

Hydrophobic Silica Nanoparticle and Anionic/Cationic Surfactants Interplays Tailored Interfacial Properties for the Wettability Alteration and EOR Applications

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ABSTRACT: *In this study, the effect of anionic and cationic surfactant solutions alone and in combination with silica AEROSIL® R⁸¹⁶ nanomaterial on the wettability alteration of carbonate rock reservoirs has been investigated. The nanofluid properties including stability, surfactant Critical Micelle Concentration (CMC), Interfacial Tension (IFT), and surfactant adsorption were studied in each case, and the synergistic effect of nanoparticles as adjacent particles along with surfactant molecules in the solution with respect to electrostatic and capillary forces has been discussed. The results show that nanoparticles generally reduce ST, CMC, and surfactant adsorption on the rock, and surfactant molecules significantly increase the stability of nanoparticles. Also, contact angle test results indicated an increase in the effect of the wettability alteration of stones in the surfactant solution by the nanoparticles from the lipophilic to the hydrophilic, and the nanopowder solution itself had the most ability to change the wettability. Finally, the results from the observations mentioned above were confirmed by performing an imbibition test based on drop experiments.*

KEYWORDS: *Enhance oil recovery; Imbibitions; Interfacial tension; SLS; AEROSIL®R⁸¹⁶; Wettability alteration.*

INTRODUCTION

Because of the significant decrement in the available oil reservoirs Enhanced Oil Recovery (EOR) methods are attracting considerable attention all around the world [1-12]. Although, the growth of these techniques has been limited by many difficulties and barriers such as probable formation damage, sweep efficiency, and cost. In the chemical EOR technique, chemicals are utilized to replace the stock oil in the pores by adjusting the characteristics of reservoir oil and rock such as interfacial tension,

wettability plus mobility ratio Furthermore, nanoparticles have demonstrated that they can improve plenty of conventional EOR challenges; nanoparticles tend to self-assemble and film-forming in contact with oil and rock porosity surfaces. The application of nanoparticles in EOR is studied in the literature[1, 13-15]. Moreover, to enhance nanoparticle stability, surfactants are added to their solution. Generally, nanoparticles are coated with surfactant molecules that their surface-active parts are modified

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the hydrophobicity-hydrophilicity of nanoparticles. These active sites accomplish nanoparticle adsorbing on the interface to modify the IFT and wettability. The (surfactant/nanoparticle) concentration ratio determines the features of the modified nanoparticles with the surfactant. If this ratio is low, surfactants are coated on a small portion of the nanoparticle's surfaces, and in high concentration ratios, a double layer of surfactant can form on the particle's surface [2, 3, 6, 15-22]. The surfactant/nanoparticle interactions can change the surface activity of surfactant molecules significantly. Ionic surfactant and charged nanoparticle with strong electrostatic interaction can form multilayers of surfactant on the nanoparticle. In general, higher concentrations of surfactants provided higher adsorption on the oil-water interface that can considerably decrease the interfacial tension and change the wettability to the water-wet condition [23, 24].

Maghzi et al. [6, 25] measured the contact angle between water with different weight percentages from the silica nanoparticles using the drop method and showed that after flooding with nanoparticles, the wetting condition of the reservoir stone changed into a strong hydrophilic situation. They used a glass micromodule to test how to move the fluid in a porous medium. Nazari investigated the changes in wettability of carbonate reservoirs in Iran using silica nanoparticles and found that with this nanoparticle the wettability of carbonate rocks in reservoirs could be varied and changed from hydrophobic to medium hydrophilic. By calculating the contact angle, he concludes that with increasing nanoparticle concentrations, the contact angle decreases, which means an increase in the hydrophilicity of the reservoir's stone [19-21].

Handringrat et al. [26], using hydrophilic silica nanoparticles, showed that nanofluids have a high potential for ultimate oil recovery as secondary flooding in comparison with the third flooding after brine water, and with the use of nanofluids, the ultimate oil recovery is increased 8%. *Maghzi et al.* showed that for a nanofluid with 0.1% weight of silica nanoparticles 8.7% and with 3% weight of silica particles 26% oil recovery was obtained compared to water flooding [25, 27]. Nanomaterials/surfactant agents reduce the capillary pressure in the reservoir's refractory and improve the flow of the reservoir in this area. Because when the dimensions of these materials are in the nanometer range, their ability to

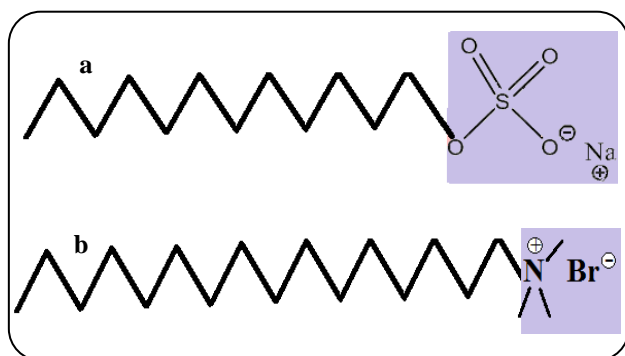
penetrate the cavities and their active surface can be dramatically increased

For following up on the significance of these studies, various surfactants types, including sulfonates of alkylbenzene, alkyl-sulfates, alkyl-phosphates, Al salts quaternary, and alkyl-glycosides, have been fabricated to investigate the abovementioned applications and active mechanisms. Plus the improved interfacial characteristics quite a few materials of the biodegradable and biocompatible surfactants are still needed. Besides the environmentally friendly nature of the green surfactants, they have indicated diverse deficiencies including rare existence in natural products; expensive production, and complex separation process. On the contrary green surfactants, fatty acids, sugar, and amino acid serve as the basis for surfactant preparation with the naturally structural origin, which mainly constitutes basic and sustainable compounds, have been replaced as a stand-in for preserving fossil resources and for mitigating environmental issues. The key roles of these materials which result in the increasing appeal to subjected industries are the super-rapid degradation, convenient biocompatibility, and low toxicity to the atmosphere. [7-9, 11, 12, 22, 27, 28]. Javadifar and colleagues examined the microscopic and macroscopic yield of heavy oil extraction in a five-point slit porous media in the injection process of two anionic surfactants (SDS) and cationic surfactants (C₁₂ TAB), as well as water-based surfactant-containing silica nanoparticles. The results showed that the presence of nanoparticles in a surfactant solution would dramatically increase oil recovery. Also, microscopic images showed that the silica nanoparticles changed the wettability of the environment from lipophilic to hydrophilic [13, 17, 29, 30]

Furthermore, it is noteworthy that wettability alteration in various interfacial tensions is different. For instance, lower interfacial tension does not always lead to remarkable alterations in wettability [13, 17, 19, 21, 25, 27]. The phase behavior of a surfactant-oil-water system and surfactant/nanoparticle affinity is another crucial factor that modulates wettability changes. It can be achieved same ST reduction at both low and high salinity conditions respectively with hydrophilic surfactants (prefer to be into the aqueous phase) and lipophilic surfactants (prefer to be into the oil phase). According to the above-mentioned, it can be designed as a hydrophilic/lipophilic surfactant formulation for specified ST reduction and more successful wettability modulating from oil-wet to water-wet [19, 31-34]

Table 1: Properties of anionic and cationic surfactants.

Properties	SLS	CTAB
Appearance	White powder	White powder
Molecular formula	$\text{NaC}_{12}\text{H}_{25}\text{SO}_4$	$\text{C}_{19}\text{H}_{42}\text{BrN}$
Molar mass g/mol	288.38	364.45
Melting point C	206	(Decomposes) 237-243

**Fig. 1: Molecular structure of a) SLS and b) CTAB.**

The purpose of this study was to investigate the effect of the presence of anionic SLS and cationic CTAB surfactants in pure form and also with the slightly Hydrophobic Aerosil® R 816 nanopowder on the adsorption of surfactants and carbonate stone wettability. The investigated properties included nano-fluid stability, critical concentration and IFT of surfactant solutions, pure and with nanoparticles, adsorption of surfactant, and finally, imbibition experiments. In each case, the presence of nanoparticles as side particles along with surfactant molecules in a soluble state is discussed with respect to electrostatic forces and capillaries. Also, contact angle and IFT tests have been performed to investigate the behavior of materials on the surface between water, oil, and rock. These studies help to better understand the behavior of nano in increasing the EOR.

EXPERIMENTAL SECTION

Chemicals

This study used anionic and cationic surfactants, sodium lauryl sulfate (SLS) and Cetyltrimethylammonium bromide (CTAB) prepared from India Mart and Merck Germany respectively. Nanopowder AEROSIL R⁸¹⁶ (AEROSIL® R⁸¹⁶ is a fumed silica after treatment with

a hexadecylsilane) is based on the Slightly Hydrophobic silica nanopowder prepared from Evonik Germany.

