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## Ionic Liquids for Low-tension Oil Recovery Processes: Phase Behavior Tests

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### Abstract

Chemical flooding with surfactants for reducing oil-brine interfacial tensions (IFTs) to mobilize residual oil trapped by capillary forces has a great potential for Enhanced Oil Recovery (EOR). Surface-active ionic liquids (SAILs) constitute a class of surfactants that has recently been proposed for this application. For the first time, SAILs or their blends with an anionic surfactant are studied by determining equilibrium phase behavior for systems of about unit water-oil ratio at various temperatures. The test fluids were model alkane and aromatic oils, NaCl brine, and synthetic hard seawater (SW). Patterns of microemulsions observed are those of classical phase behavior (Winsor I-III-II transition) known to correlate with low IFTs. The two anionic room-temperature SAILs tested were made from common anionic surfactants by substituting imidazolium or phosphonium cations for sodium. These two anionic and two cationic SAILs were found to have little potential for EOR when tested individually. Thus, also tested were blends of an anionic internal olefin sulfonate (IOS) surfactant with one of the anionic SAILs and both cationic SAILs. Most promising for EOR was the anionic/cationic surfactant blend of IOS with [C<sub>12</sub>mim]Br in SW. A low equilibrium IFT of  $\sim 2 \cdot 10^{-3}$  mN/m was measured between n-octane and an aqueous solution having the optimal blend ratio for this system at 25°C.

Keywords: surface active ionic liquid, phase behavior, surfactant blend, enhanced oil recovery



## 1. Introduction

Surfactant flooding is one of the most promising techniques in Enhanced Oil Recovery (EOR). The addition of tailored surfactants to the injection fluid reduces interfacial tension (IFT), and therefore increases the capillary number, decreasing the residual oil saturation [1, 2]. Healy *et al.* [3] found that the optimal formulation for surfactant oil recovery, with a minimum in the oil-water IFT, is achieved when equilibrium IFTs between a microemulsion phase and excess phases of oil and water become equal.

The achievement of the ultralow IFT necessary in tertiary oil recovery processes is closely related to water and oil solubilization, and hence to phase behavior. When the surfactant or surfactant blend is preferentially soluble in the aqueous phase, an oil-in-water microemulsion coexists at equilibrium with excess oil (Winsor I behavior [4]). Droplet diameter in the microemulsion and hence oil solubilization are determined by the magnitude of spontaneous curvature of its internal interfaces toward a water-continuous microstructure. Similarly, when the surfactant or blend is preferentially soluble in oil, spontaneous curvature favors an oil-continuous microstructure, and a water-in-oil microemulsion coexists with excess aqueous phase (Winsor II). Droplet size and water solubilization are again determined by the magnitude of spontaneous curvature. Near the optimal condition three phases coexist, as indicated above (Winsor III). Huh's equation [5] makes possible to estimate the value of the equilibrium IFT at the optimal condition, where spontaneous curvature is zero, from the equal values of the solubilization parameters,  $V_o/V_s = V_w/V_s$  (volume of oil or water solubilized in the microemulsion divided by volume of surfactant).

Suitable surfactants for EOR are those able to generate sufficiently low water-oil interfacial tension at reservoir conditions where the tertiary oil is trapped. Such surfactants can be found by conducting salinity or surfactant-blend scans, the proper phase behavior tests for screening surfactants before carrying out more expensive and time-consuming coreflooding experiments. Salinity scans are useful tools to determine the optimal salinity of individual ionic surfactants when monotonically altering only salinity at a fixed surfactant concentration, oil type and temperature. Blend scans are useful tools to determine the optimal blend of two surfactants when monotonically altering only surfactant ratios at a fixed surfactant concentration, salinity, oil type and temperature. A high solubilization parameter ( $>10$ ) indicates ultra-low IFT. Hence, tests of salinity and blend scans

are used to evaluate phase behavior of surfactant formulations and determine their suitability for oil recovery.

Ionic liquids (ILs) do not behave like simple molecular solvents and form spatially heterogeneous domains. This structuration between polar and non-polar regions implies the existence of differentiated and complex interactions not only in pure ILs but also in their mixtures with other compounds. Thus, this segregation provides these salts a high capacity of solvation [6]. Moreover, the amphiphilic nature of these salts makes them potential surfactants. A surfactant or surface-active ionic liquid (SAIL) reduces the surface tension of polar solvents such as water by a significant extent.

The main advantage of using SAILs in EOR is that they can be functionalized [7] according to the requirements of a specified application or reservoir. As a result, options for developing formulations are greatly expanded, especially for reservoirs at high temperatures and salinities where the choice of conventional surfactants is limited. Room temperature ionic liquids (RTILs) could be shipped in neat form to the field, which is unfeasible with most conventional ionic surfactants. Furthermore, due to the characteristic rings, of many ILs, that have a high affinity to form hydrogen bonds, the Krafft temperature for SAILs is frequently lower than for similar common surfactants. For example, imidazolium SAILs have a comparatively lower Krafft temperature than alkyltrimethylammonium compounds. This would indicate that long-chained imidazolium ILs are more able to act as surfactants at lower temperature than traditional cationic surfactants with a similar chain length [8]. On the other hand, recent studies [9-11] show that aqueous solutions of ILs (with and without oil) have a high stability in extreme conditions (high salinity and/or temperature).

Dynamic interfacial tension measurements have been a method proposed to evaluate SAILs for EOR applications [12-14]. These groups reported IFTs between aqueous solutions of ILs and oils above 0.1 mN/m. However, IFTS below 0.01 mN/m and preferably near 0.001 mN/m are needed in typical cases to mobilize trapped residual oil remaining after waterflooding of an oil reservoir.

The formulation of surfactant blends to adjust Hydrophilic-Lipophilic-Balance (HLB) or to take advantage of the synergistic behavior in mixed systems has been studied for surfactant flooding purposes [15]. Mixtures of anionic and cationic surfactants have many unique properties that can be beneficial due to the formation of ion pairs [16]. For this reason, blends of SAILs or SAIL with a common surfactant could be a solution to adjust HLB, or form ion pairs, for achieving

classical Winsor Type III microemulsions with the proper oil solubilization required for attaining ultra-low IFT. Hou *et al.* [17] have studied mixtures of a common anionic surfactant SDS with a cationic SAIL to solubilize dense non-aqueous-phase liquids and remove these compounds from the environment. However, the proposed formulations required alcohol, which was absent in the present study

In this work, for the first time, the potential of a set of SAILs alone or blended has been studied, by means of phase behavior tests, for their application in EOR. First, cationic and anionic SAILs have been studied alone by means of salinity scans. Based on the individual salinity scan results, blend scans combining different SAILs or a SAIL with the well-known EOR surfactant IOS<sub>15-18</sub>, have been tested, focusing on finding low-tension microemulsion systems that could be injected as aqueous, single-phase, compositions in hard seawater.

## 2 Experimental

### 2.1 Chemicals

The traditional cationic surfactant dodecyltrimethylammonium bromide (C<sub>12</sub>TAB) and traditional anionic surfactants dioctyl sodium sulfosuccinate (Aerosol<sup>®</sup> OT) and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich with purities > 98 %wt, > 97 %wt and >98 %wt respectively. The EOR surfactant ENORDET 0332, an Internal Olefin Sulfonate, is a twin-tailed or branched hydrophobe with 15-18 carbon atoms (IOS<sub>15-18</sub>) supplied by Shell Global Solutions International.

The anionic SAILs, namely tributylmethylphosphonium dodecyl sulfate ([P<sub>4441</sub>][DS]) and 1-butyl-3-methyl imidazolium dioctyl sulfosuccinate ([C<sub>4mim</sub>]AOT), were obtained by metathesis reaction. In the case of the SAIL [P<sub>4441</sub>][DS], an equimolar mixture of tributylmethylphosphonium chloride ([P<sub>4441</sub>][Cl], Cytec) and sodium dodecyl sulfate (SDS, Sigma Aldrich) were dissolved in water and stirred overnight at room temperature. The mixture was washed with dichloromethane. The organic phase was separated in a decanting funnel from the aqueous phase that contained the sodium chloride. For the synthesis of [C<sub>4mim</sub>]AOT, an equimolar mixture of 1-butyl-3-methyl imidazolium chloride ([C<sub>4mim</sub>]Cl, Iolitec) and dioctyl sodium sulfosuccinate (hereinafter Na-AOT) was dissolved in dichloromethane and stirred overnight at room temperature. The precipitated NaCl was filtered.

In both syntheses organic phase was washed with water and decanted several times to completely remove Cl<sup>-</sup> ions. The washing was performed until no

precipitation appeared with the addition of 0.1 M  $\text{AgNO}_3$ . Dichloromethane was removed using a rotary evaporator and the final product was dried under vacuum for 72 h [18-20]. The chemical structures were confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. The chloride content ( $<800$  ppm) was measured by ionic chromatography using an ion chromatograph (Metrohm 861) equipped with a suppressed conductivity detector, a sample processor (Metrohm 838) and a Metrosep A column ( $250 \times 4.0$  mm). A carbonate buffer ( $3.2$  mM  $\text{Na}_2\text{CO}_3$  and  $1.0$  mM  $\text{NaHCO}_3$ ) was the mobile phase at a flow rate of  $0.7$  mL  $\text{min}^{-1}$ . The water content of both ILs was measured by the Karl Fischer titration method in a Metrohm 737 KF coulometer being  $\sim 400$  ppm.

In the case of cationic SAILs, 1-dodecyl-3-methylimidazolium bromide ( $[\text{C}_{12}\text{mim}]\text{Br}$ ) was purchased from Iolitec and tributyl (tetradecyl) phosphonium chloride ( $[\text{P}_{44414}]\text{Cl}$ ) was supplied by Cytec. Both were tested as received with a purity  $>98$  %wt. The chemical structure of the SAILs used in this work is shown in Figure 1.

