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# INFLUENCE OF NaCl IN IONIC SURFACTANTS ADSORPTION IN SANDSTONE SURFACE

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**ABSTRACT**

Low interfacial tensions are one of the most important mechanisms relating to surfactant. Surfactant loss due to adsorption on the rock surfaces weakens the effectiveness of the chemical injected slurry, in reducing oil-water interfacial tension (IFT) and renders the process uneconomical. Surfactant flooding is enhanced oil recovery method (EOR) adopted in partially depleted oil reservoirs. However, surfactant adsorption can occur reducing the efficiency of EOR methods used. This work studied the influence of NaCl on anionic surfactant adsorption on sandstone. NaCl concentrations of 1.0 and 4.0% (w/w) were tested and adsorption isotherms were constructed. FTIR, XRD and thermogravimetric analysis were realized for support adsorption mechanism. The adsorption isotherms showed that salt concentration influenced the amount of adsorbed surfactant.



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## INTRODUCTION

Despite the constant current search for alternative energy sources that could eventually replace oil, this is still the main source of energy in the modern world (Chipalavela, 2013). The accelerated growth of society has demanded an increasing consumption of energy, which has encouraged the search for new methods for exploration and production of reservoirs to supply the energy needs of the planet. Oil recovery methods, especially the enhanced ones, are intended to obtain an additional oil recovery. Estimates in several locations showed an average recovery factor of 30%, considering only the conventional recovery methods. The aim of enhanced oil recovery corresponds to 70 % of the OOIP (Original Oil in Place) which is the average percentage volume remaining in reservoirs after conventional recovery (Thomas, 2004).

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Surfactant flooding is an enhanced oil recovery technique (EOR) adopted in partially depleted oil reservoirs (Agharazi-Dormani *et al.,* 1990). The solution of surfactant is used for the purpose of reducing the interfacial tension between oil and water, increasing the displacement efficiency inside the rock reservoir. One difficulty found in this method is the adsorption of surfactants onto reservoir rock surface which leads in the loss of this compound from the bulk phase. Thus, there will be less available surfactant to reduce oil-water interfacial tension which may render the method economical unfeasible (Bera *et al.,* 2013; Curbelo *et al.,* 2007). Adsorption is measured, generally, by the depletion method, where the change in surfactant concentration (depletion) after contact with adsorbents is measured. The results from the adsorption experiment are commonly expressed by adsorption isotherms, where the amount adsorbed is plotted as a function of equilibrium concentrations (Muherei and Junin, 2009). It has been shown that the nature of adsorption isotherm significantly depends on type of surfactant used, the morphological and mineralogical characteristics of the rock, the type of electrolytes present in the solution, and the presence of cosurfactants and alcohols (Scamehorn *et al.,* 1982; Liu *et al.,* 2004). The most of the reservoir rocks, such sandstone oil reservoirs, display of a net negative charge, and so, negatively charged surfactants (anionic) are usually considered in the in the surfactant flooding (Amirianshoja *et al.,* 2013). There are a lot of studies involving anionic surfactants in oil reservoir rocks (Bera *et al.,* 2013; Muherei and Junin, 2009; Amirianshoja *et al.,* 2013; Somasundaran and Krishnakumar, 1997; Weifeng *et al.,* 2011; Xing and Rankin, 2013). The action mechanism of the surfactant in the porous medium, partially filled by oil and salt, is a little complex, which encourage the development of studies in this field. Therefore, this article proposes to study the influence of different concentrations of NaCl on the adsorption of the anionic surfactant like basis soap (BS), in sandstone, used to increase the oil recovery factor.

## MATERIALS AND METHODS

### Materials

Calcined sandstone rock was kindly provided from Weatherford Lab, Texas, USA, to Núcleo Tecnológico de Cimentação de Poços de Petróleo (NTCPP), UFRN, Natal, Brazil; anionic surfactant (basis soap) was supplied by Gessy Lever and NaCl salt, analytical purity, were donated by UFRN, Natal, Brazil.

### Particle size

The sandstone sample was mashed and then sieved through sieves of 14, 48 and 100 mesh, which correspond to diameters of 1.168 mm, 0.295 mm e 0.147 mm, respectively (Foust *et al.,* 1982). The weight fraction from the sample retained on each sieve was calculated by mass balance.

