

## **A Laboratory Investigation into Wettability Alteration of Carbonate Rock by Surfactants: The Effect of Salinity, pH, and Surfactant Concentration**

**Mohsen Seid Mohammadi, Jamshid Moghadasi\*, and Amin Kordestany**

Department of Petroleum Engineering, Petroleum University of Technology, Ahwaz, Iran

*Received:* October 18, 2013; *revised:* January 07, 2014; *accepted:* February 08, 2014

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### **Abstract**

Wettability alteration is an important method for increasing oil recovery from oil-wet carbonate reservoirs. Chemical agents like surfactants are known as wettability modifiers in carbonate systems. Oil can be recovered from initially oil-wet carbonate reservoirs by wettability alteration from oil-wet to water-wet condition with adding dilute surfactant and electrolyte solutions. This paper investigates the effects of brine concentration, surfactant concentration, and the pH of injection water on the wettability alteration of carbonate reservoirs by different class of surfactants. Scanning electron microscopy images verified the formation of surfactant layer surfaces and the adsorption of surfactant molecules on the rock. The results revealed that TX-100, as a nonionic surfactant, and CTAB, as a cationic surfactant, were better wettability modifiers than SDS, as an anionic surfactant, for carbonate rocks. At the concentration of 1 wt.% and higher, the contact angle reduction was approximately unchanged. The results also proved that there was an optimum salinity for the maximum wettability alteration by surfactants. Increasing the pH of aging fluid resulted in better wettability alteration by CTAB, while, in the case of SDS, the wettability alteration was reduced. Acidic conditions had a negligible effect on the wetting behavior of TX-100.

**Keywords:** Surfactant, Wettability Alteration, Contact Angle, Carbonate Rock

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### **1. Introduction**

The flow of oil through a porous medium is governed by viscous, gravity, and capillary forces (Morrow, 1979). In carbonate reservoirs, the displacement of oil by water is mostly dictated by the spontaneous imbibition of water into the oil-containing matrix blocks. The degree of success is generally determined by the extent of spontaneous imbibition of water into the matrix blocks, which is dominated by the capillary forces, as well as being linked to the wetting conditions of the rock surface (Zhang and Austad, 2006). About 80% of carbonate reservoirs are classified as neutral to oil-wet because of the positive zeta potential of the rock surface (Chabert et al., 2010). Studies showed that the process from original water-wet calcite surfaces to oil-wet might be caused by the adsorption of polar organic components present in crude oil (Benner and Batrell, 1941; Thomas et al., 1993; Rezaei Gomari and Hamouda, 2006). Oil recovery efficiency from oil-wetted carbonate reservoirs by a water injection process is very poor.

Wettability alteration by chemical treatment is one of the techniques to recover oil from such reservoirs through the spontaneous imbibition of injection water to a micro-porosity (Gupta and Mohanty, 2008; Adibhatla and Mohanty, 2006; Austad and Milter, 1997; Standnes and Austad, 2000).

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\* Corresponding Author:  
Email: J.moghadasi@put.ac.ir

In 1997, Austad and Milter observed that cationic surfactants performed better than anionic surfactants in changing the rock wettability to a more water-wet state. They hypothesized that, for cationic surfactants, the mechanism responsible for the wettability alteration in oil-wet carbonate rock was the formation of ion pairs between the cationic heads of the surfactant molecules and the acidic components of the crude oil adsorbed on the surface of carbonate rock. For anionic surfactants, surfactant molecules could form a monolayer on the rock surface through hydrophobic interactions with the adsorbed crude oil components. The layer of the adsorbed surfactants with the hydrophilic head groups covering the originally oil-wet rock surface could change the wetting state of the rock surface toward a more water-wet state (Salehi et al., 2008; Austad et al., 1998). In 2010, Jarrahan et al. claimed that TX-100 was approached to the calcite surface by its ethoxy group and the adsorbed fatty acid was extracted from the surface instead. They stated that the presence of ethoxy group in the chemical structure of nonionic surfactants changed the bonding orientation of stearic acid groups and improved wettability alteration.