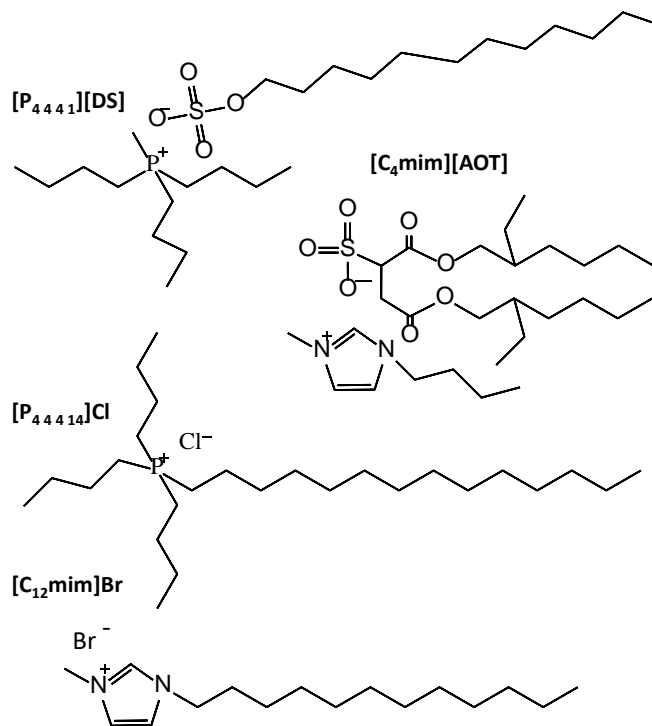


Figure 1. Chemical structure of the SAILs used in this work.

n-octane (reagent grade, 98 %wt), butylbenzene ( $>99$  %wt) and hexylbenzene (97 %wt) were purchased from Sigma–Aldrich and used in the experiments as model oils. Sodium chloride was purchased from Fisher Chemical and calcium chloride

dihydrate, magnesium chloride hexahydrate and sodium sulfate anhydrous were purchased from EMD chemicals. All the salts were certified ACS Reagent Grade with a purity  $\geq 99$  %wt. The brines were made by adding salt to deionized water.

## 2.2 Procedure

Salinity tests were done in encased glass pipettes [21] at test temperature. The pipettes for the tests were made from 5 cm<sup>3</sup> pipettes of borosilicate glass severed in half after sealed at the tip. Approximately 1 cm<sup>3</sup> of brine + surfactant and 1 cm<sup>3</sup> of test oil were weighed into individual pipettes while located on an analytical balance; thereafter pipettes were top sealed with an oxygen-acetylene torch. Water oil ratio (WOR) was  $\sim 1$  and the concentration of surfactant was 2 %wt overall. n-octane was chosen in most of the cases as oil phase because optimal salinities of various surfactants against this oil and many crude oils are somewhat similar [22]. In some cases, to decrease the optimal salinity, butylbenzene and hexylbenzene were also selected as oils. Scans were conducted by either varying salinity for obtaining optimal salinity of single surfactants while temperature, concentration of surfactant and water/oil ratio (WOR=1) were fixed or by varying surfactant ratio for obtaining the optimal blend at desired conditions of salinity and temperature.

Samples were mixed end-to-end in a rotary mixer, at room temperature, approximately 24 hours and then left to equilibrate quiescently until the phase volume remained constant. Tests at higher temperatures were carried out placing the sealed pipettes inside a test tube filled with silicone oil and locating them in a dry block heater tailored for the test tubes. Samples were removed from heater several times, mixed briefly end-to-end by hand, and replaced to remain quiescent. This procedure of mixing was continued until phase volumes remained constant. Photographs were taken and phase volumes read to calculate solubilization parameters for finding optimal salinity or optimal blend ratio.

In the case of the optimal blends with clear aqueous solutions, the hydrodynamic radius of the aggregates was measured by means of Dynamic Light Scattering from A Malvern Zen3600 Zetasizer Nano ZS apparatus.

The absence of liquid crystals was proved by the absence of birefringence using a spectral confocal microscopy (Leica model TCS SP2) with polarized light.

Interfacial tensions were measured using a spinning drop tensiometer Krüss model Site100. Temperature was controlled by circulating oil from a thermostatic bath Julabo model EH-5. The uncertainty in the temperature measurement is

0.01°C. The capillary was filled from a 5 ml syringe filled with denser phase without any air bubbles. The solution was kept in the capillary for at least 30 min and then it was replaced with fresh solution. The lighter phase was injected with a Hamilton microliter syringe at a slow speed of rotation (about 100 rpm) and a volume varying between 2 and 4  $\mu\text{l}$ . The capillary rotating speed was that necessary to obtain a drop length at least 4 times larger than its diameter. The interfacial tension was then obtained from the Vonnegut equation,

$$\gamma = \frac{\Delta\rho \cdot \omega^2 \cdot r^3}{4} \quad [1]$$

Where  $\omega$ ,  $r$  and  $\Delta\rho$  are the capillary rotating speed, drop radius and density difference between dense and light phases, respectively.

### 3. Results and discussion

#### 3.1 Individual SAILs

Anionic surfactants are most widely used in chemical EOR processes [1]. With this in mind, the well-known traditional surfactants sodium dodecyl sulfate (SDS) and dioctyl sodium sulfosuccinate (Na-AOT) were modified by changing sodium to a phosphonium or an imidazolium cation, respectively, to convert them to room-temperature SAILs.

Phase behavior of the modified-SDS SAIL [P<sub>4 4 4 1</sub>][DS] was studied with *n*-dodecane as model oil and test results were issued in a previous publication [18]. Up to about 4 %wt NaCl only two phases were present with the SAIL in the aqueous phase (Winsor I behavior) but with minimal oil solubilization. Upon further increasing salinity, a middle phase was formed. This phase had an oil solubilization parameter ( $V_o/V_s$ , ratio of oil to surfactant volume) that was difficult to determine accurately by measuring phase volumes but was below  $\sim 1.2$  up to 12 %wt NaCl – far less than for typical microemulsions. Moreover, the system never became lipophilic to form a Winsor type II microemulsion in equilibrium with excess brine at higher salinity. Similar phase behavior was found in this work when studied with *n*-octane. SAIL and brine form a coacervate in equilibrium with excess brine in the absence of oil or having miniscule oil solubilization in the presence of paraffinic octane and dodecane, when the concentration of NaCl is about 4 and 4.5 %wt.

Surfactants tested with aromatic hydrocarbons have a lower optimal salinity than when tested with paraffinics of comparable oil molar volume ( $V_{mo}$ ), according to Puerto *et al.* [23]. Thus, salinity scans with aromatic hydrocarbons as test oils



could permit to achieve an optimal salinity below that where the coacervate formed. So, butylbenzene and hexylbenzene were the test oils selected to assess the differences between  $[P_{4441}][DS]$  and its parent compound SDS.

In Figure 2 (top) the photographs of the salinity scans are shown at 25°C for 2 %wt. SAIL  $[P_{4441}][DS]$  (overall concentration) with butylbenzene (left) and hexylbenzene (right). With both oils the SAIL generated classical microemulsion phase behavior, Winsor I-III-II transition, with optimal salinities well below 1 %wt NaCl. No coacervate was observed.

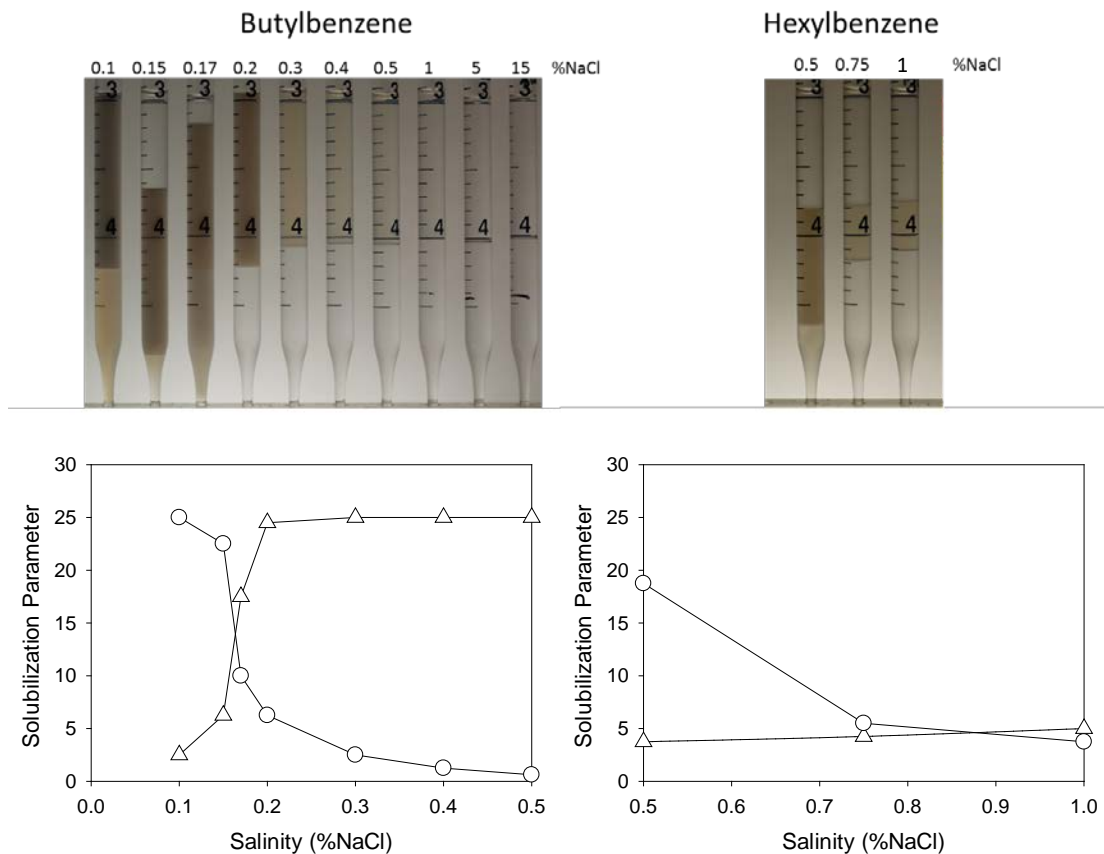


Figure 2. Top: Pictures of salinity scans, 2 %wt. overall  $[P_{4441}][DS]$ , butylbenzene or hexylbenzene oil,  $WOR \sim 1$  at 25°C. Bottom: Solubilization Parameters (  $\circ$   $V_w/V_s$  ,  $\triangle$   $V_o/V_s$  ) for both salinity scans.

