SPE-198713-MS

Lignin As a Potential Additive For Minimizing Surfactant Adsorption On Clay Minerals In Different Electrolyte Concentration

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Abstract

The use of surfactants in chemical enhanced oil recovery can recover more oil trapped in the reservoir. However, the loss of surfactant due to adsorption on porous media renders the process ineffective and economically unfeasible. In this study, the adsorption of sodium dodecyl sulfate (SDS) and 4-octylphenol polyethoxylated (TX-100) on different clay minerals (kaolinite, montmorillonite, illite and quartz) as a function of the surfactant concentration, pH and salinity has been investigated. Besides, the use of lignin alkali as a sacrificial agent to reduce adsorption of surfactants in the reservoir is proposed. Surfactant adsorption on the different minerals was determined using the surface tension technique and batch equilibrium adsorption process with lignin as sacrificial agent. The experiment was conducted at varying pH and electrolyte concentrations. Furthermore, oil displacement test was conducted in a sandpack to determine the amount of oil recovered by the surfactant before and after pre-flush with lignin alkaline. Experimental result reveals that SDS adsorbed more on kaolinite while, TX-100 on montmorillonite. The decrease in pH increased the adsorption of SDS on kaolinite and illite, meanwhile, the adsorption of TX-100 on montmorillonite increased significantly at low pH. The optimum salinity concentration for both surfactants was at 20,000ppm for all the minerals except for kaolinite which was at 30,000ppm. Lignin alkaline reduced the surfactant adsorption by 50% and 53.2% for SDS and TX-100 respectively. Oil displacement test with SDS and TX-100 surfactants after water flooding had additional recovery of 7.44% and 4.18% respectively while, after pre-flush the recovery increased by 2.2%.

Key Words: Adsorption, Clay Minerals, Quartz Sand, Surfactants, Enhanced Oil Recovery, Lignin

1.0 Introduction

Oil and gas remain the major source of energy despite contribution from renewable and other sources (Afolabi et al., 2016; Ogiriki et al., 2016). The rise in world population has resulted in increasing demand for energy. Meanwhile, the oil and gas industry is fazed with dearth of new deposits and diminishing output

from conventional oil reserves (Gbadamosi et al., 2019). Hence, enhanced oil recovery (EOR) has attracted a lot of attention to produce more oil from depleted reservoirs (Yekeen et al., 2018, Gbadamosi et al., 2018; Agi et al., 2018). To this end, several EOR methods have been proposed (Abbas et al., 2018; Gbadamosi et al., 2018a; Agi et al., 2018a). Of the numerous EOR methods, chemical EOR has been adjudged to have a high efficiency leading to its prodigious research and field applications (Gbadamosi et al., 2019a). Surfactant flooding, a chemical EOR method utilizes an amphiphilic molecule to lower interfacial tension of oil-water interface and alter wettability of the rock after waterflooding (Kamal et al., 2017; Agi et al., 2018b; Liu et al., 2010; Hirasaki et al., 2011). Both phenomena decrease capillary force trapping the residual oil in the reservoir and consequently increases the pore scale displacement efficiency. Despite all the huge potentials of surfactant in EOR, it has a lot of challenges that needed to be overcome before a project can be economically feasible. One of such challenges is the loss of surfactant to the formation rocks during flow in porous media. The high rate of adsorption can render the whole process unfeasible (Shah & Schechter, 1977). To remedy this situation, there is need to understand the adsorption mechanism in play and the factors affecting adsorption.

Numerous factors account for varying surfactant adsorption behaviour in porous media. This include reservoir temperature, pH, reservoir salinity, rock permeability, formation type and clay mineral content. Samasundaram and Hanna (1978) incorporated the impact of univalent electrolyte, and bivalent electrolyte in their review, alongside the impact of pH and salinity. They concluded that, the effect of inorganic electrolyte depends uniquely on the kind of cation and anion used. Ziegler and Handy (1979) investigated the impact of temperature on adsorption. They used nonionic surfactant at low concentration, they reported that, the adsorption of nonionic surfactant decreases with increase in temperature.

The presence of clay mineral content in reservoirs have also been adduced to be responsible for surfactant adsorption during surfactant flooding process. Multi-component statistics investigation has shown that, the sorption power of soil/sediment composition for triton follows an order of montmorillonite > organic carbon > illite > 1.4nm minerals (vermiculite + chlorite + 1.4nm integrated minerals) >> kaolinite. The sorption of surfactant on soils or sediment is the collective influence of soil/sediment organic matters and clay minerals, which depend on both the contents of soil/sediment organic matter, the type and content of clay minerals (Zhu et al., 2003). Lee et al., (2005) investigated the effect of soil properties on surfactant adsorption, they concluded that cationic surfactant has the tendency to be strongly adsorbed to soils and clays by means of electrostatic interaction. The cationic surfactants adsorption capacities were directly proportional to the cationic exchange capacity (CEC) for anionic adsorption, and the possible mechanism for adsorption is the van der Waals forces or hydrogen bonding. Besides, Paria (2008) reported that adsorption of anionic surfactant on soil also showed a positive relationship with organic material and soil content. The impact of clay type on adsorption of anionic surfactant showed significant adsorption by Ca-saturated montmorillonite than Na-saturated montmorillonite. The type of clay in the formation, the ionic strength of the aqueous solution and the exchangeable cations saturating the clay also determines the rate at which nonionic surfactant are adsorbed.

Many researchers have advocated for the use of hybrid surfactants (Reid et al. 2004), the use of co-surfactants (Riazia & Moshfeghianb, 2009) which can change the properties of the surfactant such as solubility and charge when mixed with the surfactant or the blend of at least two surfactants (Sanchez et al., 2008; Muherei & Junin, 2009; Junin et al., 2011) can reduce the CMC and the adsorption of the surfactant. Sanchez et al., (2008) studied the adsorption of three different surfactant nature non-ionic (Triton X-100), anionic (SDS) and cationic (octadecyltrimethylammonium bromide (ODTMA) on different clay minerals. They reported that the adsorption of TX 100 and ODTMA was higher for montmorillonite and illite, while that of SDS was higher for kaolinite and sepiolite. They also reported that the mineral structure and surfactant nature has influence on the adsorption capacity of surfactants by clays.

Furthermore, Muherei and Junin (2009) examined the adsorption of Triton X-100 and SDS, with two local adsorbents (sand and shale), using the surface tension technique. They reported that SDS was not

adsorbed to any of the sample while, Triton X-100 (non-ionic surfactant) adsorbed on both adsorbents. Junin et al., (2011) investigated the effects of the mineralogical composition of adsorbent on adsorption. They used noninic surfactants (TX-100 & TX N-75) in a sandpack containing different clay minerals (kaolinite & illite). They concluded that there is a relationship between the adsorption of nonionic surfactants and the quantity of clay in the adsorbent. They observed that the quantity of surfactant adsorbed increased when the percentage of clay mineral in the adsorbent increased (from 2% to 8% in the sandpack). Amirianshoja et al., (2011) investigated the effects of the mineralogical composition of adsorbent on adsorption. Using anionic and nonionic surfactant on quartz and clay minerals, they noted that a direct relationship exists between the adsorption of nonionic surfactant and the amount of clay, while the adsorption of anionic surfactant was negligible.

Goa and Sharma (2012) synthesized anionic Gemini surfactant and characterized it using the Kraft temperature (below room temperature.). The Gemini surfactant showed low adsorption compared to the conventional surfactant and also exhibited tolerance to salinity and hardness.

Behrens et al., (2013) used anionic surfactant Aerosol-OT to investigate its adsorption on kaolinite using the indirect method of measurement. Aerosol-OT adsorb onto kaolinite under high surfactant concentration and low salinity. Yekeen et al. (2016) investigated the adsorption of (SDS) on kaolinite at various surfactant concentration and added electrolyte (NaCl, $CaCl_2$ and $AlCl_3$) concentration, using the surface tension technique and two-phase titration method. They reported that the adsorption of SDS by kaolinite increases with increasing concentration of NaCl and $CaCl_2$ and decreases with temperature. While, the adsorption remained constant with increase concentration and temperature.

