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ORIGINAL ARTICLE

The effect of surfactant concentration on nanoparticles surface wettability during wettability alteration of oil-wet carbonate rock

W.M.S.M. Latif[1], M.S.M. Musa[1], A.S.M. Balakirisnan[1], and W.R.W. Sulaiman[1]

[1] School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia
Phone: +6075535555; Fax: +6075581463

ABSTRACT – Previous studies reported that the presence of surfactant increases nanoparticles surface wettability by in-situ surface activation. On the other hand, the excess of surfactant concentration has an inverse effect on particle hydrophobicity by altering it to be hydrophilic back. Hence, this study presents an experimental investigation of wettability alteration by using a surfactant-nanoparticles system by using cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) surfactant, and hydrophilic silicon dioxide (SiO_2) and partially hydrophobic silicon dioxide (PH SiO_2) nanoparticles. The nanoparticles surface wettability and the wettability alteration of oil-wet carbonate rock were measured by using the contact angle method. The result shows that the contact angle of the oil-wet carbonate rock was most reduced by using CTAB-hydrophilic SiO_2, from 112.00° to 28.35°. The excess of surfactant concentration (beyond CMC) shows an inverse effect on particle surface wettability, however, induces the water-wetness of the carbonate rock. Besides, the hydrophilic SiO_2 shows a more effective effect as a wettability modifier than the PH SiO_2, in the absence and presence of CTAB or SDS surfactant.

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INTRODUCTION

Most of the world's oil reserves are found as sandstone (water-wet) or carbonate rocks (oil-wet), which are 40% and 60% respectively [1, 2]. Two mechanisms of wettability alteration by surfactant normally cited are the removal of the oil-wet layer (a roll-up mechanism) to expose the underlying originally water-wet surfaces or setting up a water-wet layer on the top of the oil-wet layer [3].

The injected $C_{12}TAB$ cationic surfactant altered the oil-wet chalk to water-wet by desorbing the carboxylates from the chalk surface, consequently, the oil was recovered by spontaneous imbibition [4]. However, it was difficult to desorb the already adsorbed anionic organic materials (carboxylates) by using anionic surfactant due to having a similar surface charge [5]. Wettability alteration of oil-wet carbonate was studied by using various ionic types of surfactant [6]. Based on the contact angle reduction, $C_{12}TAB$ was the most effective agent, followed by TX-100 and SDS respectively. $C_{12}TAB$ irreversibly desorbed stearic acids dissolved in n-heptane from the carbonate surface via ion-pair, to change it to water-wet. Besides, TX-100 was adsorbed to carbonate surface through polarization electron and ion exchange, which adsorbed the stearic acid from carbonate surface through hydrophobic reaction; while the SDS mechanism was a hydrophobic tail of surfactant with the adsorbed acid. A similar result was obtained that the oil-wet rock with initial contact angle 140° was reduced to 56°, 98°, and 110° in the presence of 0.3 wt% of CTAB, TX-100, and POE(1) respectively [7]. Hence, CTAB cationic surfactant showed the best effect. The suggested mechanism of CTAB-sandstone was ionic pair of hydrophilic CTAB bonding, while the mechanism of TX-100 and POE(1)-sandstone was hydrophobic bonding. Thus, the binding of surfactant-rock through the hydrophilic part was much stronger than the hydrophobic part. Nevertheless, it is believed that surfactant induced wettability alteration from oil-wet to water-wet condition is expected to be completely reversible, i.e., the adsorbed surfactant is easily desorbed, hence, the surface turned to be oil-wet again [4, 8].

Nanoparticles are the newly explored discipline in wettability alteration, especially by using SiO_2 nanoparticles since it is more effective than other metal oxide nanoparticles: e.g., Al_2O_3, MgO, Fe_2O_3, Ni_2O_3, ZnO, ZrO_2, and SnO [9-11]. There are three types of main utilized SiO_2 nanoparticles in wettability alteration. First is hydrophilic SiO_2 or lipophobic and hydrophilic polysilicon nanoparticles (LHPN) which is utilized to increase the water-wetness. Second is hydrophobic SiO_2 or hydrophobic and lipophilic polysilicon nanoparticles (HLPN), which have a high percentage of ($-CH_3$) group and utilized to increase the oil-wetness. Third is neutrally wet polysilicon nanoparticles (NWPN) with an equal percentage of (-OH) and ($-CH_3$) groups on SiO_2 surface, to alter the wettability to neutral-wet.

The nanoparticles increase the water-wetness of a rock surface by removing the oil-wet layer through 'cleaning' mechanism [12, 13] and/or setting up a water-wet layer on the top of the oil-wet layer [14] through 'coating' mechanism. In the cleaning mechanism, the nanoparticles arrange themselves in wedge-film structure, resulting in structural disjoining pressure gradient at wedge vertex which enhances the ability to remove the oil phase from the rock surface [12]. The cleaning mechanism was studied by using SiO_2 nanofluid, oil-wet calcite, and oil model comprised of stearic acid which dissolved in n-hexane [15]. At the initial state, the stearate anions are adsorbed onto the primary and induce positive

*CORRESPONDING AUTHOR | W. M. S. M. Latif | ✉ mlshaharizuan@yahoo.com charge sites. As oil-wet calcite was immersed in SiO_2 solution, the negative charge of SiO_2 could interact with the positive charge of the calcite surface; while the positive species of solution help to remove the stearates through complexation process. Lastly, the stearate anions are partially removed and replaced with hydrophilic SiO_2, which altered the oil-wet to a more water-wet [15].