Reservoir rock samples

Due to the fact that the nature of the stone is very important in the change of wettability, two types of carbonate stone and sandstone are used in one of the southern reservoirs of Iran.

Fluids

Depending on the test, the water phase was distilled water and salty water. Distilled water with a density of 998.2 kg/m³ and a viscosity of 1cp at 25 °C was produced in the laboratory and used as the basis solution for IFT measurements and adsorption experiments.

It was used to measure the IFT because Kerosene is transparent compared to crude oil. The kernel viscosity was 1.7 cp (measured with the Cannon-Fensk instrument), and the density was 796.9 kg/m³ at 25 °C. Crude oil of one of the southern reservoirs of Iran was used for injection testing. Its density and viscosity at 25 °C are 88.89 kg/m³ and 28 cp, respectively.

Solutions preparation

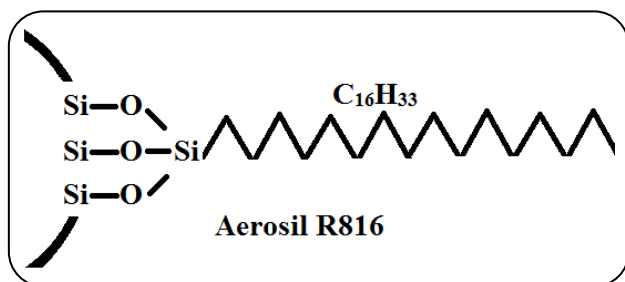
A solution of surfactant is made by adding a precise amount of surfactant powder to distilled water while on a magnetic stirrer. To overcome Solubilizing Temperature or Kraft Temperature solution will be heated to a sufficiently for 30 minutes. The nano-particles are then first soaked to the required amount of water, and then the particle mass is separated from each other by an ultrasonic device and dispersed in an aqueous phase. The sonication process was performed to ensure complete particle separation for 90 minutes.

Table 1: Properties of AEROSIL R⁸¹⁶ nanopowder.

Properties	AEROSIL R ⁸¹⁶
Behavior in the presence of water	Slightly Hydrophobic
Contact Angle (Degree)	100-120
Appearance	Fine white powder
Surface area (m ² /g)	20 ±190
particle size (nm)	12-16
Density (gr/l)	60
PH	4.0- 5.5
Carbon content Wt.%	0.9-1.8
SiO ₂ Wt.%	>99.8
Al ₂ O ₃ Wt.%	< 0.05
Fe ₂ O ₃ Wt.%	< 0.01
TiO ₂ Wt.%	< 0.03
HCL Wt.%	< 0.025

Table 3: Composition of Salt-water sample.

Composition	Concentration (mg/liter)
Mg ²⁺	6318
Ca ²⁺	20000
CL ⁻	142000
TH (Total Hardness)	76000

**Fig. 2: AEROSIL® R⁸¹⁶ is a fumed silica after being treated with hexadecylsilane.**

Interfacial tension measurement

The interfacial tension of the oil/nanofluids at ambient conditions is measured by the pendant drop method.

Pendant drop Setup

A pendant drop device typically consists of four main parts, including laboratory tubes, a lighting system, an imaging system, and ultimately a data acquisition

system. The Pendant drop device is used to measure IFT at different temperatures and pressures. This device has the ability to measure IFT and contact angle in a range of temperatures up to 200 ° C and pressure up to 10000 psig.

Fig. 3(a) shows the IFT measurement setup schematic. First, a specified diameter syringe is equipped and filled with crude oil. An optically clear vessel is filled with the nanofluid. The concentrations of the nanofluids are varied between 0 to 0.5 mg/mL. The tip of the needle is positioned in the vessel. The crude oil droplet is positioned at the tip of the needle from the topside of the vessel, and then, the image of the droplet is recorded by applying a CCD camera equipped with a macro lens. Finally, the image of the equilibrium pendant drop is analyzed by the image analyzing software and the IFT is determined.

The pendant drop method is the most appropriate and most commonly used method for IFT. In this method, by analyzing the droplet of a fluid in a fluid under the equilibrium conditions of IFT, the shape of the drop depends on the balance between the gravity forces and the surface forces.

Parameters of the pendant drop that are determined experimentally are the equatorial diameter, D_e , and the diameter D_s at a distance D_e from the top of the droplet. The IFT is then calculated from the following equation.

$$\gamma = \frac{D_e^2 g \Delta \rho}{H}$$

Where, g and $\Delta \rho$ are the acceleration of gravity and the difference between the crude oil droplet and the aqueous solution densities, respectively. The shape parameter (H) depends on the value of the shape factor ($S = ds/de$).

Adsorption Experiments

Adsorption of surfactant in a porous environment is one of the most important issues in the injection of surfactant to increase EOR. Because depending on the purpose of the injection of these chemicals, the adsorption of surfactant on the stone will have a significant effect on the resultant injection. Because the adsorption of surfactants is a function of complex parameters, an analytical method is proposed to calculate the adsorption, and the adsorption rate is usually obtained in a laboratory.

Static Adsorption

The static adsorption method was used to measure the adsorption of surfactant on the rock. In this method, surfactant solutions with different concentrations with

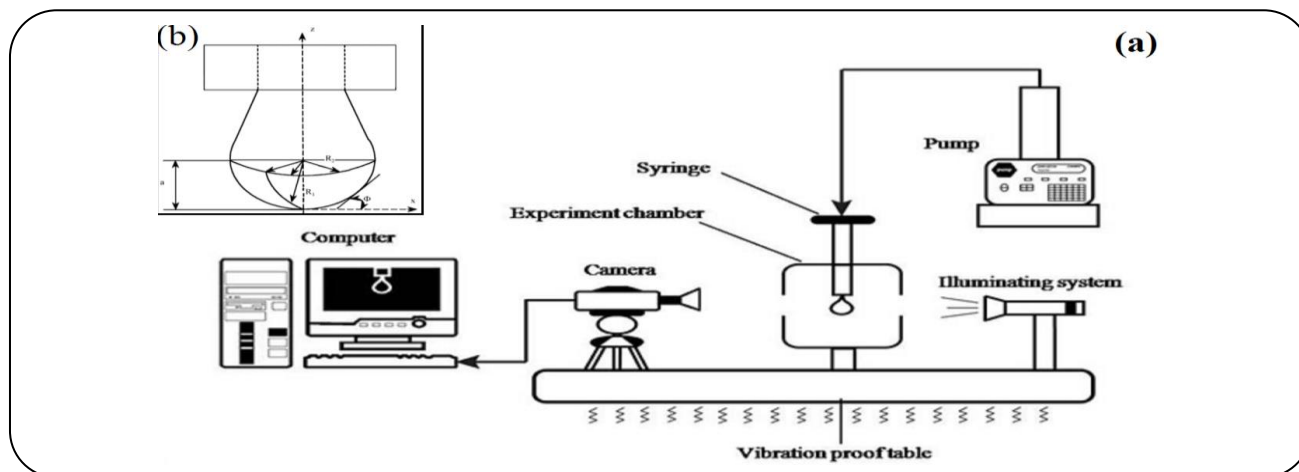


Fig. 3: (a) Schematic of the IFT measurement set up, (b) diameters of the pendant drop.

the ratio of 5 to 1, solution to the rock, in suitable containers in contact with each other, with a gentle shake for 24 hours, reach equilibrium. This time is greater than the time it takes to reach the equilibrium state in the adsorption phenomenon. However, the adsorption of surfactant at different times to prove this claim was measured. After the equilibrium, the solution of surfactant and rock was separated using centrifugation, and each test was repeated three times to ensure the correctness and repeatability of the experiments.

Dynamic Adsorption

To measure the dynamic adsorption, stone particles of different sizes were beaten in a sand pack, then 5 pvs surfactant solution was injected into the sand pack, and then 5 pvs water was injected. The injection rate is 0.5 cc/min and is sampled in 5 cc ranges. The concentration of adsorption has been calculated by analyzing the concentration of the output in the sand pack and integrating the concentration integral. It is worth noting that the surfactant solutions are made with water that is in contact with the rock for 24 hours and reaches equilibrium. By doing this, the probability of occurrence of dissolution of rock in solution in adsorption experiments and its effect on conductivity and dissolution density is prevented.

Measurement of nanofluid solution concentration

To measure the concentration, the properties of the solution should be used that changed to change the concentration. Due to the fact that IFT is constant at

concentrations higher than the Critical Micelle Concentration (CMC), this property is not an appropriate option for concentration measurement. Therefore, the conductivity coefficient and in some cases, the solution density were used to determine the concentration. Concentration levels are obtained by establishing a proper calibration graph through the properties mentioned. To measure the conductivity, the Sartorius Professional conductivity meter PP-20 and the density of 5000 DMA were used.

