

STUDY OF WETTABILITY ALTERATION MECHANISMS BY SURFACTANTS

Kh.Jarrahan^{*a}, M. Vafie-Sefti^{*a}, Sh.Ayatollahi^b, F.Moghadam^a, A.Mousavi Moghadam^a

^a Chemical Engineering Department, Tarbiat Modares University, Jalal Al-Ahmad Highway, P.O. Box: 14155-143, Tehran, Iran

^b EOR Research Centre, Shiraz University, Shiraz, Iran. (www.eor.ir),
Tel: +98-711-6474602, Po. Box: 71345-1719

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ABSTRACT

Enhanced oil recovery in fractured carbonate reservoirs by water flooding is depended on the wettability properties of rock surface that is related to the stability of water film between rock and oil. The results of recent researches showed that presence of long chain fatty acids such as adsorbed Stearic acid on the surface of calcite cause a collapse on water film between the rock surface and the oil phase. Therefore, oil recovery in these kinds of reservoirs may lead to some challenges because of changing state of reservoir rock into oil wet.

Utilization of surfactants is one of the available accesses for wettability alteration of reservoir rock, from oil wet into water wet. So that studying of wettability alteration mechanism using surfactants has been emphasized by recent researchers.

In this work, it is focused on presenting a process mechanism which has a direct effect on surfactants behavior in oil field usage, by using of analysis techniques such as Zeta Potential, TGA, and contact angel measurement. The results have shown that between useable surfactants, anionic surfactants have the least effect on wettability alteration, because of the generated repulsion between the anion of the fatty acid carboxylic group and their anionic part. Where in case of cationic surfactants, because of the appointment of electrostatic attraction and ion-pair formation, zeta potential is changed and surface is tended to water wet. These results are completely coincided with contact angle measurement tests and zeta potential and TGA tests.

INTRODUCTION

The flow of oil through a porous medium is governed by viscous, gravity and capillary forces [1]. In case of fractured carbonates, the displacement of oil by water is dictated mostly by 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 from the fractures into the matrix blocks, which is dominated by the capillary forces, and also linked to the wetting conditions of the rock surface [2].

It has been recognized that the several parameters such as pH, polar organic compound in crude oil (natural surfactants and Asphaltene), brine composition and temperature determine the wetting behavior of mineral rocks [3]. Outcrop carbonate rocks are, in general, water-wet. However, in most observed cases, carbonate oil reservoirs have neutral to oil-wet character [4]. It has suggested that the process from original water-wet calcite surfaces to oil-wet may have been caused by adsorption of polar organic components present in crude oils [5, 6].

Chemical treatment for wettability alteration is one of the techniques to recover oil from such reservoir [7-11]. Therefore, in two past decades, many researches are focused on this subject. Austad et al 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 is the formation of ion- pairs between the cationic heads of the surfactant molecules and the acidic components of crude oil adsorbed on the surface of carbonate rock. In contrast, anionic surfactant molecules with the adsorbed crude oil components on the rock surface. The layer of adsorbed surfactants with the hydrophilic head groups covering the originally oil-wet rock surface could change the wetting state of the rock surface toward more water-wet [12, 13].

Hamouda et al worked with a system of n-Decane/ fatty acid/ water on calcite plates at elevated temperature. They showed that wettability (contact angle) follows the same trend as partition coefficient of fatty acid and IFT which in turn depends on pH and thus on zeta potential of calcite [14]. The mechanisms of wettability alteration by surfactants on carbonates have not been understood completely.

This work was studied the mechanism of the change in wettability on oil-wet calcite plate by analytical techniques such as Zeta potential, TGA¹ and Contact Angle measurements.

Results and discussions

At first, modification of calcite powder was performed by Stearic acid in 0.01 M concentration as model oil. Model oil is prepared by adding Stearic acid in n-heptane. In spite of positive charge of Calcium Carbonate powder, it can be expected that its surface charge was changed due to contact with anionic form fatty acid (RCOO^-) and therefore it change to negative charge. Figure 1 shown the Calcite surface behavior before and after its placement in 0.01 M of Stearic acid solution (n-Heptane+Stearic acid). As illustrated in Fig.1, Calcite powder located at oil-water interface after oil-wetting. It is obvious that water has a significant effect on dissociation of fatty acid and oil-wetting of Calcite species. Figure 2 presents contact angle of water drop on calcite surface before and after of its modification by Stearic acid. As expected, after 3 days aging of calcite plate in