The comparison between different surfactant classes as wettability modifier and the effect of some parameters on their behavior have not been well understood yet. This work studies the change in the wettability of oil-wet calcite slices by cationic, anionic, and nonionic surfactant and investigates the effects of salinity, surfactant concentration, and pH on this phenomenon.

## 2. Experimental methods and procedures

The surfactants used in this study are cetyl trimethyl ammonium bromide (CTAB) as a cationic surfactant, sodium dodecyl sulfate (SDS) as an anionic surfactant, and Triton X-100 as a nonionic surfactant, which are supplied by Merck company; their corresponding chemical formula are  $C_{16}H_{33}N(CH_3)_3Br$ ,  $C_{12}H_{25}OSO_2ONa$ , and  $C_8H_{17}C_6H_4(OCH_2CH_2)_nOH$  respectively. The surfactant properties and their structures are tabulated in Tables 1 and 2 respectively.

Distilled water was used to prepare a brine solution in contact angle measurements with a density of  $998 \text{ kg/m}^3$  and a viscosity of 1 cp. NaCl and  $Na_2SO_4$  were used to change the salinity of the aqueous phase in contact angle tests. Crude oil was provided from Ahwaz oilfield located in the southwest of Iran with an approximate viscosity of 16 cp and a density of  $0.8629 \text{ gr/cc}$  at  $22 \text{ }^\circ\text{C}$ . Kerosene was used in pendant drop device for contact angle measurements. The core plug used in this study for contact angle measurements and the core flooding experiments was made of carbonate rock and obtained from one of the Iran oil producing formations.

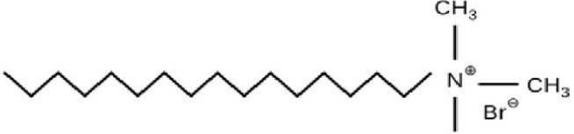
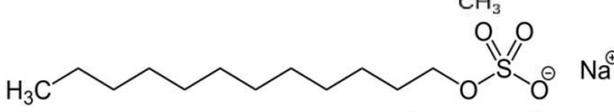
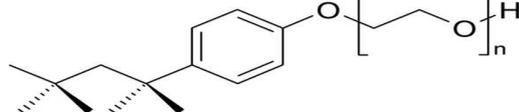
### 2.1. Wettability test

The wettability tests were conducted on mineral slices (1.2 cm diameter and 0.4 cm thickness). The slices were polished with a trimming machine to achieve a flat and smooth surface and were then equilibrated with synthetic 180000 ppm NaCl brine for two weeks.

**Table 1**  
Properties of the surfactants used in this study (all properties at  $20 \text{ }^\circ\text{C}$ ).

Surfactant	Molar mass (g/m)	Solubility in water (g/mol)	Bulk density ( $\text{Kg/m}^3$ )	pH value	CMC (ppm)
<b>Cetyl trimethyl ammonium bromide</b>	364.45	0.192	390	5-7	328
<b>Sodium dodecyl sulfate</b>	288.37	150	490-560	6-9	2307
<b>Triton X-100</b>	--	soluble	1070	5-8	1500

