Experimental and Modelling Studies on Adsorption of Anionic Surfactant in Alkaline-Surfactant-Polymer (ASP) Flooding

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Alkaline-surfactant-polymer (ASP) has recently gained interest in the petroleum industry due to its synergy. However, studies on surfactant adsorption in ASP formulation modelling are still limited and unclear, making it challenging to obtain the ideal ASP formulation. Therefore, this research focuses on adsorption of anionic sodium dodecyl sulfate (SDS) and cationic cetyltrimethylammonium bromide (CTAB) surfactants on quartz sand surface, in the presence of sodium carbonate (Na_2CO_3) alkali and partially hydrolyzed polyarylamide (HPAM) polymer and modelling of adsorption isotherms. Critical micelle concentrations (CMCs) of both surfactants were determined from surface tension method. Static adsorption tests were conducted by shaking of the mixture samples (mass-to volume ratio of 1:5), centrifuging it, and then collecting the supernatant liquid for UV-Vis analysis. Surfactant concentrations ranged from 100-2000 ppm (SDS) and 100-500 ppm (CTAB). The Na_2CO_3 and HPAM concentrations for ASP solution were fixed at 5000 and 500 ppm, respectively, while the salinity varied from 10000 to 30000 ppm. The CMC of SDS was found at 2200 ppm, higher than CTAB (370 ppm). From adsorption tests, overall, the CTAB adsorption was greater than SDS on quartz-sand with doubled the value at 10000 ppm salinity at 500 ppm concentration. The adsorption of surfactants also increased with increasing salinity. From Langmuir and Freundlich adsorption isotherms developed, the Langmuir isotherm model proved to be the best fit for the experimental data of surfactant adsorption phenomena in ASP flooding.

1. Introduction

The most promising chemical enhanced oil recovery (EOR) technique is alkaline–surfactant–polymer (ASP), which has an effective synergy of alkaline, surfactant, and polymer as its constituent components by injecting these components into a single slug (Kusumah and Vazques, 2017). The polymer improves sweep efficiency by increasing the viscosity of the solution. On the other hand, alkaline produce in situ surfactants, which reduces residual oil saturation, while surfactants reduce interfacial tension, which increases the number of capillaries in the reservoir. Li et al. (2019) also stated that these actions together contribute to increase reservoir oil recovery. Anionic surfactants are preferentially used during surfactant flooding in sandstone reservoir since the electrostatic repulsion between anionic surfactant and negatively charged quartz inhibits the retention of surfactant on the reservoir rock (Nandwani et al., 2019). Because of the high adsorption of cationic surfactants on negatively charged sandstone minerals, cationic surfactants have not been used for field application in EOR processes for sandstone reservoirs but can be used in carbonate reservoirs as carbonates are mostly positively charged (Kumari et al., 2018). In ASP flooding, the presence of polymers, alkalis, other deposition, the types and concentration of surfactant used, and the mineralogical characteristics of rocks, have different effects on the adsorption of surfactants. Adsorption is believed to be a major cause of surfactant consumption (Zargartalebi et al., 2014). However, research and studies on surfactant adsorption in ASP formulations is currently limited. Even if there was, the surfactant adsorption mechanism with presence of alkaline and polymer is still poorly understood and uncertain (Amran et al., 2022). An adsorption model relates the equilibrium surfactant adsorption at the solid or liquid interface to the equilibrium concentration of surfactant in the solution at a

constant temperature (Nandwani et al., 2019). Models of adsorption isotherms can provide mechanism information on the adsorption process, which is useful for adsorption system design. The classification, physical meaning, application, and method of solving isotherms, on the other hand, have not been systematically examined and summarized. In recent years, attention has focused on ASP formulations, which have been shown to work by taking into account the parameters involved, such as the type (Druetta and Picchioni, 2020), the characteristics (Zawala et al., 2020), and chemical conditions which includes the salinity, pH, and concentration of each ASP component (Mohd et al., 2021). However, most of the research studies focused on one or two of the three key components, and some did incorporate additional agents and substances. Previous research has highlighted the formulation of ASP, but there are still a lot of unknowns about how to acquire the best formulations. Many of them differ in terms of the materials used, the techniques employed, the parameters involved, and most importantly, the outcomes, but generally they agreed that surfactant adsorption decreases with the aid of alkali and polymer in ASP formulation. This research effort could deliver new understanding and different perspective in relation to minimizing surfactant adsorption with presence of alkali and polymer at varying salinity using anionic SDS and cationic CTAB surfactants through static adsorption test in a sandstone reservoir condition. An ideal adsorption isotherm model was selected based on two models (Langmuir and Freundlich) developed from the experimental data.

