

Research note

## Chemical Induced Wettability Alteration of Carbonate Reservoir Rocks

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### Abstract

Wettability alteration of outcrop obtained from Asmari formation was investigated using surfactants. Three different surfactants including a cationic surfactant: dodecyltrimethylammonium bromide (DTAB), an anionic surfactant: sodium dodecylbenzenesulfonate (SDBS) and a non-ionic surfactant that was Triton X-100 were used.

Wettability alterations in the presence of each surfactant for the three surfactant concentrations from 0.1 to 0.3 wt% in brine and at four different temperatures, from 25 to 80°C were examined. Surfactant solution droplets were placed on the rock surfaces after being saturated with brine and placed in crude oil. The potential of surfactants to alter the wettability was determined by estimating the contact angle ( $\theta$ ) between the surfactant droplet and the surface of the rock. The results indicated that Triton X-100 could change the wettability condition from oil-wet to water-wet more than other surfactants with the same concentrations and temperatures.

**Keywords:** Carbonate reservoir, Wettability alteration, Surfactant, Oil-wet, Water-wet

### 1. Introduction

Oil recovery by waterflooding is one of the most important methods applied to maintain the reservoir pressure above the bubble point pressure in order to increase oil-sweep efficiency [1]. Mechanism of oil recovery by water is in such a way that when water is located next to the rock, spontaneous imbibition of water into the matrix occurs and oil is extracted [2]. Most of the Iranian reservoirs which are fractured carbonate reservoirs are oil-wet [3]. In these types of reservoirs, water cannot spontaneously imbibe into the matrix due to the low and negative capillary pressure [4]. Maximum oil

recovery is obtained after the wettability alteration of reservoir rock. [5]. A proper method for increasing the sweep efficiency in this type of reservoir is to maintain oil swelling, reduce the oil viscosity, lowering the interfacial tension and changing the wettability of the rock [6]. Hence, wettability alteration of the oil wet rocks to water-wet is crucial to enhance oil recovery of this type of reservoir.

In order to improve oil recovery in fractured carbonate reservoirs, two different methods have been reported in the literature including adding a certain amount of surfactants [7-9] and wettability change by increasing

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temperature [10-12]. In order to change the wettability using surfactants, three different types of surfactants including anionic surfactants [9,13], non-ionic surfactants [7], and cationic surfactants were employed [14,15].

Oil production operations in the Aghajari oil field in the south of Iran are mature. Initially discovered in 1938, cumulative recovery from this giant oil field with more than 15 billion barrels of recoverable oil has reached 10 billion barrels so far. Iran's Aghajari Field, which experienced peak production of 1 million barrels a day in 1974, and then produced a steady 850,000 barrels per day for 17 consecutive years, is now going to consume 3 billion cubic feet of South Pars gas to prop up production of only 187,000 barrels per day. Water imbibition is still another efficient mechanism for further oil production from this reservoir. In this experimental work, three types of surfactants including an anionic surfactant, a non-ionic surfactant and a cationic surfactant were employed in order to investigate the wettability alteration of the outcrop obtained from this reservoir.

A comparison of the wettability alteration potential of the reservoir rock as a result of using three surfactants at four different temperatures was made based on the contact angles measurement between the chemical droplets and the rock pieces.

## 2. Experimental

The oil sample used in this study was obtained from well No. 90 of the Aghajari reservoir from the depth of 2600 meters under sea level. The rock was obtained from the Asmari formation outcrop, the same formation of Aghajari reservoir. The three types of surfactants were cationic, anionic and nonionic that are dodecyltrimethylammonium bromide,  $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{CH}_3\text{N}(\text{CH}_3)_2\text{CH}_3\text{Br}$  (DTAB); sodium dodecylbenzenesulfonate,  $\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ , (SDBS) and Triton X-100,  $\text{C}_{14}\text{H}_{22}\text{O}$

$(\text{C}_2\text{H}_4\text{O})_{10}$ , respectively. Cationic surfactant was purchased from Sigma-Aldrich Company and anionic and non-ionic surfactants were purchased from Merck Company.