Boyle's Two Cell is used to measure porosity where the porosity is obtained by injection of a noble gas (hydrogen gas) in two tubes, one containing the cores, and the other as the reference tuber, and the repetition of the test with a reference cylinder instead of the core is obtained. It should be noted that the use of noble gas is due to neutralize the effects of gas on the rock.

Core flood experiments

Coreflood set up

The Core Flooding Machine consists of five main parts, including an electric pump, injection and production lines, core holder assembly, and production vessel.

Core porosity and permeability measurements

For permeation measurement, distilled water with different flow rates is injected into the cores, and after the required time for the system equilibrium the pressure is recorded, and permeability with Darcy's Equation is calculated with the viscosity of the injected fluid and the core dimensions.

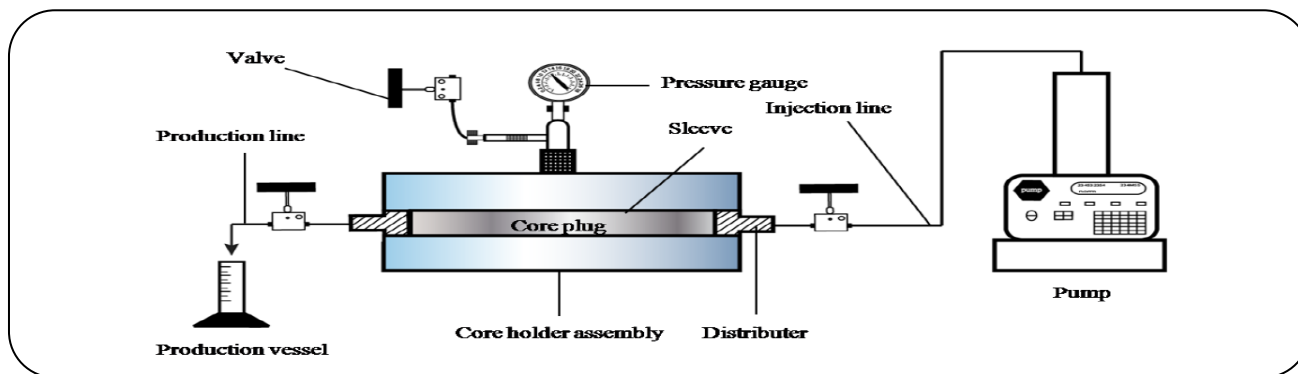


Fig. 4: Schematic of the core flood set up.

Coreflooding procedure

After measuring the permeability of the core, water is injected with low discharge in the core, and then the oil is slowly injected into the core. It should be noted that the amount of water output at this stage is very important because this water determines the amount of oil in the core.

Contact angle measurement

The commonly used method for directly measuring the contact angle for determining the properties of a specific rock-water-oil system is called the Sessile Drop method. In this method, the Pendant drop device is used to capture the image of the droplet.

To analyze the droplet, first put a drop on the stone and let the droplet find its equilibrium on the stone, then, in a situation where no other angular change occurs in the droplet, an image is taken from the droplet.

Forced and spontaneous imbibition experiments

Imbibition setup consists of three main sections, including a glass tube for maintaining the core and the desired solution, a cylinder for recording the outlet fluid, and a magnetic stirrer for keeping the fluid homogeneous during the test. In the imbibition test, the amount of oil output from the cores is measured by the penetration of an external fluid such as surfactant in the rock.

RESULTS AND DISCUSSION

Nanofluid stability

One of the crucial parameters for using nanomaterials in EOR is to increase their stability. R^{816} nanopowder and two types of surfactants SLS and CTAB have been used in this study. The stability of R^{816} nanopowder was studied in an aqueous solution. The solution with suspended particles

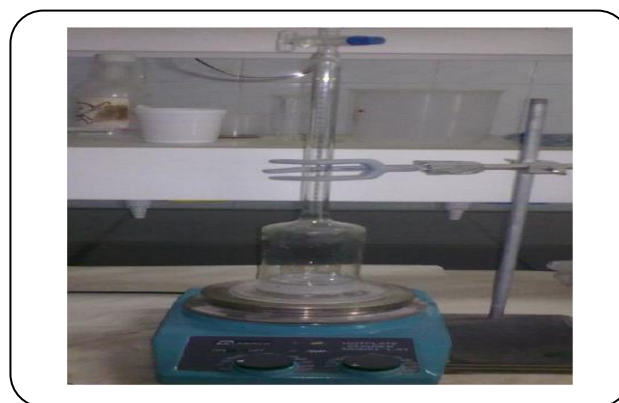


Fig. 5: Imbibition setup.

of R^{816} remained stable for about 3 to 4 days for a very short time. Instability in colloidal solutions usually occurs for two reasons. One of the reasons is the presence of relatively strong van der Waals forces between nano-powders in water. These gravity forces, in particular, make high agglomerates and eventually become flocculate. The second reason is gravity [35]. When the particles become agglomerates. Of course, the difference in density between nanoparticles and their surroundings is calculated. In states in which the particle density is greater than the density of the surrounding environment, the particles tend to move downwards, and they are deposited due to gravity. When particles are very small, their Brownian motion, which is due to kinetic energy, overcomes these forces. Moreover, if the gravitational forces are very strong, they will dissipate particles. Fig. 6 shows the process of flocculation and ultimately, sedimentation [36].

of surfactants and R^{816} on each other

The forces between surfactants and nanomaterials are further characterized by their characteristics, such as surface

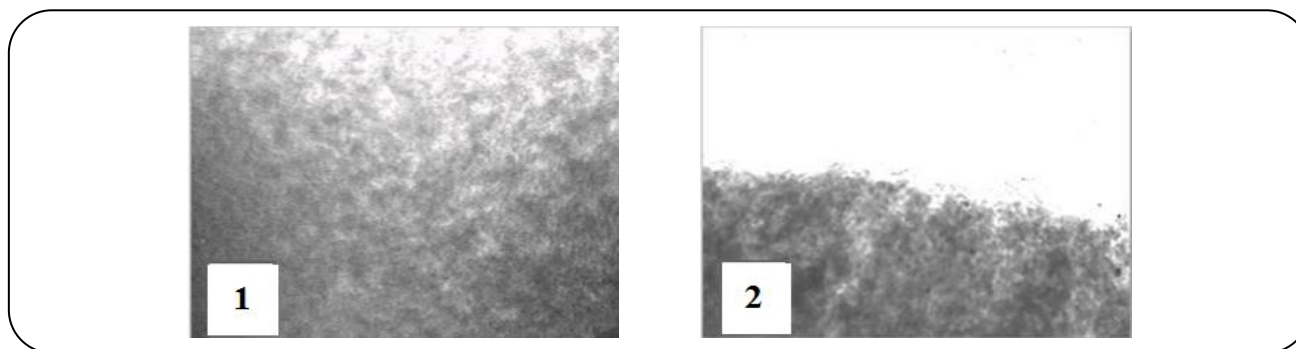


Fig. 6: R^{816} 1) Flocculation 2) Sedimentation.

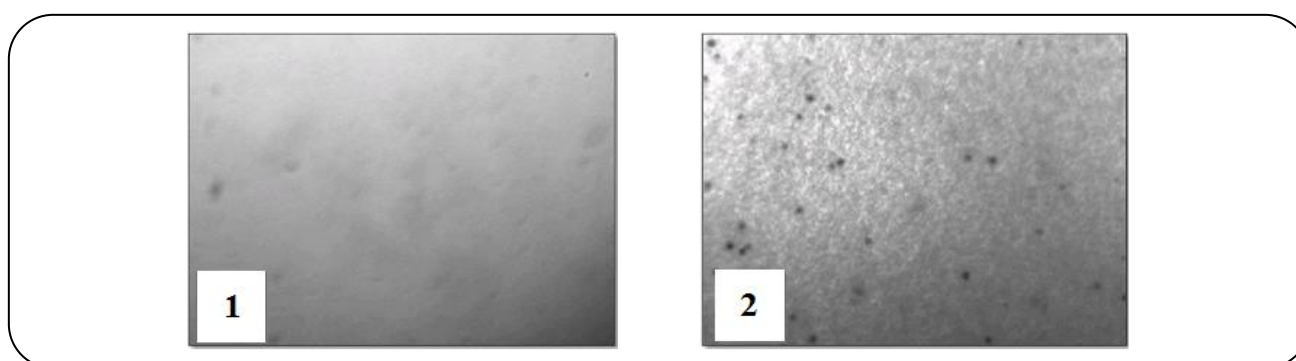


Fig. 7: R^{816} solution by adding cationic surfactant CTAB 1) before adding surfactant 2) one hour after adding surfactant.

charge. The contrast between hydrophilic nanopowders and more active surface materials is due to electrostatic forces, with the help of these forces and other forces that act simultaneously with these forces, it can analyze the contrast between anionic and cationic surfactants with nano-powders.

