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## **Effect of Scaling and Corrosion Inhibitors on the Static Adsorption of an Anionic Surfactant on a Carbonate Rock**

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### **Abstract**

About half of the world's oil reserves are in carbonate reservoirs, and most of these formations are mixed-wet or oil-wet and fractured, with extremely heterogeneous porosities and permeabilities. Implementation of enhanced oil recovery (EOR) techniques in this kind of reservoir is essential to achieve peak oil production and increase the recovery factor. Chemical EOR (CEOR) processes have been studied for many years in carbonate reservoirs but are not usually economically viable. Surfactant flooding has been considered as one of the most promising techniques among the chemical recovery methods due to the capacity of some surfactants to alter the carbonate rocks' wettability. However, the process is economically feasible only when losses of surfactant caused by adsorption into the porous media are decreased. Adsorption of surfactants can be affected by the surface charge on the rock surface and fluid interfaces. In general, the adsorption of cationic surfactants on carbonates is lower in comparison with other surfactants. Nevertheless, the high cost of cationic surfactants compared to anionic ones has led to studies aiming to evaluate the injection of the latter in the presence of a sacrificial agent in order to reduce the adsorption caused by interaction between the negative charges of the surfactant and positive charges on the carbonate surface. This work aims to study the effect of the presence of two chemicals, normally applied as scaling and corrosion inhibitors, on reducing the static adsorption of an anionic sodium olefin sulfonate surfactant on a carbonate rock. Water soluble poly(sodium methacrylate) (PSM) and diethanolamine (DEA) were evaluated as sacrificial agents in concentrations close to their scaling and corrosion inhibitor functions, respectively, to verify their sacrificial role in a co-injection chemical scenario. Adsorption studies were carried out using a pulverized carbonate rock in which low-salinity water was used as the base medium. Aqueous stability tests were carried out, which made it possible to select the correct salinity for the solutions of surfactant. Surface tension measurements were used as an indirect approach to study the adsorption of the surfactant in the presence and absence of PSM and DEA. Individually, PSM presented the best performance in reducing the adsorption of the anionic surfactant, while the DEA showed an almost null effect. However, when the chemicals were mixed, a synergistic effect was observed. The performance of PSM can probably be attributed to a steric effect of an adsorbed layer of polymer. It will be shown that even at lower concentrations, co-injection chemicals which are used for targeting other issues, such as scaling and

corrosion inhibitors, may play the role of a sacrificial agent in reducing the adsorption of anionic surfactants, which is a concern in application to carbonate reservoirs.

## Introduction

Oil recovery consists of three stages: primary recovery, secondary recovery, and enhanced recovery, sometimes named tertiary recovery. In primary recovery, crude oil is displaced from the reservoir to the well because of the effect of the pressure gradient that exists between the downhole and the reservoir. In this stage, natural energy associated with the reservoir allows the oil to reach the surface. The second stage begins if the medium's pressure becomes inadequate or significant quantities of other fluids are being produced; this stage involves injecting an external fluid such as water or gas into the reservoir through injection wells to maintain the pressure and move the hydrocarbon towards the producing wells. Possibly the quantity of oil recovered in the first two stages approximately corresponds to a range equal to 20–50% of the Original Oil in Place (OOIP); this percentage depends on the characteristics of the reservoir and the crude oil (Terry, 2003; Donaldson *et al.*, 1989). The amount of oil that remains in the reservoir may be obtained by enhanced oil recovery (EOR) methods.

EOR methods aim to optimize the secondary recovery processes by increasing the sweep efficiency and decreasing residual oil saturation, causing an increase in the oil recovery by means of fluid injection or the addition of energy to the reservoir (Al-Adasani and Bai, 2010; Abdelgawad and Mahmoud, 2014). Several EOR methods have been implemented over the years. These methods may be of chemical or physical nature. Traditionally, they have been classified in four categories: thermal processes, gas injection, chemical processes, and others.

Methods of a chemical nature, normally defined as chemical enhanced oil recovery (CEOR), consist in injecting into the reservoir a chemical solution of either surfactant, polymer, alkali, or a combination of them, which decreases the interfacial tension, alters the wettability, and enhances mobility (Green, Willhite, 1998; Sheng, 2011). Surfactant flooding has been considered one of the most promising techniques among the chemical recovery methods but is uneconomical due to the meaningful losses of surfactant on the rock surface. Currently the application of CEOR represents a small percentage of the EOR methods implemented in the industry. Because of the cost of application, interest in CEOR studies and projects is higher when the oil price is high. Even from the perspective of a more favourable economic scenario, it is necessary to decrease surfactant losses into porous media due to adsorption.

Carbonate reservoirs (dolomites and limestones) contain approximately 60% of the world's proven oil reserves (Akbar *et al.*, 2001; Roehl and Choquette, 1985). Most of these reservoirs are naturally fractured and present a high degree of heterogeneity (Jardine and Wilshart, 1982; Al-Anzi *et al.*, 2004). This kind of reservoir represents an enormous challenge regarding the selection of the best method of production, since secondary recovery techniques (waterflooding) or enhanced recovery methods are needed to achieve maximum production (Allan and Sun, 2003). Waterflooding is an effective technique in naturally fractured and water-wet formations (Hirasaki and Zhang, 2004); oil production is achieved by the imbibition of water into the matrix and subsequently the oil is expelled to the fracture network and later transported toward producer wells. Nonetheless, at least 80% of carbonates are oil-wet or possess mixed wettability (Alotaibi, Azmy, and Nasr-El-Din, 2010; Downs and Hoover, 1989). Recovery by waterflooding in fractured oil-wet/mixed-wet carbonate reservoirs is low, due to the low imbibition of water into the oil-wet matrix (Dong and Al Yafei, 2015). Additionally, few EOR processes are compatible with the formations that present the abovementioned characteristics. Surfactant flooding ("huff and puff") has been considered as one of the most promising techniques for these cases (Seethepalli, Adibhatia, and Mohanty, 2004), because of the ability of some surfactants to alter the rock wettability and increase the displacement efficiency by lowering the interfacial tension between the oil and water and mobilizing the residual oil.

