



Equilibrium Adsorption Isotherms of Anionic, Nonionic Surfactants and Their Mixtures to Shale and Sandstone

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Abstract

In this paper, the adsorptive behaviour of two surfactants (Triton X100 and SDS) and their mixtures (1:2; 1:1; 2:1 SDS:TX100 by wt) with two local adsorbents, sandstone and shale was examined. Adsorption of surfactants was assessed using a surface tension technique for aqueous phase surfactant concentrations less than critical micelle concentration (CMC). SDS (anionic surfactant) adsorption was not detected to any of the adsorbent samples. In contrast Triton X100, an ethoxylated nonionic surfactant, adsorbed to both adsorbents. Surfactant adsorbed/Kg adsorbent was lower for TX100-SDS mixtures in comparison to TX100 alone particularly for shale. Adsorption data for sub-micelle concentrations were found to fit successfully both Freundlich and Langmuir isotherms. Freundlich models pretty much represent the data than the Langmuir model. Because of their ability to minimize their amounts adsorbed to different adsorbents, mixed anionic-nonionic surfactant particularly TX100-SDS may show potential advantages in surfactant enhanced aquifer remediation (SEAR) and surfactant enhanced oil recovery (EOR) applications.

Keywords: Surfactant, CMC, Surface tension, Mixed Surfactants, Adsorption, Adsorption Isotherms

1. Introduction

The adsorption of surfactants on rock/soil/sediment solid matrix may result in the loss and reduction of their concentration, which may render them less efficient or ineffective in practical treatment. Adsorption of surfactants from aqueous solutions in porous media is very important in enhanced oil recovery (EOR) of oil reservoirs because surfactant loss due to adsorption on the reservoir rocks impairs the effectiveness of the chemical solution injected to reduce the oil-water interfacial tension (IFT) and renders the process economically unfeasible (Curbelo et al., 2007). Furthermore, the adsorption of surfactants by soils can result in much surfactant being unavailable for the micellar solubilisation of hydrophobic organic compounds (HOCs), thereby decreasing its efficiency for desorption. Nevertheless, the presence of adsorbed or immobilised surfactants in soils gives rise to the partition or adsorption of HOCs in the soil-water system, which exacerbate desorption of organic compounds (Edwards et al., 1994; Sun et al., 1995). In this sense, comparable to the selection of a surfactant to solubilise the contaminant or reduce the oil IFT is its minor tendencies to be adsorbed by the soil/sediment/reservoir rock under consideration.

Surfactant adsorption to solid-liquid interfaces is a process where transfer of surfactant molecules from bulk solution phase to the solid-liquid interface takes place. It can be considered as a partitioning of the adsorbate species between the interface and the bulk, and can occur if the interface is energetically favoured by the surfactant in comparison to the bulk solution (Paria and Khilar, 2004; Zhang and Somasundaran, 2006). In presence of soil or sediment, adsorption of surfactant as monomers may occur at low aqueous surfactant concentrations. With an increase in surfactant

concentrations, surfactant monomers adsorbed to a solid surface begin to aggregate and form micelle-like structures called admicelles or hemimicelles, depending on whether the aggregates have one or two surfactant layers. Once these structures form on a solid surface, adsorption of additional surfactant may rapidly increase until a complete bilayers of surfactant covers the solid surface. These surface aggregates form beyond a critical concentration below the CMC, and is known as critical hemimicellar concentration (HMC); hemimicellization was first hypothesized by Gaudin and Fuerstenau (Gaudin and Fuerstenau, 1955).

Kinetics and equilibrium adsorption of surfactants at the solid-liquid interface depend on the nature of surfactants and the nature of the solid surface (Zhang and Somasundaran, 2006). Three types of interactions are generally involved in the adsorption of a surfactant at solid/liquid interface. The attractive or repulsive interaction between the hydrophilic group and the surface, the attractive interaction between the hydrophobic group and the surface and the lateral interactions that occur between adsorbed surfactants. For surfactants, the most important interactions between the hydrophilic group and the surface are the electrostatic and hydrogen bonding (Paria and Khilar, 2004; Zhang and Somasundaran, 2006). Electrostatic interactions are most important for ionic surfactants. If the surfactant and the adsorbent are oppositely charged, the rate of adsorption is very fast and the equilibrium time is less. In the other hand, if surfactant and the adsorbent are similarly charged, repulsion forces take place and minor adsorption is resulted.

