Recovery of Oil in Limestone with Cationic Surfactant: Investigation of the Adsorption, Wettability, and Spontaneous Imbibition

Vanessa Cristina Santanna*, Tereza Neuma Castro Dantas, Allan Martins Neves, Juliana Rocha Dantas Lima, and Camila Nóbrega Pessoa

Department of Petroleum Engineering, Federal University of Rio Grande do Norte, Natal, Brazil

ABSTRACT

The performance of petroleum recovery methods is dependent on the characteristics of the reservoir rock, oil quality, and formation water. One fundamental feature for considering petroleum recovery methods is the wettability of the rock reservoir. Also, this feature impacts the displacement of fluids in the rock reservior. In the case of the limestone, which normally features oil wettability, enhanced recovery methods are responsible for altering surface wettability. In this study, the effect of concentration of a cationic surfactant in the oil recovery from limestone is shown. In these tests, finite-bath technique was used to investigate adsorption by varying the amount of adsorbent and contact time. By carrying out contact angle assays, the wettability of the limestone was assessed. In addition, the oil recovery was effected by spontaneous imbibition. In this study, the limestone samples with solutions of CTAB in the concentrations of 0.8596 g/L and 1.2280 g/L, using a 2% KCl solution are treated. The results showed enhanced adsorption of CTAB at the CMC. The nature of this phenomenon did not induce changes in the wettability of the rock, which was confirmed by the contact angle measurements. In the spontaneous imbibition, more oil could be recovered when using a CTAB below the CMC, possibly due to less intense adsorption by the limestone.

Keywords: Imbibition, Surfactant, Oil Recovery, Adsorption, Limestone

INTRODUCTION

Rock wettability is a decisive parameter in the production and recovery of oil for it affects the economic viability of potential projects. It can occur in diverse environments such as low-permeability and stratified limestone reservoirs, naturally fractured reservoirs, and even high-permeability sandstone reservoirs.

The great majority of carbonate rocks presents wettability that favors oil and presents low produtivity. Therefore, many studies seek to invert the wettability in this type of rock to increase productivity. The use of surfactants in advanced recovery processes in carbonate rock aims to alter the rock's wettability, promoting oil flow, and consequently, increasing recovery. The use of

*Corresponding author

Vanessa Cristina Santanna

Email: vanessasantanna@yahoo.com.br

Tel: +55 849 9988 5780

Fax: +55 849 9988 5780

surfactants in the process leads to an increase in surface wettability lowering water surface tension and promoting adsorption in the solid surfaces. Literature offers several reports on the study of the effects of wettability and heterogeneity of the rock on the production and recovery of oil [1,2,3,4,5,6]. However, when researching this subject, many gaps and inconsistencies can be found.

Imbibition experiments at 40 °C with 100% oil saturated cores, using CTAB surfactant concentration in the range of 0.13 to 5.0 wt.% were carried out by Standnes and Austad in 2000 [7]. It is observed that the imbibition rate and the oil recovery increase with increasing concentration of cationic surfactants above their critical micelle concentration (0.2 wt.%) [7]. However, concentrations much higher than the CMC from 1.0 to 5.0 wt.% impair the recovery. Moreover, this has been ascribed to the solubilization of recovered oil in the micelles. Based on this premise, this work uses CTAB concentrations 30 % below its CMC (0.8596 g/L) and at the actual CMC (1.2280 g/L).

Spontaneous imbibition assays in limestone plugs, both saturated with oil (100 %) and containing initial water (Swi > 0) were carried out by Babadagli and Boluk in 2005 [8]. Anionic, nonionic, and cationic surfactants in concentrations below and above their CMC's were tested by them [8]. Also, it was verified that for Swi = 0, the nonionic IGEPAL and the cationic CTAB were more efficient at low concentrations.

Moreover, the spontaneous imbibition in limestone plugs saturated with oil was investigated by Høgnesen in 2006 [9]. The ability of CTAB was again examined above its CMC. Then, it was confirmed that surfactant concentration directly affected recovery rates. Observations show that

when higher interfacial tensions were generated between oil and CTAB solutions, capillary forces were dominant in the oil displacement [9]. For the most part, gravity forces governed oil displacement in lower interfacial tensions.