On the other hand, the adsorption of SiO_2 nanoparticles formed a nanotextured layer on the oil-wet calcite surface as analyzed by using scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDX), hence, coating mechanism [14]. A similar finding was reported that the distribution of the SiO_2 layer on the oil-wet calcite surface was homogeneous after nano-modification as analyzed by using SEM and energy-dispersive X-ray spectroscopy (EDS). Surface roughness measurements by atomic force microscopy (AFM) also showed that the roughness of calcite increased from 18–32 nm to 1300 nm in the presence of 0.5 wt% SiO_2 [16].

Studied by using micromodel, the mechanisms involved during wettability alteration by SiO_2 dispersion were hydrophilic nature of SiO_2, hydrogen bonding between silica and water, and the increment of surface free energy [17]. The adsorption of hydrophilic SiO_2 on oil-wet calcite also studied by using kinetic, equilibrium, thermodynamic, and DLVO analysis [18]. The kinetic behavior of the SiO_2-calcite system followed the pseudo-second-order model, and the equilibrium study revealed that the Langmuir model yielded a better fit which implied that monolayer coverage of SiO_2 onto the calcite surfaces was more probable. The thermodynamic analysis showed that physical/electrostatic adsorption was expected to be the prevailing mechanism for the adsorption with a spontaneous and endothermic nature; while DLVO interaction energies showed that ionic strength of solution increased the extent of SiO_2 adsorption on calcite.

The adsorption of hydrophilic SiO_2 or LHPN on the oil-wet rock will increase the relative permeability of oil (K_{ro}), which decreasing the resistance to oil flow. Meanwhile, the relative permeability of water (K_{rw}) decreases significantly. By forming a SiO_2 nanoparticles-layer on the rock surface, the viscous forces required to overcome capillary forces were reduced dramatically [19]. Conversely, by the adsorption of HLPN on porous medium, the relative permeability of oil (K_{ro}) will decrease while the relative permeability of water (K_{rw}) will increase. When the HLPN is adsorbed on surfaces of porous walls, the hydrophobic layers are formed instead of hydrated layer, and slip effects appear on the pore wall when a driving pressure is applied to the rock cores sample [20].The calculated slip length was 0.024–0.063 μm, which makes fluid to move more quickly and the flow capacity increased greatly. As a result, the sandstones core contact angle increased from 49.1°, 38.1° and 24.1° to 105°, 101.2° and 99.8° respectively, hence, successfully altered from water-wet to oil-wet.

In summary, the parameters which influence the wettability alteration by using nanoparticles are the type of nanoparticles, concentration, particle surface wettability (surface modification), exposure time, brine salinity, and the presence of surfactant [11, 15, 21].

The utilization of surfactant-nanoparticles during wettability alteration was reported in the previous studies [22, 23]. Despite that SiO_2 nanoparticles have further increased the water-wetness by prior surfactant, the previous studies did not measure the nanoparticles surface wettability in the presence of surfactant. Due to the excess of surfactant concentration will have an inverse effect on nanoparticles surface wettability, hence, the thorough investigation on this matter is the main objective of this study. The utilization of surfactant-PH SiO_2 during wettability alteration also remain inconclusive yet, although the PH SiO_2 could be utilized in a low permeability water-wet reservoir, where water injection either for pressure maintenance or secondary oil recovery is very difficult to be operated [24].

METHODS AND MATERIALS

Surfactant and Nanofluids Preparation

The surfactants used in this study were CTAB and SDS as cationic and anionic surfactant respectively. The SDS was purchased from Sigma-Aldrich, Germany with a purity of 95% and a molecular weight of 288.38 g/mol. The CTAB was purchased from Fisher Chemical, UK with a purity of more than 95% and a molecular weight of 364.45 g/mol. Both surfactants were directly used without further purification. The CMC of surfactant in deionized water (DI) and the brine of 1 wt% NaCl were measured by using the conductivity method. The nanoparticles utilized in this study used were hydrophilic SiO_2 and PH SiO_2. The hydrophilic SiO_2 was purchased from SkySpring Nanomaterials Inc., USA with a purity of 99.5%, while the PH SiO_2 (silica-dimethyl silylate with 50% dichloromethylsie capped, 50% SiOH) was purchased from Wacker Chemie AG, Germany with a purity of above 99.8%. Both nanoparticles were directly used without further purification. The basic properties of nanoparticles are listed in Table 1 and the image of hydrophilic SiO_2 and PH SiO_2 nanoparticles size is shown in Figure 1.

