

Synthesis and Characterization of Polymeric Surfactant from Palm Oil Methyl Ester and Vinyl Acetate for Chemical Flooding

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Abstract

Surfactants for enhanced oil recovery are generally made from non-renewable petroleum sulfonates and their prices are relatively expensive, so it is necessary to synthesis the bio-based surfactants that are renewable and ecofriendly. The surfactant solution can reduce the interfacial tension (IFT) between oil and water while vinyl acetate monomer has an ability to increase the viscosity as a mobility control. Therefore, polymeric surfactant has both combination properties in reducing the oil/water IFT and increasing the viscosity of the aqueous solution simultaneously. Based on the study, the Critical Micelle Concentration (CMC) of Polymeric Surfactant was at 0.5% concentration with an IFT of 7.72×10^{-2} mN/m. The best mole ratio of methyl ester sulfonate to vinyl acetate for polymeric surfactant synthesis was 1:0.5 with an IFT of 6.7×10^{-3} mN/m. Characterization of the product using FTIR and HNMR has proven the creation of polymeric surfactant. Based on the wettability alteration study, it confirmed that the product has an ability to alter from the initial oil-wet to water-wet quartz surface. In conclusion, the polymeric surfactant has ultralow IFT and could be an alternative surfactant for chemical flooding because the IFT value met with the required standard for chemical flooding ranges from 10^{-2} to 10^{-3} mN/m.

Keywords: Enhanced Oil recovery, Interfacial Tension, Methyl Ester Sulfonate, Polymeric surfactant, vinyl acetate

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INTRODUCTION

Oil production is estimated to decline by around 4% per year due to the aging of the wells. In 2016, oil production amounted to 338 million barrels, and it is estimated to decrease to 85 million barrels in 2050. Oil exports in 2016 amounted to 128 million barrels which are predicted to decline slowly and will running out in 2035 (BPPT, 2018). To overcome this imbalance,

efforts are being made to increase oil production through Enhanced Oil Recovery (EOR) technology.

Enhanced Oil Recovery (EOR) is a method which is used to increase oil production in an oil well by collect the residual oil between the pores of rocks in the reservoir, so that oil that are thick, heavy and low permeability can be taking out to obtain more oil after declining the oil production (Green and Willhite, 2017)

There are three kinds of oil recovery in petroleum industry. First is primary recovery which is recovery by ordinary drive energy initially available in the reservoir. It does not need injection of any external heat or fluids as a driving energy. Second is secondary recovery which is recovery by injection of external fluids, include gas and/or water, particularly, for volumetric sweep efficiency and pressure maintenance purpose. The last is tertiary recovery which relates to the recovery after secondary recovery and utilize special fluids injected into the reservoir such as miscible gases, chemicals, and/or thermal energy. The latter is classified as EOR technology and one of the EOR technique is chemical flooding which use polymer, surfactant, alkali and their combination (Sheng J. J., 2011).

The primary and secondary recovery methods are able to about one third of the oil in the reservoir, whereas by applying tertiary recovery (EOR) with surfactant injection, oil production can reach 40-60% from the reservoir (Alagorni *et al.*, 2015).

Methyl ester feedstocks derived from palm stearin, palm kernel, coconut, soya and tallow have been used in sulfonation studies because they were derived from renewable oils and as a class methyl ester sulfonates have environmental properties and excellent surfactant (Sheats and MacArthur, 2005). Therefore, Indonesia has the potential as a country in developing palm oil-based surfactant. Based on Food and Agriculture Organization (FAO) data, Indonesia is the biggest palm oil production and exporter country in the world. In 2017, Palm oil production in Indonesia was recorded at 35.36 million tons (Kementan, 2017). Therefore, the surfactant based on palm oil has great potential to become an industrial scale in the future.

Methyl ester sulfonate exhibits good dispersion characteristics and detergency, especially in hard water. MES can be produced by reacting methyl ester with several sulfonating agents including chlorosulfuric acid (ClSO_3H), sulfuric acid (H_2SO_4), Oleum ($\text{SO}_3 \cdot \text{H}_2\text{SO}_4$), and SO_3 gas (Foster, 1997).

Polymeric surfactant can be synthesized from methyl ester sulfonate (MES) which is able to overcome the problem in conventional ASP (Alkali-Surfactant-Polymer) flooding without reducing its efficiency. The problems occur because of the different properties, the mixtures able to separate into two phases in a flow stream. Besides that, resulting surfactant loss to reservoir rock surface by adsorption because of the attraction of surfactant to rock-water interface (Yu, *et al.*, 2008). Other problems because of the unsuitability between surfactant and polymer, yielding in the decrease of polymer properties, such as adsorption, aggregation, and diffusion performance in porous media (Sun, *et al.*, 2010). Moreover, even ASP injection has resulted to successfully increase oil recovery in the field, the existence of the strong alkali has baneful effects on polymer performance. In many cases more polymer is requisite to reach the desired viscosity (Elraies, *et al.*, 2011).

