Study of Synthesis Polyethylene glycol oleate Sulfonated as an Anionic Surfactant for Enhanced Oil Recovery (EOR)

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Abstract. Mechanical Enhanced Oil Recovery (EOR) through chemical injection is using an anionic surfactant to improve the recovery of oil residues, particularly in a reservoir area that has certain characteristics. This case led the authors to conduct research on the synthesis of an anionic surfactant based on oleic acid and polyethylene glycol 400 that could be applied as a chemical injection. In this work, we investigate the sulfonation of Polyethylene glycol oleate (PDO) in a sulfuric acid agent. PDO in this experiment was derived from Indonesian palm oil. Variation of mole reactant and reaction time have been studied. The surfactant has been characterized by measuring the interfacial tension, acid value, ester value, saponification value, iodine value, Fourier Transform Infrared (FTIR), and particle size analyzer. There is a new peak at 1170-1178 cm⁻¹ indicating that S=O bond has formed. PDO sulfonate exhibits good surface activity due to interfacial tension of 0,003 mN/m. Thus, polyethylene glycol oleate sulfonate was successfully synthesized and it could be useful as a novel anionic surfactant.

1. Introduction
Recently, the enhanced of oil recovery (EOR) technology gains much attention in many countries due to the lack of oil resources and difficulty in finding new oil sources. Application of EOR technology gives an additional chance to get out more oil from the reservoir, possibly about another 20% [1]. This technique is more efficient than other techniques such as gas and thermal engineering. One of the chemical injection techniques is using surfactants. Basically, the surfactant for EOR made from vegetable oils and palm oil derivatives with polyester formed.

The previous study, Rafa, and Favero have conducted a petroleum-based surfactant study [4, 5], whereas biomass-based polymeric surfactants have been obtained from natural resources. It has attracted much attention as a polymeric surfactant and potential for EOR applications due to lower cost and derived from renewable sources. This polymer also has a good viscosity and interface activities. Another study from Elraies (2011) reported the esterification of sulfonated fatty acids from castor oil [6]. Synthesized of a vegetable oil based methyl ester (oleic acid) as a cationic polymeric for EOR applications was performed by Irawan (2015) [7]. Babu (2015) was synthesized an anionic surfactant (sodium methyl ester sulfonate) from castor oil [8]. An anionic surfactant have a negative charge and some properties such as stable, decreasing IFT or interface tension, and low adsorption to
rocks in petroleum reservoirs [2]. Therefore, an anionic surfactant could be considered being the effective chemical compound for EOR techniques.

The surfactant used depends on conditions and characteristics of the intended reservoirs. This statement is similar as reported by Hirasaki who investigate an anionic surfactant for adsorbing positive charges on clay surfaces in sandstone and matrix on carbonate surfaces at neutral pH [9]. The reservoir conditions containing sandstone is more suitable using an anionic surfactant which can be obtained by the process using a sulfonation agent such as concentrated sulfuric acid. Sulfuric acid could be hydrolyzed. Neutralization process is needed as soon as the sulfuric group formed [3]. When the crude oil contacts the water that contains the brine, the natural surfactant will be collected on the interface and form an adsorbed film that lowering the interface tension from the crude or water. Decreasing sources can be affected by the adsorption of the surfactant to rocks in the petroleum reservoir. The utilization of sulfonate agents can reduce the adsorption process so that the oil recovery would be increased. The composition of reservoir rock plays a role in determining the interaction between mineral-added reagent (surfactant or polymer) and the effect on liquid interface properties such as surface load and wettability [11]. Stachurski said that the charge value of a solution in the zeta potential of emulsion droplets is a function of pH and independent of the length of aliphatic hydrocarbon chains [12]. Iglauer (2010) has observed the effect of surfactant adsorption on Berea sandstone with a standard size for sandstone of 74-250µm [13]. In surfactant flooding, mechanism of the recovery process was based on decreasing interface tension between two phases (IFT). The role of IFT in oil recovery has been explained regarding capillary (Ca) numbers (Hirasaki). In fact, the presence of hydrophobic parts in water-soluble structures is also known to affect the interface properties (surface tension, IFT, wettability). The value which usually used are 10⁻³ mN / m) to support the application of EOR techniques [14]. However, some studies of surfactant flooding polymers suggest that in some cases there is no significant correlation between low IFT values and the optimum value of IFT is greater than 10⁻³ mN/m or commonly called by ultralow IFT [15]. Therefore, the effectiveness of the surfactant polymer value is very difficult to achieve, and the range of IFT value is 0.1 – 15 mN/m [4]. There is a lack of evidence about an anionic surfactant based on petroleum are more costly and non-renewable so that the current research aimed on anionic surfactant based on palm oil (oleic acid) and polyethylene glycol are renewable, more economical, and have ultralow IFT values.

