for EOR in carbonate reservoirs. To develop the formulation, the experimental procedure previously described in this chapter was applied. Two promising blends at 44.7/55.3 and 73.7/26.3 SDBS/C1EG mass ratios were found in synthetic seawater via phase behavior tests at ambient temperature. However, solubilization parameters at 50°C and 75°C significantly decreased to values below 10, indicating that the performance of the blend

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at high temperatures would be compromised. For this reason, the formulation would only be proposed to be applied in close-to-ambient temperature reservoirs.

In order to be more precise defining promising blend ratios, further optimization was carried out via IFT studies using crude oil. Very low IFT values in the order of 10^{-2} mN/m were reported for blend ratios close to the second optimum (73.7% SDBS), however, ultralow IFT (10^{-3} mN/m) was obtained for an optimal blend ratio of 40/60 SDBS/C1EG. Dynamic adsorption tests were performed on carbonate rocks using both promising blend ratios, resulting in low surfactant retention (0.36-0.51 mg_{surf}/g_{rock}). Finally, core-flooding tests were carried out and additional oil recoveries of 18.2% and 14.9% of the OOIP were obtained with the first and second optimum respectively. Therefore, due to its better injectability, lower IFT and adsorption, and better recovery, a formulation consisting of 1 wt% blend solution (40/60 SDBS/C1EG mass ratio) in SSW was defined as the definitive optimal formulation for use in carbonate reservoirs around room temperature. In addition, this formulation was found to be stable in high salinity brines (250000 ppm of TDS) containing divalent ions and high temperatures (75°C). Blending the IL C1EG with SDBS solves the main drawbacks of the application of this traditional anionic surfactant in carbonate reservoirs. Stability in harsh environmental conditions is improved, and adsorption is reduced to manageable values.

The main mechanism underlying this improvement was thoroughly examined. Literature research revealed that when anionic and cationic surfactants are combined, they exhibit strong interactions, causing the two hydrophilic groups to merge into a nonionic-like surfactant. This ion pairing phenomenon results in a surfactant commonly referred as a catanionic specie. The formation of these catanionic species leads to a reduction in micelle surface charge, resulting in a smaller area occupied by the combined surfactant head groups. As a result, the catanionic species demonstrates significantly higher surface activity. Additionally, the properties of the catanionic species differ greatly from those of the individual parent molecules. It is more lipophilic, less influenced by electrolytes, exhibits greater surface/interface activity, and possesses a lower CMC [28, 29].

Due to the very promising results obtained, it was decided to initiate the process of obtaining a patent for this formulation in order to enable commercialization and attract

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potential interest from petrochemical companies. The patent is currently in the revision process (*ES2922249 / WO2022184955*). Following the development of the patent, a collaboration was initiated with CEPSA, a Spanish petrochemical company. They allowed us testing the formulation to enhance the performance of LAS surfactants from the petrochemical industry, which they commercially market, in carbonate rocks. CEPSA provided various petrochemical LAS samples, each with different alkyl chain length and isomer content. Our objective was to study blends of these surfactants with the SAIL C1EG, aiming to develop new optimal formulations and assess the structure-performance relationship.

Three formulations were successfully designed through phase behavior studies. These formulations consisted of a LAS (C16, C15-C18 with standard isomers distribution, or C15-C18 with external isomers enriched distribution) combined with C1EG. LAS content in the blend, that led to Winsor III behavior, varied from 36-45%. Optimal solubilization parameters were found promising for the application (greater than 15) at 25°C. In addition, blends were found to be stable in SSW. The proposed formulations achieved very low IFT values. The lowest IFT value achieved was $4.99 \cdot 10^{-3}$ mN/m for the formulation containing the LAS C15-C18 with external isomers enriched distribution. For the other formulations with C16 and C15-C18 with standard isomers distribution, IFT values between $3.78 \cdot 10^{-2}$-$3.28 \cdot 10^{-2}$ mN/m were reported. In comparison to the application of LASs alone, the addition of C1EG drastically reduced the adsorption of the blend in carbonate material. Equilibrium adsorption values of 3.9 mg/g_{rock} and 2.9 mg/g_{rock} were obtained in static adsorption experiments for the blends containing C1EG and C16 or C15-C18 with standard isomers, respectively. However, the blend containing C15-C18 with external isomers enriched distribution exhibited a significantly higher adsorption value of 8.1 mg/g_{rock}. It is important to note that these results only provide a preliminary assessment of blend performance and may not fully represent real adsorption in reservoirs, due to the higher rock specific surface employed in these experiments. The use of LAS with external isomer enriched distribution increased adsorption by 179% compared to the use of LAS with standard isomer distribution. For this reason, the use of these type of LASs was discarded. Finally, it was found that LAS surfactants with varying alkyl chain lengths (C15-C18) resulted in greater oil recovery in core flooding tests, achieving an additional 20.8% of the OOIP. In comparison, LASs with a uniform alkyl chain length (C16) achieved a lower value of

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15.1% of the OOIP. It must be noted that the EOR step was performed combining surfactant and polymer flooding to improve the economy of the process. The tested formulations were found promising for reservoirs near ambient temperature. However, it is important to note that the IFT increased and stability decreased with temperature, indicating suboptimal performance at higher temperature conditions. This limitation restricts the application of these blends for EOR in high-temperature environments. In order to design a formulation with LAS surfactants with improved performance at high temperatures, the influence of SAIL structure on thermal stability was studied. In the previous studies, the formation of liquid crystals and low solubilization parameters above 50°C made the application of the catanionic species unfavorable at high temperatures. Several authors [30-32] studied the influence of polyoxyethylene groups in nonionic surfactant performance and found that more oxyethylene groups increase the cloud point, and hence enhance the thermal stability of surfactant molecules. For that reason, the SAIL N-ethyl-N-bis[poly(ethylene glycol)]-N-tallow ammonium ethylsulfate, commercially named Iolilyte T2EG, a cationic surfactant with higher content of polyoxyethylene groups than C1EG, was proposed for the design of a new optimal formulation.

A formulation was developed utilizing a C15-C18 LAS with a standard distribution of isomers, and T2EG. Following the described procedure, an optimal formulation was successfully designed, comprising 1 wt% of a surfactant blend with a mass ratio of 56.4/43.6 LAS/T2EG in SSW. Phase behavior experiments were conducted to investigate the impact of temperature and salinity on the performance of the surfactant blend. As anticipated, an increase in salinity led to a transition in microemulsion behavior, shifting from WI-WIII-WII. This shift can be attributed to the salting-out effect [33]. Regarding the influence of temperature, it was observed that the hydrophilic nature of the system decreases as temperature rises. This behavior is commonly observed in nonionic surfactants. Nonionic surfactants with polyoxyethylene groups, possess a coil-shaped structure capable of encapsulating water molecules. However, as temperature increases, the hydrogen bonds between the surfactant and water weakens, leading to a decrease in the hydrophilic properties of the system [34]. In addition, temperature increase makes the formation of catanionic micelles thermodynamically unfavourable, increasing the degree of dissociation of surfactant monomers. [35] The experiments were conducted between 25°C and 75°C, and although solubilization

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parameters decreased with temperature, values higher than 10 were achieved in all cases, indicating a promising solubilization capacity. Additionally, the absence of liquid crystals or precipitated phases further supported the feasibility of applying this surfactant blend under these conditions. The optimized formulation demonstrated good stability in high salinity environments, tolerating up to 100000 ppm TDS at 50°C and 90000 ppm TDS at 75°C. Moreover, IFT between the formulation and crude oil was measured at temperatures ranging from 25°C to 75°C, and values lower than 10^{-2} mN/m were achieved. In comparison to a similar blend featuring the same LAS surfactant with the SAIL C1EG, the current formulation exhibited superior performance at high temperatures. Furthermore, an adsorption equilibrium value of 1.35 mg/g_{rock} was obtained for this formulation in static adsorption experiments. This value was lower than the obtained for the blend containing the same LAS surfactant and C1EG (2.9 mg/g_{rock}), indicating that surfactant adsorption decreased with an increase in the ethoxylation degree of the surfactant. Core-flooding experiments involving surfactant and polymer flooding were conducted at ambient temperature. Results demonstrated significant additional oil recovery in water-wet carbonate rocks (19.53% of the OOIP), primarily attributed to the mechanism of IFT reduction. Unfortunately, due to equipment limitations, high-temperature oil recovery on oil-wet carbonate cores could not be tested.