According to (Guo, *et al.*, 2017), erosion and scaling are very common issue in ASP flooding field test. In strong base ASP flooding pilot test in Daqing oilfield, the major scale type is silica and calcium carbonate scale, while, in weak base ASP flooding, the scaling issue is less serious and the most scale type is calcium carbonate. Some research conducted by (Cheng, *et al.*, 2014a; Cheng, *et al.*, 2014b; Zhu, *et al.*, 2012) stated that the corrosion and scaling are frequent problems in field application of ASP.

Based on an earlier paper written by Jirui *et al* (2001), they mentioned the corrosion and scale problems that happened during the ASP flood in Daqing field. A strong base has a negative effect on polymer performance, and in many cases more polymer is required to attain the desired viscosity (Wang *et al.*, 2006). With the high concentration of alkaline can reduce polymer viscosity, thus more polymers will be required to get the sufficient viscosity which in turn increased cost (Sheng, 2014) (Guo, *et al.*, 2017). In ASP field applications, scaling and corrosion issues due to the use of base damaged the lifting system and thus shortened the average pump-checking period, resulting in increased workload for maintenance. Beside corrosion and scaling, ASP flooding produces a strong emulsification resulted in many produced liquid treatment issues. Strong emulsification increased in ASP flooding applications of South-5 and North-1 East zone, and it was difficult to separate between oil and water (Zhu, *et al.*, 2012).

The reaction of polymeric surfactant synthesis is to insert sulfonate groups into hydrophobic groups in the polymer chain. The previous research by (Ye, *et al.*, 2004) has synthesized poly[acrylamide-acrylic acid-N-(4-butyl) phenyl acrylamide] which was the basis for synthesizing of polymeric surfactant through the polymerization process. It is expected that it can reduce IFT value and be able to control viscosity also. So that it has properties that combine between the high viscosity of the polymer and interfacial properties of the surfactant (Cao and Li, 2002).

In chemical flooding, it is effectual to increase the fluids viscosity injected and to reduce the IFT to an ultra-low value (10^{-3} mN/m) that is between that of the fluids and the crude oil (Cao and Li, 2002; Berger and Christie, 2017), the IFT value of surfactants for EOR must reach 10^{-3} mN/m. Raffa *et al* (2016) has summarized that the IFT for EOR ranges from 10^{-2} to 10^{-3} mN/m.

Synthesis of polymeric surfactant for EOR applications was carried out by (Elraies *et al.*, 2011). Sodium methyl ester sulfonate (SMES) was prepared using a Chlorosulfonic acid as sulfonating agent from castor oil methyl ester. The polymerization reaction was carried out between acrylamide monomer and SMES. The IFT value and viscosity of the polymeric surfactant indicated that this surfactant was potential for oil recovery in the reservoir to replace the conventional ASP flooding method.

Meanwhile, Babu et al (2015) was synthesized polymeric surfactant from castor oil. The results concluded that polymeric surfactant was able to reduce the interfacial tension until 10^{-3} mN/m so that, it is a suitable candidate for increasing oil recovery by chemical flooding. Besides that, it has higher viscosity than that of SMES surfactant.

The latest study that has been done by Wibowo, *et al* (2020) on synthesis of polymeric surfactant from palm oil methyl ester for EOR application. Methyl ester sulfonate was synthesized by reacting between methyl ester and NaHSO_3 , after MES was formed then followed by polymerization with acrylamide monomer in order to synthesize polymeric surfactant. The result found that the polymeric surfactant was able to reduce the interfacial tension (IFT) up to 2.3 mN/m, although the IFT was not very low, it has the potential as an alternative surfactant for EOR applications.

Synthesis of polymeric surfactant from sulfonate ether alcohol using vinyl acetate monomer and acrylic acid for EOR applications has been patented also by (Caneba, 2010). Research on oil recovery with vinyl acetate and acrylic acid was able to recovery until 17-41% OOIP (Raffa *et al.*, 2016).

Based on some studies above, research to synthesize of polymeric Surfactant from palm oil methyl ester using vinyl acetate monomer has never been done before which become the novelty of this research. Therefore, in this research the polymerization of MES will be carried out using vinyl acetate monomer to obtain ultralow Interfacial Tension (IFT) values as well as a viscosity control, furthermore it is expected to prevent several problems mentioned before in EOR applications.