The spontaneous imbibition of limestone samples saturated with oil (S_{wi}=0) was examined by Babadagli in 2006 [10]. Nonionic, anionic, and cationic surfactants were used in concentrations below and above their CMC's. The results showed that, in general, when using concentrations above the CMC, the recovery rates are lower than when using brine, with only two exceptions for such behavior: using a fatty quaternary amine salt and the anionic hexylene glycol sulfonate.

The surfactant effects on dolomite rocks were studied by Jarrahian et al in 2012 [16]. Also, three surfactants: C_{12}TAB (cationic), TritonX-100 (nonionic), and SDS (anionic) were studied by them. Based on the results, the cationic surfactant C_{12}TAB presented the highest wettability, promoting ionic interactions, and leading to increased water wettability.

Dodecyltrimethylammonium chloride (DTAC) below and above the CMC in the spontaneous imbibition of limestone samples saturated with oil was used by Pons-Jiménezo et al in 2014 [11]. Then it was observed that the recovery rate was directly proportional to the surfactant concentration, achieving the highest percentage with the highest amount of surfactant used.

A methodology was presented by Wang et al in 2015 to determine the static adsorption of the dodecyl hydroxypropyl sulfide (DSB) over limestone using HPLC and zeta potential measures [17]. Results showed that increasing NaCl concentration caused a decrease in DSB adsorption in limestone surface due to an increase in zeta potential. In contrast,

the DSB adsorption started with a decrease and gradually increased with the increase in CaCl$_2$, in response to the zeta potential action in the surface. The wettability alteration in carbonate rock by combining brine water with surfactant during water flooding was studied by Karimi et al in 2016 [12]. Different brine formulations were tested through contact angle measurements and spontaneous imbibition experiments in oil-wet limestone core samples, both in the presence and absence of surfactant (dodecyltrimethylammonium bromide -DTAB). Contact angle measurements revealed that all low salinity brine solutions changed the wettability of oil-wet surface towards a more water-wet state. In the presence of cationic surfactant, utilizing both, with the wettability influencing ions, more water-wet surfaces are resulted. The spontaneous imbibition results show that the combination of the effect of wettability influencing ions (Mg^{+2} and SO$_4^{-2}$) along with the cationic surfactant can result in a remarkable oil production.

In the present work, the influence of the cationic surfactant cetyltrimethylammonium bromide (C$_{16}$TAB) concentration on oil recovery from limestone by wettability, adsorption, and spontaneous imbibition is examined. Traditionally, literature describes these parameters separately, but when studying them combined one can achieve interesting results.

EXPERIMENTAL PROCEDURES
Materials and Method
Fluids and Rock

The chemicals used in this investigation were the cationic surfactant cetyltrimethylammonium bromide (CTAB), purchased from VETEC, with a purity of 99 %; and potassium chloride, provided by Synth, with a purity of 99 %. Petroleum samples were collected from the Ubarana field (Brazil) and kindly supplied by Petrobras (oil = 0.8344 g/mL specific mass and 2.90 cP viscosity). Limestone samples were extracted from the Jandaíra formation, in the State of Rio Grande do Norte (Brazil), classified as calcite rock.

Corresponding to the brine solution used in the experiments, 2 % (w/v) KCl aqueous solutions were prepared. This saline solution was then used as the solvent of two surfactant systems which were tested, with CTAB concentrations of 0.8596 g/L (below the CMC) and 1.2280 g/L (at the CMC).