Karaguzel & Xu (2017) studied the effect of pH on adsorption and desorption of cationic surfactant hexadecyl trimethyl ammonium bromide from silicate surface, they concluded that ph is a critical factor in determining the adsorption and desorption process. The adsorption of surfactants cannot be foretold only based on the adsorbent attributes (Muherei & Junin, 2009). Hence, the lithological attributes such as mineralogy, texture, grain size and other petrophysical properties are very essential for determining the adsorption of surfactant to a rock for an effective EOR process. Also, the influence of environmental conditions within the reservoir such as pH and salinity could also play a significant role in the adsorption of surfactants to the rock.

Researchers in the past have studied the adsorption of surfactants on clay minerals from Somasundara & Hanna (1978) to Karaguzel & Xu (2017) but not all gave emphasis on their effect of different type of clay mineral content. Somasundaran & Hanna (1978) only focused on kaolinite, Ziegler & Handy (1979) did not consider pH in their research and Karaguzel & Xu (2017) considered only pH while, Sanchez et al., (2008) did not consider the effect of environment conditions such as salinity and pH. Since a typical reservoir consist of three dominant clay minerals namely kaolinite, illite and montmorillonite, available literatures are insufficient to draw conclusion on surfactant adsorption behaviours. Recently, Wu et al., (2017) investigated the reduction of surfactant adsorption on rock using silica nanoparticles. They reported that silica nanoparticles can reduce surfactant adsorption effectively and increase recovery. In this research therefore, the adsorption of surfactants on different clay minerals is studied. The effect of environmental factors such as salinity and pH on adsorption is also investigated and the use of lignin alkaline as a sacrificial agent to reduce adsorption is proposed. The mechanism of inhibition of surfactant adsorption by lignin is elucidated herein.

2.0: Materials and Methods

2.1: Materials
An anionic surfactant, (SDS) and a non-ionic surfactant (Triton X-100) were used for this study. The surfactants were supplied by Acros Organic Company. The SDS with the formulae $C_{12}H_{25}NaO_4S$ has

a molecular weight of 288.38g/mol with a purity of 95%, while TX-100 with a chemical formula $C_{14}H_{22}O(C_2H_4O)_{10}$ has a molecular weight of 646.37g/mol with a purity of 96%. Sodium Chloride used in the preparation of the different brine solution was supplied by Acros Organic Company with molecular weight of 58.44 g/mol and a purity of 99% assay. Sodium hydroxide (NaOH) and Sulphuric acid used for determining the pH, also lignin alkali used as a sacrificial agent were supplied by Acros Organic Company. The quartz sand was collected from Teluk Ramunia, Johor-Malaysia, kaolinite and montmorillonite were supplied by Sigma Aldrich, while the illite was collected from Kuala Rompin, Pahang-Malaysia. The chemicals were of analytical grades and were used as received without purification. The chemical structure of TX-100 and SDS is shown in Figures 1 and 2.
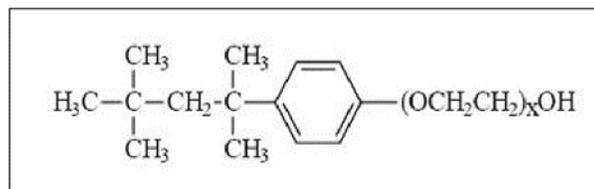
Figure 1—Chemical Structure of TX-100
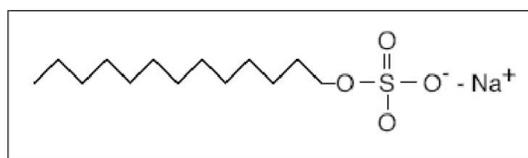
Figure 2—Chemical Structure of SDS

2.2 Preparation of Surfactant Solution

The surfactants solutions were prepared in a standard 1000 ml volumetric flask. The weight in mass of the surfactant is taken and emptied into the volumetric flask, then distilled water was used to complete the solution to obtain the required weight (1kg). Finally, the stock solution was diluted to concentration range of $0.005 - 1.0$ wt.%. To study the influence of the electrolyte concentration on surfactant adsorption on different clay minerals, different surfactant solutions were prepared using NaCl salt at different concentration. Five different salinity concentration was investigated, for the SDS, salinity of 0ppm, 5,000ppm, 10,000ppm, 20,000ppm, 30,000ppm, while for TX-100, salinity of 0ppm, 10,000ppm, 20,000ppm, 30,000ppm, 40,000ppm.

2.3 Rock and Porous Media Preparation

2.3.1 Rock Sample Preparation.
The rock samples used in this study are clay minerals and quartz sand, the rock minerals were crushed using a rock pulveriser (BICO, Inc.) to make the sample finer. The samples were then passed through USA Standard Testing Sieves, ATM Corp., New Berlin, WI. The rock samples were air dried for 24 hours and oven dried at 105°C for 24 hours, these samples were used in both the batch and displacement experiment. 5g of each sample was taken for morphological analysis and another 5g of each sample were further crushed to get a fine particle for X-Ray Diffraction (XRD) analysis.

2.3.2 Porous Media Preparation.
Polyvinyl chloride (PVC) tube with an inner diameter of 3.4cm and a length of 31cm was used as the porous media holder. For the displacement test, quartz sand and clay minerals with the highest adsorption were mixed in the proportion (95% quartz and 5% clay), then loaded gradually and pressed into the holder while shaking simultaneously to have a uniform compaction. Distilled water was added from the top through a pipe and a vacuum pump was used to extract the water from the

bottom after packing was complete. Two layers of 120-micron filter cloth and a one layer of 50-micron filter cloth was used to block the inlet and outlet to prevent fine grains from moving out of the pipe.

2.4 Characterization Technique

The crystallinity of the adsorbent was investigated by X-Ray Diffraction (XRD) analysis using a SIEMENS D500 with Cu Kα radiation, λ=0.15147nm, at a voltage of 40kV and current of 200mA, the scattered radiation was spotted at an angular range of 5-60°(2θ), with a scanning speed of 1 deg/min.

2.5 Surface Tension and CMC Determination

The surface tension measurement was carried out with Kruss tensiometer (Kruss GmbH, Hamburg), using Platinum-iridium ring at constant temperature of 26°C. The tensiometer was calibrated using the method described in ASTM designation: D1331-89. The tensiometer was operated based on the Du Nouy principle, in which the platinum-iridium ring is suspended from a torsion balance and the force (mN/m) required to pull the ring free from the surface film is measured. The surface tension value was taken when a stable reading was obtained for a given surfactant concentration. The average of a series of constant readings for each sample was corrected to account for the tensiometer configuration, yielding a corrected surface tension value (Zuidema and Waters 1941). A plot of the surface tension values versus the surfactant concentration was made to determine the CMC of the surfactant. The CMC value was taken at the inflexion point on the curve, that is, the point where there was no significant change in surface tension and the surface tension remain relatively constant after this point. This is similar to methods of determining CMC as reported in literature (Muherei and Junin, 2009).

2.6 Adsorption Study

The adsorption of the surfactant was determined by batch equilibrium adsorption process. 10 g of the mineral sample was added to the 60 ml surfactant (1:6 w/v ratio) in a 100 ml glass vial at different concentration of NaCl and was allowed to equilibrate at 25 °C. The glass vial was shaken using a gyratory shaker at 100 rpm for 3 hours and 16 hours was allowed for complete separation to take place, which was also enough for complete equilibrium. Preliminary test showed that within 3 hours contact time, almost all the adsorption has taken place, the process was repeated for all the minerals. To determine the effect of pH on adsorption behaviour, three pH points was investigated. The first point was at pH 2.0. Sulphuric acid was used to adjust the pH, the second point was at the neutral 6-7, the third point was at pH 10 to simulate the alkaline condition. NaOH was used to adjust the pH. The brine consisting of the adjusted pH was used to prepare a stock solution for surfactant solution and used for dilution purposes.