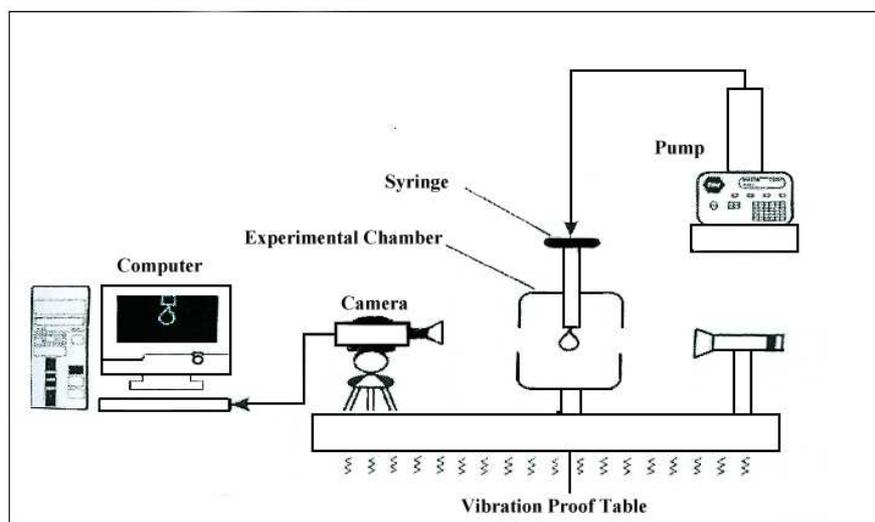
**Table 2**  
A schematic of the surfactant structures.

Surfactant	Structure
CTAB	
SDS	
TX-100	

The slices were removed from brine and aged in crude oil at an elevated temperature (60 °C) in the oven for about two weeks to change their surface to oil-wet. The elevated temperature aging is to compensate for the short aging time (compared with the geological time). After being removed from the oven, in order to recognize the initial wettability state of the carbonate slices, the slice was held in contact with 180000 ppm NaCl brine for an hour in the experimental chamber of pendant drop device and then the contact angle was measured. All contact angle tests were conducted at a temperature of 22-23 °C and atmospheric pressure.

Figure 1 illustrates the general schematic of pendant drop set components. Subsequently for investigating the effects of salinity, surfactant concentration, and pH on the wetting behavior of calcite slices, fluids of desired properties were made and then the carbonate slices were aged in these fluids for 8 hrs. To prevent the effect of time on contact angle data, the tests were performed 4 hrs after the aging process.

In order to investigate the effect of the changing salinity of aging fluid on the wettability alteration, the surfactant concentration was kept constant at 0.5 wt.%, and the salinity level was varied as 0.1%, 1%, 3%, 5%, and 10% (1000, 10000, 30000, 50000, and 100000 ppm respectively).



**Figure1**

A general schematic of pendant drop set components.

As shown in Table 3, to evaluate how the surfactant concentration affects the wettability alteration of carbonate slices, fifteen aging fluids by mixing distilled water and surfactants are made.

**Table 3**  
Fluid system used for evaluating surfactant concentration parameter.

Fluid number	Surfactant type	Surfactant concentration (% wt)	Surfactant concentration (CMC)
1	CTAB	0.02	0.61
2	CTAB	0.033	1
3	CTAB	0.5	15.15
4	CTAB	1	30.4
5	CTAB	2	60.9
6	SDS	0.1	0.43
7	SDS	0.23	1
8	SDS	0.5	2.16
9	SDS	1	4.33
10	SDS	2	8.66
11	TX-100	0.1	0.66
12	TX-100	0.15	1
13	TX-100	0.5	3.33
14	TX-100	1	6.66
15	TX-100	2	13.33

The pH of the aging fluid is believed to be very important in determining the wettability because it strongly influences the surface charge on the rock surface and fluid interfaces, which in turn affects the adsorption of surfactants into crude oil (Anderson, 1986).

The aqueous solutions are adjusted to a pre-determined pH value using  $\text{Na}_2\text{CO}_3$  (105.99g/mol) or adding drops of 37% HCl. The effect of the pH values between 4 and 10 on wettability is studied. In all the tests planned to evaluate the effect of the aging fluid pH, the concentration of the surfactant was kept constant at 0.5 wt.%.