R^{816} nano-silica powder and CTAB

As expected, the addition of CTAB to the silica nanopowder solution makes it unstable and, as shown in Figure 7, CTAB causes flocculation of colloidal particles. The main reason for this phenomenon is the presence of electrostatic attraction forces between the hydrophilic surfactant head and nanoparticles. These results are consistent with the observations [37].

Changes in effective charge on the nanopowder surface indicate this, the higher the concentration of CTAB, the more surfactant absorbed on the surface of the nanopowder, which reduces the effective charge of nanopowder [37, 38].

R^{816} nano-silica powder and SLS

Adding the SLS Surfactant to R^{816} Nano-Powder solution improves the stability of this solution (Fig. 8).

Improvements in the stability of the R^{816} solution may be due to two reasons. The first reason is surfactant adsorption through the alkyl chain on the hydrophobic branches of R^{816} and the other is because of the adsorption of surfactant head on a hydrophilic nano-side, which increases the surface charge on nano-powder in both phenomena and reduces their repulsion [37].

These observations are consistent with the findings of Mingxiang Luo *et al.* [39, 40] By performing a molecular dynamics simulation of the interaction between the SLS and the nanocrystalline silica powder, most SLS molecules point towards the nanopowder (Fig. 9) and the interesting point is the orientation of some hydrophilic SLS heads towards the nanopowder. Many sodium ions were present near the hydrophilic surfactant and nanopowder.

Further studies have shown that the hydrophilic head of surfactant is closer to the negative charge of nanoparticles. The mechanism that causes this to happen is not yet clear. The first guess is the existence of a dual-layer around the nanoparticles in which the nanoparticles with negative charge hold positive sodium ions around, and these ions absorb the negative head of the surfactant.

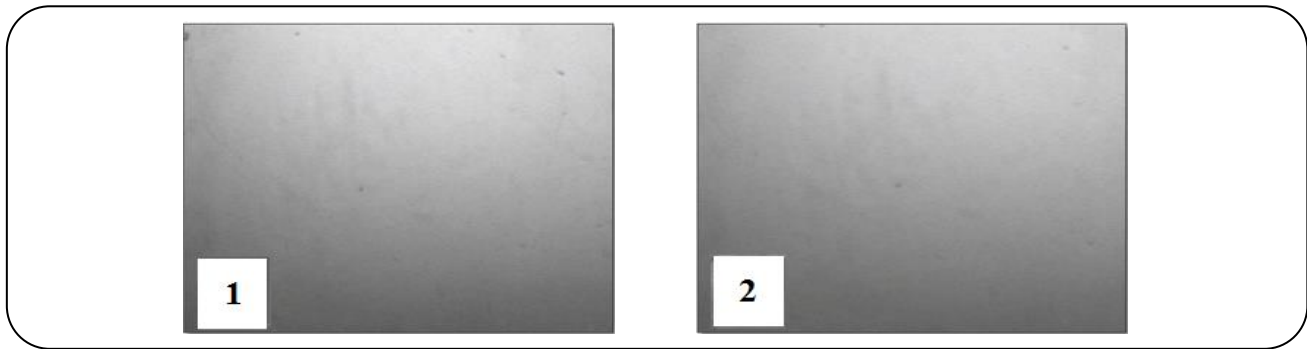


Fig. 8: R816 solution stability in the presence of SLS 1) Immediately after adding SLS 2) One week after adding SLS.

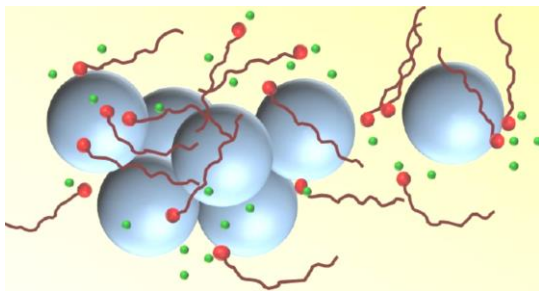


Fig. 9: The morphology of surfactant molecules in contact with nanoparticles.

Zeta potential measurements for solutions stability

The silica AEROSIL® R 816 -surfactant solutions Zeta potential was measured using electrophoresis with a WALLIS Zeta potential instrument from CORDOUAN, equipped with a highly reliable 20 mW diode @635 nm coupled to an automated optical attenuation system. The ζ -potential values were ascertained using the Helmholtz-Smoluchowski equation from the mobility measurements. ζ -Potential is a very efficient technique for ascertaining the solution stability. ζ -potential of the pure silica AEROSIL® R⁸¹⁶ was measured to be -23 mV in aqueous suspension. As Fig. 10 illustrates the ζ -potentials are altered by the addition of anionic and cationic surfactants into the AEROSIL®R⁸¹⁶ dispersion. In general, ζ -potential decreases to -34 mV which made it more stable which was in agreement with the results presented in Fig. 8. Reversely, there is a slight enhancement of the ζ -potential by the addition of CTAB to -19 mV and diminishment of stability which is reflected in Fig. 7. As shown in Fig. 8, the surfactant molecules SLS adsorption on the surface of the hydrophobic nanoparticles transformed their hydrophobic nature into partially hydrophilic, these structures of AEROSIL® R⁸¹⁶ / SLS make the solution more.

Effect of nanoparticles on the critical concentration of surfactant

The critical micelle concentration is one of the most important parameters of each surfactant and must be determined before the use of any surfactant. This parameter is usually obtained by measuring one of the properties of the surfactant that exhibits dual behavior at lower and higher concentrations than critical concentrations. Surfactant conductivity has been used to measure its critical concentration alone, as well as for various surfactant and nanoparticle compounds. The critical concentration is obtained by plotting the conductivity changes in terms of concentration variation. The critical concentration is obtained by plotting the conductivity changes in terms of concentration variation. CMC is the point where the slope of the curve changes and in other words, the change in Conductivity flux changes with increasing concentration. The results of measuring the critical concentration in different conditions are given below.

The CMC of Surfactant solutions

Conductivity changes are shown in Figure 10 on the basis of the surfactant concentration. As you can see, CMC of anionic and cationic surfactants are 2023 and 529 ppm, respectively.

The results of CMC measurements are consistent with the results of other studies [41, 42].

Surfactant/nanoparticle solutions CMC

The purpose of this study was to investigate the effect of the presence of nanoparticles on the critical concentration of surfactants, and for this reason, the SLS/R⁸¹⁶ compound was tested. It should be noted that CTAB was not used because of stability problems. Conductivity measurements of this solution showed that

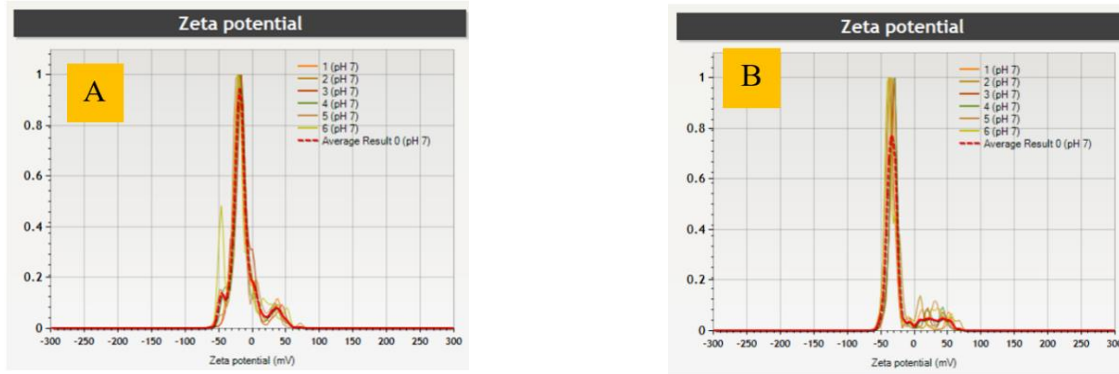


Fig. 10: Zeta potential measurements of the CTAB+ Silica (A) and Silica +SLS (B).