The schematic chemical reaction for synthesizing of methyl ester sulfonate and polymeric surfactant can be shown in Fig. 1 and 2 respectively. Two possibilities for producing free radicals in the surfactant chain are break-down of the -OH bond or cleavage of C=C (unsaturation) bond. Because of the -OH bond polarity is higher than that of C=C bond, the higher proportion of free radical for grafting on -OH will be more possible rather than breaking of C=C unsaturation bond. In fact, the polyacrylamide chain formation occurs in the hydroxyl substituents (-OH) of surfactants (MES) rather than the unsaturated bond of the surfactant (Babu *et al.*, 2016).

METHODOLOGY

Materials

Palm oil methyl ester, Sulfuric acid (H_2SO_4) Merck p.a, Sodium Hydroxide (NaOH) Merck p.a, Methanol (CH_3OH) 98% p.a, Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) Merck p.a, Vinyl acetate Merck p.a.

Experimental procedure of methyl ester sulfonate synthesis

Methyl Ester Sulfonate (MES) was made by reacting 100 mL (0.35 moles) of palm oil methyl ester and 22 mL (0.39 moles) of H_2SO_4 into a three-neck flask reactor equipped with a reflux and thermometer. The reaction was heated and stirred on a hotplate stirrer at 60°C for 1.5 hours. After reaction complete, the purification was carried out with 40% methanol at 50°C for 60 minutes. After purification, the neutralization was done using 30% NaOH solution until pH 5-6. The last step was methanol evaporation with a rotary evaporator to purify the MES product.

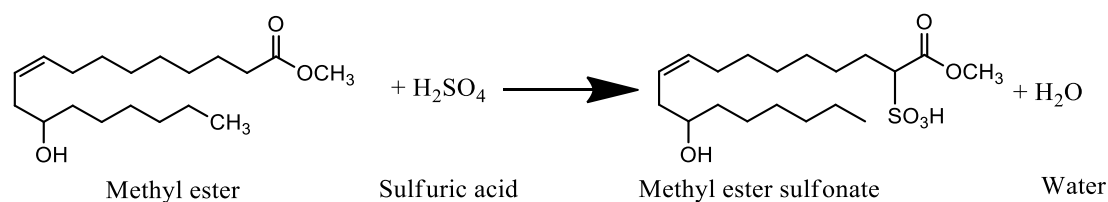


Figure 1. Synthesis reaction of MES

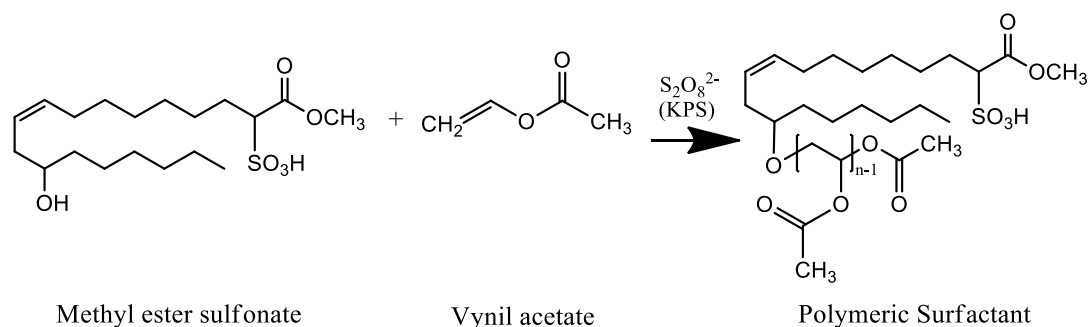


Figure 2. Synthesis reaction of polymeric surfactant

Experimental procedure of polymeric surfactant synthesis

Potassium persulfate ($K_2S_2O_8$) 1.23% as initiator was prepared by dissolving it into aquadest and the pH was adjusted to 9-10 by NaOH solution. Polymerization was carried out using a three-neck flask reactor equipped with a reflux and thermometer. MES surfactant was added to vinyl acetate with a certain mole ratio (1:0.5, 1:0.75, 1:1, 1:1.25, 1:1.5), then potassium persulfate initiator was added as well. The polymerization was heated with varied temperature (40, 45, 50, 55, 60°C) for 60 minutes with a hotplate stirrer.

Product analysis

The polymeric surfactant product was tested for viscosity using Ostwald viscometer in chemical engineering laboratory, Institut Teknologi Indonesia, Critical Miscelle Concentration (CMC) and IFT values using IK27 Spinning Drop Tensiometer in SBRC laboratory, IPB University. The best mole ratio of polymeric surfactant was measured the functional groups by Shimadzu FTIR spectrophotometry and the characteristic resonances by JEOL spectrometer FT NMR in LIPI chemical research center laboratory and contact angle measurement using Phoenix 300 contact angle analyzer in SBRC laboratory, IPB University.

