

## Adsorption of Aerosol-OT on Sand and Shale at High Sodium Salt Concentration

Azza Hashim Abbas, Mohd Zaidi Jaafar, Abdul Razak Ismail, Wan Rosli Wan Sulaiman\*

Petroleum Engineering Department, Faculty of Chemical & Energy Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.  
 r-wan@petroleum.utm.my

Surfactant flooding is a method for additional recovery of oil from partially depleted reservoirs by changing the interfacial tension. During the application of surfactant into a reservoir, a certain loss in the high equivalent weight fraction occurs. These surfactant molecules are the most efficient in lowering the interfacial tension between reservoir brine and crude oil. Introducing the surfactant to rock sediment may result in these losses and increase the partition or adsorption of hydrocarbon organic compounds (HOCs) in the rock-water system. The adsorptive behaviour of Aerosol-OT was studied under high salt concentration at room temperature in the presence of sandstone and shale. This study detected the adsorption based on the monitored changes in the initial concentration of the surfactant. The adsorption of the surfactant Aerosol-OT has been investigated using batch adsorption isotherms and the technique of UV-Vis spectroscopy. The objective of the study was to gain further insight into the surfactant adsorption for these adsorbents and to determine the appropriate isotherm model. The equilibrium results showed that the value of concentration changed from 0.03 g/L to the lowest value of 0.0124 g/L, which is lower than half. The batch adsorption isotherms that Aerosol-OT adsorption behaviour followed was found to fit Langmuir-Frandauch model.

### 1. Introduction

Chemical enhanced oil recovery (CEOR) has been under attention for decades. Researching for new formulation has attracts academic research interest, mainly in the area of harsh reservoir conditions (Watkins, 2009). Attempts to enlighten the challenges of chemical flood have been done by several studies. One of these issues was regarding to the water quality. Many potential mature reservoirs for chemical EOR application have high salinities and very high total dissolved solids (TDS) (Levitt et al., 2013). These cases are considered problematic because of high water treatment cost, sludge disposal, and potential scale problem in the formation (Zaitoun et al., 2003); thus the technical process design is tough and almost economical CEOR had not been revealed yet.

Chemically injecting surfactant contributes many benefits to the practice of exploiting oil. Surfactant provides low interfacial tension which is needed for high oil recovery. Laboratory studies showed that when interfacial tension (IFT) reached  $1 \times 10^{-2}$  mN/m and below, it may improve the oil mobility. Till today, the best surfactants can form stable microemulsion that provide ultra-low IFT between  $1 \times 10^{-4}$  to  $1 \times 10^{-5}$  mN/m.

In case of the sandstone reservoirs, which is approximately one-fourth of the world's sedimentary rocks in the world, the industrial evaluation advised that chemical techniques like polymer-surfactant flooding can result in a good recovery. Several sandstone reservoirs were nominated for surfactant practice if the appropriate surfactant is found. Fitting the surfactant to the reservoir condition is necessary for an effective chemical flood. Each design requires a sufficient surfactant to act at the oil water interfaces, without exhibiting precipitation and phase separation at reservoir conditions for the duration of the project, which could last for years.

Various surfactants for EOR measures have been investigated on lab-scale. Recent studies on their physicochemical properties such as high solubilisation capacity, surface activity, and unique micelle structure and aggregation behaviour, have revealed a more interesting anionic Gemini surfactants called Aerosol-OT.

The controversy of Aerosol-OT description to follow di chain or Gemini group raised up by (Mukherjee et al., 1993). Aerosol-OT have remarkable lower CMC than their cationic counterparts, significant water solubility which can substantially lower the surface tension, form micelles, and exhibit more interesting rheological behaviour compared to conventional anionic homologues. Aerosol-OT readily exchanges its sodium counter ion for multivalent cations, even if these are present in small concentrations only. This has made Aerosol OT a subject of interest (Nave et al., 2000) .