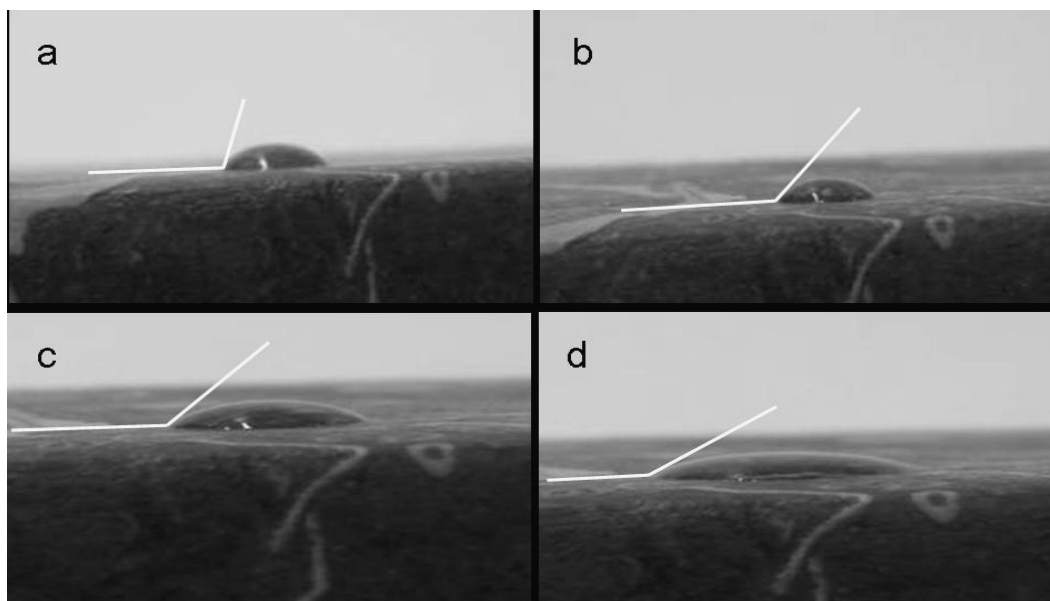
The outcrop rock used was excavated from southern parts of Iran. It was cut into small pieces sized  $20 \times 4 \times 3 \text{ cm}^3$ . The surfaces of the pieces were polished under supervision of Isfahan University geologists. Then, they were immersed in the brine for a period of 30 days. After being saturated with brine, they were immersed in a container of crude oil for a period of 50 days in order to be saturated with the oil.

Surfactant solutions of the concentrations, 0.1, 0.2 and 0.3 wt% were prepared in brine. To investigate the wettability alteration, a droplet of each surfactant solution was placed on the surface of the rock and kept there for 8 minutes. This procedure was repeated for temperatures of 25, 30, 50 and 80 °C for each surfactant solution. The contact angles were measured by means of a digital camera, Sony 8.1 mega pixel resolutions DSC-W100 Model.

## 3. Results and discussion

In the first stage, the contact angle of the brine on the fresh rock surface immersed in the crude oil was measured. The contact angle was found to be around  $100^\circ$ , indicating that the wettability of the original rock is intermediate to oil-wet. Wettability of carbonate reservoir rocks was also verified by other researchers and similar results were reported [3, 16 and 17].

Fig. 1 shows the contact angles measured for the surfactant solution droplets and the rock surfaces that represent the wettability alteration potential for Aghajari oil reservoir rock. This test was repeated for the DTAB surfactant solution at concentrations of 0.1, 0.2 and 0.3 wt% for different temperatures of 25, 30, 50 and 80°C.



**Figure 1.** Contact angles for 0.1 wt% DTAB solutions and Aghajari oil reservoir rock at different temperatures (a) 25, (b) 30, (c) 50 and (d) 80 °C

The contact angle results are also shown in Fig. 2 as a function of DTAB concentration and soaking temperature. As shown, the contact angle decreases as the DTAB concentration increases, which indicates more change in the wettability of the rock towards water wetness conditions. The same trend is observed as the soaking temperature increases. This shows the effect of temperature on the wettability alteration of the oil wet rocks towards water wetness, known as the thermally induced wettability alteration.

The same result was also reported in the literature [18] as the wettability of the carbonate rocks were altered using cationic surfactant of type  $R-N(CH_3)_3Br$ , known as  $C_nTAB$ . It was shown that by increasing the surfactant concentration below the critical micelle concentration (CMC) would change the wettability of the carbonates more to the water-wet conditions. In the current study, all of the selected concentrations were below CMC and it was observed that the wettability alteration improved as the concentration of surfactants increased.

Austad et al. [19] used C12TAB solutions in order to investigate the imbibition of the surfactant solutions into chalk cores. They reported that the oil production percentage was increased by increasing the temperature from 40 to 70 °C. In our research, it was shown that the contact angle was decreased by increasing the temperature. This is in agreement with those presented by Austad et al. as the lower the contact angle, the higher the wettability alteration.