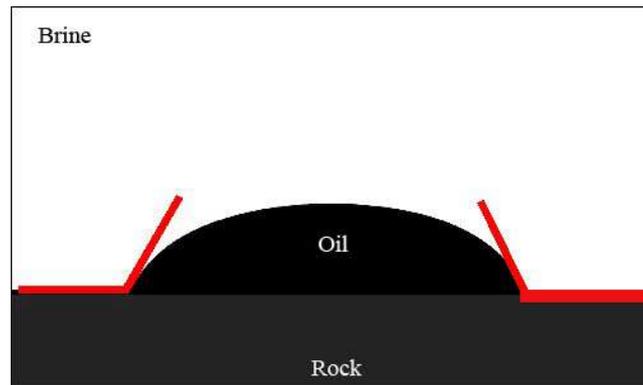
## 2.2. Scanning electron microscope

Scanning electron microscopy (1455 VP model, LEO Company) was used to analyze the surface of calcite slices before and after aging in crude oil and after aging in the surfactant fluids. The equipment was also used to characterize the surface morphology and mineralogy of calcite slices.

## 3. Results and discussion

As already mentioned, wettability evaluation was carried out by measuring the contact angle between oil drop and calcite slices in synthetic brine for several systems. The contact angle measurements were repeated for each test and the ultimate variation between the measured data for each case was observed to be about 10 degrees, and thus the contact angle data contained a maximum error of  $\pm 5$  degrees. All the contact angle experiments were performed at a temperature of 22 °C and atmospheric pressure.

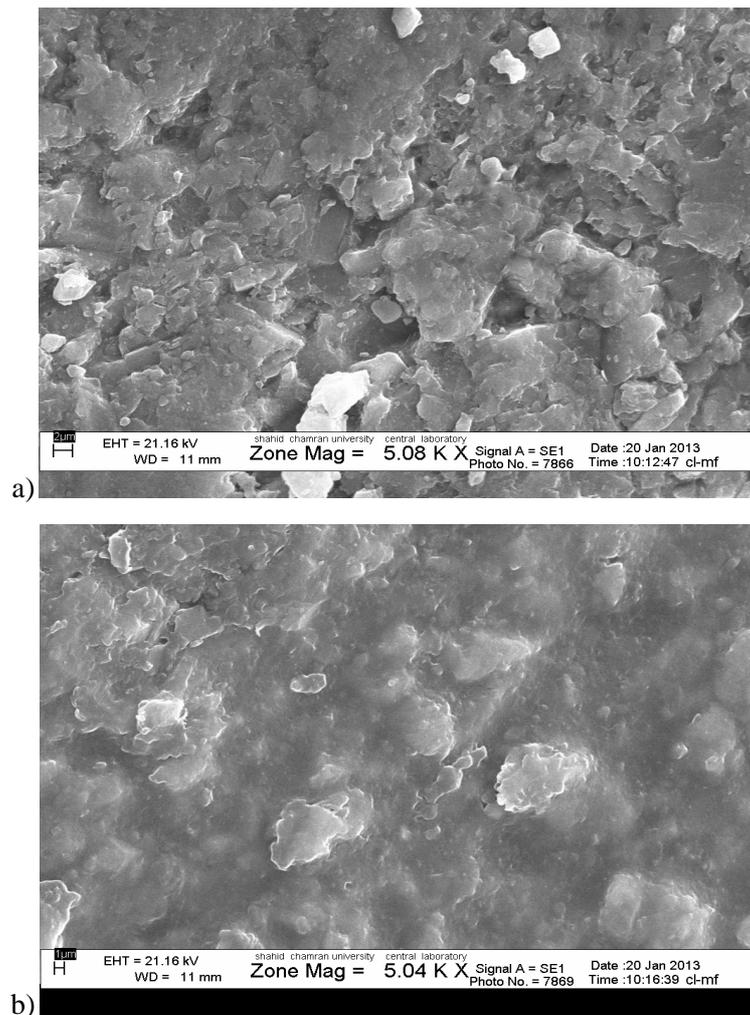
The contact angle value for calcite slices before any aging processes with the surfactant solutions was about 120 degrees as shown in Figure 2, which proved an oil-wet condition.



**Figure 2**

Contact angle test result of an oil-wetted calcite slice.

