

Adsorption and wettability study of methyl ester sulphonate on precipitated asphaltene

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Abstract. Asphaltene precipitation from crude oil and its subsequent aggregation forms solid, which preferentially deposit on rock surfaces causing formation damage and wettability changes leading to loss of crude oil production. To resolve this problem, asphaltene inhibitor has been injected into the formation to prevent the precipitation of asphaltene. Asphaltene inhibitors that are usually employed are generally toxic and non-biodegradable. This paper presents a new environmentally friendly asphaltene inhibitor (methyl ester sulphonate), an anionic surfactant, which has excellent sorption on formation rock surfaces. Result from adsorption study validated by Langmuir and Freundlich models indicate a favourable adsorption. At low volumes injected, methyl ester sulphonate is capable of reverting oil-wet sandstone surface to water-wet surface. Biodegradability test profile shows that for concentrations of 100-5000ppm it is biodegradable by 65-80%.

1. Introduction

Asphaltene has been identified in terms of its structure as possessing a poly-aromatic and poly-cyclic rings bearing alkyl side chains attached to heteroatoms. Asphaltene is defined in terms of solubility as insoluble in n-alkanes but readily soluble in aromatic solvents. Asphaltene colloidal state in the crude oil pose no serious concern but the precipitation from crude oil and subsequent flocculation or aggregation presents a serious concern. Asphaltene precipitation from crude oil is as a result of destabilization of thermodynamic equilibrium that exist between the asphaltene-resin micelle in the crude oil [1]. Three major factors that causes destabilization of thermodynamic equilibrium that exist in the crude oil are: changes in composition, temperature and pressure [1]. Precipitation of asphaltene from crude oil is common in undersaturated light crude oil with minor amount of asphaltene of which conversely, heavy crude oil with high amount of asphaltene content do not show asphaltene precipitation problem [2].



When asphaltene precipitate it gradually starts to settle on the rock surfaces and steady build-up of precipitated asphaltene will preferentially adsorb on the rock surfaces. The mechanism responsible for this phenomenon are due to interaction between precipitated asphaltene particles and chemical compounds in minerals present in the rock, necessitated by governing factors such as charge transfer interaction, Van der Waals, steric repulsion and hydrogen bonding [3]. The effect of adsorption of asphaltene particles on rock surface causes continuous accumulation of asphaltene particles which plugs the pore throat of reservoir rock leading to formation damage and changing the wettability of the reservoir rock which affect the production of crude oil [4]. Wettability changes is a big concern as explained by [5] precipitated asphaltene presents a positive core charge which enables it to penetrate thin water films around water-wet rock, then attaching to negatively charged water-wet mineral surfaces thereby reverting their wettability from water-wet to oil-wet.

The mechanism that prevent asphaltene particle adsorption on rock surfaces involves treating the rock surfaces with an inhibitor (surfactants) which will preferentially adsorb on the rock surface, presenting an electrostatic repulsive force that keeps the formation surface from adsorbing polar asphaltene particles as shown in Figure 6. Surfactants consists of hydrophobic and hydrophilic moieties and have been found to have the ability to alter properties of surfaces and interfaces. The mechanism by which surfactants adsorb on solid rock surfaces are: ion pairing, ion exchange, hydrophobic bonding, adsorption by polarization and adsorption by dispersion forces [6]. [7] Identified four regions by which surfactants adsorb on a rock surface and identified electrostatic attraction/repulsion and hydrophobic bonding as the mechanism for surfactant adsorption.

In the oil and gas industry surfactants has been utilized for diverse application most especially in enhanced oil recovery and production chemistry processes [8] [9]. [10] conducted adsorption studies with anionic surfactant on Berea sandstone and concluded that anionic surfactants adsorption performance are promoted by higher pH, higher temperature and low salinity. [11] Affirms similar observation by conducting static and dynamic adsorption of anionic surfactant. Several adsorption studies conducted reported a type 1 isotherm adsorption for anionic surfactants [10].