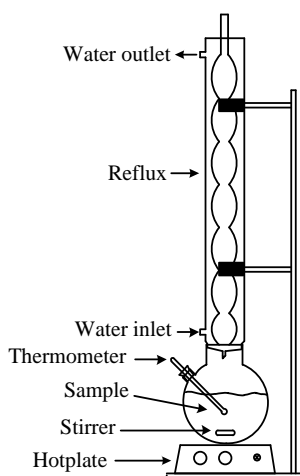


Figure 3. Experimental equipment scheme

RESULTS AND DISCUSSION

The Effect of MES to vinyl acetate mole ratio on polymeric surfactant viscosity.

According to (Raffa, Broekhuis, & Picchioni, 2016), polymerization of MES able to increase of water viscosity and reduce in interfacial tension (IFT). Based on Fig. 4, The graph illustrates that the viscosity decreases from 1:0.5 to 1:1 mole ratio at all variations of the polymerization temperature. The highest viscosity is obtained at 1:0.5 at 50°C with 6.9140 mm²/s and it goes decrease to 2.5348 mm²/s at ratio of 1:1. After that the viscosity increases along with the increase in the number of monomers at all variations of the polymerization temperature. The viscosity

increases significantly at 50°C with the highest viscosity at 1:1.5 (6.0506 mm²/s). Whereas at other temperatures, the viscosity varies between 3.8199 and 4.1081 mm²/s. at 1:1.5 mole ratio. Based on Fig. 4, it depicts that the viscosity of polymeric surfactant tends to uplift with the increasing number of monomers. This is because more monomers result in more polymer chains that are attached to the MES.

Polymeric surfactant has ability to increase the viscosity. It is similar like polymer which is an important part of the ASP flooding. Polymer is mainly used to upsurge the viscosity of the injection system and thus improve the mobility ratio (Guo, *et al.*, 2017).

Based on experiments, the viscosity of crude oil was 3.0819 mm²/s, therefore the viscosity of polymeric surfactant at mole ratio of 1:0.5 is the best because it has had not only the lowest IFT but also the viscosity resulted (4.4502 mm²/s at 60°C) had not much different from the viscosity of crude oil. According to Elraies, *et al* (2011), the viscosity difference will be inadmissible and can cause other problems in the injection process. Thus, it can be resumed that to obtain a successful chemical slug that is able to propagate into the formation once it is injected without losing its integrity and capable of producing ultralow IFT, the mole ratio of 1:0.5 is the optimum ratio for IFT reduction and viscosity control. Furthermore, the viscosity resulted was almost similar as the study conducted by Elraies, *et al* (2011) and Oladimeji, *et al* (2013).

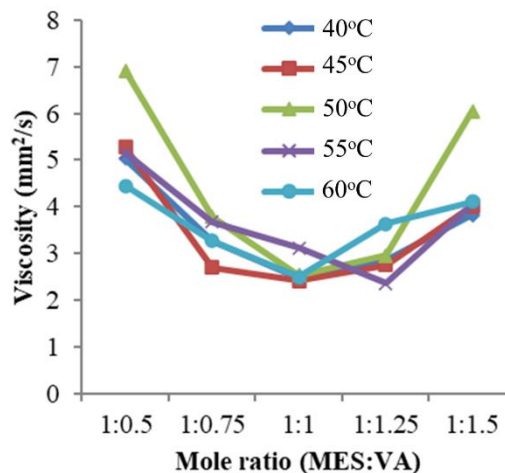


Figure 4. The Effect of MES to vinyl acetate mole ratio on polymeric surfactant viscosity

The Effect of polymeric surfactant concentration on IFT values.

In surfactants, CMC parameter is very important. CMC is a critical micelle concentration at which surfactant molecules begin to form aggregates known as micelles. It shows the point at which monolayer adsorption is finish and the surface-active properties are at an optimum. Below CMC, surfactant molecules are in the form of monomers and along with increasing concentrations of surfactants in the bulk, the surface or interfacial tension decreases dramatically. Whereas,

above the CMC, the monomers concentrations are nearly constant (Farn, 2006).

Based on Fig. 5, The chart depicts that the IFT value decreased dramatically as the polymeric surfactant concentration increased from 0.1 to 0.5% starting from 0.2854 until 7.72×10^{-2} mN/m. After that the IFT value rises slowly along with the increase of polymeric surfactants concentration until 0.1466 mN/m. Therefore, it can be concluded that the CMC of polymeric surfactant is 0.5% concentration because it has the lowest IFT value.