Wettability alteration plays a significant role in surfactant EOR, and this Thesis undertook comprehensive investigations into various catanionic blends, yielding valuable insights into the mechanisms of wettability alteration associated with these compounds. It is widely recognized that these blends exhibit nonionic behavior. Results showed that wettability alteration induced by the catanionic blends tested in this Thesis is relatively weak and reversible. The anionic/cationic blends examined in this study involve a benzene ring in the LAS anionic surfactant and several ethoxy units present in the cationic SAILs.

Jarrahian et al. [36] proposed a wettability alteration mechanism for nonionic surfactants incorporating a benzene ring in their structure. According to their findings, surfactant molecules are adsorbed onto the positively charged rock surface through electrostatic interactions, produced by the polarization of π electrons in the benzene ring. Consequently, the surface zeta potential decreases, and adsorbed carboxylic acids

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establish hydrophobic tail-tail interactions with the adsorbed surfactant molecules. On the other hand, for surfactants containing ethoxy groups, Souayeh et al. [37] suggested that the molecules are adsorbed onto the carbonate surface via hydrogen bonding between the ethoxy units and hydroxyl or carboxylic groups on the solid surface. As a result, the adsorbed organic compounds are displaced, allowing the surfactant molecules to occupy the active sites of the calcite material. Subsequently, the desorbed carboxylic acids form a new layer through hydrophobic interactions with the adsorbed surfactant. Both mechanisms can explain why tested catanionic blends were only able to change the wettability of the rock towards less oil-wet rather than a strongly water-wet condition. For this reason, the main mechanism of oil extraction using these blends was IFT reduction.

Lastly, the use of SAILs in a different area of the petroleum industry was studied. CO_2 injection is attracting new market interest, as it appears to be a promising solution for cost-effective CO_2 capture processes. The use of foams can help to address challenges such as early gas breakthrough and poor sweep efficiency caused by the large viscosity difference between CO_2 and the fluids of the reservoir. The use of foams can be favorable for both CO_2 sequestration and foam-assisted CO_2 EOR processes. However, the stability of the foam at harsh conditions of temperature, pressure, and salinity is still a challenge. For this reason, to study the application of SAILs to stabilize foams, a short stay at the University of Texas at Austin under the direction of Professor Mohanty was carried out. Six SAILs with the most common functional groups (imidazolium, pyridinium and ammonium) were evaluated in static foam experiments at two reservoir conditions: A (63°C, 1910 psi and 125356 mg/L TDS) and B (40°C, 1000 psi and 255470 mg/L TDS). High-pressure stability tests and gas-formulation co-injection experiments were performed with the most promising formulations using CO_2 to determine the apparent foam viscosity and mobility reduction factor. Initial foam height of 5.75 cm and half-life time of 5.27 min were reported for the foam produced with the SAIL 1-hexadecyl-3-methylimidazolium chloride ([C_{16}mim]Cl) at A reservoir temperature but ambient pressure. A significantly lower stability (0.69 min) but higher foamability (9.95 cm) was obtained with 1-dodecyl-3-methylimidazolium bromide ([C_{12}mim]Br), a SAIL with the same functional group but lower alkyl chain length. For the case of the SAIL 1-hexadecylpiridinium chloride ([C_{16}Py]Cl), a higher initial foam height (5.9 cm) but lower half-life time (3.58 min) compared to [C_{16}mim]Cl were

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achieved. Similar results were reported for B reservoir temperature (ambient pressure), indicating that the effect of alkyl chain length and IL functional group on foam performance are the same regardless of temperature and salinity conditions. High-pressure stability studies showed that stability was improved with increasing pressure: the highest stability was reported for the highest reservoir pressure (reservoir A). A half-life time of 7.8 days was achieved with [C_{16}mim]Cl at reservoir A conditions, several times higher than those reported in literature for foams made with regular surfactants. In addition, the high mobility factors obtained in foam flow experiments (300-1230) demonstrate the promising potential of SAILs to improve sweep and gas trapping efficiency in CO_2-EOR and CO_2 sequestration processes in high salinity, pressure and temperature reservoirs. It must be noted that tests were not performed in the presence of crude oil. Further studies are required to determine the compatibility of the foam with crude oil, as it can negatively impact foam stability by reducing surface tension, destabilizing foam lamellae, and coalescing foam bubbles.

The development of novel SAIL formulations and their integration into existing petrochemical processes is a significant step towards creating more efficient operations. Ongoing research and development efforts are clearing the path for the use of SAILs in the petrochemical industry. This Thesis makes an important contribution to the application of SAILs to EOR processes, by the design of several formulations that improve the performance of traditional surfactants.

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6. CONCLUSIONS

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This Thesis has explored the potential of utilizing formulations based on SAILs for oil recovery processes, namely: surfactant flooding and foam assisted CO_2-EOR. Through a comprehensive investigation of various SAILs, including phase behavior and stability studies, valuable insights have been gained regarding the fundamentals of their effectiveness as EOR agents. Moreover, the experimental results obtained at the laboratory scale have demonstrated the significant impact of SAIL formulations on oil extraction. It can be concluded that SAILs are interesting alternatives to traditional surfactants in the above mentioned EOR processes. The design and optimization of different SAIL formulations have shown the potential of these compounds to reduce IFT, change rock wettability, and decrease adsorption on the rock surface. These findings provide a solid foundation for further research and development in this field, opening up new possibilities for the application of SAILs in EOR. From the studies conducted in this Thesis, some specific conclusions may be established.

From the literature review carried out, it can be concluded that although there are some promising results regarding the application of SAILs in EOR, there is a lack of phase behavior and adsorption studies that should always be considered before conducting extraction experiments. Additionally, there is a very limited amount of research conducted on carbonate cores. Cationic SAILs must be proposed for carbonate reservoirs to reduce surfactant adsorption. Accordingly, a formulation based on the SAIL 1-decyl-3-methylimidazolium triflate was suggested for EOR in carbonate reservoirs. However, the main conclusion of this work is that SAILs would be better employed to improve the performance of traditional surfactants, rather than used by themselves.

The SAIL C1EG showed the ability to improve the performance of SDBS, a LAS, by enhancing its stability at high salinity conditions and reducing its adsorption on carbonate rocks. Blending this cationic SAIL with SDBS overcomes the main challenges in the application of LAS on carbonate reservoirs. This behavior can be extended to blends of C1EG and LASs obtained from the petrochemical industry.

The influence of alkyl chain length and isomer distribution of petrochemical LASs on the performance of blends containing the SAIL C1EG was examined. LASs containing a higher amount of 2-phenyl isomers exhibit lower IFT, but significantly higher adsorption compared to LASs with a lower 2-phenyl isomer content. LAS surfactants

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with varying alkyl chain lengths result in a greater oil recovery compared to LASs with a uniform alkyl chain length. Finally, the alkyl chain length distribution has little influence on wettability alteration.

