

# Evaluation of surfactant blends for enhanced oil recovery through activity maps



Nestor Tafur, Alba Somoza, Ana Soto\*

CRETUS, Department of Chemical Engineering, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, Spain

## ARTICLE INFO

### Article history:

Received 28 April 2022

Revised 4 July 2022

Accepted 29 July 2022

Available online 2 August 2022

### Keywords:

Anionic

Cationic

Ionic liquid

Microemulsion

Winsor III

## ABSTRACT

Better use of already exploited oil reservoirs using Enhanced Oil Recovery techniques is becoming essential. The use of surfactant blends is a common approach when individual surfactants are not effective. However, defining the optimum conditions for application becomes very challenging due to the number of variables involved in specific cases. In this work, blends of dioctyl sulfosuccinate sodium salt with Akypo LF2 and two surfactant ionic liquids (1-decyl-3-methylimidazolium chloride and 1-dodecyl-3-methylimidazolium bromide) were evaluated for oil recovery. Activity maps, representations of the phase behavior of the surfactants as a function of blend ratio, salinity and temperature, were found to be useful tools to describe conditions leading to Winsor type III systems. Among the blends studied, mixtures with Akypo LF2 were found of interest for application at low temperatures, showing interfacial tensions close to 0.01 mN/m in a wide range of salinity concentrations. In the case of blends with ionic liquids, even though they led to more promising solubilization parameters, the high sensitivity of these mixtures to blend ratio changes discourages, in principle, their use for practical applications.

© 2022 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

Considering the investment and other associated risks involved in discovering and developing new oil fields, hydrocarbon exploration has decreased in recent years, whilst oil reserves around the world are being depleted [1,2]. In this context, oil companies must turn to their existing oil fields and maximize the oil recovery from already exploited reservoirs. As water flooding alone is insufficient to displace all the oil in place, due to viscous and capillary trapping forces, the application of Enhanced Oil Recovery (EOR) techniques is needed to extract as much oil as possible. For this reason, these methods will probably become more relevant than in the previous decades, with an increasing imperative on their being employed wherever economically feasible. One of the main chemical EOR methods is surfactant flooding. A surfactant is a substance which lowers the surface tension of the medium in which it is dissolved, and/or the interfacial tension with other phases [3]. Anionic, cationic and non-ionic surfactants have been proposed for EOR. Recently, aqueous mixtures of two oppositely charged surfactants, so-called catanionic surfactant mixtures, have been shown promising for the application [4].

The oil droplets (residual oil), which remain trapped in the pores of the reservoir after water flooding cannot be displaced under normal oil–water interfacial tension (IFT), around 10–30 mN/m, because of the strong capillary forces. To start the mobilization of oil droplets and decrease the residual oil saturation to very low values, IFT must first be reduced to around  $10^{-2}$  to  $10^{-3}$  mN/m during surfactant flooding [5–9]. Such ultralow values of IFT correspond to Winsor Type III systems, according to the Winsor classification [10], where a surfactant solubilizes equal volumes of oil and water to form a middle microemulsion in equilibrium with excess oil (upper) and excess water (lower) phases. This behavior is preferred to Winsor Type I, with an aqueous microemulsion in equilibrium with an excess oil phase, or Winsor Type II where the biphasic system corresponds to an oily microemulsion in equilibrium with an excess water phase. The fragile equilibrium of optimal Winsor III microemulsions can be easily broken with changes in water salinity, temperature, surfactant concentration, etc., causing a shift to Winsor Type I or II [11].

The presence of a salinity gradient in the reservoir makes it difficult to keep the surfactant formulation in optimal conditions (ultra-low IFT) along its path from the injection well to the production wells. This is a typical problem found when water flooding is not carried out with the formation brine. A gradient appears between the injected and formation water salinities because of the mixing that occurs in the process, and the existence of non-

\* Corresponding author.

E-mail address: [ana.soto@usc.es](mailto:ana.soto@usc.es) (A. Soto).

swept heterogeneous zones which contain immobile oil and formation brine. This salinity gradient depends on the initial water saturation, the composition and concentration of injected and formation water, pore volume, arrangement of the injector/producer wells, and volume of injected water, among other factors. Sheng [12] suggests that a 80/20 ratio for injection water/formation brine salinity should be selected to design formulations able to produce Winsor type III systems. Thus, the influence of salt concentration on microemulsion behavior is a relevant study for EOR.

The use of surfactant blends is a common approach when single surfactants are unable to meet the demanding requirements of surfactant EOR. These blends can be adjusted to obtain an optimal microemulsion (Winsor III system) at the desired salinity by changing the surfactant mix ratios. The synergy between two surfactants encourages the formation of mixed micelles, improving the performance of the formulation [13–16]. Previous studies [4,13,16–23] have shown favorable interactions in quite different systems, such as anionic-anionic, anionic-nonionic and anionic-cationic. In this line, Anton *et al.* [24] tested the combination of sodium dodecyl sulfate with tetradecyltrimethylammonium bromide looking for an optimal formulation. The desired three-phase behavior was found with water, oil and alcohol for mixtures up to 25 % of any of the surfactants. Higher concentrations led to precipitation of flat crystals. The design of alcohol-free anionic-cationic microemulsions which avoid such precipitation problems was approached in detergency studies, and the combination of a branched surfactant and surfactants with varying tail length was proposed [18,25]. Puerto *et al.* studied the use of alkoxyglycidylether sulfonates for EOR, and proposed their combination with an internal olefin sulfonate in order to avoid the cloud-point phenomenon found at elevated temperatures [20]. To address the disadvantages of the use of alkalis during surfactant flooding, Zhang *et al.* [26] proposed the use of blends of cationic, anionic, zwitterionic and nonionic surfactants to achieve ultra-low IFT. The authors demonstrated that anionic/cationic and anionic/zwitterionic blends for highly active aggregates behave like nonionic surfactants and show a high salinity tolerance. The surfactants used and their mixing ratios can be tailored to achieve optimal formulations at different salt concentrations. The possibilities of anionic/cationic blends were further studied by Li *et al.* [22]. A polyoxyethylene ether carboxylate anionic surfactant was blended with a quaternary ammonium chloride cationic surfactant and tested for a high-temperature, low-salinity, and high-hardness condition. The ethoxy number of the anionic compound and the chain length of the anionic surfactant were tuned to obtain optimal surfactant blends able to produce ultra-low IFT. In our previous work [27], blends of traditional surfactants and surface-active ionic liquids (SAILs) were tested for EOR. To that aim, the phase behavior of the mixtures with octane and a hard brine was determined at several temperatures. The combination of an internal olefin with dodecyltrimethylammonium bromide or 1-dodecyl-3-methylimidazolium bromide was proposed for the application. However, there is a lack of studies in the literature involving the phase behavior of surfactant blends at a wide range of salinities and temperatures.

The purpose of the present work therefore is to evaluate the phase behavior of different surfactant blends with water and oil at such conditions. In order to formulate the surfactant blends, the anionic branched surfactant dioctyl sulfosuccinate sodium salt (AOT) was selected. It has a relatively short but bulky double alkyl chain and a small ionic head group. This disproportion between the hydrophilic and hydrophobic parts makes it highly lipophilic [28], thus allowing a flexible tuning through blending with more hydrophilic surfactants. It was also selected because it has been shown as a component of interest in the design of microemulsions for various applications [29,30]. To design an anionic/nonionic blend,

polyoxyethylene(8) octyl ether carboxylic acid (Akyo LF2) was selected. This is a triblock alkyl ethoxy carboxylate surfactant whose ionization level depends on the pH of the formula, behaving like a nonionic surfactant at acid pH, and an anionic one in an alkaline solution. It has a short lipophilic chain and a relatively long hydrophilic section. Due to its chemical structure, the ethoxy and carboxylate groups make it tolerant to high salinity and stable long-term to high temperature [23,31,32]. To design anionic/cationic blends, ionic liquids were selected as cationic components. These salts with long alkyl chains are being currently proposed as surfactants for EOR due to their promising features, such as the possibility of their functionalization [33–38]. However, their success in forming Winsor type III systems is low, and blends with traditional surfactants are required [27,39–41]. The selected surface active ionic liquids (SAILs) were 1-decyl-3-methylimidazolium chloride ( $[C_{10}mim]Cl$ ) and 1-dodecyl-3-methylimidazolium bromide ( $[C_{12}mim]Br$ ).

The main contribution of this paper is the proposal of activity maps to analyze the influence of salt concentration, thus considering the possible variation of this parameter from injection to production wells, and temperature, on the phase behavior of surfactant blends. Even though obtaining these maps is a time-consuming procedure, they are an extremely useful tool to determine the limits of the region with the greatest interfacial activity (three-phase zone) of a surfactant system, varying two or three formulation parameters at the same time. The information provided offers a thorough understanding of the performance of the surfactant formulation, with the aim of predicting the behavior of chemical flooding in the reservoir in the event of salinity changes, thus allowing better decisions regarding the process. To that aim, the following studies were carried out:

- Phase behavior of AOT/Akyo LF2, AOT/ $[C_{10}mim]Cl$  and AOT/ $[C_{12}mim]Br$  blends at 25 °C and seawater salinity (5 wt% NaCl).
- Influence of water salinity on phase behavior. The concentration was varied from 1 to 15 wt% NaCl. This allowed activity maps to be made of the studied blends at 25 °C.
- Influence of temperature on phase behavior. Determinations at two new temperatures (50 and 75 °C) were carried out covering the entire range of salinities. This allowed the analysis of the variation of the size of the Winsor III region with this variable.
- Measurements of IFT for promising blends at optimal conditions, to ensure the achievement of ultra-low IFT and the validity of the blends for EOR.

## 2. Materials and methods

### 2.1. Materials

The anionic surfactant dioctyl sulfosuccinate sodium salt (Aerosol<sup>®</sup> OT, AOT) and the salt sodium chloride (NaCl), with purity grade of  $\geq 97$  wt% and  $\geq 99$  wt% respectively, were purchased from Sigma-Aldrich. The polyoxyethylene(8) octyl ether carboxylic acid ( $C_8EO_8OCH_2COOH$ ), commercially named Akyo LF2 (hereinafter referred as LF2 for simplicity), was kindly provided by KAO Chemicals with a purity of  $\geq 98$  wt%. The cationic SAIL 1-dodecyl-3-methylimidazolium bromide ( $[C_{12}mim]Br$ ) was purchased from Iolitec with a purity of  $> 98$  wt%, while the SAIL 1-decyl-3-methylimidazolium chloride ( $[C_{10}mim]Cl$ ) was synthesized. To that aim, 1-methylimidazole (Aldrich, 99 wt%) was directly alkylated with 1-chlorodecane (Aldrich, 98 wt%) at 60 °C under inert atmosphere for 72 h. The product was dissolved in acetonitrile (Panreac,  $>99.9$  wt%) and washed several times with ethyl acetate (Aldrich,  $>99.5$  wt%) to eliminate unreacted starting materials. After washing, most of the organic solvent was removed in a rotary evaporator, followed by stirring and heating at 70 °C for 48 h under

high vacuum (<0.1 mbar) to complete the removal of any residual volatile compounds present. A purity > 99 wt% was estimated by chromatography. Fig. 1 shows the chemical structures of surfactants. *n*-Octane was used as a model oil because it can mimic crude oil behavior in optimal salinity determinations for many surfactants [27]. It was purchased from Sigma-Aldrich with purity grade > 99 wt%.

