

Adsorption of Anionic Sodium Dodecyl Sulfate Surfactant on Local Sand and Kaolinite Surfaces: The Prospect of Alkaline and Salinity

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Abstract: Chemical losses in surfactant flooding could substantially degrade the efficiency of the process. This study aims to analyze the prospect of alkaline in minimizing surfactant adsorption. Static adsorption tests were conducted to investigate the adsorption of anionic sodium dodecyl sulfate (SDS) surfactant on local sand and kaolinite surfaces. Alkaline (sodium carbonate) ranging from 1wt% to 3wt% were added into the surfactant formulation with local sand or kaolinite at fixed volume to mass ratio of 5:1. Brine (sodium chloride) concentrations were varied from 1wt% to 3wt%. Equilibrium adsorption test was conducted by shaking the suspension for 24 hours, centrifuged and the supernatant sample was analyzed using UV-Vis spectrophotometer. The kinetics of surfactant adsorption was also analyzed by taking the suspension samples at every 30-60 minutes interval during the shaking process. Adsorption kinetics of SDS surfactant showed a nonlinear increase of the adsorption followed by a plateau. Adsorption on the kaolinite was found higher than the local sand. Increasing SDS concentration resulted in increase of adsorption on both local sand and kaolinite surfaces until reaching its micelle concentration. The increase in brine concentration also led to higher adsorption capacity, but alkaline addition has potentially reduced the adsorption due to higher repulsion force.

Index Terms: Adsorption, Surfactant, Kaolinite, Local Sand, Alkaline.

I. INTRODUCTION

Enhanced oil recovery (EOR) is implemented to obtain higher recovery from a reservoir, not achieved by primary and secondary recoveries [1]. The basic mechanisms of EOR include increasing volumetric sweep efficiency and enhancing displacement efficiency through IFT reduction and decrease in mobility ratio [2], [3]. One of the methods to monitor the EOR process is by a real-time approach of streaming potential measurement using electrodes permanently installed downhole, preliminarily investigated by (Mohd, Jaafar [4], Mohd, Jaafar [5]) to monitor alkaline-surfactant-polymer (ASP) flooding. Surface active agents, called surfactants are the chemical substances that adsorb at the surface or fluid/fluid interface to alter the

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surface and interfacial properties, specifically lowering the surface tension or IFT [6]. A surfactant molecule consists of two functional groups, which are the polar group called hydrophilic (water-soluble) and non-polar group, called hydrophobic (oil-soluble). There are four categories of surfactants, which are anionic, cationic, nonionic and zwitterionic (amphoteric) based on the nature of the head groups [7]. In aqueous solution, the molecule of anionic surfactant ionizes, resulting in negative charge of the surfactant. It is classified as anionic due to the negative charge on the head group [6]. Anionic surfactants have been widely used in chemical EOR due to their benefits of efficiently lowering the IFT, highly stable, relatively resistant to retention, and allowing low adsorption on sandstone rock surface, which is also negatively charged. The key mechanism of surfactant is the reduction of IFT between water and oil, which assist in the residual oil mobilization, resulting in higher oil recovery. However, anionic surfactants are not suitably used in carbonate rocks (positively charged surface) due to high adsorption on the rock surface. In EOR, introduction of surfactant in carbon dioxide (CO₂) flooding will generate CO₂ foam, which have the advantages of mobility control and liquid film stabilization by the surfactant. Nanoparticle addition could further enhance the foam stability and many researchers have studied the prospect of nanoparticles in CO₂ foam flooding [8]-[13].

The main potential problem during surfactant flooding is the chemical losses due to adsorption on the rock surfaces. Surfactant has a tendency to be adsorbed onto the rock surfaces, but alkaline could provide substantial advantage to reduce the surfactant adsorption [14]. These chemical losses could substantially degrade the efficiency of the process. In surfactant adsorption, electrostatic attraction of the electrically charged solid surface with the charged head group of the surfactant molecule plays an important role in contributing to the adsorption mechanism. Thus, anionic surfactants are preferred for sandstone reservoirs leading to repulsion of similarly negative charged, resulting in lower adsorption. Adsorption of ionic polymers also results from electrostatic attraction or repulsion depending on the net ionic charged of the surface [15]. Surfactant retention involves several mechanisms including adsorption, precipitation of surfactant when divalent ions present, surfactant diffusion into dead-end pores, as well as partitioning of surfactant into the oil phase.

