

ADSORPTION CHARACTERISTICS OF SURFACTANTS ON DIFFERENT PETROLUUM RESERVOIR MATERIALS

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Abstract: The loss of injected chemical(s) in the reservoir during injection due to the adsorption of the surfactant (and co-surfactants) unto the rock materials weighs heavily on the economics and environmental footprint of the process and remains a focus of research attention. It is necessary that the surfactant loss in the reservoir during injection is minimized to improve on the process economics and ensure its wider application. In this study the adsorption of cationic and anionic surfactants onto the common reservoir rock material and drilling mud weighing agent is investigated at various surfactant concentration and salinity. The effect of pH was also studied by formulating an alkaline-surfactant mixture using various concentration of NaOH. The indirect method of residual equilibrium surfactant concentration measurement was employed to obtain the adsorption isotherm of cetyltrimethyl-ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) on kaolin, silica, alumina and ilmenite. Surfactant concentration was varied from 50-600 ppm and the conductivity of the equilibrated media at room temperature is measured at various brine concentration and pH. Both surfactants were found to adsorb strongly onto the rock materials while stabilization in the level of adsorption in the region above the CMC was observed as the monomer concentration falls due to micelles formation. At same level of salinity, it was found that cationic surfactant adsorbed more strongly on the rock materials than the anionic surfactant. The volume adsorbed was found to increase up to a maximum of 1.170 mg/g and 1.8249 mg/g for SDS and CTAB respectively on kaolin and ilmenite for instance, as the concentration was increased at constant salinity. The same trend was noted as the brine concentration was varied with adsorption increasing with salinity for anionic surfactant. As pH increases the volume adsorption for SDS decreases while the opposite was the case with the cationic surfactant, CTAB which increase with the alkalinity of the solution.

Keywords: Adsorption, Surfactant, Petroleum Reservoir

Introduction

Surfactant flooding is widely employed to manipulate the phase behaviour of the reservoir fluids to counteract the high capillary force trapping oil in the pores of the reservoir during enhanced oil recovery process (Babu *et al.*, 2015; Kamari *et al.*, 2015; Zargartalebi *et al.*, 2015). The surface active chemical promotes the formation of microemulsions at the crude oil and the displacing fluid (mostly water) interface (Ahmadi & Shadizadeh, 2015; Spildo *et al.*, 2014) thus causing a significant lowering of the fluids interfacial tension (IFT). This is required to efficiently mobilize a substantial percentage of the residual oil towards the production wells to enhance overall crude recovery (Lu *et al.*, 2014). The major problem that affects the efficiency of tertiary oil recovery during micellar flooding, steam-surfactant flooding, alkaline-surfactant (AS), surfactant-polymer (SP) or alkaline-surfactant-polymer (ASP) is the loss of surfactant through interaction with reservoir rock (Ponce F *et al.*, 2014), along with surfactant partitioning into the oil interface (Bera *et al.*, 2013).

In surfactant-water-solid systems, the quantity of surfactant adsorbed depends on the rock properties (surface charge for instance), the character of the surfactant (kind of surfactant, the chain structure), temperature, salinity in addition to the pH (Qiao *et al.*, 2012; Sheng, 2011). Other mechanisms that may cause surfactant losses include precipitation of surfactant when in the presence of electrolyte ions and surfactant diffusion into dead-end pores (Shamsi-Jazeyi *et al.*, 2014; Tichelkamp *et al.*, 2015). High adsorption of surfactants onto the reservoir rock causes surfactant chromatographic retardation while they are carried through a reservoir formation, thus turning the EOR project unproductive and economically not viable (Ma *et al.*, 2013). Dynamic and balanced surfactant adsorption at the solid/liquid interface is mainly dependent on the surfactant's nature as well as on the nature of the reservoir rock surface.

(Hosna Talebian *et al.*, 2015; Romero-Zerón & Kittisrisawai, 2015; Zhang & Somasundaran, 2006). Hence, the choice and selection of surfactant for Chemical Enhanced Oil Recovery (CEOR) operation is influenced by the oil reservoir materials and conditions as well (Kamari *et al.*, 2015).