T2EG is a cationic SAIL characterized by a higher content of polyoxyethylene groups compared to C1EG. The combination of this SAIL with a C15-C18 LAS (with standard isomer distribution) showed the most promising results for the application in EOR. The developed optimal formulation presented greater stability at high temperatures and lower adsorption in comparison to the previous proposed formulations. It can be concluded that the presence of polyoxyethylene groups in the SAIL can improve the performance of this blends in EOR processes at high temperature conditions.

The main mechanism contributing to oil recovery was IFT reduction for all the presented formulations, wettability alteration playing a minor role.

SAILs are revealed as promising agents in terms of stability and foaming ability for foam generation in CO_2-EOR injection. The findings showed that, at ambient pressure, imidazolium-based SAILs exhibit highest foam stability while pyridinium-based SAILs demonstrate superior foaming ability. SAILs with longer alkyl chain lengths exhibit reduced foaming ability but increased stability compared to those with shorter alkyl chains. High-pressure stability tests showed that the increase of pressure promotes foam stability. The design of formulations for the specific conditions of each reservoir is required. Future studies should focus on testing these foams in oil recovery applications.

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List of abbreviations and acronyms

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ABS	Alkylbenzene sulfonate
C1EG	Cocosalkylpentaethoximethylammonium methylsulfate
CMC	Critical micelle concentration
EOR	Enhanced oil recovery
IFT	Interfacial tension
IL	Ionic liquid
LAS	Lineal alkylbenzene sulfonate
Nc	Capillary number
OOIP	Original Oil in Place
SAIL	Surface-active ionic liquid
SDBS	Sodium dodecylbenzenesulphonate
SDS	Sodium dodecyl sulfate
SSW	Synthetic seawater
T2EG	N-ethyl-N-bis[poly(ethylene glycol)]-N-tallow ammonium ethylsulfate
TDS	Total dissolved solids

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References

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[1] U.S. Energy Information Administration (EIA) (2022). Annual Energy Outlook 2022 with Projections to 2050. https://www.eia.gov/outlooks/aeo/ (accessed 03 March 2023)

[2] Joint Research Centre (JRC) of the European Commission (2019). The POTEnCIA Central scenario: An EU energy outlook to 2050. https://publications.jrc.ec.europa.eu/repository/handle/JRC118353 (accessed 04 March 2023)

[3] ACS Chemistry of Life (2009). Sustainable U.S. Manufacturing: Chemical and Allied Industries. Technology Area 1: Alternative Feedstocks. https://www.acs.org/content/dam/acsorg/sustainability/acsandsustainability/sustainablemanufacturing/roadmaps/smrt-technology-area-1-alternative-feedstocks-pdf.pdf (accessed 07 March 2023)

[4] Vishnyakov, V., Baghir, S., Salmanov, A. and Zeynalov, E. (2019). Primer on Enhanced Oil Recovery. First edition. Gulf Professional Publishing, Houston, Texas. ISBN: 978-0-12-817632-0.

[5] Sheng, J.J. (2011). Modern Chemical Enhanced Oil Recovery: Theory and Practice. First edition. Gulf Professional Publishing, Houston, Texas. ISBN: 978-1-85617-745-0.

[6] Gbadamosi, A., Junin, R., Manan, M., Agi, A., Yusuff, A. (2019). An overview of chemical enhanced oil recovery: recent advances and prospects. *Int Nano Letters* 9:171–202. https://doi.org/10.1007/s40089-019-0272-8

[7] Sheng, J.J. (2015). Status of surfactant EOR technology. *Petrol* 1: 97–105. https://doi.org/10.1016/j.petlm.2015.07.003

[8] Sheng, J.J. (2013). Review of Surfactant Enhanced Oil Recovery in Carbonate Reservoirs. *Adv Pet Explor & Develop* 6(1): 1-10. http://doi.org/10.3968/j.aped.1925543820130601.1582

[9] International Energy Agency (IEA) (2023). CO_2 Emissions in 2022. https://www.iea.org/reports/co2-emissions-in-2022 (accessed 22 March 2023)

[10] Tadros, T.F. (2014). 7. An Introduction to Surfactants. First edition. De Gruyter, Berlin, Germany. ISBN: 978-3-110-31212-6

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

[11] Sheng, J.J. (2013). Enhanced Oil Recovery: Field Case Studies. First edition. Gulf Professional Publishing. Houston, Texas. ISBN: 978-0123865458.

[12] Freemantle, M. (2010). An introduction to Ionic Liquids. First edition. Royal Society of Chemistry, Cambridge, UK. ISBN: 978-1-84755-161-0.

[13] Kirchner, B., Perlt, E. (2018). Ionic Liquids II. Part of the book series: Topics in Current Chemistry Collections (TCCC). First edition. Springer International Publishing, Cham, Switzerland. ISBN: 978-3-319-89793-6.

[14] Hanamertani, A.S., Pilus, R.M., Irawan, S. (2017). A Review on the Application of Ionic Liquids for Enhanced Oil Recovery. In: Awang, M., Negash, B., Md Akhir, N., Lubis, L., Md. Rafek, A. (eds). Proceeding of the International Conference on Integrated Petroleum Engineering and Geoscience. Springer, Singapore. https://www.doi.org/10.1007/978-981-10-3650-7_11

[15] Nandwani, S.K., Malek, N.I., Chakraborty, M., Gupta, S. (2020). Insight into the Application of Surface-Active Ionic Liquids in Surfactant Based Enhanced Oil Recovery Processes–A Guide Leading to Research Advances. *Energ Fuel* 34: 6544-6557. https://dx.doi.org/10.1021/acs.energyfuels.0c00343

[16] Bera, A., Belhaj, H. (2016). Ionic liquids as alternatives of surfactants in enhanced oil recovery—A state-of-the-art review. *J mol liq* 224: 177-188. http://dx.doi.org/10.1016/j.molliq.2016.09.10

[17] Buettner, C., Cognigni, A., Schröder, C., Bica-Schröder, K. (2022). Surface-active ionic liquids: A review. *J Mol Liq* 347: 118160. https://doi.org/10.1016/j.molliq.2021.118160

[18] Pillai, P., Maiti, M., Mandal, A. (2022). Mini-review on Recent Advances in the Application of SurfaceActive Ionic Liquids: Petroleum Industry Perspective. *Energ Fuel* 36: 7925-7939. https://doi.org/10.1021/acs.energyfuels.2c00964

[19] Salah, H., Nancarrow, P., Al-Othman, A. (2021) Ionic liquid-assisted refinery processes – A review and industrial perspective. *Fuel* 302: 121195. https://doi.org/10.1016/j.fuel.2021.121195

[20] Manshad, A.K., Rezaei, M., Moradi, S., Nowrouzi, I., Mohammadi, A.H. (2017). Wettability alteration and interfacial tension (IFT) reduction in enhanced oil recovery

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

(EOR) process by ionic liquid flooding. *J Mol Liq* 248: 153-162. https://doi.org/10.1016/j.molliq.2017.10.009

[21] Tadros, T. (2013). Critical Micelle Concentration. In Encyclopedia of Colloid and Interface Science. Springer, Berlin, Germany. https://doi.org/10.1007/978-3-642-20665-8_60

[22] Ahmed, S., Elraies, K. A. (2018). Microemulsion in Enhanced Oil Recovery in Science and Technology behind Nanoemulsions. InTech Open [Internet]. https://doi.org/10.5772/intechopen.75778 (accessed 15 May 2023)

[23] Spildo, K., Sun, L., Djurhuus, K., Skauge, A. (2014). A strategy for low cost, effective surfactant injection. *J Petrol Sci Eng* 117: 8-14. https://doi.org/10.1016/j.petrol.2014.03.006