2.7 Oil Displacement Test

Lignin alkaline was used as a sacrificial agent to reduce the surfactant adsorption. Figure 3 shows the schematic diagram of the oil displacement setup. Brine and paraffin were used as the aqueous and oleic phases in the experiments. The concentration of the brine was set at 20,000ppm NaCl solution and the experiment was conducted at room temperature.
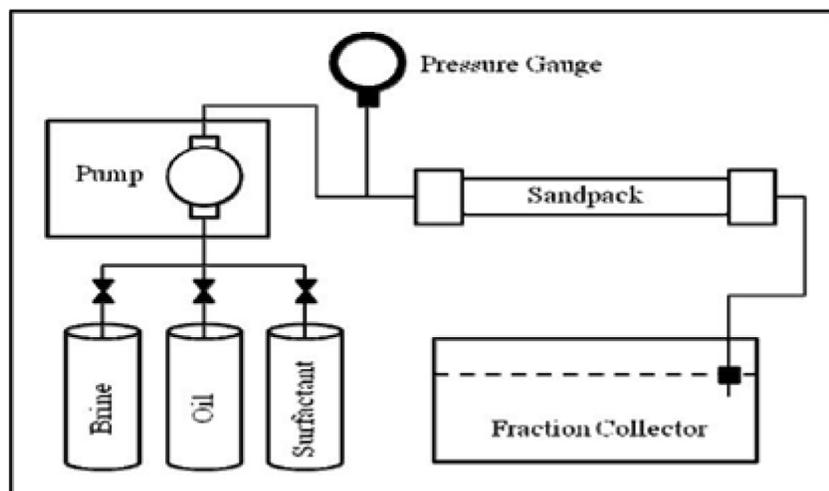
Figure 3—Experimental Setup for Oil Displacement Test

The porous media was injected with brine until it was 100% saturated, to represent oil migration, oil was injected until minimum water saturation or irreducible water saturation was reached. The porous media was then aged for 24 hours to ensure proper saturation. The porous media was again flooded with brine until oil saturation was achieved, this flood was designed to represent secondary recovery by means of water flooding and was done horizontally. The remaining oil in the sandpack was then subjected to surfactant flooding. For the pre-flush displacement test, lignin alkali was injected before the injection of surfactants. During the flooding process, the recovery performance of the original oil in place (OOIP) is measured with time and the percentage of the recovery efficiency is estimated from the measured amount of oil separated from the recovery.

3.0 Results and Discussion

3.1 Rock Mineral Composition

(a) Quartz Sand Sample.   The XRD result, was used to determine the dominant, major and minor composition in each sample. The minerals composition was determined by using the area under the graph and the intensity of the peak. Every mineral reflection can be detected reflection at certain wavelength. By using Bragg equation, the quantity of each of identified minerals can be estimated using their peak area.

Quartz is identified by its distinctive reflections at 4.24 Å and 3.33 Å. The 3.33 Å peak of quartz is more intense than the other peaks.
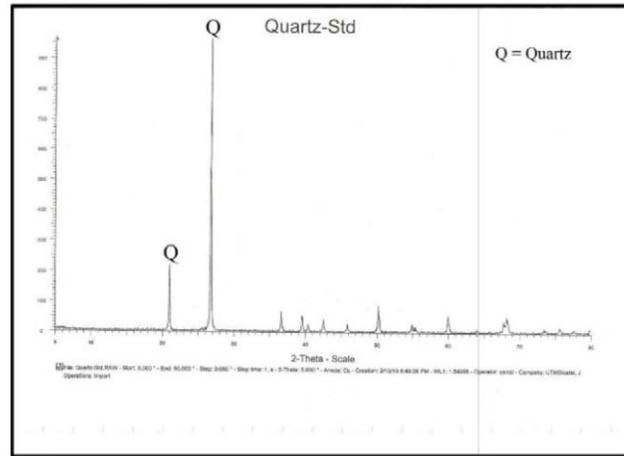
Figure 4—XRD Result for Quartz Sample

(b) Kaolinite Sample.   Kaolinite is the most abundant clay mineral present in the sample. It is represented by a basal (001) reflections at 7.13 Å and (002) reflection at 3.56 Å. Quartz is the important non-clay mineral present in the sample. Quartz is identified by its distinctive reflections at 4.24 Å and 3.33 Å. Illite is the next minor clay mineral present in the sample. Illite is identified by series of basal reflections at 9.93 Å, 4.97-5.01 Å. Therefore, the dominate mineral is kaolinite while the minor minerals are quartz and illite
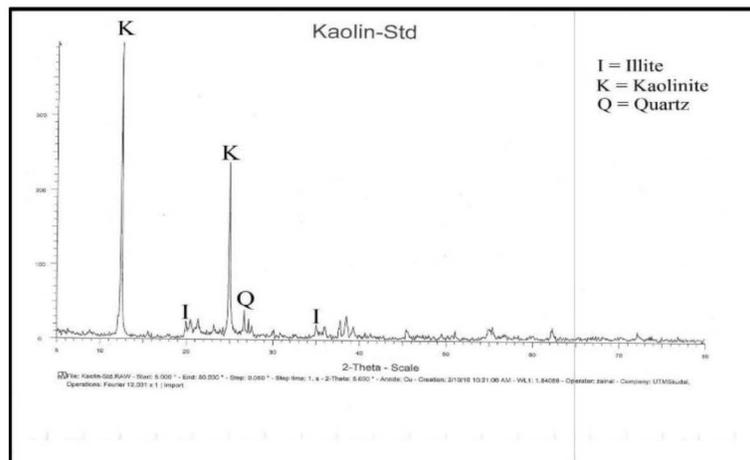
Figure 5—Result for Kaolinite Sample

(c) Montmorillonite Sample.   Montmorillonite was the most abundant clay mineral present in the sample. It was represented by reflections at 15.31 and 4.48 Å. Illite forms as minor clay mineral present in the sample. Illite was identified by a series of basal reflections at 9.93 Å, 4.97-5.01 Å. Quartz was the non-clay mineral present in the sample. Quartz was identified by its distinctive reflections at 4.24 Å and 3.33 Å. The dominate mineral therefore, was montmorillonite, while illite and quartz where minor mineral present.
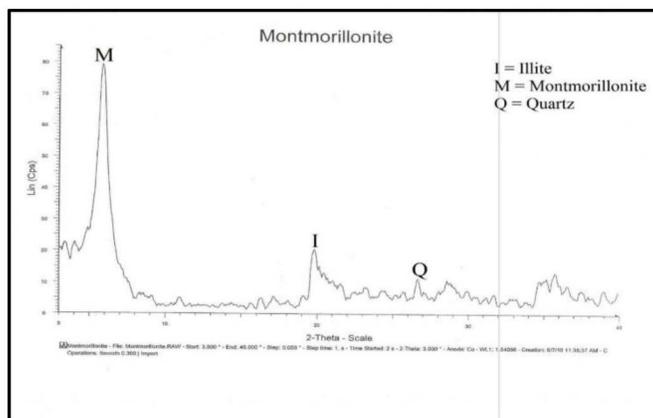
Figure 6—XRD Result for Montmorillonite Sample

(d) Illite Sample. Illite forms one of the most abundant clay mineral present in the sample. Illite is identified by a series of basal reflections at 9.93 Å, 4.97-5.01 Å. Kaolinite is the next major clay mineral present in the sample. It is represented by a basal (001) reflections at 7.10 Å. Quartz is the next important non-clay mineral present in the sample. Quartz is identified by its distinctive reflections at 4.24 Å and 3.33 Å. The dominate mineral was illite, while quartz and kaolinite where major minerals present.
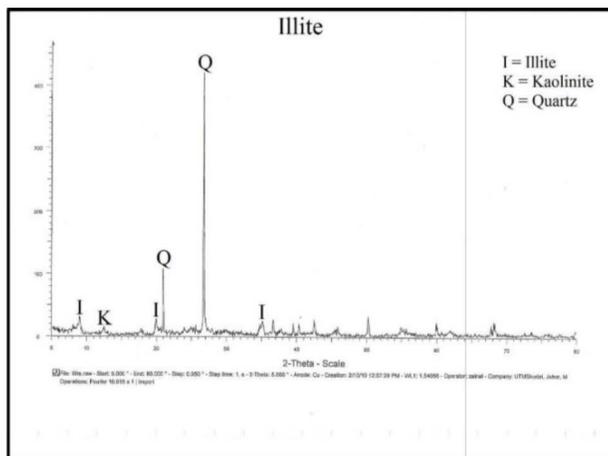
Figure 7—XRD Result for Illite Sample

The surface area of each mineral was determined using the BET method, the surface area for each mineral are shown in Table 1.