The adsorption isotherm of an ionic surfactant on an oppositely charged solid usually follows "Somasundaran–Fuerstenau" type. Somasundaran–Fuerstenau adsorption isotherm is a typical isotherm of a surfactant on a solid surface that can be subdivided into four regions (Somasundaran and Fuerstenau, 1966). In region I, adsorption obeys Henry's law, that is, adsorption increases linearly with concentration. Region II shows a sudden increase in adsorption, while region III shows a slower rate of increase in adsorption than region II. Region IV is the plateau region above the CMC. The explanations for the nature of adsorption curve in the first three regimes are well accepted. The sudden rise in adsorption in region II is due to formation of surface aggregate of the surfactant molecules on the solid surface. In Region III, the solid surface is electrically neutralized by the adsorbed surfactant ions, the electrostatic attraction is no longer operative and adsorption takes place due to lateral attraction alone with a reduced slope. However, in Region IV, the surfactant concentration reaches critical micelle concentration, the surfactant monomer activity becomes constant and any further increase in concentration contributes only to the micellization in solution and it does not change the adsorption density.

Although the adsorption of single surfactants at pure solid-liquid interface has been investigated intensively, there have been only a few studies of mixed systems, in spite of their great importance. Nevertheless, adsorption of surfactant mixtures to natural soils is even scarce. From the application point of view, adsorption from surfactant mixtures is of particular interest, since in most applications surfactants are used in combination with other surfactants. The obvious reason for this is that producing monodisperse surfactants is often too expensive, but in addition to this, many surfactants show synergistic behaviour together with other surfactants, making the use of multi-component systems favourable.

In many applications, surfactant mixtures in particular anionic-nonionic mixtures often give rise to enhanced overall performance over single component systems. For example, anionic-nonionic surfactant mixtures might show advantageous solubilisation behaviour, exhibiting cloud points higher than those of the single nonionic surfactant, along with Krafft points lower than those of the single anionic surfactant. Mixed surfactants could be employed over a wide range of temperature, salinity, and hardness conditions than the individual surfactants (Gu and Galera-Gomez, 1995; Al Ghamdi and Nasr-El-Din, 1997; Goell, 1999). Therefore, surfactant mixtures with superior properties are always required in a wide variety of practical applications. Consequently, one of the main challenges in adsorption studies is to extend the knowledge from fundamental studies on single surfactant systems to multi-component systems, thereby approaching the applied systems.

Recently, the adsorption of anionic-nonionic surfactant mixtures on natural soils was studied by Zhou and co-workers (Yu et al., 2007; Zhou and Zhu, 2007a&b). The study showed that the adsorption isotherm of TX100 from single surfactant solution was nonlinear and typical S-shape curves, reaching a plateau in adsorption amount at surfactant equilibrium concentration around the CMC. The addition of 10 mol% SDS to TX100 resulted in a 25% decrease in the maximum adsorption amount for TX100. Thus, the higher the mole fraction of SDS in mixed surfactant solutions, the greater the decrease in the maximum adsorption amount for TX100. These results showed that, when SDS was mixed together with TX100, the sorption of nonionic surfactant onto soil was severely restricted and a higher mole fraction of SDS in surfactant solution meant that a lower plateau adsorption can be reached with a smaller TX100 concentration in surfactant solution.

Zhou and co-workers findings provided the incentive for the present investigation, in which the role of mixing anionic surfactant with nonionic surfactants on adsorption is considered for local adsorbents. As the adsorption of surfactants onto different adsorbents diminishes their active concentration, it becomes economically important to reduce surfactant

adsorption. This is particularly vital to improve surfactant-facilitated transport of organic contaminants in SEAR operations as well as surfactant EOR for mature oil fields.

Generally, the most common method for the determination of the adsorption is the depletion method, where the change in surfactant concentration (depletion) after contact with adsorbents is measured and assumed to be adsorbed. The results from the adsorption experiment are generally expressed in the form of adsorption isotherms, where the amount adsorbed is plotted as a function of equilibrium concentrations. Adsorption isotherms are measured by keeping solution environment conditions, such as temperature, pH and ionic strength constant. In this study, the adsorption of TX100, SDS, and their mixtures by shale and sandstone substrates is investigated. The experimental results are fitted to Langmuir and Freundlich isotherms and the characteristic parameter of each model are obtained.