Fig. 3 shows the wettability alteration potential in reservoir rock by SDBS at different temperatures of 25, 30, 50 and 80 °C. The test was repeated at different concentrations of 0.1, 0.2 and 0.3 wt%. The overall contact angle results are also shown in Fig. 4 as a function of SDBS concentrations and soaking temperature. As shown, by increasing the temperature and the surfactant concentration, smaller contact angles were found which means more wettability alteration of the reservoir rock towards the water-wet conditions. The least contact angle measured for this surfactant was observed at 0.3 wt% and at 80 °C.

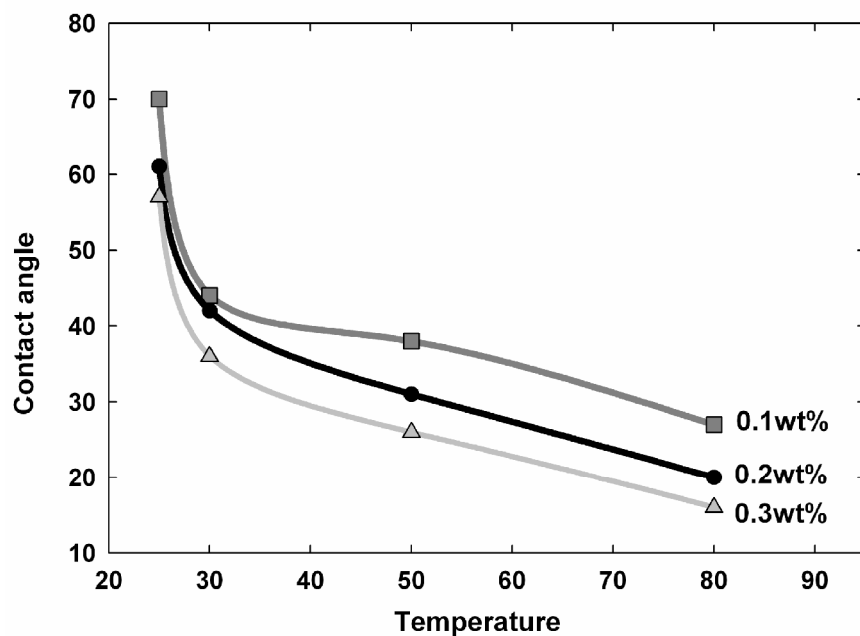


Figure 2. The effects of DTAB concentration and soaking temperature of the wettability alteration potential of Aghajari oil reservoir rock.

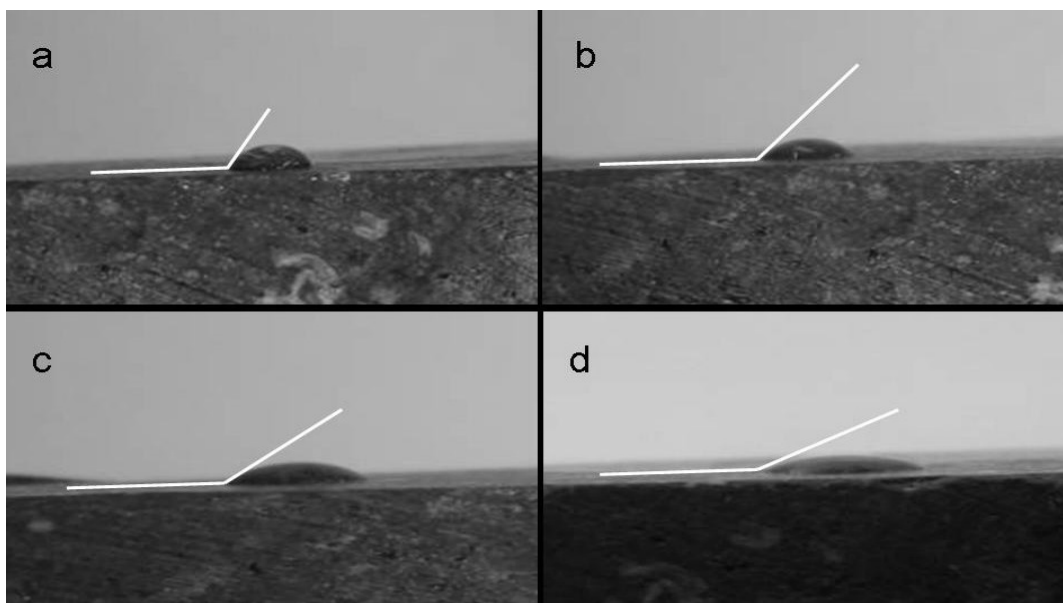
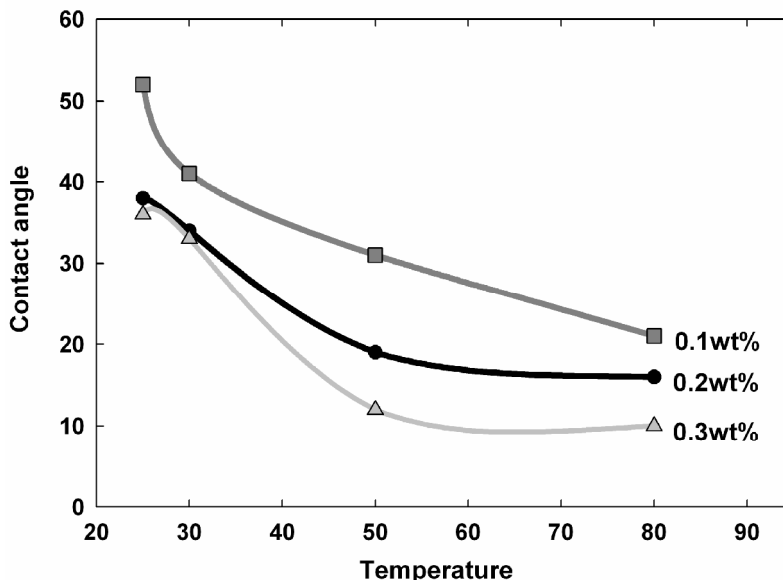