### Adsorption

According to (Curbelo, 2006), the critical micelle concentration (cmc) and molecular weight of BS surfactant are, respectively, 5.4 x $10^{-3}$mol/L (1.69 g/L) and 286.1 g/mol. Thus, for adsorption test, solutions of 1.0 and 4.0 % NaCl at surfactant concentrations below and above the cmc were prepared. Adsorption experiments of surfactants on sandstone rock, were carried out in a shaker machine (Tecnal TE-420) were conducted in 250 mL erlenmeyer flasks at room temperature (~28 $^{o}$C). Each flask contained a constant mass of sandstone adsorbent (0.1 g) and BS surfactant –salt solution (Fig. 1). The flasks were brought to the incubator under constant shaking, in order to reach equilibrium. The mixture rest long enough for complete separation between solid and solution. Then, surfactant concentrations in each sample were determined. The adsorbed amount (Γ) was calculated by a simple mass balance between the initial and final solution conditions, represented mathematically by Equation 1.

$$\Gamma = \frac{V(C_0 - C_e)}{m} \qquad \text{......................(1)}$$

Where: $C_0$ and $C_e$ are initial and equilibrium concentrations of surfactant (mg/L) respectively, $V$ is volume of surfactant solution (L), $m$ is mass (g) and $\Gamma$ is the surfactant amount adsorbed on adsorbent (mg/g).

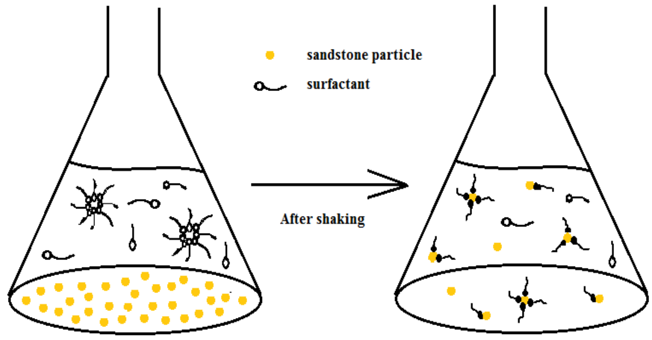



**Fig. 1. Adsorption in sandstone particle**

Adsorption Isotherms were plotted for each salt concentration studied.

### Adsorption models

The Langmuir and Freundlich models were studied to suit the experimental data. The equations of the Langmuir (2) and Freundlich (3) models are:

$$q = \frac{q_m K_L C_e}{1 + q_m C_e} \qquad \text{.................(2)}$$

$$q = K_F C_e^{1/n} \qquad \text{..................(3)}$$

Where: qis the surfactant amount adsorbed on adsorbent (mg/g), $C_e$is equilibrium concentrations of surfactant (mg/L), $q_m$is constant related to adsorption energy (L/mg), $k_L$is Langmuir constant (L/g), $k_F$is Freundlich constant (mg/g), n is empiric parameter.

### FTIR

Fourier Transform Infrared (FTIR) spectroscopy measure ments were carried out with IRPrestige-21 spectrometer (Shimadzu) using Potassium Bromide (KBr) as dispersing agent. Thin translucent disks were prepared by mixing approximately 0.7 mg of sample and 1% (w/w) of KBr and subjected to a pressure of 8.0 ton $cm^{-2}$. Spectra were obtained in range of 4500-400 $cm^{-1}$ in the transmittance mode. Five samples were analyzed: surfactant (BS); pure sandstone; sandstone adsorbed surfactant with 0.0%, 1.0% and 4.0% NaCl.

### XRD

Sandstone samples were characterized by X-ray diffraction (XRD) in XRD-7000 (Shimadzu) using CuK α radiation, 30 kV of voltage, 30 mA of current and a Ni filter. Data were collected in 2θ range of 5 - 80°.The analysis was made for: pure sandstone; sandstone with adsorbed surfactant 0.0% NaCl and 4% NaCl.

### Thermo gravimetric analysis

The thermal behavior of pure sandstone and sandstone with surfactant and 4% NaCl samples was carried out in a SDT Q600 thermogravimetric apparatus from TA Instruments. The analyzes were performed from room temperature to 900 °C with a heating rate of 10 °C $min^{-1}$, under flow of 100 mL/min of $N_2$, using approximately 30 mg of samples.