Table 1. Properties of nanoparticles

Nanoparticles type	Size (radius)	Specific surface area (SSA)	Density
Hydrophilic SiO_2 (SiO_2)	10 nm	640 m^2/g	2.17 g/cm^3
Partially hydrophobic SiO_2 (PH SiO_2)	12 nm	Hydrophilic: hydrophobic = 130–170:120 m^2/g	2.20 g/cm^3

(Source: SkySpring Nanomaterials Inc., USA and Wacker Chemie AG, Germany)

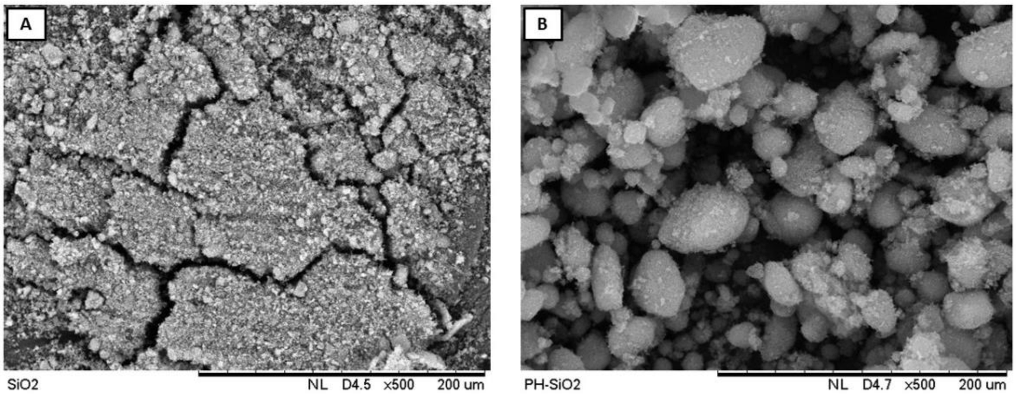


Figure 1. Scanning Electron Image (SEM) of SiO_2 (A) and PH SiO_2 (B)

The surface wettability of nanoparticles was assumed to be similar to the contact angle of glass slide which treated with nanoparticles. To determine the particle surface contact angle, first, 1 wt% of SiO_2 in DI was prepared as a thin layer on a glass slide. Then, it was allowed to dry at room temperature for five hours, before dropping one drop of water on it by using a syringe needle [25]. Instantly, the water image was captured by using a digital microscope VAKIND model 1000X 8 LED 2MP USB. Then, the contact angle was measured by using image sensor 0.3M HD CMOS (Digital 2M) where the average value of the left and right side was taken. Besides, since hydrophobic SiO_2 or PH SiO_2 cannot be dispersed in a polar liquid such as water, hence, it can only be dispersed in an organic fluid such as ethanol [21, 26].

As prior, the nanoparticles surface wettability in the presence of a surfactant is assumed to be similar to the contact angle of glass slide which treated with nanoparticles-surfactant. The adsorbed surfactant molecules could pull the particles to the air-water interface when the nanoparticles adsorbed the proper amount of surfactant molecules, especially in the presence of electrolyte [27]. Besides, the adsorption of particles at the air-water interface was mainly controlled by particle-interface and particle-particle interactions [28].

Wettability Alteration of Carbonate Rock Samples

The carbonate rock was prepared in a coin shape with a diameter of 5 cm and a thickness of 1 cm by using a coring machine. Before the test, the carbonate rock was rinsed with water and dried by oven at 80 ^{o}C to eliminate the impurities [29]. To ensure all samples have a similar contact angle of oil-wet before the experiment, it were chemically treated by immersing in 4 wt% of dichloromethylsilane in n-hexane [30, 31] for three hours, before dried inside an oven at 60 ^{o}C for three days [32].

During wettability test, firstly the carbonate rock sample was placed inside a beaker with DI. Then, one drop of oil was injected below the carbonate rock sample by using a curved-syringe needle, as shown in Figure 2 below [7, 9, 15]. The oil drop image was captured by using the digital microscope VAKIND model 1000X 8 LED 2MP USB, and the contact angle was measured by using image sensor 0.3M HD CMOS (Digital 2M). The tolerance of contact angle between the left and right side was controlled between $0.1^{o} < \Theta < 2.5^{o}$ [15, 33] and the simple average value was taken. The contact angle in DI was recorded as the initial condition or experimental basis. Then, the experiment was repeated by using another carbonate rock sample, in the presence of 1 wt% NaCl, surfactant, and nanoparticles dispersion.

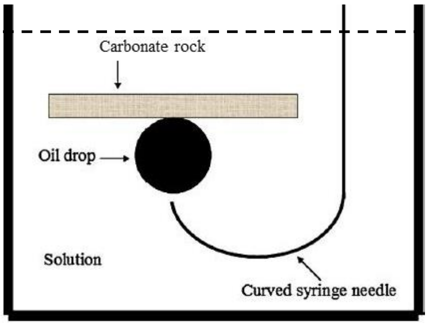


Figure 2. Wettability alteration of oil-wet carbonate rock

The first studied parameter was exposure time along which monitored hourly up to 24 hours. The effect of surfactant was studied by varying the CTAB and SDS concentrations at CMC and 2 CMC. Then, the effect of nanoparticles concentration was studied by varying from 0.01 wt% to 2.00 wt% to obtain the optimum concentration of nanoparticles, in the absence and presence of surfactant. The prepared surfactant-nanoparticles dispersion was stirred for 12 hours and followed by 30 minutes of sonication before used [34, 35].

RESULTS

Nanoparticles Surface Wettability in the Presence of Salt Concentration

By using the contact angle of the treated glass slide method, the measured hydrophillic SiO_2 and PH SiO_2 nanoparticles surface wettability in DI are 3.74° and 90.00° respectively. The repeated experiment in the presence of 1 wt% NaCl and surfactant is given in Table 2.