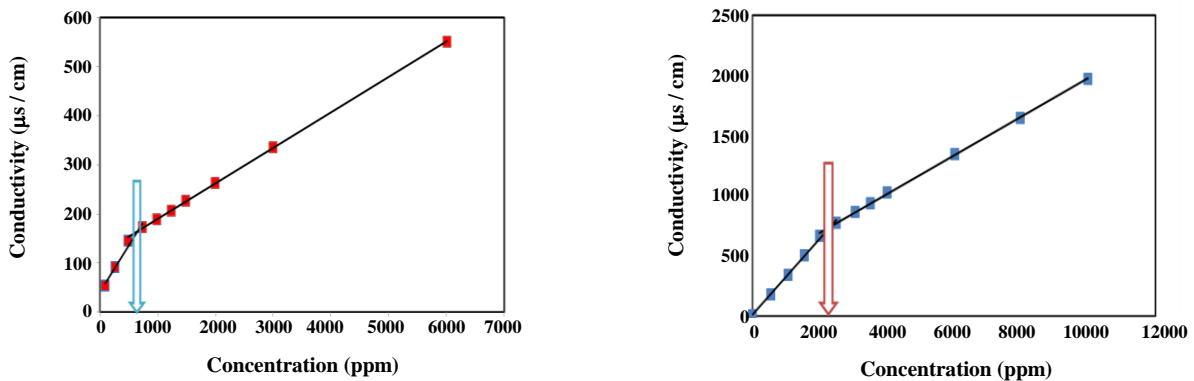


Fig. 11: The CMC of Surfactants with Conductivity Changes 1) SLS 2) CTAB.

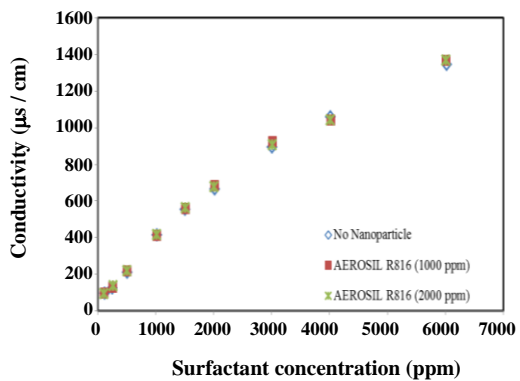


Fig. 12: The effects of nanoparticles on surfactant Conductivity.

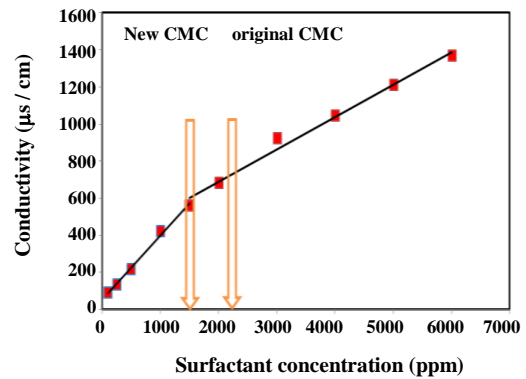


Fig. 13: Alteration of the critical micelle concentration of SLS in the presence of R^{816}

the presence of nanoparticles had minimal effect on the conductivity of surfactants (Fig. 11)

However, the presence of nanoparticles affects the critical concentration of surfactants. As you can see in Fig. 12, R^{816} nanoparticles reduced the CMC of SLS surfactant relative to pure SLS solution.

The presence of nanoparticles reduces the critical concentration of surfactant. It is worth noting that the increase in the concentration of nanoparticles further reduces the critical concentration (Fig. 13), which is probably due to electrostatic forces between nanoparticles and the hydrophilic head of the surfactant.

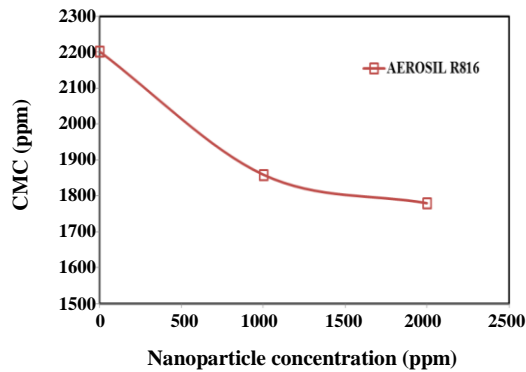


Fig. 14: Effect of Nanoparticle Concentration on Surfactant CMC.

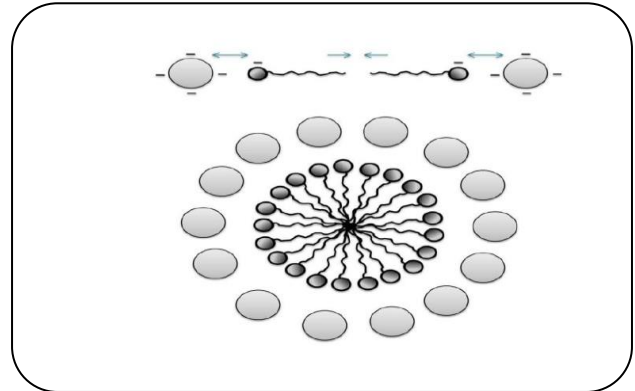


Fig. 15: Electrostatic repulsion between nanoparticles and surfactants.

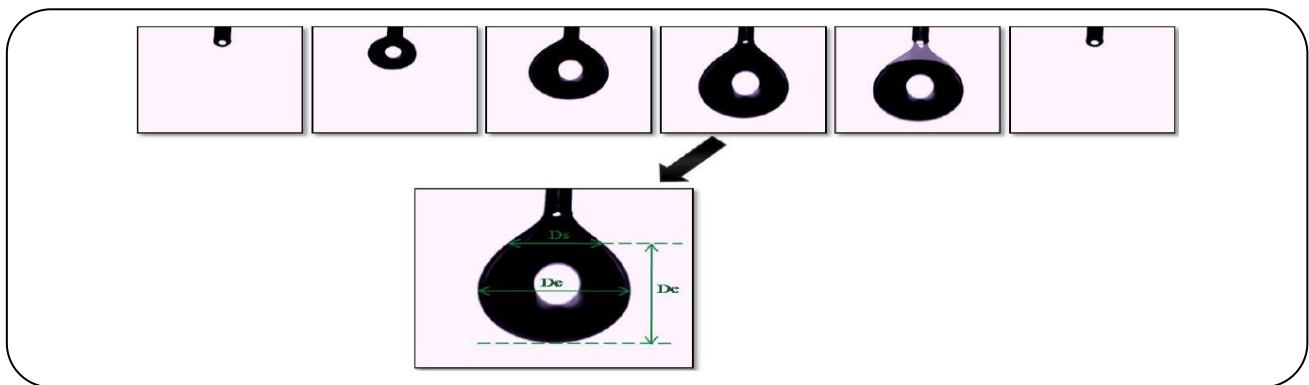


Fig. 16: The process of forming a droplet in the pendant drop setup.

Regardless of the low adsorption of surfactants on nanoparticles, the negative charge of nanoparticles and the hydrophilic head of surfactant leads to a negative electrostatic repulsion between the molecules [43]. This repulsion force moves the surfactant molecules towards each other (Fig. 14) and makes the surfactant micellization faster. Besides, the presence of hydrophilic nanoparticles in an aqueous medium makes the situation inappropriate for the hydrophobic head of surfactant and accelerates the process of micellization [44].

IFT between surfactant /Nano solution and oil

The surfactant solution is injected by a high-precision pump with a very low flow rate in the kerosene medium. Although the low flow rate of the measurement process causes the surfactant monomers to have time to equilibrate between two phases, the surfactant is released by the gravity in the kerosene, not by the injection pressure.

The suitable droplet for measuring the IFT is a drop just before falling (Fig. 15), and it is attained by determining the parameters of the D_s and D_e for IFT.

The IFT of surfactant solutions

To determine the effect of CTAB and SLS on IFT between water and oil, various concentrations of these materials were made. Fig. 16 shows droplets with different concentrations for SLS before falling. By increasing the concentration of the surfactant solution, the droplet resistance is reduced, and gravity is the only dominant force in the droplet formation process. This phenomenon is due to the reduction of IFT between aqueous and petroleum solutions. After a specific concentration, the size of droplets remains constant, which indicates that IFTs remain constant at higher concentrations than this concentration.