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All these mechanisms lead to alteration and reduction of the chemical slug composition, which in turn affect the efficiency of displacement process. However, surfactant adsorption has been the major contributor and control on the amount of surfactant loss inside the porous medium [14]. The adsorption mechanisms have been reported to involve single ions (not micelles) of ion exchange, ion pairing, π electrons polarization, hydrophobic bonding and dispersion forces [16], [17]. The physical-chemical properties affecting the adsorption of surfactant from solution were reported to be pH, temperature, ionic strength, and electrolyte concentration [16], [18]-[20]. Other factors have been reported such as clay content, surfactant structure, Eh, microemulsion viscosity, crude oil, co-solvent, mobility control [21], surfactant concentration, molecular weight and the presence of alkaline [14], [15]. These factors should be considered during investigation of adsorption in surfactant flooding.

Silica (SiO_2) has been reported to be the major component of sand and silt. Those with fine particles (less than $2\ \mu\text{m}$) are categorized as clay. Due to its most abundancy and crystalline silica phase stability, α -quartz has been broadly selected to investigate the interface of water-silica systems in environmental processes. Quartz particles, which are coarse in size, exhibit low specific surface area with no colloidal properties, yet they demonstrate adsorption. In contrast, amorphous silicas with fine particles mostly have large specific surface area. Bera, Kumar [22] have studied the adsorption of anionic sodium dodecyl sulphate (SDS), cationic cetyltrimethylammonium bromide (CTAB) and nonionic Tergitol 15-S-7 surfactants on sand surface and found higher adsorption of cationic than the anionic surfactants, while intermediate behavior of nonionic surfactant. Adsorption on the sand particles increases with increasing surfactant concentration until reaching the saturation point, while increase in salinity also enhance the adsorption capacity. Clays, also known as alumino silicates consist of a layered structure that is composed of a sheet of tetrahedrons of silicon atoms with oxygen atoms at the surrounding, while the sheet of octahedrons of aluminum ion surrounded by six hydroxyl groups or oxygen atoms. Kaolinite is the most common type of clays in reservoirs, consists of a 1:1 alumina silicate, where a tetrahedral silica sheet and an octahedral alumina sheet are bonded through the sharing of oxygen atoms aluminum and silicon atoms in nearby sheets [23]. According to Alkan, Demirbaş [24], zeta potential of the kaolinite surfaces and crystal edges could vary depending on the solution pH and ionic strength. A study by Park, Lee [25] found an unexpected highest maximum adsorption of anionic dodecylbenzenesulfonate (DBS) surfactant, since it was previously reported that zeta potential of kaolinite is approximately -10 to -40 mV (significantly negative) with high electrolyte concentration at natural pH of about 5.9 [24]. Theoretically, the negatively charged DBS molecules would undergo electrical repulsion with the kaolinite surface and expected to have low adsorption. However, hydrophobic interaction has been presumed to occur between DBS molecules with the surface of kaolinite due to low hydrophilic characteristics, thus resulting in a relatively high amount of monolayer.

Glover, Puerto [26] found a linear increase in the retention with the salinity until a certain level, where almost all surfactant injected retained in the core above that salinity

level. It indicated the formation of type II microemulsion at that salinity, which resulting in high surfactant retention. Dang, Chen [14] found that the surfactant adsorption generally increases with increase in salinity, resulting in the surfactant drive to the interface and reduces the repulsion in the adsorbed layer. This results in increase of surfactant adsorption with increasing salt concentration. Increase in the salt concentration favors the charge sites to increase and hence leading to a sudden increase in the adsorption of anionic surfactants on the negatively charged surfaces. Therefore, to a certain degree, impose of negative salinity gradient could overcome the moderate surfactant retention [27]. Alkali is a base, where hydroxide ions (OH^-) is produced when dissolved in water or alcohol. Olajire [28] reported that alkali has advantages in contributing to crude oil emulsification, enhancing ionic strength of aqueous phase and aiding in IFT reduction to ultralow values when surfactant is present. The use of alkali can also reduce costs by minimizing the amount of surfactant required for the process. These are through reduction of surfactant adsorption onto the surface and the in-situ generation of soaps from its reaction with the acidic component in the crude oils. Surfactant adsorption could be reduced since alkali addition increases the density of rock surface's negative charge, leading to water-wet condition [29]. The generated soap can broaden the optimal salinity range and create a micro-emulsion phase which provided the extension of three-phase region with water and oil [29], [30]. Wettability plays important role in oil recovery and its alteration could also be produced with the use of alkali. Wettability alteration will affect the fluid redistribution in the pores, which significantly impact the oil recovery [31].

