

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

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## ABSTRACT

Foam injection has the potential to improve CO<sub>2</sub> enhanced oil recovery (EOR) and simultaneous CO<sub>2</sub> sequestration processes by increasing sweep efficiency. However, the stability of the foam remains a challenge specially at harsh conditions of temperature, pressure, and salinity. Surface-active ionic liquids (SAILs) are promising chemicals that usually exhibit high surface activity, salinity tolerance, and thermal stability. This study investigates the performance of SAILs to produce foam for CO<sub>2</sub> EOR in two high salinity reservoirs (A and B). Both reservoirs are at high salinity conditions with salinities of 125,356 mg/L and 255,470 mg/L. Half-life time and initial foam height were considered to represent foam stability and foaming ability, respectively. An optimal formulation of 0.5 wt% [C<sub>16</sub>mim]Cl was selected for reservoir A conditions, whereas 0.5 wt% [C<sub>16</sub>Py]Cl and 0.5 wt% [C<sub>16</sub>mim]Cl formulations were studied for reservoir B conditions. Foam mobility was measured at a quality of 80% to test the validity of the proposed formulations. A promising half-life of 7.8 days was obtained for [C<sub>16</sub>mim]Cl at Reservoir A conditions in high-pressure stability tests, several times higher than those reported in literature for traditional surfactants. Mobility reduction factors higher than 300 were reported for all the cases, with the most promising result (1229) achieved for [C<sub>16</sub>mim]Cl at Reservoir A conditions. These results indicate that strong foams can be generated at high salinity conditions using SAILs. This work shows the promising possibilities of SAILs to improve the sweep efficiency in CO<sub>2</sub>-EOR methods and enhance the gas trapping in sequestration processes.

## 1. Introduction

Primary and secondary stages of oil production from conventional reservoirs produce an average of 30% of original oil in place, leaving a high percentage of oil behind [1]. With the decline in oil production from mature reservoirs and the global oil demand set to increase, improving oil recovery is still a major issue. In this context, tertiary or enhanced oil recovery (EOR) methods are developed to improve oil production. EOR techniques usually involve injection of chemical solutions (surfactant or polymer EOR), gases (miscible or immiscible EOR), or high-temperature fluids such as steam or hot water (thermal EOR) [2]. Gas flooding is a widely used EOR method; oil can be displaced by different gases, such as, carbon dioxide, hydrocarbon gas, nitrogen, or flue gas [3]. In this context, CO<sub>2</sub> injection is attracting new market interests since it is considered a promising way to ensure cost-efficient avoidance of CO<sub>2</sub> emissions to atmosphere. This technology can generate a product with a strong economic value while it can also

sequester CO<sub>2</sub> in underground formations previously occupied by oil [4]. However, the large viscosity contrast between gas and both oil and water during CO<sub>2</sub> injection usually results in early gas breakthrough and poor sweep efficiency. Even in CO<sub>2</sub> sequestration in aquifers, viscous fingering phenomenon is also a significant challenge, as it can impact the long-term storage capacity in underground formations. Injection of gas in the form of foam can help to overcome these issues [5].

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

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foam. A limited number of studies have been conducted on CO<sub>2</sub> foam performance under harsh reservoir conditions. Some authors [9–13] studied the influence of temperature and pressure on CO<sub>2</sub> foams stabilized by surfactants through foam stability and foam mobility tests. As a general conclusion, all the studies agreed that foam lifetime decreases with temperature, but the effect of pressure was complex to evaluate. Wang et al. [9] found out that the influence of this variable greatly depends on the type of surfactant used. In addition, Zhang et al. [10] and Wang et al. [11] claimed that, at the same conditions, foam stability achieved with higher alkyl chain length was better than with shorter alkyl chain length surfactants. The effect of salinity has also been assessed by several authors [8,14,15]. Studies agreed that foam stability is higher at higher salt concentrations due to the reduction of the electrostatic repulsion between surfactant molecules making the *lamellae* rigid. Nevertheless, in all these studies, half-life time of CO<sub>2</sub> foams stabilized with surfactants did not exceed 300 min. Therefore, it is desirable to develop CO<sub>2</sub> aqueous foams with improved stability at high temperature, salinity, and pressure conditions.