[24] Salager, J.L., Antón, R.E., Sabatini, D.A., Harwell, J.H., Acosta, E.J., Tolosa, L.I. (2005). Enhancing solubilization in microemulsions—State of the art and current trends. *J Surfact Deterg* 8: 3–21. https://doi.org/10.1007/s11743-005-0328-4

[25] Vonnegut, B., 1942. Rotating bubble method for the determination of surface and interfacial tensions. *Rev Sci Instrum* 13: 6–9. https://doi.org/10.1063/1.1769937

[26] Bethell, D., Fessey, R.E., Namwindwa, E., Roberts, D. (2001). The hydrolysis of C12 primary alkyl sulfates in concentrated aqueous solutions. Part 1. General features, kinetic form and mode of catalysis in sodium dodecyl sulfate hydrolysis. *J Chem Soc Perkin Trans* 2: 1489-1495. https://doi.org/10.1039/B102957F

[27] Dembicki, H. (2022). Chapter 1 – Introduction in Practical Petroleum Geochemistry for Exploration and Production. Second edition. Elsevier. Amsterdam, Netherlands. https://doi.org/10.1016/B978-0-323-95924-7.00008-9

[28] Li, Y., Zhang, W., Kong, B., Puerto, M., Bao, X., Sha, O., Shen, Z., Yhang, Y., Liu, Y., Gu, S., Miller, C., Hirasaki, G.J. (2016). Mixtures of anionic/cationic surfactants: a new approach for enhanced oil recovery in low-salinity, high-temperature sandstone reservoir. *SPE J*. 21: 1164–1177. https://doi.org/10.2118/169051-pa

[29] Jia, H., Leng, X., Hu, M., Song, Y., Wu, H., Lian, P., Liang, Y., Zhu, Y., Liu, J., Zhou, H. (2017). Systematic investigation of the effects of mixed cationic/anionic surfactants on the interfacial tension of a water/model oil system and their application to enhance

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

crude oil recovery. *Colloid Surface* 529: 621–6127. https://doi.org/10.1016/j.colsurfa.2017.06.055

[30] Inoue, T., Misono, T. (2008). Cloud point phenomena for POE-type nonionic surfactants in a model room temperature ionic liquid. *J Colloid Interface Sci* 326: 483–489. https://doi.org/10.1016/j.jcis.2008.04.047

[31] Mirchi, V., Saraji, S., Akbarabadi, M., Goual, L., Piri, M. (2017). A Systematic Study on the Impact of Surfactant Chain Length on Dynamic Interfacial Properties in Porous Media: Implications for Enhanced Oil Recovery. *Ind Eng Chem Res* 56: 13677–13695. https://doi.org/10.1021/acs.iecr.7b02623

[32] Wu, J., Xu, Y., Dabros, T., Hamza, H. (2005). Effect of EO and PO positions in nonionic surfactants on surfactant properties and demulsification performance. *Colloids Surf A Physicochem Eng Asp* 252:79–85. https://doi.org/10.1016/j.colsurfa.2004.09.034

[33] Veiskarami S, Jafari A, Soleymanzadeh A. (2020). Phase behavior, wettability alteration, and oil recovery of low-salinity surfactant solutions in carbonate reservoirs. *SPE J* 25:1784–802. https://doi.org/10.2118/200483-PA

[34] Nakama Y. (2017) Chapter 15 – Surfactants in Cosmetic Science and Technology: Theoretical Principles and Applications. Firs edition. Elsevier. New York, USA. https://doi.org/10.1016/B978-0-12-802005-0.00015-X

[35] Bhattarai A. (2015) Studies of the Micellization of Cationic-Anionic Surfactant Systems in Water and Methanol-Water Mixed Solvents. *J Sol Chem* 44:2090–105. https://doi.org/10.1007/s10953-015-0391-4

[36] Jarrahian, K., Seiedi, O., Sheykhan, M., Sefti, M.V., Ayatollahi, S. (2012). Wettability alteration of carbonate rocks by surfactants: A mechanistic study. *Colloids Surf A Physicochem Eng Asp* 410:1–10. https://doi.org/10.1016/j.colsurfa.2012.06.007

[37] Souayeh, M., Al-Maamari, R.S., Aoudia, M., Karimi, M., Hadji, M. (2018). Experimental Investigation of Wettability Alteration of Oil-Wet Carbonates by a Nonionic Surfactant. *Energ Fuel* 32:11222–11233. https://doi.org/10.1021/acs.energyfuels.8b02373

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Appendix A:

Journal articles in which this Thesis is based

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Oil recovery tests with ionic liquids: A review and evaluation of 1-decyl-3-methylimidazolium triflate

Alba Somoza[a], Alberto Arce[b], Ana Soto[a]

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[b] School of Engineering, Universidade de A Coruña, E-15403, Ferrol, Spain

Journal: Petroleum science (2022), ed. Elsevier B.V. on behalf of KeAi. (ISSN: 1995-8226), 19: 1877-1887.

DOI: https://doi.org/10.1016/j.petsci.2021.10.025

Impact factor = 4.757 (2021), ranking it 3/19 in Petroleum Engineering (Q1).

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Author contribution (CRediT taxonomy): Experimental, Formal Analysis, Writing.

Chapters reproducing the article content: Chapter 3.

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

Alba Somoza[a], Néstor Tafur[a], Alberto Arce[b], Ana Soto[a]

[a]CRETUS. Department of Chemical Engineering, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Spain.

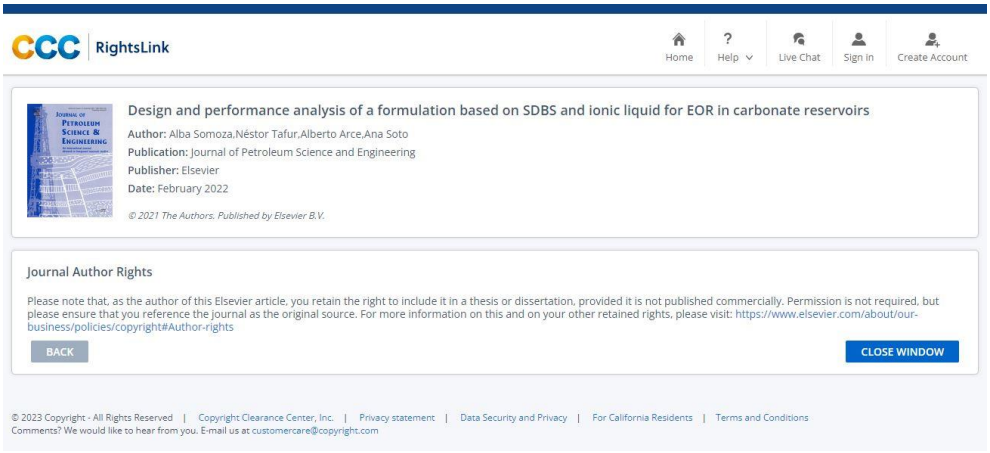
[b]School of Engineering, Universidade de A Coruña, E-15403, Ferrol, Spain

Journal: Journal of Petroleum Science and Engineering (2022), ed. Elsevier B.V (ISSN: 0920-4105) 209: 109856

DOI: https://doi.org/10.1016/j.petrol.2021.109856

Impact factor = 5.168 (2021), ranking it 2/19 in Petroleum Engineering (Q1).

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Author contribution (CRediT taxonomy): Experimental, analysis, writing.

Chapters reproducing the article content: Chapter 3

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Experimental evaluation of blends containing lineal alkylbenzene sulfonates for surfactant flooding in carbonate reservoirs

Alba Somoza[a], Borja Rodríguez-Cabo[b], Izaskun Barrio[b], M. Flor García-Mayoral[b], Ana Soto[a]

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Journal: SPE Reservoir Evaluation & Engineering (2023), ed. by the Society of Petroleum Engineers (ISSN: 1930-0212) SPE-215828-PA: 1-14

DOI: https://doi.org/10.2118/215828-PA

Impact factor = 2.672 (2021), ranking it 5/19 in Petroleum Engineering (Q2).

