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Critical micelle concentration, interfacial tension and wettability alteration study on the surface of paraffin oil-wet sandstone using saponin

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Critical micelle concentration, interfacial tension and wettability alteration study on the surface of paraffin oil-wet sandstone using saponin

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Abstract. Nowadays, the implementation of chemical enhanced oil recovery (CEOR) techniques improves the oil recovery by injecting synthetic surfactants in reservoir. However, the recent use of this synthetic surfactant is quite expensive and possesses toxicity problems when exposed to the environment. This issue has forced the search for alternative, cheaper and natural synthetic surfactant to enhance oil recovery. Hence, this study aims to provide some insights into the effect of saponin as natural plant-based non-ionic surfactant on the surface of paraffin oil-wet sandstone. The effectiveness of saponin depends on the critical micelle concentration (CMC), interfacial tension (IFT) and wettability alteration. The surfactant concentration containing saponin was varying from 0.005wt% to 0.07wt% to determine CMC value using surface tension measurement, meanwhile for IFT measurement was conducted at 0.5wt% to 8wt% concentration using Krus Tensiometer K6. The experiments were conducted at standard condition with 25ºC and 14.7psia. The findings showed that surface tension for CMC value of saponin is 0.05wt%. Approximately 27% reduction from initial IFT was achieved with 8wt% of saponin concentration. The saponin successfully alter the wetting state of oil-wet sandstone to intermediate-wet through quantitatively measurement of contact angle. Saponin with low CMC value is favourable to become a reference concentration as natural surfactant, effective to alter of reservoir rock properties, facilitate oil mobilization, increase oil recovery and suggested as an additive for mitigating wax deposition.

1. Introduction

Enhanced oil recovery (EOR) is one of the recent techniques used to satisfy the world's energy needs. However, the main obstacles faced by industry are environmental and economic issues caused by the uses of chemicals in the application of EOR [1]. Hence, the application of chemical EOR which widely used in the most of country especially in US began to decrease significantly starting from 1988. The increasing price of surfactants cause the declination use of this type of chemical. The long-term uses of surfactant also contribute to the environmental pollution. Large volume of synthetic surfactants needed during the application of EOR which affect the increment of raw material. Thus, this condition makes the surfactants no longer economical. Furthermore, synthetic surfactant has high adsorption rate which will render the flooding process inefficient [2].

In oil and gas industry, chemical enhanced oil recovery (CEOR) technique is usually applied to brownfield reservoir. The main purpose of CEOR is to increase the oil mobility. Surfactant is a main material to change the physicochemical properties in aqueous injected fluid because of its ability to reduce interfacial tension (IFT) between water-oil phase. In addition, the surfactants used in the low concentrations may change the wettability of reservoir rock to be intermediate wet or more water wet [3]. Baturaja formation in the May fields located in Indonesia, Mauddud fields in Bahrain, Cottonwood Creek fields in Wyoming, Yates fields and the Cretaceous Upper Edwards reservoir in Texas are oil drilling fields that have been achieved successful results from the application of surfactants.

There are recent researchers conducted research on natural surfactants application as an alternative to synthetic surfactants [4,5,6,7,8,9]. Natural surfactants are more environmental-friendly because of their relatively low toxicity and economically cheaper than synthetic surfactants. The utility of natural surfactants provides various benefits such as simple chemical structures which become biodegradability, environmental compatibility, composed of specific functional groups thereby increasing selectivity, detoxification of specific pollutants which allow for specificity, activity in extreme temperatures, certain pH and salinity. In general, the role of natural surfactants is to increase the spread of contaminants in the aqueous phase and increase the bioavailability of hydrophobic substrates for microorganisms, in order to eliminate pollutants through biodegradation [10].

The main source of plant-based surfactants that have been widely used in various industries is saponin [11,12,13,14]. The saponin is a non-ionic natural surfactant which consist of a non-volatile glycoside compound with a high molecular weight. It is composed of sugars and aglycones which relate to hydrocarbon groups. In oil and gas industry, saponins are used as an agent in CEOR with the same function as the synthetic surfactants application process. Figure 1 illustrated the general molecular structure of saponin.