Table 2. Nanoparticles surface wettability in 1 wt% NaCl

System	θ_{left}	θ_{right}	$\theta_{average}$	$\Delta\theta_{left-right}$
Hydrophilic SiO_2	10.80°	10.59°	10.70°	0.21°
Partially hydrophobic (PH) SiO_2	58.06°	58.50°	58.28°	0.44°
CMC CTAB-SiO_2	25.08°	23.75°	24.42°	1.33°
2 CMC CTAB-SiO_2	15.59°	15.01°	15.30°	0.58°
CMC CTAB-PH SiO_2	70.02°	71.57°	70.80°	1.55°
2 CMC CTAB-PH SiO_2	46.40°	46.03°	46.22°	0.37°
CMC SDS-PH SiO_2	74.29°	74.62°	74.46°	0.33°
2 CMC SDS-PH SiO_2	58.57°	59.04°	58.81°	0.47°

Effect of Exposure Time on Wettability Alteration

The first parameter that has been studied is the effect of exposure time. First, one piece of carbonate rock in coin shape was immersed in 1 wt% NaCl as a basis of the experiment. Then, it was immersed in a solely surfactant solution, solely nanoparticles, and surfactant-nanoparticles system which monitored by hourly up to 24 hours. The obtained contact angle of the paraffin oil which injected from below is shown in Figures 3.

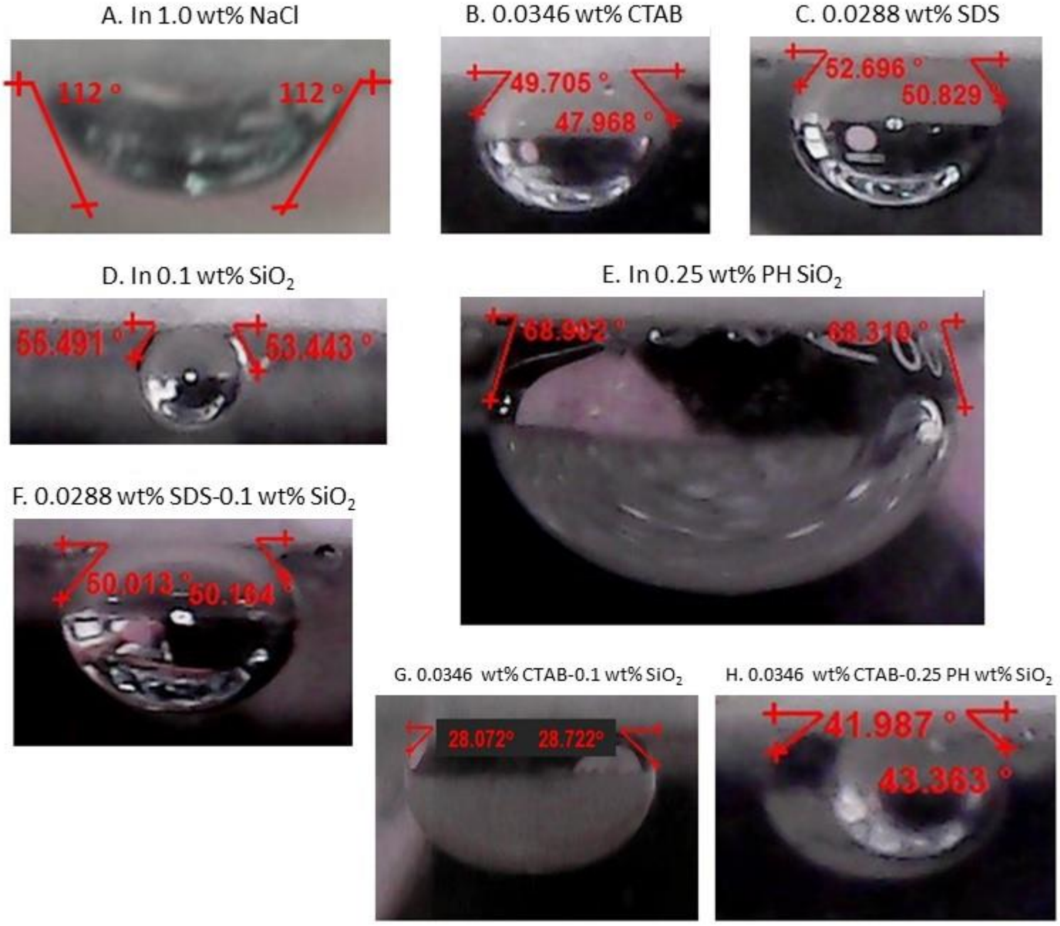


Figure 3. The contact angle of carbonate rock in solely surfactant, solely nanofluid, and surfactant-nanofluid

As can be seen in Figure 4, the minimum contact angle obtained in all systems: solely surfactant, solely nanoparticles, and surfactant-nanoparticles were all obtained since the first hour of exposure time-in, and continuously exposed the carbonate rock up to 24 hours did not further reduce the contact angle. Thus, the carbonate rock samples already reached the optimum adsorption capacity after one hour.

In a solely surfactant or solely nanoparticles system, the highest reduction of contact angle was obtained by using CTAB, followed by SDS, SiO_2, and PH SiO_2 respectively. The presence of CMC CTAB and SDS successfully reduced the contact angle of the oil-wet carbonate rock from 112° to 48.84° and 51.77° respectively, while the utilization of 0.1 wt% SiO_2 and 0.25 wt% PH SiO_2 nanoparticles reduced the contact angle of the oil-wet carbonate rock from 112° to 54.47° and 68.61° respectively.