There are four most common types of surfactants depending on the hydrophilic headgroup: anionic, cationic, non-ionic, and zwitterionic (Eastoe and Tabor, 2014; Behrens, 2013). In general, adsorption of cationic surfactants on carbonates is lower in comparison with other surfactants. However, the high cost of cationic surfactants (more than 3 US\$/kg) compared to anionic ones (approximately 1 US\$/kg) has led to studies aiming to evaluate the injection of the latter in the presence of a sacrificial agent to reduce adsorption losses in carbonates (Seethepalli, Adibhatia, and Mohanty, 2004; Shamsijazeyi, Hirasaki, and Verduzco, 2013). Adsorption of surfactants can be affected by surface charge on the rock surface and fluid interfaces; sacrificial agents reduce the increase of adsorption caused by interaction between the negative charges of the anionic surfactant and positive charges on the carbonate surface.

Over recent decades, numerous studies of the problems that occur in surfactant flooding methods have been done. The adsorption behaviour is the most well-studied issue, with the aim of finding a way to decrease losses, and the use of sacrificial agents is one of most frequently applied approaches for reducing this phenomenon. Alkalis (sodium carbonate or sodium hydroxide) are often used as sacrificial agents. Krumrine et al. (1982) evaluated the effect of alkaline additives in surfactant systems for EOR processes through static adsorption tests. Seethepalli, Adibhatia, and Mohanty (2004) suggested that adsorption of anionic surfactants on carbonates can be suppressed significantly by the addition of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). Sodium carbonate is not effective in the presence of anhydrite. It is essential to identify sacrificial agents that are effective in any environment. Shamsijazeyi, Hirasaki, and Verduzco (2013) evaluated sodium polyacrylate as a sacrificial agent, compared this polymer with many other conventional or recently recommended sacrificial agents, and demonstrated the advantages of sodium polyacrylate over all of them in the presence of anhydrite through static and dynamic adsorption studies; additionally, they showed that polyacrylate reduces the adsorption of a selected anionic surfactant on several sample rocks, including industrial calcite, Carl Pool dolomite, Berea sandstone, and limestone. Wang et al. (2014) presented a laboratory study to analyse the effect of polyacrylamide in the reduction of adsorption of an anionic surfactant on a core of a carbonate reservoir by means of dynamic adsorption tests.

The alteration of wettability also has received great attention. Austad et al (1998) investigated the application of cationic surfactants to alter wettability and thus improve spontaneous imbibition in chalk material saturated with oil. They showed that cationic surfactants, such as CTAB (dodecyltrimethylammonium bromide) are quite effective when used in the water-flooding procedure at concentrations greater than the critical micelle concentration (CMC) ( $\sim 1$  wt%), recovering approximately 70% of the OOIP. Zhou, Morrow, and Ma (1996) reviewed the oil recovery by spontaneous imbibition, addressing the influence of the wettability of the rock in the imbibition process. Many academics suggest the use of cationic surfactants in carbonates and anionic surfactants in sandstones. However, Seethepalli, Adibhatia, and Mohanty (2004) identified some anionic surfactants that can change the wettability of the calcite surface to intermediate/water-wet condition as well as or better than the cationic surfactant CTAB. On the other hand, Hirasaki and Zhang (2004) discussed the ability of an anionic surfactant to alter the wettability and reduce the interfacial tension in oil-wet carbonates by adding sodium carbonate to inhibit adsorption.

In studying the adsorption behaviour, it is important to determine the concentration of surfactant after solution makes contact with crushed rock in order to find the absorption percentage. There are several ways of determining this concentration, such as the indirect surface tension method for estimating the losses of surfactant onto dolomitic limestone surface. Muhere (2009) applied this method to create equilibrium adsorption isotherms for some nonionic and anionic surfactants on shale and sandstone. Behrens (2013) studied the adsorption of the anionic surfactant Aerosol OT on kaolinite under different conditions and applied the same method to determine the surfactant concentration.

This paper presents a study of the static adsorption of an anionic sodium olefin sulfonate surfactant on a dolomitic limestone rock in the presence of two chemicals that are normally applied as scaling

and corrosion inhibitors. First, an aqueous stability test was developed, which made it possible to select the correct salinity for the solutions of surfactant; later, the Critical Micelle Concentration (CMC) was determined. Additionally, the amount of the surfactant adsorbed in the solutions with and without the two chemicals on disintegrated rock was determined using the indirect surface tension method. Finally, water-soluble poly(sodium methacrylate) (PSM) and diethanolamine (DEA) were evaluated as sacrificial agents in concentrations close to their scaling and corrosion inhibitors' functions, respectively, to verify their sacrificial role in a co-injection chemical scenario.

## Materials and Methods

### Chemicals

**Surfactant.** The surfactant used was an alpha-olefin sulfonate anionic surfactant with the chemical structure  $C_{14-16}CH=CH-(CH_2)_n-SO_3Na$  [sodium (C14-16) olefin sulfonate], as shown in Figure 1. Its specific mass is 1.06 g/mL, with a content of 39% (w/w) in aqueous solution.

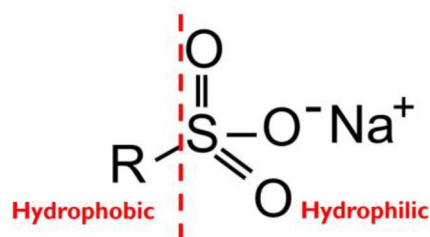


Figure 1—Structure of the anionic surfactant

**Chemicals to be evaluated as potential sacrificial agents.** DEA and PSM were evaluated with the aim of reducing the adsorption of the anionic surfactant in the rock sample.

DEA, with the chemical formula  $HN(CH_2CH_2OH)_2$ , is shown in Figure 2. A commercial grade sample was used with a content of 84% (w/w) in aqueous solution and specific mass of 1.1 g/mL.