Adsorption Assays

Limestone samples were calcined (at 250 °C for 6 hours), crushed, and sieved to be used in the adsorption assays as 100-mesh particles. Analyses of the adsorption phenomena were made with the finite-bath technique in a Dubnoff waterbath. First, the mass of adsorbent (limestone) was varied in samples of 16 g, 24 g, 32 g, 40 g, and 48 g for each solution (2% KCl without CTAB, and solutions of CTAB in 2% KCl at concentrations of 0.8596 g/L and 1.2280 g/L), for 2 hours, under constant stirring at 30 °C. Then, these samples were filtered out and surface tension measurements were acquired with a SensaDyne tensiometer. Following, the surfactant concentration was determined in each sample by plotting an analytical curve with surface tension (η) versus concentration (ln C) data [13]. The best-fit equation was η = -1.7927 (ln C) + 41.417, with R^2 = 0.9834. The adsorption capacity (q, in mg/g) was calculated by equation 1,

$$q = [V(C_0 - C_e)]/m \qquad (1)$$

where: C$_0$ is the initial surfactant concentration (mg/mL), C$_e$ is the concentration of surfactant

in the filtrate (mg/mL); V is the solution volume (mL); and m is the mass of adsorbent (g).

The equilibrium mass was determined for each solution by varying the contact time in intervals of 10, 20, 30, 60, 90, and 120 minutes, under constant stirring, at 30 °C. For each experiment carried out at a different time interval, all samples were filtered out and the surface tension of the filtrate was assessed to determine the surfactant concentration in it. Then, it was possible to establish the equilibrium time for the adsorption. Langmuir and Freundlich isotherms were compared with the experimental data to verify which adsorption model provides the best fit. These theoretical models obey the linearized equations 2 and 3 respectively.

$$C_e/q = 1/(K_L q_m) + C_e/q_m \qquad (2)$$

$$\ln (q) = \ln (K_F) + (1/n) \ln (C_e) \qquad (3)$$

where: q_m (mg/g) is the adsorption capacity; K_L (mL/mgr) is the equilibrium constant; and K_F and n are empirical constants, indicating adsorption capacity and intensity of the adsorption energy respectively.

Contact Angle Measurements

Calcined limestone plugs (at 250 °C for 6 hours) were crushed in fine particles, which were sieved and collected in a 200-mesh plate. By using a hydraulic press, cylindrical tablets were prepared with the aim of reducing roughness, which consists of surface irregularities in a small scale on the limestone surface, and aiding contact angle measurements.

The saturation of the rock tablets was performed with crude oil with density of 0.8344 g/mL and viscosity of 2.90 cP. The tablets were allowed to interact with the oil for 48 hours in an oven kept at 50 °C. After saturation, the tablets were cleansed

with toluene and n-heptane, and their dry masses were registered before and after saturation with oil [14]. Then imbibition was carried out with CTAB solutions in 2% KCl at surfactant concentrations of 0.8596 g/L and 1.2280 g/L, and also in 2 % KCl brine (without surfactant), for 30 minutes, at room temperature (25 °C). For reference, the conditions under which the tablets were tested are shown in Table 1.

Table 1: Imbibition fluids for each tablet.

Tablet	Imbibition fluid
1	KCl 2%
2	
3	
4	
5	CTAB 0.8596 g/L
6	
7	
8	
9	CTAB 1.2280 g/L
10	
11	
12	

Contact angle measurements were acquired with the imbibed tablets using the 2 % KCl solution and crude oil in a Krüss goniometer model DSA100.

Imbibition Assays

Limestone cylindrical plugs with 4.0 cm diameter and 4.0 cm length were previously calcined at 250 °C for 6 hours with the objective of removing all humidity and removing organic matter. Their average porosity was 42%. For the imbibition assays, the plugs were also saturated with oil for 48 hours in an oven at 50 °C. Later, the plugs were cleansed with toluene and n-heptane and, finally, allowed to dry and weighed [14]. Plugs dry masses were also registered before and after saturation

with oil.