This journal does not allow full reprinting of the paper in a Thesis or dissertation.

Author contribution (CRediT taxonomy): Experimental, Formal Analysis, Writing.

Chapters reproducing the article content: Chapter 3

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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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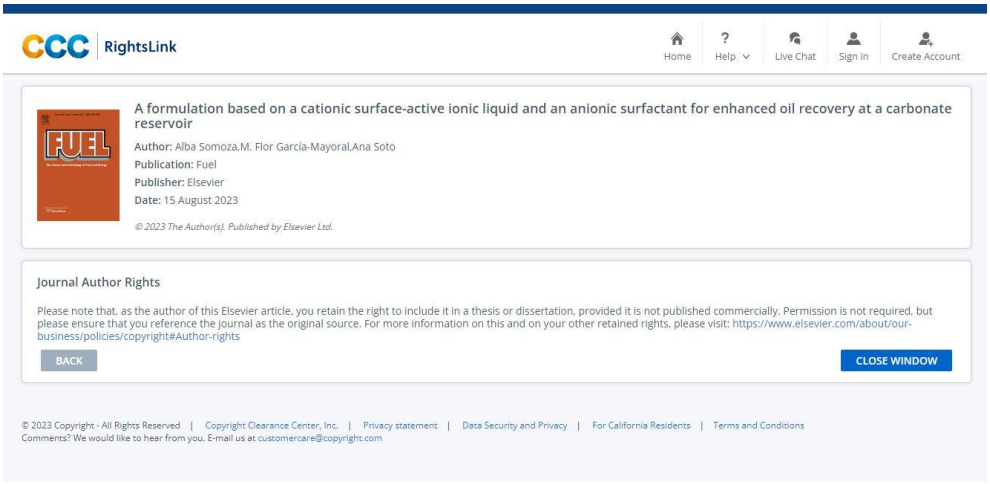
[b]CEPSA. Research Center, Madrid E-28805, Spain

Journal: Fuel (2023), ed. Elsevier B.V (ISSN: 0016-2361) 345: 128363

DOI: https://doi.org/10.1016/j.fuel.2023.128363

Impact factor = 8.035 (2021), ranking it 29/119 in Energy & Fuels (Q1) and 19/143 in Chemical Engineering (Q1).

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Author contribution (CRediT taxonomy): Experimental, Formal Analysis, Writing.

Chapters reproducing the article content: Chapter 3

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Experimental evaluation of foams stabilized by ionic liquids for enhanced oil recovery

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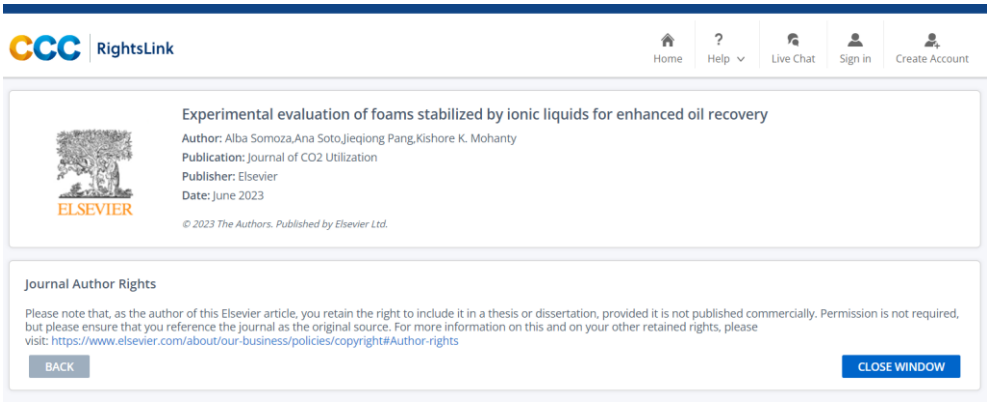
Journal: Journal of CO_2 Utilization (2023), ed. Elsevier B.V (ISSN: 2212-9820)

72: 102507

DOI: https://doi.org/10.1016/j.jcou.2023.102507

Impact factor = 8.321 (2021), ranking it 36/179 in Multidisciplinary Chemistry (Q1) and 16/143 in Chemical Engineering (Q1).

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Author contribution (CRediT taxonomy): Conducted experiments, wrote manuscript.

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Appendix B:

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Figure: Figure 2.1. Evolution of energy consumption by fuel type in the European Union.

Source: Joint Research Centre (JRC) of the European Commission (2019). The POTEnCIA Central scenario: An EU energy outlook to 2050. https://publications.jrc.ec.europa.eu/repository/handle/JRC118353 (accessed 04 March 2023)

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Appendix C:

“Resumo” (Summary, in Galician)

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Introdución

O petróleo é un combustible fósil indispensable na vida diaria dos consumidores en calquera parte do mundo. É unha fonte esencial de enerxía, pero ademais, o petróleo tamén é indispensable como materia prima para a síntese de moitos produtos que aseguran a nosa calidade de vida. É innegable que unha transición cara fontes de enerxía e materiais renovables é crucial para evitar o desastre climático. Non obstante, a pesar dos avances que se están a levar a cabo, esta transición pode levar un tempo considerable. Coa demanda global de enerxía en aumento e a diminución do número de descubrimentos de novos campos petrolíferos, é necesario maximizar a produción dos pozos existentes mediante a aplicación de novas tecnoloxías de recuperación.

Máis do 50% do petróleo permanece atrapado nas rocas dos xacementos, debido a forzas capilares, despois da aplicación dos métodos de recuperación convencionais. Ademais, máis do 60% das reservas de petróleo sitúanse en depósitos de roca carbonatada. Estes xacementos caracterízanse por posuír unha rede de poros complexa, baixa permeabilidade, condicións adversas de temperatura e salinidade, e condicións desfavorables de mollabilidade, o que dificulta a extracción de cru. Por isto, estanse a desenvolver técnicas de mellora da recuperación de petróleo (EOR polas súas siglas en inglés) para solucionar estes problemas e recuperar o petróleo de difícil acceso. Entre os métodos de EOR, a extracción con surfactantes é unha técnica amplamente empregada que aumenta a recuperación de petróleo mediante una combinación de varios mecanismos, como a diminución da tensión interfacial ou a alteración da mollabilidade. Con todo, a intolerancia destes produtos químicos a condicións adversas, como alta temperatura e salinidade, limita a súa aplicación en moitos xacementos. Ademais, os surfactantes aniónicos tradicionais, amplamente utilizados en xacementos de areniscas, non se poden aplicar en depósitos carbonatados dado que se produciría unha alta adsorción do produto químico. Neste contexto, os líquidos iónicos (LIs) están a emerxer como posibles candidatos para mellorar os procesos de EOR. A utilización destas sales na industria petroquímica é un campo que avanza rapidamente e mostra un gran potencial para futuras aplicacións. Os LIs posúen propiedades interesantes como: presión de vapor desprezable, alta capacidade de solvatación, e boa estabilidade térmica, o que os fai moi versátiles en aplicacións relacionadas co refino. A súa capacidade para disolver e estabilizar compoñentes

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complexos, como hidrocarburos pesados ou compoñentes polares, fai que sexan candidatos ideais para deseñar procesos eficientes de extracción e purificación. Cando un LI posúe unha gran actividade superficial, coñécese como líquido iónico surfactante (SAIL, das súas siglas en inglés).