Tolerating surfactant to high salinity is not the only issue facing the industry. More complexity came from other sources like porous media, reservoir heterogeneity, fluid interaction, and surfactant concentration loss. Surfactants concentration loss from aqueous solutions in porous media is a fundamental issue in EOR (Behrens, 2013). Several reasons can cause this lost such as (1) surfactant interaction with solids at the interface (adsorption); (2) surfactant precipitation because of ions; (3) immobile phase trapping the surfactant; (4) Chemical trapping in case of surfactant/polymer interactions; and (5) retention in the rock (Azam et al., 2013).

The physical and chemical process, where a substance is accumulated at the interface between the phases, which may be solid-liquid, liquid-liquid, gas-liquid or gas-solid is referred to adsorption. It is well known that adsorbate is the substance being removed from the liquid phase and adsorbent is the solid phase onto which the accumulation takes place. Base on this explanation, surfactants adsorb at solid/liquid interface. The solid surfaces are either positively or negatively charged in the aqueous medium by ionisation/dissociation of surface groups or by the adsorption of ions from solution onto a previously uncharged surface (Dąbrowski, 2001). In the oil field sandstone, reservoirs are normally composed of stable minerals (e.g., quartz, feldspar and rock fragments), accessory minerals, and pores saturated with fluids. These reservoirs cannot be found as singular sandstone. Occurrence of shale in sandstone reservoir made impact on the quality of the reservoir and the possibility for future studies. Introducing the surfactant to multi solid component is complex to explain (Ahmadi and Shadizadeh, 2015) ,these mix in reservoir matrix make the understanding of (sand-surfactant) or (shale-surfactant) is not enough for reservoir practicing.

To simplify the basic understanding in case of single adsorbent, we can say that: at low surfactant concentrations, the surfactant molecules are adsorbed on rock surface or sediments as a single monomer and form monomeric layer. As the surfactant concentration increases, the adsorbed surfactant monomers tend to aggregate and form micelles. These layers are considered to be the losses due to the adsorption. Adsorption weakens the efficiency required to reduce the IFT of oil-water (Park et al., 2015).

To illustrate these layering behaviours, two characters are needed. First the certain time to reach the equilibrium (adsorption equilibrium); and second, the mathematical model that govern the trend of adsorption (adsorption isotherm curve). An adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at constant temperature and pH. Adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration.

This paper discusses on the determination of isothermal of Aerosol-OT shale-sandstone samples. To the best of author knowledge, information on the absorptive characterisations of surfactant Aerosol-OT onto shale and sandstone is lacking and inappropriate. Though many approaches have been taken to understand the Aerosol-OT more, no suitable solution were found and to explain its adsorption behaviour in reservoir.

Quantitative determination using UV-Vis were used to derive isotherm that can fit the equation and adsorption behaviour of the surfactant. Outcome of the adsorbent dose on adsorption density were determined through batch experiments done at constant pH and temperature, single salinity, and single initial concentration. Data from the adsorption were analysed by using Langmuir, Freundlich isotherm model.

## **2. Methodology**

### **2.1 CMC experiment**

#### **2.1.1 Materials**

The experiment began by preparing brine through distillation to obtain a solution containing 35,000 ppm of NaCl concentration in a standard volumetric flask of 1,000 mL. This solution represents high salinity. The surfactant solution was then prepared by adding one (1) g of Aerosol-OT Dioctylsulfonate into the sodium salt (96 % purity) which was purchased from Acros Organic, were used without further purification to the prepared brine. The surfactant was allowed to equilibrate for 24 h before any measurement. For CMC test, several concentrations were prepared by dilution of the stock solution in the brine. The pH for the solutions was carried out using eco tester pH 1 from thermos scientific company, it found to be 6.4.

### 2.1.2 Measurement

The surface tension measurements of surfactant solutions were made using the Du Noüy ring tensometer from Kruss Company using a platinum ring. The CMC values were determined at the breakpoint of nearly two straight line portions in the surface tension versus concentration plots. The CMC of the surfactant in the brine were measured for 35,000 at fixed room temperature (25 °C).