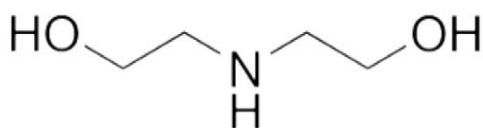


Figure 2—Structure of diethanolamine

PSM with the chemical formula  $[CH_2C(CH_3)(CO_2Na)]_n$  is shown in Figure 3. The sample used has a weight-average molecular weight (Mw) of around 9500, specific mass of 1.18 g/mL, and content of 30% (w/w) in water.

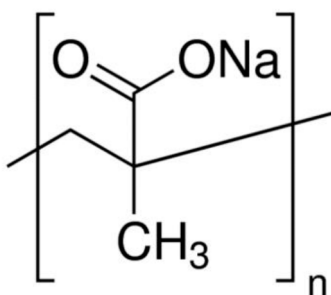


Figure 3—Structure of the PSM (Sigma-Aldrich, 2018).

**Brines.** Sodium chloride (NaCl) and distilled water were used to prepare a saline base medium. Brines have been used as the base medium for injection of surfactants since the beginning of its implementation. (Donaldson *et al.*, 1989).

For the aqueous stability tests, brines with different concentrations of NaCl were used: from 2000 to 75000 ppm.

As will be shown further, it was decided that the adsorption studies would be developed using NaCl at 2000 ppm as well as for the surface tension measurements to determine the CMC and for the indirect adsorption tests. The main reason for choosing this concentration was the result of the aqueous stability tests. Some studies indicate that the injection of low-salinity water improves the recovery of oil in the reservoir (Al-Adasani and Bai, 2010).

**Adsorbent: rock sample for adsorption test.** The mineralogical composition of the carbonate rock sample was characterized by X-ray fluorescence and the loss on ignition test (1020 °C), by which it was possible to verify that it was a dolomitic limestone.

The adsorption of the surfactant in the rock is determined by equilibrium tests using crushed rock. To crush the rock, the procedure was to place the rock sample of dolomitic limestone in a jaw crusher and later in a roller crusher to obtain the desired granulometry of the material. Then, the material resulting from this process was sieved on meshes of 0.15 and 0.074 mm and thus a grain size of less than 0.074 mm was obtained.

### Aqueous Stability Tests

Injection of a monophasic is important since precipitates, liquid crystals, or a second phase could be formed, leading to a nonuniform distribution and transport of the injected materials. In this way, the transparency and homogeneity of the injected solution may be associated with the stabilization of the surfactant in an electrolyte concentration (Sheng, 2011).

For these tests, the concentration of the surfactant (1000 ppm) was selected with fixed concentrations of DEA and PSM of 1.5 mM and 100 ppm, respectively; saline base medium was in the range from distilled water (0 ppm) to 75000 ppm of NaCl, as previously mentioned.

After preparation in 100-mL reagent flasks with caps, the solutions were manually shaken slowly for 10 minutes and then left to settle for 60 minutes. Finally, the stability of the solutions was evaluated after 1, 8, 12, and 24 hours, recording whether the formation of precipitates, turbidity, phase separation, or gel formation occurred.

### Surface tension measurements

A KRÜSS K6 tensiometer (ring method) was used for the surface tension measurements for both CMC determination and surfactant adsorption tests (indirect method). The surface tension values were measured at room temperature ( $23 \pm 1$  °C) and corrected using a correction factor obtained from the literature surface tension value for the water and experimental value obtained for the distilled water.

### CMC Characterization

Surfactant solutions at different concentrations from 100 to 1000 ppm in distilled water and from 5 to 1000 ppm in 2000-ppm NaCl solution were prepared for the determination of CMC.

**Adsorption tests.** The surface tension method is an indirect approach to study the adsorption of surfactant. An estimate of the adsorption of surfactant on the particles is obtained by this method. The simplicity and practicality of this method were among the reasons why it was chosen (Behrens, 2013).

The application of the surface tension methodology requires a previous study; therefore, surface tensions of surfactant solutions must be measured under a wide range of known concentrations to create a plot. The disadvantage of using this method is that the surface tension only changes with the concentration if the

concentration of surfactant is lower than the CMC value (Muherei and Junin, 2009). In this way, adsorption tests were carried out using surfactant concentrations lower than the CMC value.

It will be shown that because the CMC at the selected salinity (2000 ppm), for the adsorption tests, surfactant concentration range was less than 100 ppm.

#### Procedure

Surfactant solutions at different concentrations (30, 60, and 90 ppm) lower than the CMC were prepared at the selected salinity (2000 ppm) and were used as baselines. In addition, three additional solutions were prepared, as follows: surfactant + DEA; surfactant + PSM; and surfactant + DEA + PSM. An additional condition with only DEA + PSM in the saline solution was prepared to verify whether these chemicals had an influence on the surface tension measurements. Table 1 shows the formulation for each concentration of surfactant used in the adsorption tests.

**Table 1—Surfactant concentrations of formulations at a salinity of 2000 ppm for adsorption tests in calcareous dolomite rock sample.**

Surfactant concentration [ppm]	Total salinity [ppm]	DEA concentration [mM]	PSM concentration [ppm]
30	2000	0	0
30	2000	1.5	0
30	2000	0	100
30	2000	1.5	100
60	2000	0	0
60	2000	1.5	0
60	2000	0	100
60	2000	1.5	100
90	2000	0	0
90	2000	1.5	0
90	2000	0	100
90	2000	1.5	100
0	2000	1.5	100

A known mass of surfactant-containing solution ( $m_{tot.solution}$ ) is mixed with a known mass amount of the crushed rock ( $m_{carbonate}$ ). The solid-to-liquid weight ratio used was 1:5, that is, around 8 g of crushed rock was added to 40 g of surfactant-containing solution. The solutions and rocks were mixed using a magnetic stirrer for 4, 10, 18, 24, and 28 hours at 1128 RPM and then left to settle for sedimentation of solids. All the tests were carried out at room temperature ( $23 \pm 1$  °C). Subsequently, filtration was carried out to separate the surfactant-containing solution from the rock sample, followed by surface tension measurements. Surface tension measurements of surfactant-containing solutions were also carried out before contact with the carbonate rock.