Recently, some researchers have investigated the use of ionic liquids (ILs) as alternative chemicals in enhanced oil recovery processes [16–18]. Surface active ionic liquids can reduce the surface tension of water to about 30–40 mN/m [19]. The water-crude oil interfacial tension can be reduced to about 1 mN/m from about 40 mN/m by the addition of ionic liquids [20]. These compounds are salts with melting or glass transition temperatures below 100 °C. Their negligible vapor pressure, high thermal stability and high solvating capacity makes them ideal compounds for the application. In addition, cations and anions of these salts can be selected to design task-specific compounds that meet the requirements of each specific reservoir. In comparison to traditional surfactants, it has been proven that ILs show advantages regarding stability at high salinity and temperature conditions [20,21]. In this context, ILs seem promising candidates to overcome stability problems of CO<sub>2</sub> foams.

Only a few researchers have investigated the use of ILs in EOR foam applications. Hu et al. [22] and Ouyang et al. [23] studied the effect of imidazolium ILs structure on foam features using Density functional theory (DFT) simulations and foam stability experiments. They concluded that the introduction of hydroxyl groups and longer alkyl chain lengths in the imidazolium cation was favorable for foam features. More applied approaches can also be found in the Literature. Sakthivel and Salin [5] studied the use of imidazolium ILs, with varying alkyl chain length, as additives to a non-ionic surfactant to improve foam stability. They performed bulk and porous-scale dynamic foaming experiments at high-pressure (2200 psi) and high-temperature (80 °C). Stability of the foam in the presence of IL increased by more than 50% compared to their neat surfactant solution. They also concluded that, as in the case of traditional surfactants, longer alkyl-chain exhibited higher stability and higher foamability than shorter alkyl-chain ILs. However, even though they tested different gases in bulk foam experiments, they only worked with N<sub>2</sub> in porous media tests. Deep eutectic solvents (DESs), constituted by choline chloride and two short-alkyl chain imidazolium ILs, were employed by Hanamertani et al. [24] as additives to a mixture of anionic and amphoteric surfactants. Bulk foam experiments at ambient and high temperature (80 °C) were performed to study foam stability. Results showed that ILs and DESs were able to improve surfactant foam stability. In their subsequent work [25], the most promising ILs and DESs were tested on dynamic foam mobility test using N<sub>2</sub> as the foaming gas. Unfortunately, permeability of the core, flow rate and temperature and pressure conditions were not reported. All these results provide an indication of the capability of ILs to reduce gas mobility and increase mobility reduction factor during injection processes.

In this paper, six surface-active ILs (SAILs) with the most common functional groups are tested for CO<sub>2</sub> foam EOR. The influence of the alkyl chain length and ethoxylation degree on the SAILs performance is analyzed. Two different reservoir conditions are evaluated: Reservoir A (63 °C, 125,356 mg/L salinity, and 1910 psi) and Reservoir B (40 °C,

255,470 mg/L salinity, and 1000 psi). Aqueous stability and bulk foam stability experiments at ambient pressure are carried out, aiming to test the performance of the different foams and select the most promising SAILs. Finally, the effectiveness of the proposed SAIL formulations is evaluated via high-pressure stability studies and foam mobility tests. Air but also, for the first time, CO<sub>2</sub> is selected as foaming gas in combination with SAILs. Foam apparent viscosity and mobility reduction factor are determined. This work offers a significant advance in the application of SAILs in CO<sub>2</sub> EOR processes.

## 2. Materials and methods

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

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

CO<sub>2</sub> with a purity of 99.9 wt% was purchased from Linde Gas & Equipment. Ottawa sand F95 was used in sand-packs; it was obtained from US Silica.

### 2.1. Compatibility tests

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

### 2.2. Static foam experiments

Static foam experiments were performed to compare the foaming ability of the proposed SAILs. These tests are a fast-screening method to evaluate the suitability of the different surfactants for the application. In this study, initial foam height and foam stability were assessed over time. Two foaming gases were screened: air and CO<sub>2</sub>. Experiments were performed at 40 °C (B) and 63 °C (A) according to each reservoir temperature.