Table 1—Summary of XRD and Surface Area Result

Sample	Mineral Composition				Total	Surface Area(m²/g)
	Quartz	Kaolinite	Illite	Montmorillonite		
Quartz-std	~100	-	-	-	100	1.5
Kaolinite-std	~5	90	~5	-	100	11.62
Illite	~20	~35	~45	-	100	21.56
Montmorillonite	~5	-	~5	90	100	157.05

*std = Standard

Table 2—Chemical composition of Minerals

Minerals	Chemical Formula	Chemical Structure
Quartz	SiO_2	Oxygen is shared with two tetrahedra
Kaolinte Group	$Al_2SiO_5(OH)_4$	Silicate sheet bonded to aluminium oxide/hydroxide layers (gibbsite layer)
Illite group	$(K,H)A_{l2}(Si,Al)_4O_{10}(OH)_2\text{-}xH_2O$	Silicate layers at the top and bottom of gibbsite layer
Montmorillonite Group	$(Ca, Na, H)(Al, Mg, Fe, Zn)_2(Si, Al)_4O_{10}(OH)_2\text{-}xH_2O$	Gibbsite in between two silicate layers

3.2 Effects of Mineralogy on Adsorption

Mineralogy plays a very important role in adsorption. In fact, the types of minerals determined how much the surfactant adsorbs, it also determines what type of interaction happened at solid-liquid interface.

3.2.1 Triton X-100 Adsorption Behaviour.
Figure 8 shows the result of adsorption test for TX100 with different minerals. The CMC for TX100 was found to be around 0.015 wt%. This is in agreement with previous studies Zhu et al., (2003); Zhou and Zhu (2004); Sanchez-Martin et al., (2008). The highest adsorption was by clay minerals (kaolinite, illite and montmorillonite) compared to the quartz sand, which is also in agreement with the findings of Podoll et al., (1987). The adsorbed surfactant for quartz was found to be approximately 0.12g/kg, the lowest value compared to other minerals (Table 3), the reason is, the surface group of quartz sand is responsible for the formation of hydrogen bonds between the surface and the surfactant during the adsorption process. Quartz also does not have any additional charge, making the adsorption by other mechanism almost impossible (Nevskaia et al.,1995).
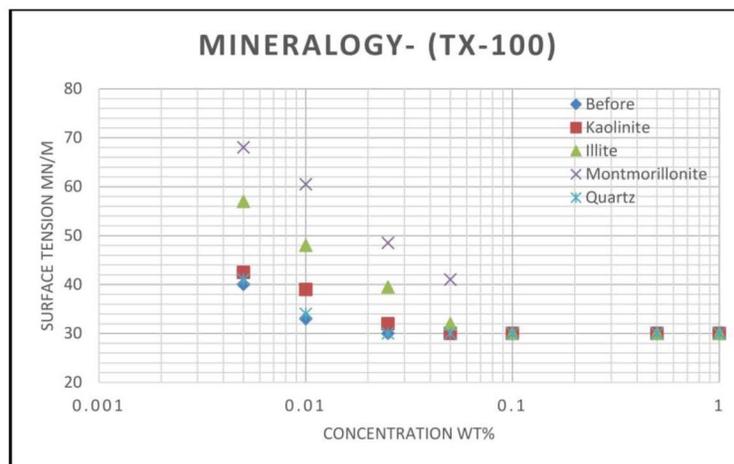
Figure 8—Surface Tension of TX-100, before and after Adsorption Test with Minerals

Table 3—Adsorption of TX-100 Surfactant on Minerals.

Minerals	CMC before (wt.%)	CMC after (wt.%)	Adsorbed amount (g/Kg)
Kaolinite	0.015	0.032	1.02
Illite	0.015	0.060	2.70
Montmorillonite	0.015	0.130	6.90
Quartz	0.015	0.017	0.12

The results also show a strong interaction of the surfactant with montmorillonite and illite, the surfactant adsorption for both mineral is 6.9g/kg and 2.7g/kg respectively. Non-ionic surfactants tend to adsorb on

montmorillonite due to the dispersion of clay in the presence of elevated surfactant concentration, which leads to a rapid increase in the retention capacity of the surfactant micelles in the remaining voids of the clay surface or between the structure, forming admicelles after a sufficiently large critical mass of the surfactant was adsorbed (Deng et al., 2003; Sonon & Thomson, 2005). The surface area also plays a very important role, the larger the surface area, the more the interaction that occur and the higher the adsorption. From the surface area test, montmorillonite has the highest surface area of 157.05m²/g. Illite and montmorillonite has high affinity for TX100, while kaolinite has less affinity, this is attributed to the large surface area of illite and montmorillonite compared to kaolinite (Zhu et al., 2003; Rodriquez-Cruz et al., 2005; Sanchez-Martin et al., 2008).

3.2.2 SDS Adsorption Behaviour.

From Figure 9, the CMC is about 0.1%wt, which is higher than that of TX-100. This is because, non-ionic surfactants aggregation or micellization is mainly due to the hydrophobic interaction among the hydrocarbon chains. The hydrocarbon group are easily separated from the aqueous environment, whereas, for ionic surfactants, high concentration is necessary to overcome the electrostatic repulsion between ionic head group during aggregation (Joshi et al.,2005). Generally, anionic surfactants are composed mainly of high polar and non-polar functional group, hence, hydrogen bonding, adsorption by dispersion force and hydrophilic bonding may all be operative mechanism (Lee et al., 2005). Kaolinite and illite interact strongly compared to quartz and montmorillonite, however, kaolinite adsorption was higher than that of illite due to the purity of the kaolinite used. Despite large surface area of illite compared to kaolinite (Sanchez-Martin et al., 2008). The amount of kaolinite adsorbed as seen in Table 4 is 4.8g/kg, this is also due to the ability of kaolinite to develop a variable charge and adsorb completely dissociated anions by ligand exchange (Sastry et al., 2005). However, the adsorption of SDS onto other layered clay minerals like montmorillonite and illite is not possible through the same principle. Because of the negative charge of the clay surface that repels the anionic surfactants, so there is no interaction such as ion exchange (Yang et al., 2007).
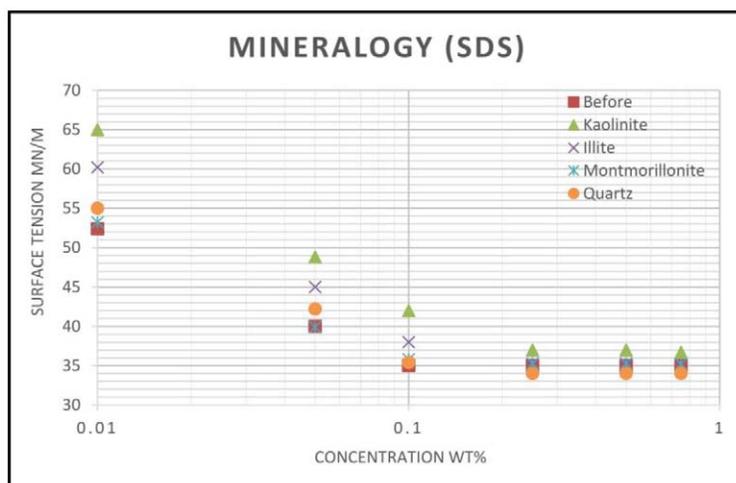
Figure 9—Surface Tension before and after Adsorption Test with Minerals

Table 4—Adsorption of SDS Surfactants with Minerals

Minerals	CMC before (wt.%)	CMC after (wt.%)	Adsorbed amount (g/Kg)
Kaolinite	0.1	0.18	4.8
Illite	0.1	0.15	3.0
Montmorillonite	0.1	0.12	1.2
Quartz	0.1	0.13	1.8

3.3 Effect of pH on Adsorption

The charge on the surface is dependent on the pH, as the pH of an aqueous solution is reduced, the solid surface become more positive or less negative due to the adsorption of proton from the solution onto the charged site, which will lead to increase in the adsorption of anionic surfactants