According to the Gibbs adsorption theory, the reduction of IFT between aqueous and oil solutions is due to the adsorption of surfactant molecules in the interphase of water and oil, and the higher the surfactant concentration, IFT is also reduced to the extent that the middle surface of surfactant molecules saturated. According to other researchers, the strong opposition

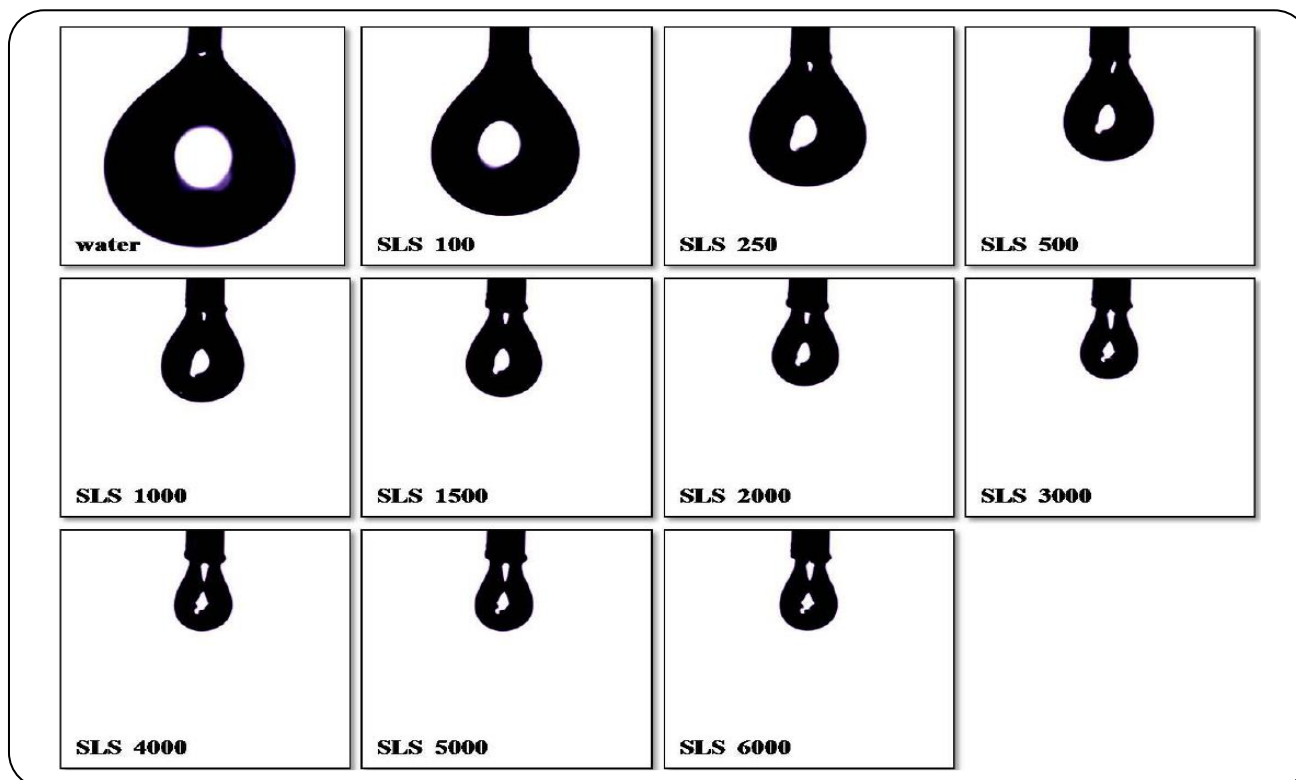


Fig. 17: The final shape of SLS droplets with increasing concentrations.

between surfactant and oil molecules has led to the reduction of IFT [45, 46].

The IFT between water and oil in various concentrations of surfactants is calculated and plotted in Fig. 17.

The difference between the CTAB and SLS IFT graphs show that the IFT reduction process depends on the type of surfactant. The determining parameter in the reduction of IFT for different surfactants is the size of the hydrophobic alkyl chain and the hydrophilic head. The smaller the molecule size, the greater the number of molecules is located at this median level and further reduces IFT. Therefore, it can be said that the number of more molecules of CTAB in the space between two phases is located and further reduces IFT. Another important point is the steady-state IFT at a specific concentration of surfactant. As already mentioned, this concentration is the critical concentration of surfactant, and the addition of surfactant to the solution formed micelles of the monomers, and the number of free monomers remains constant to the two-phase mid-level. As can be seen, the critical concentration calculated with the IFT is consistent with the one calculated by the conductivity property.

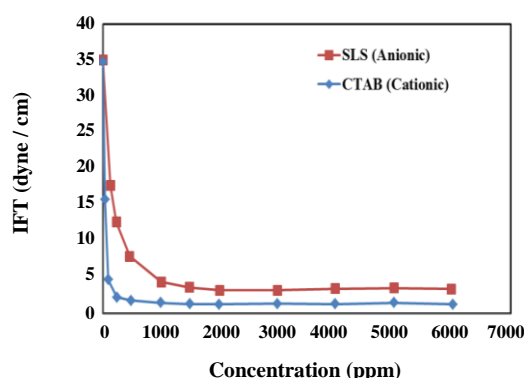


Fig. 18: The effect of surfactant concentration on IFT between water and kerosene.

Nanoparticle and surfactant IFT

In this section, the presence of nanoparticles on surfactant IFT behavior was investigated. Due to the persistence of CTAB, the SLS/R816 composition was tested. For this test, a certain amount of surfactant has been dissolved in the suspended solution of nanoparticles. To determine this phenomenon, the IFT between the water and petroleum phases was calculated (Fig. 18). Observing

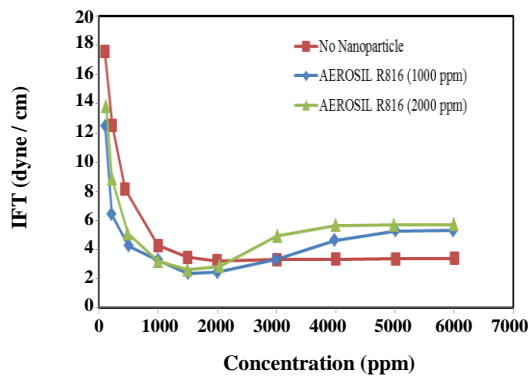


Fig. 19: Variation of IFT with surfactant concentration for SLS /R⁸¹⁶ and pure SLS.

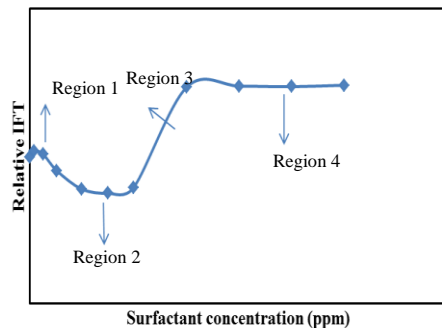


Fig. 20: Relative IFT of SLS/R816 and pure SLS.

the results, we noticed the strange behavior of surfactant with nanoparticles at a constant concentration.

To clarify this phenomenon, the concept of relative IFT, in which the IFT ratio of surfactant solution and IFT of the SLS/R⁸¹⁶ composition was used in a constant concentration of surfactant (Fig. 19). In very low concentrations of surfactant, the entry of nanoparticles has a negligible effect on the IFT of surfactant (region 1), with a significant increase in surfactant concentration, there is a significant change in IFT with the presence of nanoparticles. With the presence of nanoparticles, to concentration under the critical point, the reduction of IFT decreases, so that at all concentrations below the critical point, the IFT with the presence of nanoparticles is less than normal (region 2). However, when surfactant concentrations reach critical points, the presence of nanoparticles results in different behavior and increases IFT (region 3). Ultimately, IFT with the presence of nano is more than normal (without the presence of nano). This

phenomenon was also predicted from the analysis of the shape of droplets (area 4)

In low concentrations of surfactant, nanoparticles are soaked in water and remain in an aqueous medium, and do not move toward the space between the two phases [37, 47]. The second region's behavior is explained with a different look. First, with increasing surfactant concentration, the repulsive force between surfactant and nanoparticles increases, and this causes the surfactant to move toward the interphase space as a result of IFT [43]. Another view says that by increasing the concentration of surfactant, the number of surfactants on the surface of nanoparticles increases and they tend to increase to the two-phase space. Thus, with the increase in the number of nanoparticles in this space, they can carry SLS itself, and their presence in this space or the release of SLS, of which can lead to a decrease in IFT. The more marked reduction of IFT may be due to the self-depositing of nanoparticles alone. The nanoparticles tend to stay in the space between the two phases [48]. With increasing surfactant concentration, more nanoparticles are located in the space between water and oil. In this way, the justification for increasing the IFT between the two phases can be explained by the forces of the capillary. When the particles are placed in the space between two phases, they are classified into two categories, Floation, and Immersion, depending on their type of placement (Figure 20) they are floating on another phase and in a restricted state between two phases. In both cases, the capillary force comes along the surface of the contact due to its deformation.