Obxectivos

O obxectivo principal desta Tese é o deseño de formulacións baseadas en SAILs para a súa aplicación en EOR. Para acadar este obxectivo, establecéronse algúns obxectivos específicos. O primeiro foi realizar un estudo exhaustivo do estado da arte no uso de Lis para a recuperación de cru. A atención centrouse nos traballos máis aplicados, aqueles nos que estes compoñentes químicos eran probados en estudos de inundación (extracción de petróleo). Dado que o número de aplicacións con LIs en rocas carbonatadas era moi baixo, o segundo obxectivo centrouse en deseñar unha formulación baseada nun SAIL para mellorar o rendemento dos actuais procesos de extracción con surfactantes en rocas carbonatadas. Posteriormente estableceuse o obxectivo de mellorar a aplicación dos surfactantes aniónicos tradicionais da familia dos alquilbencenosulfonatos, mediante a súa mestura con LIs, para este tipo de xacementos. Seguindo nesta liña, tamén se propuxo investigar a influencia da lonxitude de cadea e a distribución de isómeros, desta familia de surfactantes, na eficacia da mestura. O seguinte obxectivo foi o deseño dunha formulación que mellorase a aplicación destes surfactantes tradicionais en xacementos a alta temperatura. Por último, e movendo o foco cara a outras técnicas de EOR, decidiuse avaliar a aplicación de SAILs en procesos de extracción e almacenamento de CO_2 mediante espumas.

Discusión

A revisión bibliográfica realizada mostrou que as principais vantaxes do uso de LIs en EOR son a súa versatilidade e alta estabilidade en condicións ambientais adversas. Con todo, a pesar das case ilimitadas posibilidades estruturais dos LIs, o número de estudos que proporcionan un enfoque práctico na súa aplicación son aínda moi escasos. Moitos autores realizaron probas de inundación usando leitos de area non consolidados, caracterizados por unha alta permeabilidade e porosidade. Os resultados destes experimentos deben ser considerados con cautela, xa que a extracción de petróleo pode estar sobreestimada en comparación cos xacementos reais, debido a que en rocas non consolidadas existen menores forzas capilares e polo tanto unha menor retención de

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petróleo nos poros. Neste tipo de experimentos, reportáronse recuperacións adicionais de petróleo (despois da extracción con auga) de ata o 32% do petróleo in situ (OOIP, das súas siglas en inglés). Con respecto aos experimentos que usaron rocas de xacementos reais, acadáronse recuperacións adicionais de petróleo con LIs puros de ata o 16,5% do OOIP. Hai que indicar que a cantidade de estudos de adsorción atopados na literatura é sorprendentemente escaso, a pesar de ser un estudo fundamental para a aplicación. Por outra banda, os compostos químicos aplícanse nalgúns casos en concentracións demasiado altas, o que fai que as formulacións propostas non sexan factibles para aplicacións reais. Tamén cómpre sinalar que a maioría dos LIs foron propostos para xacementos de areniscas, o que implica unha alta adsorción dado que a gran maioría de LIs son catiónicos e este tipo de rocas teñen carga superficial negativa. Ata o inicio desta Tese, só o SAIL cloruro de 1-octadecil-3-metilimidazolio ([C_{18}mim]Cl) tíñase ensaiado en extracción de cru de rocas carbonatadas.

Co fin de deseñar unha formulación baseada nun SAIL capaz de mellorar o rendemento dos procesos de extracción con surfactantes en xacementos carbonatados, utilizouse o SAIL triflato de 1-decil-3-metilimidazolio ([C_{10}mim][OTf]), debido á súa solubilidade en auga e á súa capacidade de reducir a tensión interfacial. Estudiouse o comportamento da mestura auga, n-octano e SAIL, e atopouse un sistema Winsor I no intervalo de salinidade 0-15% en peso de NaCl. Posteriormente, realizouse a optimización da formulación mediante medidas de tensión interfacial entre a fase acuosa e cru. Propúxose unha formulación que consistía en 4000 ppm de SAIL, 2% en peso de NaCl e 1% en peso de NaOH, resultando nun valor de tensión interfacial de 0,58 mN/m. Os estudos de adsorción dinámica revelaron que a adsorción do SAIL nas rocas carbonatadas podía considerarse o suficientemente baixa para que a formulación fose adecuada para a aplicación neste tipo de depósitos. Obtívose unha recuperación adicional de petróleo, despois da inxección de auga, do 10,5% do OOIP ao inxectar 4 PV (volumes de poro) da formulación de surfactante. O mecanismo principal asociado á mellora na recuperación de petróleo para a formulación proposta foi a redución da tensión interfacial. O aumento das forzas viscosas tiveron un efecto menor, e os mecanismos de alteración da mollabilidade non se estudaron.

Ainda que se obtivo unha boa recuperación de cru, a tensión interfacial entre a formulación proposta e o petróleo estaba lonxe dos valores ultrabaixos requeridos

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(0,001 mN/m) para aumentar o número capilar varias ordes de magnitude. Para abordar este problema, buscouse mesturar o SAIL triflato de 1-decil-3-metilimidazolio con outros compostos en busca dun comportamento de fases Winsor III, asociado a valores baixos de tensión interfacial e polo tanto a alta recuperación de cru.

Encontráronse dúas mesturas prometedoras que levaron ao comportamento de fase desexado. Estas mesturan consistiron en triflato de 1-decil-3-metilimidazolio e os surfactantes aniónicos tradicionais dodecilsulfato de sodio (SDS) e dodecilbencenosulfonato de sodio (SDBS). No caso da mestura de SDS co LI imidazolio, os parámetros de solubilización obtidos foron altos (requisito para optimizar o proceso de extracción), pero a formulación en ausencia de fase orgánica non era estable e precipitaba. No caso do SDBS, os parámetros de solubilización eran demasiado baixos, o que implica que non sería capaz de alcanzar os valores ultrabaixos de tensión interfacial desexados. Tendo en conta que a combinación destes dous surfactantes tradicionais cun SAIL resultaba nun comportamento de tipo Winsor III, decidiuse explorar outras mesturas de surfactantes tradicionais con novos SAILs.

O SDBS é máis estable a altas temperaturas que o SDS, o que fai que o primeiro sexa potencialmente máis adecuado para aplicacións de EOR. Con todo, o SDBS (como calquera alquilbencenosulfonato de sodio) non se pode empregar como composto puro en xacementos carbonatados, debido á súa incompatibilidade cós ións divalentes e á súa alta adsorción neste tipo de rocas. Por esta razón, escolleuse o SDBS como un surfactante tradicional de interese para mesturar con SAILs, co obxectivo de resolver os problemas mencionados.

Iolilyte C1EG é o nome comercial do SAIL metilsulfato de cocosalquilpentaetoximetilamonio. A pesar de que en moitas ocasión os LIs levan asociado un custo elevado, o Iolilyte C1EG destaca como unha opción económica entre os LIs actualmente dispoñibles no mercado, xa que o seu prezo ten a mesma orde de magnitude que outros surfactantes convencionais utilizados para EOR. Por outra banda, o Iolilyte C1EG obtense a partir de ácidos graxos derivados do aceite de coco, polo que é unha opción respectuosa co medio ambiente. Por estas razóns, a mestura SDBS/C1EG foi seleccionada como unha opción interesante para desenvolver unha nova formulación. Mediante estudos de comportamento de fase a temperatura ambiente, atopáronse dous óptimos nas relacións de masa 44,7/55,3 e 73,7/26,3 de SDBS/C1EG

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en auga de mar sintética. Como inconveniente, os parámetros de solubilización a 50°C e 75°C diminuíron de forma significativa. Isto implica unha perda de eficacia da formulación coa temperatura.