## 2.2 Adsorption experiment

### 2.2.1 Materials

It is familiar in sand stone reservoir to have up to 80 % sand and not more than 20 % shale. To study the initial adsorption behaviour, 3 different amounts of sand and shale was used in a 50 mL batch of Aerosol-OT solution to address this comparison.

### 2.2.2 Measurement

In order to determine surfactant adsorption for dispersed systems, it can be done by adding a known amount of surfactant to the system, then wait for the system to reach equilibrium, and then extricate the dispersed solids, after which the concentration of surfactants in the solution were measured. Pilot experiments revealed that within the first 12 h, approximately the entire adsorption happened. For settling the experiment to maximum limit the batches remain up to 24 h contact time at rest was for equilibrium and complete separation to be obtained. For this experiment, the UV-vis spectroscopy was used to determine the absorbance value and the calibration curve for Aerosol-OT.

## 2.3 Adsorption models

Evaluation on the ideal adsorption system is vital because the outcome can lead to generation of the most appropriate equilibrium correlation. In this case, a quantitative comparison of adsorbent behaviour for different adsorbent systems (or for varied experimental conditions) is needed for future comparison and optimum selection. The adsorption model is represented by a curve. The curve can describe phenomena of retention or release or mobility of a substance from aqueous porous media, and its role is to predict the capacity of the matrix to be adsorbed at certain concentration and condition. The curve is plotted against residual concentration or time. It can be described in mathematical form (mathematical correlation). The well-known monolayer Langmuir and empirical Freundlich model are two adsorption isotherms that can explain the relation of adsorption equilibrium. The Langmuir isotherm model was used to quantify and contrast the performance of different bio-sorbents (adsorption isotherm). The Langmuir isotherm model is known to be one of the most commonly used model for measuring the adsorption isotherm.

## 3. Results

### 3.1 Critical micelle concentration (CMC)

In order to extract the CMC value, a standard solution of 0.005, 0.1, 0.5 and 0.7 g/L was prepared in 50 mL volumetric flasks from stock solution of 1 g/L. A graph of the surface tension values was plotted against the salinity concentrations at room temperature. The CMC values were determined at the breakpoint of the nearly two straight line plots as shown in Figure 2. The CMC value of the brine 35,000 at fixed room temperature (25 °C) was found at the range of 0.5 – 0.65 g/L as shown in Figure 1. The test was conducted at low concentration, where CMC is ten time higher than the selected solution. This selection was made as part of the initial screening to evaluate Aerosol-OT effectiveness.

### 3.2 Adsorption behaviour

In order to investigate the adsorbents with the highest adsorption rate, we first carried out the adsorption isotherm test by adding 2 g, 5 g, and 7.5 g of adsorbents into 50 mL of Aerosol-OT surfactant and weighed them to get 4 %, 10 % and 15 % sample concentrations of the adsorbents. Next, 4 samples were prepared for each adsorbent. These selections were made based on 4 time intervals. Each of these samples was then placed in a stirring plate and stirred by the magnetic stirrer at 200 rpm in room temperature. The absorbance readings were then recorded as presented in Tables 1 and 2.

It should be noted that for sand, the 4 % sample concentration was not selected because it was too low (Table 1). Each sample solution was centrifuged at 4,000 rpm for 40 min. The solutions were analysed using UV-spectrophotometer to obtain the absorbance values for the determined wavelength until the equilibrium concentration was reached.

From the absorbance values of each standard solution at the determined wavelength, the generated calibration curve (which records the concentration vs absorbance curve for Aerosol-OT) found the highest peak at 198 nm, while the adsorption value was recorded as 1.213, as shown in Figure 2.