Depending on the rock formation, oil reservoirs are typically categorized into two types: carbonate and sandstone (Dandekar, 2013; Lashkarbolooki *et al.*, 2014). Anionic surfactants are generally preferred in sandstone reservoir formations owing to the fact that they are relatively less adsorbed in comparison to any of nonionics, cationics as well as zwitterionics surfactants (Ma *et al.*, 2013). These reservoirs comprises of huge quantities of quartz (silica) and less of silicate and carbonate rock crystals and the arrangement is dependent on the sedimentology of the reservoir formation. The majority of solid surfaces of reservoir rocks are charged, for instance silica is predominantly negative charge, while calcite, alumina and dolomite are positively charged at neutral pH (Cappelletti *et al.*, 2006; Yoshihara *et al.*, 1996). If the surfactant being injected and the reservoir material (adsorbent) have different charges, the degree of adsorption is very rapid and the time of equilibrium time is reduced (Muherei & Junin, 2009). In contrast, if the surfactant and the reservoir material have the same charge, repulsive interaction occur which results in negligible adsorption (Wesson & Harwell, 2010). Surfactant adsorption has been found to increase as the surface charge of the reservoir rock increases in the direction of the more positive charges (Pei *et al.*, 2014), which is in accordance with the mechanism of electrostatic. Bastrzyk and Sadowski (2012) reported that CTAB exhibited higher adsorption comparing to SDS on both natural dolomite and magnesite in a low-salinity solution consisting of 0.0001 M of sodium chloride. Significant adsorption of cationic surfactants may be expected to occur if the carbonate formation is rich in clay and/or silica (Ma *et al.*, 2013).

To fully comprehend the scheme of surfactant adsorption taking place on carbonates and precisely select the right surfactants for CEOR processes in carbonate rock formations, Ma *et al.* (2013) studied the adsorption of anionic and cationic surfactants using natural and synthetic carbonate materials. They also looked into likely impurities in natural carbonate, for example clay and silica. Sodium dodecyl sulfate (SDS) and cetylpyridinium chloride (CPC) were selected as the cationic and anionic surfactants, correspondingly. CPC showed insignificant adsorption when synthetic calcite was used but then again quite high adsorption on a number of natural carbonates. It was observed that the adsorption plateau of CPC on carbonates was highly dependent on the amount of silica in the carbonate samples as a result of the strong electrostatic interaction among CPC and the negative binding sites in clay and/or silica. Other researchers have studied the effect of pH and salinity on the adsorption of surfactants (Delshad *et al.*, 2013; Dong *et al.*, 2013; Olajire, 2014; Sheng, 2013a; 2013b; Yuan *et al.*, 2015; Zhao *et al.*, 2015). Generally, addition of alkali to raise the pH is able to change the surface charge to alter the adsorption quantity; the salinity may alter the electrical potential of surface sites for the adsorption (Wesson & Harwell, 2010; Yuan *et al.*, 2015). Adding salts of multivalent cations can sometimes cause a significant increase in the adsorption of anionic surfactants but a considerably decrease in the adsorption of cationic surfactants (Salari *et al.*, 2011).

In general, the most used technique to determine the surfactant loss through adsorption onto the porous medium during a surfactant core flood, is the method of depletion, where the change in the amount of surfactant after it comes in contact with adsorbents is registered and said to be adsorbed. The results obtained from determining the adsorption experimentally are usually represented as adsorption isotherms, where the quantity of surfactant adsorbed is given as a function of equilibrium concentrations (Bera *et al.*, 2013; Salari *et al.*, 2011; Xiao *et al.*, 2003). Adsorption isotherms are determined by maintaining solution environment states, for instance pH, temperature and ionic strength constant (Touhami *et al.*, 1998). When determining surfactant adsorption in dispersed systems, a known quantity of surfactant is added to the system and allowed to reach equilibrium. Afterwards the dispersed solids are separated and the surfactant concentration in the solution measured (Salari *et al.*, 2011). Surfactant adsorption is given by the relationship:

$$\Gamma = \left(\frac{(C_i - C_e) \times M_s}{(M_c)} \right) \times 10^{-3} \quad (1)$$

where,

Γ is the adsorption density (mg/g), C_i is the initial surfactant concentration (ppm), C_e is the equilibrium surfactant concentration in solution (ppm), M_s is the mass of the surfactant solution (g) and M_c is the mass of the dry adsorbents (g).

Adsorption models are normally needed to estimate the loading on the adsorption medium at a certain concentration of the element being studied. The two most common adsorption isotherms which are utilized to model the equilibrium

adsorption relation are the well-known monolayer Langmuir and empirical Freundlich models (Salari *et al.*, 2011). The Langmuir isotherm has been extensively used in various adsorption studies. The Langmuir theory works with the assumption that the sorption occurs at precise homogeneous sites on the adsorbent (Zhang & Somasundaran, 2006). A basic assumption of the Freundlich isotherm is that the adsorbent has a heterogeneous surface constituted of diverse classes of adsorption sites (Salari *et al.*, 2011). He showed that at different solution concentrations the ratio of the quantity of solute adsorbed onto a certain amount of an adsorbent (or porous) material to the concentration of the solute in the solution changes. His theory does not estimate any overload of the adsorbent material by the adsorbate. Hence, infinite surface coverage can be estimated using mathematical terms, which indicates multilayer sorption of the surface (Rawajfih & Nsour, 2006).

