



Impact of Anionic Surface Active Agent on the Wetting Behavior of the Different Reservoir Rock in the Presence of Colloidal Silica Nanoparticles

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Abstract

Wettability of the surface is one of the most vital variables affecting crude oil mobilization inside the pore spaces. The wettability of the reservoir is characterized by the contact angle measurement. The composition of the reservoir has a direct impact on the contact angle of the fluid. Hence, the present study focuses on the wettability studies of the different rock surfaces with and without aging with the crude oil using surfactant solution. The results suggested that the positively charged rock surface has a strong interaction with the negatively charged surfactant molecules. However, surface coated with crude oil almost nullifies the effect of different compositions on the contact angle. Furthermore, Colloidal Silica Nanoparticles (CSNs) improve the efficiency of surfactants in modifying the wettability of the rock.

Introduction

Nanoparticles are of a great piece of interest in the advancement of any technology because of their smaller size and higher surface area (Gbadamosi et al., 2019; Munshi et al., 2008; Pal et al., 2019). The application of nanoparticles in the oil and gas industry has dragged the attention of researchers due to the efficacy of NPs in enhancing the performance of chemical EOR, drilling fluid, cement strength. Oil recovery from the matured reservoir is one field in which the application of the costly NPs can be justified because of the increase in the residual oil mobilization. After water flooding, injection of NPs along with the some chemical has been stated to amplify the efficiency of the slug in reducing surface tension as well as in shifting the reservoir rock wettability. The wettability of the reservoir rock is characterized by the contact angle formed by the fluid on the surface of the rock. The reservoir rocks are known to be water wet originally which is altered to oil-wet during the movement of hydrocarbon from the originating pore spaces to the accumulating pore spaces. Since water-wet reservoirs are known to have lower residual oil saturation hence the objective of the reservoir and production engineers is to again modify the wetting characteristics of the reservoir towards water-wet. The alteration of the wettability during production from the matured fields is generally achieved by the injection of surfactant. However, NPs along with surfactants have been proved to be highly efficient in the process.

Several additives have been used for the alteration of wettability. Different mechanisms have been proposed for different additives. Application of anionic surfactant involves the hydrophobic interaction for the modification of wetting behavior of oil-wet rock whereas cationic surfactants involve the ion pair formation for the same (Hou et al., 2018). The addition of nanoparticles for the same purpose involves the formation of wedge film that applies a disjoining pressure on the adsorbed oil layer which helps in removing the oil droplet from the layer resulting in the modification of wettability of reservoir rock (Hou et al., 2018). A lot of researchers have focused on the application of nanoparticles in the oil and gas industry. Various studies are available stating the reduction of surfactant loss because of its adsorption on the rock surface upon the application of nanoparticles mixed with surfactant. Furthermore, nanoparticles have also been shown promising results upon minimizing the surface tension of the



chemical slug. However, a common problem of the agglomeration of the nanoparticles remains consistent throughout different studies involving nanoparticles.

To encounter the problem of agglomeration, the present study focuses on the application of Colloidal Silica Nanoparticles (CSNs) on the wetting character modification of different reservoir rocks. CSNs are a stable dispersion of silica nanoparticles in ethanol and water mixture which doesn't agglomerate at all when kept for several days. This provides an edge over the conventional nanoparticles which tend to form a cluster and ultimately settle down. The present study is based on the contact angle measurement of a chemical slug composed of surfactant and CSNs on different reservoir rocks (shale, carbonate and sandstone). This could provide an understanding of the characteristics of the CSNs for different types of rocks for the alteration of wettability.

Methodology

Materials required

Colloidal Silica Nanoparticles (CSNs) having industrial name CC401 in colloidal dispersion state was procured from Nouryan Chemicals Pvt Ltd. CSNs have a viscosity of 8 cP whereas the average particles size was 12 nm. Anionic surfactant (sodium dodecyl sulfate) of analytical grade was procured from SRL chemicals. Common beach sand was used to simulate sandstone reservoir after washing whereas shale and carbonate samples were procured from ONGC.

Contact angle measurement

The contact angle was measured using the Goniometer from Apex India of the model Acam-NSC series. Pellet of different reservoir rock was created by first grinding the reservoir rock into the powdered form using Analytical mill and then pellet of distinct formation was created using a hydraulic pellet formation machine of 25 tons load. A stock solution of 2500 ppm of surfactant was first prepared which was then used to create three different solutions mixed with CSNs at 5v%, 15v% and 25v% respectively. The sessile drop method was then used for the formation of a drop on the surface and the image was then captured and analyzed (Gupta et al., 2021). Each observation was repeated three times to reduce the error during the experimentations and to check the repeatability of the measurements. Measurement were recorded up to 600 s under ambient pressure temperature conditions.