Para ser máis precisos á hora de definir as proporción óptimas de mestura, realizouse unha optimización adicional mediante estudos de tensión interfacial entre a formulación (1% en masa da mestura de surfactantes en auga de mar sintética) e cru. Obtivéronse valores moi baixos de tensión interfacial (10^{-2} mN/m) para proporcións de mestura próximas ao segundo óptimo (73.7% SDBS). Máis prometedor foi o valor ultra baixo (10^{-3} mN/m) obtido cunha proporción 40/60 SDBS/C1EG. As probas de adsorción dinámica en rocas de carbonato mostraron baixa retención destas prometedoras mesturas (0,36-0,51 mg/g_{roca}). Leváronse a cabo ensaios de extracción en núcleos de roca carbonatada obtidos de pozos reais e, tras a inxección de auga, proporcionaron recuperacións adicionais de petróleo entre 18,2% e 14,9% do OOIP. A formulación óptima definitiva foi definida como unha disolución cun 1% en peso da mestura de surfactantes (40/60 SDBS/C1EG) en auga de mar. A súa selección foi debida a súa maior estabilidade, menor adsorción, e maior recuperación de cru. Tamén se comprobou que era estable en augas con alta salinidade (250000 ppm de sólidos totais disoltos) incluíndo ións divalentes e a altas temperaturas (75°C). A mestura de SDBS con C1EG resolve as limitacións da aplicación de SDBS en xacementos carbonatados, mellorando a súa estabilidade en condicións ambientais adversas, e reducindo a adsorción a valores manexables.

Debido a que os resultados obtidos foron moi prometedores, decidiuse iniciar o proceso de obtención dunha patente (*ES2922249 / WO2022184955*) para esta formulación, co fin de posibilitar a súa comercialización e atraer o interese de compañías petroquímicas. Tras o desenvolvemento da patente, iniciouse unha colaboración con CEPSA (compañía petroquímica española) para probar a formulación con diferentes sulfonatos de alquilbenceno lineales (LASs). CEPSA proporcionou diversas mostras destes compostos, cada unha con diferentes lonxitudes de cadea alquílica e contido de isómeros. O obxectivo centrouse en validar e adaptar a formulación patentada para o traballo cos surfactantes petroquímicos, coa intención de desenvolver novas formulacións óptimas e avaliar a relación entre estrutura e rendemento.

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Deseñáronse tres formulacións que contiñan un LAS (C16, C15-C18 con distribución estándar de isómeros, ou C15-C18 con distribución enriquecida en isómeros externos) combinado con C1EG. O contido de LAS na mestura, que levou a sistemas Winsor III, variou entre o 36% e o 45% en masa, obtendo parámetros de solubilización altos (superiores a 15) a 25°C. Ademais, comprobouse que as mesturas eran estables en auga de mar sintética con salinidade de ata 49700 ppm de sólidos totais disoltos. As formulacións propostas acadaron valores moi baixos de tensión interfacial. O valor máis baixo obtido foi $4{,}99 \cdot 10^{-3}$ mN/m para a formulación que contiña o LAS C15-C18 cunha distribución enriquecida de isómeros externos. Para as outras formulacións con C16 e C15-C18 con distribución estándar de isómeros, obtivéronse valores de tensión interfacial entre a formulación e cru de entre $3{,}78 \cdot 10^{-2}$ e $3{,}28 \cdot 10^{-2}$ mN/m. En comparación coa aplicación de LAS en solitario, a adición de C1EG reduciu drasticamente a adsorción da mestura en rocas carbonatadas. Obtivéronse valores de adsorción de 3,9 mg/g de roca e 2,9 mg/g de roca en experimentos de adsorción estática para as mesturas que contiñan C1EG e C16 ou C15-C18 con isómeros estándar, respectivamente. Porén, a mestura que contiña C15-C18 con distribución enriquecida de isómeros externos resultou nun valor de adsorción significativamente máis alto (8,1 mg/g_{roca}). É importante ter en conta que estes resultados proporcionan unicamente unha avaliación preliminar do rendemento da mestura e non reflicten completamente a adsorción real en xacementos, debido á maior superficie específica da roca utilizada nos ensaios de laboratorio. O uso de LASs con distribución enriquecida de isómeros externos aumentou a adsorción nun 179% en comparación co uso de LASs con distribución estándar de isómeros. Por esta razón, descartouse o uso deste tipo de LAS. Por último, nos ensaios de extracción, observouse que os surfactantes LAS con lonxitude de cadea alquílica variable (C15-C18) resultaron nunha maior extracción de petróleo, cunha recuperación adicional do 20,8% do OOIP. En comparación, os LASs cunha lonxitude uniforme de cadea alquílica (C16) alcanzaron un valor menor, 15,1% do OOIP. O proceso de EOR levouse a cabo combinando extracción con surfactante e con polímero para mellorar o balance económico do proceso. As formulacións testadas mostráronse prometedoras para xacementos próximos á temperatura ambiente. É importante destacar que a tensión interfacial aumentou e a estabilidade diminuíu ao aumentar a temperatura, o que restrinxe a aplicación destas mesturas para EOR en ambientes de alta temperatura.

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Para mellorar o rendemento deste tipo de formulacións a altas temperaturas, propúxose o uso do SAIL etilsulfato de N-etil-N-bis[poli(etilén glicol)]-N-sebo amonio, comercialmente coñecido como Iolilyte T2EG (T2EG), un surfactante catiónico con maior contido de grupos polioxietileno que o C1EG, o que teoricamente mellora a súa estabilidade térmica. Deseñouse unha formulación que contiña un 1% en peso dunha mestura de LAS C15-C18 cunha distribución estándar de isómeros e T2EG, cunha relación másica de 56.4/43.6 LAS/T2EG en auga de mar sintética (49700 ppm de sólidos totais disoltos). Esta formulación demostrou boa estabilidade en ambientes de alta salinidade, tolerando ata 100000 ppm de sólidos totais disoltos a 50°C e 90000 ppm a 75°C. Ademais, a formulación presentou unha tensión interfacial notablemente baixa en contacto con cru (en torno a 10^{-2} mN/m) en todo o rango de temperaturas de 25°C a 75°C. Leváronse a cabo experimentos de adsorción estática en roca carbonatada e obtívose un valor de adsorción en equilibrio de 1,35 mg/g_{roca}. Este valor foi inferior ao obtido para a mestura do mesmo LAS con C1EG (2.9 mg/g_{roca}). A formulación mostrou un rendemento claramente superior a altas temperaturas en comparación coas formulación semellantes propostas anteriormente nesta tese. Os experimentos de extracción a temperatura ambiente, combinando extracción con surfactante e con polímero, resultaron nunha recuperación de petróleo adicional moi significativa (19.53% do OOIP), atribuída principalmente ao mecanismo de redución da tensión interfacial. Desafortunadamente, debido a limitación do equipo, non se puido estudar a extracción a alta temperatura.

A alteración da mollabilidade é un dos principais mecanismos de extracción en EOR con surfactantes. Nesta tese leváronse a cabo estudos con diversas mesturas de SAIL catiónico e surfactante aniónico, que proporcionaron información valiosa sobre os mecanismos de alteración da mollabilidade destes compostos. Cando se combinan surfactantes catiónicos e aniónicos xérase unha gran sinerxia. As interaccións electrostáticas entre as cabezas dos tensioactivos de carga oposta, e a atracción intermolecular entre as cadeas hidrofóbicas de hidrocarburos, dan lugar a complexos electrostáticamente neutros tamén chamadas especies cataniónicas. É amplamente recoñecido que estas mesturas exhiben comportamento non iónico. Os resultados dos experimentos de alteración da mollabilidade, mostraron que a alteración inducida por este tipo de mesturas cataniónicas é relativamente débil e reversible. Por esta razón, o

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principal mecanismo de extracción de cru con estas formulacións é a redución da tensión interfacial.