1 - Thermal gravimetric analysis

model oil, contact angle increased from 0° to 138° , which is indicated the wettability alteration of the surface in contact with fatty acid. After assure Carbonate powders of oil wetting, they were aged in different surfactant solution. The results of zeta potential of Calcite surface, which was placed in different surfactants solution, are shown in Fig. 3. According to the Fig.3, cationic surfactants were more effective respect to the other ones in surface charge variation of calcite powder. This behavior is resulted from adsorption of cationic surfactants due to electrostatic attraction between polar side of the surfactants and fatty acid. So that surface charge changed from -22 to $+22.4$ mV. Increasing of surfactant concentration ($\sim 1\%$ wt) led to higher entrance of it into the system and zeta potential enhanced to $+44.8$ mV. About non-anionic surfactant TX-100, it was approached to the calcite surface by its ethoxy group and adsorbed fatty acid was brought out of surface instead. Finally, the performance of anionic surfactant in the wettability alteration process was investigated. The obtained results shown hydrophobic interaction formation between non-polar tail of surfactant and carbon chain adsorbed fatty acid was main mechanisms of wettability alteration in this surfactant. Since hydrophobic interaction is weaker than electrostatic attraction, intensity of water-wetting in this case is lower than other ones. TGA experiments were also confirmed the recent obtained results. So that, the residue amount of fatty acid measured by TGA analysis on calcite surface after treatment by surfactant for cationic type was the least and for the anionic one was the most (Fig.3). According to the TGA results, three steps were observed during heat treatment. First step, the temperature of 25°C to 230°C , was related to the eliminated of the existed water available in crystal matrix or physisorbed acid. The main stage, temperature of 230 to 400°C , was related to elimination of chemisorbed components and the last stage, temperature of 400 to 600°C , illustrated the powder thermal decomposition. The effect of concentration and surfactant types on water-rock-air interface contact angle were presented in Fig 4 to 5. The results shown that contact angel was decreased by increasing of surfactant concentration. As expected, the lowest contact angle belonged to the cationic surfactant.

CONCLUSION

In this study, effect of surfactants on wettability alteration was investigated and following conclusion can be drawn:

- 1- Surfactants can be altered wetting conditions by changing of Calcite surface charge.
- 2- Based on surfactant types, wettability alteration from oil-wet to water-wet occur by different mechanism. For instant, cationic surfactant presents good performance relative to other ones due to electrostatic attraction between its positive charge and adsorbed acid groups on Calcite surface.
- 3- Presence of ethoxy group in chemical structure of Nonanionic surfactant changes bonding orientation of Stearic acid groups and improved wettability alteration. However, weak hydrophobic interaction between the tail sections of the anionic surfactant molecules and oil component (Stearic acid) causes that anionic surfactant has low performance in altering the wettability of Calcite rock to water-wet.

4- As can be found from zeta potential results, above the CMC, all surfactants show similar effect on surface charge changing.

5- The results of the contact angle measurements indicated that contact angle decreased with surfactants concentration increasing. This decline trend is minimum in cationic surfactant due to ion-pair formation between surfactant and anionic mode of the Stearic acid.

6- Thermal gravimetric analysis (TGA) shows that the content of adsorbed acid on Calcite powder after treatment by cationic surfactant is lower than other ones surfactants. These results are agreement with the contact angle measurements.

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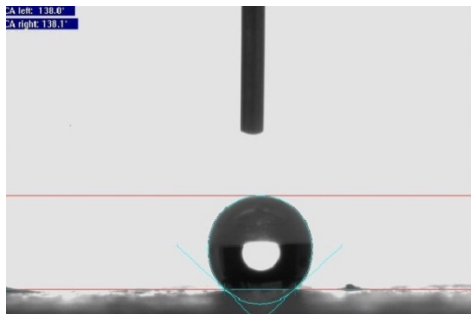


(a)

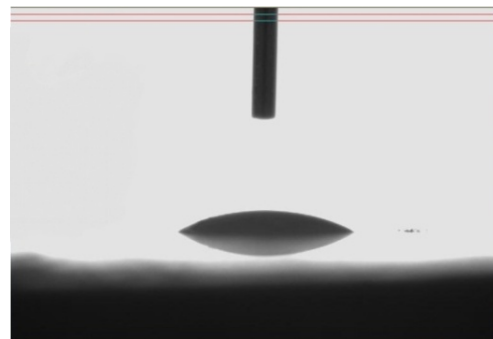


(b)

Figure1. Visual Observation demonstrates the change of wettability of Calcite Powders When Stearic acid is added to system. Picture (a) it is shown, where the Stearic acid is added, calcite powders stay in the oil phase or at interface and Picture(b) where calcite powders are suspended in the water phase.