2. Materials

2.1 Surfactants

Polyethylene glycol tert-octylphenyl ether-Triton X100 (TX100) was supplied by Scharlau Chemie, Spain. It is a nonionic surfactant ($C_8H_{17}C_6H_4[OCH_2CH_2]_xOH$) with a CMC which spans between 0.13-0.2 g/L (0.2-0.31 mmol/L) (Zhou and Zhu, 2004; Zhou and Zhu, 2007a&b; Zhu and Feng, 2003; Rodriguez-Cruz et al., 2005; Zhao and Zhu, 2006). It has an average of 9.5 ethylene oxide units per molecule with an average molecular weight of 646.37g/mol. Sodium Dodecylsulfate-SDS ($C_{12}H_{24}NaSO_4$) is an anionic surfactant with a CMC which spans between 1-2.4 g/L (3.32-8.4 mmol/L) (Zhou and Zhu, 2004; Zhu and Feng, 2003; Rodriguez-Cruz et al., 2005). SDS molecular weight is 288.4 g/mol and was supplied by Merck with a high grade of purity (99%). All chemicals were used as received without further purification.

2.2 Adsorbents

Shale Samples were collected from an outcrop of a local shale formation (Batu Arang, Selangor, Malaysia). Sandstone Samples were collected from an outcrop of a local sandstone formation (Bukit Bangkong, Kuala Rompin, Pahang). Samples were disintegrated into small pieces by jaw crusher and then ground using rock pulveriser (Fritsch, Germany). Samples were air dried for 24hrs followed by oven drying at 105°C for 24hrs. Dried rock samples were sieved to obtain particles less than 2mm and larger than 1mm in all experiments.

3. Methods

3.1 Preparation of Surfactant Solutions

The surfactant solutions were prepared in a standard 1000mL volumetric flasks, surfactants were weighed on mass basis and emptied into the volumetric flask and then double distilled water was used to complete the solution to the final weight (1Kg). After the preparation of the stock solution, it was diluted to obtain desired concentration. TX100 and SDS solutions were prepared at concentrations ranged from 0.0025wt% to 1wt% corresponding to molar concentrations of 0.039-15.47mM for TX100 and 0.0867-34.68mM for SDS. Mixed surfactant solutions were prepared by mixing SDS and TX100 solutions of the same weight concentrations with different mass ratios of 2:1, 1:1, and 1:2 SDS:TX100. This results in a mole fraction of SDS in the total mixtures of 0.82, 0.69 and 0.53, respectively. Mixed surfactant solutions were allowed to equilibrate for at least 5hrs before any measurements were made.

3.2 Surface Tension Measurements

The surface tension technique was applied to determine the CMC in various combinations of shale/sandstone and/or surfactant systems. The surface tension measurements were carried out with Krüss tensiometer (Krüss GmbH, Hamburg, Instrument Nr, K6) using a platinum-iridium ring at constant temperature ($25\pm 1^\circ C$).

3.3 CMC Measurements

The CMC values were obtained through a conventional plot of the surface tension versus the surfactant concentration. The CMC concentration corresponds to the point where the surfactant first shows the lowest surface tension. The surface tension remains relatively constant after this point.

3.4 Adsorption Experiments

Adsorption isotherms were determined by batch equilibrium adsorption procedures. 10g of shale/sandstone are added to a set of 60mL surfactant solutions (surfactant initial concentrations spans from 0.0025wt% to 1wt%) in a 100mL glass vials and allowed to equilibrate at $25\pm 1^\circ C$. Preliminary experiments indicated that within the first 16hrs- almost all adsorption takes place. 24hrs contact time at rest was long enough for equilibrium and complete separation to be obtained. Surfactant sample aliquots are taken for surfactant concentration determination before and after adsorption. All experiments were conducted with 3 replicates at $25\pm 1^\circ C$. To determine the maximum sorption of surfactants into shale/sandstone, a surface tension method was used. The amount of surfactant adsorbed and/or abstracted was computed from the difference of surface tension values before and after adsorption, and means of three replicates were used. The amount of solute adsorbed, Γ , is expressed in g/Kg and was determined as:

$$\Gamma = (C_i - C_e) \frac{V}{W} \quad [1]$$

Where C_i and C_e are the initial and equilibrium liquid phase concentrations of surfactant solutions (g/L), respectively; V is the volume of the surfactant solution (L); and W is the mass of the dry adsorbents (Kg).

