The Effect of Clay Content in the Adsorption of Surfactant by Reservoir Rock in the Enhanced Oil Recovery Process

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Abstract. Surfactant flooding aims at lowering the interfacial tensions between the oil and water phases to improve the displacement efficiency during oil recovery. However, high adsorption of surfactant by reservoir core is undesirable since it could decrease the ability of surfactant to reduce the interfacial tension between oil and brine which makes injection ineffective. This study was done to get better understanding of the effect of clay content on oil displacement. The procedures of adsorption process are as follows: crushed core were put into flasks which filled with surfactant and heated up at different temperature for three days operation. The clean solution was then measured its absorbance using UV spectrophotometer. The result of adsorption experiments show that the adsorption decreased up to 25 % when temperature was increased from 25 to 70 oC. The experimental for studying the effect of clay content on the adsorption also shows the right behavior. The experimental results also show that adsorption of surfactant is higher in the clean core than in the core filled with oil. This phenomenon is true since the contact area between surfactant and core is much higher when the core is clean. The oil displacement experiments show that the oil recovery also depends on type of reservoir rock used in the process.

1. Introduction

The production of some reservoir wells in Indonesia (old wells) decline after being exploited years by years. The alternative ways to increase oil production can be done by finding new wells or using new technology for the old wells. The cost of finding a field is extremely expensive, because the chance of a successful oil well drilling is very low. It took about a million dollar per well. Due to this expensive cost, the alternative ways will be the interesting for researches in order to increase the crude oil production. Secondary and tertiary recovery (Enhanced Oil Recovery / EOR) is at present to be the good choice. Chemical Enhanced Oil Recovery refers to processes in which alkali, surfactants and/or polymers are being used to lower interfacial tension, change the wet ability, and control mobility in order to increase the amount of oil recovered from a previously water-flooded reservoir. After a long term water-flooding process, some amount of oil is left trapped in the reservoir due to a high capillary pressure. To get movable oil, surfactant agents are introduced into the reservoir to increase oil recovery by lowering the interfacial tension between oil and water [1].

Several methods of EOR are encouraging in Indonesia as well as in the world today. In compliance with this, research in the area of EOR is still carried out by many examiners. In fact, experiments are becoming more and better developed. One of these research areas is in the exploitation of chemicals for seeking the enhancement of oil recovery. Surfactant flooding is a well-known concept that has been practiced in the field for many decades. Current technology is a progressive and gradual development of technologies and ideas that have existed for a long time. Surfactant flooding is usually carried out after a water flood. There are two main types of surfactant flooding – Alkaline Surfactant Polymer (ASP) or Surfactant Polymer (SP) flooding. Even though several experiments have been done in this area, the application in the field often fails. This not only is caused by expensive cost of chemicals, but also because the process as it is applied in the field is not compatible with the process in the laboratory. Surfactant flooding is considered to be a method of additional recovery of oil from partially depleted reservoirs. The mechanism of action of the surfactant in a porous medium, partially filled with oil and brine, is still not very well understood. There are still many problems that need to be solved in the area of EOR basic research to allow that research to be applied in the field for improving oil
recovery. The complexity of the system increases with the effects of other parameters, such as: heterogeneity of the rock, interaction of the surfactants with reservoir fluids, coalescence of the oil drops and surfactant adsorption.

One of the main challenges in this process is the loss of surfactant due to adsorption on formation rocks. Surfactant adsorption is a process of transfer of surfactant molecules from bulk solution phase to the surface/interface. Surfactant adsorption in porous media at the solid-liquid interface play an important role and is one of the major criteria which decide the economic viability of surfactant flooding in chemical enhance oil recovery applications. In fact, high adsorption of surfactant can make the chemical EOR processes economically-unfeasible [2, 3, 11, 13]. In the surfactant injection for EOR process, the surfactant adsorbed by reservoir core is caused by clay content in the core. High adsorption of surfactant by reservoir core is undesirable since it could decrease the ability of surfactant to reduce the interfacial tension between oil and brine which makes injection ineffective. Besides, for clay minerals in reservoir rocks, their presence has an important impact upon reservoir properties such as porosity and permeability.