2. Materials and Methods

2.1. Materials

For an anionic surfactant synthesis, laboratory grade chemicals such as sulfuric acid (H₂SO₄) pro analysis (95-97%) from E.Merk cat. 1.00731.2500, Hydrogen peroxide (H₂O₂) pro analysis (35-37%) from E.Merck Cat. 1.07209.2500, Polyethylene glycol oleate (PDO) technical. For titrimetric analysis using Potassium hydroxide (KOH) pro analysis from E.Merck.Cat. 1.05033.1000, technical ethanol, a reagent for ester value analysis, acid value, iodine value, and saponification value.

2.2. Methods

In this study, the sulfonation reaction was carried out with the polyethylene glycol oleate (PDO) ester as an anionic surfactant. This reaction has been performed by using Li [17], for PEG Dioleate (PDO), the sulfonation process was carried out using 50% of total weight H₂O₂ reactants. Furthermore, the sample is washed using 50% methanol to convert all remaining fatty acids [18]. The following sulfonation process: (1) amount of sulfuric acid as a sulfonation agent, was added with varying mole ratio of 1:0.5; 1:1; and 1:1.5. While the PDO has been stirred in a reactor, sulfuric acid was added gradually. The reaction temperature has been maintained at 80°C for 2, 4 and 6 hours. PDOS (Polyethylene glycol Oleate Sulfonate) was bleached with H₂O₂ 50% total reactant weight at 75°C for 2 hours. The product and methanol (50% total reactant weight) were mixed in 2 hours at 50°C; PDOS
was neutralized with NaOH solution at 50°C for 2 hours; then the residue was evaporated and characterized.

2.3. **Characterization of PDOS an anionic surfactant**

The chemical and physical properties of oleic acid and PEG based anionic surfactant was analyzed by titration method based on ASTM D4662-03 to obtain the acid value (Av), ester value (Ev), saponification value (Sv), and iodine value (Iv). The functional group present in the PDOS surfactant was determined used FTIR spectrophotometer (Shimadzu-IR Prestige21). Interfacial Tension (IFT) measurement on the surfactant solution was conducted to measure the interfacial stress of the surfactant solution with oil. The result was expected with smaller than 10⁻³ mN/m. IFT measurement using Spinning Drop Interfacial Tensiometer TX 500. The particle size analysis of surfactants was determined using HORIBA Nano Particle Analyzer SZ-100 at 25°C. All samples were prepared in deionized water and sonicated using Elmasonic E 15H for 10 minutes.

3. **Result and Discussion**

3.1. **Synthesis of PDOS based an anionic surfactant**

Figure 1 shows the results of iodine value at 1:1-mole ratio for 2 hours was still high, then decreased by 4 hours, but increased again at 6 hours reaction. While the mole ratio of 1:0.5, sulfuric acid as sulfonation agent used is not optimal, so iodine value is still high. The highest number of iodine on TM (without methanol) indicates that there are still many reactants that do not react [6, 8, 18].

![Fig.1. Iodine value graph](image1)

![Fig.2. Ester value graph](image2)

In Figure 2, ester value is an indicator of the ester compound. From the variation of time and mole ratio, the TM sulfonation (without methanol) has shown the significant number, the smallest ester value among all variables. In figure 3, the optimum value is at a mole ratio of sulfuric acid and PDO of 1: 1 for 4 hours, the smallest value compared to other variables. The odds are already reacting all over the reactant. This also is seen in stark contrast to the saponification value of TM (without methanol). In figure 4, it shows that the smallest acid value which means the optimum result is in the reaction of 1:1-mole ratio for 4 hours. From the four images of the curves, concluded the optimum reaction of sulfonation is at a mole ratio of 1:1 during 4 hours.
3.2. Characterization of PDOS based an anionic surfactant

Characterization of Polyethylene glycol oleate sulfonated based an anionic surfactant was recorded in Table 1. Analysis of acid value was conducted to find out the progress of the synthesis of PDOS. Decreasing acid value from oleic acid into PDO occurred because of extension chain of reactive carboxyl from oleic acid formed an anionic surfactant, whereas the decline acid value from PDO into PDOS occurred due to neutralization process on sulfonation reaction with NaOH and formation of NaSO\(_3\) or sodium sulfonate. On the other hand, the ester value increased with sulfonation reactions. Increasing ester value occurred because of extension chain of reactive carboxyl from PDO, it will react with the base which means the residual acid in the anionic surfactant product is reduced [6, 8, 18]. Babu in his study made sodium methyl ester sulfonate from ricinoleic acid, with the result of acid value, saponification value and iodine value are 10-12, 185-190, and 80-90 respectively.