3.3.1 TX-100 Adsorption Behaviour. The adsorption test result for different pH condition for TX-100 is shown in Figures 10 to 12. It shows a slight increase in the CMC value for TX-100, which shows that pH, has an effect on the CMC.
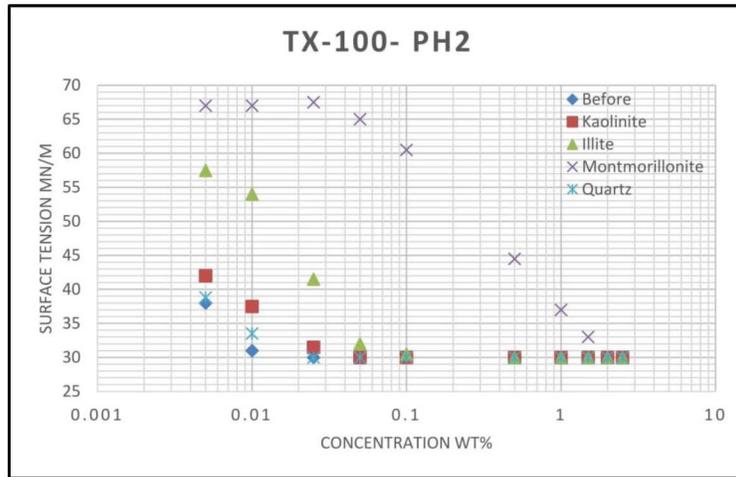
Figure 10—Surface Tension of TX-100 before and After Adsorption Test with Minerals at pH 2
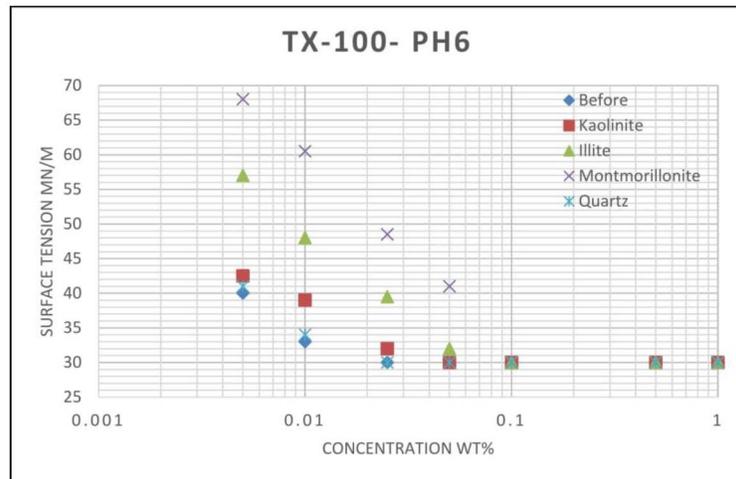
Figure 11—Surface Tension of TX-100 before and after Adsorption Test with Minerals at pH 6
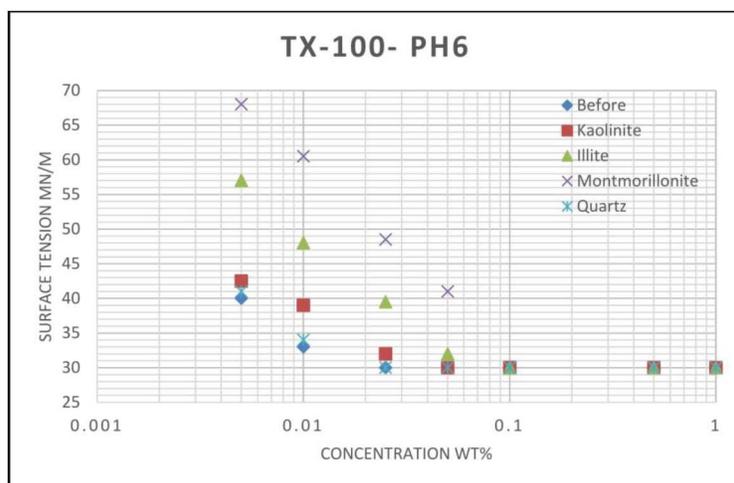
Figure 12—Surface Tension of TX-100 before and after Adsorption Test with Minerals at pH 10

From the graph, the CMC of non-ionic surfactant after adsorption increases in acidic condition than the basic. Montmorillonite had high adsorption, while there was no significant increase in surfactant for illite, quartz and kaolinite. The quantity of surfactant adsorbed is shown in Table 5. The high adsorption rate of montmorillonite is as a result of the low point zero-charge (PZC) which is lower than 3 pH (Kosmulski & Dahlsten, 2006). That is at pH 2, the surface of montmorillonite was filled with hydronium ions, which gives a positive charge on the surface, hence, attracting the TX-100 molecule to adsorb to it. Also, high surface area of montmorillonite makes it have a more positive charge than other minerals, hence, attracts more TX-100 molecules to it. Illite and kaolinite does not have high surface area, hence the effect was not much. Quartz on the other hand increased significantly at pH 2, because it also has a low PZC between 2-3 (Clausen et al., 2001). At pH 2 the surface of quartz is positively charged and attracts more molecules of the surfactant to it.

Table 5—Adsorption of TX-100 on Minerals at Different pH

Minerals	Adosrbed amount (g/Kg)		
	pH 2	pH 6	pH 10
Kaolinite	1.14	1.2	0.96
Illite	2.7	2.82	3.42
Montmorillonite	19.28	6.96	7.98
Quartz	0.24	0.12	0.06

3.3.2 SDS Adsorption Behaviour.   The surface tension result for SDS adsorption at different pH values is shown in Figures 13 to 15, there was a significant decrease at the acidic condition for CMC of SDS. The value dropped from 0.1wt% to 0.038wt% at pH 2, this could be attributed to the effect of hydrogen ions at low concentration (Rahman & Brown, 1983).
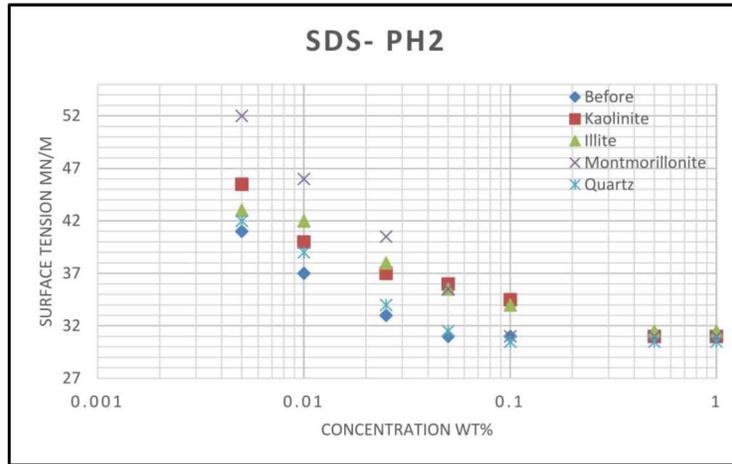
Figure 13—Surface Tension of SDS before and after adsorption test with minerals at pH 2.
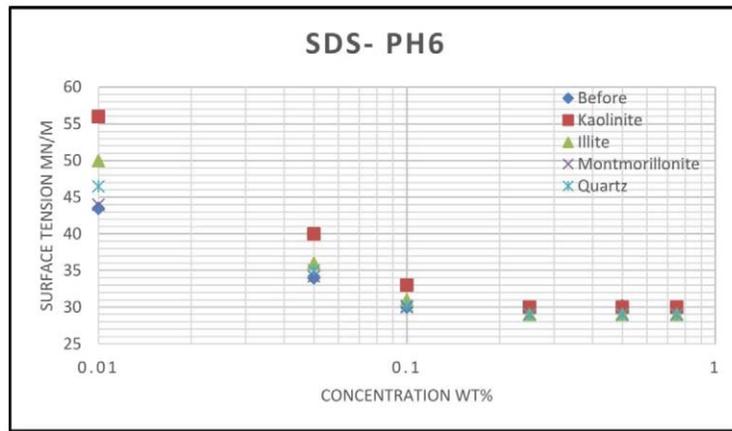
Figure 14—Surface Tension of SDS before and after Adsorption Test at pH 6
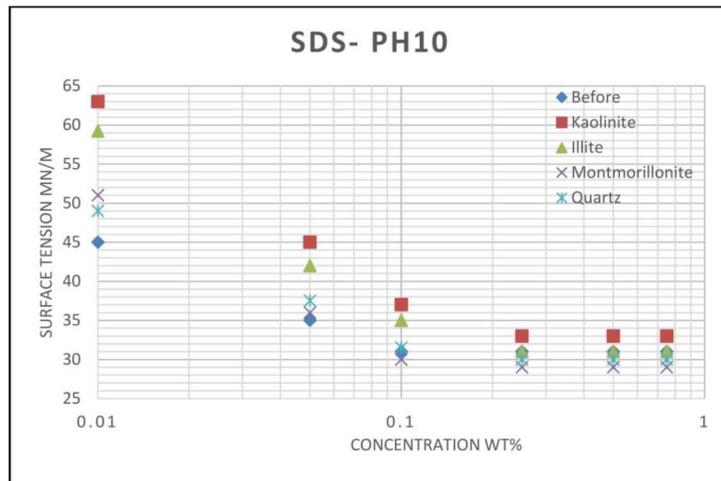
Figure 15—Surface Tension of SDS before and after Adsorption Test at pH 10