## RESULTS AND DISCUSSION

### Particle size

Sandstone particles were evaluated for Tyler sieves. The particles retained in range of - 48 + 100 mesh was used for adsorption experiments, with average diameter was 0.221 mm.

### Adsorption

The influence of NaCl concentration on adsorption isotherm is showed in Fig.2.

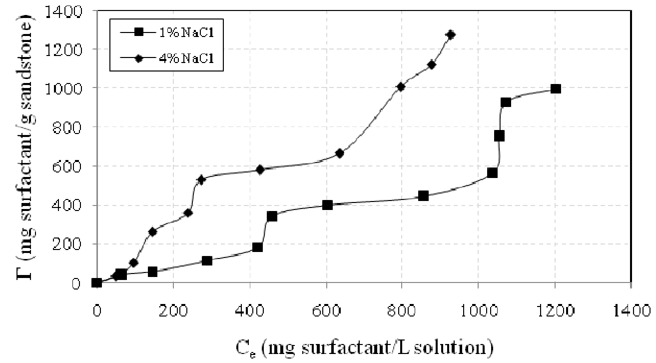



**Fig. 2. Influence of NaCl concentration on the adsorption isotherm**

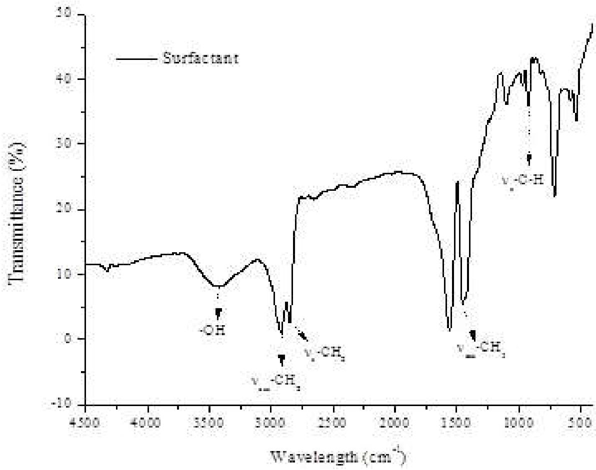
It observed (Fig. 2) that the adsorption was more pronounced at salt concentration of 4% NaCl, as noted by comparing surfactant's adsorbed amounts at the same equilibrium concentrations, for example, at 600 mg surfactant /L solution, the adsorbed amount is always higher for 4% NaCl, approximately, 400 mg surfactant/g sandstone rock than for 1% NaCl, 620 mg surfactant/g sandstone. For this sample, adsorption will persist until there is no more mass transfer between surfactant solution and the rock surface. The monolayer may be achieved, and later a multilayer was formed, probably when the equilibrium concentration get close to thecmc of the surfactant. The reduction of electrostatic repulsion between adsorbed species as result of high salt concentrations will contribute for increase surfactant's adsorption. Furthermore, the fact that NaCl be more soluble than SB also results in an increase adsorption capacity. Fig.2 show also the adsorption isotherm for the surfactant solution with 1% NaCl, which is observed that the monolayer starts from the equilibrium concentration ($C_e$) of, approximately,460 mg/L, until 1040 mg/L, with a maximum amount adsorbed of 560 mg surfactant/g rock, due to interactions among surfactant's no polar tails in concentrations close to the cmc. For surfactant solution with 4% NaCl, a maximum amount adsorbed was greater and equal to 660 mg surfactant/g rock. Fig. 2 show that the curves described have different behaviors according to surfactant concentration. Table 1 shows Freundlich model parameters that admit adsorption in multilayers, adjusted to experimental data obtained for surfactant adsorption, with 1% NaCl and 4% NaCl. Langmuir Model did not adjust the experimental data because it only admits monolayer adsorption. Freundlich model was well represented by the experimental data, showing an unfavorable adsorption, n = 0,71 and 0,96 to 1% and 4% NaCl, respectively (Table 1), because values of n in the range of 1 <n <10 indicate favorable adsorption. These is a good result for the objective of this work, because it decreases the surfactant loss by adsorption in rock during the EOR.

