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JOINT CONVENTION YOGYAKARTA 2019, HAGI – IAGI – IAFMI- IATMI (JCY 2019)

Tentrem Hotel, Yogyakarta, November 25th – 28th, 2019

Bubbling Nitrogen Techniques for Esterification of Nonionic Surfactant for EOR Application

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Abstract

Many industrial sectors, especially cosmetics, food, and pharmaceuticals have high interest in surfactants, due to the unique chemical properties of the molecule which containing two groups with different polarity properties. Petroleum industry also has an interest for applying surfactants to increase oil production in mature oil fields which experience a decline in oil production. This method is known as Enhanced Oil Recovery (EOR) technology. The development of vegetable materials for surfactant synthesis is preferably in association with the abundant availability, renewable and environmentally friendly raw materials. In this research, surfactant synthesis was carried out using vegetable materials as a hydrophobic group and polyethylene glycol as a hydrophilic group that forming an ester. There are various techniques to produce esters, such as reflux technique using a condenser, the azeotrop technique using dean-stark, enzymatic techniques using enzymes from a bacterium, and the bubbling technique using nitrogen gas. Esterification of this nonionic surfactant was performed by nitrogen bubbling method with the oleic acid and polyethylene glycol (PEG) 400 as substrate. Since bubbling method are environmentally friendly without the use of organic solvents and economically efficient in large scale applications, this method was favorable to be conducted.

Reaction optimization was carried out through equivalent variations of oleic acid and PEG (1: 1.1; 1:2; 1:3; 1:4) and variations in

reaction time (3, 4, 5, and 6 hours). The ester product was identified by thin layer chromatography test for optimum condition determination. Confirmation the surfactant structure was performed by H1NMR. The optimized surfactant was further characterized by an interface tension test (IFT) to see the surfactant's ability to reduce IFT between water and oil. The results showed that the optimum conditions for esterification of Oleate-PEG 400 which produced the best reaction conversion was obtained with the equivalent ratio oleic acid and PEG 1: 3 and reaction time of 6 hours. The surfactant structure has been confirmed using H1NMR and able to decrease the oil and water interfacial tension up to 10^{-4} dyne/cm in brine salinity condition 18000 ppm and oil 34,39 °API

Introduction

In spite of the recent worldwide interest for alternative sources of energy, with especial and strategic interest in fuels derived from renewable products, the situation of petroleum in many countries stills drives much concern. Brazil, for example, is continuously advancing in the discovery of novel oil reservoirs and in the devise of potential ways to exploit oil both onshore and offshore. Many research projects are joining industry and university personnel, aiming to improve the technology to enhance oil productivity. In addition to the primary recovery techniques and several physical methods conceived as enhanced oil recovery (EOR) methods, the development of

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EOR processes based on operations which involve chemicals is greatly promising, many of which employing surfactants. Knowledge on the interfacial properties between oil, water and solid rock reservoirs, especially under extreme conditions, with occasional presence of natural gas, is important to better implement the EOR method (Gurgel et al., 2008).

In general, EOR chemical methods are classified in terms of the main chemical agents used to modify the equilibrium established in the reservoirs after recovery via conventional or physical methods. We particularly focus our attention on general EOR activities involving the use of polymers, surfactants, foams and certain chemicals such as alkali, or suitable mixtures containing them, as in polymer-alkaline, surfactant-polymer and alkaline surfactant-polymer (ASP) flooding mixtures (Li et al., 2000; Nedjhioui et al., 2005).

Surfactant molecular structures consist of two parts. One is called the hydrophilic group which is soluble in water and has hydrophilic nature. The other part is called the lipophilic group which is insoluble in oil but is not soluble in water and has lipophilic nature (Bhattacharya et al., 2011; Schramm et al., 2003; Czajka et al., 2015; Raffa et al., 2015). Two kinds of groups are in the opposite directions, and both ends are connected to bond in the same molecule, forming an asymmetric and polar structure. The structure is usually referred to "parent structure" (Amphiphilic structure) (Yuan et al., 2014). Surfactant molecules have amphiphilic structure including an affinity for water and an affinity for oil (Figure 1).

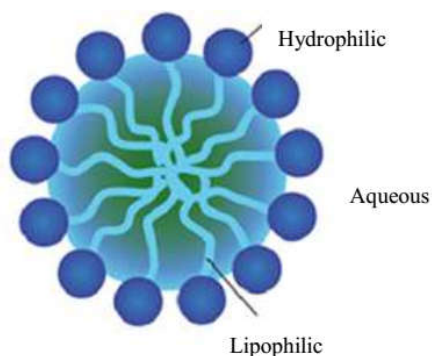


Figure 1. The structure of the surfactant

Surfactants are the compounds which can reduce the surface tension (or interfacial tension) of water by adsorbing at the water-air interface (or water-oil interface) (Snell et al., 1958; Gushe et al., 1959; Schramm et al., 2003; O'Rear, 2015).