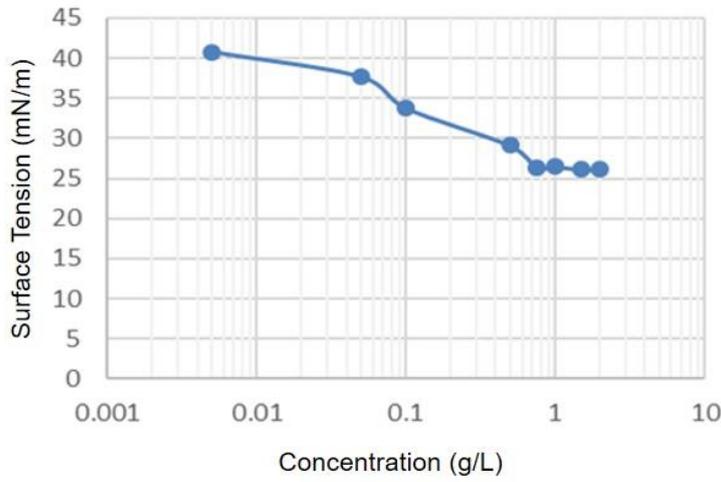


Figure 1: CMC value plot

Table 1: Shale samples

Name of adsorbent	30 min	60 min	120 min	1,440 min
Shale - 4 %	1.185	0.988	0.949	0.827
Shale - 10 %	0.865	0.895	0.794	0.772
Shale - 15 %	0.903	0.789	0.794	0.697

Table 2: Sand samples

Name of adsorbent	30 min	60 min	120 min	1,440 min
Sand - 10 %	0.933	0.917	0.829	0.846
Sand - 15 %	0.844	0.803	0.829	0.770

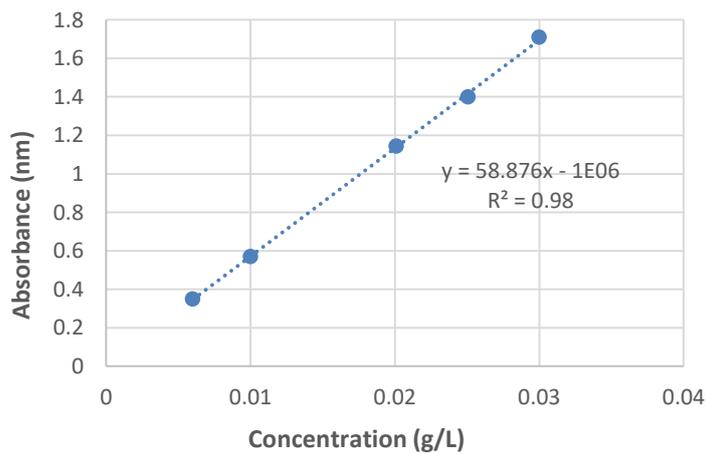


Figure 2: Aerosol-OT calibration curve

### 4. Discussion

CMC results for the surfactant were found to be in the range of 0.5 - 0.65 g/L. These results are comparable with (Behrens, 2013) and previous research (De and Maitra, 1995). The low CMC values came with the agreement of high salinity which indicate reasonable concentration needed for future field application. The suggested dose of the surfactant to be used was at the range of the CMC (0.55 g/L), adsorption of the surfactant onto the adsorbents was determined for the same time interval. This study conducted at very low concentration to address the sensitivity of Aerosol-OT at in the presence of reservoir rock.

For the same time interval, the remaining concentration of surfactant in the sand batch was considered to be higher than in shale. For the first 30 min, the sand showed high capacity to adsorb as fast as shale.

From the equilibrium end point, 10 % of shale has similar adsorption capacity of sand. This comparison makes it clearer that the shale is not the only source of surfactant loss in the reservoir, as even the clean sand stone is the source of adsorption.

