

Experimental Studies of an Anionic Surfactant Adsorption onto Silica Surface

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Abstract: Adsorption is a unit operation in which dissolved constituents is removed from the solvent (water) by interphase transfer to the surfaces of an adsorbent particle. The basic objective of this paper is calculating adsorption density and modeling of the equilibria of adsorption processes on Silica Surface. This paper describes the equilibrium adsorption was investigated by examining adsorption behavior in a system of solid phase silica and of an aqueous phase of surfactant. Effects on surfactant adsorption density for different surfactant concentration were conducted in on crushed silica. The range of initial surfactant concentrations were from 500 to 5000 ppm in the crushed silica. Sodium dodecyle sulphate surfactant used as an ionic surfactant. An adsorption isotherm is used to characterize the equilibria between the amount of adsorbate that accumulates on the adsorbent and the concentration of the dissolved adsorbate. The Langmuir adsorption isotherm, Freundlich isotherm used to describe equilibria. The equilibrium time was approximately one day. The rate of adsorption dependent on availability of surfactant in the system, it was found that the adsorption of surfactant increased with increasing surfactant concentration. The phenomenon of adsorption at solid/liquid interface is of major importance in the process of enhanced oil recovery with the application of surfactant.

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1. Introduction

Loss of surfactants owing to their interactions with reservoir rocks and fluid is possibly the most important factor that can determine the efficiency of a micellar flooding process (Somasundaran, 2000). The adsorption of surface-active agents at the interface of a solid and a liquid phase is a fundamentally important phenomenon, both scientifically and technologically. The facility and strength of that adsorption are very largely controlled by three factors, which are related to the materials in question: (1) the chemical nature of the species being adsorbed, including the nature of the head group (anionic, cationic, nonionic, etc.) and that of the hydrophobe (length and nature of the chain, degree of branching, etc.), (2) the nature of the solid surface onto which the surfactant is being adsorbed (highly charged, nonpolar, etc.), and (3) the nature of the liquid environment (in water, the pH, electrolyte content, temperature, additives, etc.). A slight change in one of these or other factors can result in a significant change in the adsorption characteristics of the system. The adsorption of a surfactant molecule onto a solid surface can be significantly affected by relatively small changes in the characteristics of the system (Drew, 2006). Foam application involves injecting a surfactant along with water and gas into the reservoir

(Enick et al., 2000). The economics of foam flooding depend significantly on the quantity of surfactant required to generate and propagate foam. Surfactant loss through partitioning into the crude oil phase and through adsorption onto the rock surfaces often consumes more than 90% of the surfactant in the system.⁶ Surfactant loss through partitioning into the crude oil can be responsible for surfactant losses of as much as 30%. However, for the very hydrophilic surfactants chosen for many foam flooding applications, the partitioning onto crude oil is near zero (Schramm, 2000; Grigg and Mikhalin, 2007). Adsorption does not depend on the nature of the surfactant alone, but also (though not inclusively) on temperature, brine salinity and hardness, rock type, wettability, and the presence of the residual oil phase (Schramm, 1994). The classification of the surfactant comes from the hydrophilic group of the surfactant. Up to this point we have covered three of the four general classes of surfactants defined so far: anionic, nonionic and cationic. Anionic surfactants, Surfactants that carry a negative charge on the surface-active portion of the molecule; Cationic surfactants, Surfactants carrying a positive charge on the surface-active portion of the molecule. Nonionic surfactants, Surfactants that carry no electrical charge, as their water solubility is derived from the presence

of polar functionalities capable of significant hydrogen bonding interaction with water (e.g., polyoxyethylenes, sugars, polyglycidols) (Drew, 2006).

Calcite and dolomite are carbonate minerals with similar structures. Calcite is formed by alternate layers of calcium ions and carbonate-ion groups. Dolomite is composed of alternate layers of calcium, magnesium, and carbonate ions. Both solids are salt-type minerals; therefore, the solubility in water is higher than for oxides and silicates. The surface charge on the two carbonate minerals in aqueous systems seems to be generated by the preferential dissolution of lattice ions, either Mg^{2+} , Ca^{2+} , or CO_3^{2-} . This dissolution process is determined by interactions between the dissolved ions and the solution constituents; complexes formed by the reactions can then be adsorbed again or precipitated on the solid surface. Although not all work reported in the literature agrees, some studies indicate that hydrogen ions also appear to act as potential determining ions for carbonates which means that the surface charge on the minerals also depends on the equilibrium pH of the solution. At high pH values, more hydroxyl anions are present in the bulk solution and a net negative surface charge is observed. At low pH in the presence of an excess of hydrogen cations, however, the surface charge is positive. These results suggest that cationic surfactants can exhibit very low adsorptions on carbonates-adsorptions significantly below those exhibited by anionics (Grigg et al., 2002).