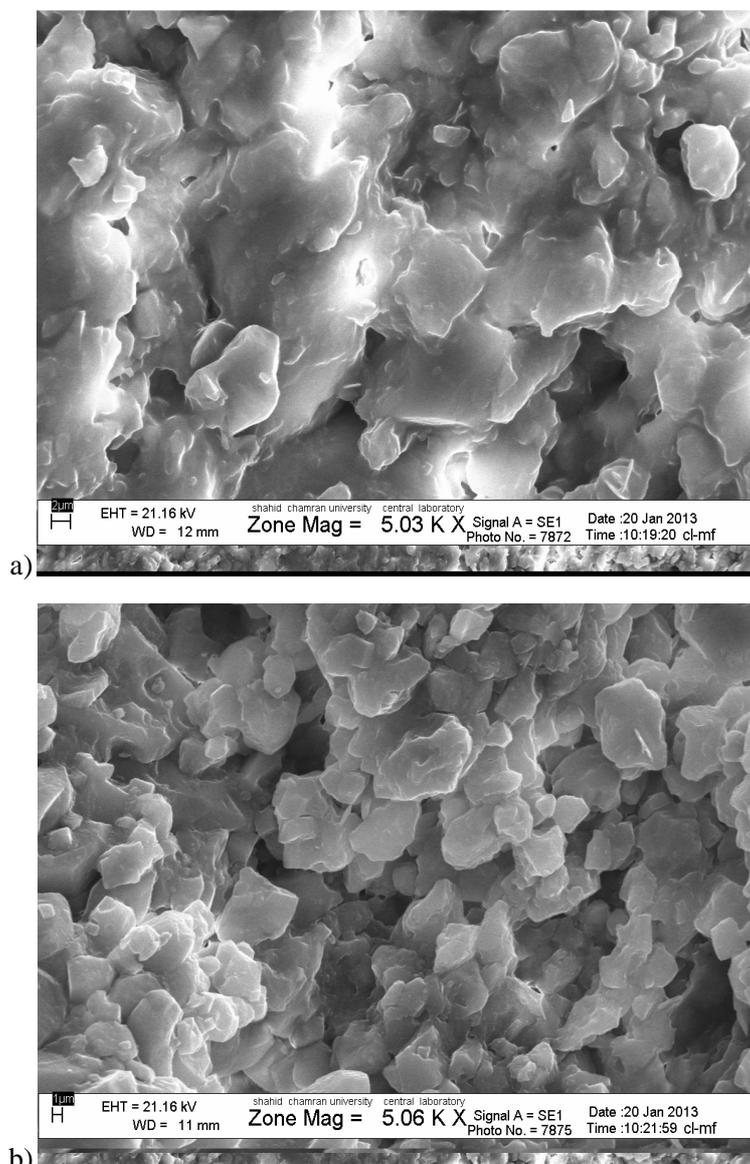
The change of wettability from a water-wet to strong oil-wet condition, as verified by SEM images (Figure 3), was due to the presence of an oil film on the solid surfaces of the slices that were aged in the crude oil. It can be observed that the cleaned slices have a surface containing carbonate particles with sharp edges, while the slices aged in the oil have a relatively smooth surface covered with oil.



**Figure 3**

SEM image of a calcite slice surface: a) before aging in crude oil; b) after aging in crude oil.