2. Methodology

2.1 Materials

Two types of surfactants were used, namely anionic Sodium Dodecyl Sulphate (SDS) with molecular weight of 288.4 g/mol, and cationic Cetyl Thrimethyl Ammonium Bromide, (CTAB) with a molecular weight of 308.34 g/mol (Zawala et al., 2020), respectively purchased from Sigma Aldrich. Sodium carbonate (Na_2CO_3) from QReC as the alkali constituent, while for the polymer constituent, partially hydrolyzed polyacrylamide (HPAM) obtained from VChem (China) was used. This is to mimic the ASP flooding solution. Meanwhile, quartz sand purchased locally (Malaysia) was used to mimic sandstone reservoir conditions, which also include brine (NaCl) which was acquired from Sigma Aldrich. All chemicals were used as received without further purification.

2.2 Methods

2.2.1 Critical Micelle Concentration (CMC) Determination

The surface tension measurement was used to calculate the CMC of anionic (SDS) and cationic (CTAB) surfactants. The results were obtained using a tensiometer (KRUSS K20 EasyDyne) with the du Noüy ring technique. The interaction of a platinum ring with the liquid surface was used in this method. Before the experiment, the platinum ring was completely cleaned with acetone and then flame-dried before each measurement. The measurement of surface tension was taken at each surfactant concentration for both SDS and CTAB samples. The graph of surface tension data against surfactant concentrations was then plotted. The CMC was found at the intersection of two lines which were the baseline of minimal surface tension and the slope of linear surface tension decline.

2.2.2 Static Adsorption Test of surfactant

The experimental work began with the preparation of ASP formulation with varying surfactant and brine concentrations as summarized in Table 1.

Table 1: Concentrations of the chemical solution

Chemical	Type	Concentration (ppm)
Surfactants	Anionic: SDS	100, 300, 500, 1000, and 2000
	Cationic: CTAB	100, 200, 300, 400, and 500
Alkaline	Na_2CO_3	10000
Polymer	HPAM	500
Brine	NaCl	10000, 20000, and 30000

The static adsorption test was carried out by mixing the quartz sand with ASP solution at a mass-to-volume ratio of 1:5 and then setting it on an incubator shaker for 24 hours at a constant temperature of 25±1 ℃. After that, a refrigerated benchtop centrifuge was used at 3000 rpm for 30 mins to effectively separate the solid and the solutions. After that, the supernatant solution was collected for further UV-Vis analysis. The procedures were conducted for both SDS and CTAB surfactants in ASP solutions.

2.2.3 Adsorption Measurement and Analysis

The UV-Vis Spectrophotometer was used to measure surfactant adsorption on quartz sand. A calibration curve was generated by graphing the absorbance versus initial surfactant concentration. The accuracy of the

calibration curve is important, where R-squares must be close to 1. This standard calibration plot is crucial to get the final concentration of the samples with different salinities. Following calibration, graphs for the adsorption rate of surfactant against their respective surfactant concentration were established. The adsorption rate was calculated using Eq(1) in mg/g (Saxena et al., 2019).

$$A(t) = \frac{\Delta C(t) \cdot V}{m} = \frac{(Ci - Cf) \cdot V}{m}$$

(1)

Where Ci and Cf are the initial and final equilibrium concentrations of surfactant (mg/L), V is volume of the solution used (L), and m is the mass of adsorbent represented by the mineral samples (g).

2.2.4 Adsorption Isotherm Model

The adsorption experimental data obtained were examined using two different adsorption isotherm models which are Langmuir and Freundlich. The Freundlich model is the most often used optimal isotherm to depict the data of many forms of organic contaminants onto adsorbents, followed by the Langmuir model (Ebaga-Ololo and Chon, 2018). These two models are the most commonly used in adsorption investigations due to their simplicity (linear regression method). The list of formula for Langmuir and Freundlich (Kalam et al., 2021) adsorption isotherm models is shown in Eq(2) and Eq(3), respectively.

$$q_e = \frac{q_o \, K_L \, C_e}{1 + K_L \, C_e}$$

(2)

Where q_e is amount of adsorbate adsorbed (mg/g), q_o is the maximum amount of adsorbate adsorbed (mg/g); K_L is the Langmuir constant (L/mg) and C_e is equilibrium concentration (mg/L).

$$q_e = K_F \, C_e^{\,1/n}$$

(3)

Where C_e is equilibrium concentration (mg/L), q_e is the amount adsorbed onto the rock surface (mg/g), K_F is the adsorption capacity (mg/g), 1/n is the Freundlich adsorption parameter, and its value is related with adsorption intensity or surface heterogeneity.