## 2.2. Methods

Fig. 2 shows a schematic representation of the methodology used in this work. It involves phase behavior determinations and IFT measurements.

### 2.2.1. Phase behavior

The phase behavior of mixtures of water, oil (*n*-octane) and surfactant (AOT, LF2, [C<sub>10</sub>mim]Cl, [C<sub>12</sub>mim]Br and their blends) was visually analyzed following the so called encased-glass-pipette method [20,42]. The borosilicate glass pipettes were sealed at the tip, then once the reagents of the formulations were placed inside the pipettes (water oil ratio was ~ 1 and the concentration of surfactant in the aqueous phase 4 wt%), they were heat-sealed at the top and gently mixed for 24 h in a rotary mixer at ambient temperature. Thereafter, each pipette was enclosed in a 10 cm<sup>3</sup> test tube filled with silicone oil, to favor thermostatisation, and placed in a dry block heater OVAN model BD200-RE at the required temperature (25, 50 or 75 °C). When no change in the interfacial surface position was noticed, equilibrium condition was assumed. A surfactant concentration higher than that usually found in formulations was used to facilitate the visualization of the interfacial surface and the estimation of solubilization parameters. This procedure is frequently used in this kind of study [20,23,27,41].

Solubilization parameters were determined as the volume of oil or water solubilized in the microemulsion divided by volume of surfactant ( $V_o/V_S$  and  $V_w/V_S$ ), assuming all the surfactant is present in the microemulsion phase. To attain an optimal formulation, three phases must coexist (Winsor type III system) and the solubilization parameters must be equal and of large value. According to Hugh's correlation [43] (Eq.1), this condition leads to ultra-low IFT.

$$IFT_{Huh} = c/(V_i/V_S^*)^2 \quad (1)$$

where  $V_i/V_S^*$  is the optimal solubilization parameter, and  $C$  is an empirical constant which ranges from 0.1 – 0.35 mN/m. A value of 0.3 was assigned to this constant to estimate  $IFT_{Huh}$  for the evaluated blends.

In order to find the hydrophilic or lipophilic character of the target surfactants, salinity scans were carried out for LF2 and [C<sub>10</sub>mim]Cl at 25 °C. To that aim, several pipettes were prepared with different salt concentrations ranging from zero to 15 wt%, at 2 wt% intervals, in the aqueous phase. In the case of AOT and [C<sub>12</sub>mim]Br, the information was taken from a previous work [27].

The blending of surfactants can be used to adjust the hydrophilic-lipophilic balance and obtain a Winsor type III system. As in the case of the salinity scan, a blend scan is one-dimensional phase behavior evaluation with changes in a formulation variable, in this case the blend ratio. Its main objective is the determination of the optimal blend ratio required to achieve a triphasic system with a middle microemulsion. The blend scans were carried out at 25 °C with AOT and LF2, [C<sub>10</sub>mim]Cl or [C<sub>12</sub>mim]Br. Blend ratios were prepared at 5 wt% intervals, maintaining 4 wt% as the concentration of surfactant in the formulation. When a transition from Winsor I to Winsor II was observed without triphasic systems in the middle, the step was reduced to 1 wt%. Water salinity was initially set to 5 wt% NaCl to approximate the salinity of seawater (5 wt% TDS).

With the purpose of evaluating the effect of salinity and temperature on the phase behavior, blend scans were also carried out at salinities ranging from 1 wt% NaCl to 15 wt% NaCl, and temperatures of 50 and 75 °C. The interval for the salinity changes was adapted to the needs of each system. Thus, for the very electrolyte sensitive systems, the evaluation was done with increments of 1 wt% NaCl concentration, while for less sensitive mixtures increments of 5 wt% NaCl were used.

An activity map has as its main target the visualization of the greatest activity zone, as a function of two or three formulation variables, which can offer helpful insights into the development of a surfactant flooding strategy providing the highest oil recovery [12,44]. Thus, as the present study is particularly focused on optimizing the phase behavior of the systems during a hypothetical blend injection in an EOR process, the chosen formulation variables were: blend ratio, aqueous phase salinity (mimicking the salinity gradient that could be encountered in the reservoir during chemical flooding), and temperature. Thus, the type of Winsor system was analyzed through the preparation of activity maps as a function of these three variables.

### 2.2.2. Interfacial tension (IFT)

If the surfactant blends were clear or translucent, dynamic IFTs were measured between *n*-octane (representing oil) and the aqueous phase at 1 wt% blend concentration using a spinning drop tensiometer (Krüss model Site 100), as in our previous reports [38,41]. For all measurements, the capillary tube of the spinning drop was filled with the aqueous phase, and a 4 µL drop of *n*-octane was left inside. Measurements were taken at a fixed rotation speed of 3000 rpm, making sure that length of the drop was 4 times greater than its diameter. Measurements were taken at 25 °C, along the three-phase region, at different blend ratios and salinities.

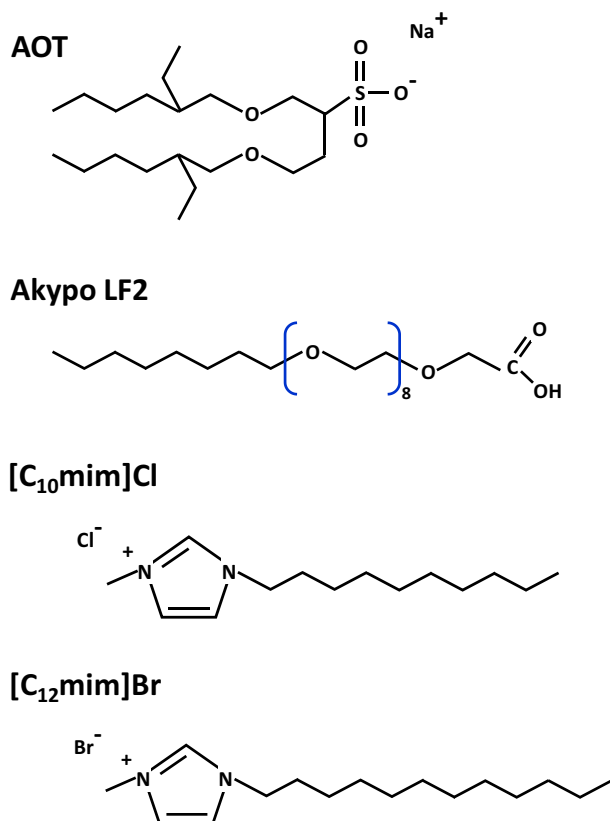


Fig. 1. Chemical structure of surfactants and ionic liquids.

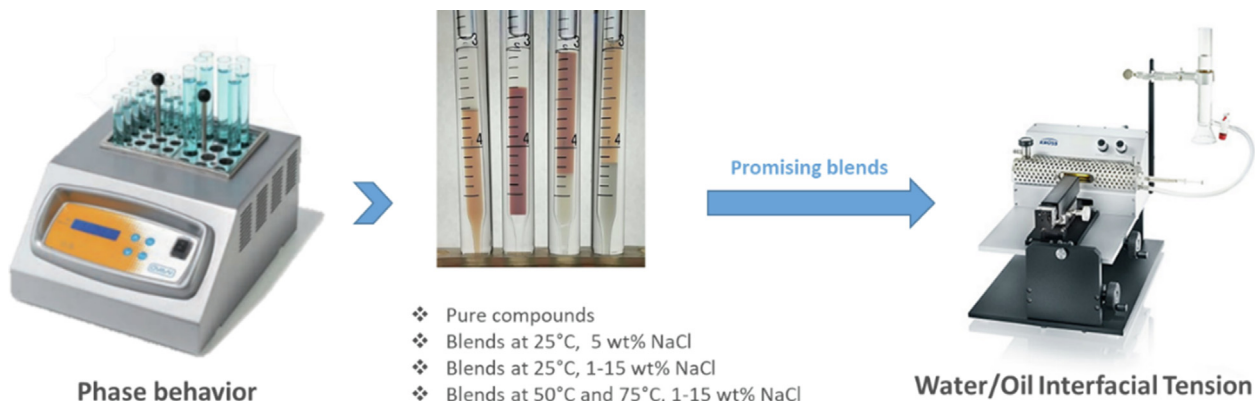


Fig. 2. Schematic representation of the methodology used in this work.

### 3. Results and discussion

#### 3.1. Phase behavior

Salinity scans were carried out for LF2 and [C<sub>10</sub>mim]Cl at 25 °C. Results can be seen in Figures S1 and S2 from Supporting Information (SI). Both surfactants were found to be highly hydrophilic, remaining Winsor I systems along the salinity interval evaluated. A similar behavior was previously found [27] in the case of the SAIL [C<sub>12</sub>mim]Br, microemulsions of Winsor type I were found up to 15 wt% NaCl. Conversely, the pure surfactant AOT is highly lipophilic, changing from Winsor I to Winsor II at 0.21 wt% NaCl optimal salinity [27]. Therefore, fixing a salt concentration of 5 wt% NaCl in water/oil systems, AOT was mainly located at the upper phase (Winsor II), while the rest of the surfactants were found in the lower phase (Winsor I). The lipophilic character of the AOT was then used as a tuning tool to find optimal blend ratios (leading to three phase systems with equal and large solubilization parameters), in combination with more hydrophilic surfactants.