Solubilization parameters  $V_o/V_s$  and  $V_w/V_s$  as a function of salinity are shown for both oils in Figure 2 (bottom). Optimal salinity,  $C_{\phi}$  increases in %wt NaCl from  $\sim 0.16$  with butylbenzene to  $\sim 0.85$  with hexylbenzene. This means that the optimal salinity increases when  $V_{mo}$  increases. In contrast, the solubilization parameter at the optimal salinity ( $V_o/V_s = V_w/V_s$ ) decreases from 14 to 5. This effect of  $V_{mo}$  on

optimal salinity and solubilization parameters (Figure 3) is in good agreement with the three-parameter representation of surfactant/brine/oil interaction published by Puerto *et al.* [23].

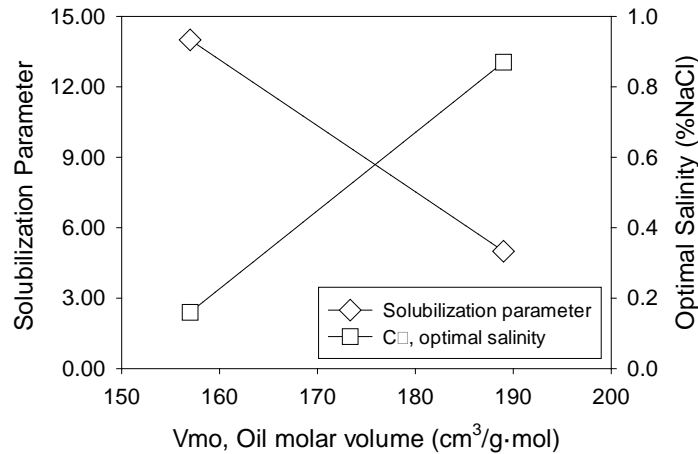


Figure 3. Effect of oil molar volume on optimal salinity and solubilization parameters.

When same samples as in Figure 2 were tested at 50°C, the volume of the oleic phase was found to be greater than the initial value for the range of salinity tested, which means the existence of an upper phase microemulsion or Winsor type II behavior. Therefore optimal salinity decreases when temperature increases.

Similar tests were carried with the parent compound SDS, and Winsor I behavior was found up to 15 %wt. NaCl. Thus, in the presence of these aromatic oils, SDS-modified as a SAIL is much more lipophilic than the parent compound, as expected due to the alkyl chains of the phosphonium cation. This is in agreement with a much lower CMC of the SAIL (0.9 mmol/kg) than the corresponding value for SDS (8.2 mmol/kg) [18].

As surfactants in EOR can be injected as a microemulsion or as an aqueous surfactant solution, the behavior in the absence of oil at 25°C was also studied. The SAIL was soluble in brine up to 4.5 %wt NaCl (higher than optimal salinity), thereafter a coacervate phase formed. On the contrary, SDS that appears very hydrophilic in the presence of oil, at 1.5 %wt NaCl formed a clear solution but at 2 %wt the Krafft point was reached and a precipitate appeared, confirming that the SAIL has a lower Krafft point than SDS

As has been shown, the SAIL [P<sub>4 4 4 1</sub>][DS] appeared unsuitable to generate Winsor III microemulsion with *n*-octane, a model oil that could mimic crude oil behaviour on optimal salinity determination for many surfactants. Lipophilic interactions can be modified in different ways [24] to adjust optimal salinity that include varying the oil, as disclosed in Figure 2 where *n*-octane was substituted by aromatic oils, or altering the lipophile. In particular, a branched lipophile would also lower optimal salinity. Accordingly, a SAIL based in the common branched surfactant Na-AOT was selected to carry out new tests.

In Figure 4 are plots of solubilization parameters as a function of salinity at 25, 50 and 83°C for aqueous solutions of [C<sub>4</sub>mim]AOT (left) and its parent compound Na-AOT (right), equilibrated with equal volumes of *n*-octane, the surfactant concentration being 2 %wt overall. The corresponding photographs of salinity scans are shown in Figure S1 in supplementary information. In this case, the branched SAIL [C<sub>4</sub>mim]AOT generated classical phase behavior with an optimal salinity of 0.06 %wt NaCl at 25°C, while the optimal salinity for the parent compound under same conditions was 0.21 %wt NaCl. So, in the presence of *n*-octane, [C<sub>4</sub>mim]AOT (modified-AOT) is more lipophilic than the parent compound Na-AOT, again probably due to the alkyl chains of the imidazolium cation. This is in agreement with a lower CMC of the SAIL (1.78 mM) than the corresponding value for Na-AOT (2.88 mM) [20]. Furthermore, the modified compound has a solubilization parameter at optimal salinity of ~20 at 25 and 50°C, indicating ultra-low IFTs. This value is higher than the solubilization parameter of the parent compound (~14 at 25°C and ~6 at 50°C), meaning that the SAIL has more potential for EOR applications at very low salinities and temperatures, conditions that are hard to satisfy with known available surfactants. In the case of the SAIL, optimal salinity increases (from ~0.06 %wt NaCl to ~0.18 %wt NaCl), and the solubilization parameter decreases (from 20 to 8), with the increase of temperature to 83°C. In the case of the parent compound, the optimal salinity also increases with temperature (from ~0.21 %wt NaCl to ~1 %wt NaCl) and the solubilization parameter decreases (from 14 to 5).

In the absence of oil, the behavior of the common surfactant Na-AOT has been widely studied [25], and issued test results have indicated that at the tested surfactant concentration (4 %wt) and salinity range (optimal salinities: 0.05-1 %wt NaCl), a dispersion of liquid crystalline particles exists. In the case of the modified compound, [C<sub>4</sub>mim]AOT, a similar behavior was found. This behavior, dominated by the nature of the surfactant anion, has been previously described in literature for other AOT compounds [26].

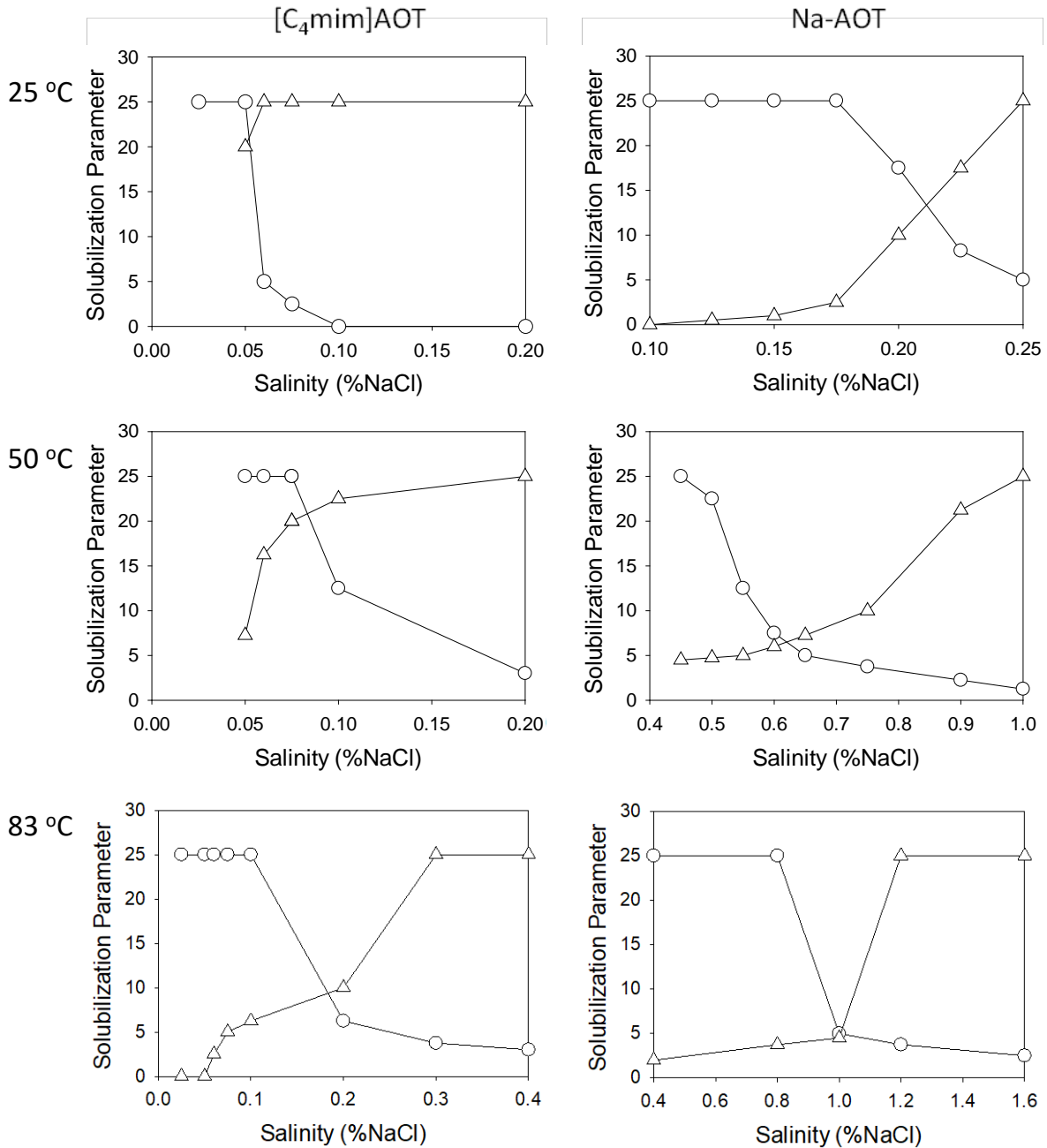


Figure 4. Solubilization parameters (  $\circ$   $V_w/V_s$  ,  $\triangle$   $V_o/V_s$  ) from salinity scans at 25, 50 and 83 °C for 2 %wt [C<sub>4</sub>mim]AOT (left) and its parent compound Na-AOT (right), WOR~1, *n*-octane, NaCl brine.