This study investigated the adsorption characteristics of anionic and cationic surfactants on different reservoir materials including alumina, silica and kaolin, a form of clay that is found in reservoirs all over the world. Since surfactant is typically added to drilling mud, its adsorption on the emerging drilling mud weighing agent, ilmenite is also investigated, at different pH and salinity. Modelling of the equilibria of adsorption processes on the mentioned materials is investigated. Langmuir and Freundlich isotherms were utilized to model adsorption data to determine the isotherm which gives the best correlation with experimental data.

Materials and Methods

Anionic surfactant, Sodium dodecylsulfate, SDS (Sigma Aldrich, 98%) and cationic surfactant, cetyltrimethylammonium bromide, CTAB (Sigma Aldrich, 98%) are employed. The alkalinity (that is pH) was adjusted with NaOH (Sigma Alrich, 97%) while NaCl (Sigma Alrich, 99%) was used to prepare the synthetic brine solution for salinity adjustment. In this study three types of adsorbents material (to represent reservoir rock materials) is used: alumina powder (Sigma Aldrich, 99.5% metals basis), fine silica flour (Sigma Aldrich, 99.8 %, with a surface area of 175-225 m²/g), kaolin (Al₂Si₂O₅(OH)₄) (Sigma-Aldrich, 98%) and ilmenite (FeTiO₃) obtained from South Africa ore is used as typical drilling fluid weighing agent.

The kaolin powder is dried in a convection electric oven at 120 °C overnight so as to eliminate water and any other adsorbed substances. The result from BET analysis of the kaolin powder is measured using a Quantachrome Autosorb-3b BET Surface Analyzer (Table 2).

Table 1: BET characterization of kaolin clay

Parameter	Kaolin Clay
Area, m ² /g	14.91
Total pore volume, cm ³ /g	0.082731
Average Pore size, Å	221.9

Static adsorption experiments were run to analyze the adsorption characteristics of SDS and CTAB surfactants from aqueous solution onto synthetic kaolin clay, silica, alumina and ilmenite surfaces. Initial surfactant concentrations prepared from a 30 mL surfactant solution in 2 wt.% NaCl ranged from 50-600 ppm were used. The absorbent-dispersed surfactant solution samples were combined at a mass (solid-liquid) ratio of 1:20 in 500 mL glass bottles and shaken at 240 rpm (revolutions/minute) for 24 h at a temperature of 25 ± 2°C using a temperature controller horizontal electrical shaker machine. To ensure equilibrium, the absorbent-surfactant solution mixtures were agitated for 24 h at room temperature and ambient pressure. After adsorption, the surfactant-solid system was separated by means of filtration using a vacuum pump. Surfactant sample aliquots are taken for determination of surfactant concentration before and after adsorption. The equilibrium surfactant concentrations of both surfactants were evaluated so as to determine the maximum quantity of surfactant adsorbed into reservoir material.

The effects of pH and NaCl concentrations on the adsorption capacity of the adsorbent (kaolin clay) to the anionic and cationic surfactants were also investigated. To adjust the required pH values of the maximum adsorption of the surfactant solutions were considered and NaOH (0.2 M) solutions ranging from 0 wt. % to 1 wt. % were used. The salinity of the solution was altered with NaCl (0.2 M) solutions from 0-5 wt. %. A conductivity meter (Mi 170 Bench Meter, EC/TDS/NaCl/Temperature) from Martini Instruments was used to obtain the residual surfactant concentration before and after contact with the reservoir materials. The amount of surfactant adsorbed (adsorption density) was expressed as the unit of mass of surfactant adsorbed per 1 gram of solid adsorbent (mg/g). Adsorption density on reservoir materials was determined by using the expression in Equation (1). Adsorption data have been evaluated by

fitting with Langmuir and Freundlich isotherm models.

Findings

In Figures 1 and through 4 illustrates the adsorption isotherm for SDS and CTAB on the representative reservoir rock materials, that is, synthetic kaolin powder, alumina and silica and the weighing agent, ilmenite at ambient temperature and constant pH of 6.0. The solution salinity was kept constant with 2 vol % NaCl solution. It could be seen from the Figure 1 that both the anionic and cationic surfactant exhibit significant adsorption unto the kaolin clay. This is due to the presence of both negative and positive binding sites happen on this mineral surface at the prevailing pH. This was reported to be the case in other published works (for instance, (Xu *et al.*, 1991), Zhou and Gunter (1992), Jiang *et al.* (2010), Ma *et al.* (2013)). The same happened when ilmenite was used (see Figure 2) as its surface is net negatively charged. With an increase in surfactant concentration, it could be seen that SDS adsorption density increased from 0.3960 mg/g at 50 ppm to 1.170 mg/g at surfactant concentration of 250 ppm when kaolin clay was used. On ilmenite however, a very small increase in the adsorption of SDS is observed from 0.27 mg/g to 0.99 mg/g over 50 to 300 ppm.