The spontaneous imbibition assays were carried out with a simple glass cell, vertically disposed and attached to a graduated tube at a higher level. During the imbibition assays, oil-saturated plugs were immersed in the cell containing brine (2% KCl) to simulate conventional oil recovery, with surfactant solutions (CTAB) at the concentrations listed previously (0.8596 g/L and 1.2280 g/L in 2 % KCl) to simulate enhanced oil recovery. All assays were carried out at 25 °C. The volume of oil that was displaced by capillary and gravity forces was obtained by readings along the graduated tube (to an error of 0.1 mL), and recorded every 5 days, during 60 days. The total oil recovery rate (RR), in percentage (%), was calculated with equation 4:

$$RR = (V_{or} / V_{ooip}) * 100 \% \tag{4}$$

where: V_{or} is the volume of residual oil and V_{ooip} is the original oil in place (in mL).

RESULTS AND DISCUSSIONS
Adsorption

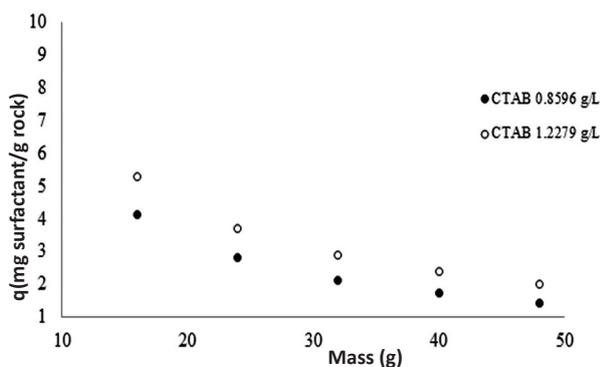Figure 1 shows the adsorption data acquired when using the surfactant below and at the CMC.

It indicates that adsorption in finite-bath experiments with varying adsorbent mass is more effective at the CMC. According to [15], when studying the adsorption of a cationic surfactant, Cetylpyridinium chloride (CPC), and an anionic surfactant, sodium dodecyl sulfate (SDS), in carbonate materials, verified that the adsorption of cationic surfactants in natural carbonates is linked to the silica composition present in the carbonate samples. There is a strong electrostatic interaction between CPC and the negative poles of silica and clay.

The equilibrium adsorption masses for both surfactant concentrations were established as 40 g of rock sample with 0.8596 g/L and 1.2280 g/L (Figure 1). The equilibrium is observed in the point where the adsorption practically stops varying with the increase in adsorbent mass. After this finding, new finite-bath experiments were devised with the optimized adsorbent mass by changing the contact time. This is depicted in Figure 2, which shows that the variation in the amount of adsorbed matter is minimal within the studied time interval, and therefore the contact time is not a much influent parameter in the investigation.
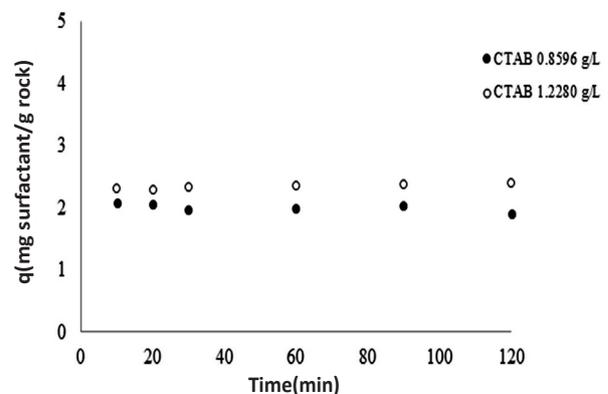

Figure 1: Adsorption data when using CTAB below the CMC (0.8596 g/L) and at the CMC (1.2280 g/L).

Figure 2: Adsorption of CTAB below and at the CMC as a function of contact time.

Langmuir and Freundlich isotherms were applied to the experimental adsorption data with the surfactant solutions in the limestone samples. Figures 3 and 4 show the fittings of such data with both models.
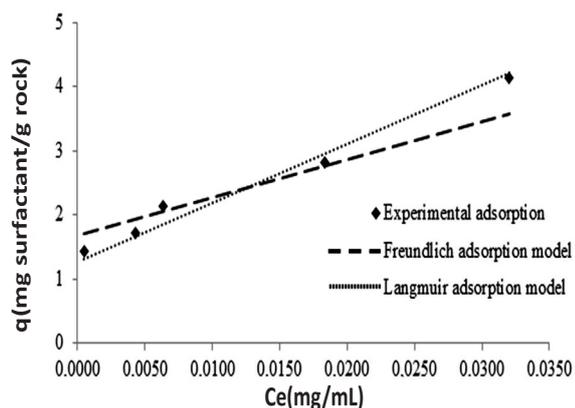