The phase behavior of the SAILs [C<sub>12</sub>mim]Br and [P<sub>4 4 4 14</sub>]Cl as function of salinity was also studied. These cationic SAILs formed, in the presence of *n*-octane, with a WOR~1 and 2 %wt surfactant at 25°C, microemulsions of Winsor type I up to 15 %wt NaCl, so they could appear too hydrophilic to be used alone for many EOR

applications. Properties of several cationic SAILs have been disclosed in literature by means of time-consuming techniques (interfacial tension, core flooding experiments, etc.). For example,  $[C_{12}mim]Cl$  has been studied [12] by measuring dynamic interfacial tension and doing core flooding experiments. The test results were unfavorable because a poor tertiary oil recovery was found.  $[C_{12}mim]Cl$  is too hydrophilic (same as  $[C_{12}mim]Br$ ) and microemulsions with a good solubilization parameter (necessary for ultralow interfacial tensions) were not found. Thus, conducting salinity and blend scans of SAILs would be advisable before considering another type of experimentation.

### 3.2 Blend scans

Winsor III behavior can be achieved, not only changing salinity, but also mixing at a fixed salinity pairs of surfactants (hydrophilic + lipophilic) or (cationic + anionic, seeking ion pair formation), to adjust interactions between  $\overline{W}$ ,  $\overline{O}$ ,  $\overline{C}$  (Water region, Oil region and amphiphilic membrane) [4] to make  $R=1$  where  $R$  is the ratio of cohesive energy,  $A$ , per unit area between  $CO$  and  $CW$  [27].

Test results of salinity scans presented above have shown that the studied anionic SAILs were very lipophilic with the selected oils ( $C\phi < 0.8$  %wt NaCl for both SAILs at all tested temperatures) while cationic ionic liquids were the opposite, very hydrophilic ( $C\phi > 15$  %wt). Therefore, the studied SAILs are unsuitable for EOR processes when used alone to cover broad salinity range. However, their blending with each other or another surfactant is a design option for application with a brine of an ionic strength similar to, for example, seawater. In this section, phase behavior tests of blends of two SAILs or a SAIL with the well-known EOR surfactant  $IOS_{15-18}$  are disclosed. The goal was to find optimal blends with  $n$ -octane as the oil phase and with a hard brine (containing divalent ions) as the aqueous phase of ionic strength similar to seawater.

#### ***$[C_{12}mim]Br / [C_4mim]AOT$***

A first salinity scan was done (Figure S2) for a 2 %wt blend of  $[C_{12}mim]Br/[C_4mim]AOT$  in 5 %wt NaCl brine with  $n$ -octane at 25°C. The cationic SAIL,  $[C_{12}mim]Br$ , is very hydrophilic with an optimal salinity higher than 15 %wt NaCl, so at 5 %wt NaCl it has Winsor I behavior. However the anionic SAIL,  $[C_4mim]AOT$ , with a low optimal salinity ( $\sim 0.06$  %wt) at the fixed test salinity has

Winsor II behavior. When mixed, the inversion point from Winsor I to Winsor III, or optimal blend  $B_{\phi}$ , occurred at a composition ratio between 7/3 and 6/4 of  $[C_{12}mim]Br/[C_4mim]AOT$ . The large difference in optimal salinities dominates the electrostatic anionic-cationic attraction in determining phase behavior; this is in contrast to situations discussed below where both individual surfactants exhibited Winsor I behavior at test conditions.

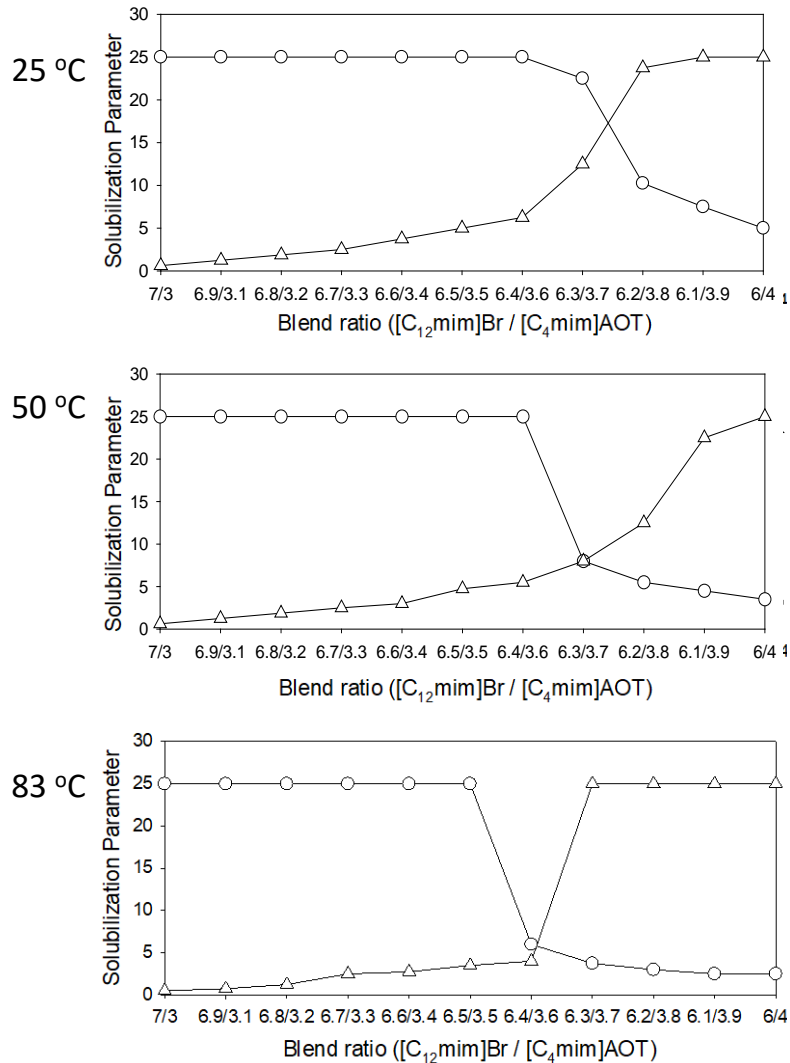


Figure 5. Solubilization parameters (  $\circ$   $V_w/V_s$  ,  $\triangle$   $V_o/V_s$  ) from blend scans at 25, 50 and 83 °C for 2 %wt  $[C_{12}mim]Br/[C_4mim]AOT$ ,  $WOR \sim 1$ ,  $n$ -octane, 5 %wt NaCl brine.

The chances of finding samples in the three-phase region are low when blending at 10 %wt ratio intervals for two surfactants of very dissimilar optimal salinities. Blending surfactants that are so dissimilar in optimal salinity should be a reason of concern when designing for EOR processes for obvious reason: too narrow IFT

region, chromatographic separation, etc. However, from a scientific point of view, this study allows for gaining insight into the behavior of blends with SAILs. There are no data so far with ionic liquid blends screened in the manner described here.

A narrower blend scan between 7/3 and 6/4 ratios of [C<sub>12</sub>mim]Br/[C<sub>4</sub>mim]AOT was carried out at 25, 50 and 83°C (Figure S3). Solubilization parameters are shown in Figure 5. The optimal Winsor III condition ( $V_o/V_s = V_w/V_s$ ) occurred when cationic surfactant was in excess, and the solubilization parameter of the optimal blend at 25°C was ~ 18, which should produce ultralow IFT (below 0.001 mN/m), according to Huh's correlation [5] used to calculate IFT from the solubilization parameters. According to that correlation,

$$\gamma_{mo} = C/(\sigma_o)^2 \quad [2]$$

Where  $C=0.3$ ,  $\sigma_o = V_o/V_s$ .

The classical transition, Winsor I-III-II, occurred at all tested temperatures; however, a large temperature effect was found. As temperature increases the optimal blend ratio, rich in the cationic SAIL, becomes more hydrophilic and the solubilization parameter decreases from ~20 at 25°C to ~5 at 83°C. The reason for the large temperature effect needs to be further evaluated.

To determine if these surfactants are tolerant to divalent ions, a hard brine with a similar ionic strength to the previous test brine (5 %wt NaCl) was prepared (see Table 1) and blend scan tests were conducted. Hardness is important because the presence of divalent ions in reservoirs and seawater often causes precipitation of surfactants, especially if they are not alkoxyated.

Table 1. Seawater composition	
	g/Kg solution
Na <sub>2</sub> SO <sub>4</sub>	4.84
CaCl <sub>2</sub> ·2H <sub>2</sub> O	1.89
MgCl <sub>2</sub> ·6H <sub>2</sub> O	15.06
NaCl	27.94

Figure S4 and Figure S5 in supplementary information are for showing the phase behavior test results for this blend scan. It was found that the SAIL blend is tolerant to the presence of divalent ions and that solubilization parameters,

optimal blend ratio and effect of temperature were almost equivalent to those without divalent ions.