##### 3.1.1. Blend scans at 25 °C and seawater salinity

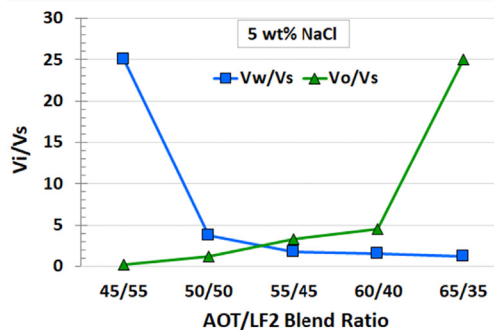
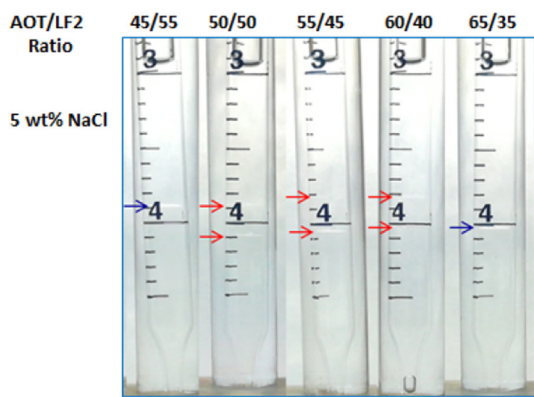
Three surfactant systems, AOT/LF2, AOT/[C<sub>10</sub>mim]Cl and AOT/[C<sub>12</sub>mim]Br, were subjected to blend screening at a fixed salinity of 5 wt% NaCl and 25 °C to determine the optimal mixing ratios. Fig. 3a shows the blend scan of the AOT/LF2 mixture. Both surfactants show very different hydrophilicity. At low proportions of AOT (left side Fig. 3a), the blend behaved as hydrophilic and pipettes were in the Winsor I region. Increasing the AOT ratio made the formulation more lipophilic, and Winsor type II systems were found passing through the three-phase region. Winsor type III systems were found at ratios between 50/50 and 60/40 AOT/LF2. However, the volume of the microemulsion phase was limited. As expected, similar tendencies were found for the other two blends (Fig. 3b and 3c left) due to the hydrophilic character of the SAILS. In the case of the blend with [C<sub>10</sub>mim]Cl, a change from Winsor I to Winsor III was initially observed (tests not shown) close to a composition ratio of 45/55 AOT/[C<sub>10</sub>mim]Cl, which is why a narrower blend scan was carried out from 40/60 to 48/52 ratios (Fig. 3b). A narrower three-phase region than in the case of LF2 was found (between 43/57 and 45/55), however, the volume of the microemulsion was greater. Also, the dissimilar optimal salinities of AOT and [C<sub>12</sub>mim]Br lead to a very narrow region of optimal salinities. In fact, a Winsor type III system was only found at 35/65 AOT/[C<sub>12</sub>mim]Br ratio, the volume of the middle microemulsion being very significant (Fig. 3c left).

The capacity of solubilization of the evaluated blends was studied through the solubilization parameters ( $V_o/V_s$  and  $V_w/V_s$ ). Fig. 3 right shows these relative volumes, for the three blends studied, as

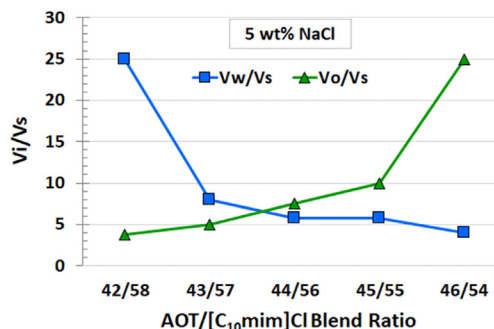
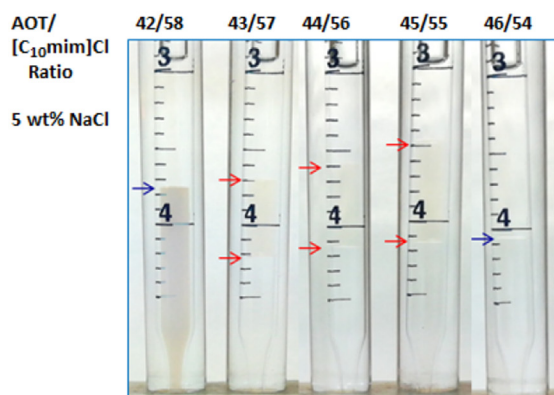
a function of blend ratio. As shown, the AOT/LF2 blend had the lowest optimal solubilization parameter ( $V_o/V_s^*$ , when  $V_o/V_s = V_w/V_s$ ) of 2.5 (Fig. 3a right). Numerical data are shown in Table 1. A low value of  $V_o/V_s^*$  indicates a low capacity of the formulation to solubilize large volumes of oil and water in the middle phase. Based on Huh's equation (Eq. (1)), the  $IFT_{Huh}$  was approximately  $4.8 \times 10^{-2}$  mN/m at the optimal blend ratio AOT/LF2 = 53/47. The solubilization parameter plot for the mixture AOT/[C<sub>10</sub>mim]Cl (Fig. 3b right) shows a higher value of the optimal solubilization parameter ( $V_o/V_s^* \sim 6.6$ ) at a 44/56 blend ratio, giving rise to  $IFT_{Huh}$  of about  $6.9 \times 10^{-3}$  mN/m. The blend AOT/[C<sub>12</sub>mim]Br showed the highest value of  $V_o/V_s^*$ , about 14.5 at an optimal blend ratio of 35/65 (Fig. 3c right), deriving on an ultralow  $IFT_{Huh}$  of about  $1.4 \times 10^{-3}$  mN/m at that optimal point, a promising value for EOR applications.

The justification for these remarkable differences in solubilization capabilities between AOT/LF2 and AOT/SAILS blends lies in the electrostatic activity between the oppositely charged head groups of the surfactants. They tend to form ion pairs, so that synergy between surfactants increases when their charges are opposite [22,45]. AOT is anionic whereas SAILS are cationic surfactants. LF2 is a weak carboxylic acid sensitive to the surrounding solution's pH. In alkaline environments it behaves as an anionic surfactant ( $-\text{COO}^-$ ), while in acid solutions it acts as a nonionic surfactant ( $-\text{COOH}$ ), similar to the nonionic surfactant C<sub>8</sub>EO<sub>8</sub>OH. In neutral conditions, it behaves more like a nonionic surfactant [32]. Thus, the anionic/nonionic blend is less synergic than the anionic/cationic ones. Electrostatic interactions between oppositely charged surfactant head groups lead to an effective reduction of the area of the combined surfactant-head groups, leading to a higher surface activity and greater capacity of solubilization [22].

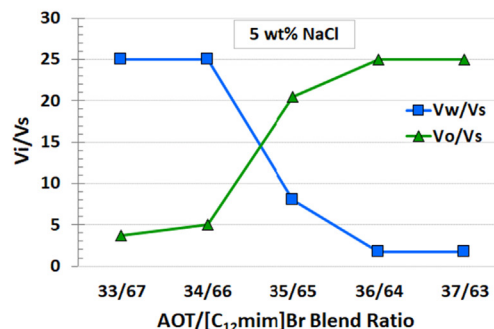
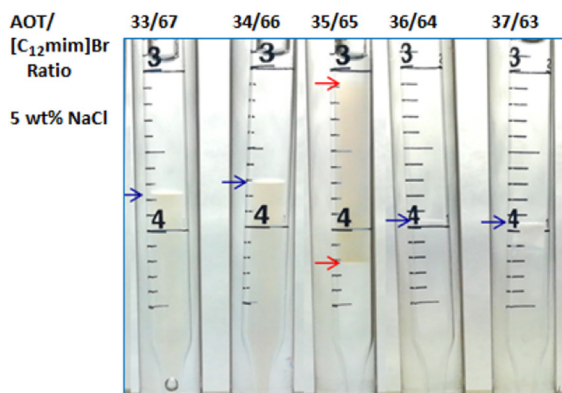
Some works have evaluated the synergy between AOT and nonionic polyoxyethylene alkyl ether (C<sub>10</sub>EO<sub>8</sub>/C<sub>10</sub>EO<sub>10</sub>/C<sub>13</sub>EO<sub>10</sub>) [46] or [C<sub>n</sub>mim]Br (n = 8, 10, 12, 14) SAILS [47,48], by means of the determination of the micellar interaction parameter ( $\beta^m$ ). Positive values of  $\beta^m$  are associated with repulsion between two surfactant molecules, while negative values with attraction in the mixed micelles. Therefore, at higher negative values, the synergy between the head groups of two surfactants is also higher. Those studies [46–48] estimated lower negative values for AOT/nonionic surfactant blends (in the range of  $-0.902$  to  $-6.34$ ), and higher negative values for AOT/SAIL blends (between  $-17.6$  and  $-23.1$ ). The negative values in the first case are due to the insertion of ethylene oxide chains in nonionic surfactants reducing the repulsion between these and anionic head groups in mixed micelles. The negative values in the second case are associated to the formation of ion-pairs, leading to an increase of the aggregation number or even the formation of microstructures such as vesicles. Such syner-



(a)



(b)



(c)

Fig. 3. Blend scans and solubilization parameters ( $V_i/V_s$ ) for the studied blends at 5 wt% NaCl and 25 °C. (a) AOT/LF2, (b) AOT/[C<sub>10</sub>mim]Cl, (c) AOT/[C<sub>12</sub>mim]Br.

getic effects favor solubilization. When a very high synergism is found between surfactants, the surface area charge of mixed micelles is reduced practically to zero and blends can show less hydrophilic behavior or even behave like nonionic surfactants. Thus, catanionic mixtures interact more strongly with the oil, so as their concentration at the interface increases, the interaction of the surfactant mixture with the oil phase is also increased, a change which is compensated by decreasing the salinity in order to increase the interaction on the water side [24]. Then stronger interactions of the surfactant mixture with both oil and water result in a higher solubilization. In the case of AOT/SAILS, parameter  $\beta^m$  reduced with the increase of the alkyl chain length, and consequently micellar radius, which explains the larger solubilization capacity of AOT/[C<sub>12</sub>mim]Br with respect to AOT/[C<sub>10</sub>mim]Cl.

### 3.1.2. Effect of salinity

It is well-known that increasing the aqueous phase salinity reduces the polar interaction between water molecules and head-groups of ionic surfactants, inducing surfactants to be expelled from the aqueous phase to the oil phase, while nonionic surfactants are more insensitive to electrolyte concentration [9,49]. Aiming to analyze the influence of salt concentration on the phase behavior of the studied blends, tests were also carried out at 1, 10 and 15 wt% NaCl.

Fig. 4 shows AOT/LF2 blend scans at different salt concentrations and 25 °C. In this case, the maximum salt concentration tested was 13 wt% since higher concentrations led to the appearance of a coacervate. As shown, the effect of salinity is rather significant on this blend. The increase of salt concentration has two effects: the size of the Winsor III regions (the range of composi-

**Table 1**  
Optimal blend ratios and corresponding solubilization parameters for AOT/LF2, AOT/[C<sub>10</sub>mim]Cl and AOT/[C<sub>12</sub>mim]Br blends at several salinities and temperatures and atmospheric pressure.