There are many kinds of surfactants, and they are classified by use, properties and chemical structure. The surfactant classification depends on water dissociation and the structure of hydrophilic group (Schramm et al., 2003; . According to the water-soluble, surfactants can be classified into ionic surfactants and nonionic surfactants. Ionic surfactants can be divided into anionic surfactants, cationic surfactants and amphoteric surfactant. Special features or new type surfactant is as special surfactant (Wang et al., 2003; Zhang, 2001).

The hydrophilic group has common-COOH,-SO₃H, and a polyoxyethylene chain; lipophilic group has common-Si,-CF,-CF₂, and a polyoxypropylene chain. The hydrophilicity and lipophilicity of surfactant molecules change with molecule composition and structure. When the hydrophilic is stronger than lipophilic, it is the water-soluble surfactant; when hydrophilic is stronger than lipophilic, it is the oil-soluble surfactant. Water-soluble or oil-soluble reflects important physical and chemical parameters of surfactant application. It is an important basis for a reasonable choice of surfactant.

Current development of the majority of novel substances/ chemicals, irrespective of their intended use, is based on the Green Chemistry Program, established at the beginning of 1990s (Shonnard et al., 2007). Since then, the development of many green chemistry approaches and environment-friendly chemical syntheses have been driven by this program. Green chemistry is defined as the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances, whereas a hazard is anything that could have a negative effect on human health and the environment. Hence, a permanent priority for both chemical industry and academic community became the development of greener or more environmentally benign processes and materials (Jessop et al., 2015). Similar to

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other fields, industry needs are brought to the focus of academic work, which is achieved through continual communication and collaboration between industry and academia (Constable et al, 2007). In this manner, research areas are tailored according to the actual needs.

In the paper study the synthesis of vegetal-based nonionic surfactants with catalytic reactions and without solvents. The solvent azeotropic technique using ethyl acetate to reduce the concentration of water as a side-product was replaced by nitrogen gas. Replacing the function of ethyl acetate with nitrogen due to its non-toxic and environment-friendly nature, and the application of industrial-scale reactions will reduce production costs. Ini mengacu pada Green Chemistry. Di mana reaksi kimia diarahkan pada efek kesehatan dan lingkungan

Data and Method

Technical grade oleic acid from palm oil and PEG-400 were used as raw material of the surfactant. Nitrogen technical grade were used as azeotropic agent with a by-product water. Sulfuric acid, sodium sulfate anhydrate, and cerium sulfate pentahydrate with analytical grade were used for product analysis. Crude oil "A" with 34.39 °API was used for IFT measurement.

1. Screening of Bubbling Nitrogen

Oleic acid with 70% purity was reacted with PEG-400 by the mol equivalent ratio 1:1.1 as much as 7.05 grams and 11 grams of PEG-400 in the presence of 10 % mol sulfuric acid (0.13 mL) as catalyst. The reaction runs with nitrogen flow and heated up to 100°C. Thin layer chromatography (TLC) was used to monitor the reaction with the cerium sulfate tetrahydrate ($\text{CeSO}_4 \cdot 4\text{H}_2\text{O}$) as the staining reagent. Esterification product was then identified by Spinsolve 43 MHz Proton Magritek and .

2. Optimization of esterification

In order to obtain the highest yield, optimization were accomplished by varying equivalent ration of oleic acid and PEG-400 as follows 1:1,1; 1:2; 1:3 and 1:4. The addition of catalyst sulfuric acid and nitrogen flow with

heated up to 100°C. Reaction was monitored by TLC method and the structure was confirmed by NMR 43 MHz.

3. Interfacial tension (IFT) measurement

The ability of surfactant to decrease the IFT of oil and water as the main function of surfactant was evaluated by measuring the IFT using Spinning Drop Tensiometer TX-500 C/D. Surfactant solution with different concentration at 18000 ppm salinity was prepared and filled into the IFT tube. Two microliters of oil was added and put into the IFT unit. Setting the device at 60 °C and run the measurement at 6000 rpm.

Result and Discussion

1. Screening of Bubbling Nitrogen

The esterification reaction carried out is the development of the solvent azeotropic technique. The esterification reaction products not only produce esters, but also water as a side-product. The esterification reaction is a reversible reaction.