Figure 3: Langmuir and Freundlich isotherms for CTAB below the CMC (0.8596 gr/L).
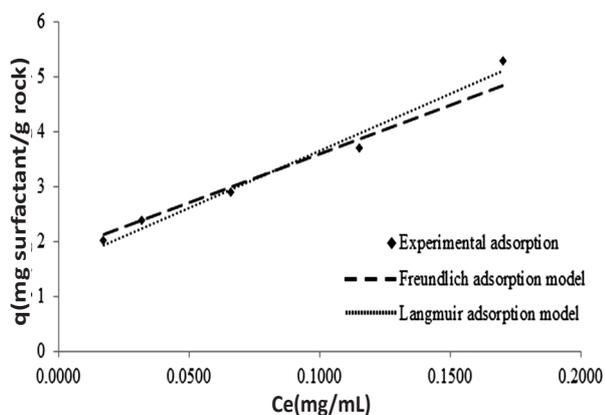

Figure 4: Langmuir and Freundlich isotherms for CTAB at the CMC (1.2280 g/L).

Table 2 shows the equations of the isotherms for the CTAB samples at concentrations below the CMC (0.8596 g/L) and at the CMC (1.2280 g/L).

Table 2: Non-linear isotherm equations for CTAB.

Concentration	Equation	Correlation coefficient
Below the CMC (0.8596 g/L)	Langmuir $q = (4.4228*188.4167*C_e)/ (1+188.4167*C_e)$	0.9165
	Freundlich $q = 7.6860*(C_e^{0.2364})$	0.8439
CMC (1.2280 g/L)	Langmuir $q = (6.3694*17.4444*C_e)/ (1 + 17.4444*C_e)$	0.8863
	Freundlich $q = 9.3933*(C_e^{0.3948})$	0.9380

The correlation coefficients shown in Table 2 and the plots depicted in Figures 3 and 4 confirm that the experimental data for the surfactant concentration of 0.8596 g/L are better adjusted with the Langmuir model (in this adsorption model, a continuous monolayer of adsorbate molecules is formed surrounding a homogeneous solid surface), also, for the surfactant concentration of 1.2280 g/L, the Freundlich isotherm is a better fit. One can conclude that surfactant adsorption on the reservoir possibly occurs as monolayers in lower concentrations, as suggested by the Langmuir model, with surfactant molecules behaving as monomers. When more surfactant is added, the formation of multilayers is favored, which is suggested by the Freundlich model. One can also point out that micelles were probably formed under such circumstance, since the CMC was reached.

Contact Angle

In the contact angle assays, the tablets were saturated with oil. The experiments analyzed twelve different samples. The amounts of remaining oil in each experiment are shown in Table 3, and the corresponding contact angles are shown in Table 4.

Table 3: Oil volumes in the tablets.

Tablet	Initial mass (g)	Mass after saturation (g)	Mass of remaining oil (g)	Oil volume (mL)
1	0.4094	0.4293	0.0199	0.0240
2	0.3990	0.4281	0.0291	0.0351
3	0.4150	0.4445	0.0295	0.0355
4	0.3917	0.4163	0.0246	0.0296
5	0.3890	0.4150	0.0260	0.0313
6	0.4115	0.4413	0.0298	0.0359
7	0.3865	0.4124	0.0259	0.0312
8	0.4124	0.4423	0.0299	0.0360
9	0.3895	0.4179	0.0284	0.0342
10	0.4014	0.4285	0.0271	0.0326
11	0.3982	0.4269	0.0287	0.0346
12	0.3968	0.4244	0.0276	0.0332

Table 4: Contact angles for the assays with the limestone tablets.