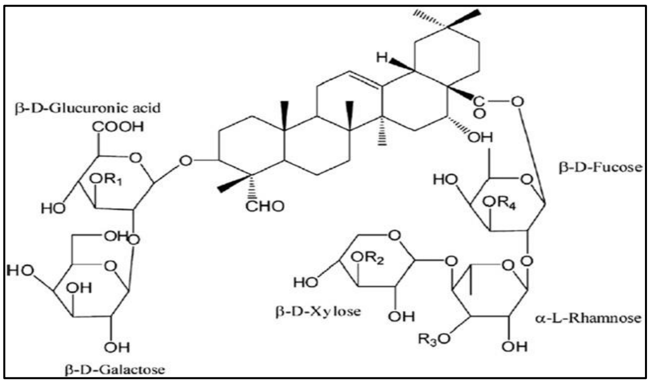

Figure 1. General molecular structure of saponin [12].

The aim of this study is to determine the critical micelle concentration (CMC) of saponin based on surface tension measurement from Du Noüy ring method. Besides that, this study was conducted to identify the effect of saponin on reservoir rock and fluid properties which include the IFT measurement from the same method as conducted in surface tension measurement. The wettability alteration from quantitatively evaluation in contact angle measurement by implementation of sessile drop method also has been discovered. In addition, oil-wet sandstone was used as porous media in this study as about 61% of giant fields in the world is sandstone reservoir.

Many researchers conducted a CMC measurement of saponin extracted from various type of plant by using surface tension as a parameter. According to Chen et al. [13], the additional of extracted saponins from *Quillaja saponaria* with 13.9% purity gives the CMC value of saponin which ranging from 0.01-0.02 wt% at neutral pH of 6.5 s.u. Meanwhile, Stanimirova et al. [12] conducted the same experiment from the same source of saponin, but the CMC value obtained was 0.025 wt%.

As the natural surfactant, saponin could reduce IFT of water-oil phase which considered as a factor that supports the use of saponins in the CEOR technique. Many researchers have successfully implemented the application of saponin in CEOR method throughout their studies. Shahri et al. [14] conducted a study in IFT reduction and wettability alteration to ensure the effects of saponin addition in distilled water as the surfactant solution. The results shows that saponin able to reduce IFT from 48 to 9 dynes/cm which makes saponin has similar ability as conventional surfactants that commonly used in chemical flooding process. The average contact angle of 50.24° was obtained which is in a relatively hydrophilic range. Since IFT is affected by capillary pressure, this pressure governs the wetting changes due to its dependency on contact angle. In addition, IFT reduction between water-oil assist to mobilize oil which can reduce the tendency of oil from stick on the rock grains. Moradi et al. [15] stated that wettability alteration on oil-wet quartz identified by using saponins extracted from *Tribulus terrestris* which indicated by the reduction of contact angle from 160.3° to 80.6° with 0.9 wt% saponin concentration.

2. Materials and Methods

2.1. Materials
The natural nonionic surfactant used from saponin extracted from bitter leaf was supplied by Sigma Aldrich located at Selangor, Malaysia. This surfactant was in powder form with the total amount of 11 grams used to prepare the surfactant solution. In this study, distilled water was used as the solvent in solution preparation. For the evaluation of wettability alteration, sandstone plate from Mount Santubong, Sarawak was used as a porous media with diameter of 50 mm and thickness of 9 mm. In addition, paraffin oil was used as an oil-phase. After aging process, the sandstone was cleaned out with toluene before conducting wettability alteration mechanism and n-heptane was used for washing the sandstone plate.

2.2. Preparation of surfactant solution
Surfactant solution is a mixture of distilled water and saponin powder at different concentrations. This process started by preparing the stock solutions due to minimize the utility of saponin powder. 8 wt% is the concentration for stock solution by mixing 8 grams of saponin powder into 100 ml distilled water. Furthermore, lower concentrations prepared through the dilution process which is carried out by adding distilled water according to the desired concentration based on the equivalent of the concentration and volume of stock solution to the additional volume of concentration. Surfactant solutions with concentrations of 6 wt%, 3 wt%, 1 wt%, 0.1 wt%, 0.07 wt%, 0.06 wt%, 0.05 wt%, 0.03 wt%, 0.01 wt%, and 0.005 wt% were prepared in this study.

2.3. CMC measurement
Du Noüy ring and Krüss Tensiometer K6 used to measure the surface tension at ambient condition with temperature of 25°C and pressure at 14.7 psi [16]. The effect of surfactant solution towards the surface tension was measured by using tensiometer. Afterwards, the result of surface tension at different concentrations were plotted to determine the CMC value. The concentration of surfactant solutions by various amount of saponin that has been used are 0.005 wt%, 0.01 wt%, 0.03 wt%, 0.05 wt%, 0.06 wt%, and 0.07 wt% which is carried out alternately from low to higher concentrations.