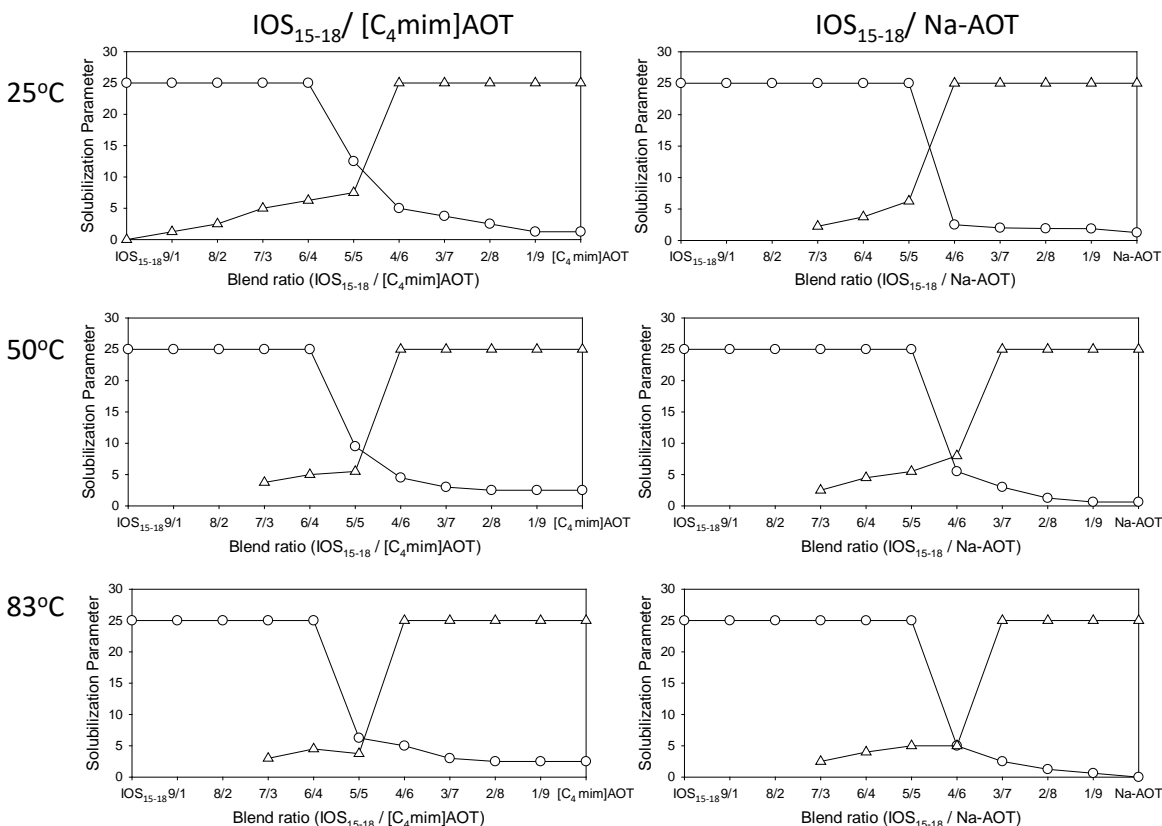


Figure 6. Solubilization parameters (  $\circ$   $V_w/V_s$  ,  $\triangle$   $V_o/V_s$  ) for blend scans at 25, 50 and 83 °C for 2 %wt  $[C_4mim]AOT/IOS_{15-18}$  (left) and  $Na-AOT/IOS_{15-18}$  (right),  $WOR \sim 1$ , *n*-octane, 5 %wt NaCl brine.

### **$IOS_{15-18}/[C_4mim]AOT$ and $IOS_{15-18}/Na-AOT$**

One interesting feature of SAILs for creating microemulsions suitable for EOR with traditional EOR surfactants comes from their low Krafft points. Therefore, it was of interest to study blends of SAILs with anionic  $IOS_{15-18}$ , of high Krafft point and more hydrophilic than  $[C_4mim]AOT$  or  $Na-AOT$ , which are also anionic. Blend scans were conducted for these systems with 2 %wt blend concentration overall, a soft 5 %wt NaCl brine, and *n*-octane as oil at 25, 50 and 83°C (Figure S6). Solubilization parameters are shown in Figure 6. As 5 %wt NaCl is well above optimal salinity of  $[C_4mim]AOT$  (0.06 %wt NaCl) and  $Na-AOT$  (0.21 %NaCl) and below optimal salinity of  $IOS_{15-18}$  (~7.5 %wt NaCl [28]),  $[C_4mim]AOT$  and  $Na-AOT$  have Winsor II behavior and  $IOS_{15-18}$  Winsor I. The phase behavior without



divalent ions is similar for both blends. Optimal Winsor III microemulsions occurred at a mass ratios of  $\sim 5/5$  IOS<sub>15-18</sub>/[C<sub>4</sub>mim]AOT and  $\sim 4/6$  for IOS<sub>15-18</sub>/Na-AOT at all tested temperatures. In both cases, when temperature increases the optimal blend,  $B_\phi$ , is almost constant but solubilization parameter at 25°C ( $\sim 10$ ) is reduced by half at 83°C.

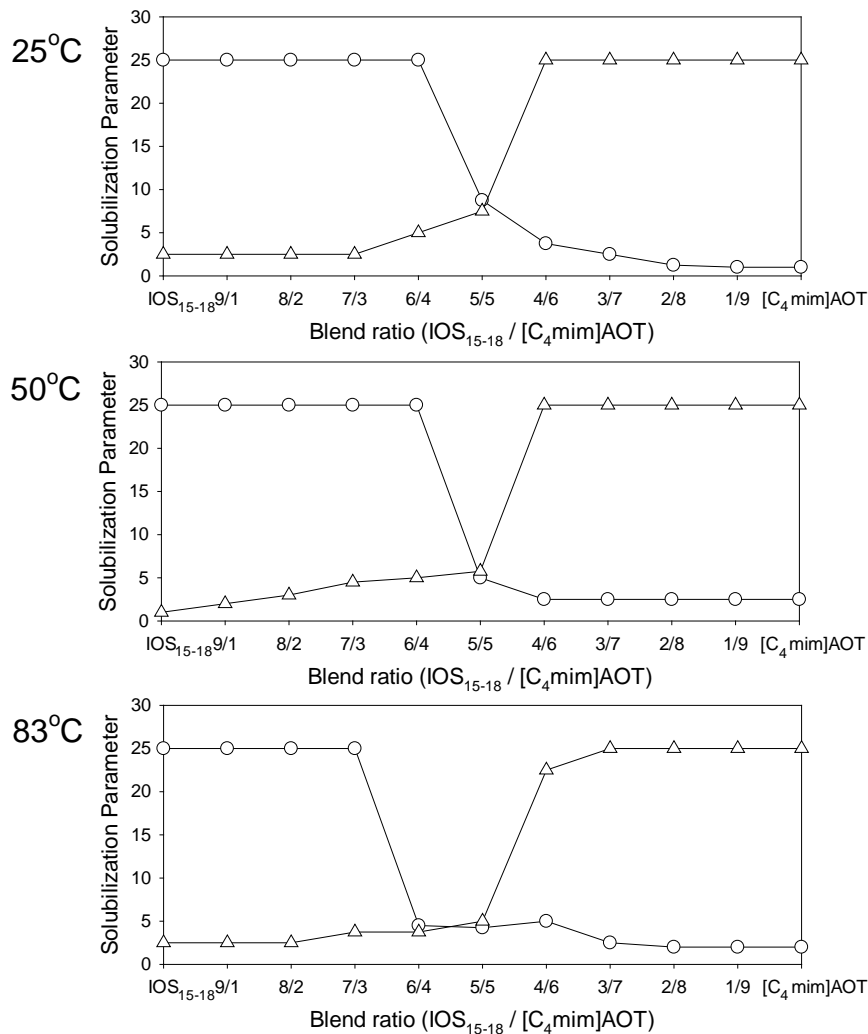


Figure 7. Solubilization parameters (  $\circ$   $V_w/V_s$  ,  $\triangle$   $V_o/V_s$  ) from blend scans at 25, 50 and 83 °C for 2 %wt IOS<sub>15-18</sub>/ [C<sub>4</sub>mim]AOT, WOR $\sim$ 1, *n*-octane, seawater.

However, when testing with hard seawater, the blend having the common surfactant Na-AOT is intolerant at 25°C to divalent ions (Figure S7, right). Instead of the middle-phase microemulsion with significant oil and brine solubilization, a small viscous phase with minimal solubilization (volume practically equal to volume of surfactant) appears. On the contrary, when modified-AOT SAIL ([C<sub>4</sub>mim]AOT) is blended with IOS<sub>15-18</sub>, the system presents a microemulsion

similar behavior to that found with NaCl (Figure S7, left). A surfactant below its Krafft point may precipitate or form what have been coined as 'VCP' or Very Condensed Phase. Further studies are required to understand if the different behavior of these blends is related to the higher Krafft point of the blend with Na-AOT.

The effect of temperature on the phase behavior was evaluated for the system tolerant to divalent ions, the one involving SAIL. Test results shown in Figures 7 and S8 indicate that solubilization parameters, optimal blends and the effect of temperature were almost equivalent to those without divalent ions.

### ***IOS<sub>15-18</sub>/[P<sub>4 4 4 14</sub>]Cl***

Because of the importance of finding surfactants or blends of surfactants tolerant to divalent ions, it was decided to continue the studies by testing with the hard-synthetic seawater defined in Table 1. Figure 8 is to indicate the solubilization parameters from the phase behavior test results (Figure S9) for a 2 %wt overall blend scan of IOS<sub>15-18</sub>/[P<sub>4 4 4 14</sub>]Cl in hard seawater with *n*-octane at 25, 50, 83 and 100°C. The situation is different than the previous blend of anionic and cationic surfactants with Winsor I and Winsor II behavior because in this case both surfactants are in Winsor I region in hard seawater when unblended. However, when blended they generated optimal blends in Winsor III region caused by the strong electrostatic interaction between them; the uncharged catanionic entities are more lipophilic than the individual ionic surfactants. At 25°C two optimal blends, B<sub>φ</sub>, appear. A monotonic change in IOS<sub>15-18</sub>/[P<sub>4 4 4 14</sub>]Cl ratio produces Winsor I→III→II→III→I phase behavior transitions. As [P<sub>4 4 4 14</sub>]Cl proportion increases, the blend becomes more lipophilic until Winsor III behavior appears at ~15 %wt and Winsor II behavior at 20 %wt. As the proportion of [P<sub>4 4 4 14</sub>]Cl continues to increase, the formulation becomes again more hydrophilic remaining Winsor II at 70 %wt but changing to Winsor III at 80 %wt and to Winsor I again.