This method of measuring the adsorption of the surfactant in carbonate rocks is based on determining the difference between the concentration of the surfactant in solution before and after the adsorption test. The adsorption of the surfactant in the solution was determined using the following equation, based on Ahmadi and Shadizadeh (2013):

$$q = \frac{m_{tot.solution} \times (C^o - C)}{m_{carbonate}} \times 10^{-3} \quad (\text{Eq. 1})$$

where:

$q$ : surfactant adsorption on rock surface [mg/g rock]

$m_{tot.solution}$ : total mass of solution in original bulk solution [g]

$C^o$ : surfactant concentration in initial solution before equilibration with carbonate rock [ppm]

$C$ : surfactant concentration in aqueous solution after equilibration with carbonate rock [ppm]

$m_{carbonate}$ : total mass of crushed carbonate [g]

## Results and Discussion

### Aqueous stability test

Table 2 presents the results of the aqueous stability test. It was observed that at a salinity of 25000 ppm, the solution became clouded, and at concentrations greater than 50000 ppm, the formation of precipitates took place. In the solutions with concentrations of 2000 and 5000 ppm, no turbidity or precipitation was observed until after 24 hours. In this way, the salinity of 2000 ppm (a low-salinity condition) was selected since it is an intermediate value within said range. Also, this condition was considered as it did not present precipitates or turbidity (Figure 4).

Table 2—Aqueous stability test results

Test	1	2	3	4	5	6
Anionic Surfactant [ppm]			1000			
DEA [mM]			1.5			
PSM [ppm]			100			
NaCl [ppm]	0	2000	5000	25000	50000	75000
Results after 1 h	C	C	C	C	C	P
Results after 8 h	C	C	C	C	CL	P
Results after 12 h	C	C	C	C	CL	P
Results after 24 h	C	C	C	CL	P	P

C – Clear; CL – Cloudiness; P – Precipitate; S – Separation



Figure 4—Images showing examples of the aqueous stability test results at salinities of 2000 and 75000 ppm at fixed concentrations of the surfactants (1000 ppm) DEA (1.5 mM) and PSM (100 ppm).

### Critical micelle concentration (CMC)

The plots of surface tension versus surfactant concentration in distilled water at a salinity of 2000 ppm are presented in Figure 5. The point of intersection between the negative slope and the straight line corresponds to the CMC value for both conditions. Microsoft Excel<sup>®</sup> was used to estimate trend lines next to and after the CMC values. The CMC was calculated as the point where the equations were equal, solving in terms of y. Table 3 presents CMC values and equations describing the variation of surface tension (y) as a function of concentration (x).

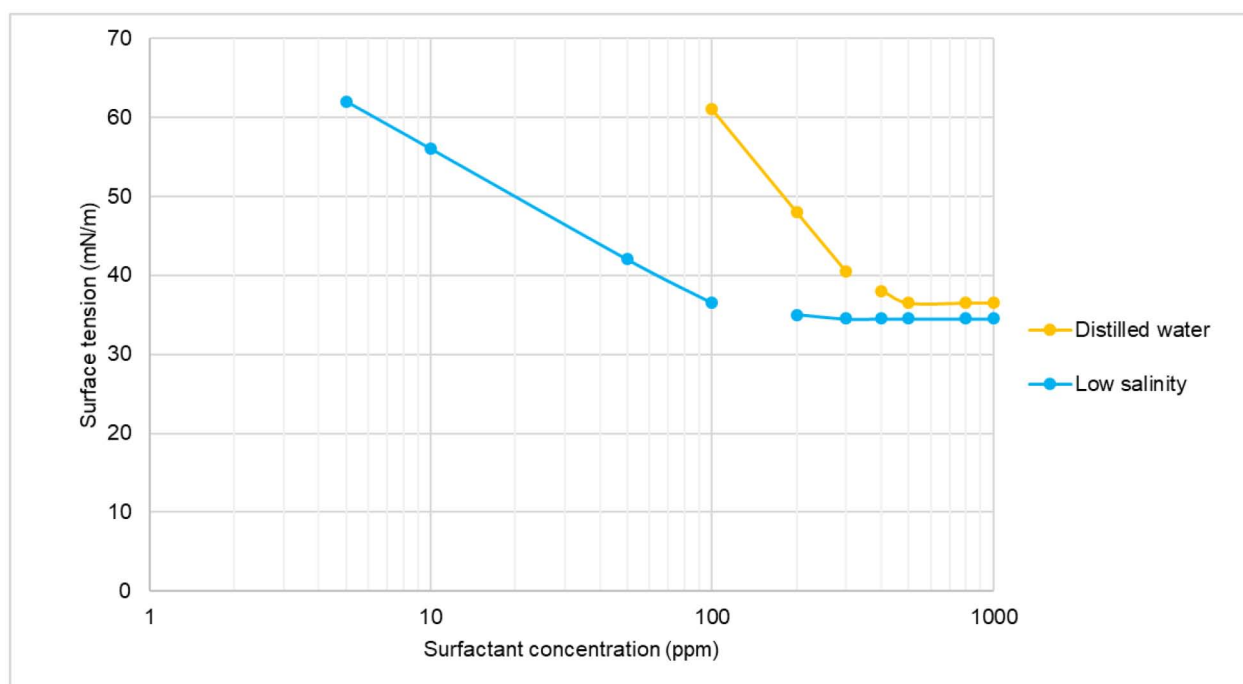


Figure 5—Surface tension versus anionic surfactant concentration in distilled water and low-salinity water (2000 ppm NaCl)

Table 3—CMC values and equations describing the modification of surface tension (y) (mN/m) as a function of concentration (x) (ppm)

Salinity [ppm]	CMC [ppm]	Surface tension (y) = f [Concentration(x)]
0	349.23	$-18.66\ln(x) + 146.9 = -1.295\ln(x) + 45.215$
2000	117.95	$-8.554\ln(x) + 75.705 = -0.23\ln(x) + 35.997$

The effect of salinity on the CMC value was evidenced since it decreased drastically when electrolytes were added to the solution. The presence of electrolytes at a fixed temperature reduces CMC (Miyagishi, Okada and Asakawa, 2001) and increases the micelle aggregation or number of molecules per micelle. As previously mentioned, in this work surfactant concentrations were limited by the CMC value.