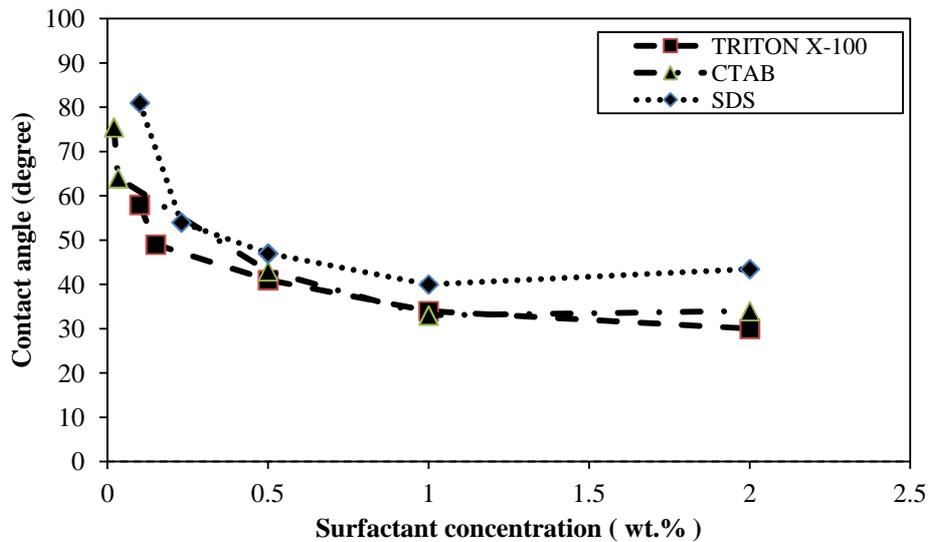
Aging the oil-wet slices in CTAB and SDS fluids results in the construction of a surfactant layer on the rock surfaces (Figure 4). These surfactant layers can be responsible for the alteration of the wettability of an oil-wet rock surface to a strongly water-wet surface.



**Figure 4**

SEM image of an oil-wet calcite slice surface: a) after aging in 0.5 wt.% CTAB solution; b) after aging in 0.5 wt.% SDS solution.

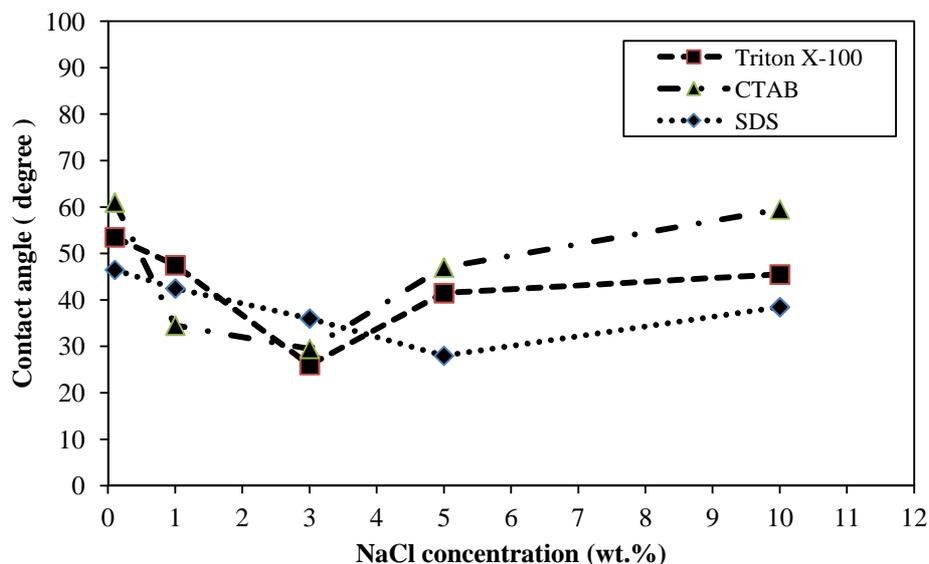
Figure 5 shows the dependency of the final contact angle on surfactant concentrations. For the three surfactants employed in this research, when the concentration was held below the critical micelle concentration (CMC), an increase in the surfactant concentration resulted in a drastic reduction in contact angle. However, at concentrations above the CMC, increasing the surfactant concentration declined the reduction rate of contact angle due to the tendency of surfactant molecules toward forming micelles. At concentrations greater than 1 wt.%, monomer activity was essentially constant. Moreover, the adsorption did not undergo any changes under such conditions and the contact angle value remained approximately unchanged.



**Figure 5**

Effect of different surfactant concentrations on the contact angle of calcite slices.