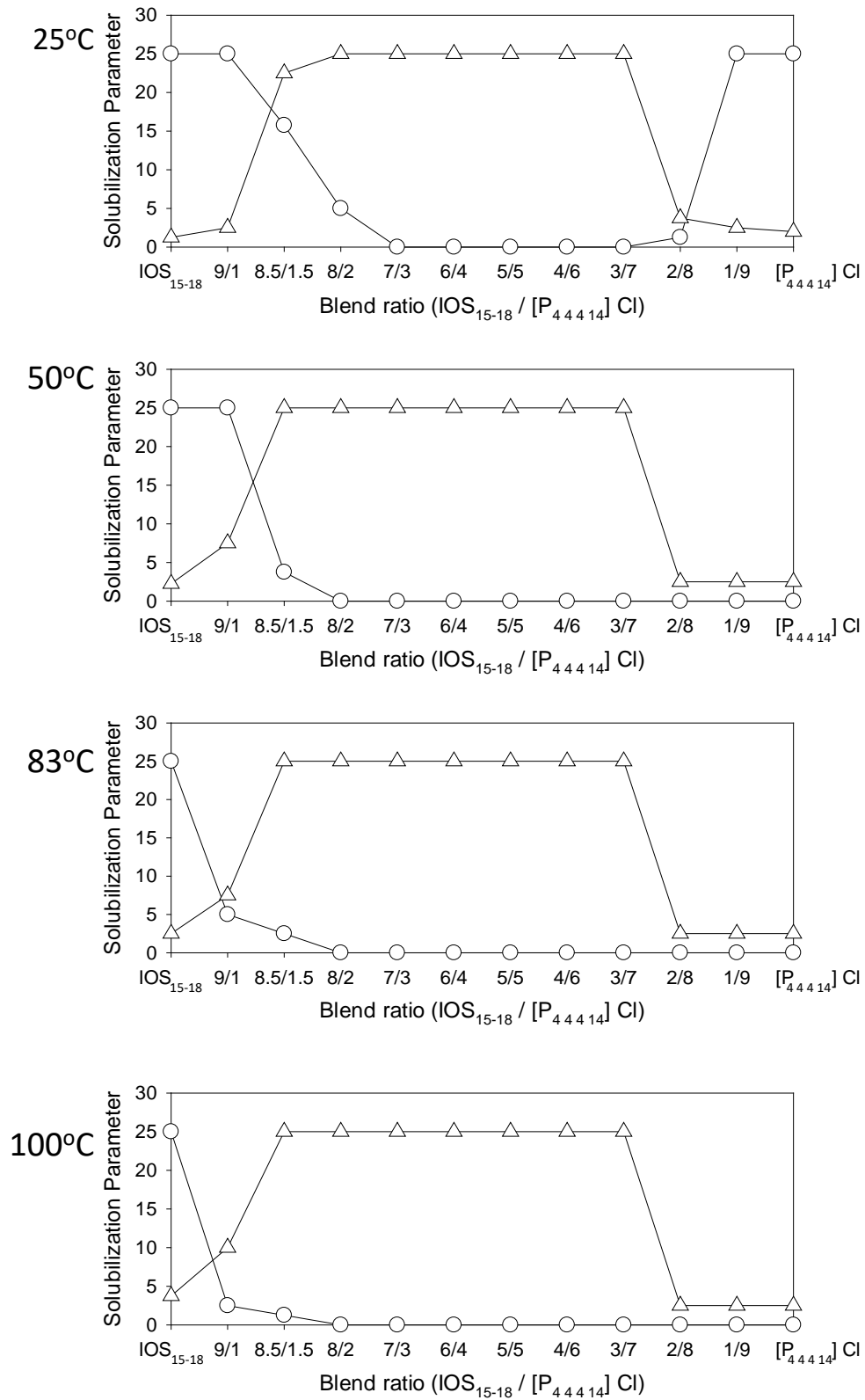


Figure 8. Solubilization parameters (  $\circ$   $V_w/V_s$  ,  $\triangle$   $V_o/V_s$  ) from blend scans at 25, 50, 83 and 100°C for 2 %wt IOS<sub>15-18</sub> / [P<sub>44414</sub>]Cl, WOR~1, *n*-octane, seawater.

As depicted in Figure 8, there are two optimal blends for 2 %wt IOS<sub>15-18</sub> / [P<sub>4 4 4 14</sub>]Cl, WOR~1, *n*-octane, seawater, a phenomenon which has been reported previously for anionic/cationic surfactant systems containing no ionic liquids [29, 30]. The first optimal is found at approximately 15 %wt of [P<sub>4 4 4 14</sub>]Cl, where there is an excess of anionic surfactant, while the second is found at approximately 80 %wt with a cationic surfactant excess. The two optimal Winsor III microemulsions have very different solubilization parameters, the first one ~15 and the second one less than 5. Therefore, only the optimal blend with excess of IOS<sub>15-18</sub> seems to have significant potential for EOR applications. When temperature increases, this optimal blend becomes richer in IOS with lower oil solubilization. However, the optimal blend enriched in SAIL disappears and a coacervate is formed at temperatures above 25°C.

### ***IOS<sub>15-18</sub>/[C<sub>12</sub>mim]Br and IOS<sub>15-18</sub>/C<sub>12</sub>TAB***

In this test case, as in the previous one, all the individual surfactants are in Winsor I region for the given conditions. Figure 9 (left) is for depicting the solubilization parameters obtained from phase behavior test results for a 2 %wt overall blend scan of IOS<sub>15-18</sub>/[C<sub>12</sub>mim]Br in hard seawater with *n*-octane at 25, 50, 83 and 100°C (Figure S10, left). Because of the oppositely charged surfactants, two optimal blends having equal solubilization of oil and brine appear. As [C<sub>12</sub>mim]Br content increases from zero, the blend becomes less hydrophilic with Winsor II behavior appearing at ~30 %wt. As the proportion of [C<sub>12</sub>mim]Br continues to increase, the formulation first becomes more lipophilic, then reverses and becomes again more hydrophilic, remaining Winsor II at 60 %wt but changing to Winsor I at 70 %wt.

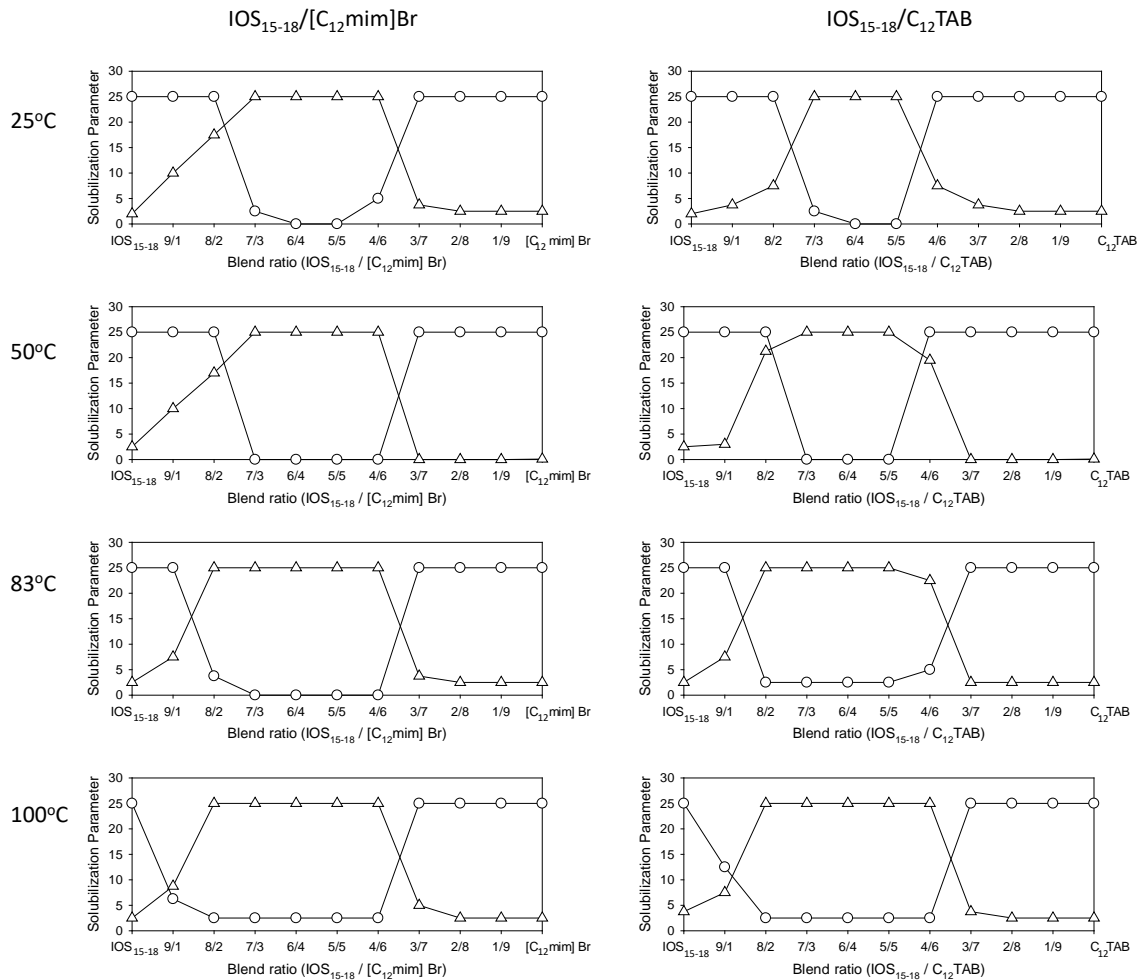


Figure 9. Solubilization parameters (  $\circ$   $V_w/V_s$  ,  $\triangle$   $V_o/V_s$  ) from blend scans at 25, 50, 83 and 100°C for 2 %wt IOS<sub>15-18</sub>/ [C<sub>12</sub>mim]Br (left) and IOS<sub>15-18</sub>/ C<sub>12</sub>TAB (right), WOR~1, *n*-octane, seawater.