### Adsorption tests

It should be noted that a previous study was carried out to measure the surface tensions of the solutions chosen for the investigation. That study evaluated whether DEA and PSM would have an effect on the surface tension measurements; however, the result was null (there was no air–water interface effect). This behaviour can also be verified from the results listed in Table 4, which presents the surface tension measurements at different concentrations of anionic surfactant in the presence of both the abovementioned chemicals.



**Table 4—Surface tension measurements at different concentrations of anionic surfactant (30, 60, and 90 ppm) before contact with the carbonate rock in 2000 ppm NaCl medium and fixed concentrations of DEA (1.5 mM) and PSM (100 ppm)**

SURFACE TENSION (mN/m)			
30 ppm			
Surfactant	Surfactant + DEA	Surfactant + PSM	Surfactant + DEA + PSM
46	46	46	46
60 ppm			
Surfactant	Surfactant + DEA	Surfactant + PSM	Surfactant + DEA + PSM
41.5	41.5	41.5	41.5
90 ppm			
Surfactant	Surfactant + DEA	Surfactant + PSM	Surfactant + DEA + PSM
38	38	38	38

As shown in Table 5, the equilibrium time was reached at 24 hours; after this time (at 28 hours) it was observed that the surface tensions were equal to the values obtained at 24 hours.

**Table 5—Surface tension measurements with time at different concentrations of anionic surfactant (30, 60, and 90 ppm) after contact with the carbonate rock in 2000 ppm NaCl medium and fixed concentrations of DEA (1.5 mM) and PSM (100 ppm)**

SURFACE TENSION (mN/m)				
30 ppm				
	Surfactant	Surfactant + DEA	Surfactant + PSM	Surfactant + DEA + PSM
4 hours	57	56.5	55	54.5
10 hours	58.5	58	56.5	56
18 hours	59	58.5	57	56.5
<b>24 hours</b>	<b>59.5</b>	<b>59</b>	<b>57.5</b>	<b>57</b>
28 hours	59.5	59	57.5	57
60 ppm				
	Surfactant	Surfactant + DEA	Surfactant + PSM	Surfactant + DEA + PSM
4 hours	49.5	49.5	47	46
10 hours	50.5	50.5	48	47.5
18 hours	52	52	49.5	47.7
<b>24 hours</b>	<b>53.5</b>	<b>53</b>	<b>51</b>	<b>48</b>
28 hours	53.5	53	51	48
90 ppm				
	Surfactant	Surfactant + DEA	Surfactant + PSM	Surfactant + DEA + PSM
4 hours	46.5	46.5	43.5	43
10 hours	47.5	47.5	44.5	44.5
18 hours	48.5	48.5	45.4	45.4
<b>24 hours</b>	<b>49</b>	<b>49</b>	<b>46</b>	<b>46</b>
28 hours	49	49	46	46

Generally, in an indirect way, it was observed that after adsorption tests, the concentrations of the surfactant decreased with time (in the solution containing only surfactant).

The first chemical evaluated as a sacrificial agent was DEA, which had no effect on adsorption when mixed with the surfactant. On the other hand, the PSM caused a more significant decrease in the adsorption, acting as a sacrificial agent by decreasing the interaction between the surfactant and the disintegrated rock.

When the three chemicals were mixed, it was observed in most cases that the surface tensions measured were lower. This allows us to affirm that when the three chemicals are mixed (surfactant, DEA, and PSM), the concentration of surfactant available in solution after contact with the rock is higher and therefore the adsorption is lower.

These surface tension values were taken and interpolated on the graph of surface tension versus surfactant concentration to obtain the concentration values after contact with the rock (Table 6).

**Table 6—Indirect surfactant concentration (ppm) with time after contact with carbonate rock in 2000 ppm NaCl medium and fixed concentrations of DEA (1.5 mM) and PSM (100 ppm). Surfactant concentrations in the initial solution were 30, 60, and 90 ppm**

Surfactant concentration (ppm) after equilibration with carbonate rock				
30 ppm surfactant				
	Surfactant	Surfactant + DEA	Surfactant + PSM	Surfactant + DEA + PSM
4 hours	9	9.5	11.9	12.5
10 hours	7.6	8	9.5	10
18 hours	7	7.4	8.8	9.2
<b>24 hours</b>	<b>6.7</b>	<b>7</b>	<b>8.5</b>	<b>9</b>
28 hours	6.7	7	8.5	9
60 ppm surfactant				
	Surfactant	Surfactant + DEA	Surfactant + PSM	Surfactant + DEA + PSM
4 hours	21.5	21.5	28	31.7
10 hours	19.4	19.4	25.5	27
18 hours	16.8	16.8	21	26.4
<b>24 hours</b>	<b>14.4</b>	<b>15</b>	<b>18.7</b>	<b>26</b>
28 hours	14.4	15	18.7	26
90 ppm surfactant				
	Surfactant	Surfactant + DEA	Surfactant + PSM	Surfactant + DEA + PSM
4 hours	29.5	29.5	42	46
10 hours	27	27	37	37
18 hours	24	24	33.5	33.5
<b>24 hours</b>	<b>23</b>	<b>23</b>	<b>32.5</b>	<b>32.5</b>
28 hours	23	23	32.5	32.5

The adsorptions of the surfactant on carbonate rock were obtained by using the equation previously presented (Eq. 1) and are shown in Table 7.