Therefore, this study is conducted to evaluate the prospect of alkaline and salinity in altering the adsorption of anionic sodium dodecyl sulphate (SDS) surfactant on the local sand and kaolinite surfaces. The outcomes could provide the potential of alkaline in minimizing the surfactant adsorption on both local sand and kaolinite, but the presence of higher salinity environment could in turn increase the ionic strength, thus resulting in higher adsorption. Kaolinite as the porous media (adsorbent) also has significant impact on the adsorption, which reacts differently with anionic surfactant from the local sand. Thus, it is significant to analyze the adsorption behavior with proper consideration on those elements.

II. METHODOLOGY/MATERIALS

A. Materials

There are two main types of chemicals used in the laboratory experiments for adsorption tests, namely surfactant and alkaline. The surfactant used in the study was anionic sodium dodecyl sulphate (SDS) purchased from Merck (the molecular structure is shown in Fig. 1), while sodium carbonate (Na_2CO_3 or soda ash) obtained from QREC was selected for alkaline. Those chemicals have been selected based on the common and widely used chemical solutions for EOR application.



Others are brine solution (sodium chloride) obtained from Vchem for salinity investigation and the indicator solution for SDS detection on UV-Vis spectrophotometer, including patent blue from Sigma Aldrich, while dimidium bromide, sulphuric acid and chloroform were purchased from Merck. All chemicals were used as received without further purification. Local sand was obtained from the sea sand at the Pantai Port Dickson, sieved at desired range of size (90 – 180 μm) and purified, while kaolinite, purchased from Sigma Aldrich is the most common type of clays present in reservoirs, which is known to attribute to the surfactant adsorption in sandstone reservoirs [32].

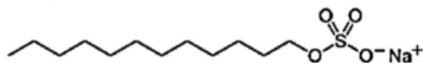


Fig. 1. Molecular structure of SDS surfactant used in the study [22].

B. Experimental Procedures

1) Determination of critical micelle concentration (CMC)

Surface tension measurement of surfactant is significant to determine its CMC. In this study, surface tension was measured using tensiometer (KRUSS K20 EasyDyne) using the Du Noüy ring method at atmospheric pressure with different concentrations of SDS surfactant solutions (0 – 0.6 wt%). From the surface tension data acquired, a plot of surface tension against surfactant concentration was constructed to determine the CMC of the SDS surfactant. CMC is the concentration identified from the curve at the inflexion point. The measurement was conducted at ambient temperature. During the experiment, acetone was used to thoroughly clean the platinum ring, which was then flame-dried before each measurement.

2) Adsorption kinetics

The adsorption kinetics of SDS surfactant on local sand and kaolinite surfaces was preliminarily investigated by addition of 10 g clean local sand into a 100 mL schott bottle containing 50 mL surfactant solution (no salt) at 0.15 wt%. The adsorption kinetics experiments were carried out at room temperature and the SDS concentration in the solution was analyzed at regular intervals until achieving the equilibrium concentration. The bottle was placed on an orbital shaker controller (PROTECH Orbital Shaker 720) for approximately 6 hours and the samples were collected for every 30 to 60 minutes. The collected samples at each interval were then centrifuged (Centrifuge Hettich ROTOFIX 32 A) and the supernatant was taken for UV-Vis spectrophotometer (Shimadzu model UV-1800) analysis for measurement of surfactant adsorption. The same procedures were repeated for SDS solution in 2 wt% sodium chloride. The adsorption kinetics were observed by a plot of surfactant adsorption against time.