A reversible reaction is a type of reaction that takes place in two directions when equilibrium is reached. Reaksi ketika keseimbangan dapat terjadi terhadap pembentukan produk, tetapi juga terhadap dekomposisi produk. To increase the conversion of reactions can be done by several techniques following the principle of Le Chatelier which reads "When a system at equilibrium changes in concentration, temperature, volume, or pressure, the system adjusts itself to negate the effect of the changes applied and the new balance is achieved".

Based on this theory, an increase in the rate of reaction towards product formation can be done by reducing the amount of product formed during the reaction. So that the reaction equilibrium will shift towards the formation of a product that will increase the reaction conversion.

The esterification is the reaction between a carboxylic acid and an alcohol with an ester as the main product and water as a by-product.

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Water produced as a side-product can be removed by the technique of flowing nitrogen gas into the mixture continuously. With the hope that the water formed will evaporate with nitrogen. So it is expected that the reaction will continue in the direction of product formation. The reaction was carried out with an equivalent ratio of oleic acid 1: 1.1 with PEG-400. The reaction is monitored every hour. It aims to analyze esterification products by using bubbling nitrogen to form esters and to determine the optimum reaction time.



Figure 2. The Chromatogram of reaction for the 1st hour (a) Oleic acid and (b) Crude reaction; Eluen *n*-hexsane:ethyl acetate (8:2)

Based on the TLC results (Figure 2) shows a new polar stain compared to the substrate of oleic acid. PEG-400 stains cannot be seen using cerium sulfate stain. The TLC chromatogram shows the esterification reaction of oleic acid and PEG-400 can take place using nitrogen bubbling. Then the reaction is continued for up to 6 hours of reaction. Every hour monitoring is carried out.



Figure 3. The Chromatogram of reaction for the 1st until 6th hour (s) Oleic acid and (1st until 6 th) Reaction time; Eluen *n*-hexsane:ethyl acetate (8:2)

The results of monitoring using TLC showed a significant change in reaction conversion per hour to the fourth hour (Figure 3). This is indicated by the thickness of the stain of the oleic acid substrate which decreases from the first hour to the fifth hour. But from the fourth

hour to the sixth hour it does not show significant substrate reduction and can be considered the same. Thus the reaction is stated to have reached its optimum condition with these conditions. Then the results of the work up a reaction using a salt solution to remove the remaining unreacted PEG-400 and acid catalyst. The product of the subsequent reaction is measured ¹H NMR to prove the product formed is the desired ester.

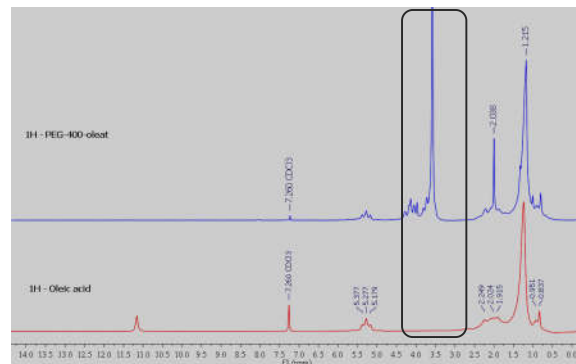


Figure 4. The spectrum of ¹H NMR oleic acid and PEG-400-oleate

Combining the spectrum of measurement results of ¹H NMR substrate and reaction products (Figure 4). The combined spectrum shows the emergence of new peaks in the 3-4.5 ppm area of the friction shift. The peak of the chemical shift area 3-4.5 ppm is the peak that shows the hydrogen atom bond on the oxygenated carbon. This shows that oleic acid and PEG-400 ester products have been formed.

Because the esterification reaction between oleic acid and PEG-400 is a chemoselective reaction to the ester product formed. Two possible ester products formed are PEG-400-oleate and PEG-400-dioleate (Figure 5). Because the desired ester product is a PEG-400-oleic ester. Thus the amount of PEG-400 used in the reaction must be more than the number of moles of oleic acid.

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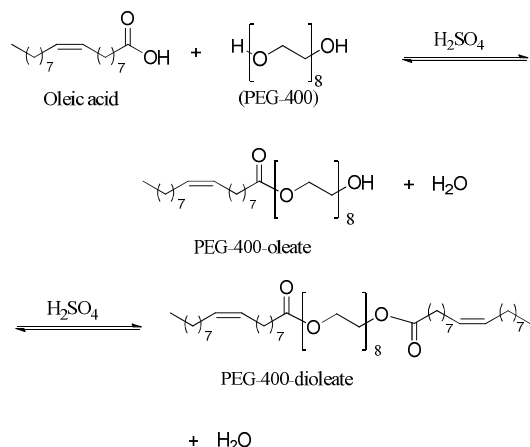


Figure 5. Esterification of oleic acid and PEG-400

In the reaction screening, the mole equivalent of oleic acid is 1: 1.1 with PEG-400. To show the ester product formed is monooleate or dioleate, it is necessary to compare the integration between the alkene part and the region of the oxygenated protons that form the ester. If the ratio between alkene integration and the integration of oxygenated protons 1:18 shows that the formed ester is PEG-400-oleate. Conversely, if the comparison between the integration of alkene protons and oxygenated protons 1:36 shows the ester formed PEG-400-dioleate.