**Table 7—Surfactant adsorption with time on carbonate rock surface (mg/g rock) in 2000 ppm NaCl medium and fixed concentrations of DEA (1.5 mM) and PSM (100 ppm). Surfactant concentrations in the initial solution were 30, 60, and 90 ppm**

Surfactant adsorption on carbonate rock surface (mg/g rock)				
30 ppm				
	Surfactant	Surfactant + DEA	Surfactant + PSM	Surfactant + DEA + PSM
4 hours	0.1055	0.1030	0.0911	0.0880
10 hours	0.1126	0.1106	0.1031	0.1006
18 hours	0.1156	0.1136	0.1066	0.1046
<b>24 hours</b>	<b>0.1171</b>	<b>0.1156</b>	<b>0.1081</b>	<b>0.1056</b>
28 hours	0.1171	0.1156	0.1081	0.1056
60 ppm				
	Surfactant	Surfactant + DEA	Surfactant + PSM	Surfactant + DEA + PSM
4 hours	0.1935	0.1935	0.1609	0.1423
10 hours	0.2040	0.2041	0.1734	0.1659
18 hours	0.2171	0.2172	0.1961	0.1690
<b>24 hours</b>	<b>0.2292</b>	<b>0.2262</b>	<b>0.2076</b>	<b>0.1710</b>
28 hours	0.2292	0.2262	0.2076	0.1710
90 ppm				
	Surfactant	Surfactant + DEA	Surfactant + PSM	Surfactant + DEA + PSM
4 hours	0.3041	0.3041	0.2413	0.2213
10 hours	0.3166	0.3167	0.2665	0.2665
18 hours	0.3317	0.3318	0.2841	0.2841
<b>24 hours</b>	<b>0.3368</b>	<b>0.3368</b>	<b>0.2891</b>	<b>0.2892</b>
28 hours	0.3368	0.3368	0.2891	0.2892

If the maximum adsorption of the surfactant for each concentration was obtained when this chemical was not in the presence of the other ones (DEA and PSM), calculations were made concerning the reduction of adsorption.

At 30 ppm, the surfactant in the presence of DEA had a reduction in adsorption of 1.28%. When PSM was added to the solution, the percentage adsorption reduction obtained was 7.68%. When surfactant, DEA, and polymer were present, the percentage reduction was 9.82%. In this way, there was a positive interaction between the chemicals, which helped to reduce the surfactant adsorption. At 60 ppm of surfactant, when the surfactants DEA and PSM were mixed, a more significant percentage reduction of adsorption was observed, with a value of 25.39%.

At 90 ppm, it could be observed that the DEA had no effect on the reduction of the adsorption of the surfactant. The percentage reduction in adsorption when PSM was added and when the three chemicals were mixed was the same (14.15%), probably because of the PSM alone.

These results indicate that the maximum synergy was obtained when using a surfactant concentration of 60 ppm. However, it can be observed that when the concentration of surfactant increases to a value above that mentioned, the synergy between the chemicals is null due to the possible reactions or mechanisms of adsorption that the surfactant has with the rock. In addition, a higher surfactant concentration implies a greater presence of surfactant ready to be retained in the surface of the rock.

Figure 6 shows the adsorption of the surfactant with time at a concentration of 30 ppm.

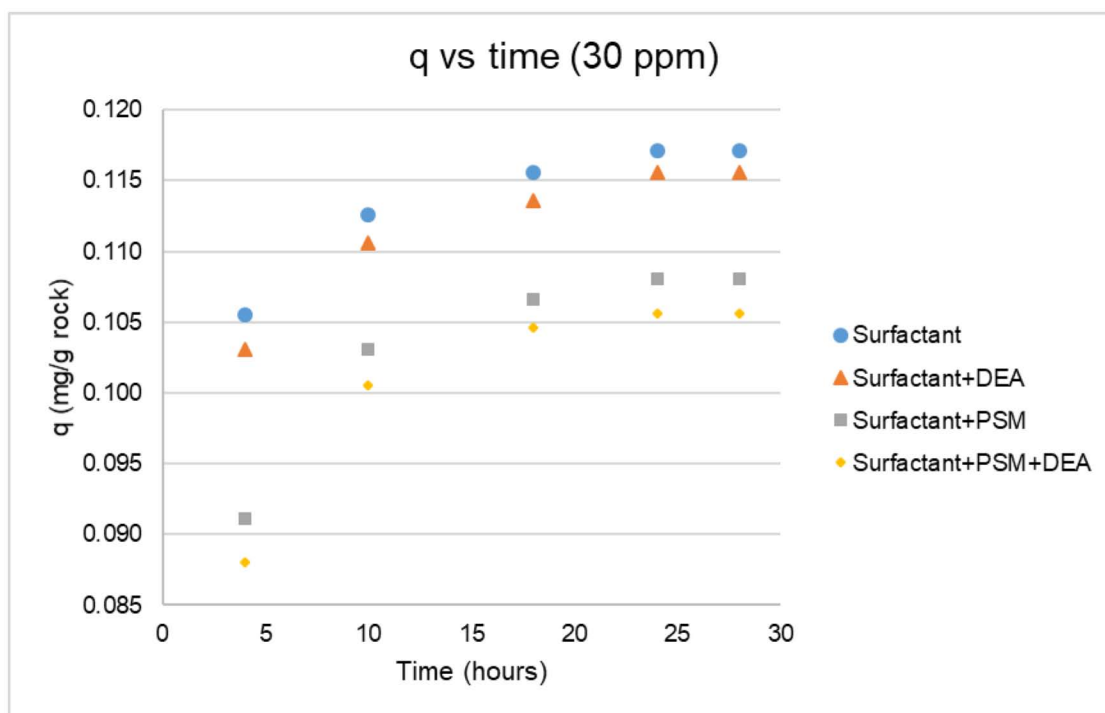


Figure 6—Surfactant adsorption with time on carbonate rock surface (mg/g rock) in 2000 ppm NaCl medium and fixed concentrations of DEA (1.5 mM) and PSM (100 ppm). The surfactant concentration in the initial solution was 30 ppm.

According to the results shown in Figure 6, when the surfactant was accompanied by the two chemicals, the adsorption was reduced compared to when there was only the surfactant in the saline medium. Also, it was possible to note that at early times (when the slope was more pronounced), a quick adsorption was achieved, followed by equilibrium, when the adsorption was almost constant, which implies that there would be no more interaction between the surfactant and the rock since much of the surface area of the latter had already been occupied.

As can be seen in Figures 7 and 8, the behaviour is similar for surfactant concentrations of 60 and 90 ppm, respectively. As the concentration of surfactant increases, a higher adsorption of the chemical will occur because there is a greater amount of surfactant available so that they can interact with both the rock surface area and the other components. Figure 8 shows similar behaviour between the surfactant system containing only the polymer chemical (PSM) and the system containing the two chemicals (DEA and PSM), which demonstrates the null action of the DEA agent on the retention of the chemical in the rock.