Tablet	Imbibed fluid	Fluid used in the contact angle assay	Contact angle
1	Brine	Brine	126.20
2	Brine	Brine	109.40
3	Brine	Oil	23.00
4	Brine	Oil	26.98
5	CTAB 0.8596 g/L	Brine	119.77
6	CTAB 0.8596 g/L	Brine	119.45
7	CTAB 0.8596 g/L	Oil	26.77
8	CTAB 0.8596 g/L	Oil	25.74
9	CTAB 1.2280 g/L	Brine	118.69
10	CTAB 1.2280 g/L	Brine	120.99
11	CTAB 1.2280 g/L	Oil	27.39
12	CTAB 1.2280 g/L	Oil	20.50

These results show that the rock wettability was not much affected by the surfactant solutions. Moreover, better results would have been obtained if the wettability of oil-wet limestone had changed to water-wet conditions because this would enhance oil recovery by imbibition. For tablets imbibed with 2% KCl, the values indicate that the limestone is oil-wet, since the angles are higher than 90º when brine is used and much lower than 90º when oil is used in the contact angle assays. When imbibition is promoted by the surfactant solutions, the contact angles remained the same, which is an indication that the wettability of the rock is not altered. The ionic character of the surfactant is possibly the most relevant parameter to justify such findings. Adsorption on the rock surface may mainly occur through the ionic moiety of the surfactant molecule; therefore, leaving the nonpolar tails away from more intense interactions with the surface. Then the rock wettability maintains its original oil-wet feature.

Imbibition

In the imbibition assays, it could be verified that the oil recovery is enhanced with CTAB solutions below the CMC, as shown by Figure 5. Oil production could only be observed from the tenth day after imbibition started, and was kept constant until the end of the study.
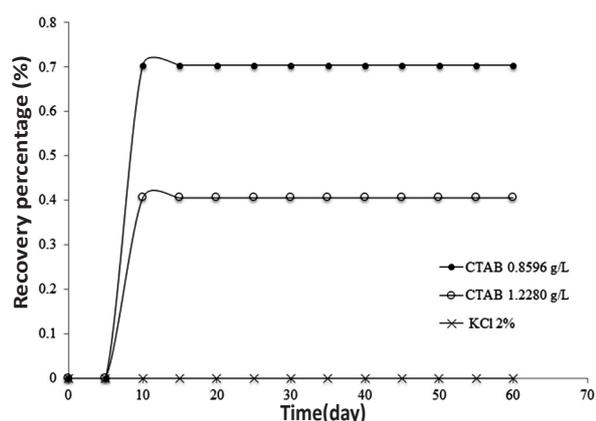

Figure 5: Spontaneous imbibition assays with the limestone in different solutions.

The oil recovery rates were 0.7 % (with CTAB below CMC), 0.4 % (with CTAB at the CMC), and 0 % (with 2 % KCl brine), because fewer surfactant molecules are adsorbed on the rock surface below the CMC, thereby increasing the concentration of free surfactant molecules. The presence of these free surfactant molecules help reduce surface tension. Ultimately, this favors oil recovery because the surfactant at the CMC (1.2280 g/L) is in the micellar form and cannot further decrease surface tension.

CONCLUSIONS

Surfactant concentration is an important parameter to be considered when its effects on adsorption which take place in oil recovery is investigated. This work typically establishes the limits for enhanced surfactant adsorption with increasing surfactant concentration in the case of CTAB-limestone

systems. Surfactant monolayers are formed below the CMC, but multiple layers are favored when more surfactant is added. However, the rock wettability barely is affected by surfactant concentrations, and, in the case of limestone, its original oil-wet character is maintained. In another approach, imbibition assays could confirm that oil recovery is actually affected by surfactant concentration, in that more oil could be extracted below the CMC, possibly due to less intense adsorption between the surfactant molecules and the rock surface.

ACKNOWLEDGMENTS

NOMENCLATURES

CMC	: Carboxymethyl Cellulose
CTAB	: Cetyl Trimethylammonium Bromide
KCl	: Potassium Chloride

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