The ions may decrease the electrostatic repulsion of the charge head by decreasing the charge density on the surface of the micelle. The quantity of SDS adsorbed at different pH is shown in Table 6. From the Table, illit and kaolinite adsorption increased at pH 2, which was as a result of large amount of hydronium ion which covered the surface of the minerals. Also, kaolinite has a point zero charge at the range of 2.8-4.8 (Tschapek

et al., 1974), at pH 2 the surface of kaolinite becomes positively charged as a result of the hydronium ion, hence attracting more anionic surfactant to it. For illite, the point of zero charge was at pH 2.8. The increase can be seen in montmorillonite and quartz, the positive hydrogen ion at the surface has attracted more SDS molecules to be adsorbed. The PZC of quartz is around 2-3, so it is expected that the adsorption will increase, but because of the low surface area, the effect was not pronounced as that of illite and kaolinite. No significant increase at pH 10 for all the minerals, but a little in surfactant adsorption was detected for kaolinite, which may have resulted from the adsorption was detected for kaolinite, which may have resulted from the adsorption of SDS on the edge of the kaolinite layer which has point zero charge at pH 7.8 (Micheals & Bolger, 1964).

Table 6—Adsorption of SDS on Minerals at different pH

Minerals	Adosrbed amount (g/Kg)		
	pH 2	pH 6	pH 10
Kaolinite	21.12	3.12	3.60
Illite	13.32	1.92	3.00
Montmorillonite	3.72	0.72	1.20
Quartz	1.50	1.32	1.80

3.5 Effect of Salinity on Adsorption

The effect of salinity on pH was conducted using the batch experiment. Salinity affected adsorption through the increase of the ionic interaction and electrical double layer phenomena.

3.5.1 Triton X-100 Adsorption Behaviour. The surface tension result for TX-100 adsorption test at different salinity concentration is shown in Figures 16 to 19. The CMC showed no significant change, in non-ionic surfactant solution, there were no ionic interaction between charged head (Rosen, 2004). This is due to the neutral charge pose by non-ionic surfactant.
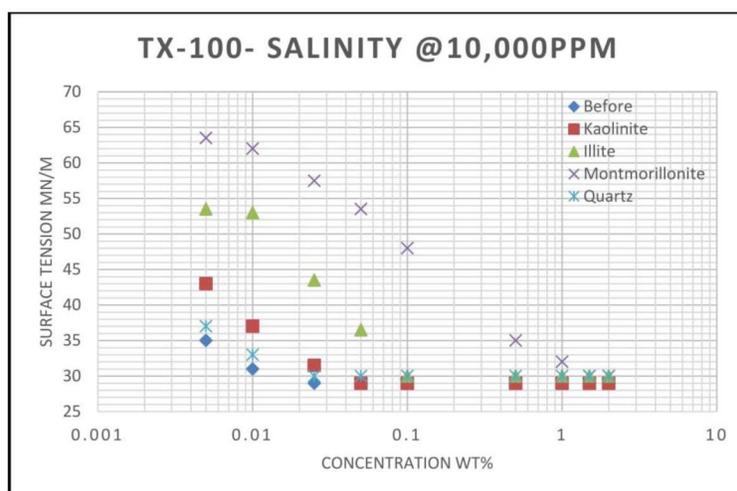
Figure 16—Surface Tension of TX-100 before and after Adsorption Test with Minerals at 10000ppm Salinity.
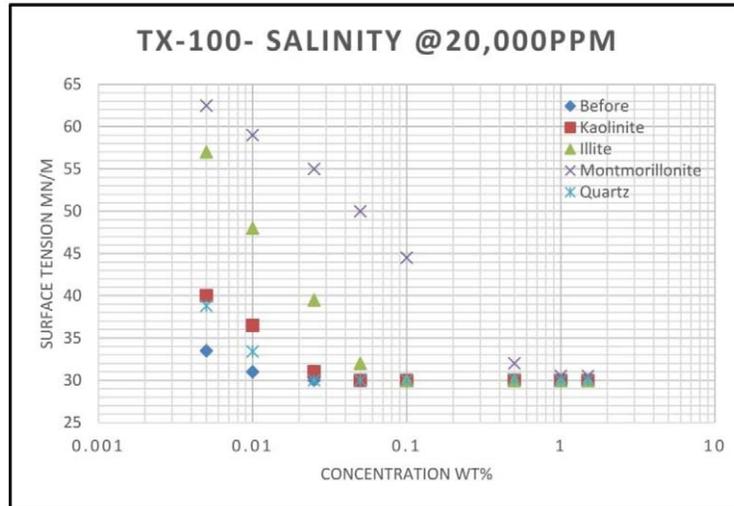
Figure 17—Surface Tension of TX-100 before and after Adsorption Test at 20000ppm
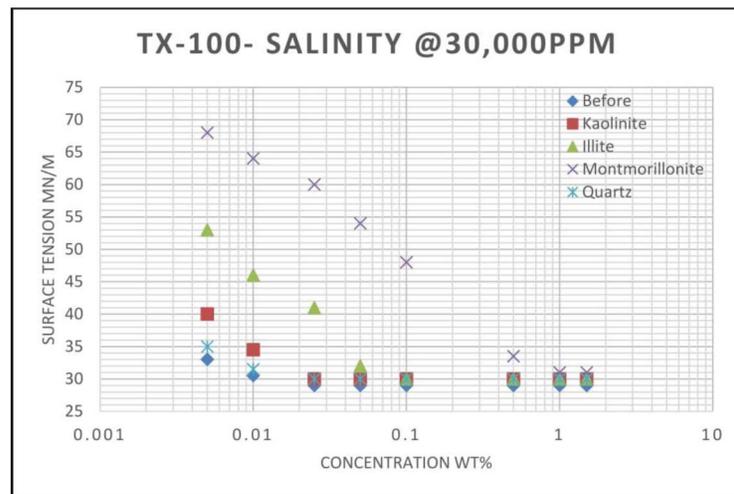
Figure 18—Surface Tension of TX-100 before and after Adsorption Test with Minerals at 30000ppm
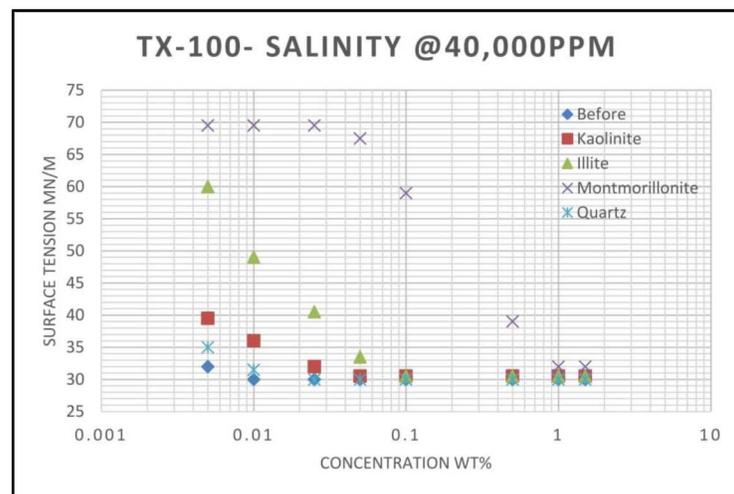
Figure 19—Surface Tension of TX-100 before and after Adsorption Test with Minerals at 40000ppm.

The result showed that the adsorption of TX-100 on montmorillonite, illite and quartz decreases with the addition of 0 to 20000ppm of the electrolyte, but increases after that amount. For kaolinite, the adsorption was lowest at 30000ppm, but increases after wards, the quantity of TX-100 adsorbed is shown in Table 3.5.