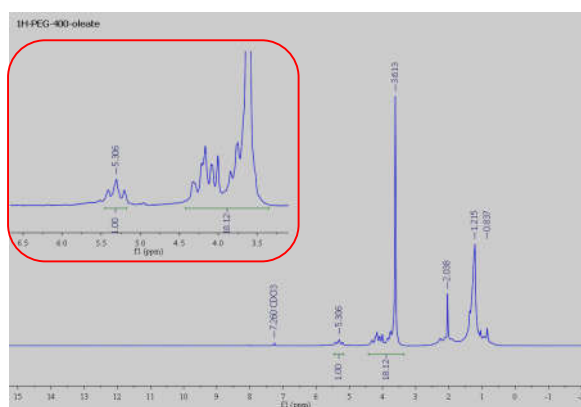


Figure 6. The spectrum of ¹H NMR PEG-400-oleate

Based on the results of the proton spectrum analysis of the product (Figure 6) shows a comparison between the alkene protons (protons in double bonds) and oxygenated

protons (polyethylene glycol chain protons) showing a ratio of 1: 18. This shows that the ester product formed is a PEG-400-oleic ester. The reaction product selectivity is also influenced by the equivalence ratio between oleic acid and PEG-400 used and not influenced by reaction time (Abdullah et al, 2017).

2. Optimization of esterification

In order to obtain the highest yield, optimization were accomplished by varying equivalent ration of oleic acid and PEG-400 as follows 1:1,1; 1:2; and 1:3. The addition of catalyst sulfuric acid were at the same amount with the previous reaction. Reaction was monitored by TLC method.

Based on the TLC results of each reaction for 6 hours, the most optimum reaction was achieved with an equivalent ratio of 1: 3 oleic acid with PEG-400. The TLC chromatogram showed a reaction with an equivalent ratio of 1:3 and 1:4 oleic acid with PEG-400 having no substrate stain (Figure 7). This proves that the reaction lasts 100% towards the formation of an ester product. This is in accordance with the principle of equilibrium, where when increasing the mole of one substrate, the reaction will shift the equilibrium towards the opposite. Thus the number of products from the reaction will increase. The increase in reaction conversion in this way applies to reactions that are reversible. Some other ways that can be done are like using the nitrogen bubbling technique to reduce the amount of water that is formed during the reaction. While other ways can also be done to optimize the reaction with variations in pressure and volume.



Figure 7. Profile results of TLC chromatograms

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3. Interfacial tension (IFT) measurement

Synthesized surfactants at optimum conditions were tested for IFT values to see their ability to reduce the interfacial tension of water and oil. The results showed that surfactant was able to decrease the IFT to the ultralow level 10^{-3} dyne/cm in the range of 0.3-1.0% w/w (Figure 8), which indicating the good performance of mixed PEG-400-Oleate surfactant, and potential to be used as chemical injection for chemical flooding EOR.

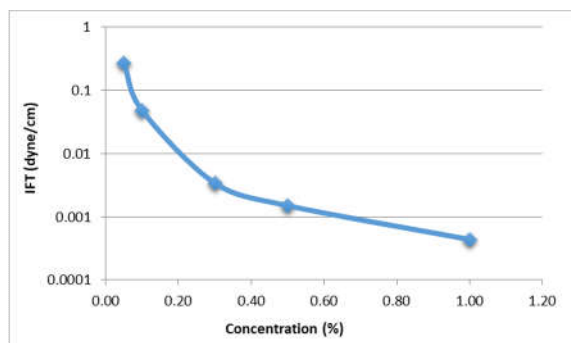


Figure 8. IFT of esterification product PEG-400-Oleate

Conclusions

The esterification reaction of the nitrogen bubbling technique was successfully carried out to obtain a PEG-400-Oleate Ester. The optimum condition with the best conversion is the equivalent ratio of 1: 3 oleic acid and PEG-400 with 10% mol sulfuric acid as a catalyst. The product of the reaction is identified using $^1\text{H NMR}$ 43 MHz. The IFT measurement proved that mixed-surfactant is having the ability to lower the IFT of oil and water levels, which can be used as a candidate for chemical flooding EOR.

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