When the concentration of particles increases, their number increases, and the particles that lie next to the particles at the mid-level, tend to be oriented toward the mid-level and create a state such as the immersion state in which the capillary forces are very effective. As the two particles become closer together, the capillary force between them increases, and this force opposes the change in the middle position between the two phases and thus increases the IFT. Prolongation of IFT in a higher amount than the normal surfactant (without the presence of nanoparticles) (in high concentrations may be justified by absorbing surfactant on the nanoscale. Charged nanoparticles cause the deformation of a carbon fiber branch. The carbon atoms near the hydrophilic head are tilted toward the middle of the two phases, due to the

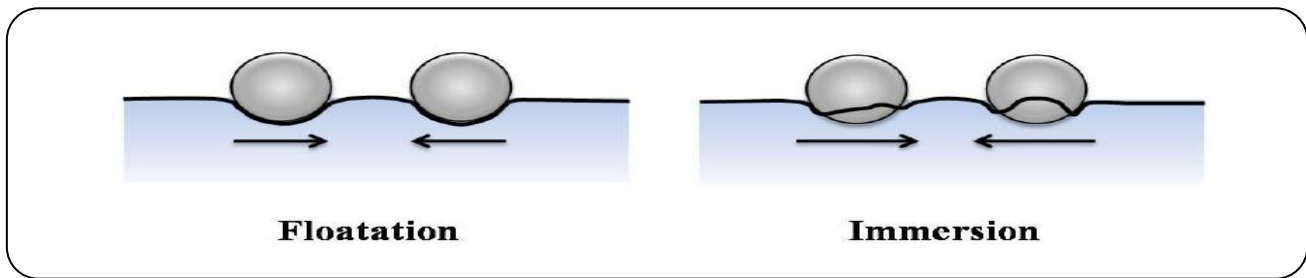


Fig. 21: A schematic of two particles along with the interface of the two phases.

presence of nanoparticles at the middle surface, the forces between hydrophobic branches surfactant and nano, and the forces between hydrophilic surfactant, the charged nanoparticles, and sodium ions. For this reason, the SLS's ability to reduce IFT due to its deformation at the middle level of the two phases decreases.

The other theory involves the capillary forces in this phenomenon. According to this theory, after increasing the concentration of nanoparticles at the midpoint of the two-phase, the space between the two phases of the saturated nanoparticles and the force of the capillary can not increase the IFT, which is why the IFT is in a higher degree than the normal surfactant [48].

As shown in Figures 18 and 19, there is no apparent change in regions 1 and 2 (up to 2000 ppm of surfactant) with changes in nanoparticle concentrations, but in zone 3 (concentration 2000 ppm to 4000 ppm), with increasing the concentration of nano the IFT increases, and it seems that the molecular forces act at higher concentrations of nanoparticles stronger and faster. Finally, in concentrations above 4000 ppm, due to the presence of more nanoparticles in the space between the two phases, there are fewer molecules of surfactant in this space, and thus the IFT is fixed at a higher value.

Nanoparticle impact on the process of surfactant adsorption

The surfactant adsorption process is the movement of surfactant molecules to a solid surface. The behavior of surfactant molecules on the solid surface depends on forces such as electrostatic forces, covalent bonding, hydrogen bonding, carbon bonds, and solubility of various components.

Surfactant adsorption

The precision of the surfactant concentration measurement methods was investigated, and a calibration

graph was made for each surfactant. The error obtained for these methods is 5% for the conductivity method and 0.0028% for the density measurement method which is acceptable. For example, the calibration chart and test points for the SLS surfactant are shown in Fig. 21.

To schedule the surfactant adsorption onto the rock, for experiments designing, unsustained adsorption of SLS at a concentration of 1000 ppm on the rock was first statically performed. Surfactant non-equilibrium adsorption was investigated using both Conductivity and Density Measurement methods, which both had perfect matching. As shown, the adsorption process can be divided into three regions. In the first region, a linear increase in adsorption is observed with increasing concentrations, and then the adsorption process passes through a transition region; in this region, the adsorption rate decreases until it is established at a specific rate.

According to Fig. 22, it can be said that the time required to balance the adsorption process is between 5 to 6 h and nearly 90% of adsorption occurs in the first 2 hours.

Equilibrium adsorption is the measurement of the maximum amount of absorbed surfactant per unit surface area or a specific rock mass unit. To ensure that surfactant adsorption is completed, the surfactants are exposed to stone for 24 hours. The adsorption of SLS on the rock by both concentrations is shown in Fig. 23 and both methods are well matched.

The adsorption of surfactant (adsorption isotherm) can be divided into three regions. The first region is the electrostatic adsorption region of the surfactant monomers with the hydrophilic head on the rock. The second region relates to the time of opposition, the surfactant monomers, and the formation of a series of rock accumulations called Hemimicelle. Other monomers, due to the fact that there is no additional surface on the surface of the stone, can not be absorbed onto the surface and remain in the solution, which is why the adsorption rate remains constant.

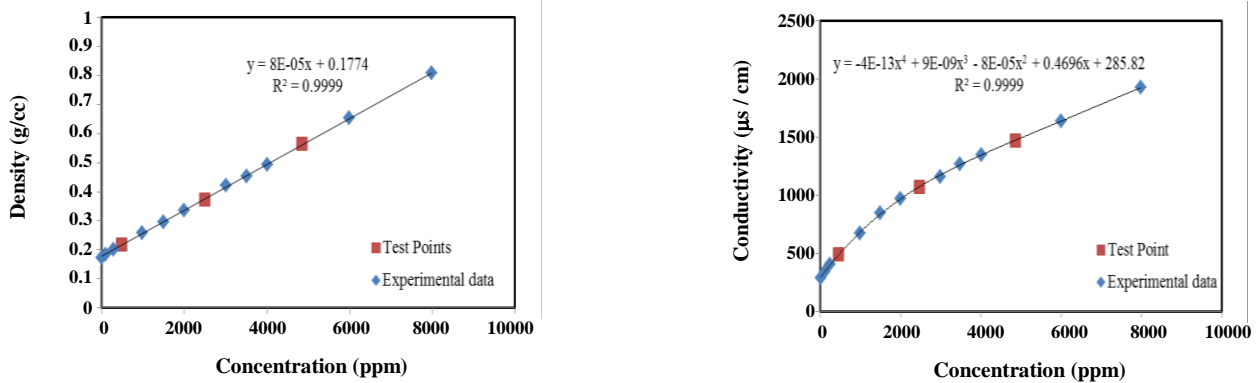


Fig. 22: SLS calibration curve 1) density 2) conductivity.

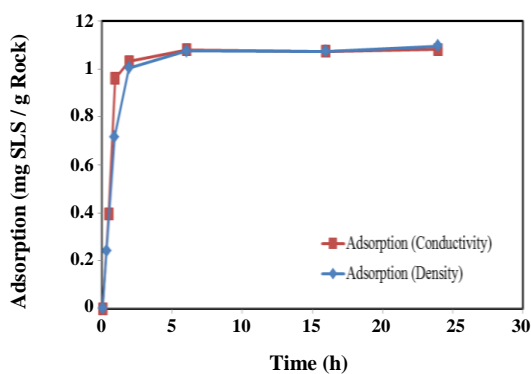


Fig. 23: SLS non-equilibrium adsorption on the sandstone.

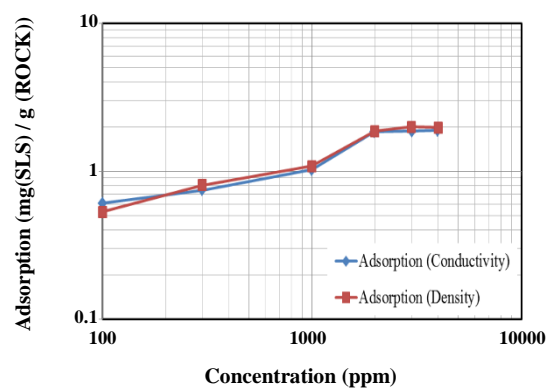


Fig. 24: The SLS equilibrium adsorption on the sandstone.

The impact of R^{816} nanoparticle on the process of adsorption of surfactant

In this test, the SLS/ R^{816} is in contact with sandstone. As shown in Fig. 24, the adsorption rate with the presence of these nanoparticles with 1000 ppm becomes lower at all concentrations.

There are two possibilities for interpreting this phenomenon. First, the R^{816} particles, due to their hydrophobic nature, always compete with surfactant molecules to absorb the stone and reduce the amount of adsorption in all concentrations. The second possibility is that the hydrophobicity of the R^{816} nanoparticles tends to remain pendant surfactant molecules in the solution.

The effect of the concentration of nanoparticles, both on the void and the surface of the rock, has been investigated on the adsorption of surfactant (Fig. 25). One noteworthy point is the decrease in adsorption rate by increasing the concentration of nanoparticles at a

concentration of 2000 ppm of surfactant, which is due to the reduction of free surface for surfactant by increasing the concentration of nanoparticles. Surfactant adsorption on nanoparticles is also low and has little effect on the results. At high concentrations of surfactant, due to the greater tendency of surfactant molecules to absorb on the surface of the rock, as well as the presence of gradients, the concentration of nanoparticles is rolled out of the surface of the rock and suspended in the solution, and the adsorption of surfactant on the rock surface is further increased.