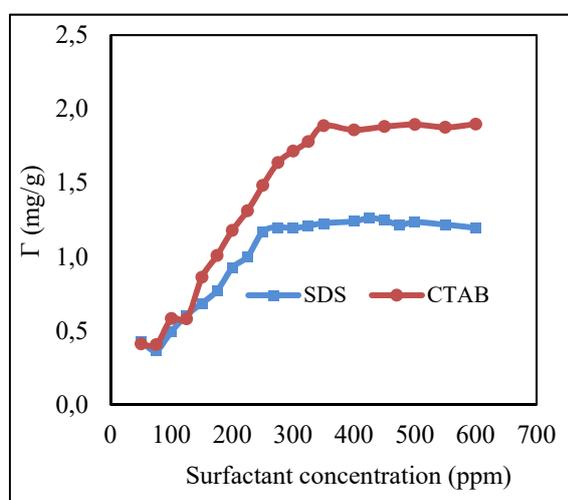


Figure 1: Static adsorption on Kaolin clay

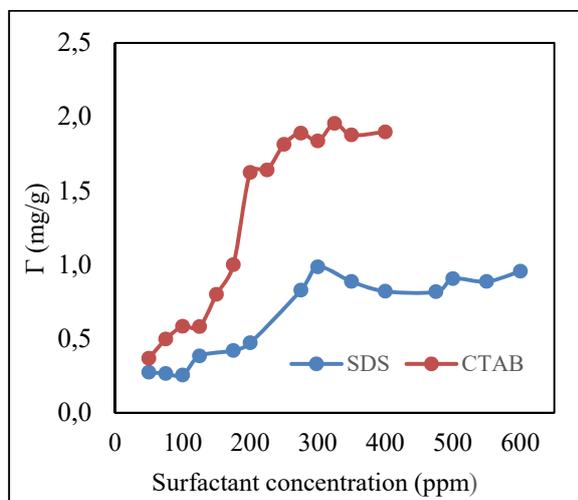


Figure 2: Static adsorption on Ilmenite

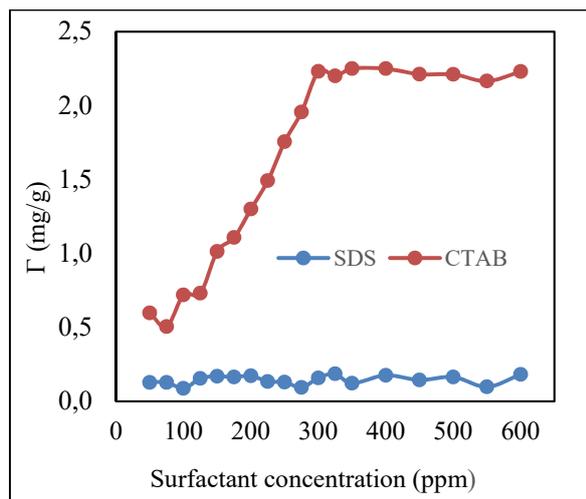


Figure 3: Static adsorption on Silica

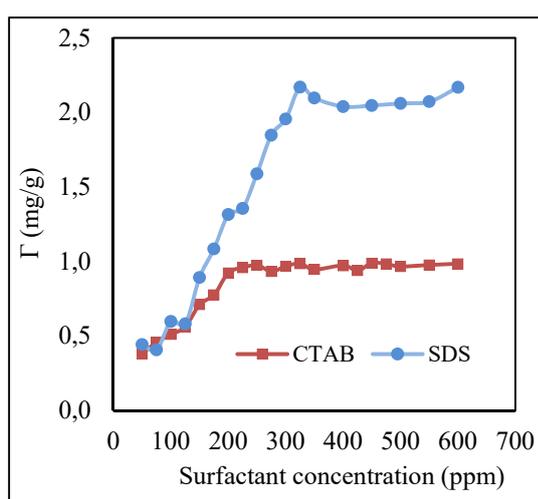


Figure 4: Static adsorption on Alumina

At low surfactant concentration, adsorption takes places mostly because of individual ion interchange without contact between the adsorbed molecules (Tichelkamp *et al.*, 2015). SDS can be adsorbed by kaolin clay as well as on ilmenite

as an anion due to the capability of the mineral to generate a variable charge and to adsorb totally disassociated anions by means of ligand exchange {Sastry, 1995 #329; Ko, 2014 #564}. An increase of surfactant monomer adsorption happens for all the rock crystals as soon as the surfactant concentration in solution rises up to a point when the surfactant concentration in the equilibrium solution attains a value near to or somewhat higher than the CMC (Liljeblad, 2006). Initially SDS adsorption occurs through scatter interactions between the hydrophobic kaolin surface and the non-polar hydrocarbon chain of the probe particle. Then, as the SDS concentration exceeded 250 ppm, the adsorption became more stabilized with the escalation in the amount of surfactant. This shows that the adsorption overcome the electrostatic repulsion between the anionic heads groups of the SDS and the alike charges existing on the edge surface of the kaolin and ilmenite mineral until saturation adsorption is attained.