Foam was prepared according to the methodology developed in

**Table 1**  
SAILs used in this study.

Abbreviature	Compound	Chemical structure	Appearance	Molecular Weight (g/mol)	CMC	Density at 25 °C (g/cm <sup>3</sup> )	Viscosity at 25 °C (mPa·s)
C1EG	Cocosalkylpentaethoxymethylammonium methylsulfate		Liquid	Not available	88.1 mg/L [26]	1.085466	2477.6
T2EG	N,N-Diethoxylated-N-tallow-N-ethylammonium ethylsulfate		Liquid	Not available	36.32 mg/L [27]	1.077613	609.25
[C <sub>12</sub> Py]Cl	N-Dodecylpyridinium chloride		Solid	283.88	15.27 mmol/L [28]	-	-
[C <sub>16</sub> Py]Cl·H <sub>2</sub> O	Hexadecylpyridinium chloride monohydrate		Solid	358.00	1.22 mmol/L [29]	-	-
[C <sub>12</sub> mim]Br	1-Dodecyl-3-methylimidazolium bromide		Solid	331.34	10.6 mmol/kg [30]	-	-
[C <sub>16</sub> mim]Cl	1-Hexadecyl-3-methylimidazolium chloride		Solid	343.00	0.99 mmol/L [29]	-	-

**Table 2**  
Formation brines composition.

Ion	Reservoir A (Canada)	Reservoir B (Michigan)
Na <sup>+</sup>	29,900 mg/L	51,802.3 mg/L
K <sup>+</sup>	4210 mg/L	5286.32 mg/L
Ca <sup>2+</sup>	12,000 mg/L	32,697.7 mg/L
Mg <sup>2+</sup>	2020 mg/L	5898.2 mg/L
Cl <sup>-</sup>	79,000 mg/L	152,318 mg/L
HCO <sub>3</sub> <sup>-</sup>	896.7 mg/L	152.5 mg/L
SO <sub>4</sub> <sup>2-</sup>	690 mg/L	4763.505 mg/L
Total salinity	125,356 mg/L	255,470 mg/L

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

### 2.3. Gas-surfactant co-injection experiments

The experimental set-up used for high pressure stability and foam mobility tests is shown in Fig. 1. The equipment contained two ISCO pumps and two accumulators for SAIL solution and CO<sub>2</sub> injection. A sand-pack and a high-pressure view cell were connected in two parallel circuits to work with one of them while keeping the other circuit closed. A back pressure regulator (BPR) was used to maintain the system pressure at either 1000 or 1910 psi. All the equipment was kept inside an oven to perform experiments at the reservoir temperature (40 °C or 63 °C). A pressure transducer was used to monitor pressure drop.