Wettability studies are usually conducted by United States Bureau of Mines (USBM) method, Amott-Harvey technique and contact angle measurement. Each of these techniques has its own limitation relating to absolute measurement and heterogeneity of the rock surfaces [12]. [13] Used zeta potential measurement to study the effect of wettability changes on carbonate rocks treated with inhibitors. The inhibitor preferential adsorb on the carbonate rock surfaces thereby repelling the oil into the bulk phase. Zeta potential measurement point of inflexion is indicative of change in wettability of the carbonate rock from oil-wet to water-wet.

In this paper, a new green anionic surfactant Methyl Ester Sulphonate (MES) is presented. Static adsorption study of methyl ester sulphonate was conducted on a crushed Berea sandstone sample. Wettability study was conducted by electrical conductivity techniques by observing the point of inflexion when varying volumes of MES was titrated into precipitated asphaltene mix with crushed Berea sandstone. MES is an environmentally friendly surfactant, biodegradability test was conducted according to APHA 5210B standard method to determine biodegradation.

2. Material and method

Methyl ester Sulphonate was purchased from Chemithon and n-heptane was purchased Sigma Aldrich (purity > 99%). Crude oil used for this experiment has API gravity of 29° API and SARA components as follows: saturates (51.36 wt%), aromatic (38.16 wt%), Resins (7.15 wt%) and Asphaltene (3.33 wt%).

The Berea sandstone to be used for the adsorption study was crushed and sieved using a 125 μ m to ensure an approximate uniform sand particle size. Composition of crushed Berea sandstone was determined by X-Ray Fluorescence (XRF) shown in Table 1.

Table 1. Composition of Berea sandstone sample

| Composition | Amount (wt.%) |
|------------------------------------------------|---------------|
| Silica (SiO ₂) | 73.54 |
| Alumina (Al ₂ O ₃) | 19.57 |
| Magnesium Oxide (MgO) | 0.82 |
| Calcium Oxide (CaO) | 0.65 |
| Ferric Oxide (Fe ₂ O ₃) | 3.47 |
| Ferrous Oxide (FeO) | 0.71 |
| Potassium Oxide (K ₂ O) | 1.15 |
| Others | 0.09 |

800mg of sandstone was measured of which 100mg each was transferred to eight 50ml beakers. Known initial concentrations of methyl ester sulphonate was prepared in the range 100-5000ppm. The absorbance value measurement was conducted using a Perkin Elmer UV-Visible spectrophotometer to establish the calibration curve. 30ml of MES was transferred to each beaker and all eight beakers placed in an orbital shaker and agitated at a constant speed of 200 rpm at 23-25°C and allowed to reach 24 hours equilibrium period. At the completion of the equilibrium period, the samples are allowed to settle for 10 minutes and samples are collected, centrifuged at 3500rpm which the supernatant was carefully collected and analysed using the UV-Vis spectrophotometer. The final equilibrium concentration was obtained by re-entry measured absorbance value into the calibration curve to obtain the equilibrium concentration. The sorption efficiency and adsorption capacity or amount of MES adsorbed by sandstone was calculated as given:

$$\% \text{ Sorption Efficiency} = \frac{C_i - C_e}{C_i} \times \frac{100}{1} \quad (1)$$

$$q_e = \frac{(C_i - C_e) \cdot V}{m} \quad (2)$$

Where q_e adsorption capacity (mg/g), C_i is the initial concentration (mg/L), C_e is the final concentration (mg/L), V is the solution volume (L) and m is the mass of sand (mg).