3. Results and discussion

3.1 Critical micelle concentration (CMC)

Surface tension measurement, the Du Noüy technique, was used to estimate the CMC of a surfactant. The CMC was calculated by graphing surface tension in mN/m versus surfactant concentration in ppm, as illustrated in Figure 1a and Figure 1b for SDS and CTAB, respectively. The surface tension of the anionic surfactant, SDS, was observed to decline as the surfactant concentration increased until it reached the inflexion point, at which point the curve began to deflect.
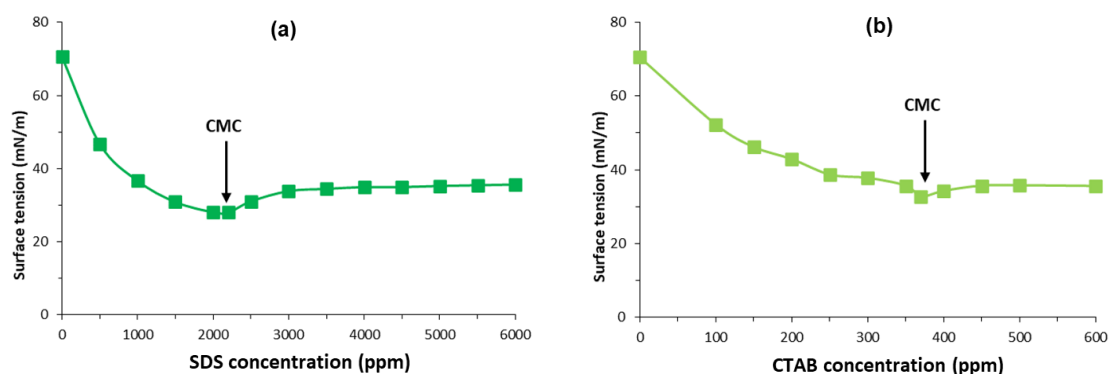

Figure 1: CMC of (a) SDS surfactant; (b) CTAB surfactant

The CMC was discovered to be 2200 ppm for SDS (Mohd et al., 2023). CTAB, a cationic surfactant, shows a similar pattern to SDS but a more linear decreasing value. CTAB's CMC value was estimated to be 370 ppm, relatively lower than SDS (Kumari et al., 2018). Surfactant adsorption on the solid surface was unaffected by

the increment in surfactant concentration above the CMC (Azam et al., 2013) because a large proportion of micelles began to form in the surfactant solution at the CMC point. As a result, the surfactant concentration after the CMC point is mostly stable or only slightly different in an increasing manner.