<b>AOT/LF2</b>							
<b>25 °C</b>							
1 wt% NaCl		5 wt% NaCl		10 wt% NaCl		13 wt% NaCl	
Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$
84/16	5.7	53/47	2.5	39/61	2.2	35/65	1.9
<b>50 °C</b>							
1 wt% NaCl							
Mass ratio	$V_i/V_s^*$						
88/12	4.25						
<b>AOT/[C<sub>10</sub>mim]Cl</b>							
<b>25 °C</b>							
1 wt% NaCl		5 wt% NaCl		10 wt% NaCl		15 wt% NaCl	
Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$
45/55	8.6	44/56	6.6	43/56	6.4	43/57	8.1
<b>50 °C</b>							
1 wt% NaCl		5 wt% NaCl		10 wt% NaCl		15 wt% NaCl	
Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$
49/55	5.9	43/57	3.7	43/57	3.7	43/57	3.7
<b>75 °C</b>							
1 wt% NaCl		5 wt% NaCl		10 wt% NaCl		15 wt% NaCl	
Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$
43/57	2.8	42/58	3.2	41/59	2.5	40/60	2.2
<b>AOT/[C<sub>12</sub>mim]Br</b>							
<b>25 °C</b>							
1 wt% NaCl		5 wt% NaCl		10 wt% NaCl		15 wt% NaCl	
Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$
36/64	14.8	35/65	14.5	34/66	14.0	32/68	15.3
<b>50 °C</b>							
1 wt% NaCl		5 wt% NaCl		10 wt% NaCl		15 wt% NaCl	
Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$
37/63	6.7	35/65	6.1	33/67	7.2	32/68	8.4
<b>75 °C</b>							
1 wt% NaCl		5 wt% NaCl		10 wt% NaCl		15 wt% NaCl	
Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$	Mass ratio	$V_i/V_s^*$
37/63	5.4	35/65	3.8	32/68	3.7	31/69	3.7

tions leading to three equilibrium phases) increases, and the proportion of AOT leading to optimal formulations decreases. At 1 wt% NaCl, three-phase systems are found from 80/20 to 90/10 AOT/LF2 ratios, and in the case of 13 wt% NaCl, a middle microemulsion is found from 20/80 to 50/50 blend ratios. Moreover, at low salinity (1 wt% NaCl), the optimal AOT/LF2 ratio was estimated to be 84/16 and decreased in AOT fraction to 39/61 and 35/65 at 10 wt% and 13 wt% NaCl, respectively. The blend becomes more lipophilic when salinity concentration increases, and the concentration of AOT required to achieve the hydrophilic-lipophilic balance decreases. Regarding the optimal solubilization parameter, it decreases from 5.7 to 1.9 when NaCl concentration increases from 1 to 13 wt% (see Table 1). The behavior found for this blend is typical of anionic surfactants. This may be explained by the lower synergism between the surfactants of this blend, the interactions between negatively charged AOT head groups being more significant than those of the nonionic ethoxy-lated groups of LF2 with water. The addition of NaCl reduces the electrostatic interaction between water molecules and the sulfonate group of AOT making it partition to the oil phase.

Fig. 5 shows AOT/[C<sub>10</sub>mim]Cl blend scans at 1, 10 and 15 wt% NaCl concentrations and 25 °C. As shown, the blend is less sensitive to salinity than the mixture with LF2. In fact, salt concentration hardly affects the size of the Winsor III region, which is very narrow at all concentrations. The salinity has also little influence on the blend optimal ratio that goes from 45/55 AOT/[C<sub>10</sub>mim]Cl at 1 wt% to 43/57 at 15 wt% NaCl. Regarding optimal solubilization parameters,  $V_i/V_s^*=8.6$  at 1 wt%, and this value decreases down to 6.6 and 6.4 at 5 and 10 wt% NaCl (Fig. 5 right) then increases up

to 8.1 at the highest salt concentration. The same qualitative behavior was found in the case of the blend with the other SAIL, [C<sub>12</sub>mim]Br. The salinity has a negligible influence on the size of the three-phase region and likewise on the optimal blend ratio, with optimal solubilization parameters first decreasing and then increasing with salt concentration. Fig. 6 shows that at 1 wt% NaCl,  $V_i/V_s^*=14.8$  at 36/64 AOT/[C<sub>12</sub>mim]Br, while at 10 wt% NaCl the optimal solubilization parameter is 14.0 at 34/66. The greatest solubilization capacity was found at 15 wt% NaCl,  $V_i/V_s^*=15.3$  at 32/68 optimal ratio. Lower concentrations of SAIL were required to achieve optimal formulations with [C<sub>10</sub>mim]Cl than with [C<sub>12</sub>mim]Br, however in the last case solubilization parameters are higher (better synergy between surfactants) and could be of interest for EOR.

Based on the results shown in Figs. 4, 5, and 6 a more detailed screening was carried out at 25 °C to generate activity maps, a clear visual representation of phase behavior of the blends studied, as a function of surfactant ratio and salinity. The activity map corresponding to the AOT/LF2 blend is shown in Fig. 7. Due to the high sensitivity of this mixture to salinity, new pipettes were prepared at intermediate salt concentrations between those initially studied. Circles in Fig. 7 show all the tests carried out. Black circles represent pipettes with two phases (Winsor I or Winsor II) and red circles show pipettes with three phases and a middle microemulsion. The highlighted area shows promising formulations for EOR due to their Winsor type III behavior. The figure also shows blend ratios and salinity concentrations leading to optimal formulations (dashed line) associated to low IFT. The activity map (Fig. 7) clearly shows that blends with AOT concentrations higher than 65 wt% are

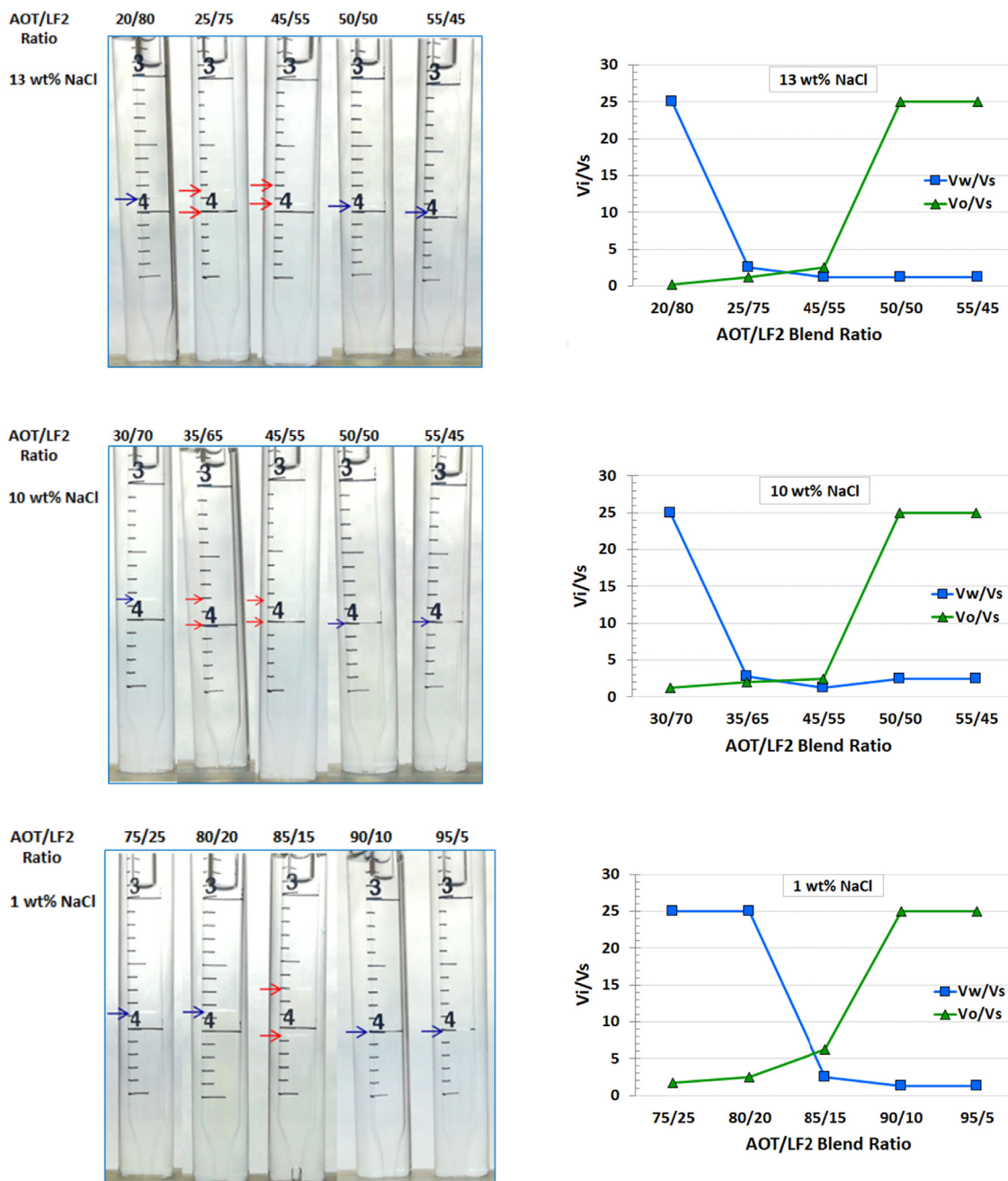


Fig. 4. Effect of salinity on blend scans and solubilization parameters ( $V_i/V_s$ ) for AOT/LF2 at 25 °C.

the most sensitive to salinity, where a small difference in wt% NaCl produces a significant change in the composition of the optimal blend ratio. In this sense, the use of this blend at low salinities is discouraged, because slight variations in either salt concentration or composition of the injected blend inside the reservoir would shift the formulation away from its optimal behavior. Conversely, at the highest concentrations of salt, the slope of the line corresponding to optimal formulations is high and the Winsor III region large. Even with significant variation in salinity or blend ratio, the Winsor III system remains, although the formulation moves away from its optimal behavior. The higher sensitivity of the blend at AOT compositions >65 wt% is accounted for by the excess of anionic surfactant, which makes it behave like an ionic surfactant. The increase of salinity in the water phase diminishes water activity and affinity of the surfactant for that phase. Increasing the concen-

tration of LF2, a change in the trend is noticed and the blend becomes more tolerant to NaCl increases. The ethoxylate block is likely the main cause of the interaction with the aqueous phase, and the presence of the inorganic salt has no significant influence, since the solubility of the surfactant in water is mainly due to the hydration of the ethoxy groups and not to electrostatic interactions [19,32].