#### 2.3.1. High pressure stability study

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

#### 2.3.2. Foam mobility test

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

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

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

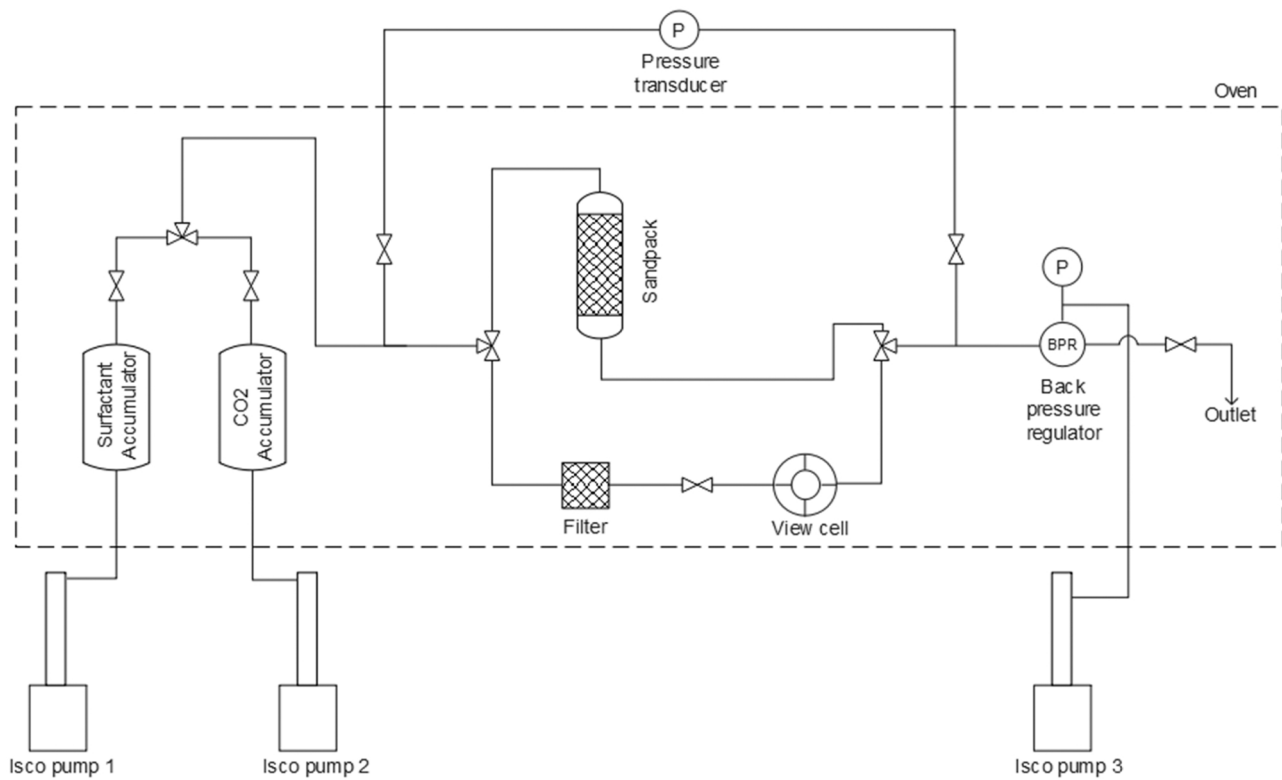


Fig. 1. Experimental set-up for high pressure stability and foam mobility tests.

injection rate of 5 mL/min (to avoid the influence of surfactant adsorption in the subsequent experiments). Surfactant concentration in formation water was 0.5 wt%. Pressure of the system was increased to the target pressure. Subsequently, CO<sub>2</sub> and surfactant formulation were co-injected at 80% foam quality from the top of the sand-pack. Total flow rates of 0.122 mL/min (4 ft/day) and 0.304 mL/min (10 ft/day) were studied. Pressure drop ( $\Delta P$ ) was recorded using a pressure transducer until it remained constant. Distilled water was injected through the sand-pack at a constant pressure after each test to clean it. Permeability was checked to ensure its consistency through the different experiments.

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

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

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

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

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

### 3. Results and discussion

#### 3.1. Compatibility tests

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

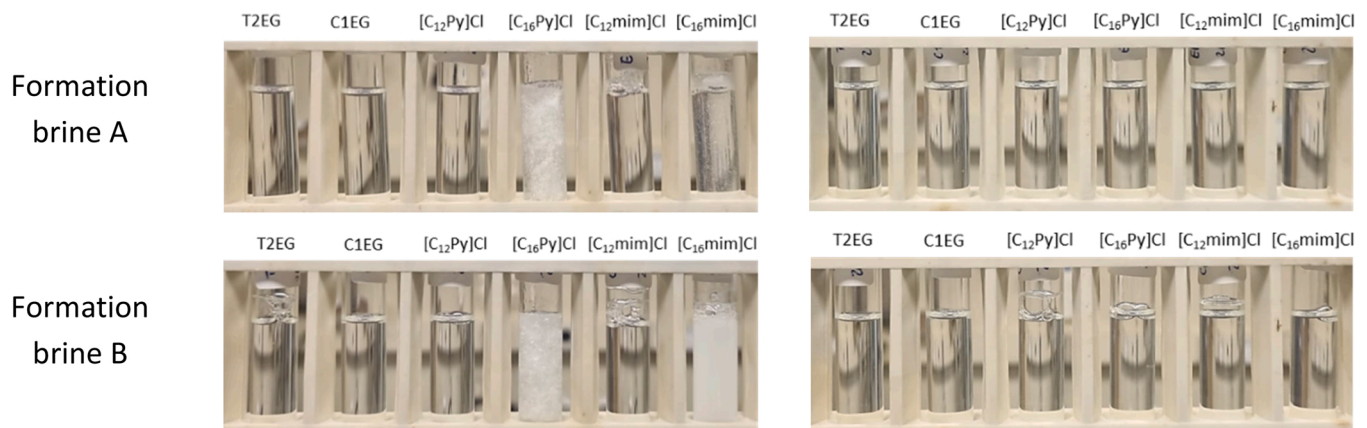


Fig. 2. Stability tests. Pictures taken after 1 week.