The adsorption isotherm also indicates that once the SDS surfactant concentration reaches 600 ppm, the volume adsorbed peaked and stabilized. However, SDS exhibits a lower adsorption plateau compare to CTAB, which is most probably because of the strong electrostatic repulsion between the anionic SDS and the negatively-charged kaolin ions. The maximum amount of SDS surfactant adsorbed on the kaolin clay and ilmenite surfaces is found to be 1.17 mg/g at concentration of 250 ppm and 0.99 g and attained at concentration of 300 ppm, respectively. In case of CTAB, a higher and substantial increase in adsorption density with surfactant concentration in contrast to SDS can be observed from 0.3975 mg/g to 1.8249 mg/g while on ilmenite was 0.3675mg/g to 1.6233 mg/g from at concentrations of 50 ppm to 275 ppm.

The basal planes of kaolin clay, ilmenite as well as silica are totally negatively charged, which causes a significant adsorption of CTAB (Ma *et al.*, 2013) as presented in Fig. 1, 2 and 3. The CTAB adsorption occurs mostly due to the presence of some charged components of kaolin and ilmenite particles such as silica (on kaolin) and TiO₂ (on ilmenite) which are negative in nature at neutral pH or in water. Salari *et al.* (2011) also noticed the same pattern where the CTAB adsorption density increase with surfactant concentration on carbonate material. According to Ma *et al.* (2013) if kaolin is present as a contaminant in natural carbonate material, its negative binding sites possibly will cause substantial CTAB adsorption particularly in alkaline systems. Here, the adsorption occurs via electrostatic interaction between the positively charged CTAB head groups and the negatively charged kaolin surfaces. This attraction follows Henry's law that the adsorption increases linearly with concentration (Paria & Khilar, 2004).

From Figures 1 and 2, CTAB adsorption attains its maximum and equilibrium state at 350 ppm and 275 ppm with an adsorption density of 1.8871 mg/g-kaolin and 1.6233 mg/g-ilmenite, respectively. It can be said that the adsorption density in this system is a function of the amount and availability of CTAB, as well as kaolin clay and ilmenite to surfactant solution proportion (Salari *et al.*, 2011). As the hydrophobic mass increases, the hydrophobic attraction between the surfactant and the absorbent molecules increases which in turn also causes an increase in the adsorption density. Here, increasing the surfactant concentrations appears to also cause an increase in the quantity of surfactant adsorbed. As the CMC is attained, the adsorption density stabilizes (or saturates) owing to the surfactant ions having filled all of the kaolin surface sites as well as the chemical potential of the surfactant monomers present in solution are practically steady beyond the CMC (Liljeblad, 2006). In this region as additional surfactant is injected beyond the CMC, a slight or no increase in adsorption with increasing surfactant concentration is observed. The micelle concentration (MC) increases and begin to agglomerate in bulk solution but then again the concentration of monomer stays almost steady because these micelles act as a chemical potential sink for any additional surfactant introduced into the system.

The positively-charged CTAB is also strongly adsorbed onto synthetic silica whereas the negatively-charged SDS shows minor adsorption (Fig. 3). The high adsorption capacity of CTAB on silica particles can be described on grounds of electrostatic interaction which happens between the positively-charged head group of CTAB and the negatively-charged silica (Bera *et al.*, 2013). Silica is mostly negatively charged over a large range of pH and at that pH of 6 the surface of the silica is strongly negatively charged, which goes in accordance with the literature of Ma *et al.* (2013). Thus, the electrostatic repulsion among the formation containing silica material and the anionic surfactant constrains the adsorption.

The behaviour of SDS is totally different over alumina is used as the solid material (Fig. 4). At low CTAB concentrations the surfactant adsorbs randomly, with no associated structure. As the surfactant concentration increases, the existence of hemimicelles on the surface is noticed. Consequently, if natural carbonates have a considerable quantity of silica, substantial adsorption of CTAB may be expected to take place. The adsorption plateau of CTAB is slightly similar to that exhibited on kaolin, however it is to some extent higher with and adsorption density

of 2.2305 mg/g at surfactant concentration of 300 ppm and the maximum adsorption for SDS surfactant was 0.19 mg/g at 325 ppm. However, SDS adsorption on synthetic alumina is higher in comparison to that of CTAB as presented in Fig. 5, which is in compliance with the literature (Paria and Khilar, 2004). This is because negatively charged surfactant strongly adsorbs on positively charged alumina at pH 6. The adsorption of CTAB on alumina is quite low due to the fact that its concentration in the vicinity of alumina surface is inferior to that in the bulk. This is probably attributed to the resilient electrostatic repulsion among the cationic CTAB surfactant and the positively-charged aluminium ions on alumina.