This study was done to get better understanding of the effect of clay content on oil displacement. Clay minerals can occur as pore-linings, pore-bridging, and/or pore-fillings in sandstone, so clay minerals can greatly reduce permeability by effective blocking pore throats of the fluid flow routes. Another important feature of clay mineral is their ability to swell and ability in cation exchange in the presence of water.

2. Experimental

2.1. Chemicals and crude oil used in the process

All chemicals needed for this experiment were obtained from the laboratory and have very high purity. The crude oils used for the experiments were the Indonesian crude oils.

2.1.1. Surfactant. Surfactant used for this experiment was synthesized in our laboratory. A good surfactant has to have two parts in its molecule: oil soluble portion (lipophile) and water soluble portion (hydrophile), and sometimes called amphiphile because of its dual nature. Usually aliphatic and aromatic hydrocarbons are considered as oil soluble portion, whereas the sulphonate or sulphate polar head are considered to be the water soluble portion.

The surfactant produced in this research is mainly Sodium Ligno Sulfonate (SLS) from waste of pulp industries and from waste of palm oil industries. The experimental procedure is as follows: first, the palm oil husks at a certain weight were put into an autoclave while added with Sodium Hydroxide solution at a certain amount and concentration. The mixture was then heated while stirred at a desired temperature. In this process, the length of the hydrolysis process was also varied. The procedure of isolation of lignin produced in this study is similar to the lignin isolation from black liquor [4, 5].

From this experiment, black solution was obtained as product of hydrolysis. This black solution is similar to the black liquor produced by paper industries. In this study, lignin was bound as sodium lignate which could be separated in the acid atmosphere using chloroform. The procedure of lignin isolation is as follows. In the first step of the study, isolation of lignin was done by precipitation using acid. The procedures of precipitation are as follows: firstly, the black liquor was combined with concentrated chloric acid and continuously stirred. The addition of acid was stopped when the solution reached a predetermined degree of acidity (pH). Secondly, chloroform was added to the solution to make precipitation and filtering of sediment easier. The sediment which formed was then filtered and washed using dilute chloric acid. To get a high purity of lignin, the washing was done for several times. The last step was to dry the sediment at 45°C for several hours.

The lignin formed from the above procedures was processed further to become SLS. The procedures of sulphonation are as follows: lignin formed from the precipitation was diluted and combined with sodium hydroxide and then mixed for several minutes. Then oleum was added while mixed continuously. The mixture was dried for several hours.

The results of hydrolysis process show that maximum temperature achieved was 170°C while the length of the cooking process was one hour. The incremental of temperature results a better hydrolysis reaction. However, at high temperature, lignin is degraded to be other materials resulting the decrease of lignin production. This condition is shown at temperature of 200°C.
2.1.2. Characteristic of rock. The rock used as an adsorbent was obtained from several fields in Indonesia having variety in permeability and porosity. All rock samples analyzed were cut from cores. The core was mechanically grinded to a powder with an average particle size of 50–30 mesh and dried well before use. The porosity and permeability were measured using Helium Porosimeter whereas the clay content was measured using Gamma Ray Index in the Geological Department.

2.2. Procedure of measuring adsorption
The procedures of adsorption process are as follows:
1. Surfactant at a certain concentration was put into several reaction flask and then crushed core were put into those flasks slowly. 2. Water bath was turned on to heat the mixture up to the desired temperature for 5 hours per day during 3 days operation. To see the effect of temperature, the water bath was set at three different temperatures: 25, 40, and 70 °C. After three days of operation, the solution was then filtered using very fine filter paper. The clean solution was then measured its absorbance using UV spectrophotometer. From the figure of relationship between the absorbance and concentration of lignin, the surfactant concentration can be determined.