(a)



(b)

Figure2. Visual illustration of Contact Angle of untreated and treated Calcite surface with Stearic Acid (0.01 M). t Picture(a), it is shown, where the Stearic acid is added, Contact angle is 138° and Picture(b) where Water-wet calcite plate, Contact angle is 0°

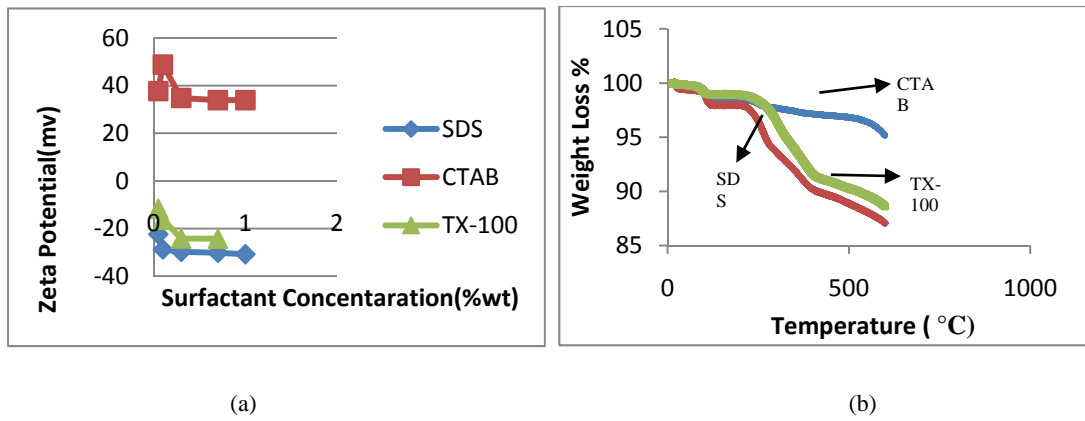


Figure3. Zeta Potential (mV) measured in distilled water(Picture a) and TGA for modified Calcite powders by 0.01M Stearic acid aged for 2 days in different concentrations Surfactant solutions(Picture b).

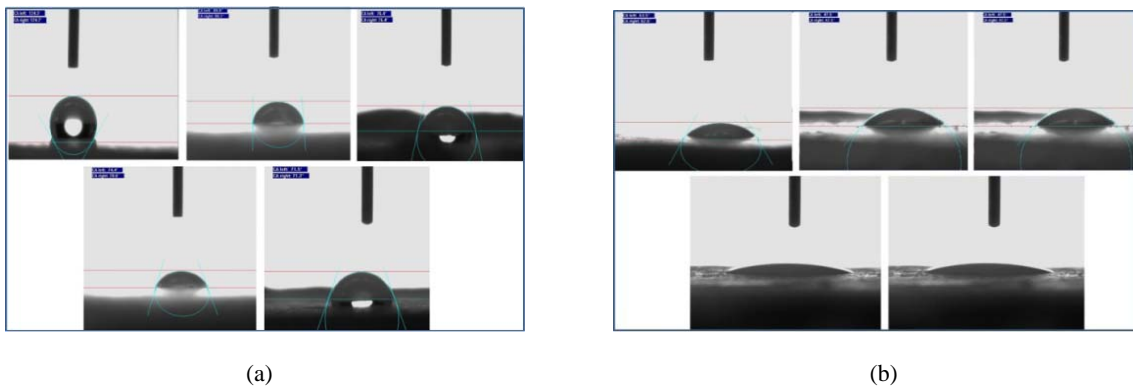


Figure4. Visual illustration of Contact Angle of treated Calcite surface with Stearic Acid (0.01 M) aged for 2 days in different concentrations Surfactant solutions. Picture (a) it is shown, where the Cationic Surfactant added and Picture(b) is related to Anionic Surfactant.



Figure5. Visual illustration of Contact Angle of treated Calcite surface with Stearic Acid (0.01 M) aged for 2 days in different concentrations of Nonionic Surfactant solutions.