Two optimal blends at all tested temperatures were found; the first was found at approximately 25 %wt of [C<sub>12</sub>mim]Br (excess of anionic surfactant), while the second was found at approximately 65 %wt (excess of cationic SAIL). Both optimal Winsor III microemulsions have good solubilization parameters, the first ~20 and the second ~ 15, which should produce ultra-low IFT. The optimal blend enriched in IOS<sub>15-18</sub> becomes richer in IOS when temperature increases. The solubilization parameter for this optimal blend remains constant when temperature increases to 50°C, and is reduced by half at 100°C. The optimal blend enriched in SAIL remains unchanged with temperature.

Figure 9 (right) is for depicting the solubilization parameters obtained from phase behavior test results for a 2 %wt overall blend scan of IOS<sub>15-18</sub>/C<sub>12</sub>TAB in hard

seawater with n-octane at 25, 50, 83 and 100°C (Figure S10, right). The phase behavior when cationic surfactant C<sub>12</sub>TAB is blended with IOS<sub>15-18</sub> is almost the same as that described for [C<sub>12</sub>mim]Br.

The surfactant concentration in the blend scans was fixed at ~2 %wt overall (or 4 %wt in the aqueous solution) for an accurate measurement of the phase volumes to calculate solubilization parameters. However, this concentration is considered high for injection into the reservoir. For this reason, the phase behavior was evaluated again for these two promising mixtures near the optimal blend ratio containing higher concentration of IOS<sub>15-18</sub> (most attractive blend from the economical point of view). Blend scans were carried out (Figure 10 a and b, left) for a 0.5 %wt overall (or 1 %wt in the aqueous solution) blend scan of IOS<sub>15-18</sub>/[C<sub>12</sub>mim]Br and IOS<sub>15-18</sub>/C<sub>12</sub>TAB in hard seawater with n-octane (WOR~1) at 25°C. It was found that the phase behavior of both blends is independent of the surfactant concentration.

Aqueous solutions to be suitable for injection into the reservoir should not exhibit phase separation or be turbid solutions. In the case of IOS<sub>15-18</sub>/[C<sub>12</sub>mim]Br and IOS<sub>15-18</sub>/C<sub>12</sub>TAB, contrarily to the previously discussed blends that could be only injected as microemulsions after addition of a suitable paraffinic oil, clear solutions were found at the optimal blend (~75% IOS<sub>15-18</sub>) in absence of oil (Figure 10 a and b, right). The hydrodynamic radius, *R<sub>h</sub>*, of the aggregates in these aqueous solutions was measured by means of Dynamic Light Scattering. Aggregates with average *R<sub>h</sub>* of ~20 nm and ~12 nm were found for IOS<sub>15-18</sub>/[C<sub>12</sub>mim]Br and IOS<sub>15-18</sub>/C<sub>12</sub>TAB blends, respectively. The aggregates could be nonspherical micelles or small vesicles with one or more bilayers separating inner and outer aqueous phases.

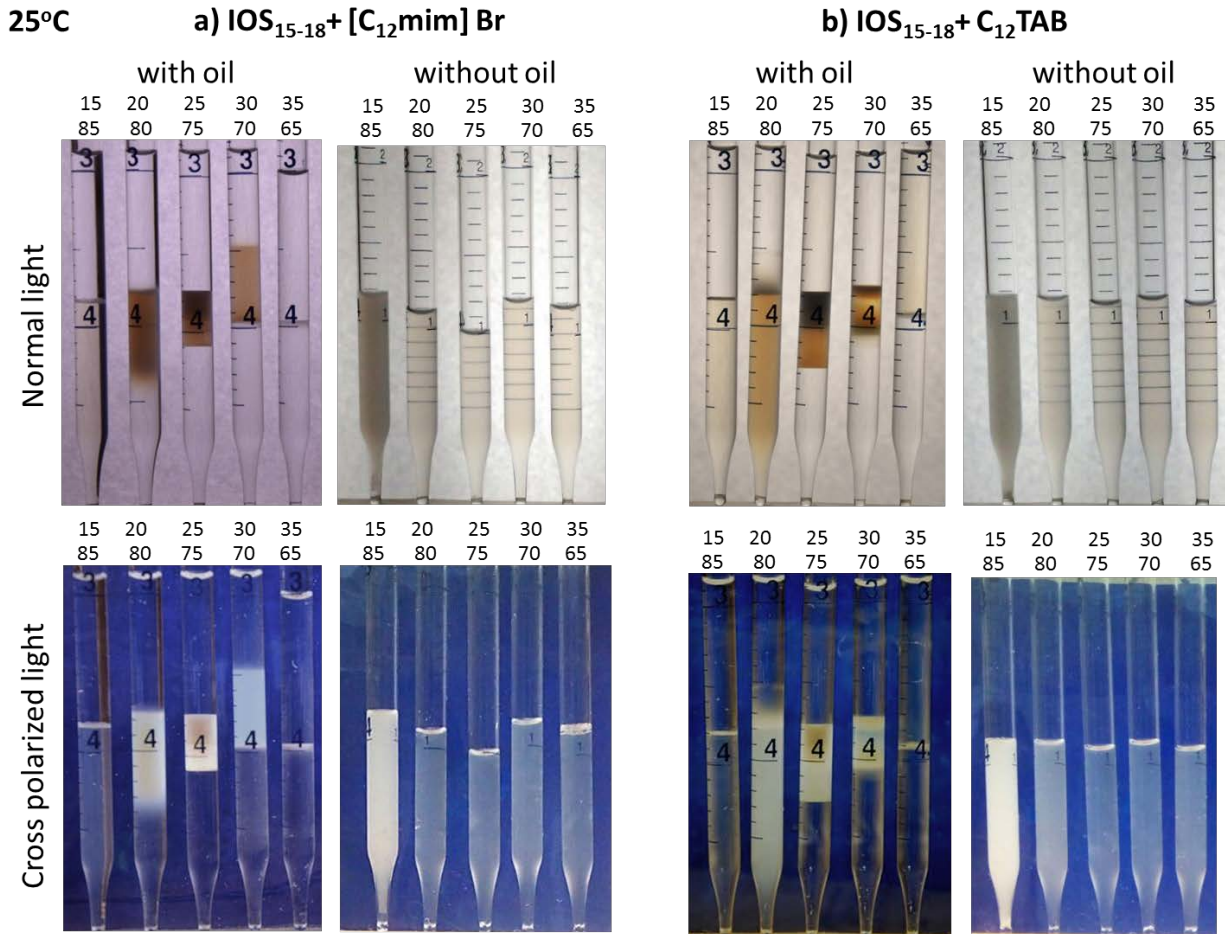


Figure 10. (a) 0.5 %wt overall Blend scan  $\text{IOS}_{15-18} + [\text{C}_{12}\text{mim}]\text{Br}$  (left) 1 %wt aqueous solution of surfactant blend in the absence of oil (right). (b) 0.5 %wt overall Blend scan  $\text{IOS}_{15-18} + \text{C}_{12}\text{TAB}$  (left) 1 %wt aqueous solution of surfactant blend in the absence of oil (right).

In absence of oil or alcohol,  $\text{IOS}_{15-18}$  solubility is poor in hard brine with an ionic strength similar to seawater; the presence of divalent ions causes its precipitation. Besides, this particular IOS surfactant has been extensively studied [28] and researchers concluded that because of the lack of solubility at optimal brine, it has to be injected below optimal in Winsor I with 1 %wt alcohol addition to produce injectable solutions. So it is important to highlight that in this research with SAILS, it has been found that addition of ~20 %wt of cationic surfactant (either  $[\text{C}_{12}\text{mim}]\text{Br}$  or  $\text{C}_{12}\text{TAB}$ ) to  $\text{IOS}_{15-18}$ , generates, in the presence of divalent ions comparable to those in seawaters, clear aqueous solutions in its Winsor III

region and very high solubilization parameters ( $V_o/V_s \sim 20$  at 25 and 50°C) with *n*-octane as oil (see figures 9 and 10).

The existence of liquid crystals in the injection fluid, whether aqueous solution or microemulsion, can lead to non-uniform distribution of the injected material and non-uniform transport owing to phase trapping or different mobilities of coexisting phases. Therefore the existence of liquid crystals was tested for the aqueous solutions at optimal conditions. The samples failed to show birefringence under polarized light, as may be seen from Figure 10. Moreover, dark pictures were obtained with polarized light microscopy, which confirmed the absence of anisotropic ordered phases. However, of particular note is the birefringent region in equilibrium with excess oil and brine, with high apparent solubilization of both, for the samples with 75/25 ratio of IOS to cationic (Figure 10). This behavior near optimal conditions differs from classical Winsor III behavior with coexisting microemulsion, oil, and brine. Although the birefringent region was not studied further, it likely consists of a mixture of bicontinuous microemulsion and lamellar liquid crystal [31]. Systematic tests for birefringence were not conducted for the systems of previous sections though a few tests revealed birefringence at 25°C in some samples. This matter should be an issue for future study.