3.5 Adsorption Models

An adsorption model is required to predict the loading on the adsorption matrix at a certain concentration of the component. The two general adsorption isotherms that can be used to describe the equilibrium adsorption relation are the well-known monolayer Langmuir and empirical Freundlich model.

3.5.1 Langmuir Isotherm

The Langmuir adsorption isotherm has been widely applied to many adsorption processes. It has produced good agreement with a wide variety of experimental data for adsorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that the sorption takes place at specific homogeneous sites in the adsorbent. Moreover, when a site is occupied by a solute, no further adsorption can take place at that site.

The rate of adsorption to the surface should be proportional to a driving force and area. The driving force is the concentration in the solution, and the area is the amount of bare surface. The Langmuir equation relates solid-phase adsorbate concentration Γ , the uptake, to the equilibrium liquid concentration at a fixed temperature. The equation was developed by Irving Langmuir in 1916 (Langmuir, 1916). The Langmuir equation is expressed as:

$$\Gamma = \frac{\Gamma_{\max} K_L C_e}{1 + K_L C_e} \quad [2]$$

Where Γ = amount adsorbed (g/Kg); Γ_{\max} = maximum amount adsorbed (g/Kg); K_L = Langmuir equilibrium constant (L/g); C_e = equilibrium aqueous concentration (g/L).

Equation [2] can be rewritten in the well known linearized expression of the Langmuir model as follows:

$$\frac{1}{\Gamma} = \frac{1}{C_e K_L \Gamma_{\max}} + \frac{1}{\Gamma_{\max}} \quad [3]$$

A plot of $1/\Gamma$ versus $1/C_e$ yields a slope = $1/(\Gamma_{\max} K_L)$ and an intercept = $1/\Gamma_{\max}$.

3.5.2 Freundlich Isotherm

Freundlich (Freundlich, 1906) developed an empirical equation to describe the adsorption process. His development was based on the assumption that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites. Freundlich demonstrated that the ratio of the amount of solute adsorbed onto a given mass of an adsorbent to the concentration of the solute in the solution was not constant at different solution concentrations. This isotherm does not predict any saturation of the adsorbent by the adsorbate; thus, infinite surface coverage is predicted mathematically, indicating multilayer sorption of the surface (Rawajfih and Nsour, 2006). The Freundlich isotherm assumes that if the concentration of the solute in the solution at equilibrium, C_e , is raised to the power $1/n$, the amount of solute adsorbed being Γ , the $C_e^{1/n}/\Gamma$ is constant at a given temperature:

$$\Gamma = K_F C_e^{1/n} \quad [4]$$

Where Γ = amount adsorbed (g/Kg); K_F = Freundlich equilibrium constant (L/g); C_e = equilibrium aqueous concentration (g/L); n =Freundlich constant.

Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. This equation can be rearranged in the linear form by taking the logarithm of both sides as:

$$\log \Gamma = \log K_F + \frac{1}{n} \log C_e \quad [5]$$

K_F and $1/n$ are the Freundlich constants related to sorption capacity and sorption intensity, respectively. The intercept and the slope of the linear plot of $\log \Gamma$ versus $\log C_e$ at a given experimental conditions provide the values of K_F and $1/n$, respectively.

4. Results and Discussion

4.1 Surfactant Aqueous Solutions

The CMC of pure surfactants and mixtures were obtained from surface tensions vs. concentration plot (Figure 1). The CMC of SDS is obtained at 0.1wt% (3.468 mM/L or 1g/L) while the CMC value of TX100 achieved is about 0.02

wt%, much lower than that obtained for SDS. These values are comparable well with values reported in previous published studies (Zhou and Zhu, 2004; Zhou and Zhu, 2007a&b; Zhu and Feng, 2003).

As seen in Figure 1, the CMC values for the mixtures were not lower than that obtained by TX100. This is in agreement with previous studies (Janczuk et al., 1995; Paria et al., 2003; Mata, 2006). The CMCs of mixed surfactants are lower than that of sole SDS and very close to that of pure TX100. In this respect, our experimental results for fresh solutions agrees with those observed by Mata (2006) who found a decrease in the CMC of mixtures with increase in mole fraction of TX100, however, the CMC of the mixed system at any composition could not be reduced than that of pure TX100.