**Table 1. Parameters of Freundlich Model**

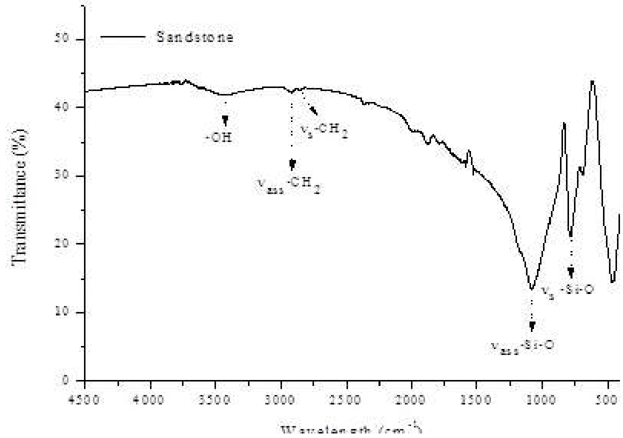
| | Model equation linearized | Parameters | |
|---|---|---|---|
| | | $K_L$ | n |
| 1 % NaCl | Ln qe = -3,0546 + 1,4 Ln Ce | 0,0471 | 0,71 |
| 4 % NaCl | Ln $q_e$ = 0,0245 + 1,0408 Ln $C_e$ | 1,0248 | 0,96 |

### FTIR

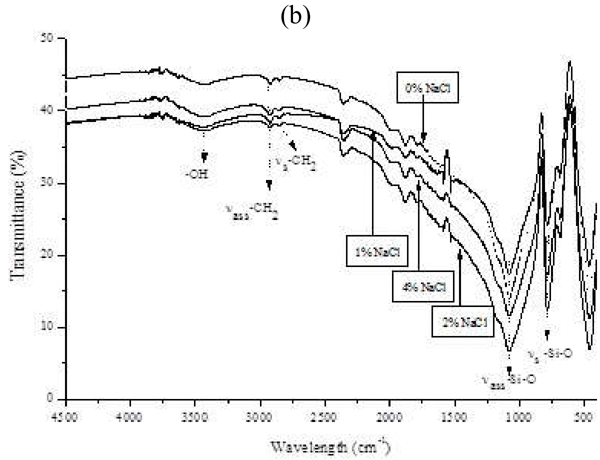
FTIR spectra of pure BS (Fig.3, a), pure sandstone (Fig.3,b) and sandstone with adsorbed surfactant (Fig.3,c) were obtained to evaluate some chemical interaction between BS and sandstone through chemical bong vibration.




(a)




(b)




(c)

**Fig. 3. Transmittance (%) versus wavelength ($cm^{-1}$) to pure BS (a), pure sandstone (b) and sandstone with adsorbed surfactant (c).**

By Fig.3 (a), (b) and (c) is observed that some of BS wavelengths, 3438, 2927, 2844 and 1446 $cm^{-1}$, are found in pure sandstone and sandstone with BS adsorbed, but in this latest, the transmittance's values are different from the pure sandstone rock, represented by more pronounced peaks, indicating the adsorption of BS in sandstone. Table 2 show the vibrations identified corresponding to each wavelength indicated in the graphs.

**Table 2. Corresponding vibration to each wavelength indicated in Fig.4 (a), (b) and (c)**

| Wavelength ($cm^{-1}$) | Vibration |
|---|---|
| 785 | Symmetrical axial deformation of Si-O-Si bound |
| 916 | Symmetrical angular deformation of C-H, in alkenes |
| 1081 | Asymmetrical axial deformation of Si-O-Si bond |
| 1446 | Asymmetrical angular deformation of $–CH_3$ |
| 2844 | Symmetrical axial deformation of $-CH_2$ |
| 2927 | Asymmetrical axial deformation of $-CH_2$ |
| 3438 | Axial deformation of O-H bond (associated) |

## XDR

Fig. 4 shows the XRD of pure sandstone; sandstone with surfactant (0% NaCl); sandstone with surfactant and 4% NaCl.