Table 7—Quantity of TX-100 Adsorbed for Salinity Effect

Minerals	Adosrbed amount (g/Kg)				
	0 ppm	1,0000 ppm	2,0000 ppm	30,000 ppm	40,000 ppm
Kaolinite	1.02	1.26	1.02	0.24	1.62
Illite	2.70	4.56	2.82	2.88	3.48
Montmorillonite	6.90	83.16	37.02	42.36	52.20
Quartz	0.12	0.24	0.18	0.12	0.24

The significant increase after 10000ppm salt addition was due to the electrode double layer formation on the minerals Na^+ acted as a counter ion and adsorbed onto the mineral after the first adsorption layer by TX-100. This counter ion then attracted another layer of TX-100 molecule to be adsorbed onto it, montmorillonite had the highest adsorption rate due to the large surface area it possesses. The adsorption lowered after that before increasing again at 30000ppm concentration. This trend occurred on all minerals except kaolinite which increase again at 30000ppm.

3.5.2 SDS Adsorption Behaviour. The surface tension result for SDS adsorption test to investigate the effect of salinity on surfactant adsorption is shown in figures 20-23. For the CMC, the value decreases significantly with increase in concentration of electrolyte. The CMC for 0 ppm concentration was around 0.1wt% and decreases significantly to about 0.011wt% with addition of 30000ppm of electrolyte.
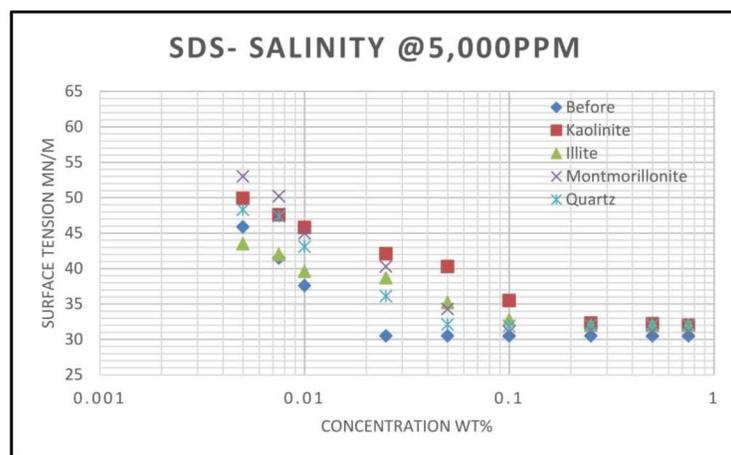
Figure 20—Surface Tension of SDS before and after adsorption Test with Minerals at 5000ppm
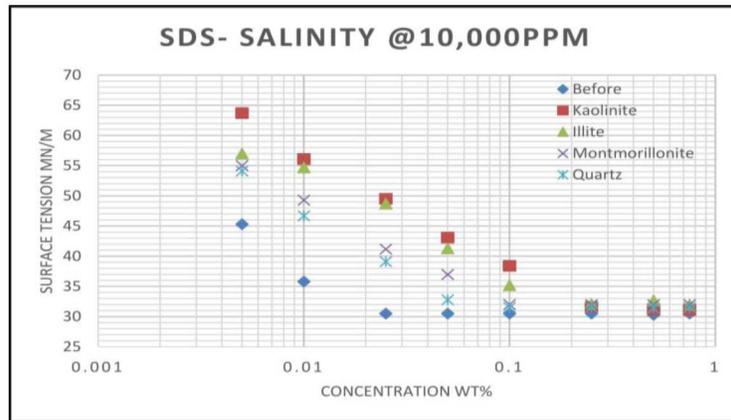
Figure 21—Surface Tension of SDS before and after Adsorption Test with Minerals at 10000ppm.
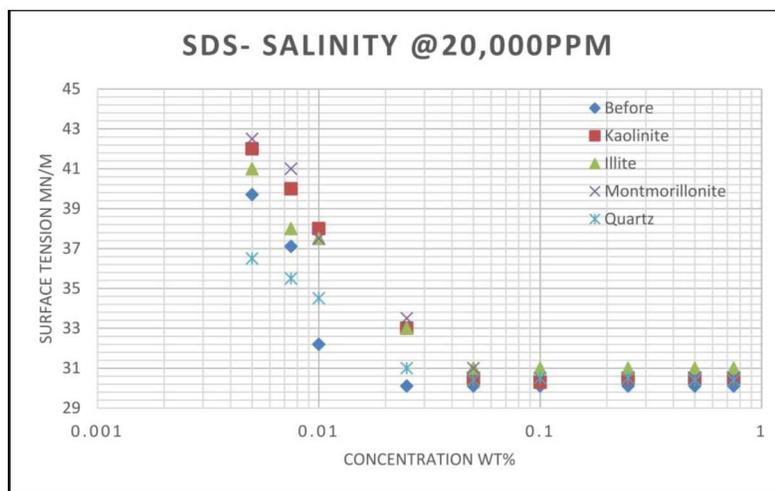
Figure 22—Surface Tension of SDS before and after Adsorption Test with Minerals at 20000ppm
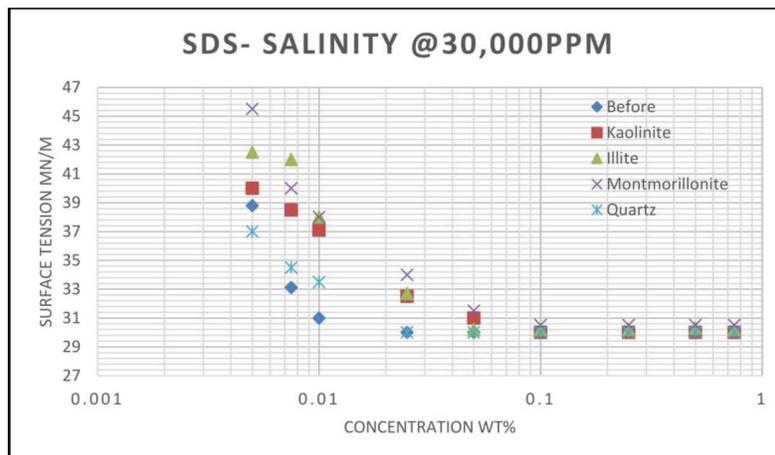
Figure 23—Surface Tension of SDS before and after Adsorption Test with Minerals at 30000ppm.

The electrolyte tends to screen the electrostatic repulsion between head groups and make the surfactant more hydrophobic. The hydrophobic interaction between the surfactant monomers will increase and cause them to aggregate at lower concentration, thereby decreasing the CMC (Muherei & Junin, 2009). Table 8 shows the quantity of SDS adsorbed.

Table 8—Quantity of SDS Adsorbed for Salinity Effect

Minerals	Adosrbed amount (g/Kg)				
	0 ppm	1,0000 ppm	2,0000 ppm	30,000 ppm	40,000 ppm
Kaolinite	4.80	10.92	12.50	1.68	3.24
Illite	3.00	6.72	8.70	1.56	1.62
Montmorillonite	1.20	3.42	4.68	2.58	3.06
Quartz	1.80	1.50	2.70	1.08	0.54

The results show that all the minerals have the lowest adsorption rate at 20000ppm salinity except for kaolinite, after which the CMC starts increasing this was observed for all the minerals. Electrolyte affect amphiphile self-assembly since there can stabilize the micelle formation at lowest concentration. Consequently, the addition of electrolyte to anionic surfactant solution can both increase the micelle aggregation number and decrease the adsorption (Rosen, 2004; Tharwat, 2005). The adsorption increases at 30000ppm due to the solubility of the SDS in the salt, this shows that SDS may precipitate at higher salinity, hence, will reduce the number of SDS ions in solution, which result to higher adsorption rate.