On the other hand, in surfactant-nanoparticles system, the contact angle of the oil-wet carbonate rock reduced from 112° to 28.40°, 42.68°, and 50.18° in CTAB-SiO_2, CTAB-PH SiO_2, and SDS-PH SiO_2 systems respectively. Considering the previous studies that found 100% of contact angle reduction within 20 minutes, and 75.4% reduction within 60 minutes [16, 33], hence, the wettability alteration by utilizing surfactant-nanoparticles in the following experiment will be monitored up to one hour.

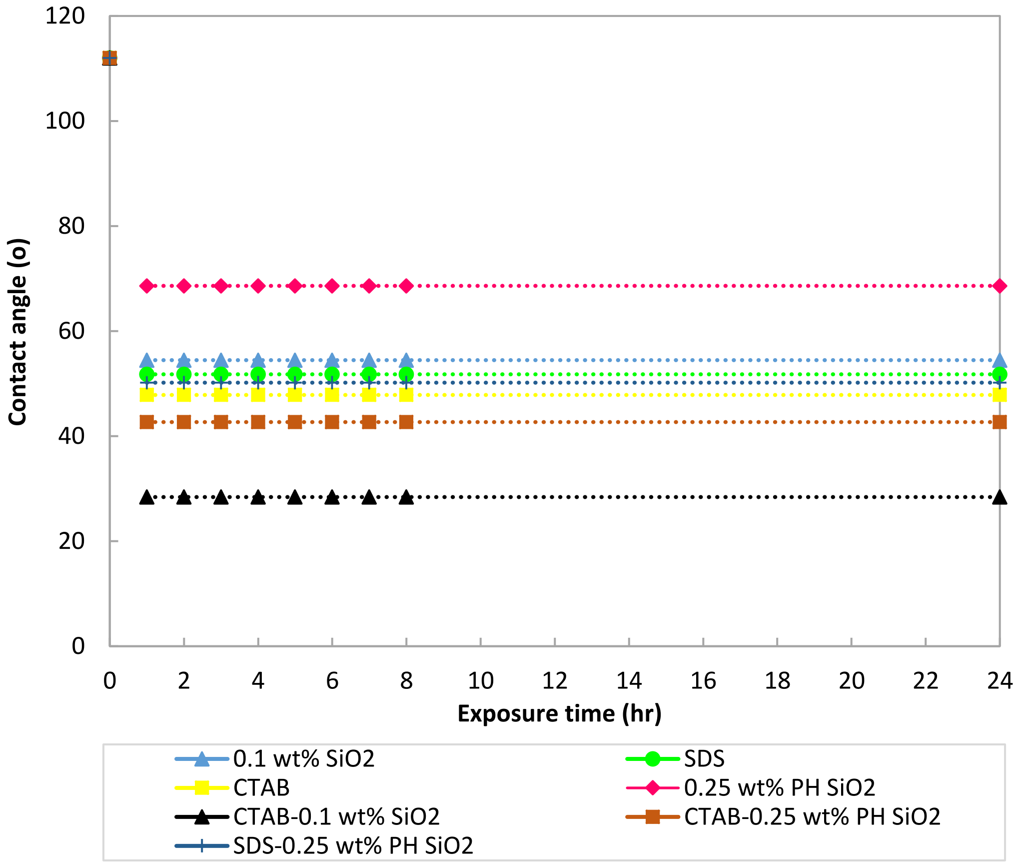


Figure 4. Effect of exposure time on contact angle in surfactant-nanoparticles

Effect of Nanoparticles Concentration on Wettability Alteration

The effect of SiO_2 and PH SiO_2 nanoparticles concentration on wettability alteration was studied in the absence and presence of surfactant, and the effect of surfactant concentration at CMC and 2 CMC.

The concentration of nanoparticles was varied from 0.01 to 0.25 wt% and the result is shown in Figure 5. As the nanoparticles concentration increases until it reaches the optimum value, the contact angle decreases until it reaches the constant value. The optimum particle concentration in all systems was within the range of 0.04–0.08 wt%. Hence, only small particle concentration already capable of altering the oil-wet to the water-wet, where the hydrophilic SiO_2 showed better effect than PH SiO_2. The surface modification at PH SiO_2 makes them the best to obtain the neutral-wet system, hence, the lower contact angle was obtained by using hydrophilic SiO_2. The optimum concentration of SiO_2 and PH SiO_2 in CTAB and SDS system at CMC and 2 CMC were between 0.04–0.06 wt% and 0.05–0.08 wt% respectively. Thus, the higher particle concentration was required by using PH SiO_2.

The CTAB-nanoparticles system showed a higher increase of water-wetness compared to SDS-nanoparticles, suggested that CTAB was a better wettability modifier than SDS. A similar result was reported in the previous study, that CTAB reduced more contact angle than SDS [6, 36]. Thus, the selection of surfactant is crucially significant despite the presence of nanoparticles.