The pH of the aqueous solution is one of the key controlling factors during surfactant adsorption to the reservoir rocks. In Fig. 5 the effect of pH on the adsorption isotherms of the two different surfactants (anionic and cationic) on synthetic kaolin clay surface is represented. Different sodium hydroxide (NaOH) concentrations ranging from 0 wt. % to 1 wt. % were used in this study and measurement carried out at ambient temperature. The SDS and CTAB surfactant concentrations was kept constant at 250 ppm and 350 ppm, correspondingly.

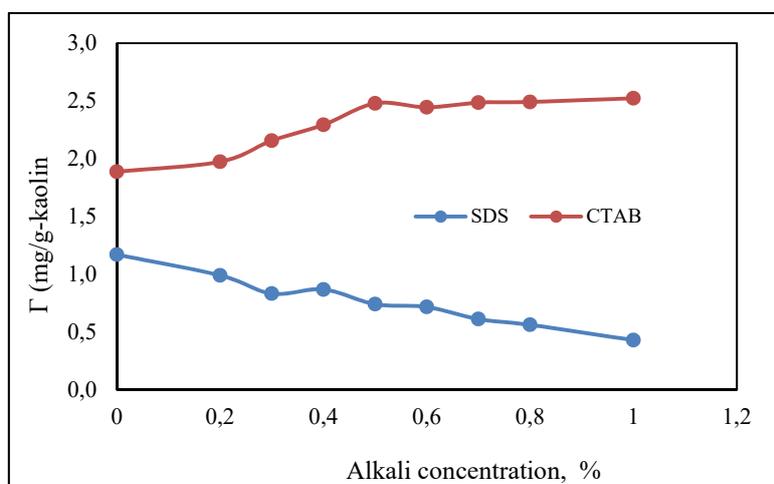


Figure 5: Adsorption isotherms of SDS and CTAB on kaolin at different pH

The adsorption of anionic surfactants decreases with the increase in concentration of alkali to raise the pH (to about 10-12). This makes the mineral surface (absorbent) more negatively charged; which in turn repulses the anionic surfactant and drive more surfactant to the solution, causing a decrease in the adsorption. Fig 5 shows that at an alkali concentration of 0.2 wt %, the SDS surfactant adsorption was instantly decreased from 1.17 mg/g-kaolin to 0.99 mg/g-kaolin. Then as the alkali concentration exceeded 0.6 wt. %, the adsorption of the surfactant on kaolin reaches saturation and its maximum adsorption is assessed to be about 0.4305 mg/g-kaolin. However in case of CTAB, as the pH of the solution increases the CTAB adsorption capacity also increases due to the fact that the cationic surfactant positively-charged head groups are strongly attracted at high pH with negatively-charged kaolin clay surface. Fig 5 also shows that at alkali concentration of 0.2 wt %, the CTAB surfactant adsorption increased from 1.887 mg/g-kaolin to 1.974 mg/g-kaolin. When the alkali concentration is raised to 0.6wt. %, the adsorption of the cationic surfactant on kaolin clay attains equilibrium and its maximum adsorption is evaluated to be around 2.523 mg/g-kaolin. Consequently, it can be concluded that ionic surfactant adsorption on mineral rock surfaces can be minimized or modified by adjusting the pH of the solution which is a very crucial to the economic viability of surfactant use in EOR processes.

Generally, Enhanced Oil Recovery (EOR) is carried out using brine injection or sea water which contains hard ions. In actual fact, nought concentration of divalent ions in a genuine application of an EOR process is very uncommon. For that reason, it is indispensable to study the effect of divalent ions on surfactant adsorption. Adsorption isotherms for SDS and CTAB surfactant solutions at different salinities on synthetic kaolin clay is presented in Figure 6.

The addition of salts of multivalent cations may in some instances originate a substantial increase in the anionic surfactants adsorption while causing a decrease in the adsorption capacity of cationic surfactants (Bera *et al.*, 2013). At the interface between surfactant and the kaolin particles, there is always an imbalanced dispersal of electrical

charges. This uneven charge distribution contributes to the rise of a potential through the interface and creates a so-called electrical double layer (Pethkar and Paknikar, 1998). When the concentration of NaCl is increased, the electrical double layer on the adsorbent's surface is compressed, thus causing a decrease in the electrostatic repulsion between the adsorbed surfactant species and the adsorbent. This results in an increase of adsorption capacity of anionic surfactants. Thus, there is a monotonic increase in the adsorption capacity of SDS as more NaCl solution is added. This is attributed to the fact that the concentration of divalent ions (Na^+) in the solution increases with increase in the added quantity of sodium chloride. A raise of the adsorption plateau of anionic surfactants with increase in the equilibrium amount of hard ions was reported by (Bera *et al.*, 2013). However a different trend is observed with CTAB, increase in the NaCl salt concentration causes the electrostatic attraction between the adsorbed surfactant species to fall resulting in the decrease of the adsorption capacity for CTAB. The surface of the kaolin clay becomes more positively-charged and as a result it repulses the cationic surfactant, thus causing a decrease in its adsorption.