Figure 3. Contact angles for 0.1 wt% SDBS solutions and Aghajari oil reservoir rock at different temperatures (a) 25, (b) 30, (c) 50 and (d) 80 °C



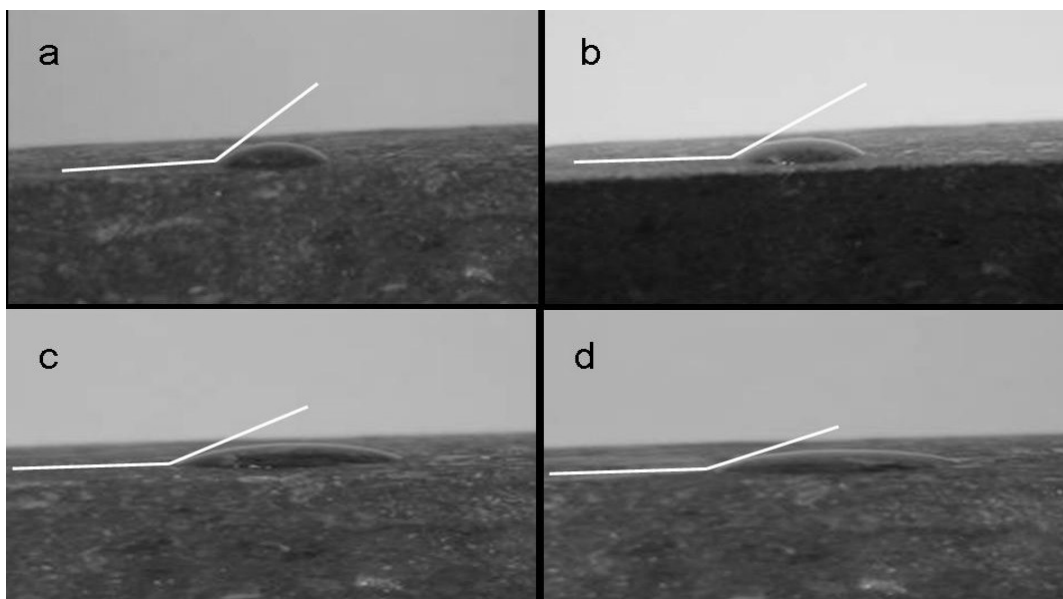
**Figure 4.** The effects of SDBS concentration and soaking temperature of the wettability alteration potential of Aghajari oil reservoir rock.

Cationic surfactant and anionic surfactants were used to alter the wettability of oil-wet rock in several studies. Seethepalli et al. [20] reported that anionic surfactant have been more effective than cationic surfactant. They utilized anionic surfactants including SS-6656 and Alforterra-35, -38, -63, -65 and -68 as well as cationic surfactants such as DTAB. It was reported that the anionic surfactants would change the wettability of the calcite surface to intermediate/water-wet conditions the same or more than the cationic surfactants like DTAB. Similar results were obtained in this study comparing the effects of anionic to the cationic surfactants. The anionic surfactant (SDBS) changed the wettability of Aghajari carbonate reservoir rock to more water wet conditions compared to the cationic surfactant (DTAB).