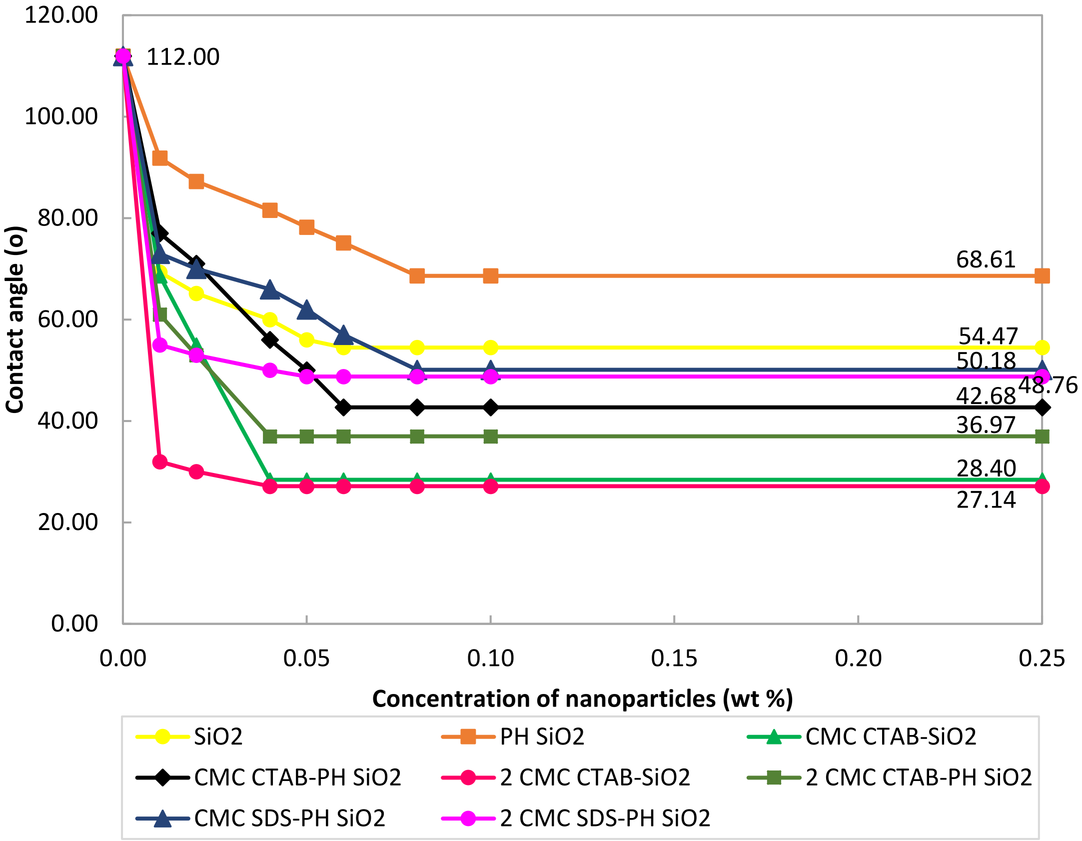


Figure 5. Effect of nanoparticles concentration on wettability alteration

Effect of Surfactant Concentration on Wettability Alteration by Nanoparticles

As shown in Figure 5, the presence of surfactant on nanoparticles dispersion further reduced the contact angle by the solely nanoparticles. The presence of CMC CTAB (0.0346 wt%) and 2 CMC CTAB (0.0692 wt%) further reduced the contact angle in the SiO_2 system from 54.47° to 28.40° and 27.14° respectively to obtain the strongly water-wet state. A similar result was occurred in CTAB-PH SiO_2 system, that contact angle of 68.61° in PH SiO_2 nanofluid reduced to 42.68° and 36.97° respectively in the presence of CMC and 2 CMC CTAB. The presence of CMC SDS (0.0288 wt%) in the PH SiO_2 system reduced the contact angle from 68.61° to 50.09° while the presence of 2 CMC SDS (0.0577 wt%) further reduced the contact angle to 46.57° respectively.

DISCUSSION

Effect of Salinity on Nanoparticles Surface Wettability

The presence of 1 wt% NaCl increased the hydrophobicity of hydrophilic SiO_2 as the contact angle increased from 3.74° to 10.70°. The presence of electrolytes alters the free energy of double-layer formation at particle surfaces as well as at the air-water interface, which in turn be reflected in the value of the contact angle and the tendency of the particles to adsorb at the air-water interface [37]. Conversely, the presence of electrolyte decreased the surface contact angle of PH SiO_2 from 90.00° to 58.28°. More hydrophobic the particle, the lower the electrolyte concentration needed to allow adsorption of individual charged particles to the air-water interface [38]. Due to the critical salt concentration (CSC) value of hydrophilic SiO_2 was occurred at 1 wt% of NaCl [39], hence, it is suggested that the CSC of PH SiO_2 is below in 1 wt% NaCl. Consequently, the excesses of salinity prevent the repulsion of particles by screening them, which leads to the coagulation of the partially hydrophobic or hydrophobic nanoparticles, resulting in the reduction of the contact angle. Further studies should be conducted to verify this matter.