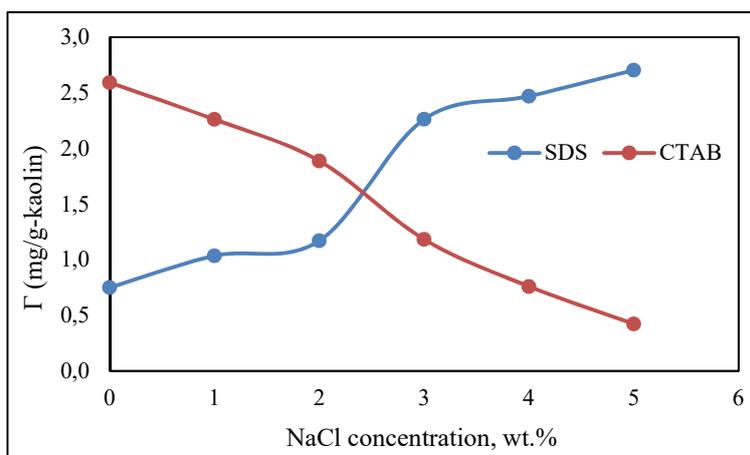


Figure 6: Adsorption isotherms of SDS and CTAB on kaolin at different salinity

Adsorption data obtained were fitted to Freundlich and Langmuir models and suitability of the isotherm equations were related by comparing the correlation coefficients, R^2 . The best-fitted parameters in conjunction with the regression coefficients for the anionic and cationic-surfactant systems adsorbed in synthetic kaolin clay, silica, alumina and ilmenite are presented in Tables 2 through 5 (for Langmuir models) and Table 6 through 8 (for Freundlich models).

Table 2: Parameters for Langmuir model fitted to synthetic kaolin clay data

Surfactants	Fitted Langmuir Equation	R_L^2	Γ_{\max} (mg/g)	K_L (g/L)
SDS	$(1/\Gamma) = 52.397 \times 1/C_e + 0.7469$	0.7364	1.17	29.58
CTAB	$(1/\Gamma) = 60.072 \times 1/C_e + 0.407$	0.7877	1.89	200.66

Table 3: Parameters for Langmuir model fitted to silica data

Surfactants	Fitted Langmuir Equation	R_L^2	Γ_{\max} (mg/g)	K_L (g/L)
SDS	$(1/\Gamma) = 61.109 \times 1/C_e + 6.9879$	0.0324	0.19	-253.21
CTAB	$(1/\Gamma) = 19.233 \times 1/C_e + 0.5654$	0.5031	2.23	187.70

Table 4: Parameters for Langmuir model fitted to alumina data

Surfactants	Fitted Langmuir Equation	R_L^2	Γ_{\max} (mg/g)	K_L (g/L)
SDS	$(1/\Gamma) = 53.41 \times 1/C_e + 0.8787$	0.9191	2.17	214.51
CTAB	$(1/\Gamma) = 58.277 \times 1/C_e + 0.3687$	0.7461	0.92	-11.2

Table 5: Parameters for Langmuir model fitted to ilmenite data

Surfactants	Fitted Langmuir Equation	R_L^2	Γ_{\max} (mg/g)	K_L (g/L)
SDS	$(1/\Gamma) = 121.69 \times 1/C_e + 1.0542$	0.715	0.99	-2.355
CTAB	$(1/\Gamma) = 64.109 \times 1/C_e + 0.4755$	0.9152	1.6233	105.20

Table 6: Parameters for Freundlich model fitted to synthetic kaolin clay data

Surfactants	Fitted Freundlich Equation	R_F^2	1/n	K_F (L/Kg)
SDS	$\text{Log}(\Gamma) = 0.4488 \times \text{LogCe} - 1.0448$	0.8521	2.23	0.1157
CTAB	$\text{Log}(\Gamma) = 0.6363 \times \text{LogCe} - 1.2975$	0.834	1.57	0.0597

Table 7: Parameters for Freundlich model fitted to silica data

Surfactants	Fitted Freundlich Equation	R_F^2	1/n	K_F (L/Kg)
SDS	$\text{Log}(\Gamma) = 0.056 \times \text{LogCe} - 0.9871$	0.0318	17.86	0.1377
CTAB	$\text{Log}(\Gamma) = 0.5191 \times \text{LogCe} - 0.9422$	0.7884	1.93	0.1648