2.4. IFT measurement
The experiment was conducted at ambient condition with temperature of 25°C and pressure at 14.7 psi. The concentration of surfactant solution by various amount of saponin was used with 0.1 wt%, 0.5 wt%, 1 wt%, 3 wt%, 5 wt%, 6 wt%, and 8 wt% which is carried out alternately from low to higher concentrations. Identical apparatus was used as for surface tension measurement with all similar

instrument preparation and procedure. The difference in this experiment is only in the use of paraffin oil and surfactant solution. The solution surfactant was poured into a sample container and followed by pouring paraffin oil. The hooked platinum ring was later submerged inside surfactant solution for about 5 mm deep by moving the movable platform upward. As the platinum ring detached from the liquid interface, the IFT between surfactant solution and paraffin oil was analysed which can be directly recorded [1].

2.5. Contact angle measurement

Sessile drop method was implemented in this contact angle measurement which must be initially prepare the oil-wet sandstone through aging process. Initially, the sandstone core was cleaned with toluene to remove fatty acid in sandstone plate which heated at 60°C for 24 hours and the core must be dried at 40°C for 24 hours. The aging process of sandstone in paraffin oil was performed by immersing the plate in paraffin oil for 2 weeks at 60°C and continued for 30 days at ambient temperature which is 25°C in order to induce the adsorption of carboxylic component on the rock surface [15]. The sandstone plate after aging process must be washed with n-heptane and distilled water, then heated in the oven at 60°C for at least 3 hours to be ready for wettability assessment and used in evaluation of wettability alteration as an oil-wet rock.

After the preparation of oil-wet sandstone, this sandstone plate was immersed in 0.05 wt% (according to its CMC value) of surfactant solution for 10 days at 25°C and 14.7 psia, then the measurement was taken for every day by sessile drop method. The paraffin oil was injected to form a droplet on the sandstone plate immersed in surfactant solution and side image of oil drops were captured using digital camera Nikon D90 and Nikon 60 mm micro lens which the angle was analysed from Image software [17,18,19].

3. Results and Discussion

3.1. Critical micelle concentration (CMC)

In this study, surface tension measurement was conducted in the air-surfactant solution at different concentrations with ambient conditions of 25°C and 14.7 psia. The addition of concentrations in saponins succeeded in reducing the value of the initial surface tension from the air-water. The surface tension reduction occurs during the reduction of contraction force. The molecules in the water are replaced by the saponin molecule when adsorption occurs by the saponin molecule on the water surface. This condition causing the attraction forces between water and saponin molecules lower than two water molecules represented by the hydrophobic tail of the skewed skew into the air and the hydrophilic head of saponin leads to water as a surface anchor [20]. This phenomenon will further drop until the minimum surface tension by increasing of saponin concentration. Figure 2 shows surface tension against surfactant concentration with the addition of saponin.

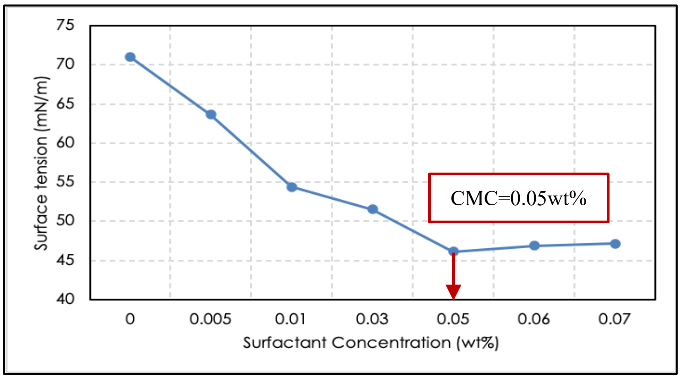

Figure 2. Surface tension against surfactant concentration with the addition of saponin.

Based on figure 2, initial surface tension of surfactant flooding starts from 71 mN/m which significantly decrease to 54.4 mN/m at saponin's concentration of 0.01 wt% and decreases continuously until it reaches the minimum surface tension of 46.13 mN/m at 0.05 wt% of saponin's concentration. The addition of saponins at the minimum surface tension consider the CMC of saponin. Addition of saponin concentration after CMC value shows an increase with an insignificant value on surface tension changes, therefore CMC of saponin is recommended as the most efficient concentration of surfactant in CEOR. Thus, the CMC of saponin is 0.05 wt% which indicated as a minimum surface tension and concentration on the break points from slope of -268.5 (before CMC) which turns into the slope of 52 (after exceeds CMC) as the indicator to be almost constant value of surface tension. This trend changes likely to occur because some of the adsorbed saponin molecules are distorted from the interface to the bulk phase.