The mechanism responsible for the surfactant adsorption is mainly the electrostatic attraction between the charged surface of the solid and the charged head group of the surfactant molecule (Grigg et al., 2002).

Also, while the addition of salts of multivalent cations can increase (sometimes significantly) the adsorption of anionic surfactants, it can significantly decrease the adsorption of cationic surfactants. One reason for the decreased adsorption is that the added cations, lattice ions of the carbonate minerals, can affect the surface charge of the mineral to enhance anionic surfactant adsorption while reducing cationic surfactant adsorption (Grigg et al., 2002).

2. Surfactants

Surfactants are defined as a group of chemicals consisting of hydrophobic and hydrophilic tails that alter the surface activity of an aqueous media. When a surfactant is dissolved in an aqueous solution its hydrophobic group distorts the hydrogen bonds between the water molecules around the hydrophobic group resulting in decreased surface tension between the hydrophobic groups and water. Both hydrophobic and hydrophilic groups of surface active agents play

an important role in this phenomenon. The hydrophobic portion is normally made up of hydrocarbons ranging from C8- C18, and can be aliphatic, aromatic, or a mixture of both. The main sources of hydrophobes are normally natural fats, oils, petroleum fractions or synthetic alcohols or polymers (Tabatabal et al., 1993).

3. Experimental Setup and Procedures

3.1. Material

The surfactant used in this study was sodium dodecyle sulphate, which is a good foaming agent. sodium dodecyle sulphate is a mixture of sodium alkyl sulphates consisting chiefly of sodium dodecyl sulphate. 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. sodium dodecyle sulphate is an anionic surfactant, by lowering the surface tension of aqueous solutions; surfactants can act as wetting agents by enhancing the spread of water over surfaces.

3.2. CMC Measurement

Generally, there are several methods to measure CMC; in this work conductivity method was selected. Concentrations of SDS were varied from 500 ppm to 5000 ppm. Conductivity of solutions was determined from high concentration to low one. Conductivity detector which was applied for experiments is from Crison Company. At first Conductivity detector should calibrated with standard solution. In all of experiments electrode was washed up with distilled water and after that with peculiar solution. This is so necessary for accuracy of solutions conductance and immersing the probe of conductometer in solution. In the next step, conductivity of terms of SDS solutions was measured. For getting the CMC, data should be drawn a graph of conductivity versus concentration and figure out the value of CMC from the turning point in the curve (Fig. 1). When concentration of surfactant solution increases to a certain value, its ions or molecules will come to association reaction, and start to be micelles, hence a sharp change in trend of curve. Careful experimental measurements using highly purified systems revealed that somewhat gradual and continuous changes in physicochemical properties occurred near the CMC. The micelles appeared to be polydisperse and that monomer activities changed above the CMC.

3.3. Test Procedures

Adsorption of surfactant on reservoir rock is determined by batch equilibrium tests on crushed core material. In batch equilibrium tests on crushed core a known volume of surfactant solution at a known concentration is mixed with a specified mass of crushed rock in a sealed container (Table 1). The container was placed in the shaker and placed in the

thermostatic air bath. Samples of surfactant solution were taken from container in one day, and we used conductometer to determine residual concentration at equilibrium time. Adsorption is computed from a material balance on the surfactant. Initial surfactant concentrations tested were 500 to 5000 ppm. The solid to liquid weight ratio was 1:1.5. All the adsorption experiments on crushed rocks were performed at 28°C and atmospheric pressure (Paktinat et al., 2006; Meyers and Salter, 1983).

The amount of surfactant absorbed (adsorption density) was expressed as the unit mass of surfactant

adsorbed per 1 gram of rock (mg/g). Adsorption density of crushed rock was calculated by the following formula⁴:

$$\Gamma = ((C_i - C_e) * M_s / (M_c)) * 10^{-3}$$

Where:

Γ : adsorption density, mg/g

C_i , C_e : initial and equilibrium surfactant concentration in solution, ppm

M_s : mass of the solution, g

M_c : mass of the core sample, g.

Table 1: Surfactant Adsorption onto Crushed Cores.