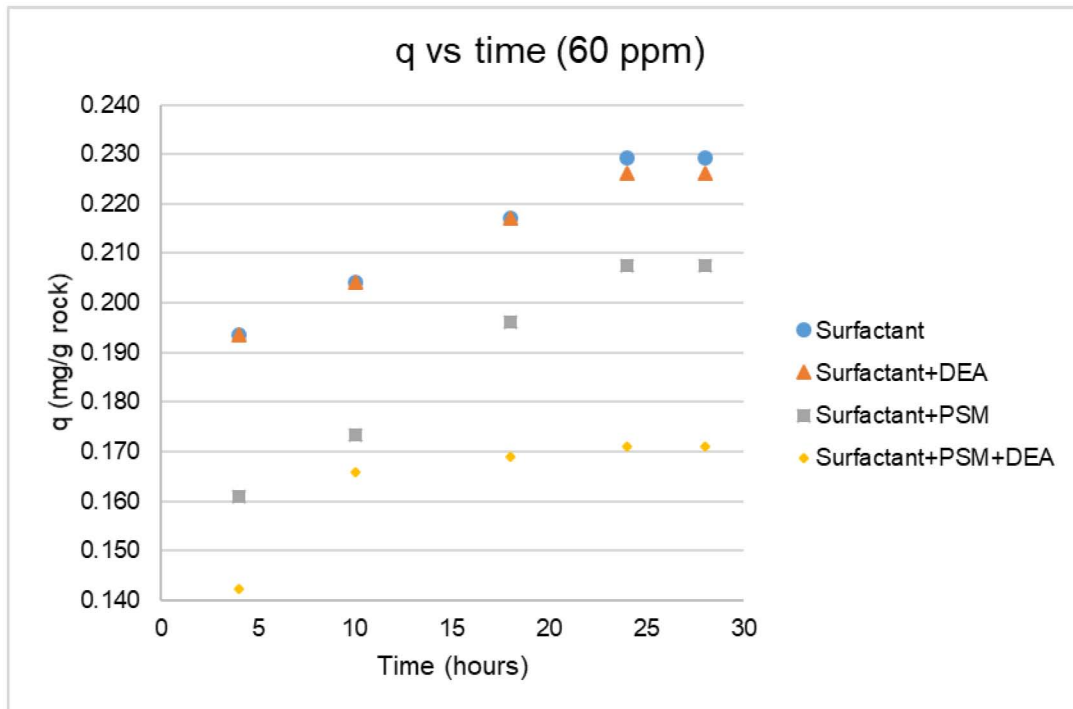


Figure 7—Surfactant adsorption with time on carbonate rock surface (mg/g rock) in 2000 ppm NaCl medium and fixed concentrations of DEA (1.5 mM) and PSM (100 ppm). The surfactant concentration in the initial solution was 60 ppm.

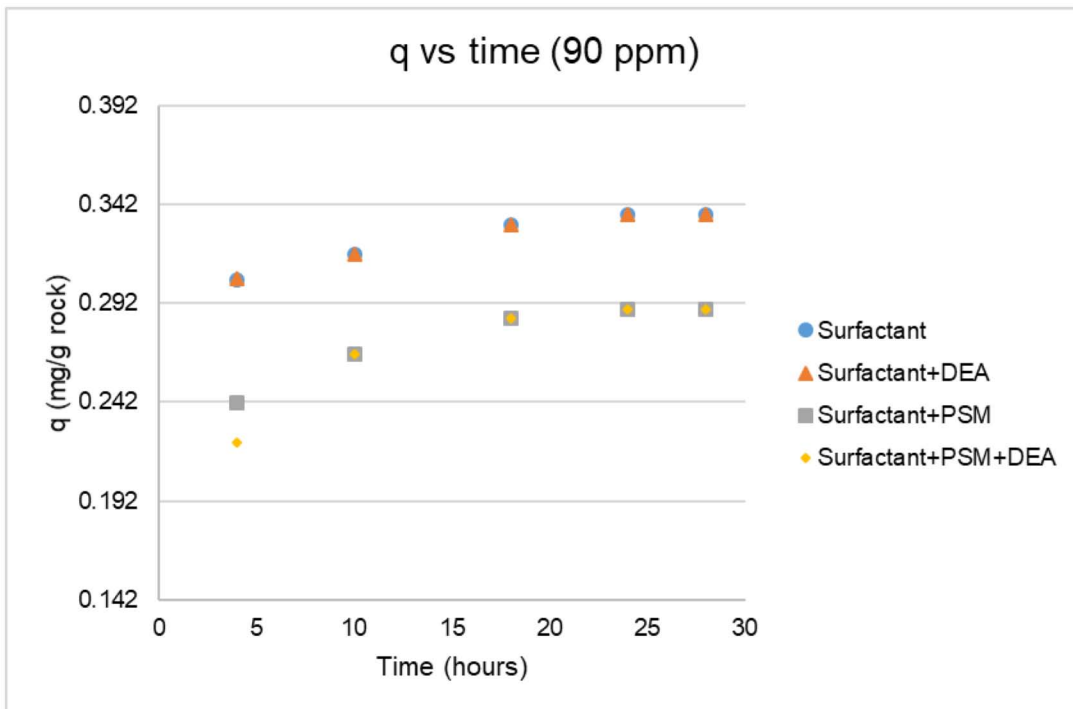


Figure 8—Surfactant adsorption with time on carbonate rock surface (mg/g rock) in 2000 ppm NaCl medium and fixed concentrations of DEA (1.5 mM) and PSM (100 ppm). The surfactant concentration in the initial solution was 90 ppm.

Figure 9 presents a summary of the absorption results when the surfactant was mixed with both chemicals (DEA and PSM).