*Figure 1. Schematic diagram of equipment set up for adsorption experiment*

The concentration of surfactant after mixing is compared with that before performing adsorption to measure the amount of surfactant loss due to adsorption. Adsorption is found by calculating the difference between the concentrations of the surfactant in the solution before and after equilibrium with the rock.

2.3. Oil displacement process
The effectiveness of the chemicals was tested through micro displacement using artificial porous medium.

2.3.1. Experimental set-up. Figure 2 shows the schematic diagram of the oil displacement apparatus. The flow rates of oil, water and surfactant were controlled using flow meters. The porous media used in the oil displacement process were core-blocks and core prepared from stainless steel cylinder and contain fine crushed core which is proposed to be an artificial reservoir with dimension about 3.75 cm ID x 10.8 cm L. The porosity of the porous media was between 20 and 40 %. For the stainless steel cylinder, the cores were crushed to 30 / 60 mesh size which resulted in a mean particle size of 2.41 x 10-4 m in diameter. Porosity of a rock depends on the pore or grain size distribution, in which the small grains can fill the space between larger grains. Porosity is a strong function of grain size distribution (sorting).

2.3.2. Procedure of operation. The procedure is as follows: initially the reservoir model was filled with brine (1 to 3 % salt concentration) until it was 100 % saturated. Then, to represent oil migration, oil was injected into the medium until minimum water saturation (Swc) of about 30 % is reached. After this, the medium was flooded by the same brine until minimum oil saturation, Sow, which was about 10 %. The oil remaining in the reservoir after this water flood was then subjected to various injections of different chemicals for further oil recovery.

*Legend :*
1. Pressurized gas
2. Oil tank
3. Brine tank
4. Surfactant tank
5. Porous media
6. Collector
Figure 2. Schematic diagram of equipment for oil displacement experiment

3. Results and discussion

3.1. Lithology, Texture and Composition of the Core.

Mudrock in thin section shows matrix supported poorly sorted grain, with angular to sub rounded shape. It composed of monocrystalline quartz, feldspar, biotite and heavy minerals as grains; whereas fine silt occurs as matrix. Quartz has some small vacuoles and needle shaped mineral inclusions. Some feldspar has been partly or totally replaced by clay minerals. It has partial dissolution, inhomogeneity packing and corroded grains porosity. Table 1 shows the characteristic of core used in this experiment.

Table 1. Characteristic of rock

| No | Type of rock     | Clay content (%) | Porosity (%) | Permeability (mD) |
|----|------------------|------------------|--------------|------------------|
| 1  | Sand stone       | 5.8              | 32.4         | 249.4            |
| 2  | Volcanic stone   | 20.4             | 25.2         | 180.8            |
| 3  | Carbonate stone  | 28.5             | 11.7         | 119.4            |

Clay minerals can occur as pore-linings, pore-bridging, and/or pore-fillings in sandstone, so clay minerals can greatly reduce permeability by effective blocking pore throats of the fluid flow routes. Another important feature of clay mineral is their ability to swell and ability in cation exchange in the presence of water. The relationship between cation exchange capacity (CEC), clay content more than 5 (five) %, and permeability can be seen. The CEC will increase relative to the increase of clay content. Therefore, in this experiment the clay content was chosen as one variable in the oil displacement process.

3.2. Adsorption experiment

The result of adsorption experiments are presented in Figure 3. Adsorption and desorption processes are dynamic processes in which molecules are continually transferred between the bulk liquid and solid surface. Adsorption and desorption of chemicals in soils depend upon various factors like soil pH, temperature, clay content, organic matter and metal oxides.

The figures show that the adsorption decreased when temperature was increased. The experimental for studying the effect of clay content on the adsorption also shows the right behavior. Further experimental results also show that adsorption of surfactant is higher in the clean core than in the core filled with oil, effect of organic matter. This phenomenon is correct since the contact area between surfactant and core is much higher when the core is clean. Whereas when the oil is presence in the core, some of the surface area is covered by the oil.