3) Equilibrium adsorption

The static adsorption test was conducted by using local sand as the adsorbent. SDS solution was prepared in 100 mL schott bottles by dissolving the SDS powder with deionized (DI) water at different concentrations below CMC (0 to 0.15 wt%). Clean local sand was added into each bottle of SDS solution with a fixed volume (SDS) to mass (sand) ratio of 5:1, which was placed on an orbital shaker controller for approximately 24 hours at constant room temperature. Centrifuge was then applied for 20 minutes to effectively

separate between the solid (adsorbent) and the supernatant. The supernatant sample was collected for UV-Vis spectrophotometer test to analyze the concentration after adsorption for measurement of surfactant adsorption. Calibration curve was required to determine the surfactant concentration after adsorption. Those procedures were repeated using kaolinite as the adsorbent. Effects of salinity and alkaline were then investigated by preparing the SDS solution in 1 to 3 wt% of sodium chloride and sodium carbonate, respectively. A plot of surfactant adsorption versus equilibrium concentration was constructed to observe the equilibrium adsorption.

4) Adsorption Measurement

The adsorptions of SDS surfactant was determined from the calibration curve constructed for surfactant solution. Calibration curve is a standard linear plot of absorbance against concentration, which could be applied to predict the concentration of known absorbance from UV-Vis measurement. UV-Vis spectrophotometer was used to analyze the concentration of the SDS solution after adsorption from the absorbance value obtained at specific wavelength. Since SDS solution is colorless and could not be detected directly from the UV-Vis spectrometer, the analysis was conducted by a variation method from Zerbe et al. (2000) [33]. From the method, 0.04 g patent blue, 0.16 g dimidium bromide and 40 mL of 1.25 M sulphuric acid were dissolved in doubly-distilled water in order to prepare 1 L indicator solution. This indicator solution can be used for several measurements of the UV-Vis analysis. For UV-Vis analysis of SDS surfactant, 0.5 mL of sample solution (SDS supernatant after adsorption) was added to 39.5 mL doubly-distilled water, followed by mixing with 10 mL indicator solution and 20 mL chloroform. The mixture was manually shaken for approximately 1 min and then allowed for phase-separation. After the phase separation, sample of the chloroform phase were taken for a few milliliters and put into the cuvette (quartz) for UV-Vis analysis. The UV-Vis spectrophotometer was set at 526 nm wavelength for SDS concentration measurement, where pure chloroform was used as the reference. The raw data obtained for each sample was calibrated using the calibration curve to acquire the SDS concentration in the samples. The surfactant adsorption on the adsorbent (local sand and kaolinite) was determined by a mass balance relation from Equation 1 [22].

$$\Gamma = (C_o - C_e) \frac{V}{M} \quad (1)$$

where Γ is the amount adsorbed per unit mass (mg/g), V is the volume of the solution used (L), M is the weight of the solid sample (g), C_o and C_e are the initial and equilibrium concentration of surfactant (mg/L), respectively.

III. RESULTS AND FINDINGS

A. Critical Micelle Concentration of Surfactant

Surface tension was plotted against surfactant concentration for CMC determination of surfactant sample is illustrated in Fig. 2. It was found that CMC of SDS surfactant to be 0.22 wt%. The surface tension decreases with increase in surfactant concentration until a specific point is reached, where the surface tension changes drastically in pattern and keeps constant. The CMC was identified as the concentration at the inflexion point, at which the curve starts to deflect. At the CMC, the surfactant solution starts to form micelles in large amount [34], thus further increase in surfactant concentration above this CMC does not enhance the adsorption of surfactant on the solid surface [35]. Due to this fact, the range of surfactant concentration in this study was selected below its CMC to ensure that adsorption occurred along the experimental works.