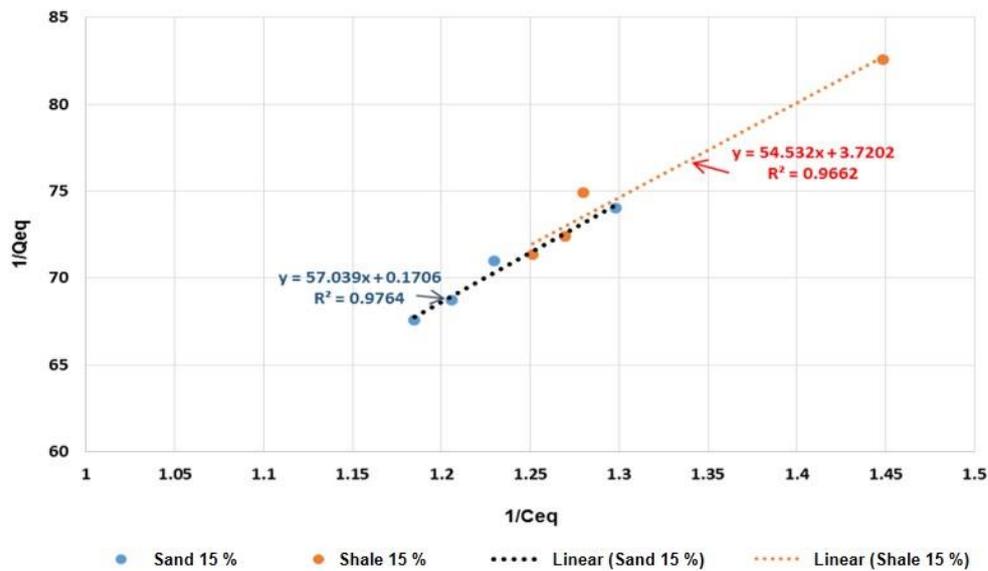


Figure 3: Langmuir adsorption for Aerosol-OT to shale and sand

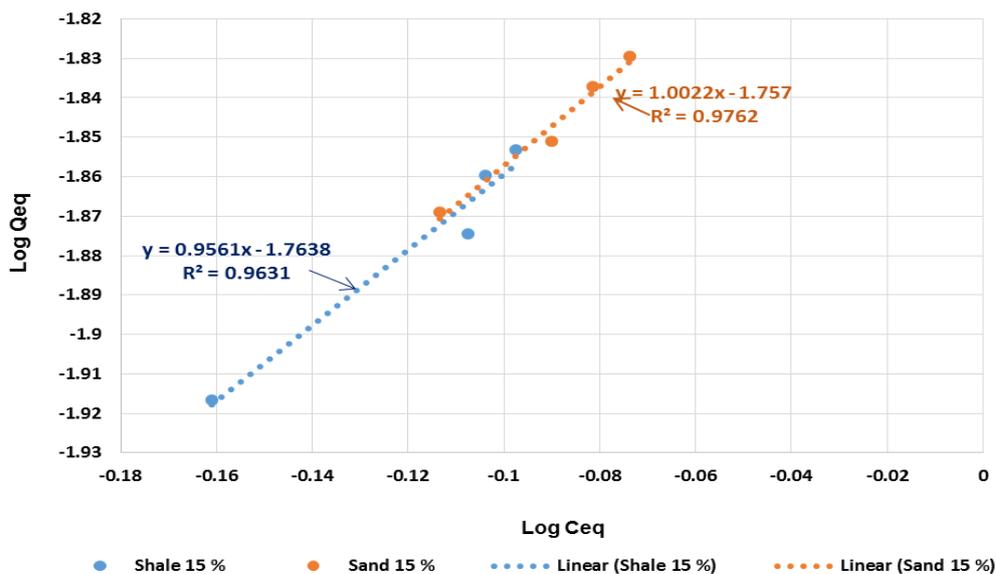


Figure 4: Frandluich adsorption for Aerosol-OT to shale and sand

To fit the data in Langmuir curve of the capacity equilibrium domain as shown in Figure 3, both adsorbents are fit with high  $R^2$  between 0.96 and 0.89 the range was acceptable for fitting. In case of 15 % shale concentration, the data observed to be scattered after 3 h. In case of 15 % shale concentration, the data observed to be scattered after 3 h. The data were also fitted for Frandluich model as the result shown in Figure 4 also indicated high fitting  $R^2$  for the model. These results were more appropriate for Langmuir model in term of stability of the model. More analysis need to be done in term of higher concentration for better understanding.