Effect of Surfactant on Nanoparticles Surface Wettability

CTAB was adsorbed on hydrophilic SiO_2 by electrostatic attraction. The increase of CTAB concentration leads to the increase of hydrophobic interactions between the hydrocarbon tails of CTAB and particle surface [40]. Through this hydrophobic interaction, the hydrophobicity of particles increased while the maximum collision occurred at CMC value. Hence, the particle surface contact angle increased from 10.70° to 24.42°. However, the excesses of surfactant concentration at 2 CMC formed a double-layer structure with the hydrophobic tails of the two layers interfingered and the headgroups of the second layer pointing to the solution, thus, the particle surface became hydrophilic again [41]. As a result, the contact angle decreased from 24.42° to 15.30°. A similar result was obtained in the CMC CTAB-PH SiO_2 system that the adsorption of monolayer CMC CTAB molecules on PH SiO_2 nanoparticles surface increased particle hydrophobicity. As a result, the particle contact angle increased from 58.28° to 70.80° by hydrophobic bonding. Whereas, the adsorption of bilayers molecules decreased the contact angle from 70.80° to 46.22°, resulted in completely unattached CTAB molecules on PH SiO_2 surface.

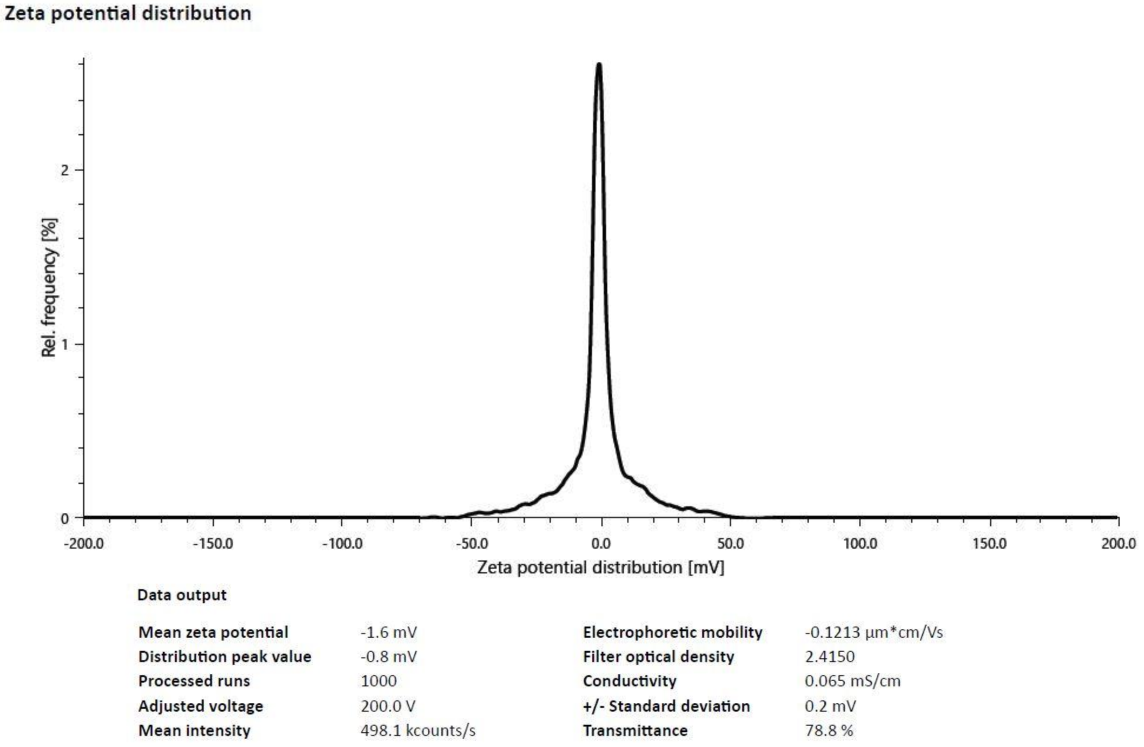
On the other hand, the adsorption of SDS molecules on PH SiO_2 nanoparticles surface increased the hydrophobicity of PH SiO_2 through hydrophobic interaction and left the negative hydrophilic head group exposed outside [42]. Through this hydrophobic interaction, the hydrophobicity of particles increased due to surfactant coverage on the surface of particles [43]. Hence, at CMC value, the contact angle of PH SiO_2 increased from 58.28° to 74.46°. However, as the SDS concentration increased to 2 CMC, the presence of double layer SDS molecules on PH SiO_2 surface and free SDS molecules which adsorbed competitively on the interface rendered the PH SiO_2 nanoparticles became more hydrophilic, consequently reduced the nanoparticles surface wettability.

Effect of Surfactant in a Surfactant-Nanoparticles System during Wettability Alteration

Due to CTAB-SiO_2 system produced the lowest contact angle, followed by CTAB-PH SiO_2 and SDS-PH SiO_2 respectively, hence, the selection of surfactant has a vital role although in the presence of nanoparticles. It is suggested that in surfactant-nanoparticles system, the primary effect is the cleaning/roll-up mechanism by surfactant while the nanoparticles act as secondary agents through the coating mechanism on the cleaned surface, where the nano-textured layer is directly proportioned to particle concentration.

As the negative charge of the oil-wet carbonate rock was immersed in CTAB-SiO_2 dispersion, the positive charge of CTAB could interact with the negative charge of calcite (CO_3^{2-}) while the sodium positive ions from the electrolyte solution could help to remove the negative charge silane [44] through the complexation process, making the adsorption amount of CTAB on the carbonate surface increased [15, 45]. Meanwhile, by the adsorption of the negative charge of SiO_2 (-OH group) on the positive sites of calcite surface (Ca^{2+}), the viscous forces required to overcome capillary forces were reduced [19]. Thus, the oil-wet carbonate was altered to water-wet.