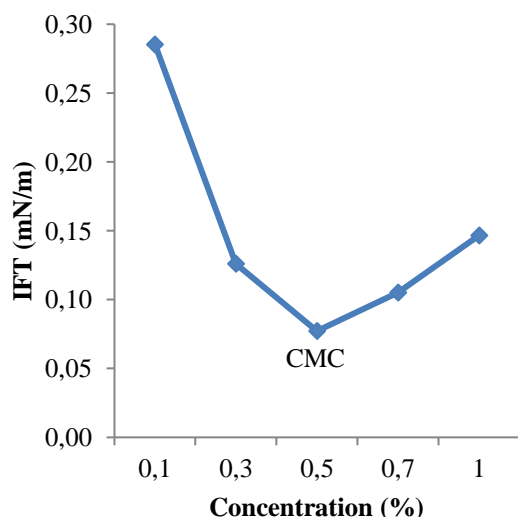


Figure 5. The Effect of polymeric surfactant concentration on IFT values.

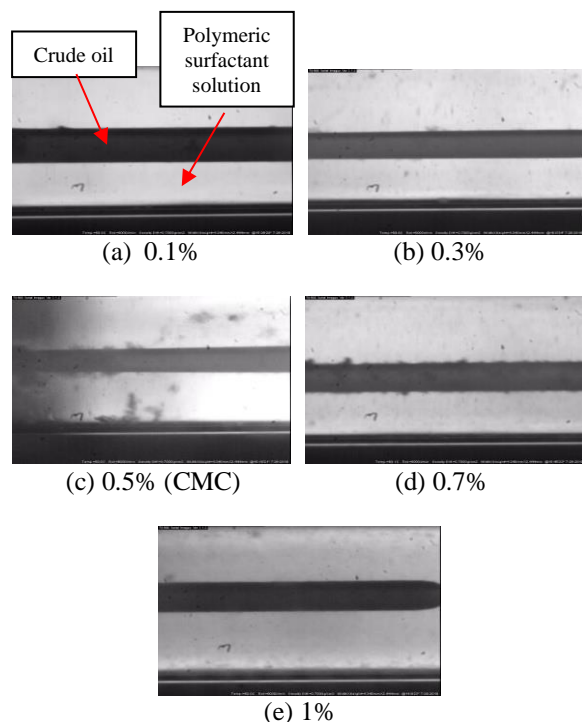


Figure 6. Interfacial tension (IFT) photograph at various concentration of polymeric surfactant

Figure 6 from a to e illustrates the visualization of IFT measurements between crude oil and formation water with adding by various concentration of polymeric surfactant solution between 0.1 and 1% using IK27 Spinning Drop Tensiometer. Based on figure 6(c), it shows that the crude oil layer was the thinnest at concentration of 0.5% from any other concentration which means that the oil was well emulsified. This is also evidenced by the lowest IFT value at CMC among other concentrations of polymeric surfactant.

The Effect of MES to Vinyl acetate mole ratio on IFT values.

According to Babu *et al* (2015) the mole ratio of monomer to sulfonate can affect the IFT value of polymeric surfactant products. The IFT measurement was carried out at 0.5% concentration of polymeric surfactant in formation water (at CMC values). Based on Fig.7 shows that the smaller mole ratio of MES to vinyl acetate (VA), the IFT values increase significantly from 6.7×10^{-3} to 1.4×10^{-1} mN/m. Therefore the 1:0.5 ratio is the best composition because the product of polymeric surfactant has the lowest IFT value.

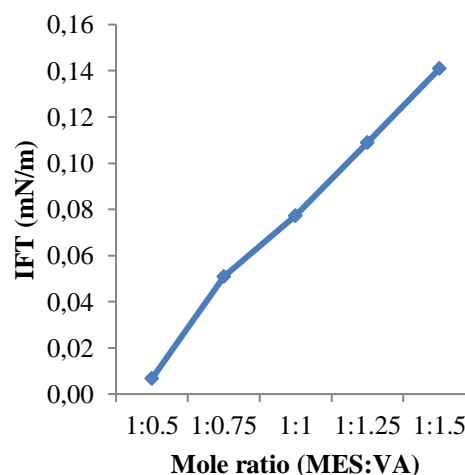


Figure 7. The effect of MES to vinyl acetate (VA) mole ratio on IFT values

Figure 8 from a to e represents the visualization of IFT measurements between crude oil and formation water with adding by various mole ratio of MES to VA at 0.5% concentration of polymeric surfactant (CMC). The mole ratio of 1:0.5 delineates the thinnest layer of crude oil which was proven by the lowest IFT value therefore this ratio was the best for emulsifying oil-water layer.

FTIR measurement results

The infrared spectrum of methyl ester is shown in Figure 9. The strong band from 1463.07 to 1437.03 cm^{-1} usually correlates with the asymmetrical bending vibration band of methyl group (C-H).