The solution was tested by elemental analyser, the observed percentages showed that the Aerosol-OT involved not only with electrostatic force but also hydrogen chemical bond. The change in the initial hydrogen element lost showed a decrease around 1.3 % from the initial concentration. The strength of this bond was not investigated in this study. However, the main goal was to find the suited model and capacity.

## 5. Conclusion

The findings provide fundamental knowledge on the adsorption capacity of single surfactant on single adsorbent. Based on the findings, the value of the adsorption capacity increased with time for each concentration. These findings imply that the adsorption capacity was increased by the increasing of the adsorbent concentration. The results of the study were found to not only fit into the Langmuir model (in the case of high concentration of shale) but also in this work compares the capacity of sandstone and shale. This comparison helps to predict the loss in surfactant flooding by providing reliable information on the adsorption behaviour and concentration losses of Aerosol-OT surfactants. The major limitation of this study is that the result is not an indication of the true adsorption capacity of Aerosol-OT on rock minerals given that the shale is not always clean (has impurities such as clay minerals), which can lead to the difference in adsorbent quantity and consequently different concentrations. The suggested adsorption phenomena also revealed to be a combination with hydrogen bond. It is worth to say that the volatility of Aerosol-OT surfactant is issued in addressing suitable answers to its chemical reaction.

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## References

- Ahmadi M.A., Shadzadeh S.R., 2015, Experimental investigation of a natural surfactant adsorption on shale-sandstone reservoir rocks, Static and dynamic conditions, *Fuel* 159, 15-26.
- Azam M.R., Tan I.M., Ismail L., Mushtaq M., Nadeem M., Sagir M., 2013, Static adsorption of anionic surfactant onto crushed Berea sandstone, *Journal of Petroleum Exploration and Production Technology* 3, 195-201.
- Behrens E.J., 2013, Investigation of loss of surfactants during enhanced oil recovery applications-adsorption of surfactants onto clay materials, MSc Thesis, Norwegian University of Science and Technology, Trondheim, Norway.
- Dąbrowski A., 2001, Adsorption—from theory to practice, *Advances in colloid and interface science* 93, 135-224.
- De T.K., Maitra A., 1995, Solution behaviour of Aerosol OT in non-polar solvents, *Advances in Colloid and Interface Science* 59, 95-193.
- Levitt D., Klimenko A., Jouenne S., Chamerois M., Bourrel M., 2013, Overcoming design challenges of chemical EOR in high-temperature, high salinity carbonates, SPE Middle East Oil and Gas Show and Conference, 10-13 March 2013, Manama, Bahrain, DOI: 10.2118/164241-MS.
- Mukherjee K., Moulik S., Mukherjee D., 1993, Thermodynamics of micellization of Aerosol OT in polar and nonpolar solvents, A calorimetric study, *Langmuir* 9, 1727-1730.
- Nave S., Eastoe J., Penfold J., 2000, What is so special about Aerosol-OT? 1. Aqueous systems, *Langmuir* 16, 8733-8740.
- Park S., Lee E.S., Sulaiman W.R.W., 2015, Adsorption behaviors of surfactants for chemical flooding in enhanced oil recovery, *Journal of Industrial and Engineering Chemistry* 21, 1239-1245.
- Watkins C., 2009, Chemically enhanced oil recovery stages a comeback, *Inform* 20, 682-685.
- Zaitoun A., Fonseca C., Berger P., Bazin B., Monin N., 2003, New surfactant for chemical flood in high-salinity reservoir, International Symposium on Oilfield Chemistry, 5-7 February 2003, Houston, Texas, United States, DOI: 10.2118/80237-MS.