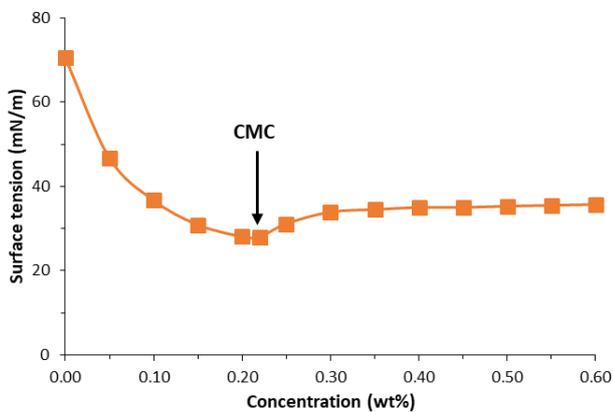


Fig. 2. CMC of SDS surfactant

B. Adsorption Kinetics

The adsorption kinetics of SDS surfactant was analyzed on the local sand-water and kaolinite-water interfaces. Local sand comprises of quartz mineral, while kaolinite is a clay mineral commonly found in the reservoirs. Fig. 3(a) and 3(b) show the adsorption kinetics of SDS surfactant on local sand and kaolinite, respectively, at 0.15 wt% initial SDS concentration with and without the presence of salt.

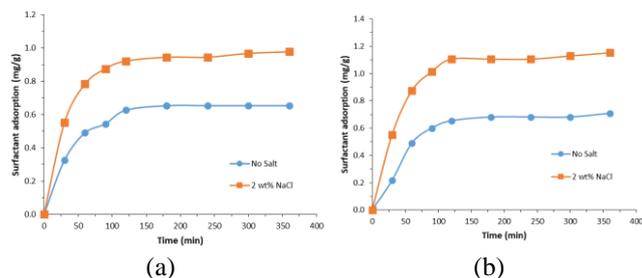


Fig. 3. Adsorption kinetics of 0.15 wt% SDS surfactant on (a) local sand, (b) kaolinite

Generally, it can be observed that the plots have similar pattern, where they start with a non-linear increase in the amount of surfactant adsorption against time followed by a gradual increase until reaching a constant adsorption (plateau) at equilibrium state [36]. The presence of salt has enhanced both the rate of surfactant adsorption and the equilibrium extent of adsorption as shown on those figures.

From Fig. 3(a), amount of adsorption on local sand surface without the presence of salt reaches the equilibrium at approximately 0.654 mg/g. Addition of 2 wt% sodium chloride has increased the equilibrium adsorption at 0.977 mg/g. However, changing the local sand to kaolinite as the adsorbent, shown in Fig. 3(b) has enhanced the surfactant adsorption for both without salt and at 2 wt% sodium chloride, which reached the equilibrium adsorption at approximately 0.708 mg/g and 1.153 mg/g, respectively. Surface charge on the solid surface and the charge brought by the fluid play important roles in surfactant adsorption [37]. For this case, the anionic SDS surfactant with negative charges is attracted to positively charged surfaces, but repulsion occurs with negatively charged surfaces. Local sand (silica) normally has negative charged surface of weak acidic in water near neutral pH [22], thus SDS surfactant experiences a repulsion forces when it was introduced to the local sand. Weak interaction occurs between the local sand and the surfactant with negatively charged head part. Hence, the SDS adsorption capacity on sand particles is not significantly high and decreases on a negatively charged local sand surface [35]. The salinity strongly affects the surface charge, where the electrical double layer (EDL) on the adsorbent surface is compressed leading to decrease in the electrostatic repulsion between the adsorbed surfactant, resulting in higher adsorption capacity [38]. Kaolinite, an alumino silicate has a 1:1 layer unit structure comprising of a single silica tetrahedral sheet and a single alumina octahedral sheet. In anionic surfactant adsorption on kaolinite surface, the amphoteric edge sites are crucial. According to Tertre, Castet [39], the point of zero net proton charge of the edge of kaolinite was found to be at pH range of 4 to 7 (negatively charged near neutral environment), depending on the ionic strength and kaolinite composition. The point of zero charge (PZC) of kaolinite is higher than that of quartz sand, thus weaker repulsion force occurs between the kaolinite surface and the negatively charged SDS surfactant, resulting in higher adsorption capacity.