| Materials         | Physical properties | Av (mg KOH/g) | Ev(mg HCl/g) | Sv(mg HCl/g) | Iv(mg HCL/100g) | HLB |
|-------------------|---------------------|---------------|--------------|--------------|-----------------|-----|
| PDO               | Liquid, dark yellow | 61.78         | 56.28        | 105.73       | 45.63           | 8.25|
| PDOS 1:1 4 hours | Liquid, brown       | 20.63         | 144.42       | 83.52        | 42.72           | 10.09|
| Oleic acid 4 hours| Liquid, yellow      | 180.04        | 22.04        | 117.77       | 85.59           | ~1.0*|
| PEG 400           | Viscous, colorless  | 2.87          | 25.24        | 18.67        | -               | 12.69-13.1*|

The saponification number of the nonionic surfactant in the present invention has decreased by 60%. The saponification number and acid number of the nonionic surfactant of the present invention can be used to calculate the HLB value based on the Griffin method [16] with the formulas as follows:

\[
HLB = 20 \times (1 - S/A), \quad \text{where} \quad S=\text{saponification number of the ester} \quad A=\text{acid number of fatty acids}
\]

To obtain an HLB value for the 8 to 13 surfactant PDO, as seen in Table 1, an anionic surfactant in the present invention categorized in an O/w emulsion, for example, surfactant application for EOR.
3.3. Mechanism of reaction

Figure 5 shows the complete reaction mechanism:

\[ \text{C}_{18}H_{37}H_{2}CC + \text{H}_{2}\text{SO}_4 \rightarrow \text{C}_{18}H_{37}HCC
\text{OCCH}_{2}\text{C}_{18}H_{31} \]

The scheme of PDO sulfonation is shown in Figure 5. When \( \text{H}_2\text{SO}_4 \) as a sulfonating agent reacted with PDO, \( \text{SO}_3^- \) ion binds with C alpha atom in the oleic chain in the PDO structure. The possibility of such reactions also describes the reaction of sulfonation in the fatty acid molecule. Indications for determine the formation of sulfonate in the PDO can be seen from the emergence of the S=O stretch peak at wavelengths 1170,79 cm\(^{-1}\) (PDOS) which did not appear at the PDO as shown in figure 6. Elraies has stated the sulfonate group is presented in peaks between 1160-1120 cm\(^{-1}\), whereas the peaks at 1410 and 1068 cm\(^{-1}\) are another indication of the presence of sulfonate groups due to the S=O stretching vibration. Babu has identified the sulfonate group at wave number 1158 cm\(^{-1}\).

![Infrared Spectrum of PDOS and PDO](image)

3.4. Interfacial Tension (IFT) and Particle Size Analyzer (PSA)

Figure 7 shows that the smaller surfactant concentration has been used for the reservoir well formulation X. The IFT value obtained is also high, more concentration of surfactant, experienced an increase in IFT value and reached a minimum number in the range of 0.3% surfactant. IFT scores
ranging from $10^{-3}$ mN/m or so-called ultralow IFT indicated that it could be used as a surfactant for EOR applications.

![Fig.7. Interfacial Tension (IFT) Graph](image1)

![Fig.8. Particle Size and Potential Zeta of PDOS](image2)

As previously mentioned, the surfactant size has an effect on the adsorption process by rocks, where the rock size in the maximum sandstone is 250 μm. The particle size of the surfactant is smaller than the standard size so that the surfactant could not be adsorbed by the surface of the rocks. Therefore, particle size analysis is also required. In figure 8, the PDOS with a mole ratio of 1:1 acid for 4 hours sulfonation has obtained PSA value of 4.723μm. Thus, the particle size of PDOS as an anionic surfactant has required in the EOR technique. Zeta potential value is a parameter that controls electrostatic interaction in dispersion particles [19]. In this case, Zeta potential may confirm that the surfactant solution is anionic because of the negatively charged (-). From the figure 8, PDOS with 1:1-mole ratio at 4 hours has a high zeta potential value, which is about \(-78.8\), an anionic.

4. Conclusion
Synthesis of an anionic surfactant has been carried out by sulfonation reaction with time variation of 2 hours; 4 hours and 6 hours and the mole ratio of sulfuric acid to polyethylene glycol oleate (PDO) ester are 1:0.5; 1:1; 1:1.5. Results of PDOS product analysis showed the optimum result at 1:1-mole ratio for 4 hours. Product characterization using FTIR exhibit a new peak at 1170 cm\(^{-1}\) (PDOS) indicating S = O bond for sulfonation process. Acid value, ester value, saponification value, and iodine value was obtained to confirm the synthesis of PDOS. The particle size was observed for PDOS at 4.723μm and zeta potential at -78.8. It has indicated that the anionic surfactant could be used in EOR system.

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