Test #	Core mass [g]	Ratio S:L	Mass of Surfactant Solution [g]	Initial SDS Conc. [ppm]	Duration of the experiment [hrs]	Residual SDS Conc. [ppm]	SDS Ads. density [mg/g]
1	20	1:1.5	30	500	24	277.8093443	0.263285984
2	20	1:1.5	30	750	24	470.6722203	0.32899167
3	20	1:1.5	30	1000	24	661.6098918	0.387585162
4	20	1:1.5	30	1250	24	835.2807235	0.460789148
5	20	1:1.5	30	1500	24	1020.470266	0.499294601
6	20	1:1.5	30	1750	24	1201.36484	0.54295274
7	20	1:1.5	30	2000	24	1386.761324	0.599858013
8	20	1:1.5	30	2250	24	1597.907036	0.690813945
9	20	1:1.5	30	2500	24	1812.030147	1.119170269
10	20	1:1.5	30	2750	24	2037.988649	1.118146968
11	20	1:1.5	30	3000	24	2281.123535	1.127075231
12	20	1:1.5	30	3250	24	2522.79395	1.121837216
13	20	1:1.5	30	3500	24	2765.441856	1.111061775
14	20	1:1.5	30	3750	24	3009.262548	1.117805505
15	20	1:1.5	30	4000	24	3250.1463	1.124123171
16	20	1:1.5	30	4250	24	3491.725122	1.126810303
17	20	1:1.5	30	4500	24	3738.793131	1.129881791
18	20	1:1.5	30	5000	24	4234.078806	0.263285984

4. Adsorption Models

An adsorption isotherm is used to characterize the equilibria between the amount of adsorbate that accumulates on the adsorbent and the concentration of the dissolved adsorbate. In this case two adsorption isotherms were used, Freundlich and Langmuir isotherm. The Langmuir adsorption isotherm and the Freundlich isotherm are two common isotherms used to describe equilibria. The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer exists on an adsorbent and is described by:

$$q_e = \frac{Q_0 K C_e}{K C_e + 1} \quad (1)$$

Where q_e is the amount adsorbed per unit mass of adsorbent (wt/wt), Q_0 and K are empirical constants and C_e is the equilibrium concentration of adsorbate in solution after adsorption. The constants Q_0 and K can

be determined by plotting $\frac{1}{q_e}$ vs. $1/C_e$ and rewriting equation (1) as:

$$\frac{1}{q_e} = \frac{1}{Q_0 K C_e} + \frac{1}{Q_0} \quad (2)$$

However, an empirical equation describes the Freundlich isotherm and typically proves to be the better relation. For the Freundlich isotherm, adsorption is described by:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

Where K_F and n are constants. Rewriting the equation (3) as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

And plotting $\log q_e$ vs. $\log C_e$ allows for the determination of K_F and $1/n$ (Green et al., 1998; Song and Islam, 1994; Thomas and Crittenden, 1998; Mannhardt and Novosad, 1988; Novosad et al., 1986).

5. Result and discussion

Based on Results obtained from this work following conclusions can be drawn:

Static adsorption experiments were run to analyze the adsorption of SDS onto silica crushed rock. For this system the ratio of solid and liquid is 1:1.5. All experiments were performed at 28°C, at ambient pressure. Initial surfactant concentrations ranged from 500 to 5000 ppm in the silica crushed rock. Table 1 summarized the SDS adsorption values and conditions measured in the crushed silica crushed system. The adsorption experiments with a weight ratio of 1:1.5 between surfactant solution and crushed silica showed that with a linear increase of surfactant concentration the SDS adsorption density increases linearly from 0.2632 mg/g to 1.119 mg/g over the range of initial surfactant concentrations from 500 ppm to 5000 ppm (Table 1). It was found that SDS adsorption density increases when the surfactant concentration increases. For the lower concentrations the availability of surfactant was not high enough to reach a plateau. Thus further tests are required to reach completely adsorption. Adsorption density for crushed silica in the range of initial concentrations of 500 to 5000 ppm and solid to liquid ratio of 1:1.5 increased with availability of surfactant with a significant change of adsorption from 0.2632 to 1.11 mg/g (Fig. 2).