4.2 Adsorption to Shale

Adsorption of surfactants onto shale at a particular surfactant dose can be determined by comparing surface tension measurements in aqueous and in shale/aqueous systems. As illustrated in Figure 2, Surface tensions for SDS have not been changed before and after equilibration with shale. However, surface tensions for TX100 were increased significantly after equilibration with shale. This is a result of less surfactant concentrations in solutions after equilibration with shale. This significant loss of TX100 monomers is attributed to their adsorption to organic matter/clay minerals in shale.

For instance, in a shale/aqueous system consisting of 10g of shale, 60mL of surfactant aqueous solution, the minimum amount of TX100 required for the aqueous-phase CMC to be attained is 1.5wt%. However, TX100 attain CMC in aqueous phase at much lower concentrations, i.e., 0.02wt%. Thus, the mass of TX100 that must be added before the aqueous-phase CMC is attained in a shale/aqueous system is much greater than that in an aqueous system without shale.

Generally, micelles do not appear to adsorb onto soil, and the amount of surfactant that is adsorbed thus plateaus at a maximum value at the aqueous-phase CMC. At the CMC values, the concentration of the bulk solutions will be saturated with surfactant monomers. As the fresh surfactant solution monomer reaches the CMC, it is assumed that surfactant/shale supernatant would reach the CMC at the same monomers indicating the same surface tension at both CMCs. Hence, the amount of surfactant adsorbed to shale can be calculated from difference between CMC obtained after equilibration with shale and the original CMC. The difference in CMCs as determined from surface tension curves was found to be 0.13 wt% (0.15-0.02). This concentration can be normalized to shale mass to yield g-TX100 to Kg-shale, i.e., 7.8g-TX100/Kg-shale. Similar values have been reported in literature for natural soil (Zhou and Zhu, 2007a; Zheng and Obbard, 2002).

It is obvious from Figure 2 that SDS-TX100 mixtures at all SDS molar fractions do improve behaviour of the nonionic surfactant. All CMCs of SDS-TX100 are similar to that of pure SDS at 0.1wt% and lower than that of pure TX100 (0.15wt%). Hence, the maximum adsorption for mixtures ($\Delta\text{CMC} = 0.1 - 0.02 = 0.08\text{wt}\%$) are lower than that of pure TX100 ($\Delta\text{CMC} = 0.15 - 0.02 = 0.13\text{wt}\%$), approximately around 39% less. Accordingly, it can be said that the presence of SDS (at molar ratios used in this work) did reduce adsorption of TX100 to shale. This is in agreement with the observation made by other researchers (Yu et al., 2007; Zhou and Zhu, 2007a).

4.3 Adsorption to Sandstone

Surface tension trend for TX100 was also increased after equilibration with sandstone (Figure 3). However, TX100 sorption to sandstone was much lower than in case of shale. The difference in CMCs obtained for sandstone case is 0.03 wt% (0.05-0.02) which is much lower than 0.13wt% obtained in case of shale. This concentration when normalized to sandstone mass yield a value of 1.8g-TX100 to Kg-sandstone. TX100-SDS mixtures at all SDS molar fractions have similar adsorption capacities as pure TX100 (Figure 3).

4.4 Sub-CMC Adsorption Isotherms

The amount of surfactant adsorbed at sub-CMC doses can be estimated from the difference in dose necessary to attain a specified value of surface tension. Data were fitted to Langmuir and Freundlich models and applicability of the isotherm equations was compared by judging the correlation coefficients, R^2 . The best-fitted parameters together with regression coefficients for the four-surfactant systems and both adsorbents are given in Tables 1-4. Tables 1 and 2 show Freundlich-fitted equations, constants, and correlation coefficients (R^2) for the four-surfactant systems adsorbed to shale and sandstone, respectively. Similarly, Tables 3 and 4 provide the Langmuir-fitted equations, constants and correlation coefficients (R^2) for the four-surfactant systems adsorbed to shale and sandstone, respectively.

The data obtained from the adsorption of the four surfactant systems were fitted to the Freundlich model by plotting $\log \Gamma$ versus $\log C_e$. The linear plot obtained has a slope that has the value of $1/n$ and y intercept that is $\log K_F$. K_F is a constant in the Freundlich model which is related to the bonding energy. K_F can be defined as an adsorption or distribution coefficient and represents the quantity of adsorbate adsorbed onto adsorbents for a unit equilibrium concentration. As seen in Tables 1 and 2, the K_F values of TX100 on both shale and sandstone are the highest, while the

TX100-SDS mixtures are more or less identical. Furthermore, K_F values are higher for the four-surfactant systems in case of shale as compared to sandstone. This result expressed the high adsorption capacity of shale for the surfactant systems in comparison to sandstone.