Different behavior is observed in Fig. 8, showing activity maps for the blends of AOT with SAILs at 25 °C. These systems were clearly less sensitive to salt concentration than the blend with LF2. At the optimal blend ratios, with the dashed lines corresponding to the optimal formulations being practically vertical (especially in the blend with  $[C_{10}mim]Cl$ ), an increase in NaCl concentration would keep the system as Winsor III and at the optimal formulation (or very close to it). This is of great importance,

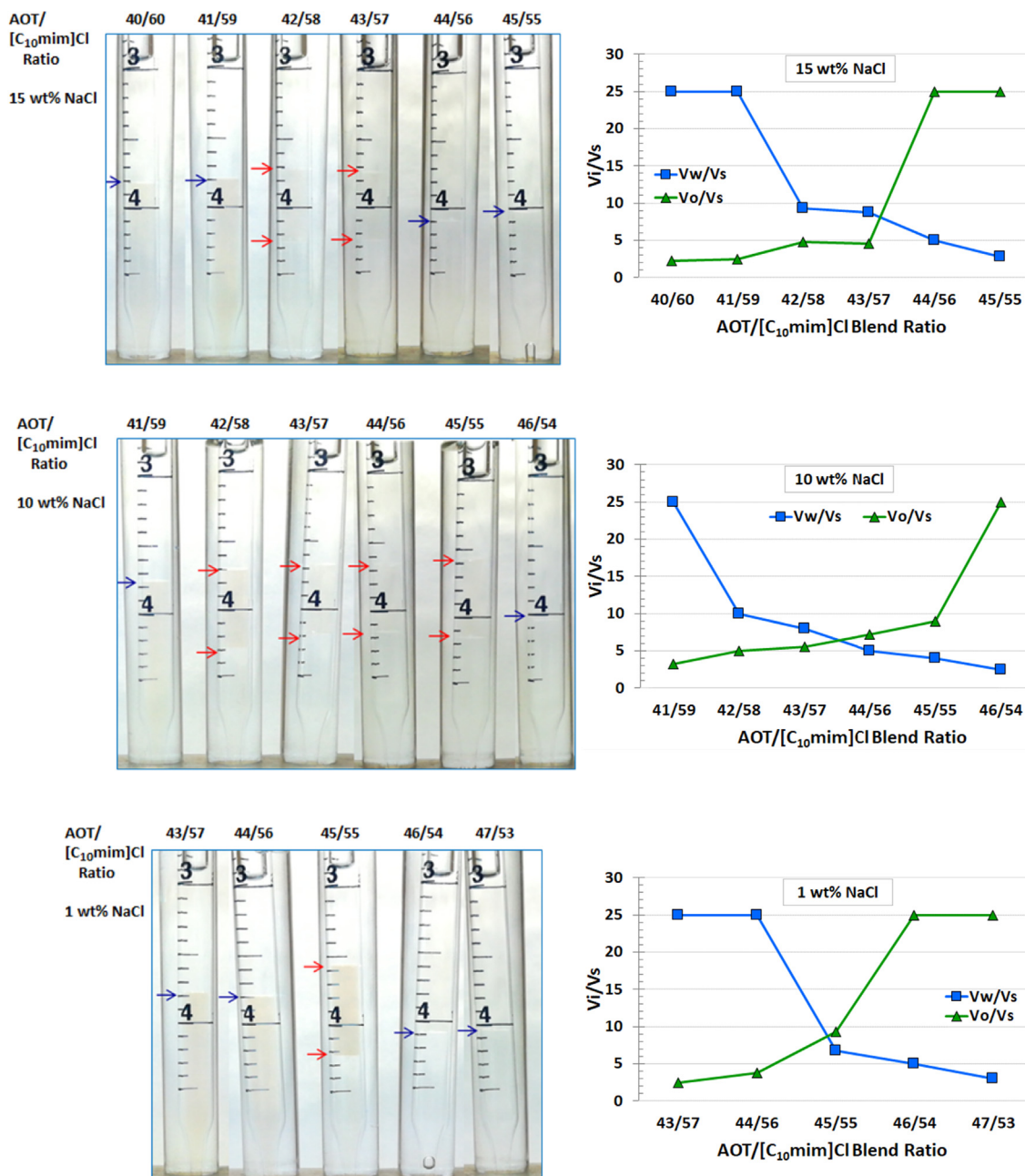


Fig. 5. Effect of salinity on blend scans and solubilization parameters ( $V_i/V_s$ ) for AOT/[C<sub>10</sub>mim]Cl at 25 °C.

because the injection water used in EOR frequently differs from the formation brine found in the reservoir, and salinity varies in the flooding process. The lipophilic AOT and hydrophilic SAILs were mixed seeking Winsor III behavior, however electrostatically neutral complexes are also formed due to the different charge of the components of the blend. When the synergy is high enough and the oppositely charged surfactants interact strongly, the mixed surfactants behave as nonionic and are less salinity sensitive [4,50]. On the other hand, Fig. 8 also shows that blends with SAILs are very sensitive to blend ratio. In mixtures with [C<sub>10</sub>mim]Cl, and more significantly in the case of [C<sub>12</sub>mim]Br, a small change in blend ratio generates distancing from the optimal region and low IFTs. This problem could be a concern in practice, due to the possible adsorption of surfactants on the rocks of the reservoir. Figure S3 in the Supporting Information allows the comparison of the activity maps of the three blends studied, and shows an advantage of

the mixture with LF2 regarding variations of blend ratio, in comparison to those with SAILs.

### 3.1.3. Effect of temperature

The effect of the temperature on phase behavior of the studied blends was analyzed. To that end, blend scans were carried out at 50 °C and 75 °C (pipette photographs and solubilization parameters can be seen in SI, Figures S4-S13).

Fig. 9 shows the activity map for the AOT/LF2 blend including the effect of temperature. The solubilization capacity of the system was drastically affected by this variable. Even though the range of blend ratios in which Winsor III systems appear is greater at 50 °C than at 25 °C, the middle microemulsions found had low volumes, hard to estimate accurately, especially at salt concentrations above 4 wt% NaCl. In some cases, coacervates were also identified by the

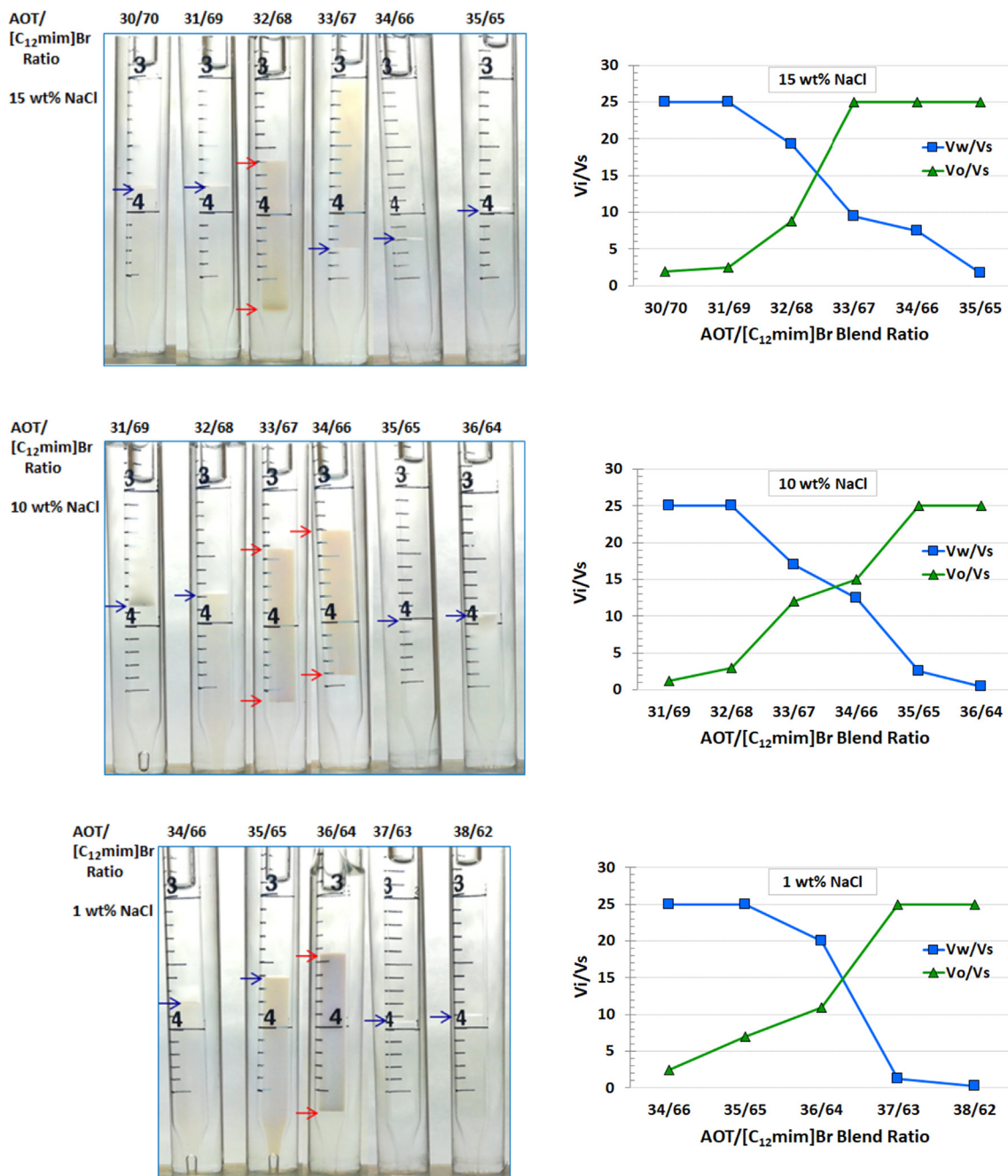


Fig. 6. Effect of salinity on blend scans and solubilization parameters ( $V_i/V_s$ ) for AOT/[C<sub>12</sub>mim]Br at 25 °C.

high curvature of the interface. The problem is even worse at 75 °C, reason why measurements were not carried out.

Figs. 10 and 11 show the activity maps for AOT/[C<sub>10</sub>mim]Cl and AOT/[C<sub>12</sub>mim]Br, respectively, including the effect of temperature. A widening of the triphasic areas with temperature was observed for the two blends. This is in agreement with results previously reported for anionic, nonionic and cationic-anionic mixtures [4,51–54].

Fig. 12 allows the visualization of the salinity and temperature effects on the optimal AOT/SAIL blend ratios. These mixtures behaved like non-ionic surfactants due to the formation of electrostatically neutral complexes. High temperature breaks hydrogen bonds between blends and water, thus decreasing the affinity of the surfactant for the aqueous phase and increasing its lipophilic character. Consequently, higher temperatures required lower pro-

portions of AOT (very lipophilic) in the blend to achieve an optimal behavior. This effect is more apparent in the case of SAILs of shorter alkyl length and at higher salt concentrations (see Fig. 12).

### 3.1.4. Solubilization parameters

Optimal blend ratios and corresponding solubilization parameters for AOT/LF2, AOT/[C<sub>10</sub>mim]Cl and AOT/[C<sub>12</sub>mim]Br blends at several salinities and temperatures and atmospheric pressure are presented in Table 1.