Ampliando as posibilidades dos SAILs en EOR, na última etapa deste traballo, analizouse a súa aplicabilidade na estabilización de espumas. A inxección de CO_2 está a atraer novos intereses no mercado, entre eles o seu uso para EOR. Non obstante, a diferencia de viscosidade entre o gas e os fluídos do xacemento fai que non se trate de procesos eficientes. O uso de espumas pode axudar a afrontar problemas habituais como a liberación anticipada de gas ou a baixa eficiencia de barrido. Cómpre indicar que a aplicación de espumas pode ser favorable tanto para procesos de almacenamento de CO_2 como para procesos de EOR empregando CO_2. Non obstante, a estabilidade da espuma en condicións adversas de temperatura, presión, e salinidade, aínda é un desafío. Para levar a cabo este estudo, realizouse unha breve estadía na Universidade de Texas en Austin baixo a dirección do profesor Mohanty. Avaliáronse seis SAILs cos grupos funcionais máis comúns (imidazolio, piridinio e amonio) en experimentos de espuma estáticos para dúas condicións de xacemento distintas: A (63°C, 1910 psi e 125356 mg/L TDS) e B (40°C, 1000 psi e 255470 mg/L TDS). Realizáronse probas de estabilidade en condicións atmosféricas e a alta presión, e experimentos de inxección simultánea de CO2 e formulación acuosa de SAIL. Determinouse a viscosidade aparente da espuma e o factor de redución de mobilidade das formulacións máis prometedoras. A espuma producida co SAIL cloruro de 1-hexadecil-3-metilimidazolio ($[C_{16}mim]Cl$), ás condición do xacemento A pero a presión ambiente, resultou nunha altura inicial de 5,75 cm e un tempo de vida media de 5,27 minutos. O tempo de vida media foi significativamente inferior (0,69 minutos) no caso do bromuro de 1-dodecil-3-metilimidazolio ($[C_{12}mim]Br$), co mesmo anelo do LI e unha cadea máis corta, e a altura inicial foi notablemente maior (9,95 cm). No caso do cloruro de 1-hexadecilpiridinio ($[C_{16}Py]Cl$), en comparación co ($C_{16}mim]Cl$, obtívose unha espuma cunha lixeira maior altura inicial (5,9 cm), e menor estabilidade cun tempo de vida media de 3.58 min. O efecto do grupo funcional do SAIL e a lonxitude de cadea foron os mesmos nas condición do xacemento B. Os estudos de estabilidade a alta presión mostraron que a estabilidade melloraba co aumento da presión, en outras palabras, a maior estabilidade obtívose para a condición de presión máis alta. Coa formulación que contiña o SAIL $[C_{16}mim]Cl$ obtívose un tempo de vida media de 7,8 días nas condicións do xacemento A, resultado varias veces máis alto do que se obtivo na bibliografía para espumas de surfactantes

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tradicionais. Ademais, obtivéronse altos factores de mobilidade (300-1230) en experimentos de fluxo de espuma, o que demostrou o prometedor potencial dos SAILs para mellorar a eficiencia de barrido e captura de gas en procesos de CO_2-EOR, e almacenamento de CO_2 en xacementos de alta salinidade, presión e temperatura.

Conclusións

Os estudos recollidos nesta Tese refrendan o interese dos SAILs para a súa aplicación como surfactantes en procesos de EOR. No caso dos SAILs catiónicos, os máis comúns, a súa aplicación proponse para xacementos carbonatados co fin de evitar altos valores de adsorción, parámetro que debe ser medido antes de presentar unha nova formulación para a aplicación. Non obstante, a principal conclusión deste traballo é o maior interese dos SAILs para mellorar o rendemento dos surfactantes tradicionais, e así cumprir todos os requisitos que unha formulación para EOR require, mais que para o seu uso como único surfactante.

O SAIL C1EG é capaz de mellorar o rendemento do SDBS, o arquetipo de LAS, incrementando a súa estabilidade a salinidades moi altas e reducindo a súa adsorción en rocas carbonatadas. Isto permite superar as principais limitacións da aplicación de SDBS neste tipo de formacións. Esta mellora é extensible a diferentes LASs obtidos na industria petroquímica. As formulacións acuosas de mesturas de C1EG e LAS cunha maior cantidade de isómeros de 2-fenilo, presentan unha menor tensión interfacial en contacto con cru pero unha adsorción notablemente maior que no caso dos LASs cun menor contido de isómeros en posicións externas. Por outra banda, os surfactantes LAS con diferentes lonxitudes de cadea alquílica dan como resultado unha maior recuperación de petróleo en comparación cos LASs cunha lonxitude de cadea alquílica uniforme.

A combinación do SAIL T2EG co LAS C15-C18 (cunha distribución estándar de isómeros) é a máis prometedora para a recuperación de cru. A formulación deseñada a partires de esta mestura demostrou posuír maior estabilidade a alta temperatura e menor adsorción en rocas carbonatas, en comparación coas formulacións propostas previamente. O aumento dos grupos polioxetileno no SAIL mellorou o seu rendemento en condicións de alta temperatura.

Os SAILs son sales prometedoras en termos de estabilidade e capacidade espumante, e

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polo tanto compostos químicos de interese para a xeración de espuma na inxección de CO_2-EOR. Os SAILs baseados en imidazolio demostraton ser máis estables, mentres que os SAILs baseados en piridinio foron os máis eficaces para xerar espuma. As probas de estabilidade a alta presión indicaron que o aumento desta variable promove a estabilidade da espuma. Tanto no caso do uso de SAILs como tensioactivos como no caso do seu uso como axentes espumantes, é necesario deseñar formulacións específicas para cada xacemento e as súas condicións. Os estudos futuros deben enfocarse cara a compatibilidade da espuma co petróleo, para asegurar que o cru non ten un impacto negativo na estabilidade da espuma, e na realización de ensaios de inundación.

Os obxectivos da Tese cumpríronse, como se deriva da patente: Composición para a extracción mellorada de petróleo (*ES2922249 / WO2022184955*), e da publicación dos seguintes traballos:

- Oil recovery tests with ionic liquids: A review and evaluation of 1-decyl-3-methylimidazolium triflate. Petroleum Science 19 (2022) 1877-1887.

- Design and performance analysis of a formulation based on SDBS and ionic liquid for EOR in carbonate reservoirs. Journal of Petroleum Science and Engineering 209 (2022) 109856.

- Experimental evaluation of blends containing lineal alkylbenzene sulfonates for surfactant flooding in carbonate reservoirs. SPE Reservoir Evaluation & Engineering (2023) SPE 215828:1-14.

- A formulation based on a cationic surface-active ionic liquid and an anionic surfactant for enhanced oil recovery at a carbonate reservoir. Fuel 345 (2023) 128363.

- Experimental evaluation of foams stabilized by ionic liquids for enhanced oil recovery. Journal of CO_2 Utilization 72 (2023) 102507.

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This Thesis focused on the design of formulations based on ionic liquids to enhance oil recovery methods. A literature review on their application in surfactant flooding was conducted. Preliminary formulations showed promise, but ionic liquids were found to be better use to improve the performance of traditional surfactants. Several formulations were developed to enhance the application of alkyl benzene sulfonates in carbonate reservoirs. Increasing the ethoxylation degree of the ionic liquid improved high-temperature performance. Some ionic liquids were also evaluated for foam generation in CO_2 flooding, showing enhanced stability and increased mobility ratio compared to traditional surfactants. These studies provide a foundation for the application of ionic liquids in enhanced oil recovery.