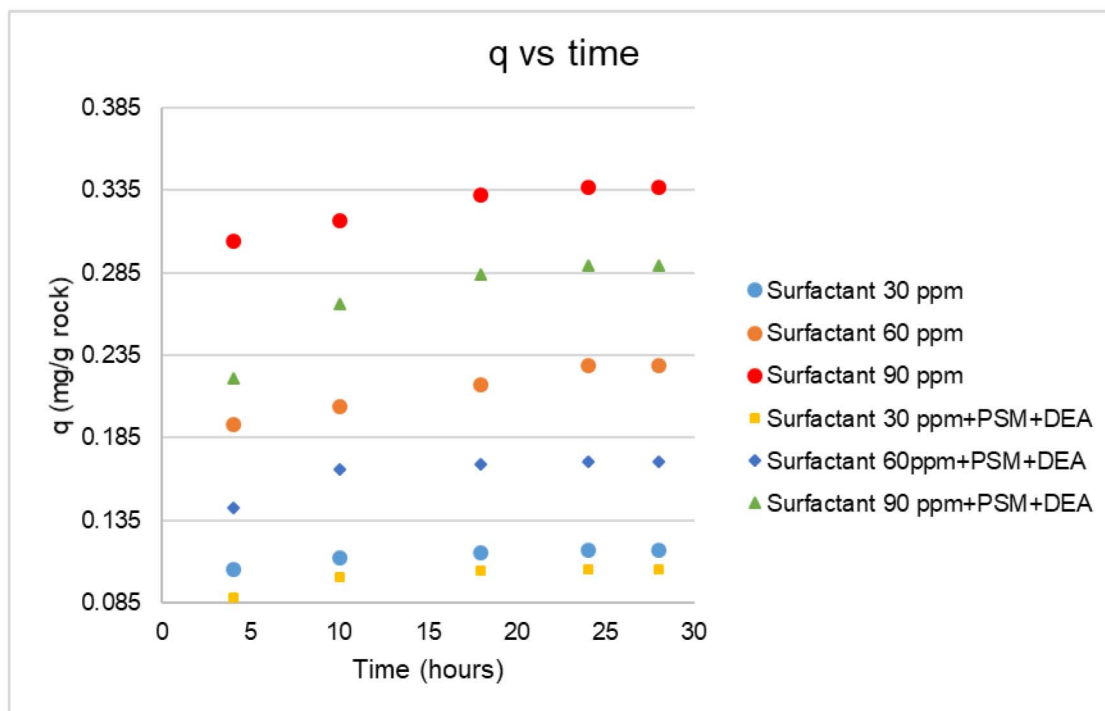


Figure 9—Surfactant adsorption with time on carbonate rock surface (mg/g rock) in 2000 ppm NaCl medium and fixed concentrations of DEA (1.5 mM) and PSM (100 ppm). The surfactant concentrations in the initial solution were 30, 60, and 90 ppm.

**Possible interaction between the chemicals and the disintegrated carbonate rock.** Normally it is supposed that the surface charge of carbonate rocks is of a positive nature. The anionic surfactant of this investigation is negatively charged; on the other hand, the chemicals to be evaluated as sacrificial agents (DEA and PSM) also present negative charges.

In this case, it can be said that the interaction between the rock and the surfactant is of an electrostatic nature, generated by opposite charges (negative surfactant head, positive rock charge) (Figure 10). In this way, it can be assumed that there is a competitive mechanism of adsorption between the chemicals (DEA and PSM), reducing the adsorption of the surfactant.

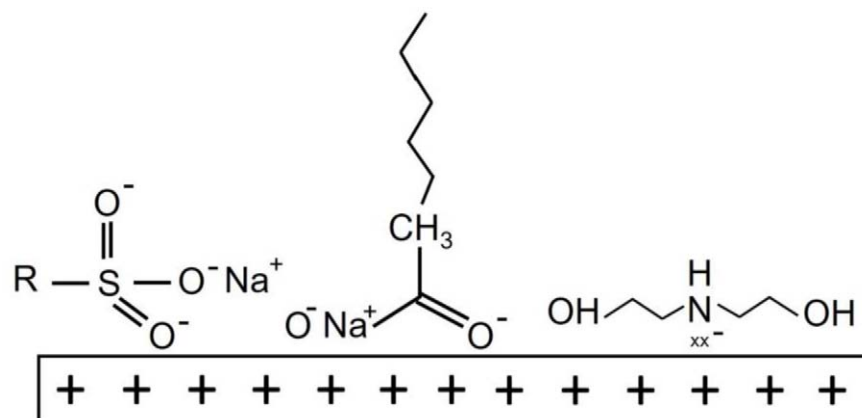


Figure 10—Possible interaction between the chemicals and the disintegrated carbonate rock

As already mentioned, the solutions with PSM showed a lower surfactant adsorption percentage in relation to the surfactant and surfactant + DEA solutions. Being a larger molecule, the PSM, upon reaching

the surface of the rock, may be adsorbed and the volume occupied by the molecule will prevent both the DEA and the surfactant from interacting with the surface area of the carbonate, presenting a steric effect.

## Conclusions

Based on the results of surface tension of the surfactant solutions after the contact with the rock, it was possible to determine the remaining concentration of the anionic surfactant in the saline solutions in the presence and absence of the chemicals DEA and PSM, indicating the capacity to act as a sacrificial agent.

In a saline medium (in this specific case, at low salinity), probably due to the presence of electrolytes, the value of the CMC is reduced.

The tests performed showed that as the concentration of surfactant increased, the adsorption also increased due to the greater number of molecules and hence a higher interaction with the rock's surface area.

In the research, is observed that the chemical DEA does not influence the adsorption of the surfactant; this is reflected in the values of adsorption reduction (as a percentage), which was not greater than 3%; nevertheless, the PSM had greater importance in the reduction of the losses of the surfactant.

In the tests performed, it was shown that when the surfactant was accompanied by the two chemicals, adsorption of surfactant was lower.

The results indicated a sacrificial function synergy between the chemicals (DEA and PSM) at the surfactant concentration of 60 ppm. This may possibly be attributed to a synergy interaction with the components of the disintegrated rock in this surfactant concentration; however, when the concentration of surfactant increased to a value above 60 ppm, the synergy between the chemicals was null.

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