Figures 6 and 7 show the dependency of the final contact angle on the salinity ( $\text{NaCl}$  as a monovalent and  $\text{Na}_2\text{SO}_4$  as a divalent salt) at a fixed surfactant concentration of 0.5 wt.%. All of the surfactant classes led to a non-monotonic behavior in contact angle; it decreases to a minimum and then increases again. The minimum contact angle (MCA) for the CTAB, SDS, and TX-100 accrued at 3, 5, and 3 wt.% respectively in the case of  $\text{NaCl}$  and 5, 3, and 1 wt.% in the case of  $\text{Na}_2\text{SO}_4$  respectively. The MCA explains the partitioning of surfactants; surfactants tend to stay in the aqueous phase at low salinities and move to the oil phase at high salinities due to the electrostatic interactions between electrolytes and surfactants.

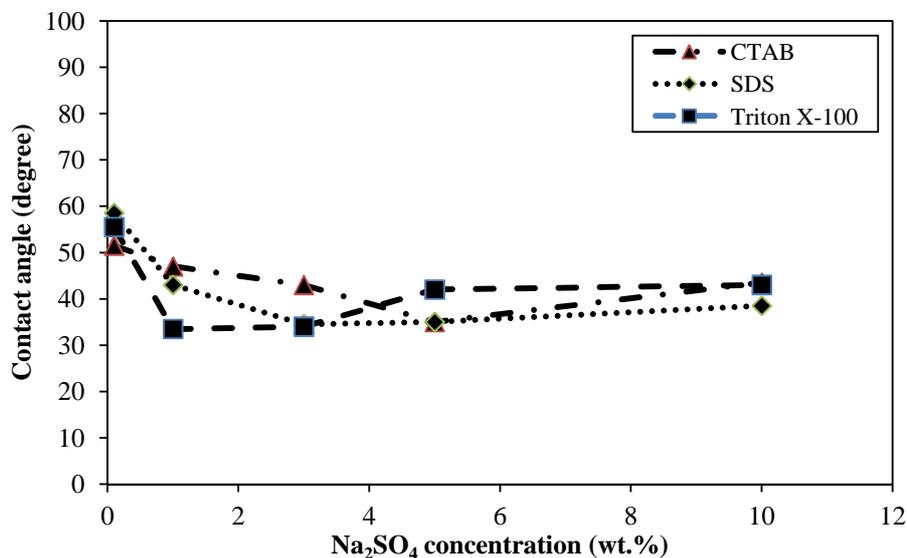


**Figure 6**

Effect of  $\text{NaCl}$  concentration on contact angle in the presence of different surfactants.

However, at an intermediate salinity, the surfactant has equal affinity for both aqueous and oleic phases. The amount of surfactant is at its highest value at the interface in this condition. It is possible that the surfactants at the oil-brine interface solubilize the adsorbed acid on calcite and thus change

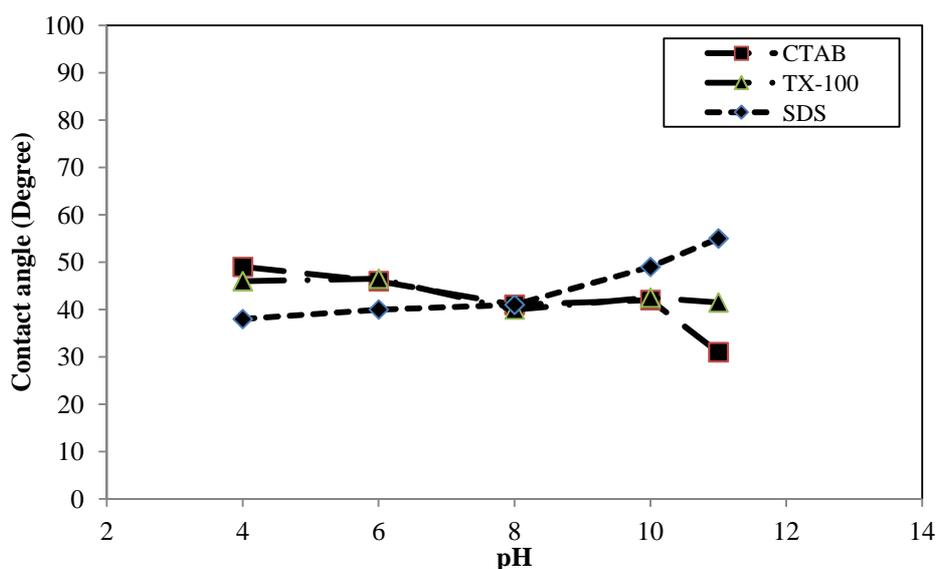
the contact angle, which can explain the minimum point in the contact angle trend. It is also possible that the micelle head-head spacing is smaller at high salt concentrations and its capacity to solubilize the adsorbed acid decreases as the salt concentration is increased (Gupta and Mohanty, 2008).