Results and Discussion

Contact angle studies

One of the most critical variable having a direct impact over the oil mobilization inside the matured oil fields is the preferential wetting character of the reservoir rock which is characterized by the measurement of contact angles (Babu et al., 2015). The lower the contact angle formed by the fluid, the higher the affinity of the reservoir rock would be to adhere that fluid on its surface. The contact angle on three distinct rock surface (carbonate, sandstone and shale) pellets were examined in this study. The surfactant solution (500 to 4000 ppm) was prepared to examine the role of surface active agent on the wettability of the rock surface. Deionized water was used to prepare the surfactant solution. The contact angle for the deionized water on the carbonate pellet surface was found to be 101° which reduced up to 90° after 600 s of contact time. The reduction in the contact angle could be explained by the adsorption of the water molecules on the carbonate rock surface. It is worth noting that the wettability of the rock surface was modified towards oil-wet by coating it with a layer of crude oil for a time span of 24 h (Fig. 1a). This explains the obtuse angle formation when the drop of water

came in contact with the carbonate surface during experiments. Furthermore, as the surfactant particles were introduced in the solution, a drastic reduction in the contact angle was observed. This can be elucidated by the adsorption of surface active agent's monomers on the oil-wet rock (Kesarwani et al., 2021b, 2021c). This phenomenon has been explained previously in various research papers. Interaction among the non-polar part of the crude oil and the alkyl chain of the surfactant leads to the adsorption of surfactant molecules on top of the crude oil layer. This leads to the superimposition of the surfactant particles exposing their hydrophilic head thus making the surface water wet again (Kesarwani et al., 2021a). Another crucial thing that was observed from the contact angle results was the trend of the contact angle. The reduction of the contact angle after the critical micelle concentration of the surfactant was found to be insignificant. This can be explained by the micelle formation of the surfactant monomers that leads to fixing the number of free monomers of surfactant in the solution which is available for the adsorption on the contact surface. Another possible explanation for the same could be the saturation of the adsorption sites available for the adsorption of surfactant particles. Up to the CMC value of the surfactant, these sites can become saturated with the surfactant particles, hence more surfactant particles can not be adsorbed on the surface which leaves insignificant variation in the contact angle after the CMC value.

An analogous trend of the result was found for other rock surfaces as well. However, for the sandstone surface, the contact angle was found to be slightly higher than that of the carbonate surface (Fig. 1b). This can be explained by the strong electrostatic attraction between the opposite charged anionic surfactant head group and the positively charged carbonate rock surface. However, due to the coating of oil on the pellet, the exposed surface was of the carboxylic group of the crude oil and hence the variation in the results were minimal. The lowest contact angle was obtained for the shale pellet which could be because of the complex charge distribution of the clays present in shale (Fig. 1c). The three rock surfaces had an almost similar trend of the contact angle even having different charges and mineral compositions present in them. This can be because of the coating of the rock surface with the crude oil in all three cases. This made the contact surface for every case the same i.e. surfactant solution and crude oil layer. It can be deduced from these experiments that if the rock surface would not have been coated with the crude oil, distinct curves for three surfaces would have been formed.

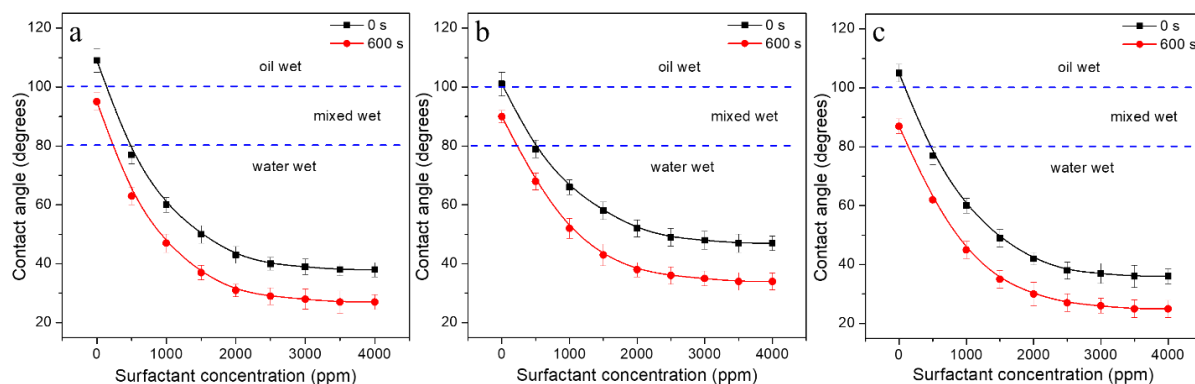


Fig. 1: Effect of surfactant concentration on the contact angle of the oil-wet surface: a) carbonate; b) sandstone; c) shale