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

### 3.2. Static foam experiments

Static foam experiments were performed to compare foam ability and bulk foam stability of SAIL formulations. Foams are thermodynamically unstable, and eventually collapse due to gravity drainage of the liquid film and diffusion through gas bubbles, also known as Ostwald ripening. When ionic surfactants like the SAILs tested in this paper are used as surface active agents, the liquid film is charged. Therefore, the overlapping of similarly charged electric double layers opposes film thinning, thus strengthening the stability of foam [36]. Foaming ability was measured by means of the initial foam height ( $H_0$ ), and half-life time was used to determine foam stability. The study was performed for the two reservoir (A and B) conditions of salinity and temperature. SAIL concentration was fixed at 0.5 wt%, as it is a typical surfactant concentration used in field applications [31]. Two different foaming gases (air and CO<sub>2</sub>) were studied. Measurements were repeated twice, and mean deviation was less than 10% for half-life time results and less than 5% for  $H_0$  values.

Table 3 shows  $H_0$  values and half-life times for the different SAILs at reservoir A conditions. Air based foams were found more stable than CO<sub>2</sub> foams, as it was expected due to the higher solubility of CO<sub>2</sub> in the foaming solution [5]. Solubility of gases in water has a negative effect on foam stability because it can accelerate the foam coalescence [9]. The effect of the different SAILs on the analyzed parameters was the same regardless of the foaming gas. Focusing on CO<sub>2</sub> EOR, due to the environmental benefits of the method, the discussion in this section refers to the numerical values of CO<sub>2</sub> foam. A  $H_0$  = 5.75 cm and half-life time of 5.27 min were achieved with the SAIL [C<sub>16</sub>mim]Cl. Half-life time was significantly lower (0.69 min) in the case of [C<sub>12</sub>mim]Br, but  $H_0$  was remarkably higher (9.95 cm). A similar result was obtained with the SAILs [C<sub>16</sub>Py]Cl and [C<sub>12</sub>Py]Cl. Therefore, longer alkyl chain length compounds resulted in a lower foaming ability, but a higher stability. These results are in agreement with other studies previously carried out with different ILs. Hu et al. [22] studied the foaming performances of different alkyl chain length imidazolium ILs. They found that the  $H_0$  was lower for C<sub>8</sub> than for C<sub>6</sub> ILs. They claimed that this reduction is probably caused by the increase of hydrophobic groups, that leads to the decrease of solubility in water, resulting in an inferior foaming performance. They also concluded that the longer the alkyl chain length, the higher the foam stability. Zhang et al. [37] found that the longer the alkyl chain length, the stronger is the interaction between molecules, resulting in greater external forces required for the bursting of foam, and therefore a more stable foam. Comparing SAILs functional groups, pyridinium SAILs showed better foaming ability, but lower stability than imidazolium compounds.

C1EG and T2EG are two quaternary ammonium SAILs. Half-life time

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

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

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

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

**Table 3**  
Static foam test results for reservoir A.

	[C <sub>16</sub> mim]Cl	[C <sub>16</sub> Py]Cl	[C <sub>12</sub> mim]Br	[C <sub>12</sub> Py]Cl	C1EG	T2EG
	Air					
$H_0$ (cm)	6.5	7.25	9.3	10.5	11	4.15
Half-life (min)	21.80	17.20	2.53	1.24	1.99	0.72
	CO <sub>2</sub>					
$H_0$ (cm)	5.75	5.9	9.95	12.05	11.15	4.35
Half-life (min)	5.27	3.58	0.69	0.53	0.47	0.34

**Table 4**  
Static foam test results for reservoir B.

	[C <sub>16</sub> mim]Cl	[C <sub>16</sub> Py]Cl	[C <sub>12</sub> mim]Br	[C <sub>12</sub> Py]Cl	C1EG	T2EG
	Air					
$H_0$ (cm)	2.35	4.95	10	10.45	8.35	2.85
Half-life (min)	81.25	54.74	7.81	4.72	6.13	16.64
	CO <sub>2</sub>					
$H_0$ (cm)	2.95	4.6	10.15	11.85	8.65	5.35
Half-life (min)	8.60	3.37	1.94	1.58	0.87	0.67

**Table 5**

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

	[C <sub>16</sub> mim]Cl	
	Air	CO <sub>2</sub>
Height (cm)	3.8	3.95
Half-life (min)	19.47	4.36