As explained above, in the case of AOT/LF2 blend at 50 °C, solubilization parameters could only be estimated at 1 and 2 wt% NaCl (Figure S5 in SI). At 1 wt% NaCl, a value  $V_i/V_s^* = 4.25$  was found at an optimal blend ratio 88/12 AOT/LF2. In comparison with results achieved at 25 °C at the same salt concentration, the optimal solubilization parameter decreased (leading to a higher IFT and lower

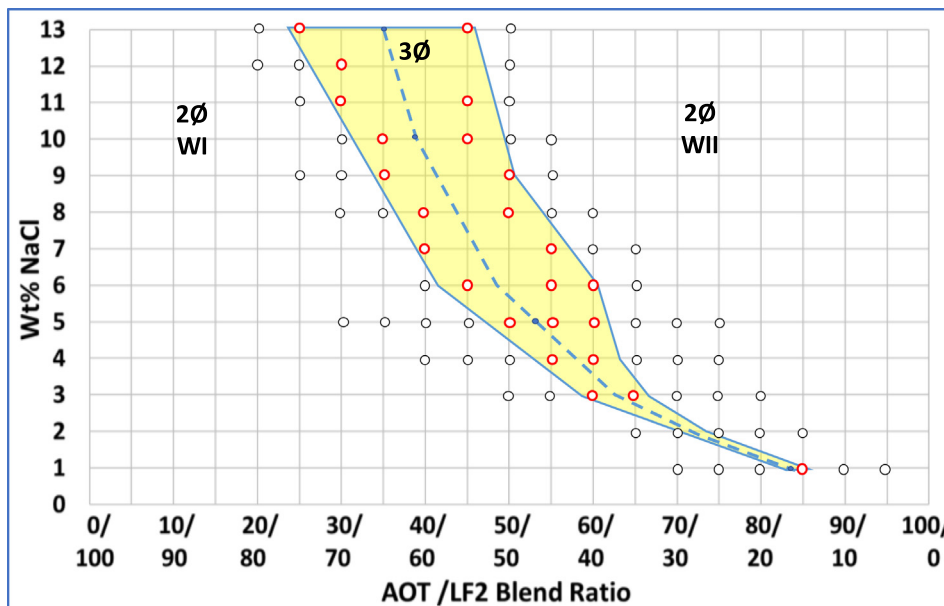


Fig. 7. Activity map for AOT/LF2 blend, as a function of salinity and blend ratio, at 25 °C. Black and red circles represent two- and three- phase systems, respectively. Blue dashed line represents optimal blend ratios.

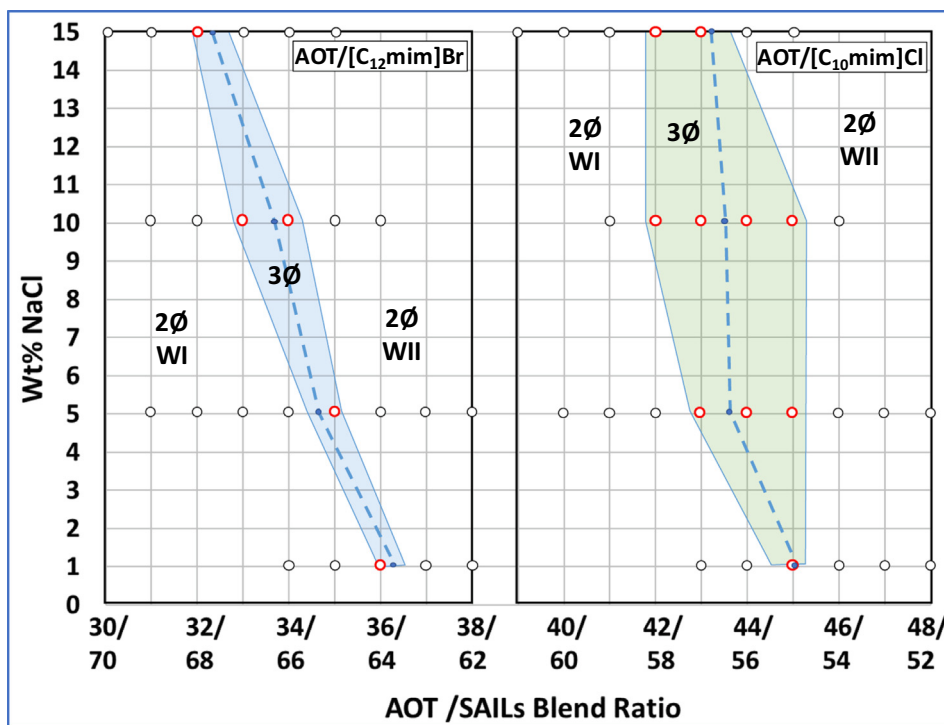


Fig. 8. Activity map for AOT/SAIL blends, as a function of salinity and blend ratio, at 25 °C. Black and red circles represent two- and three- phase systems, respectively. Blue dashed lines represent optimal blend ratios.

oil recovery), and the concentration of AOT slightly increased. Higher temperatures increase the hydrophilic character of the blend. It is worth mentioning that a previous study [32] shows the appearance of cloudy solutions when Akypo LF2 was used at 50 °C, however these problems disappear when combined with AOT. No further evaluations were carried out at higher temperatures for this blend that, among the temperatures studied, shows optimal behavior at 25 °C.

Fig. 13 allows the visualization of the salinity and temperature effects on the optimal solubilization parameters for AOT/SAIL blends. At all the studied salt concentrations, optimal solubilization parameters decrease with temperature, an effect more pronounced when the temperature increases from 25 to 50 °C and with the SAIL of longer alkyl chain length. Further studies (out of the scope of this work), based for instance on molecular simulation, are required to understand the combined effect of all the involved variables on the phase behavior of the different blends.

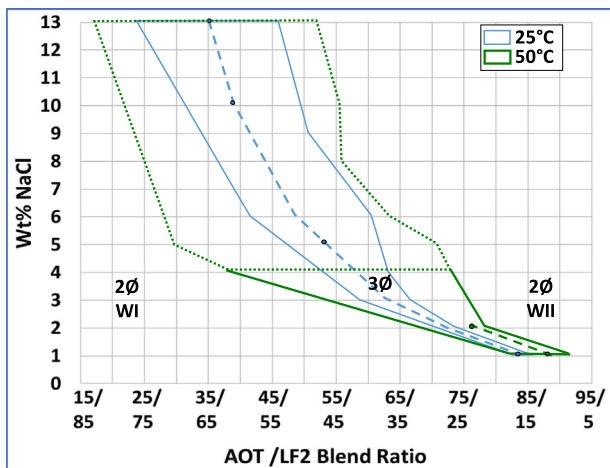


Fig. 9. Effect of temperature on the activity map of the AOT/LF2 blend.

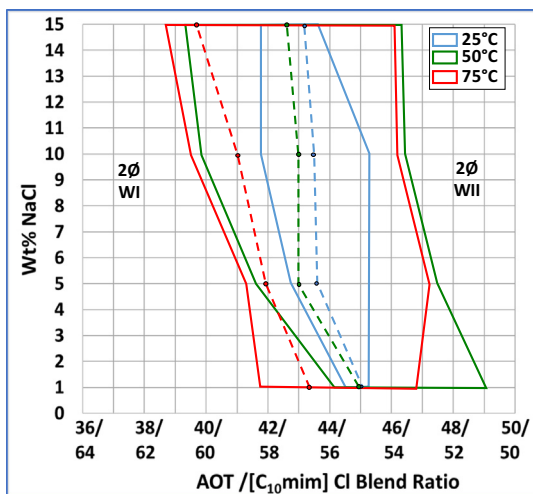


Fig. 10. Effect of temperature on the activity map of the AOT/ [C<sub>10</sub>mim]Cl blend.

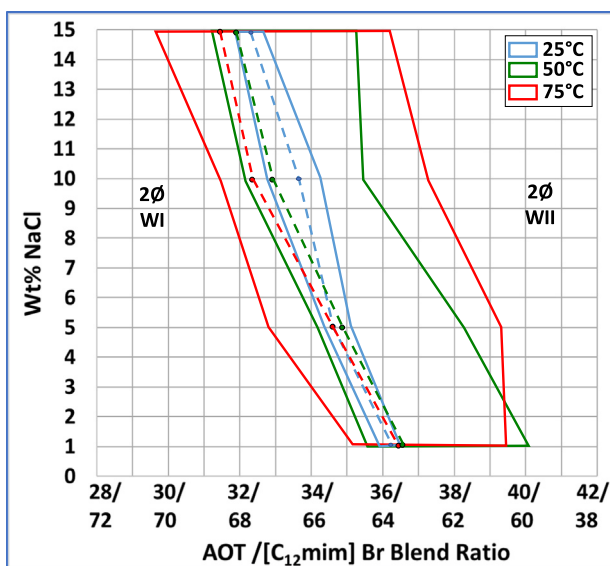


Fig. 11. Effect of temperature on the activity map of the AOT/ [C<sub>12</sub>mim]Br blend.

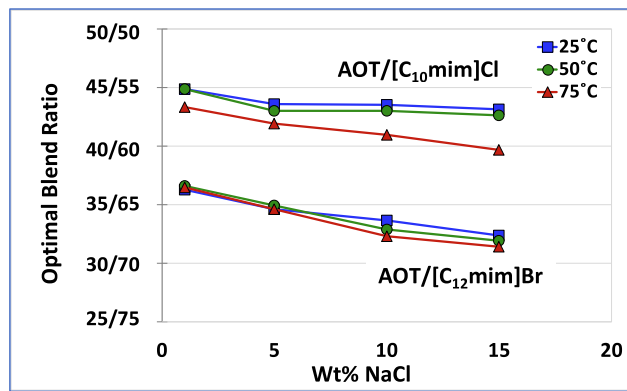


Fig. 12. Effect of salinity and temperature on the optimal blend ratio for AOT/ [C<sub>10</sub>mim]Cl blend (above) and AOT/ [C<sub>12</sub>mim]Br blend (below).

### 3.2. Interfacial tension measurements

Blends with SAILs were found to be too sensitive to blend ratios. Moreover, in absence of the oil, the injection fluids were found unstable, so they only could be injected as microemulsions. In the case of the blend AOT/LF2, a temperature of 25 °C was established as the best for the operation. For that reason, and focusing on IFT reduction as the main goal of surfactant EOR, measurements of this variable were carried out for the blend AOT/LF2 at 25 °C at optimal blend ratios. The surfactant concentration in the aqueous phase was 1 wt%. Experimental values of IFT and those calculated with Huh's equation for optimal conditions are shown in Table 2. Except in the case of 1 wt% NaCl, values of IFT estimated by the Huh's equation are over-estimated. Some experimental measurements were also carried out at blend ratios close to optimal (always in the Winsor III region). Results are shown in Fig. 14. As shown, optimal blend ratios achieved through experimental IFT measurements slightly differ from those previously obtained through solubilization parameters. Promising values of IFT, close to 0.01 mN/m in all cases, are found for the application of this blend at 25 °C.

## 4. Summary and conclusions

In this work, three blends (AOT/LF2, AOT/[C<sub>10</sub>mim]Cl and AOT/ [C<sub>12</sub>mim]Br) were evaluated for EOR. Both the carboxylic acid and the SAILs can be used to balance the hydrophilic-lipophilic character of the surfactant blend, thus improving the properties of the overly lipophilic AOT for the application. In the case of the anionic (AOT) - cationic (SAILs) mixtures, the properties of the blend depend on the formation of electronically neutral complexes due to their opposite charges. Activity maps, representations of the type of phase behavior of the surfactants as a function of blend ratio, salinity and temperature, were found to be useful tools for a clear visualization of the conditions of interest for the application of blends to EOR.