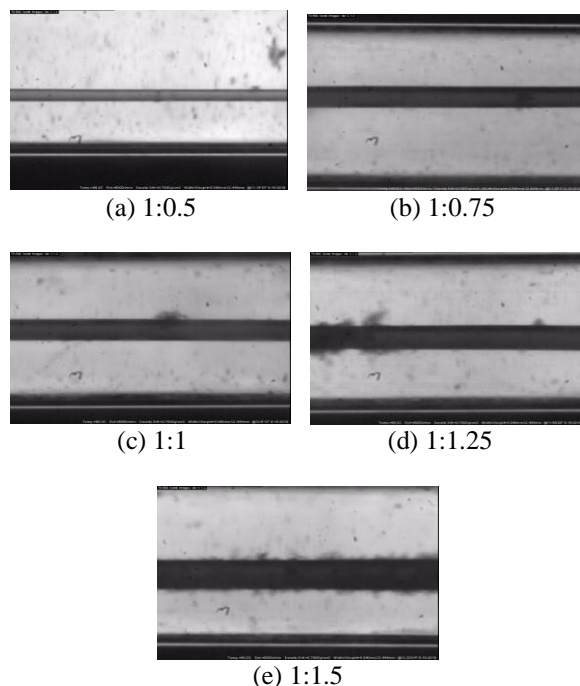


Figure 8. Interfacial tension (IFT) photograph at various mole ratio of MES to VA

In addition, between 2925.17 and 2680.2 cm^{-1} shows the symmetric and asymmetric C-H stretching modes of the terminal $-\text{CH}_3$ group. Whereas C=O stretching vibration in the spectrum of 1743.72 cm^{-1} is indicated as esters. Ether is identified by stretching of C-O in the peak from 1246.07 to 1116.83 cm^{-1} . Moreover, the wave number between 3676.48 and 3468.16 cm^{-1} are stretching of O-H alcohol. Furthermore, double bond of alkene (C=C stretching) is detected in the wave number of 1655.96 cm^{-1} .

Analysis of functional group was determined on the best mole ratio of MES to VA (1:0.5). The result illustrates in Fig. 10. It represents the functional group of polymeric surfactants.

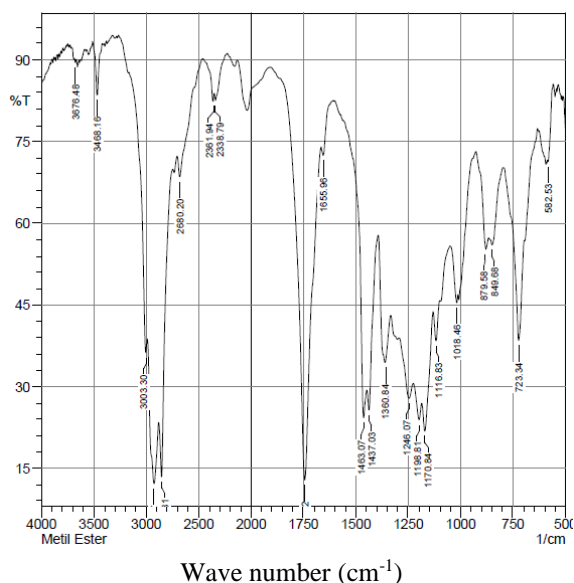


Figure 9. The infrared spectrum graph in the FTIR measurement for methyl ester.

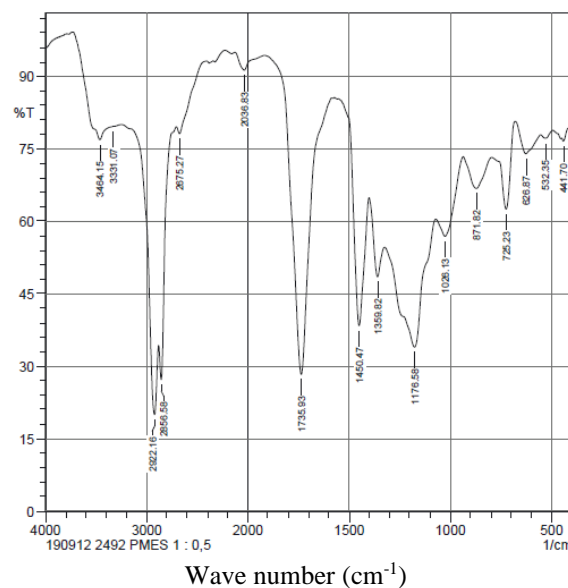


Figure 10. The infrared spectrum graph in the FTIR measurement for polymeric surfactant at mole ratio of MES to VA (1:0.5).