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

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

### 3.3. High pressure stability study

In order to use foams in tertiary oil production, the dispersion of CO<sub>2</sub> bubbles in surfactant solution must be stable at the harsh conditions of the studied reservoirs, including not only high salinity and temperature but also high pressure. For this reason, bulk foam experiments at pressure conditions of each reservoir (1910 psi for A and 1000 psi for B) were performed in a high-pressure cell to determine foam stability. Fig. 3 shows the stability study for [C<sub>16</sub>mim]Cl at reservoir A conditions. Rate of foam decay was low and half-life time was estimated as 7.8 days, several times higher than those reported in literature for regular surfactants at similar conditions [11]. Figs. 4 and 5 present the high pressure stability study at reservoir B conditions for [C<sub>16</sub>Py]Cl and [C<sub>16</sub>mim]Cl (half formation brine salinity), respectively. Half-life time for [C<sub>16</sub>Py]Cl was estimated as 0.98 h and for [C<sub>16</sub>mim]Cl, 4.5 h. Salinity has a positive effect in foam stability. Although salinity was lower in the case

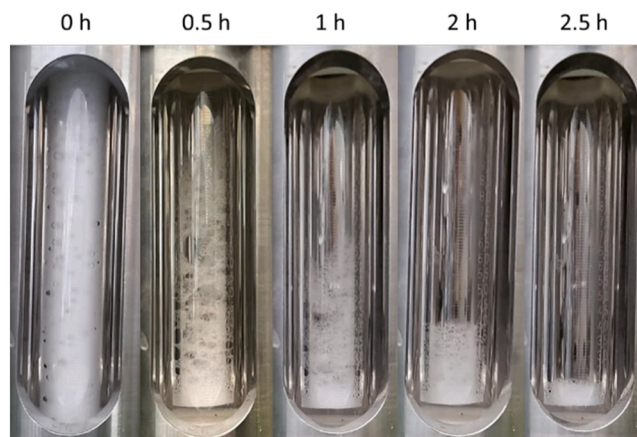


Fig. 4. High pressure stability study of [C<sub>16</sub>Py]Cl for reservoir B project.

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

Foam stability of [C<sub>16</sub>mim]Cl at reservoir A conditions is considerably higher than for reservoir B conditions. It should be noted that in both cases salinity is ~125,000 ppm of TDS since half concentration of reservoir B formation brine was applied. Reservoir A conditions of pressure and temperature (63 °C and 1910 psi), unlike reservoir B conditions (40 °C and 1000 psi), are above the CO<sub>2</sub> critical point (31.1 °C and 1068.93 psi). When temperature and pressure conditions exceed this critical point, gaseous CO<sub>2</sub> transformed into a liquid-like fluid with a density significantly higher than that of gaseous CO<sub>2</sub>, thus reducing the water drainage from lamellae [45].

It is known that as pressure increases, the solubility of CO<sub>2</sub> in brine increases according to Henry's Law, with a negative effect on foam stability. However, at high pressures, the density of CO<sub>2</sub> increases due to the compression of gas [9]. The density increase lowers the liquid drainage and stabilizes foam. We observed that the half-life increases with pressure implying that the density effect was more important than the solubility effect for SAIL foams. However, there is no agreement in the literature about how pressure affects CO<sub>2</sub> foams stability. Some authors concluded that stability increases with pressure [10,46], whereas other authors claimed that it decreases [47,48]. Furthermore, Szabries et al. [44] studied foam stability of Triton X-100, a non-ionic surfactant, at 45 °C and for a pressure range of 0–1233 psi. The authors found that, between 0 and 1087 psi, stability decreased with