The slope $1/n$, ranging between (0.33-1.18), is a measure for the adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for $1/n$ below one indicates a normal Freundlich/Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption. Furthermore, a relatively slight slope (and hence a high value of n) indicates that the adsorption is good over the entire range of concentrations studied, while a steep slope (and hence small n) means that adsorption is good at high concentration but is much poorer at lower concentrations. Accordingly, the result in Tables 1 and 2 allow to conclude that TX100 adsorption to shale involves cooperative adsorption ($1/n=1.18$).

Adsorption data fitting to Langmuir isotherm was achieved by plotting $1/\Gamma$ versus $1/C_e$ which yields a slope = $1/(\Gamma_{\max}K_L)$ and an intercept = $1/\Gamma_{\max}$. Langmuir isotherm allows determining the adsorption grade by means of its K_L and Γ_{\max} parameters. K_L is homologous to K_F in Freundlich isotherm and indicates the adsorption capacity of the adsorbent to the respective solutes: the greater the K_F/K_L the greater the Γ value. Similar to the Freundlich model, K_L values of TX100 on both adsorbents are by far higher than those of the binary mixtures of SDS-TX100 and again they are higher for the four surfactant systems in case of shale as compared to sandstone (Tables 3 and 4). The relation of greater to lower K_F/K_L value is: shale > sandstone and TX100 > TX100-SDS mixtures.

Langmuir constant, Γ_{\max} , represents the maximum amount of the surfactant adsorbed. As seen from Table 3 and 4, Γ_{\max} values are higher for the shale than for the sandstone indicating higher capacities of shale to different surfactant systems. However, as it is the case with 'n' values of the Freundlich model, the Γ_{\max} values of the four systems are more or less identical.

According to the values of the correlation coefficients, R^2 , it can be concluded that the Freundlich model represents the adsorption data reasonably well. Correlation coefficients range between 0.978-0.997 for Freundlich-fitting while they range between 0.910-0.997 for the Langmuir-fitting. However, a better criterion for the assessment of experimental isotherm data is a parameter known as normalized percent deviation (Ayranci and Duman, 2007) which is defined by the following equation:

$$P = \frac{100}{N} \sum_{i=1}^N \frac{|\Gamma_{(pred)} - \Gamma_{(exp)}|}{\Gamma_{(exp)}} \quad [6]$$

Where $\Gamma_{(exp)}$ is the experimental Γ at any C_e and $\Gamma_{(pred)}$ the corresponding predicted Γ according to the equation under study with the best-fitted parameters and N is the number of observations. It is clear from this equation that the lower the P value, the fit is considered to be excellent (Ayranci and Duman, 2007). The calculated P values for the Freundlich model are seen to be much lower than those for Langmuir model (Table 5). Therefore, it can be concluded that the Freundlich model represents the experimental isotherm data of surfactants at 25 °C better than the Langmuir model.

In light of the results obtained with shale and sandstone, it seems that adsorption of TX100 in a natural system depend largely on the adsorbent properties including chemical (mineralogical and organic) composition. The low affinity of SDS to both adsorbents is attributed mainly to repulsion forces between adsorbents and surfactants. This is because soils in aqueous solutions often obtain negative charges on the surface thus; maintain repulsion with anionic surfactants.

Adsorption of a nonionic surfactant such as TX100 is commonly thought to involve hydrogen bonding. Hydrogen bonding (also known as hydrophobic bonding) is weaker than electrostatic interactions. Hydrophobic bonding can also be important for adsorption on solids that possess a fully or partially hydrophobic surface. In this case, surfactant molecules can adsorb flat on the hydrophobic sites on the solid.

Another probably influential factor is the clay minerals and organic matter which are abundant in shale compared to sandstone. Surfactant adsorption by soils/sediments depends on the type of surfactant and the soil properties. In this sense, the results of different studies addressing the adsorption of anionic and nonionic surfactants by soils/sediments with different compositions have revealed the relative importance of soil/sediment organic matter and clay minerals on the adsorption of anionic and nonionic surfactants. Furthermore, Nonionic surfactants were found to adsorb extensively to pure clay minerals, however, adsorbed amounts of anionic surfactant were significantly lower (Rodriguez-Cruz et al., 2005).