**Figure 7**

Effect of Na<sub>2</sub>SO<sub>4</sub> concentration on contact angle in the presence of different surfactants.

The effect of the aging fluid pH on the wettability alteration of calcite slices has been investigated. According to Figure 8, in the case of CTAB, contact angle value is drastically reduced and wettability is shifted to more water-wet conditions. Nevertheless, at pH values greater than 10, contact angle reduction is more obvious. As pH is increased, the calcite surface charge is changed from positive to negative since it crosses its point of zero charge (PZC) (Somasundaran and Agar, 1967). The PZC for carbonates is around 8-10 (Alotaibi et al., 2011). Therefore, by increasing the surface negative charge (SNC) of calcite (by increasing pH), the efficiency of wettability alteration by CTAB molecules through ion-pair formation mechanism is increased.



**Figure 8**

Effect of pH parameter on contact angle of calcite slices aged in different surfactant solutions.

In the SDS solution tests, the contact angle value is increased by increasing the pH of the aging fluid and its changes is more remarkable at pH values larger than 8. By increasing pH, the SNC of calcite slices is increased and the repulsion forces between the surface charge and the SDS head charge are increased. Therefore, crossing PZC reduces the adsorption of anionic surfactants on carbonate rocks, which consequently causes poor wettability alteration by SDS. In the case of TX-100, the contact angle values show a slight variation by increasing the pH of the aging fluid. The maximum contact angle reduction is about 6.5 degrees, which is approximately equal to the maximum error of the contact angle data.

#### 4. Conclusions

1. TX-100, as a nonionic surfactant, and CTAB, as a cationic surfactant, are better wettability modifier than SDS, as an anionic surfactant, for carbonate slices;
2. For all of the surfactant classes, contact angle is reduced by increasing the surfactant concentration. At concentrations greater than 1 wt.%, monomer activity is essentially constant. Moreover, the adsorption does not undergo any changes under such conditions and the contact angle value remains approximately unchanged;
3. There exists an optimal salinity concentration for any surfactant concentration at which the wettability alteration of carbonate rock is the maximum. The variation of MCA with salinity can be explained in terms of surfactant partitioning and the maximum tendency of the surfactants to stay at the interface between the aqueous and oleic phases at an optimal salinity;
4. As the SNC of the calcite increases, the efficiency of wettability alteration by CTAB molecules is increased through ion pair formation mechanism, while, in the case of SDS, the repulsion forces between the surface charge and the SDS head charge are increased. Therefore, crossing PZC reduces the adsorption of anionic surfactants onto carbonate rocks and causes a poor wettability alteration by SDS;
5. The change in the pH of carrying fluids in carbonate slices does not have a significant effect on the wettability alteration induced by TX-100.

#### Nomenclature

cp	: Centipoise
CTAB	: Cetyl trimethyl ammonium bromide
CMC	: Critical micelle concentration (ppm)
MCA	: Minimum contact angle
PPM	: Part per million
PZC	: Point of zero charge
SDS	: Sodium dodecyl sulfate
SEM	: Scanning electron microscope
SNC	: Surface negative charge
TX-100	: Triton X-100

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