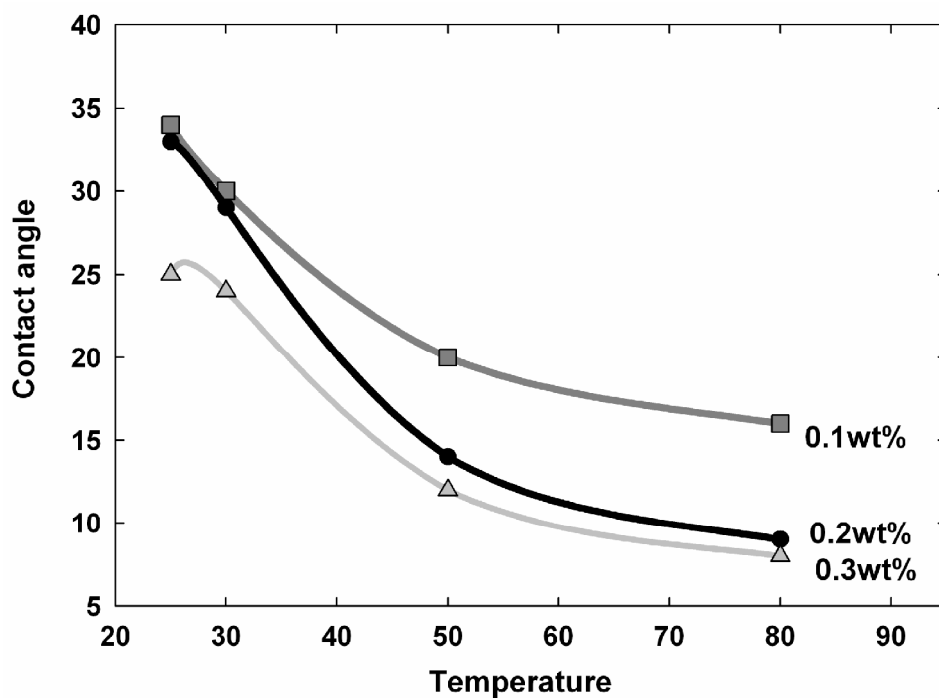
Fig. 5 shows the wettability alteration potential of Aghajari oil reservoir rock by Triton X-100 at different temperatures of 25, 30, 50 and 80 °C. This test was also repeated for different concentrations of 0.1, 0.2 and 0.3 wt%. The contact angle results are also shown in Figure 6 as a function of Triton X-

100 concentrations and soaking temperature. Comparing the results presented in Figs. 1 to 6, it is concluded that the surfactant concentration, as well as the temperature, are two effective parameters for the wettability alteration towards more water-wet conditions. As shown, increasing the two parameters would result in greater wettability alteration.

Xie et al. also investigated the effect of non-ionic and cationic surfactant on the wettability alteration using 50 cores obtained from two different carbonate reservoirs. They reported that the non-ionic surfactant enhanced the oil recovery more than the cationic surfactant due to the lower interfacial tension. Their results revealed that the non-ionic surfactants resulted in greater wettability alteration towards water-wet conditions which lead to more oil recovery [15]. The results of the present study also showed that Triton X-100 is more effective than DTAB and SDBS for wettability alteration of outcrop rock towards water-wet condition.



**Figure 5.** Contact angles for 0.1 wt% Triton X-100 solutions and Aghajari oil reservoir rock at different temperatures (a) 25, (b) 30, (c) 50 and (d) 80 °C



**Figure 6.** The effects of Triton X-100 concentration and soaking temperature of the wettability alteration potential of Aghajari oil reservoir rock.

#### 4. Conclusions

The change in the wettability of the outcrop reservoir rock from intermediate wet and near to oil-wet types is represented in this study. The results show that by increasing the surfactant concentration and temperature, more wettability alteration of the rock towards water-wet condition was obtained. Compared to anionic and cationic surfactants, Triton X-100 as a non-ionic surfactant has higher potential for wettability alteration of the reservoir rock towards the water-wet condition compared to DTAB and SDBS. Increasing the surfactant concentration and temperature result in more wettability alteration of the rock towards water-wet condition. More investigation is needed to find the wettability alteration for the same rock using different types of surfactants at reservoir conditions.

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