The results of this study are insignificantly difference with some previous studies using surface tension as a parameter to determine the CMC of saponins. Chen et al. [13] shows13.9% purity obtained the CMC value of 0.01-0.02 wt% at near neutral pH of 6.5 s.u. Meanwhile, Stanimirova et al. [12] use the same source of saponin observed at 25ºC acquired the CMC value of 0.025 wt%. Moreover, Zhou et al. [11] performed an experimental study using conventional saponins from manufacture which identified 0.003-0.015 wt% of CMC value. Another CMC value of saponins from three different manufacturers (Sigma Chemical Co. in St. Louis, MO; Acros Organics in Fair Lawn, NJ; and Penco of Lyndhurst Inc. in Lyndhurst, NJ) is ranged from 0.051-0.072 wt% at 25°C studied by Mitra and Dungan [21].

3.2. Interfacial tension (IFT)

Paraffin oil was used in this study as an oil-phase. It is categorized as the light-oil that compatible with surfactants performance in the CEOR process which is effectively used in low to medium viscosity of oil. In addition, the aqueous phase consists of the distilled water and various concentrations of saponins were used to observe the performance of saponins at ambient conditions. Figure 3 shows the effect of saponin in surfactant solution to the interfacial tension.

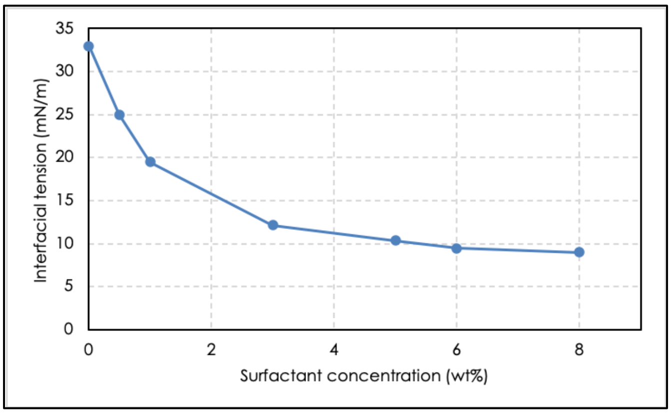

Figure 3. The effect of the saponin in surfactant solution to the interfacial tension.

This study proves that the IFT measurement of the saponins in surfactant flooding against paraffin oil showed a significant reduction. Figure 3 shows that the initial IFT between surfactant solution and paraffin oil is 33 mN/m which falls most significantly when reaching 0.5 wt% of saponin to become 25 mN/m and reaches a decrease of more than half after adding 3 wt% of saponin. The IFT reduction that occurred gradually reached 9 mN/m with an increase in saponin concentration of 8 wt%. This phenomena of IFT reduction occurs because the addition of surfactant concentration. This condition causes a single layer of surfactant monomer accumulation to interact more strongly interwoven by the surfactant structure with water-oil which is hydrophilic tail with paraffin oil and hydrophilic head with aqueous phase.

If the addition of surfactant concentration continues further, the interaction between water-surfactant-oil is getting stronger and the surfactant molecule gradually becomes denser towards the polar substance which resulting in the interfacial tension between water and oil to be more reduced. When the surfactant concentration reaches CMC, it causes the monomers to begin joining and forming the micelles. As concentration increases after CMC, micelle concentration increases without a significant increase in monomers concentration. As referred to this study, because of the water acts as a solvent, the concentration of surfactant above CMC is highly capable to dissolve oil rather than using water alone [22]. Figure 4 shows the comparison study on the effects of saponin addition towards interfacial tension using different saponin extraction sources.

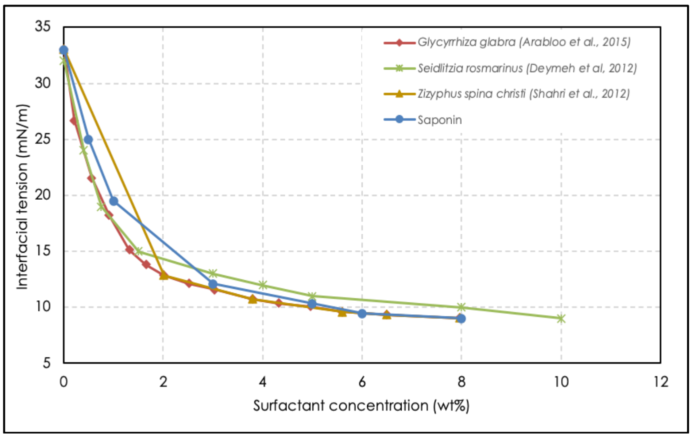

Figure 4. Comparison study on the effects of saponin addition towards interfacial tension using different saponin extraction sources [14,25,26].