C. Equilibrium Adsorption

1) Effect of salinity on surfactant adsorption

Static adsorption of SDS surfactant was conducted isothermally and the adsorption isotherms were developed by plotting the amount of adsorption (mg/g) obtained from Eq. 1, against the equilibrium concentration of surfactant, as shown in Fig. 4. Fig. 4(a) illustrates the surfactant adsorption on local sand, while Fig. 4(b) indicates the adsorption on kaolinite surface, both investigated at various salinity from 0 to 3 wt% sodium chloride.

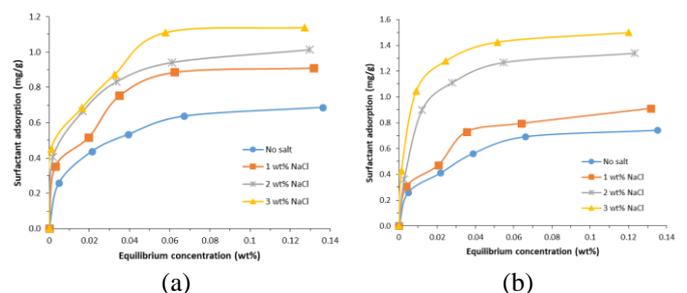


Fig. 4. Static adsorption of SDS surfactant at different salinity on (a) local sand, (b) kaolinite

From those figures, it was found that increase in surfactant concentration has led to a sudden increase in adsorption isotherm, followed by a gradual increase until reaching the plateau, where little or no increase in surfactant adsorption with increasing surfactant concentration. At the initial stage of surfactant adsorption (low surfactant concentration), the adsorption occurs due to electrostatic interaction of the electrically charged surfactant ion (the head groups of the surfactants) with the EDL of the solid surfaces (local sand and kaolinite), where Henry's law is obeyed that a linear increase of adsorption is observed with concentration [16]. At this low surfactant concentration, hydrophobic attraction between surfactant hydrocarbon chains and the solid surfaces takes place during the surfactant adsorption in almost neutral pH condition. The increase in surfactant concentration leads to hydrophobic interactions of alkyl-alkyl between adsorbed surfactant molecules with the bulk surfactant molecules, which provides additional adsorption, resulting in the formation of small sized surfactant aggregates, known as "hemi micelles" at the solid surface [32]. Hemi micelles of the surfactant molecules is formed on the solid surfaces due to lateral interaction between hydrocarbon chains. Additional driving force is generated from this lateral attraction force, which superimposes existing electrostatic attraction resulting in a dramatic increase in surfactant adsorption. This adsorption keeps increasing with increase in surfactant concentration up to a certain point, where no increase in adsorption is observed and plateau has been approached. Beyond this point, bilayer and multilayers are formed when adsorption of surfactant molecules occurs [16]. Strong repulsion occurs with increasing surfactant concentration between negatively charged solid surfaces with surfactant molecules due to negative head groups of SDS surfactant. Thus, it might be possible for adsorption level to reach plateau at the earlier stage before the CMC with increase in surfactant concentration [22]. From Table I, it can be seen that surfactant adsorptions on sand and kaolinite surfaces at this plateau without salinity effect are 0.687 mg/g and 0.741 mg/g, respectively. Basically, the SDS adsorption capacity on local sand surface is not significantly high compared to adsorption on the kaolinite surface due to weak interaction between the negatively charged sand surface and the anionic SDS surfactant with negatively charged head part. The presence of charged components, such as silica in the sand particles which are negatively charged in nature at neutral pH or in water [22] leads to smaller adsorption capacity compared to kaolinite surface, as the PZC of sand is lower than the kaolinite. Thus, stronger repulsion force between SDS ions and negative charges of sand surface. In adsorption of anionic surfactant to kaolinite, amphoteric edge sites are very significant. The PZC of the edge of kaolinite was discovered to be in the range of pH 4.0 to pH 7.0 [39], where ionic strength and kaolinite composition have the substantial effects. In this study, the adsorption tests were conducted at almost neutral condition (pH above the PZC) without adjusting any pH, therefore the net proton charge of the edge is negative, resulting in negatively charged of kaolinite surface. At almost natural pH, the zeta potential of kaolinite

was discovered to be approximately -10 to -40 mV, which is significantly negative with high concentration of electrolytes [40], [41].