Because of the promising results obtained with these blends, dynamic interfacial tensions between near-optimal formulations and oil were determined. Aqueous solutions with mass ratio=8/2 of IOS<sub>15-18</sub>/[C<sub>12</sub>mim]Br or C<sub>12</sub>TAB, i.e., slightly more hydrophilic than the optimal blend, and with equilibrium solubilization parameter high enough to expect low IFT were prepared. Surfactant blend concentration was 1 wt%. The capillary tube of the tensiometer was filled with this surfactant solution and set in rotation. A fresh drop of *n*-octane was injected and its diameter and aspect ratio that varied with centrifugal force measured until equilibrium (successive equal values). The interfacial tensions obtained were  $2 \cdot 10^{-3}$  mN/m and  $7 \cdot 10^{-3}$  mN/m for IOS<sub>15-18</sub>/[C<sub>12</sub>mim]Br and IOS<sub>15-18</sub>/C<sub>12</sub>TAB, respectively. Equilibrium was reached after 25 min for IOS<sub>15-18</sub>/[C<sub>12</sub>mim]Br and 50 min for IOS<sub>15-18</sub>/C<sub>12</sub>TAB. Both IFTs are probably low enough to displace substantial oil. Huh's correlation (Eq. [2]) was used to calculate IFT from the solubilization parameters. Interfacial tensions experimentally determined and those obtained with Huh's correlation are shown in Figure 11. A good agreement was found between calculated and measured interfacial tensions.



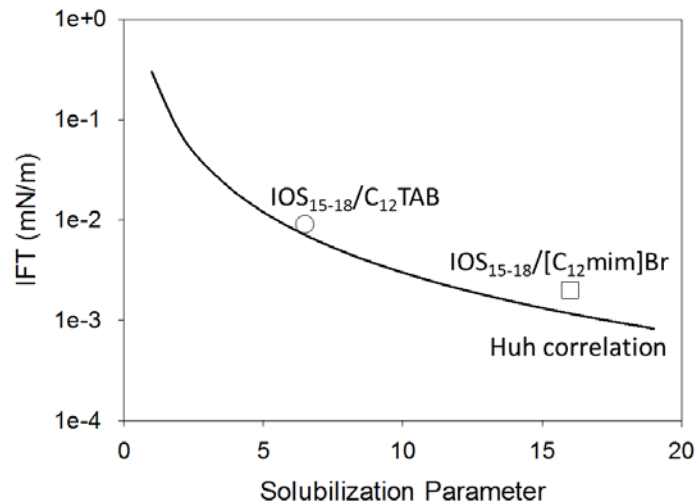


Figure 11. IFT versus solubilization parameter. Huh correlation (solid line) and experimental values for blends containing 80 %wt IOS<sub>15-18</sub> and 20%wt cationic surfactant (circle) or cationic SAIL (square).

## Conclusions

SAILs are being investigated for surfactant EOR based on their interesting features. Dynamic interfacial tension measurements have been a method proposed to evaluate SAILs for EOR applications [12-14]. However, the absence of salinity scans with these salts has led to studies at conditions where interfacial tensions are far from the required ultra-low values. In this work, for the first time, salinity scans with SAILs and blends containing SAILs were carried out to find optimal formulations where ultra-low IFTs were confirmed by measurement or are expected based on magnitudes of solubilization parameters.

Salinity scans of equilibrium phase behavior for two room-temperature cationic SAILs, [P<sub>4 4 4 14</sub>]Cl and [C<sub>12</sub>mim]Br, with n-octane as the oil indicated that, if used alone, they are too hydrophilic for application in EOR except perhaps at high salinities exceeding 15 %wt NaCl.

Replacement of Na<sup>+</sup> as counterion by less polar [C<sub>4</sub>mim]<sup>+</sup> and [P<sub>4 4 4 1</sub>]<sup>+</sup> for common anionic surfactants Aerosol OT (Na-AOT) and sodium dodecyl sulfate (SDS)

respectively yielded anionic room-temperature SAILs which were much less hydrophilic than the original surfactants, i.e., had much lower optimal salinities corresponding to their lowest IFTs [18,20].

Blend scans for mixtures of anionic and cationic SAILs, [C<sub>4</sub>mim]AOT and [C<sub>12</sub>mim]Br, were carried out at temperatures up to 83°C with n-octane as oil and 5%wt NaCl and synthetic hard seawater (SW) as brines. The large difference in hydrophilicity between the SAILs dominated the electrostatic anionic/cationic interactions in influencing phase behavior, making it very sensitive to blend ratio. An optimal blend ratio was found at which a microemulsion phase having high solubilization of both oil and brine was formed, an indication of low enough IFT to recover substantial oil.

Blend scans for mixtures of the anionic surfactant IOS and anionic SAIL [C<sub>4</sub>mim]AOT revealed that they had nearly equal weight fractions for the optimal blend ratio. Nearly the same optimal blend ratio was found when [C<sub>4</sub>mim]AOT was replaced by Na-AOT. However, the IOS/[C<sub>4</sub>mim]AOT mixture was superior to IOS/Na-AOT in SW because highly viscous phases were seen near the interface in Na-AOT samples near the optimal condition.

Blend scans for mixtures of anionic IOS with cationic SAILs [P<sub>4 4 4 14</sub>]Cl and [C<sub>12</sub>mim]Br exhibited optimal behavior with high oil and brine solubilization for blends containing about 10-20% of the respective SAILs. Because anionic and cationic surfactants were both hydrophilic, the uncharged “catanionic” surfactant produced by their electrostatic interaction made phase behavior with the mixed surfactants less hydrophilic than the individual surfactants.

The optimal blend of the IOS/[C<sub>12</sub>mim]Br system with n-octane and SW at 25°C was most promising of blends tested containing a SAIL. It exhibited a birefringent middle region in equilibrium with excess oil and brine at the optimal condition instead of the single-phase isotropic microemulsion seen in classical Winsor III behavior. IFT as measured in a spinning drop tensiometer was ~0.002 mN/m after equilibrium was reached following injection of a drop of fresh n-octane into an aqueous SW solution having 1 %wt total surfactant content with optimal blend ratio. Such low IFT suggests possible high oil recovery.

The same aqueous solution appeared suitable for injection in an EOR process because it exhibited no phase separation and contained micelles or vesicles with a

hydrodynamic radius of  $\sim 20$  nm, much smaller than typical pore sizes. This result is of interest because blends of other surfactants with such high proportions of IOS usually exhibit precipitation in hard brines at low temperatures [28].

Similar behavior of both microemulsion phases and aqueous solution was seen when the cationic SAIL was replaced by cationic surfactant  $C_{12}TAB$ . In this case IFT and hydrodynamic radius were  $\sim 0.007$  mN/m and  $\sim 12$  nm respectively.

Core floods should be conducted for the IOS/[ $C_{12}mim$ ]Br and IOS/ $C_{12}TAB$  systems to assure injectivity of the aqueous solution, surfactant transport through the core, and oil displacement without excessive surfactant retention or pressure drop.

Research on the use of SAILs in EOR is still in its infancy. The ability to design and synthesize a wide variety of SAILs should be utilized in the search for optimal formulations, especially for high temperatures and salinities where the choice of conventional surfactants is limited. The study of SAIL-SAIL and surfactant-SAIL blends and catanionic SAILs, with improved properties compared with those of individual surfactants or SAILs, should lead future research.

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## Figure Captions

Figure 1. Chemical structure of the SAILs used in this work.

Figure 2. Top: Pictures of salinity scans, 2 %wt. overall  $[P_{4.4.4.1}][DS]$ , butylbenzene or hexylbenzene oil, WOR~1 at 25°C. Bottom: Solubilization Parameters (  $\circ$   $V_w/V_s$  ,  $\triangle$   $V_o/V_s$  ) for both salinity scans.

Figure 3. Effect of oil molar volume on optimal salinity and solubilization parameters.

Figure 4. Solubilization parameters (  $\circ$   $V_w/V_s$  ,  $\triangle$   $V_o/V_s$  ) from salinity scans at 25, 50 and 83 °C for 2 %wt  $[C_4mim]AOT$  (left) and its parent compound Na-AOT (right), WOR~1, *n*-octane, NaCl brine.

Figure 5. Solubilization parameters (  $\circ$   $V_w/V_s$  ,  $\triangle$   $V_o/V_s$  ) from blend scans at 25, 50 and 83 °C for 2 %wt  $[C_{12}mim]Br/ [C_4mim]AOT$ , WOR~1, *n*-octane, 5 %wt NaCl brine.

Figure 6. Solubilization parameters (  $\circ$   $V_w/V_s$  ,  $\triangle$   $V_o/V_s$  ) for blend scans at 25, 50 and 83 °C for 2 %wt  $[C_4mim]AOT/IOS_{15-18}$  (left) and Na-AOT/ $IOS_{15-18}$  (right), WOR~1, *n*-octane, 5 %wt NaCl brine.

Figure 7. Solubilization parameters (  $\circ$   $V_w/V_s$  ,  $\triangle$   $V_o/V_s$  ) from blend scans at 25, 50 and 83 °C for 2 %wt  $IOS_{15-18}/ [C_4mim]AOT$ , WOR~1, *n*-octane, seawater.

Figure 8. Solubilization parameters (  $\circ$   $V_w/V_s$  ,  $\triangle$   $V_o/V_s$  ) from blend scans at 25, 50, 83 and 100°C for 2 %wt  $IOS_{15-18} / [P_{4.4.4.14}]Cl$ , WOR~1, *n*-octane, seawater.

Figure 9. Solubilization parameters (  $\circ$   $V_w/V_s$  ,  $\triangle$   $V_o/V_s$  ) from blend scans at 25, 50, 83 and 100°C for 2 %wt  $IOS_{15-18}/ [C_{12}mim]Br$  (left) and  $IOS_{15-18}/ C_{12}TAB$  (right), WOR~1, *n*-octane, seawater.

Figure 10. (a) 0.5 %wt overall Blend scan  $IOS_{15-18}+ [C_{12}mim] Br$  (left) 1 %wt aqueous solution of surfactant blend in the absence of oil (right). (b) 0.5 %wt overall Blend scan  $IOS_{15-18}+ C_{12}TAB$  (left) 1 %wt aqueous solution of surfactant blend in the absence of oil (right).

Figure 11. IFT versus solubilization parameter. Huh correlation (solid line) and experimental values for blends containing 80 %wt  $IOS_{15-18}$  and 20%wt cationic surfactant (circle) or cationic SAIL (square).