2.1 Wettability Measurement

Wettability study was conducted by electrical conductivity measurement. Asphaltene was separated from a crude oil with colloidal instability index (CII) of 1.21 (CII>0.9). The asphaltene sample was separated by adding 1:40 by volume of crude oil sample to n-heptane. The mixture was shaken vigorously and kept in a dark place for 24 hours. After 24 hours the supernatant was decanted and the visibly seen precipitated asphaltene blended with a mixer at 5000rpm for 10 minutes, electrical conductivity of the blended asphaltene was measured using electrical conductivity meter and the result was 0.00 μ S/cm. 100g of measured crushed berea sandstone was used for this experiment and treated with 50ml brine of composition: 1.5 wt% NaCl, 1 wt% MgCl and 0.5 wt% K₂SO₄. 100g of treated crushed Berea sandstone was placed in a beaker and gradually 50ml of asphaltene mixture

was poured into the beaker containing sandstone sample and mixed vigorously. MES was titrated into the asphaltene-crushed sandstone slurry. For every 2ml MES titrated into the beaker conductivity measurement was recorded by inserting the electrical conductivity meter probe into the sand-asphaltene mix.

2.2 Critical Micelle Concentration measurement (CMC)

Electrical conductivity method was employed to measure CMC of methyl ester sulphonate surfactant for different concentrations using Mettler Toledo conductivity meter. Concentrations of MES was plotted against electrical conductivity and the point where the linear plot changes abruptly is indicative of CMC for methyl ester sulphonate as shown in Figure 2.

2.3 Biodegradability test

Methyl ester sulphonate is a new anionic surfactant and has been established as a new green surfactant with similar detergency efficiency as Linear Alkylaryl Sulfonates (LAS). Biodegradability of methyl ester sulphonate was tested according to APHA 5210B standard method for five days Biochemical Oxygen Demand (BOD) in the presence of Nitrogen fixing bacteria (Nitrosomonas). 100-5000ppm concentrations of methyl ester sulphonate was used for this experiment.

3. Result and discussion

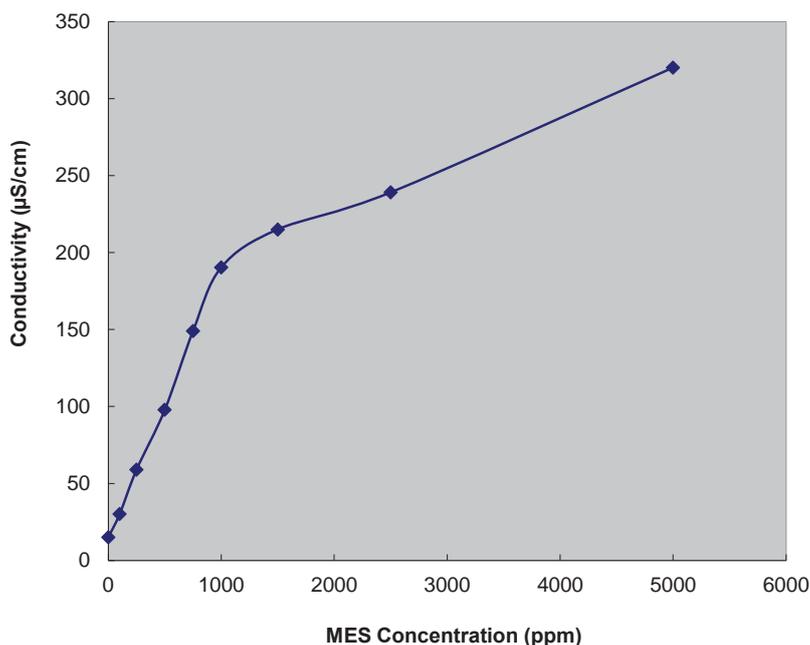


Figure 1. CMC measurement for MES by electrical conductivity

CMC measurement of MES shows an increase in the slope until and abrupt change in slope as shown in Figure 1, the point where the change was observed is known to be CMC. Thus, below the CMC MES adsorption will increase while above the CMC further increase in MES concentration does not affect adsorption. The observed CMC for MES is at 1000ppm. This point can be correlated with similar observation from adsorption isotherm shown in Figure 2 at 1000 ppm.