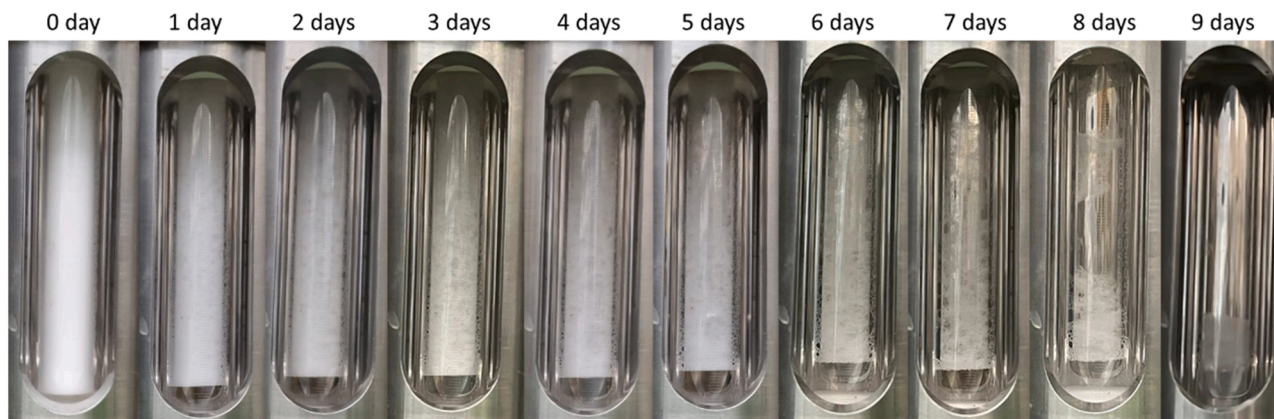


Fig. 3. High pressure stability study of [C<sub>16</sub>mim]Cl for reservoir A project.

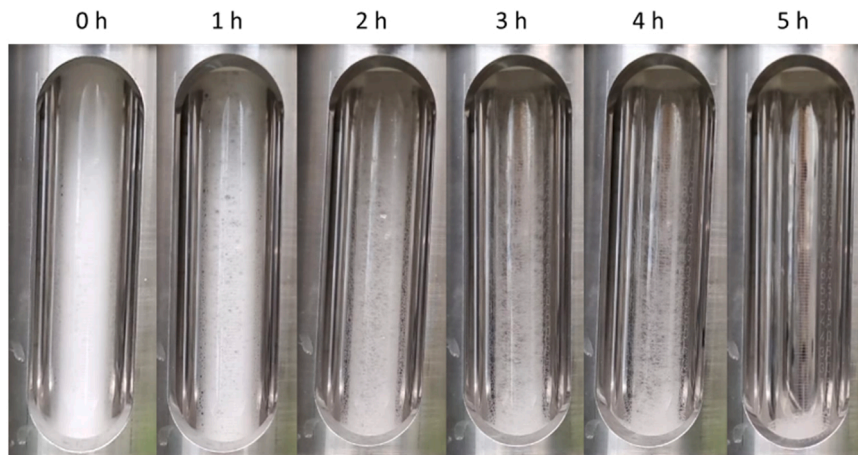


Fig. 5. High pressure stability study of [C<sub>16</sub>mim]Cl for reservoir B project using half concentration of formation brine.

increasing pressure. However, the contrary behavior was found between 1087 and 1233 psi, and foam stability improved with increasing pressure. In accordance with our results, Zhang et al. [10] found out that foams of tertiary amines were more stable with rising CO<sub>2</sub> density.

The behavior of CO<sub>2</sub> foam stability with pressure is complex, with different classes of surfactants behaving differently with pressure. Wang et al. [9] and Zhang et al. [10] concluded that the effect of pressure on foam stability depends on the hydrophilic-lipophilic balance (HLB) of the surfactant used. The solvation of hydrocarbon tails increases with the density of CO<sub>2</sub>, as it becomes more hydrophobic. As a result, strong surfactant hydrophilic heads are needed to balance this interaction. However, if the surfactant is too hydrophilic it can be embedded into the water phase and weaken the liquid film. On the contrary, surfactants with low HLB values can disorder the arrangement of surfactant molecules leading to unstable foams. In conclusion, for surfactants with relatively high HLB values, high pressures can increase the interaction between surfactant molecules and CO<sub>2</sub>, making the foam to be at the most stable state. In this state, the arrangement of the molecules at the interface is tightened and foam stability is improved by reducing water drainage and gas diffusion [9]. In this study, [C<sub>16</sub>mim]Cl and [C<sub>16</sub>Py]Cl are two hydrophilic surfactants with long carbon chains, therefore the hydrophilicity is not as high as for other surfactants with shorter alkyl chains. For the three cases studied, stability was improved with increasing pressure comparing half-life time at atmospheric (Section 3.2) and reservoir pressure. In addition, the highest stability was reported for the highest reservoir pressure (reservoir A).