The saponins addition in this study showed the same results with extracted saponins from *Seidlitzia rosmarinus*, *Glycyrrhiza glabra*, and *Zizyphus spina christi* under the same oil phase. Saponins with concentrations of 8 wt% of saponins, *Zizyphus spina christi*, and *Glycyrrhiza glabra* showed non-significant difference with the same results on IFT between surfactant flooding and paraffin oil which is 9 mN/m. Meanwhile, extracted saponins from *Seidlitzia rosmarinus* at a concentration of 8 wt% showed a significant difference compared to others saponin extraction sources with an IFT of 10 mN/m and succeeded in achieving an IFT of 9 mN/m at a concentration of 10 wt%. As a comparison, the IFT reduction process in each saponin shows a different trend of graph. Based on figure 4, it can be observed that saponins from different sources which are *Seidlitzia rosmarinus*, *Glycyrrhiza glabra*, *Zizyphus spina christi* and saponin show a significant decrease in IFT which is also different in respective concentration of 0.75 wt%, 1.5 wt%, 2 wt%, and 1 wt%. This phenomenon occurs due to the differences in the saponin structure of each plant-source. The interfacial thickness in surfactant flooding and oil will change in response to structural differences in surfactants which are closely related to the micelle formation process during CMC which render the differences in IFT value.

3.3. Wettability alteration

The natural wetting state in the sandstone which is water wet is able to change through the drainage process that involves the aging process using oil. This stage was performed to ensure the ability of saponins to change oil-wet state conditions into water-wet or tends to be more water wetness. Therefore, oil-wet sandstone performed under imbibition process by immersing the surfactant solution with saponin content in accordance with its CMC value. The concentration of saponins in CMC is intended to be the most efficient concentration both in terms of economy and the effect on oil mobilization. Figure 5 shows the effect of saponin in surfactant solution on contact angle of oil-wet sandstone.

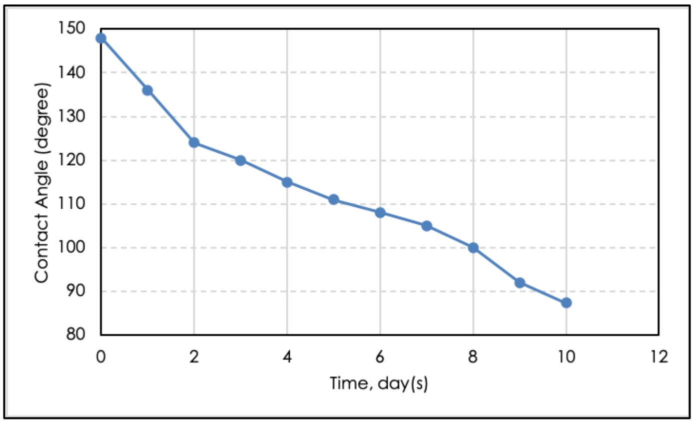

Figure 5. The effect of saponin in surfactant solution on contact angle of oil-wet sandstone.

Based on figure 5, the contact angle for distilled water only is 148°. Decrement in contact angle observed in about 16.2% on the second day with a value of 124°. On the following day, the decrease in contact angle is not more than 10° per day until the tenth day when the contact angle reaches less than 90° which is 87° as indicated to be an intermediate-wet state since the final contact angle is still in the range of 60°-120°. The proposed reason of the wettability alteration of the oil-wet sandstone prevail through the adsorption process caused by hydrogen bonding and/or hydrophobic interaction between surfactants and adsorbed paraffin oil on sandstone rock which not provided any evidence in this study [23,24].

4. Conclusion

Saponin has relatively low CMC value which is favorable to become a reference concentration in CEOR technique as natural surfactant. Based on the experimental results on surface tension at different saponin concentrations, the minimum surface tension and breakpoint of two slope values achieved the concentration of 0.05 wt% which is indicated as CMC of saponin in this study.

Saponin as natural surfactant is effective to alter the reservoir rock and fluid properties, facilitate oil mobilization, increase oil recovery and suggested as an additive to mitigating wax deposition. A 27% reduction from initial IFT between water and paraffin oil achieved by 8 wt% of saponin concentration. Observation from the IFT reduction also proved the effectiveness of saponins that can change oil-wet sandstone to intermediate-wet sandstone by the additional of saponins at CMC values.

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