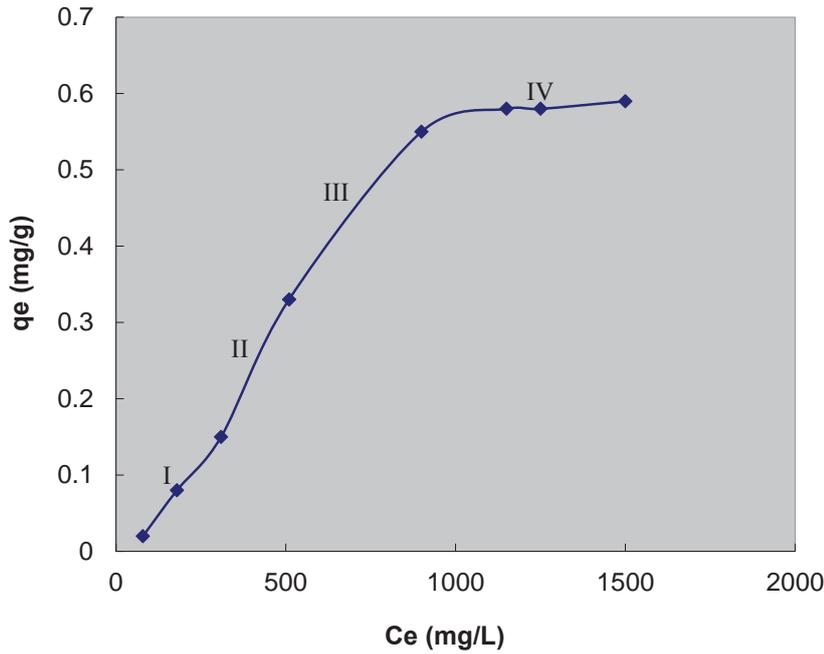


Figure 2. Adsorption isotherm of MES on Berea sandstone

Table 2. Adsorption Isotherm values for Langmuir and Freundlich models

| Langmuir | | | |
|------------|--------|-------|-------|
| q_m | K_L | R_L | R^2 |
| 50.5 | 0.0912 | 0.099 | 0.962 |
| Freundlich | | | |
| n | K_F | R^2 | |
| 1.158 | 0.017 | 0.982 | |

Langmuir adsorption isotherm describes the formation of monolayer adsorption of adsorbate on the surface of adsorbent. For Langmuir isotherm once the adsorbate occupies the surfaces, no further adsorption will occur. The Langmuir isotherm model and the dimensionless separation factor is represented as follows:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \cdot \frac{1}{C_e} \tag{3}$$

$$R_L = \frac{1}{1 + K_L C_i} \tag{4}$$

Where q_e is the adsorption capacity (mg/g), q_m is the amount of adsorbate required to form a single monolayer on unit mass of adsorbent (mg/g), K_L is the adsorption equilibrium constant (L/mg), C_e is the equilibrium constant (mg/L) and C_i is the initial concentration (mg/L). For values $0 < R_L < 1.0$, the adsorption is favourable and R^2 value of 0.96 shown in Table 2, also indicates that the adsorption data fits the model.

Freundlich adsorption isotherm describes the adsorption effect on heterogeneous surfaces. The Freundlich isotherm model is represented in the form:

$$q_e = K_F \cdot C_e^n \quad (5)$$

$$\log q_e = \log K_F + n \log C_e \quad (6)$$

Where K_F is the Freundlich constant, n is the heterogeneity factor or Freundlich coefficient. For n values greater than 1.0, adsorption is termed favourable, Table 2 shows n value of 1.158 indicating a favourable adsorption. R^2 values of 0.982 is indicative of well fitted data. [14] Stated that for Freundlich isotherm model R^2 values greater than 0.89 indicates that the model can be used to validate adsorption data.