The sulfonate group (S=O) is detected in the peak of 1026.13 cm^{-1} . Whereas ether is showed with infrared absorption characteristics due to stretching of C-O in the peak of 1176,578 cm^{-1} . In addition, the alkane chain scissoring of CH_2 and CH_3 is seen in the wave number of 1450.47 cm^{-1} . Ketones which are characteristic of esters is detected with infrared absorption characteristics on the C=O stretching vibration in the spectrum of 1735,934 cm^{-1} . The main band that appears in the IR alkane spectra is caused by stretching of CH in the wave number from 2856,576 to 2922,156 cm^{-1} . Whereas in the wave number between 3331.065 and 3464.154 cm^{-1} are stretching of O-H alcohol. Based on the functional group analysis using FTIR, it can be concluded that the polymeric surfactant has been successfully synthesized because it has sulfonate, ketone, ether and CH_3 groups detected in the product.

According to the figures, it is clear that the difference between Fig. 9 and 10 is that the latter has already detected sulfonate group which indicates that surfactant has been formed while the former is only methyl ester.

H-NMR measurement results

According to Bharti and Roy (2012), analysis of HNMR (H Nuclear Magnetic Resonance) provides a lot of information about intra-molecular and inter-molecular resonances. The most important fundamental relationship of NMR is that the signal intensity in the NMR spectrum is directly proportional to the number of nuclei present at a particular resonance. The HNMR spectrum used CdCl_2 solvent to confirm the polymerization of anionic surfactant (MES). The Resonance characteristics was tested by NMR on polymeric surfactant at mole ratio of MES to VA (1:0.5). The spread of the spectrum can be seen in Fig.11.

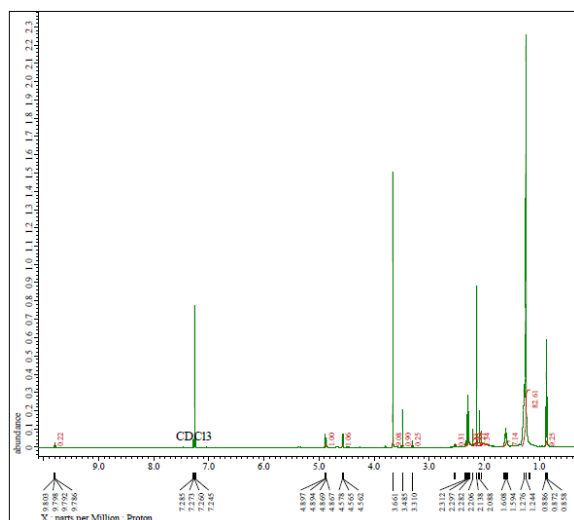


Figure 11. The H-NMR spectrum of the polymeric surfactant at mole ratio of MES to VA (1:0.5).

Resonance characteristics associated with the polymeric surfactant structure are observed in the chemical shift of $\delta = 0.858\text{-}0.886$ ppm for alkyl (methyl) (R-CH_3), $\delta = 1.244\text{-}1.276$ ppm for alkyl (methylene) ($\text{R-CH}_2\text{-R}$) where both shows the presence of long carbon chains. A chemical shift at $\delta = 1.594\text{-}1.608$ ppm indicates alkyl (methine) ($\text{R}_3\text{C-H}$) and confirms the formation of the polymer from the monomer. The chemical shift for the triple bond is shown at $\delta = 2.088\text{-}2.138$ ppm for alkyne ($\text{RC}\equiv\text{C-CH}_2\text{-}$) and $\text{RC}\equiv\text{CH}$. The acetate group (RO-CO-CH_3) in the polymer is depicted at the chemical shift of $\delta = 2.206$ ppm. The sulfonate group ($\text{R-SO}_3\text{H}$) attached to the surfactant chain is represented at the chemical shift of $\delta = 2.282\text{-}2.312$ ppm. Attachment of the surfactant chain to the polymer to form polymeric surfactant is confirmed in the chemical shift of $\delta = 3.310\text{-}3.485$ ppm in the form of ether ($\text{R-O-CH}_2\text{-}$). The methyl ester (R-COO-CH_3) group on the surfactant is shown at the chemical shift of $\delta = 3.661$ ppm. Chemical shift resulted from the two protons of the double bond alkene ($\text{RCH}=\text{CH-}$) is seen at $\delta = 4.562\text{-}4.897$ ppm. The presence of 2 and 3 double bonds in polymeric surfactants proves that there is no addition of monomer chains into it.

Contact angle measurement results

Interfacial tension (IFT) and contact angles measurement are several effective ways to identify the suitable surfactant for enhanced oil recovery by chemical flooding. Contact angle is crucial for wettability of rock surface and alteration (Bera *et al.*, 2012; Chinnam, *et al.*, 2015) which shows the degree of wetting when a liquid and solid interact. Large contact angles ($>90^\circ$) correspond to low wettability, while small contact angles ($<90^\circ$) correspond to high wettability (Yuan and Lee, 2013).