### 3.4. Foam mobility test

Foam-flow experiments in the absence of oil were conducted in a vertically oriented sand-pack column. Pore volume, porosity and permeability of the sand-pack are presented in Table 6. SAIL concentration was kept at 0.5 wt%. Experiments were performed at 80% foam quality for each reservoir conditions of pressure and temperature. Total flow rates of 0.122 mL/min (4 ft/d) and 0.304 mL/min (10 ft/d) were studied, however unstable values of pressure difference were observed for 0.122 mL/min. Several researchers [49–52] have investigated the importance of a critical injection velocity (related to a minimum pressure gradient) in porous media for transition from “coarse” to “strong”

foam. Injection rate should be greater than the critical injection velocity to obtain a stable foam. The minimum pressure gradient for mobilization of liquid lamellae and foam generation depends on different factors such as permeability of the medium, surfactant type and concentration, gas type and foam quality [3]. The velocity of 4 ft/day is likely below the critical velocity of the system, and therefore results were discarded.

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

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

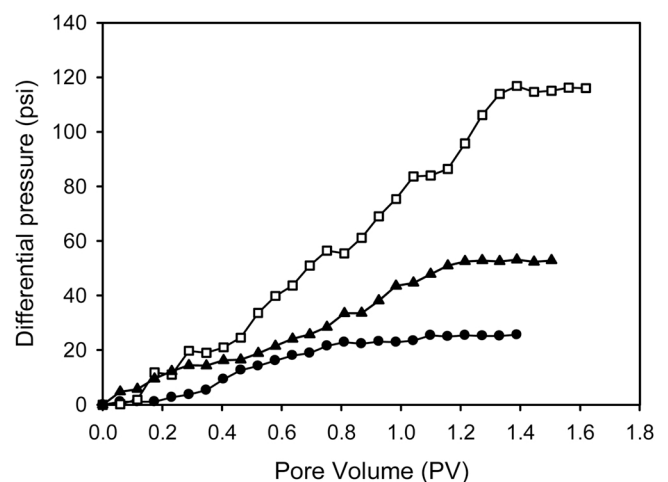


Fig. 6. Foam mobility tests for [C<sub>16</sub>mim]Cl reservoir A (□), [C<sub>16</sub>Py]Cl reservoir B (●) and [C<sub>16</sub>mim]Cl reservoir B using half concentration of formation brine (▲).

Table 6  
Sand-pack properties.

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

**Table 7**  
Results of sand-pack experiments.

	ΔP (psi)	MRF	μ <sub>af</sub> (cp)
[C <sub>16</sub> mim]Cl reservoir A	115.97	1229.01	1356.61
[C <sub>16</sub> mim]Cl reservoir B (1/2 FB)	52.86	560.19	618.35
[C <sub>16</sub> Py]Cl reservoir B	25.60	303.46	299.47

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

#### 4. Conclusions

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

- At ambient pressure, foams produced with imidazolium SAILs were the most stable, while pyridinium SAILs showed the best foaming ability.
- SAILs with longer alkyl chain length resulted in lower foam ability but higher stability compared to shorter alkyl chain length SAILs.
- SAILs with higher number of ethoxylated groups (higher hydrophilicity) resulted in lower foam performance.
- An optimal formulation of 0.5 wt% [C<sub>16</sub>mim]Cl was selected for reservoir A conditions. For reservoir B conditions, two optimal formulations of 0.5 wt% [C<sub>16</sub>Py]Cl and 0.5 wt% [C<sub>16</sub>mim]Cl with half concentration of formation brine, were identified.
- A half-life time of 7.8 days was achieved with [C<sub>16</sub>mim]Cl at high pressure reservoir A conditions, several times higher than those reported in literature for foams made with regular surfactants. Lower half-life times up to 4.5 h were obtained for the reservoir B conditions.
- Mobility reduction factors obtained in foam flow experiments were high (more than 300), with the most promising result reported for [C<sub>16</sub>mim]Cl at reservoir A conditions (1229).
- SAILs have a promising potential for increasing foam apparent viscosity and improving mobility control during EOR and CO<sub>2</sub> sequestration processes in high salinity reservoirs and aquifers.

#### CRedit authorship contribution statement

**Alba Somoza:** Conducted experiments, wrote manuscript. **Ana Soto;**

Co-directed research and edited manuscript. **Jieqiong Pang:** Conducted experiments, helped with manuscript. **Kishore Mohanty:** Directed research, edited manuscript.

#### Declaration of Competing Interest

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

#### Data Availability

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

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