Wettability Alteration of reservoir rock

In carbonate rock, pure water has a minimal ability to change the wettability and reduce the contact angle by a maximum of 7% of the initial value (Fig. 26).

The ability of the anionic surfactant SLS to reduce the contact angle in carbonate rocks at best would reduce up to 15% of the initial value (Fig. 27)

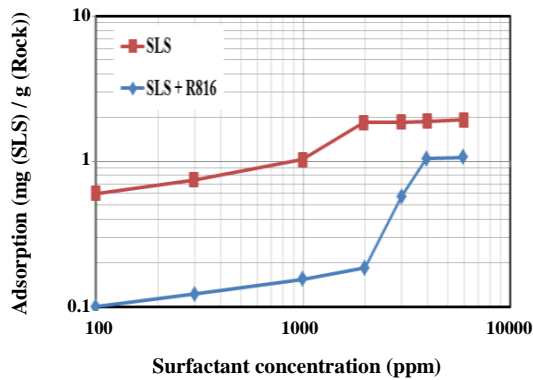


Fig. 25: The effect of R^{816} on the SLS adsorption process.

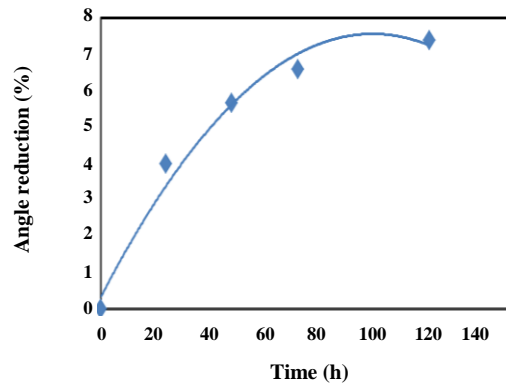


Fig. 27: Angle reduction with water on carbonate rocks.

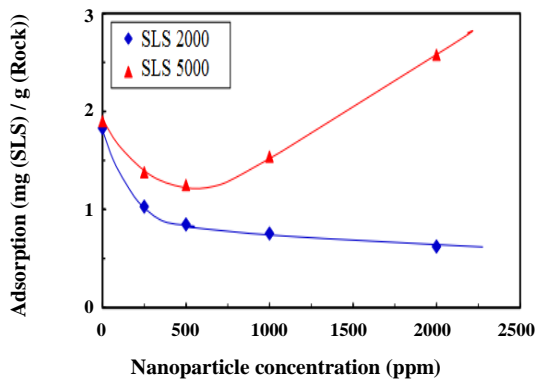


Fig. 26: The effect of nanoparticle concentrations on the adsorption of surfactants when particles are present in the solution and on the sandstone.

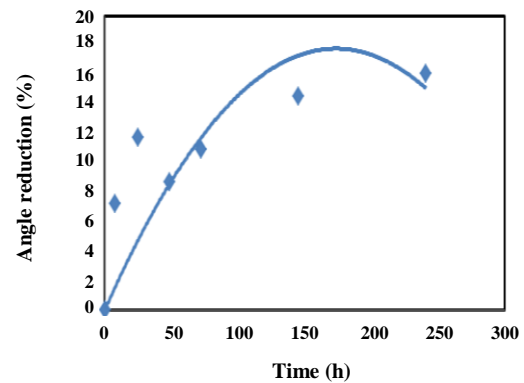


Fig. 28: Angle reduction with SLS on carbonate rocks.

Surfactant/ R^{816} in Wettability Alteration of reservoir rock

Adding R816 to anionic surfactant improved its performance slightly in the wettability alteration process of carbon rock, and slightly improved with increasing nanoparticle concentration. (Fig. 28).

Forced and spontaneous imbibition experiments

Imbibition is a process in which a wetting phase enters a medium through capillary or gravity to a porous medium, and the fluid that is present in the porous medium from the beginning is displaced and exhausted by the absorbing fluid. In split reservoirs, if imbibition is not used spontaneously, injection of water or water excitation due to low scanning efficiency will not have much success in improving the oil recovery. After the oil is discharged from the connected slots, the speed and spontaneous imbibition determine the amount of excess oil extraction from the block matrix.

The experiments were carried out for five different solutions consisting of water and nano solutions and selected according to the results of the droplet angle tests. The process of experiments shows that the mechanism of oil production with respect to the direction of the movement of oil (from the bottom to the top) is mainly gravitational and the capillary forces are less effective. Therefore, a solution without nanoparticles can also penetrate the rock (Fig. 29). It is necessary to add this point that water-soluble salts also have active ions and help the Imbibition in the rock.

Adding nanoparticles to the solution increases the role of the capillary mechanism, and this mechanism, along with the gravity forces, increases the amount of oil produced so that the oil yield is increased by adding up to 5% the nano concentration is more than normal condition. (Fig. 30)

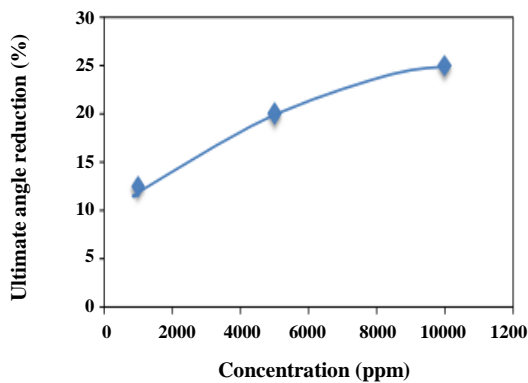


Fig. 29: Angle reduction with R^{816} concentration for R^{816}/SLS (5000 ppm) on carbonate rocks.

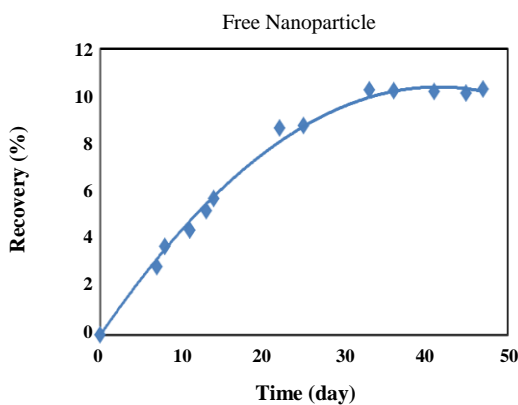


Fig. 30: Imbibition of free nanoparticle solution in sandstone.

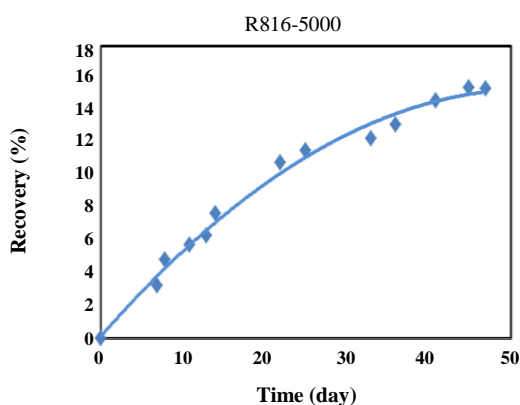


Fig. 31: Imbibition of R^{816} nano-silica solution into the sandstone.

In this study, the effect of new nanoparticles (with the addition of new groups) on the trend of wettability changes with a special look at the process of material stability in the presence of surfactants in temperature and pressure conditions of the reservoir can also be considered. Also, the use of different fluids and rocks to thoroughly examine the different points of the gapping tanks to find the best spatial conditions for the extraction process and the use of new surfactants to compare different surfactants is valuable.

CONCLUSIONS

IFT measurements showed that CTAB (cationic surfactant) has the potential to reduce the IFT between water and oil systems in comparison with SLS (anionic surfactant). The presence of nanoparticles leads to an abnormal interfacial behavior for anionic surfactants so that the IFT at lower concentrations decreased more intensely and by reaching close to a critical concentration, IFT gradually increases, and eventually (high concentrations of surfactants) its value rises from normal (without nanoparticles). At low concentrations of surfactant, the adsorption of molecules in the presence of hydrophilic nanoparticles is less than that of anionic surfactant alone present in the solution. Increasing the concentration of nanoparticles does not have much effect on the performance of this substance in the change of wettability and has practically the same effect at all concentrations. The combination of Aerosil R^{816} with anionic surfactant has improved the wettability of the product compared with when it is present in the solution alone. Increasing the concentration of nanoparticles in carbonate rocks such as sandstone has little effect on the trend of rock solidification. The ability of anionic surfactant to reduce the contact angle in carbonate rocks is very low. In carbonate rock, pure water has a very small ability to change the wettability so that the contact angle is reduced to a maximum of 7% of the initial value. The imbibition tests have confirmed the droplet tests, and the experimental process shows that the addition of nanoparticles to the solution increases the process of changing the wettability of stones from hydrophobic to hydrophilic.

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