3.6 Batch Pre-flush Test

The pre-flush test was conducted using lignin alkaline as the sacrificial agent. Kaolinite and illite were the minerals selected for this experiment and the brine used was 20000ppm NaCl. The reason for using these two minerals is because kaolinite adsorbed strongly to SDS, while, illite to TX-100. Montmorillonite was not used as the mineral with highest adsorption rate to TX-100, because of its swelling problem, making it difficult to handle, however, illite is a common mineral in the reservoir. The 20000ppm concentration is because from the batch adsorption test, all the minerals showed high adsorption rate at that salinity. The result of the batch pre-flush test is shown in Figures 24 and 25.
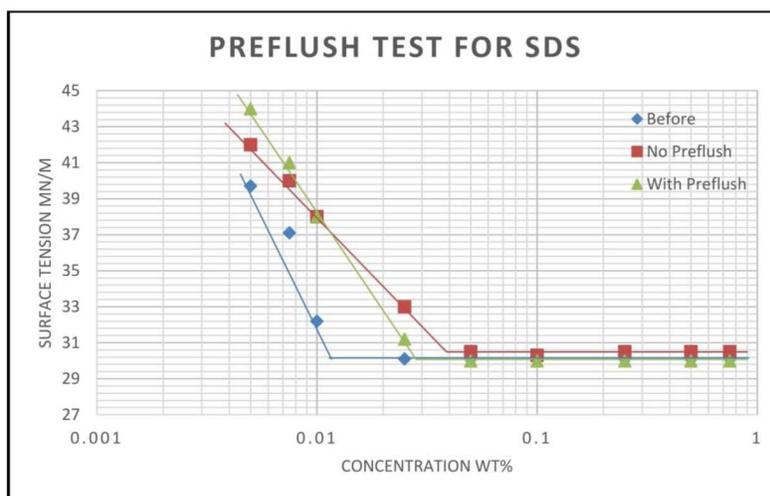
Figure 24—Batch Pre-Flush Test for SDS
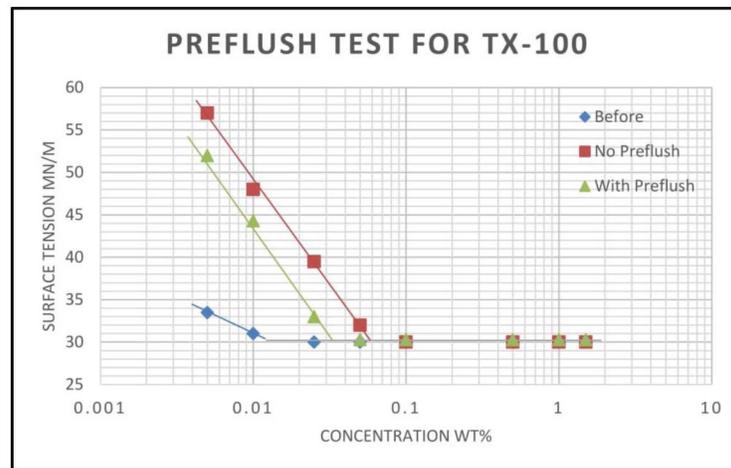
Figure 25—Batch Pre-Flush Test for TX-100

From Figure 24, the adsorption of SDS was lowered significantly, the CMC for batch experiment without pre-flush was approximately 0.04wt% and with pre-flush was approximately 0.028wt%. The quantity adsorbed was 1.68g/kg without pre-flush and 0.96g/kg for pre-flush experiment. The adsorption decreased about 50%, the decrease in the adsorption was due to the behaviour of lignin which adsorbed onto the kaolinite. The adsorption occurred as a result of the electrostatic charge and ion exchange. Lignin has a highly negative head which was attracted by the positive charge adsorption site on the kaolinite. Lignin molecules which adsorb on the adsorption site blocked the SDS molecules from being adsorb to it, hence lowering the adsorption.

The CMC of TX-100 lowered from 0.06wt% without pre-flush to around 0.035wt% with pre-flush (Figure 25), which correspond to the adsorption amount of 2.82g/kg without pre-flush and 1.32g/kg with pre-flush.

Table 9—Quantity of SDS and TX-100 Adsorbed in the Batch Pre-Flush

Surfactant/Mineral	CMC (wt.%)		Adsorbed amount (g/Kg)	
	Without preflush	Preflush	Without preflush	Preflush
SDS (Kaolinite)	0.04	0.028	1.68	0.96
TX 100 (Illite)	0.06	0.035	2.82	1.32

The results show that there is a 53.2% decrease in adsorption rate after pre-flush. Lignin first adsorbed first at the surface of illite, preventing the TX-100 from being adsorbed onto it (Daud et al., 2009).

3.7 Oil Displacement Test

Oil displacement test was conducted to know the effect of lignin alkaline as a sacrificial agent in the surfactant adsorption and oil recovery. Paraffin was the oil face used, which was dyed with red oil, water flooding was carried out before pre-flush, followed by surfactant flooding. The ratio of 95:5 of sand to kaolinite was used for the SDS, while, 95:5 of sand to illite was used for the TX-100 surfactant.

3.7.1 SDS Displacement Test. A sand pack of ratio 95:5 of sand to kaolinite was used for the displacement test. The pore volume calculated was 110cm³. The permeability for the sand pack was 4.37mD and the porosity was 39.10%, 2.87 PV of water was injected until no more oil was recovered, then 0.25PV of surfactant solution were injected. The oil recovery after water flooding was approximately 59.61% of OOIP. After surfactant flooding, the recovery increased by 7.44%. Lignin alkaline was used as the sacrificial agent for the second sand pack after water flooding process. The pore volume of the sand pack was 115cm³, with

permeability of 4.25mD and porosity of 39.98%. The oil recovery after water flooding was 59.15% of OOIP. 3.0 PV of lignin was injected during the water flooding, followed by SDS at 3.25PV. The injection of lignin alkaline and SDS produced an additional recovery of 8.78%.

3.7.2 Triton X-100 Displacement Test. A sand pack of ratio 95:5 of sand to illite was used, the pore volume calculated was 105cm^3, the permeability of the sand pack was 4.30mD, with porosity of 37.33%. The oil recovery after water flooding is 60% of OOIP, the injection of TX-100 produced 4.18% of additional oil. For TX-100, lignin was also used as the sacrificial agent, the sand pack has a pore volume of 115cm^3, permeability of 4.32mD, with a porosity of 40.9%. The oil recovery after water flooding is 60% of OOIP, lignin was injected after 2.8 PV of water was injected during waterflooding, followed by TX-100 at 3.05 PV. The injection of TX-100 and lignin produced an addition recovery of 2.2 of OOIP.
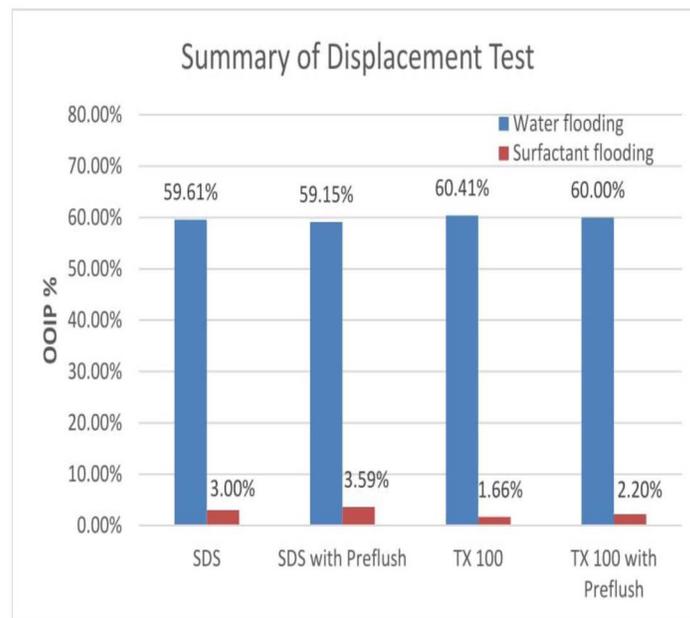
Figure 26—Summary of Displacement test

Conclusions

1. SDS adsorbed mostly on kaolinite, the adsorption sequence for the mineral is as follows; kaolinite > illite > quarz > montmorillonite.
2. The adsorption of TX-100 was higher on montmorillonite, the sequence is as follows; montmorillonite > illite > kaolinite > quartz.
3. The CMC of SDS decreased at acidic condition, the adsorption of SDS on illite and kaolinite increased.
4. Addition of electrolyte decreased the CMC of SDS significantly, the adsorption also decreased until a minimal value before it increases again.
5. The adsorption of TX-100 increased significantly at acidic condition.
6. Salinity has no effect on CMC of TX-100, adsorption also decreased with the addition of salt before increasing again.
7. The injection of surfactants produced more oil, the results also showed that anionic surfactant can mobilize more oil compared to nonionic surfactant.
8. The pre-flush batch method, there was decrease in adsorption of TX-100 and SDS on illite and kaolinite respectively. The adsorption reduced by 53.2% for TX-100 and 50% for SDS.
9. Oil displacement test with SDS and TX-100 surfactants after water flooding had additional recovery of 7.44% and 4.18% respectively.

10. The displacement test after pre-flush showed an incremental oil recovery of 2.2%.

Acknowledgement

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