More importantly, surfactant adsorption is related to the chemical potential of the surfactant molecules (monomers) in solution. Under mixed micellization conditions, the chemical potential of monomers will be lower than that for the single surfactant system and this in turn can reduce adsorption at the solid-liquid interface. Beyond the CMC, the aqueous monomer concentration will not increase with any further addition of surfactant since the additional surfactant

will form micelles. Adsorption of TX100 surfactant as well as SDS-TX100 mixtures to shale/sandstone is limited by their CMCs and reaches a plateau at their CMCs. The CMC-limited adsorption of surfactants reflects the significant effects in reducing the CMC of surfactant systems; in other words, a reduction in their CMCs reduces their adsorption.

5. Conclusion

The adsorption of surfactant onto shale/sandstone results in the dose to achieve micellization being much greater than that for an aqueous system without shale/sandstone. From this study, it can be concluded that nonionic surfactants tended to be strongly adsorbed to shale compared to sandstone. The possible sorption mechanism for nonionic surfactant is the adsorption by hydrogen bonding and it strongly seems to show correlation with clay minerals. Anionic surfactant, SDS, on the other hand showed minor adsorption capacities to both shale and sandstone. It has been shown that the maximum adsorption amounts of SDS on both shale and sandstone were lower compared with that of TX100. This was attributed to repulsion forces between the negatively charged SDS and the negatively charged shale/sandstone.

The results emphasise that for adsorption from surfactant mixtures, it is necessary to take into account the changes in the CMC with changes in composition. For adsorption from mixtures of surfactants with similar properties, i.e., CMC is same as ideal mixing; the adsorbed amount from the mixtures will fall between that of the individual surfactants. In contrast, adsorption from mixtures of surfactants that exhibit synergism in CMC (CMC is lower than ideal mixing) may show even lower adsorption tendencies. This is related to the lower chemical potential of the surfactant monomers in solution.

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Table 1. Parameters of Freundlich models fitted to shale data

Shale	Surfactant	Fitted Freundlich Equation	R_F^2	n	K_F [L/Kg]
	TX100	$\text{Log}[\Gamma]=0.3969 \times \text{Log } C_e + 1.1758$	0.9966	2.52	14.99
	SDS-TX100 [1:2 by wt]	$\text{Log}[\Gamma]=0.3839 \times \text{Log } C_e + 0.7703$	0.9878	2.60	5.89
	SDS-TX100 [1:1 by wt]	$\text{Log}[\Gamma]=0.5496 \times \text{Log } C_e + 0.9909$	0.9934	1.82	9.79
	SDS-TX100 [2:1 by wt]	$\text{Log}[\Gamma]=0.4132 \times \text{Log } C_e + 0.8641$	0.9972	2.42	7.31

Table 2. Parameters for Freundlich model fitted to sandstone data

Sandstone	Surfactant	Fitted Freundlich Equation	R_F^2	n	K_F [L/Kg]
	TX100	$\text{Log}[\Gamma]=0.6682 \times \text{Log } C_e + 0.7285$	0.9901	1.50	5.35
	SDS-TX100 [1:2 by wt]	$\text{Log}[\Gamma]=0.7465 \times \text{Log } C_e + 0.4325$	0.9899	1.34	2.71
	SDS-TX100 [1:1 by wt]	$\text{Log}[\Gamma]=0.7369 \times \text{Log } C_e + 0.3476$	0.9777	1.36	2.23
	SDS-TX100 [2:1 by wt]	$\text{Log}[\Gamma]=0.6953 \times \text{Log } C_e + 0.3301$	0.9921	1.44	2.14

Table 3. Parameters for Langmuir model fitted to shale data

Shale	Surfactant	Fitted Langmuir Equation	R_L^2	Γ_{\max} [g/Kg]	K_L [L/g]
	TX100	$1/\Gamma=0.0009 \times 1/C_e + 0.2762$	0.9102	3.62	306.89
	SDS-TX100 [1:2 by wt]	$1/\Gamma=0.0051 \times 1/C_e + 0.4225$	0.9652	2.37	82.84
	SDS-TX100 [1:1 by wt]	$1/\Gamma=0.0086 \times 1/C_e + 0.356$	0.9559	2.81	41.40
	SDS-TX100 [2:1 by wt]	$1/\Gamma=0.0042 \times 1/C_e + 0.3983$	0.9498	2.51	94.83