Table 8: Parameters for Freundlich model fitted to alumina data

Surfactants	Fitted Freundlich Equation	R_F^2	1/n	K_F (L/Kg)
SDS	$\text{Log}(\Gamma) = 0.3291 \times \text{LogCe} - 0.8389$	0.8286	3.04	0.2698
CTAB	$\text{Log}(\Gamma) = 0.6787 \times \text{LogCe} - 1.3523$	0.8253	1.47	0.0318

Table 9: Parameters for Freundlich model fitted to ilmenite data

Surfactants	Fitted Freundlich Equation	R_F^2	1/n	K_F (L/Kg)
SDS	$\text{Log}(\Gamma) = 0.5686 \times \text{LogCe} - 1.5353$	0.8471	1.76	0.0444
CTAB	$\text{Log}(\Gamma) = 0.5803 \times \text{LogCe} - 1.2463$	0.8903	1.72	0.0823

The adsorption data acquired from the two surfactant-systems were fitted to the Langmuir model by plotting $1/\Gamma$ against $1/C_e$ which gives a slope of $1/(\Gamma_{\max}K_L)$ and an intercept of $1/\Gamma_{\max}$. Langmuir isotherm makes possible to evaluate the adsorption grade through the aforementioned K_L and Γ_{\max} factors. K_L is a constant in the Langmuir model which shows the adsorption capability of the solid material to the corresponding solutes: the higher the K_F/K_L the higher the Γ value. K_L values of SDS on alumina and CTAB on kaolin are by far higher than those of SDS on silica and ilmenite and CTAB on the alumina surface. This due to the fact that on these minerals their adsorption capacity is almost negligible.

The adsorption data was also fitted to the Freundlich isotherm by plotting a graph of $\log\Gamma$ against $\log C_e$ which yields a slope = $1/n$ and an intercept = $\log K_F$. K_F is equivalent to K_L in the Langmuir model which is related to the bonding energy. K_F can be described as an adsorption coefficient plus it denotes the amount of adsorbate adsorbed on adsorbents for a unit equilibrium concentration. Alike the Langmuir isotherm model, from Tables 6 to 9, the K_F values of SDS on alumina and CTAB surfactant when it is adsorbed on silica are the highest. From the obtained results it can be noticed that there is a high adsorption capacity of alumina for the anionic surfactants in comparison to silica.

The slope $1/n$, starting from 0.9422 to 1.5353 is an indication of the surface heterogeneity and intensity of adsorption and as its value approximate to zero. According to Muherei (2009) if the value of $1/n$ is lower than 1, the Freundlich/Langmuir isotherm is considered to be normal whereas if it is above 1 means that there was cooperative adsorption. Moreover, a greater value of n (and considerably small slope) is an indication that the adsorption is good over the series of concentrations studied, but a low value of n (and sharp slope) reveals that the adsorption is good at high concentration but then again is considered to be much poorer at very low concentrations. From Tables 2 to 9 it can be concluded that the adsorption of adsorption of SDS onto ilmenite involves cooperative adsorption ($1/n=1.5353$). The Langmuir constant, Γ_{\max} , is an indication of the highest amount of the surfactant adsorbed. As observed in Table 4 to 7, Γ_{\max} values are higher for CTAB adsorbed on silica and SDS on alumina which indicates silica and alumina higher capacity to adsorb cationic and anionic surfactants.

Conclusions

In summary, the amount of adsorption in terms of mass per unit surface area varies a lot with different minerals. From this study, it can be concluded that cationic surfactants had a tendency to be strongly adsorbed to silica > kaolin > ilmenite surfaces compared with the anionic surfactant. With increase in the surfactant concentration, adsorption on the surface of reservoir materials particles increases until the saturation point is reached. With increasing alkali concentration (pH) of the solution the anionic surfactant adsorption on synthetic kaolin clay surface decreases on

account of an increase in the electrostatic repulsive forces among the absorbent and the adsorbed surfactant molecules whereas the contrary occurs when cationic surfactant is used. With the addition of NaCl salt to the surfactant solution, the adsorption of anionic surfactant on synthetic kaolin clay surface increases owing to the low electrostatic repulsion between the adsorbed surfactant species and the reservoir material surface. While an opposite trend was observed in the adsorption plateau of the cationic surfactant. Thus, these facts suggests that the adsorption capacity of anionic surfactant increases (or is favoured) with the increase in salinity while the adsorption capacity of cationic surfactant is favoured with the increase in alkalinity of the system at ambient temperature. Adsorption factors for the Langmuir and Freundlich isotherms were determined thru the use of adsorption experimental data.

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