Table I: Summary of surfactant adsorption at 0.15 wt% equilibrium concentration at different salinity

Salinity (wt%)	Surfactant adsorption (mg/g)	
	Local sand	Kaolinite
0.0	0.687	0.741
1.0	0.911	0.911
2.0	1.014	1.339
3.0	1.139	1.499

From Fig. 4, salinity demonstrates significant impact on SDS surfactant adsorption to sand surface as in Fig. 4(a) and kaolinite surface as shown in Fig. 4(b). Increasing the sodium chloride concentration from 0 to 3 wt% in the surfactant solution has led the charge sites to increase, resulting in an abrupt increase of the anionic SDS surfactant adsorption on the negatively charged surfaces. Increasing the salt concentration also increases the ionic strength as shown in Table II. It can be seen that the ionic strength at 1, 2 and 3 wt% of sodium chloride was calculated from Eq. 2 to be 0.171 M, 0.342 M and 0.513 M, respectively. However, the presence of divalent ions (calcium chloride) demonstrates higher ionic strength at similar salt concentrations, thus higher surfactant adsorptions on sand and kaolinite surfaces are forecasted when calcium chloride salt is present. High adsorption resulted from high ionic strength is related to the salting-out effect of the surfactant. The thickness of the EDL at the sand and kaolinite surfaces has been diminished due to increase in ionic strength leading to reduction in repulsion of anions. Introducing negative salinity gradient was reported to be able to overcome moderate surfactant retention to a certain degree [27]. The amount of surfactant adsorption for each salinity effect is given in Table I. Surfactant adsorptions on the local sand at the plateau (0.15 wt% surfactant concentration) are shown as 0.911 mg/g, 1.014 mg/g and 1.139 mg/g at 1, 2 and 3 wt% sodium chloride concentrations, respectively. However, kaolinite demonstrates higher surfactant adsorption at similar salt concentrations, which are 0.911 mg/g, 1.339 mg/g and 1.499 mg/g, respectively. At the interface between surfactant and sand particles or kaolinite, an unequal distribution of electrical charges always occur. This unequal electrical charge distribution leads to a rise in the potential across the interface, resulting in the formation of EDL [38]. As the sodium chloride concentration increases, the EDL on the surface of adsorbent (sand and kaolinite) is compressed, which in turn decreases the electrostatic repulsion between the adsorbed surfactant species. Consequently, the adsorption of surfactant capacity increases. Therefore, increase in salinity of the system results in the increase of the surfactant adsorption capacity at a constant ambient temperature. High salinity, which provides high ionic strength could favor the adsorption of SDS on the sand and kaolinite surfaces.

$$I = \frac{1}{2} \sum C_i Z_i^2$$



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(2)

where C_i and Z_i are the molar concentration and the valence of ion i , respectively.

Table II: Ionic strength of brine at various concentration

Concentration		Ionic strength (mol/L)	
(wt%)	(g/L)	Sodium chloride	Calcium chloride
0.0	0	0.000	0.000
1.0	10	0.171	0.270
2.0	20	0.342	0.541
3.0	30	0.513	0.811

2) Effect of alkaline on surfactant adsorption

In surfactant flooding, the presence of alkali has the potential to reduce surfactant adsorption during the displacement process through the formation. In situ soap formation from the acidic component in the crude oil could further reduce adsorption when the surfactant is injected at lower salinities. Alkali also provides wettability alteration of the formation to either more water-wet or more oil-wet state [42]. In this study, surfactant adsorption has been investigated at different alkaline concentrations as shown in Fig. 5(a) and Fig. 5(b) for local sand and kaolinite as the solid adsorbents, respectively. From Fig. 5(a), it was found that surfactant adsorption keeps decreasing with increase in alkaline concentration. No addition of alkaline demonstrates the highest adsorption of 0.687 mg/g, followed by 0.522 mg/g, 0.303 mg/g and 0.139 mg/g at equilibrium surfactant concentration with 1, 2 and 3 wt% sodium carbonate, respectively, given in Table III. However, higher adsorption was observed on kaolinite surface as illustrated in Fig. 5(b), where the amount of adsorbed surfactant are 0.741 mg/g, 0.632 mg/g, 0.522 mg/g and 0.358 mg/g with 0, 1, 2 and 3 wt% alkaline, respectively. Basically, alkali can increase the solution pH with increasing alkaline concentration. The number of positively charged sites on the solid surfaces can be reduced by increasing solution pH, resulting in lower adsorption of the negatively charged surfactant [43]. For local sand which is negatively charged in the common environment, alkali addition could enhance the negative charge of the surface to be more electronegative leading to stronger repulsion force with anionic SDS that reduce the adsorption. In addition, alkali could also function in consuming the multivalent cations in the solution, where precipitation of surfactant molecules could occur. Comparing with salinity effect, substitution of sodium chloride with sodium carbonate alkaline has significantly reduced the surfactant adsorption on both sand and kaolinite surfaces. However, according to Lv, Bazin [44], small pH dependence of adsorption was reported and the adsorption reduction is closely related with the sodium ion activity as well as types and valences of inorganic anions present in the aqueous solution. From the alkaline affect investigation, addition of sodium carbonate at different concentrations is concluded to sustain the pH values above PZC of Gibbsite for the kaolinite. It was reported that zero adsorption could only occur above pH 12.5 for negatively charged surfactant and alumina systems [45].