Table 4. Parameters for Langmuir model fitted to sandstone data

Sandstone	Surfactant	Fitted Langmuir Equation	R_L^2	Γ_{\max} [g/Kg]	K_L [L/g]
	TX100	$1/\Gamma=0.0186 \times 1/C_e + 1.8183$	0.9727	0.55	97.76
	SDS-TX100 [1:2 by wt]	$1/\Gamma=0.1002 \times 1/C_e + 1.2657$	0.9904	0.79	12.63
	SDS-TX100 [1:1 by wt]	$1/\Gamma=0.1151 \times 1/C_e + 1.7052$	0.9803	0.59	14.81
	SDS-TX100 [2:1 by wt]	$1/\Gamma=0.0887 \times 1/C_e + 1.8708$	0.996	0.53	21.09

Table 5. Estimated 'P' Values

Surfactant	Estimated 'P' Values			
	Freundlich		Langmuir	
	Shale	Sandstone	Shale	Sandstone
TX100	3	7	19	23
SDS-TX100 [1:2 by wt]	4	8	9	9
SDS-TX100 [1:1 by wt]	4	9	13	13
SDS-TX100 [2:1 by wt]	2	6	13	9

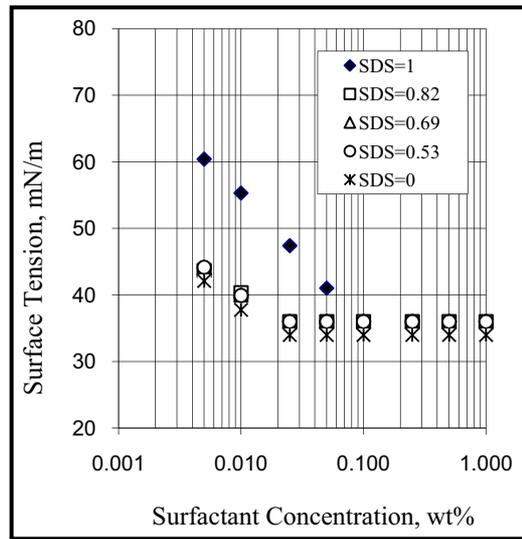


Figure 1. CMCs of surfactants systems in Aqueous Solutions

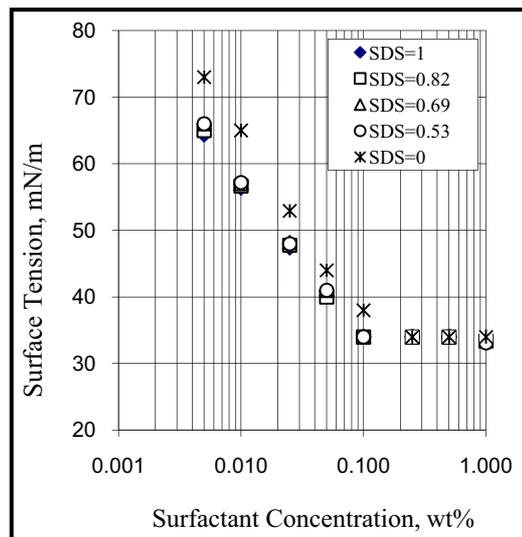


Figure 2. CMCs of surfactant systems after equilibration with shale

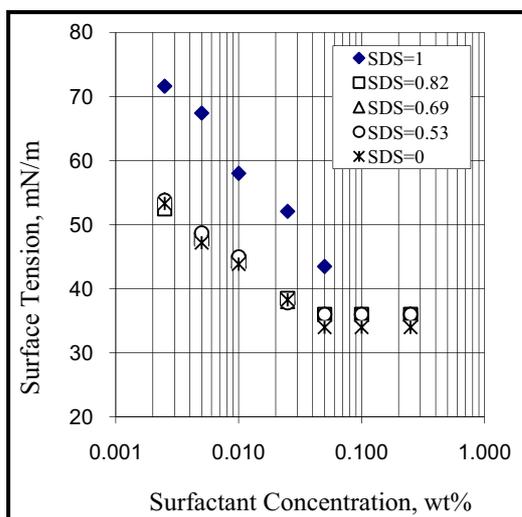


Figure 3. CMCs of surfactant systems after equilibration with sandstone