### 4.1. AOT/LF2 blend

Among all the studied blends, AOT/LF2 was found to be the most salinity sensitive, with significant changes in both optimal blend ratio and solubilization parameters, as NaCl concentration varies.

The effect of salt was more significant in the case of blends with AOT concentrations higher than 65 wt%, at which the mixture behaved like anionic surfactants, and less significant for lower con-

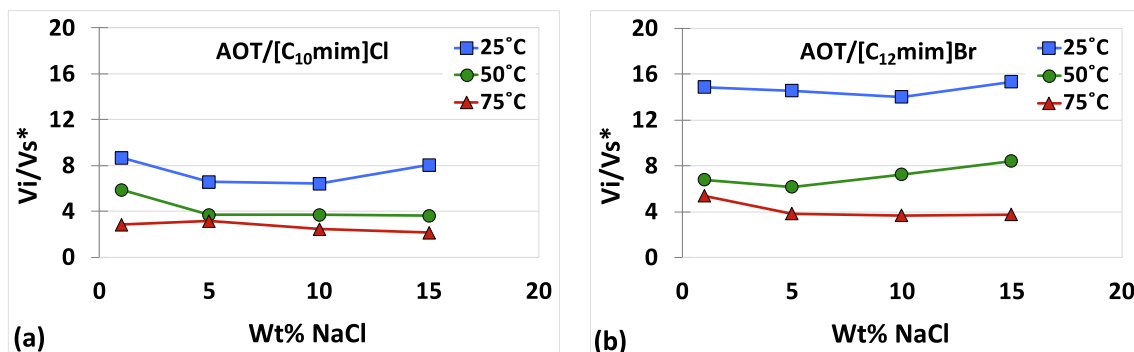


Fig. 13. Effect of salinity and temperature on the optimal solubilization parameters for (a) AOT/ [C<sub>10</sub>mim]Cl blend and (b) AOT/[C<sub>12</sub>mim]Br blend.

Table 2

Experimental and calculated, through Huh's equation, IFT for AOT/LF2 optimal blend ratios at 25 °C and different salinities.

Salinity (wt% NaCl)	Optimal mass ratio	Experimental IFT (mN/m)	Calculated IFT (mN/m)
1	84/16	$1.51 \times 10^{-2}$	$9.2 \times 10^{-3}$
5	53/47	$1.21 \times 10^{-2}$	$4.8 \times 10^{-2}$
10	39/61	$1.23 \times 10^{-2}$	$6.3 \times 10^{-2}$

centrations at which the behavior approached nonionic surfactants.

The main advantage of this blend lies in its low sensitivity to the blend ratio, allowing good performance even if there are changes in surfactant composition inside the reservoir. The increase of temperature led to middle microemulsions of low volumes and small solubilization parameters.

The application of this blend would be of interest at low temperatures. At 25 °C and the optimal blend ratios, IFTs close to 0.01 mN/m were found throughout all the range of salinities studied. Futures studies should focus on core flooding experiments to confirm the oil recovery capacity of the blend.

#### 4.2. AOT/SAILs blends

Both AOT/SAILs performed similarly. With a behavior similar to nonionic surfactants, they were shown to be more tolerant to salinity changes. Thus, the variation of NaCl hardly affected optimal

blend ratios or solubilization parameters. These last being higher, and promising, in the case of the SAIL of higher alkyl chain length.

As in the case of the blend with LF2, the increase of temperature led to wider Winsor III regions and lower solubilization parameters. However, problems of stability in the absence of oil, and the high sensitivity of these mixtures to blend ratio changes discourage, in principle, the use of these blends for practical applications.

#### CRediT authorship contribution statement

**Nestor Tafur:** experimental, analysis, first-draft writing. **Alba Somoza:** experimental orientation, editing. **Ana Soto:** conceptualization, supervision, writing, funding acquisition.

#### Declaration of Competing Interest

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

#### Acknowledgements

The authors acknowledge the Ministry of Science and Innovation and State Research Agency (AEI, 10.13039/501100011033) for financial support throughout project PGC2018-097342-B-I00, including European Regional Development Fund. A. Somoza also acknowledges predoctoral financial support (grant ref. PRE2019-089101). We would also like to thank Kao Corporation S.A. for supplying the Akypo LF2 surfactant.

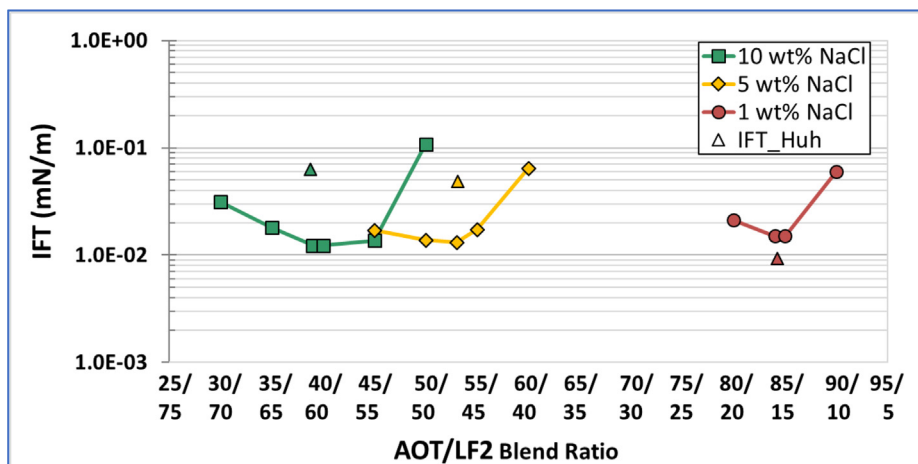


Fig. 14. IFT measurements for AOT/LF2 blend, as a function of blend ratio and salt concentration, at 25 °C.