To encounter a similar contact surface, the contact angle on different rock surfaces (without aging) was determined using water as a fluid. Surfactant solution (2500 ppm) prepared in the deionized water was used as a fluid to examine the contact angle at the pellet. The contact angle for carbonate rock surface was found to be 23° which reduced up to 11° as the contact time was increased up to 600 s. Since adsorption is a time-dependent phenomenon, hence the contact angle reduced with contact time. Furthermore, the contact angle for sandstone and shale surface was found to be 35° and 32°

respectively which were observed to be decreasing with time up to 23° and 19° corresponding to 600 s. Now, the difference between the contact angle using the same fluid could be because of the different compositions of the rock surface. Carbonate surface being positively charged offers strong Coulombic attraction towards the negatively charged surfactant head groups resulting in the lowest contact angle. Shale surface having clay minerals as a major component have a complex arrangement of charge and structure which exchange the cation (Na^+) released by the surfactant results in the interaction between the surfactant particles and shale surface and hence lower contact angle was observed. It can be deduced from the results that the anionic surfactant should perform better in carbonate surfaces however, considering the amount of surfactant lost due to its adsorption on the positively charged surface remains significantly higher. Hence, anionic surfactants are not generally preferred for carbonate rock surfaces.

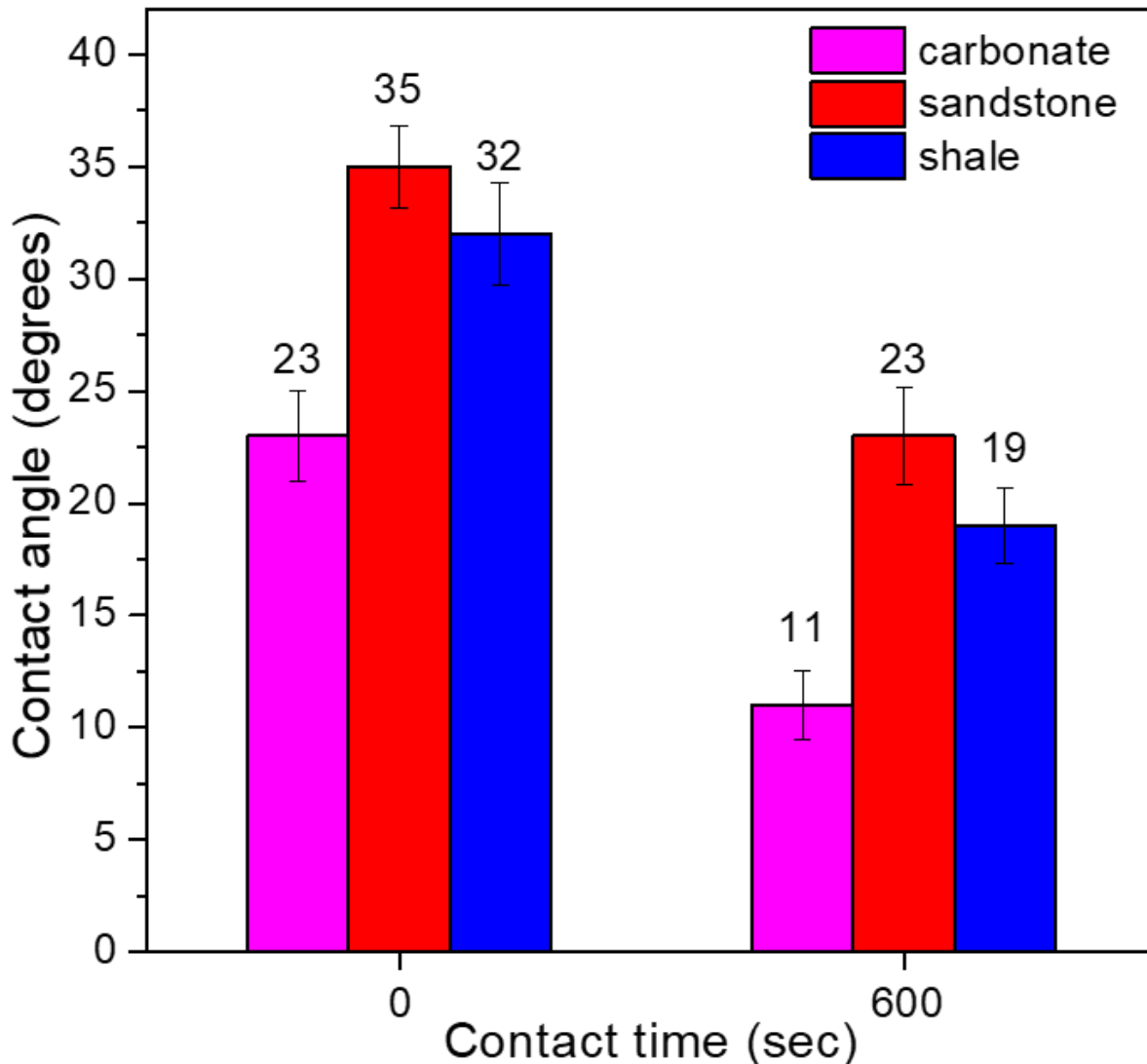


Fig. 2: Contact angle on different rock surfaces using 2500 ppm surfactant solution

Effect of CSNs on the contact angle