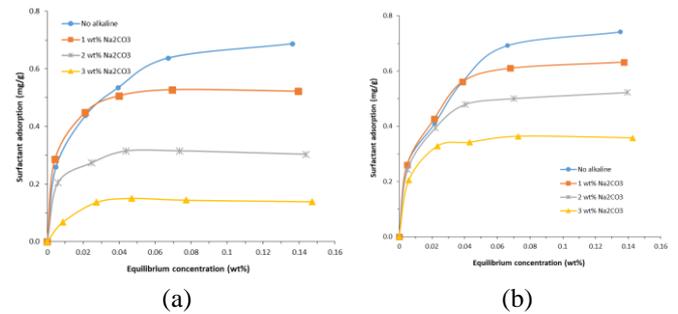


Fig. 5. Effect of various alkaline concentrations on adsorption of SDS surfactant on (a) local sand, (b) kaolinite

Table III: Summary of surfactant adsorption at 0.15 wt% equilibrium concentration at different alkaline concentration

Alkaline (wt%)	Surfactant adsorption (mg/g)	
	Local sand	Kaolinite
0.0	0.687	0.741
1.0	0.522	0.632
2.0	0.303	0.522
3.0	0.139	0.358

IV. CONCLUSION

It was found that the CMC of SDS surfactant from surface tension method to be at 0.22 wt%. Thus, the range of surfactant concentration was selected below this CMC value (0 to 0.15 wt%) for further adsorption analysis. Adsorption kinetics indicated the same pattern, but higher surfactant adsorption on kaolinite surface than the surface of local sand. A nonlinear increase in adsorption amount was observed followed by a plateau to indicate equilibrium condition. For static adsorption of SDS, similar trend of adsorption behavior has been observed with equilibrium surfactant concentration. Increase in surfactant concentration has led to a sudden increase in adsorption capacity, followed by a decrease in the slope until reaching the plateau, where small or no increase in surfactant adsorption with increasing equilibrium surfactant concentration. Electrostatic interaction (repulsion or attraction) of the negatively charged SDS ion with the EDL of the sand and kaolinite surfaces have determined the behavior of the SDS adsorption. In addition, the electrostatic interaction between the SDS ion with the sand and kaolinite surface charges is influenced by their PZCs. Salinity has significant effect on surfactant adsorption, which increases with increasing sodium chloride concentration. 3 wt% sodium chloride concentration demonstrates the highest adsorption of 1.139 mg/g on local sand, while 1.499 mg/g on kaolinite surface at equilibrium surfactant concentration. High adsorption resulted from high ionic strength of the salt, resulting in diminish of the EDL thickness at the sand and kaolinite surfaces, thus reducing the repulsion of anions. Alkaline also has significant impact on surfactant adsorption, which decreases with increase in sodium carbonate concentration. Alkaline could increase the solution pH, which can reduce the number of positively charged sites on the solid surfaces. Thus, the negatively charged SDS surfactant has undergone stronger repulsion with the negatively charged sand and kaolinite surfaces, resulting in lower adsorption.



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