3.2 Surfactant adsorption in ASP system at different salinities

The effect of salinity on the static adsorption of SDS and CTAB surfactants onto sand particle surfaces in an ASP system was examined, and the results are shown in Figure 2. For both surfactants, a sudden increase in surfactant adsorption at higher concentrations was seen for 0 ppm salinities between 1000 and 2000 ppm for SDS, and between 300 and 500 ppm for CTAB. In general, surfactant adsorption increases with increasing concentration, followed by a steady increase until reaching a plateau where adsorption is constant. Additional concentrations supplied to the solution had no effect on surfactant adsorption in this system because most of the active sites were surfactant-adsorbed, and micelles were repelled by the adsorbed surfactant molecule (Elias et al., 2016). In this research, both surfactants exhibit a gradual increase in adsorption rate pattern with their respective sets of concentration samples. In terms of salinity, brine concentrations of 30000 ppm demonstrated the highest surfactant adsorption, followed by 20000 and 10000 ppm. For example, at a concentration of 500 ppm, the adsorption rate for SDS at 0 ppm is 0.49 mg/g, 0.58 mg/g at 10000 ppm, 0.89 mg/g at 20000 ppm, and 1.01 mg/g at 30000 ppm. The same pattern was seen in CTAB. Theoretically, an increase in salinity can boost surfactant adsorption onto sand particles. In a paper by Saxena et al (2019), it was stated that most of the surfactant has low tolerance level towards high salinity brine which would significantly lead to high surfactant absorption. This is due to the effect of metallic ions in the brines such as Na+, Ca+ and Mg+ that will absorb the surfactant thus reducing the surfactant effectiveness. This pattern is consistent across all three salinity instances and corresponds to the common adsorption curve discovered in earlier studies (Mohd and Jaafar, 2019). When the surfactant adsorption rates of SDS and CTAB were compared, it was discovered that CTAB had a higher surfactant adsorption rate onto sand particles than SDS at the same concentrations (100, 300, and 500 ppm). At 500 ppm surfactant concentration, it was observed that the surfactant adsorption exhibited by CTAB (0.90 ppm) was found to be almost doubled compared to SDS (0.51 ppm) at 10000 ppm brine. Overall, the SDS adsorption rate increases significantly as salinity concentration increases (Mohd et al., 2021), though it remains lower than the adsorption rate of CTAB, which increases consistently. Generally, cationic surfactant like CTAB will adsorb more to sandstone rocks due to its positive charge which will be attracted to the negatively charged sandstone rocks. Anionic surfactant, SDS, on the other hand showed minor adsorption capacities. This was attributed to repulsion forces between the negatively charged SDS and the negatively charged sandstone (Muherei and Junin, 2009). Since the outcome of experimental works depicts as per assumption, the results are accepted.
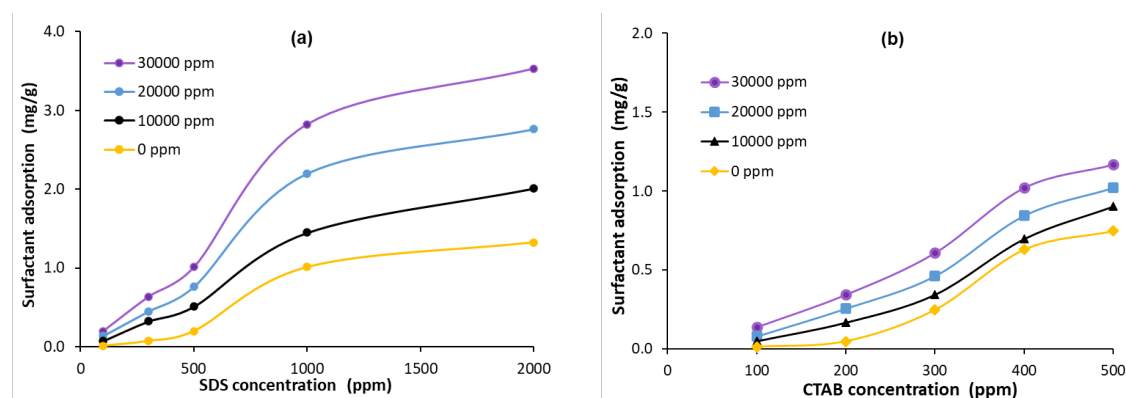

Figure 2: Surfactant adsorption on sand particles in ASP system at different salinity for (a) SDS surfactant; (b) CTAB surfactant

3.3 Adsorption Isotherm Models

3.3.1 Langmuir Model

The Langmuir isotherm model for a specific surfactant solution was assessed using Eq(2). Graphs of $1/q_e$ versus $1/C_e$ were plotted for SDS and CTAB surfactants according to salinities of 0, 10000, 20000, and 30000 ppm, respectively. The parameters for Langmuir model fitted for both surfactants are summarized in Table 2. Generally, the linearity and straight-line results for SDS surfactant are better than CTAB. In general, it may be assumed that both surfactants plotted exhibits an excellent fit that clearly follows the Langmuir isotherm. This assertion is supported by the R^2 values, which are near to unity, implying 1. SDS's R^2 values are greater than

0.97 for all salinities and even resulted in as high as 0.99 for 20000 and 30000 ppm, whereas CTAB R^2 values are on average stands at 0.98. Furthermore, the adsorption is favorable because the separation factor, R_L values are slightly greater than zero and all lesser than one (Ebaga-Ololo and Chon, 2018) as shown in Table 3 and estimated using Eq(4). The intercept and slope of the graph were used to calculate the K_L and q_o values, respectively as indicated in Table 2.

$$R_L = \frac{1}{1 + K_L\,Ce}$$
(4)

Table 2: Parameters for Langmuir model fitted for SDS and CTAB surfactants at different salinities