It has been observed that an increase in temperature leads to considerable decrease in the maximum quantity adsorption of surfactants. The lower the temperature, the higher the maximum of surfactant adsorbed. This decrease in maximum adsorbed at higher temperature is expected as an increase in the kinetic energy of the species. Consequently, there is an increase in the entropy of the system, which results in a decrease of aggregate organization on the surface of the adsorbent [6].

Further studies by Durovic et al., [7] who studied the adsorption of some chemicals in the soil containing clay, also show the same behavior that increasing in clay content results in increasing adsorption of chemical in the solution.
Figure 3. Results of adsorption experiment

Chain length is also an important factor in determining the adsorption behavior of a surfactant. There have been studies on effect of surfactant chain length on surfactant adsorption. With the increasing hydrocarbon chain length of the surfactant molecules become more hydrophobic, which leads to the change in bulk properties of the solution. As a general rule, in aqueous medium, the greater the dissimilarity between the surfactant and solvent, the greater the aggregation number. As a result, surfactants with longer hydrocarbon chains have a much greater driving force for the aggregation [8].

Surfactant adsorption is a process of transfer of surfactant molecules from bulk solution phase to the surface/interface. The adsorption of surfactant at the solid–liquid interface plays an important role in many technological and industrial applications, especially in Oil and Gas industries due to high amount surfactant needed for EOR. In the surfactant injection, the surfactant adsorbed by reservoir core is caused by clay content in the core. High adsorption of surfactant by reservoir core is undesirable since it could decrease the ability of surfactant to reduce the interfacial tension between oil and brine which makes injection ineffective. Such adsorption of surfactants on solid can lead to changes in a variety of interfacial phenomena such as wetting behavior (oil displacement, flotation, and detergency) and colloid stability (dispersion, flocculation). This experiment was done to get better understanding of the effect of clay content on oil displacement. The results show that the lower the clay content in the reservoir rocks, the better of oil displacement can be achieved.

3.3. Oil displacement

In the EOR process, after injection of water (water flooding), some oil is still left in the reservoir due to high viscosity or high interfacial tension (IFT) between oil and the reservoir rocks. Therefore, after injection of chemicals, especially surfactant, which are able to decrease the IFT, more oil can be recovered. A good surfactant has to have two parts in its molecule: oil soluble portion (lipophile) and water soluble portion (hydrophilic), and sometimes called amphiphile because of its dual nature. Usually aliphatic and aromatic hydrocarbons are considered as oil soluble portion, whereas the sulphonate or sulphate polar head are considered to be the water soluble portion. To ensure that the porous media itself was not active, the experiments for oil displacement were conducted in an artificial porous medium.

Figures 4 troughs 6 show the results of oil displacement for different clay content in different types of core namely sandstone, volcanic stone and carbonate stone. The experiment of oil displacement in Figure 4 used the core prepared from stainless steel cylinder and contain fine crushed core. The porous media used in the oil displacement process depicted in Figures 5 and 6 were core-blocks.
From the figures, it can be seen that the lower the clay content in the reservoir rocks, the better of oil displacement can be achieved. The nature of the surfactants, minerals and solution conditions as well as the mineralogical composition of reservoir rocks play a governing role in determining the interactions between the reservoir minerals and externally added reagents (surfactants / polymers) and their effect on solid-liquid interfacial properties such as surface charge and wet ability [9, 10]. In addition, the formation water having salinity between 7000 and 11000 also pH between 7.9 and 9 contribute to the oil displacement results.
4. Conclusions

Oil displacement plays an important role in enhanced oil recovery. It has been shown that oil displacement is affected by many factors including surfactant / polymer, mineralogical composition, and solution conditions such as pH and salinity. The adsorption surfactant at various conditions onto reservoir rock was investigated in this study. Static adsorption experiments at various salinity and temperature conditions were performed. Based on the results of surfactant adsorption experiments using reservoir rock, the following conclusions can be drawn: an increase in temperature leads to a considerable decrease in the maximum quantity adsorption of surfactants, the surfactant adsorbed by reservoir core is caused by clay content in the core, and lower the clay content in the reservoir rocks, the better of oil displacement can be achieved.

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