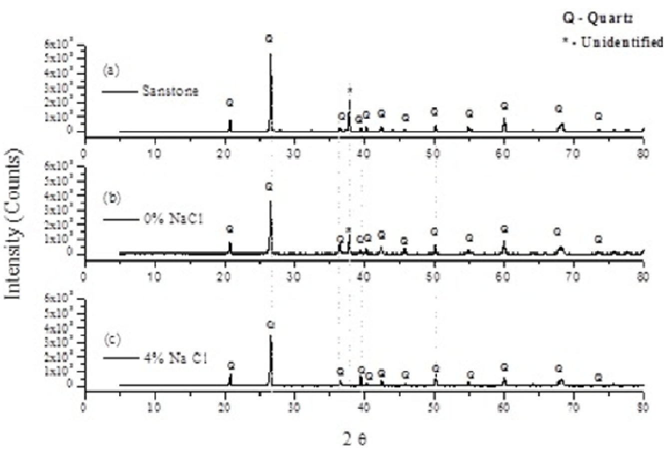



**Fig. 4. XRD of pure sandstone (a) of sandstone with BS (b) and sandstone with BS and 4% NaCl (c)**

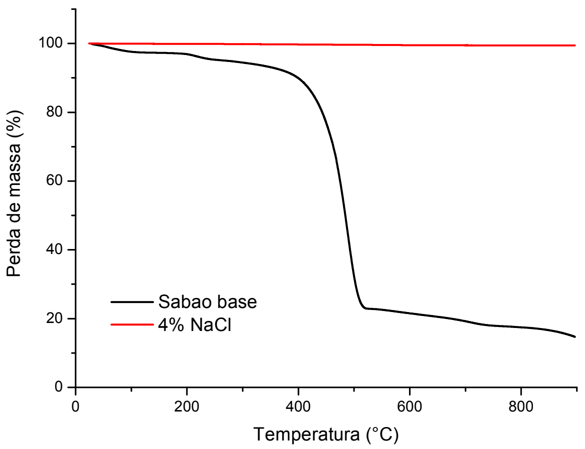



**Fig. 5. Loss of mass (%) for pure BS and sandstone with BS and 4% NaCl**

According to X-ray diffraction results, the sandstone shows a crystal structure, predominantly of alpha quartz (Q), with hexagonal crystal structure, identified in file nº 089 277 ICSD by peaks sited at 2θ: 20.84°; 26.6°; 36.51°; 39.4°; 40.3°; 42.43°; 45.7°; 50.16°; 54.81°; 59.98°; 60.06°; 67.68°; 64.06°; 68.25°; 73.4°; 75.66° and 77.54° (Fig.4). The addition (or adsorption) of BS (Fig.5b - 0% NaCl) and BS plus 4% NaCl (Fig.4 c) did not changed the crystalline structure of sandstone, however influenced in the crystallinity, observed by intensity reduction of quartz main peak, located at 2θ 26.6°. The decrease in crystallinity may be associated with surfactant adsorption on the surface layer of the adsorbate. As there wasn't almost no variation in intensity between the Fig.4 (b and c) compared with the variati on between Fig.4 (a and b) and Fig.5 (a and c), it seems that the NaCl influences the amount adsorbed surfactant.

### Thermogravimetric analysis

Fig.5 shows the loss of mass (%) for pure BS and sandstone with BS surfactant and 4% NaCl. BS sample showed a weight loss of about 70% in the temperature range of 327-527 °C associated with the decomposition of organic compounds in these surfactants. However, the sandstone sample 4% NaCl did not exhibit thermal event, showing thermally stable. Thus, BS with 4% NaCl in the sandstone is resistant to the high temperatures exposed in the oil reservoirs during the processes of enhanced oil recovery, without losing its properties. So, there will be no efficiency reduction due to loss of mass.

### Conclusion

Adsorption isotherms for solutions containing 1 and 4% NaCl showed a monolayer adsorption of surfactant. The 4% NaCl solution showed a higher adsorption capacity than 1% NaCl concentrations, since salt helped reduce electrostatic repulsion between adsorbed surfactant species, increasing the adsorption capacity of the sandstone. So, petroleum wells which use surfactant flooding (BS) as EOR, oil recovery factor, in this case, will be significantly affected by high salt concentrations, since the higher is the concentration of salt, the higher will be surfactant adsorption on rock and, therefore, the greater will be the amount of surfactant necessary to achieve the same oil recovery factor.

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