The charge of the carbonate rock used in this study was confirmed by using Litesizer 500 Anton Paar instrument. Zeta potential measurement has also been used as a quantitative technique for characterization of colloidal stability [46]. Higher magnitude of zeta potential (less than −15 mV or higher than 15 mV) signified higher electrostatic repulsion forces and low aggregation of particles in the aqueous solutions [47] . By using 1 wt% of the carbonate rock in DI, at pH 7.3, the obtained mean zeta potential was -1.6 mV with SD ± 0.2 mV as displayed in Figure 6. This result is consistent with the previous studies, that the surface charge of carbonate rock in deionized water was a negative charge, with the point of zero charge (pzc) is between pH 6 and 7.5 [18, 48, 49]. Conversely, the surface charge of carbonate rock is positive below this pH, while the increase in pH drives the zeta potential of the carbonate towards the negative direction [50, 51].



Data output

Mean zeta potential	-1.6 mV	**Electrophoretic mobility**	-0.1213 µm*cm/Vs
Distribution peak value	-0.8 mV	**Filter optical density**	2.4150
Processed runs	1000	**Conductivity**	0.065 mS/cm
Adjusted voltage	200.0 V	**+/- Standard deviation**	0.2 mV
Mean intensity	498.1 kcounts/s	**Transmittance**	78.8 %

Figure 6. Zeta potential distribution and mean value of the carbonate rock

The wettability test was then compared with the surface tension and interfacial test as shown in Figure 7, which has a linear agreement with Young's equation. According to Young's equation, for a given solid, as the wetting tendency is larger, the smaller the contact angle or the surface tension, which including SDS and CTAB surfactant [52, 53]. Besides, the high IFT was obtained in functionalized SiO_2 nanoparticles compared to hydrophilic SiO_2 since the functional groups make the nanoparticles less water-wetness [54].

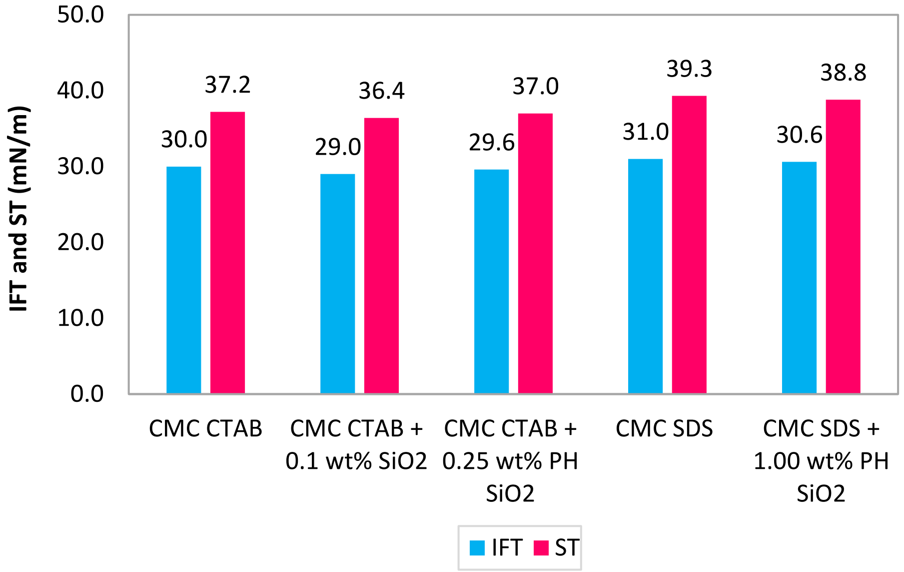


Figure 7. Surface tension and IFT of surfactant-nanoparticles system

CONCLUSIONS

In this study, the wettability of oil-wet carbonate rock in the presence of surfactant-nanofluid has been studied by varying the surfactant type, surfactant concentrations, and nanoparticles concentration. The results are summarized below:

1) Solely surfactant system was a more effective wettability modifier compared to solely SiO_2 nanofluid system. The water-wetness increased with the increases of surfactant concentration from CMC to 2 CMC.
2) The presence of 2 CMC surfactant inversed the nanoparticles to be hydrophilic back, hence, the reduced of particle surface wettability compared to CMC.
3) Although the presence of 2 CMC surfactant have an inverse effect on nanoparticles surface wettability, however, the contact angle of oil-wet carbonate rock further decreased compared to CMC surfactant-nanoparticles. Hence, the wettability alteration in surfactant-nanoparticles system was governed by surfactant rather than nanoparticles.
4) The effectiveness of hydrophilic SiO_2 compared to PH SiO_2 in increasing the water-wetness, either in the absence or presence of surfactant despite having a smaller optimum nanoparticles concentration.
5) The wettability result showed a linear agreement with Young's equation, due to surface tension and IFT reduction in surfactant-hydrophilic SiO_2 nanoparticles systems was lower than surfactant-PH SiO_2 system.
6) The selection of hydrophilic SiO_2 nanoparticles is recommended in increasing the water-wetness compared to PH SiO_2, however, in the presence of surfactant to obtain the strongly water-wet state.

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