Adsorption isotherm obtained as shown in Figure 2 is similar to those reported by [7]. Four regions where depicted on the adsorption isotherm and the adsorption isotherm shows a type 1 adsorption. Region I, MES adsorption on the surfaces of Berea sandstone is predominantly by electrostatic interaction between MES head group and charged sites on the sandstone surfaces. Region II is notably marked with increase in MES adsorption resulting from electrostatic interaction occurring on the surfaces and hydrophobic interaction between adsorbed MES molecules. Region III is predominantly as a result of hydrophobic interaction and electrostatic repulsion build up. Region IV, which is above the CMC show no further adsorption as observed, as adsorption activity remains constant and a maximum adsorption of 0.59 mg/g of sandstone was recorded.

Wettability study by electrical conductivity shown in Figure 43 For the crushed Berea sandstone treated with precipitated asphaltene electrical conductivity measurement values was constant as asphaltene predominantly occupy the surface of the sandstone resulting to an oil-wet surface. Gradual addition of 2ml up to 10ml for 5000ppm MES causes conductivity value to change as MES displaces the asphaltene from the sandstone surfaces and preferentially adsorb at the surface. This occurrence reverts the wettability as MES displaces the asphaltene to occupy the surfaces thus, becoming water-wet which is important for production. The same scenario was observed for 2500ppm, 1000ppm and 500ppm and their respective point of inflexion was 18ml, 20ml and 26ml respectively. Figure 5 shows the schematics of MES displacing asphaltene by electrostatic tail-to-tail repulsion. Higher concentration of MES with less volume applied to the sample causes the reversal while higher volume of MES at low concentrations is required to effect the wettability reversal, this is as a result of fewer ion charges to interact with the charges on the surface of the sandstone.