Phoenix 300 contact angle analyzer was used to determine the contact angle of polymeric surfactant solution. The effect of polymeric surfactant on wettability alteration mechanism is done by measuring

contact angles of crude oil–surfactant interface (Babu *et al.*, 2015). In this experiment, polymeric surfactant was dropped in contact with a rock oil-wet surface. The rock surface was created by hydrophilic SiO_2 glass (quartz). Contact angle between crude oil and quartz surface was determined in the existence of polymeric surfactant solution.

Polymeric surfactant has a very positive result in terms of wettability alteration by decreasing contact angles dramatically. The initial state of the quartz was oil-wet. By the application of polymeric surfactant, the oil-wet surface altered gradually to water-wet state which is privileged need for chemical flooding. Figure 12 represents the contact angle behaviors of polymeric surfactants with time.

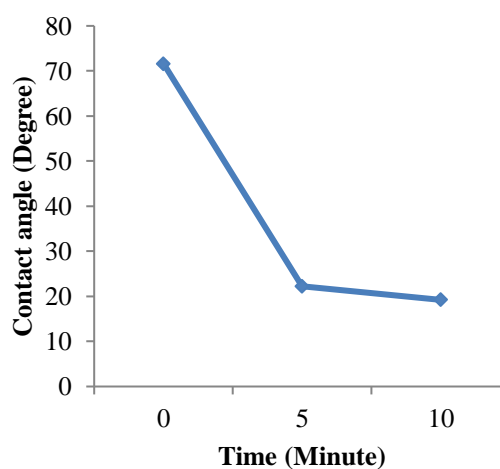


Figure 12. Variation of dynamic contact angle for polymeric surfactant on oil-wet quartz surface

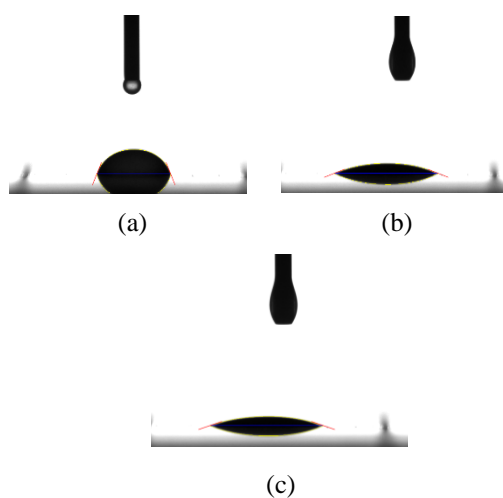


Figure 13. Photograph of polymeric surfactant solution drops on oil-wet quartz surface during contact angle measurement. a 0 min (initial), b after 5 min, c after 10 min

The contact angle measurement of polymeric surfactant was carried out on the best mole ratio of MES to VA 1:0.5 with a concentration of 0.5%. Based on Fig.12, the initial contact angle was 71.6433°, then after 10 minutes the contact angle decreased dramatically to 19.2207°. As time goes, it became less than 10° with elapse of time.

The initial contact angle of polymeric surfactant is higher because of the nature of viscous solution of the product. As the polymeric surfactant is viscous in nature, therefore, the formation of thin film on the quartz surface is stable which helps to offer a higher contact angle at the beginning (Babu *et al.*, 2015).

Figure 13 shows the polymeric surfactant solution which drops on the oil-wet quartz surface for a certain time, and it was successful to alter from the oil-wet quartz surface to water-wet because the contact angle less than 90° which represent high wettability.

CONCLUSION

According to the study, based on the viscosity test, polymeric surfactant product has viscosity of 4.4502 mm²/s at 60°C polymerization reaction temperature at mole ratio of MES to VA (1:0.5). Referring to CMC analysis, it could be concluded that the CMC of polymeric surfactant was at 0.5% concentration because it has the lowest IFT value (7.72x10⁻² mN/m). The best mole ratio of MES to vinyl acetate monomer for polymerization to synthesize polymeric surfactant was obtained at ratio of 1:0.5 which has the lowest IFT value (6.7x10⁻³ mN/m). Characterization of polymeric surfactant product using FTIR and HNMR confirmed that the product was successfully formed in this study. According to wettability alteration study of oil-wet quartz surface with the polymeric surfactant, it proved that the polymeric surfactant has an ability to alter from the initial oil-wet to water-wet quartz surface. In conclusion, based on the test results, the parameter of viscosity, concentration (CMC), IFT and contact angle needs to be considered in polymeric surfactant products which has ultralow IFT and could be an alternative surfactant for EOR applications because the IFT value met with the required standard for chemical flooding from 10⁻² to 10⁻³ mN/m.

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