As it was shown in (Fig. 2), after reaching an adsorption density of 1.11 mg/g at 2750 ppm of surfactant concentration, adsorption goes to steady condition and reach plateau. So the maximum adsorption for crushed core system is about 1.1 mg/g. In general, it was found that the adsorption density in this system is a function of SDS concentrations, SDS available in the system and solid to solution ratio. The correlation between the chain length and the adsorption density is explained by the increasing hydrophobic attraction as the hydrophobic mass increases. As the CMC is reached the adsorption density levels off because the chemical potential of the monomers in solution is almost constant above CMC. As more surfactant is added above CMC, the micelle concentration increases but the monomer concentration remains approximately constant (Liljeblad, 2007).

5.1. Adsorption Isotherms

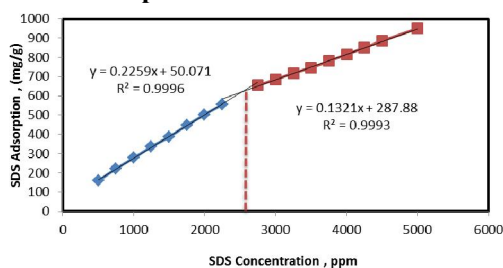


Figure 1: Conductivity of SDS Vs. Surfactant Concentration

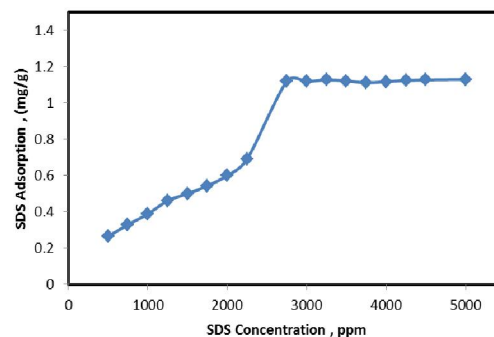


Figure 2: Adsorption Density with Respect to Surfactant Concentration.

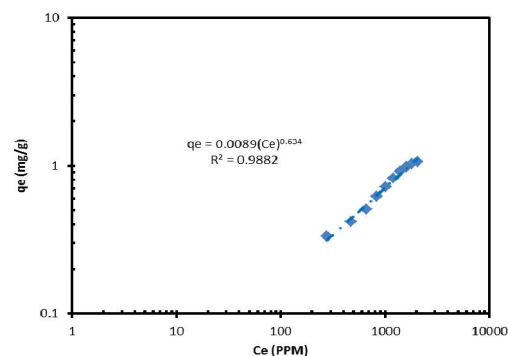


Figure 3: Freundlich Isotherm, Crushed core.

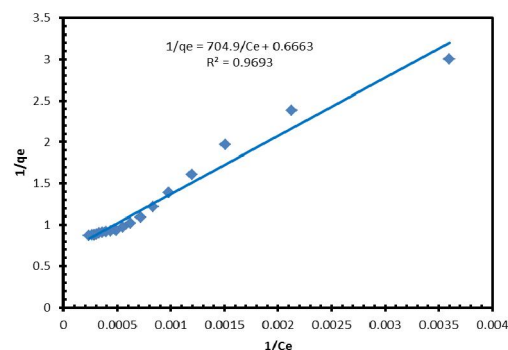


Figure 4: Langmuir Isotherm Crushed Core.

An adsorption isotherm consists of a series of measurements of the surface excess as a function of concentration of surfactant at constant temperature. In this case two adsorption isotherms were used; Freundlich and Langmuir isotherms. The adsorption isotherms of surfactant are presented in Figs3 to 4. The data presented on these graphs show a linear relationship between the surfactant equilibrium concentration and adsorption density. Adsorption density for crushed silica, in the range of initial concentrations of 500 to 5000 ppm and solid to liquid ratio of 1:1.5 increased with availability of surfactant. The plotted curves of adsorption density versus residual concentration for Langmuir isotherm have a

constant slope with increasing surfactant concentration compared to Freundlich isotherm (Fig. 3 and fig. 4). The mechanism responsible for the surfactant adsorption is mainly the electrostatic attraction between the charged surface of the solid and the charged head group of the surfactant molecule.

6. Conclusion

Based on results obtained from this work following conclusions can be drawn:

- The rate of adsorption dependent on availability of surfactant in the system, it was found that the adsorption of surfactant increased with increasing surfactant concentration.
- Adsorption of surfactant increases as the rock surface charge increases toward more positive values, consistent with an electrostatic adsorption mechanism.
- The plotted curves of adsorption density versus residual concentration for Langmuir isotherm have a constant slope with increasing surfactant concentration compared to Freundlich isotherm.

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