## References

- [1] Y. Chen, Y. Lu, Features of O&G supply and demand and trend of E&D under the low oil price cycle, Soc. Pet. Eng. - SPE/IATMI Asia Pacific Oil Gas Conf. Exhib. 2019, APOG 2019. (2019) 1–9. <https://doi.org/10.2118/196537-ms>.
- [2] IFP Energies Nouvelles, Exploration-production investments, Onshore and offshore drilling activities and markets, geophysics and offshore construction, 2019. <https://www.ifpenergiesnouvelles.com/article/exploration-production-investments-onshore-and-offshore-drilling-activities-and-markets-geophysics-and-offshore-construction>.
- [3] M.J. Rosen, J.T. Kunjappu, *Surfactants and interfacial phenomena*, 4th ed., John Wiley & Sons, New Jersey, 2012.
- [4] Y. Li, W. Zhang, K. Bailing, M. Puerto, X. Bao, S. Ou, S. Zhiqin, Y. Yiqing, L. Yanhua, G. Songyuan, C. Miller, G.J. Hirasaki, Mixtures of anionic/cationic surfactants: A new approach for enhanced oil recovery in low-salinity, high-temperature sandstone reservoir, SPE J. 21 (2016) 1164–1177. <https://doi.org/10.2118/169051-pa>.
- [5] K. Spildo, A. Johannessen, A. Skauge, Low salinity waterflood at reduced capillarity, SPE - DOE Improv Oil Recover. Symp. Proc. 2 (2012) 1264–1276. <https://doi.org/10.2118/154236-ms>.
- [6] J. Sheng, *Enhanced oil recovery field case studies*, 2nd ed., Elsevier Inc., Amsterdam, 2013.
- [7] N. Ghadami, D. Arsanti, M. Faizal Sedaralit, Uncertainty assessment of chemical EOR in one of the offshore fields in Malaysia, Soc. Pet. Eng. - SPE Asia Pacific Enhanc. Oil Recover. Conf. EORC (2015). (2015) 522–536. <https://doi.org/10.2118/174614-ms>.
- [8] M.S. Kamal, I.A. Hussein, A.S. Sultan, Review on surfactant flooding: phase behavior, retention, IFT, and field applications, Energy and Fuels. 31 (2017) 7701–7720. <https://doi.org/10.1021/acs.energyfuels.7b00353>.
- [9] D. Green, G.P. Willhite, *Enhanced oil recovery*, 2nd Ed, Society of Petroleum Engineers, Inc, Richardson, Texas, 2018.
- [10] P.A. Winsor, Hydro-tropy, solubilisation and related emulsification processes. Part I, Trans. Faraday Soc. 44 (1948) 376–398. <https://doi.org/10.1039/TF9484400376>.
- [11] J.L. Salager, J.C. Morgan, R.S. Schechter, W.H. Wade, E. Vasquez, Optimum formulation of surfactant-water-oil systems for minimum interfacial tension or phase behaviour., Soc. Pet. Eng. J. 19 (1979) 107–115. <https://doi.org/https://doi.org/10.2118/7054-PA>.
- [12] J. Sheng, *Modern chemical enhanced oil recovery: Theory and practice*, 2nd Ed., Elsevier Inc., Amsterdam, 2011.
- [13] S. Bharadwaj, J.C. Ahluwalia, Mixed-surfactant system of dodecylbenzene sulfonate and alpha-olefin sulfonate: Micellar and volumetric studies, JAOCS, J. Am. Oil Chem. Soc. 73 (1996) 39–45. <https://doi.org/10.1007/BF02523446>.
- [14] M.S. Bakshi, S. Sachar, N. Mahajan, I. Kaur, G. Kaur, N. Singh, P. Sehgal, H. Doe, Mixed-micelle formation by strongly interacting surfactant binary mixtures: Effect of head-group modification, Colloid Polym. Sci. 280 (2002) 990–1000. <https://doi.org/10.1007/s00396-002-0717-9>.
- [15] I.J. Park, B.H. Lee, Mixed micellization of sodium dodecylbenzene sulfonate with polyoxyethylene lauryl ether surfactants (POLE4 and POLE23) in n-butanol aqueous solution, J. Surfactants Deterg. 15 (2012) 41–46. <https://doi.org/10.1007/s11743-011-1287-y>.
- [16] P.M. Holland, D.N. Rubingh, Mixed surfactant systems, Fuel Sci. Technol. Int. 11 (1993) 241–242. <https://doi.org/10.1080/08843759308916065>.
- [17] K. Holmberg, B. Jönsson, B. Kronberg, B. Lindman, *Surfactants and polymers in aqueous solution*, 2nd Ed, John Wiley & Sons, Ltd., Chichester, England, 2002. <https://doi.org/10.1002/0470856424>.
- [18] T. Doan, E. Acosta, J.F. Scamehorn, D.A. Sabatini, Formulating middle-phase microemulsions using mixed anionic and cationic surfactant systems, J. Surfactants Deterg. 6 (2003) 215–224. <https://doi.org/10.1007/s11743-003-0264-3>.
- [19] Y. Li, X. He, X. Cao, G. Zhao, X. Tian, X. Cui, Molecular behavior and synergistic effects between sodium dodecylbenzene sulfonate and Triton X-100 at oil/water interface, J. Colloid Interface Sci. 307 (2007) 215–220. <https://doi.org/10.1016/j.jcis.2006.11.026>.
- [20] M. Puerto, G.J. Hirasaki, C.A. Miller, J.R. Barnes, Surfactant systems for EOR in high-temperature, high-salinity environments, SPE J. 17 (2012) 11–19. <https://doi.org/10.2118/129675-PA>.
- [21] P. Ghosh, H. Sharma, K.K. Mohanty, Chemical flooding in low permeability carbonate rocks, Proc. - SPE Annu Tech. Conf. Exhib. (2017) 9–11. <https://doi.org/10.2118/187274-ms>.
- [22] Y. Li, M. Puerto, X. Bao, W. Zhang, J. Jin, Z. Su, S. Shen, G. Hirasaki, C. Miller, Synergism and performance for systems containing binary mixtures of anionic/cationic surfactants for enhanced oil recovery, J. Surfactants Deterg. 20 (2017) 21–34. <https://doi.org/10.1007/s11743-016-1892-x>.
- [23] J. Montes, N. Blin, A.E. Alvarez, I. Barrio, A. Panadero, R. Rodriguez, M. Coca, F. Trujillo, Novel anionic surfactant formulation for high temperature carbonate reservoirs, Soc. Pet. Eng. - SPE EOR Conf. Oil Gas West Asia (2018). <https://doi.org/10.2118/190353-ms>.
- [24] R.E. Antón, D. Gómez, A. Graciaa, J. Lachaise, J.L. Salager, Surfactant-oil-water systems near the affinity inversion part IX: Optimum formulation and phase behavior of mixed anionic-cationic systems, J. Dispers. Sci. Technol. 14 (1993) 401–416. <https://doi.org/10.1080/01932699308943413>.
- [25] A. Upadhyaya, E.J. Acosta, J.F. Scamehorn, D.A. Sabatini, Microemulsion phase behavior of anionic-cationic surfactant mixtures: Effect of tail branching, J. Surfactants Deterg. 9 (2006) 169–179. <https://doi.org/10.1007/s11743-006-0387-6>.
- [26] G. Zhang, J. Yu, C. Du, R. Lee, Formulation of surfactants for very low/high salinity surfactant flooding without alkali, Proc. - SPE Int. Symp. Oilf. Chem. 1 (2015) 399–414. <https://doi.org/10.2118/173738-ms>.
- [27] I. Rodriguez-Escontrela, M.C. Puerto, C.A. Miller, A. Soto, Ionic liquids for low-tension oil recovery processes: phase behavior tests, J. Colloid Interface Sci. 504 (2017) 404–416. <https://doi.org/10.1016/j.jcis.2017.05.102>.
- [28] E.Y. Sheu, S.H. Chen, J.S. Huang, Structure and growth of Bis(2-ethylhexyl) sulfosuccinate micelles in aqueous solutions, J. Phys. Chem. 91 (1987) 3306–3310. <https://doi.org/10.1021/j100290a049>.
- [29] B. Wu, B.J. Shiau, D.A. Sabatini, J.H. Harwell, D.Q. Vu, Formulating microemulsion systems for a weathered jet fuel waste using surfactant/cosurfactant mixtures, Sep. Sci. Technol. 35 (2000) 1917–1937. <https://doi.org/10.1081/SS-100100627>.
- [30] W. Wan, J. Zhao, J.H. Harwell, B.-J. Shiau, Characterization of crude oil equivalent alkane carbon number (EACN) for surfactant flooding design, J. Dispers. Sci. Technol. 37 (2) (2016) 280–287.
- [31] C. Negin, S. Ali, Q. Xie, Most common surfactants employed in chemical enhanced oil recovery, Petroleum. 3 (2017) 197–211. <https://doi.org/10.1016/j.petlm.2016.11.007>.
- [32] P. Denk, A. El Maangar, J. Lal, D. Kleber, T. Zemb, W. Kunz, Phase diagrams and microstructures of aqueous short alkyl chain polyethylene glycol ether carboxylate and carboxylic acid triblock surfactant solutions, J. Colloid Interface Sci. 590 (2021) 375–386. <https://doi.org/10.1016/j.jcis.2021.01.061>.
- [33] A.Z. Hezave, S. Dorostkar, S. Ayatollahi, M. Nabipour, B. Hemmateenejad, Investigating the effect of ionic liquid (1-dodecyl-3-methylimidazolium chloride ([C12mim][Cl])) on the water/oil interfacial tension as a novel surfactant, Colloids Surfaces A Physicochem. Eng. Asp. 421 (2013) 63–71. <https://doi.org/10.1016/j.colsurfa.2012.12.008>.
- [34] A.Z. Hezave, S. Dorostkar, S. Ayatollahi, M. Nabipour, B. Hemmateenejad, Effect of different families (imidazolium and pyridinium) of ionic liquids-based surfactants on interfacial tension of water/crude oil system, Fluid Phase Equilib. 360 (2013) 139–145. <https://doi.org/10.1016/j.fluid.2013.09.025>.
- [35] S. Sakhitvel, S. Velusamy, R.L. Gardas, J.S. Sangwai, Use of aromatic ionic liquids in the reduction of surface phenomena of crude oil-water system and their synergism with brine, Ind. Eng. Chem. Res. 54 (2015) 968–978. <https://doi.org/10.1021/ie504331k>.
- [36] A.K. Manshad, M. Rezaei, S. Moradi, I. Nowrouzi, A.H. Mohammadi, Wettability alteration and interfacial tension (IFT) reduction in enhanced oil recovery (EOR) process by ionic liquid flooding, J. Mol. Liq. 248 (2017) 153–162. <https://doi.org/10.1016/j.molliq.2017.10.009>.
- [37] 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>.
- [38] A. Somoza, A. Arce, A. Soto, Oil recovery tests with ionic liquids: a review and evaluation of 1-decyl-3-methylimidazolium triflate, Pet. Sci. (2021). <https://doi.org/10.1016/j.petsci.2021.10.025>.
- [39] H. Jia, X. Leng, M. Hu, Y. Song, H. Wu, P. Lian, Y. Liang, Y. Zhu, J. Liu, H. Zhou, 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 Surfaces A Physicochem. Eng. Asp. 529 (2017) 621–627. <https://doi.org/10.1016/j.colsurfa.2017.06.055>.
- [40] S.K. Nandwani, M. Chakraborty, H.J. Bart, S. Gupta, Synergism, phase behaviour and characterization of ionic liquid-nonionic surfactant mixture in high salinity environment of oil reservoirs, Fuel. 229 (2018) 167–179. <https://doi.org/10.1016/j.fuel.2018.05.021>.
- [41] 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). <https://doi.org/10.1016/j.petrol.2021.109856>.
- [42] J.R. Barnes, J.P. Smit, J.R. Smit, P.G. Shpakoff, K.H. Raney, M.C. Puerto, Development of surfactants for chemical flooding at difficult reservoir conditions, SPE Symp. Improv. Oil Recover. 1 (2008) 435–452. <https://doi.org/10.2118/113313-ms>.
- [43] C. Huh, Interfacial tensions and solubilizing ability of a microemulsion phase that coexists with oil and brine, J. Colloid Interface Sci. 71 (1979) 408–426. [https://doi.org/10.1016/0021-9797\(79\)90249-2](https://doi.org/10.1016/0021-9797(79)90249-2).
- [44] R.C. Nelson, J.B. Lawson, D.R. Thigpen, G.L. Stegemeyer, Cosurfactant-Enhanced Alkaline Flooding, Soc. Pet. Eng. AIME. (1984) 413–424. <https://doi.org/10.2118/12672-ms>.
- [45] G. Kume, M. Gallotti, G. Nunes, Review on anionic/cationic surfactant mixtures, J. Surfactants Deterg. 11 (2008) 1–11. <https://doi.org/10.1007/s11743-007-1047-1>.
- [46] R.K. Mahajan, D. Nandni, Micellization and phase behavior of binary mixtures of anionic and nonionic surfactants in aqueous media, Ind. Eng. Chem. Res. 51 (2012) 3338–3349. <https://doi.org/10.1021/ie202463w>.
- [47] S. Novak, S. Morasi Piperčič, S. Makarič, I. Primožič, M. Čurlin, Z. Štefanič, D. Domazet Jurašin, Interplay of noncovalent interactions in ionic liquid/sodium bis(2-ethylhexyl) sulfosuccinate mixtures: from lamellar to bicontinuous cubic liquid crystalline phase, J. Phys. Chem. B. 120 (2016) 12557–12567. <https://doi.org/10.1021/acs.jpbc.6b10515>.
- [48] M.T. García, I. Ribosa, J.J. González, F. Comelles, Surface activity, self-aggregation and antimicrobial activity of cationic mixtures of surface active imidazolium- or pyridinium-based ionic liquids and sodium bis(2-

- ethylhexyl) sulfosuccionate, *J. Mol. Liq.* 303 (2020), <https://doi.org/10.1016/j.molliq.2020.112637> 112637.
- [49] J.L. Salager, A.M. Forgiarini, J. Bullón, How to attain ultralow interfacial tension and three-phase behavior with surfactant formulation for enhanced oil recovery: a review. Part 1. Optimum formulation for simple surfactant-oil-water ternary systems, *J. Surfactants Deterg.* 16 (2013) 449–472, <https://doi.org/10.1007/s11743-013-1470-4>.
- [50] R.E. Antón, J.M. Andérez, C. Bracho, F. Vejar, J.L. Salager, Practical surfactant mixing rules based on the attainment of microemulsion-oil-water three-phase behavior systems, *Adv. Polym. Sci.* 218 (2008) 83–113, [https://doi.org/10.1007/12\\_2008\\_163](https://doi.org/10.1007/12_2008_163).
- [51] C.L. Sassen, A. Gonzalez Casielles, T.W. de Loos, J. de Swaan Arons, The influence of pressure and temperature on the phase behaviour of the system H<sub>2</sub>O + C12+ C7E5 and relevant binary subsystems, *Fluid Phase Equilib.* 72 (1992) 173–187, [https://doi.org/10.1016/0378-3812\(92\)85025-4](https://doi.org/10.1016/0378-3812(92)85025-4).
- [52] R.E. Antón, A. Graciaa, J. Lachaise, J.L. Salager, Surfactant-oil-water systems near the affinity inversion, Part VIII: Optimum formulation and phase behavior of mixed anionic-nonionic systems versus temperature, *J. Dispers. Sci. Technol.* 13 (1992) 565–579, <https://doi.org/10.1080/01932699208943334>.
- [53] K.-H. Oh, J.R. Baran, W.H. Wade, V. Weerasooriya, Temperature insensitive microemulsion phase behavior with non-ionic surfactants, *J. Dispers. Sci. Technol.* 16 (2) (1995) 165–188.
- [54] M.G. Aarra, H. Høiland, A. Skauge, Phase behavior and salt partitioning in two- and three-phase anionic surfactant microemulsion systems: Part I, phase behavior as a function of temperature, *J. Colloid Interface Sci.* 215 (1999) 201–215, <https://doi.org/10.1006/jcis.1999.6228>.