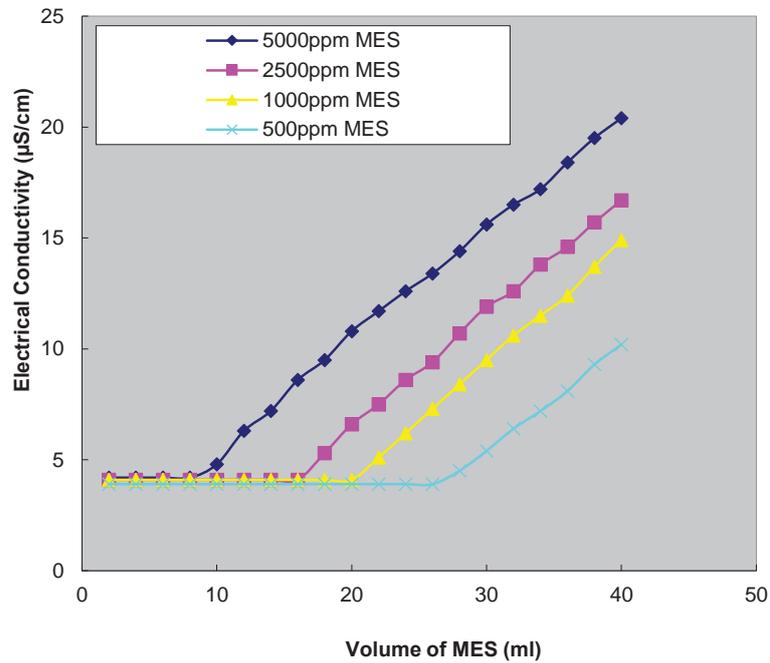


Figure 3. Wettability measurement of MES on Berea sandstone

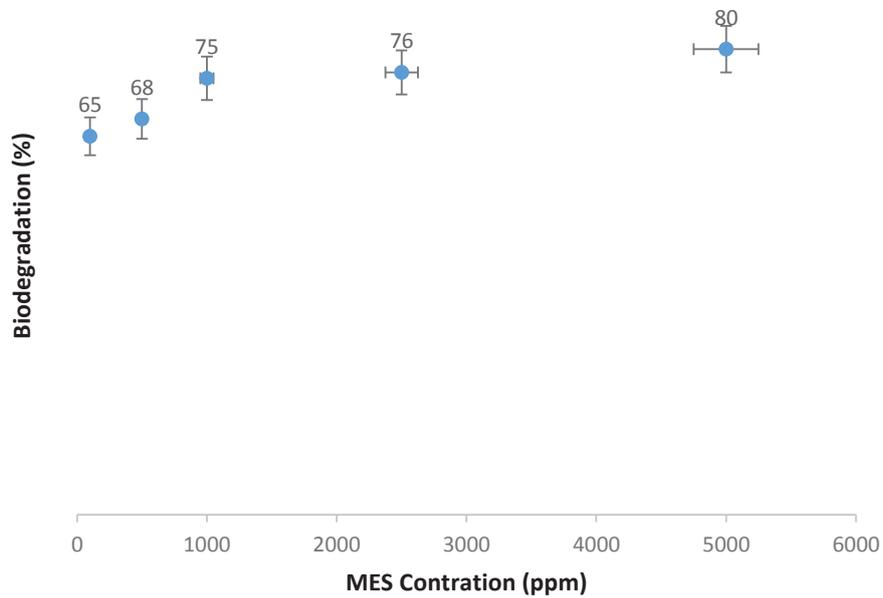


Figure 4. Biodegradation of MES Concentrations

Biodegradation test result for MES concentrations is shown in Figure 4. MES degraded in the range 65-80%, as 5000ppm MES degraded the highest by 80%. Technically, biodegradation criteria for 5 days is 60%. Results obtained meets the criteria requirement. Similar result was obtained by [15]

using different method to test the biodegradation of MES. [16] Conducted biodegradation test according to OECD 301D and reported 80% biodegradation of palm based alpha-sulphonated methyl ester an active ingredient for formulating powder detergent.

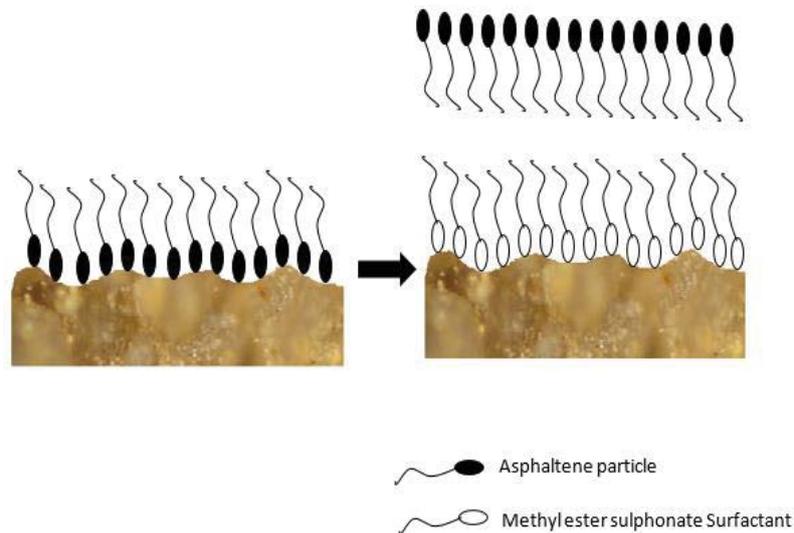


Figure 5. Schematic of MES displacing asphaltene from sandstone surface

Conclusion

Anionic surfactant methyl ester sulphonate has an excellent adsorption capacity capable of preferentially adsorbing on rock surfaces thereby reverting the state of wettability of the surface and preventing further deposition of precipitated asphaltene on the rock surfaces. As a result of MES excellent sorption capacity it can find application in chemical enhanced oil recovery processes especially in alkaline and surfactant flooding. MES is shown to be highly biodegradable, which makes it environmentally friendly surfactant.

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