The addition of CSNs with the surfactant solution was also determined and it was found to have a synergistic effect on wetting behaviour. The contact angle of the 2500 ppm solution of surface active agent with the variation of CSNs (0 v%, 5 v%, 15 v% and 25 v%) was determined. A decreasing trend of the contact angle with an increasing CSNs concentration was observed for all three surfaces (Fig. 3). The contact angle for the shale surface was found to be reduced from 38° to 31° upon the addition of 25 v% of CSNs with 2500 ppm surfactant. The further reduction of the contact angle confirms the synergy between surfactant and nanoparticles. The addition of smaller size nanoparticles having a negative surface charge leads to the formation of the wedge film around the crude oil droplets that applies a disjoining pressure on the adsorbed layer of crude oil. This mechanism has also been explained previously by several scholars (Kesarwani et al., 2021c; Nazari Moghaddam et al., 2015). The further reduction of the contact angle signifies the efficacy of the CSNs to increase the effectiveness of the surfactant molecules to amend the oil wetting nature of the reservoir rock.

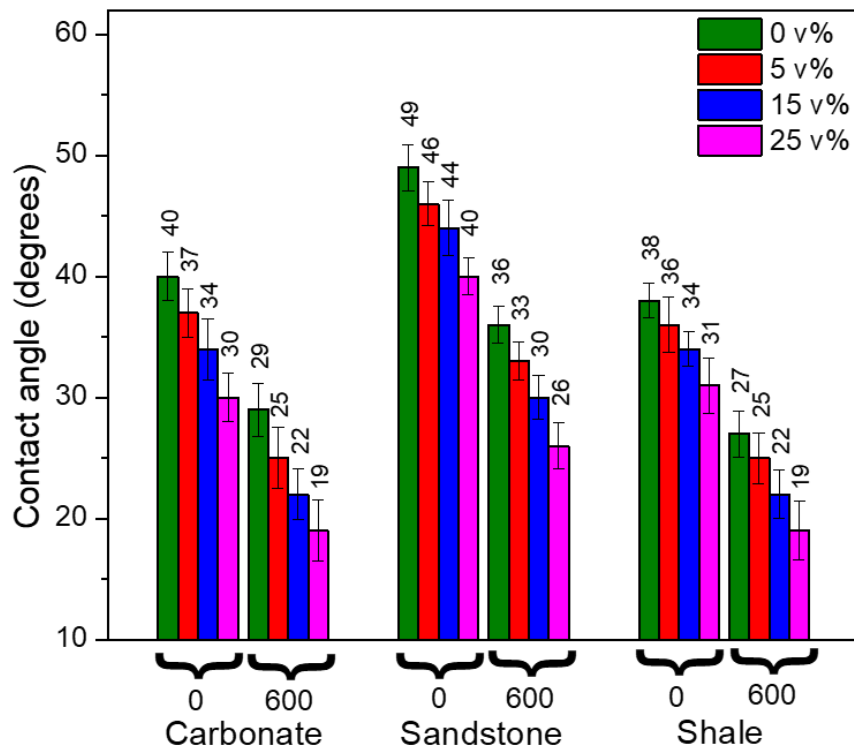


Fig. 3: Synergistic effect of CSNs and anionic surfactant on the contact angle

Conclusions

Different rock surfaces can have a distinct theory that explains the modification of wettability. Carbonate surface offers strong electrostatic attraction to the anionic surfactant leading to the lowest contact angle. It can be deduced from the experimental results that the anionic surfactants perform best for carbonate surfaces for the modification of their wetting characteristics. Moreover, the addition of CSNs has a synergistic effect on the efficiency of the surfactant to modify the wetting behavior of the different reservoir rocks.



Acknowledgments

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