Salinity (ppm)	SDS surfactant				CTAB surfactant			
	Fitted Eqn.	R^2	q_o (mg/g)	K_L [L/mg]	Fitted Eqn.	R^2	q_o (mg/g)	K_L [L/mg]
0	y=10187x-13.193	0.9735	-0.0013	-0.0758	y=11168x-36.719	0.9860	-0.0026	-0.0272
10000	y=1232x-1.132	0.9837	-0.0009	-0.8835	y=2429x-7.550	0.9895	-0.0114	-0.1325
20000	y=587x-0.661	0.9992	-0.0011	-1.5126	y=1409x-4.621	0.9802	-0.0133	-0.2164
30000	y=316x-0.254	0.9901	-0.0008	-3.9448	y=662x-2.040	0.9885	-0.0148	-0.4902

Table 3: RL values for SDS and CTAB surfactants

Salinity (ppm)	SDS	CTAB
0	0.00664	0.07926
10000	0.00057	0.01533
20000	0.00033	0.00933
30000	0.00013	0.00410

3.3.2 Freundlich Model

The linearized Freundlich isotherm is simple and straightforward, and its mathematical model for the Freundlich isotherm can be employed as an Eq(3). A graph of Log qe against Log Ce was plotted for SDS and CTAB surfactants according to salinities of 0, 10000, 20000, and 30000 ppm, respectively. The parameters for Freundlich model fitted for both surfactants are presented in Table 4. It was found that R^2 values for CTAB are higher when compared to SDS at salinities greater than 10000 ppm. However, SDS's R^2 values are still acceptable because they do not fall below 0.90. The slope equals to 1/n, whereas the intercept equals the log of K_F. It was mentioned that adsorption is deemed favourable when 1/n is in between the ranges of 0 to 1. Adsorption is unfavourable when 1/n > 1, and it is irreversible when 1/n = 1 (Ebaga-Ololo and Chon, 2018). According to the results, both SDS and CTAB have a majority of 1/n values greater than 1, only at salinity of 10000 ppm for CTAB where the value of 1/n is 0.3127, is within the favorable range. Hence, the Freundlich model is unsuitable to fit the experimental data because it implies that the adsorption is unfavourable (Muherei and Junin, 2009).

Table 4: Parameters for Freundlich model fitted for SDS and CTAB surfactants at different salinities

Salinity (ppm)	SDS surfactant				CTAB surfactant			
	Fitted Eqn.	R^2	1/n	K_F [mg/mg]	Fitted Eqn.	R^2	1/n	K_F [mg/mg]
0	y=1.7953x-5.495	0.9567	1.7953	6.48×10^{-5}	y=3.4382x-8.841	0.9226	3.4382	1.45×10^{-4}
10000	y=1.1689x-3.307	0.9639	1.1689	1.25×10^{-2}	y=0.3127x-1.486	0.9502	0.3127	2.26×10^{-1}
20000	y=1.0726x-2.811	0.9427	1.0726	1.78×10^{-2}	y=2.0987x-5.140	0.9800	2.0987	5.86×10^{-3}
30000	y=0.9892x-2.367	0.9124	0.9892	2.79×10^{-2}	y=1.7353x-4.091	0.9639	1.7353	1.67×10^{-2}

4. Conclusion

The adsorption of anionic (SDS) and cationic (CTAB) surfactants on the surfaces of sandstone reservoir minerals, specifically quartz sand, was analyzed in this research for surfactant formulation with alkaline and polymer as ASP system. SDS was found to have a CMC value of 2200 ppm while CTAB had a CMC value of 370 ppm, in agreement with the estimated values from past studies. It was found that the cationic CTAB surfactant, had a much higher adsorption rate onto sand particles than anionic SDS surfactant. Both surfactants adsorbed more at higher salinities, but it was highlighted that SDS adsorption remains lower than CTAB despite the increment of salinity. In term of selecting the most suited adsorption model, the Langmuir adsorption model was observed to fit the experimental data better than the Freundlich adsorption model for both surfactants with presences of alkaline and polymer. This is due to the linearity and closeness of the R^2 values to unity when plotting the Langmuir model (R^2 values range: 0.97-0.99), as compared to Freundlich model (R^2 values range: 0.91-0.98). It should be carefully addressed when selecting the type of surfactant to be used in EOR procedures

since they may enhance surfactant adsorption and thus decrease effectiveness. For future improvement, it is recommended to apply other similar adsorption isotherm models such as the Temkin model, Redlich–Peterson model, and Sips model for best fitting analysis. Lastly, to investigate other parameters, such as varying the alkaline and polymer concentrations, as well as utilizing other reservoir minerals such as kaolinite clay to acquire more comprehensive data on surfactant adsorption.

Acknowledgments

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