The Initial Comparison Study of Sodium Lignosulfonate, Sodium Dodecyl Benzene Sulfonate, and Sodium p-Toluene Sulfonate Surfactant for Enhanced Oil Recovery

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Abstract. Surfactant (surface active agent) exhibit numerous interesting properties that enable their use as additional component in mobilising of residual oil from capillary pore after secondary recovery process using gas injection and water flooding. In this study, Sodium Lignosulfonate (SLS) surfactant was successfully synthesized by applying batch method using lignin from oil palm empty fruit bunches as precursor. Furthermore, its performance in reducing interfacial tension of crude oil and formation water colloidal system was compared with commercial available surfactant including Sodium Dodecyl Benzene Sulfonate (SDBS) and Sodium p-Toluene Sulfonate (SpTS). The synthesized SLS surfactant was characterized by using Fourier Transform Infrared (FTIR) spectroscopy. Meanwhile, its performance in reducing interfacial tension of crude oil and formation water colloidal system was analyzed by using compatibility test, phase behaviour analysis, and interfacial tension (IFT) measurement. The compatibility test shows that SLS, SDBS, and SpTS surfactants were compatible with formation water. In addition, the phase behaviour analysis shows that SLS surfactant was better than SpTS surfactant, while SDBS surfactant generates the highest performance proved by the best microemulsion formation resulted by SDBS. Furthermore, the optimum concentration of SLS, SDBS, and SpTS surfactants in reducing the interfacial tension of crude oil and formation water was 1.0%. The IFT measurement indicates that the performance of SLS with the value of 1.67 mN/m was also better than SpTS surfactant with the value of 3.59 mN/m. Meanwhile, SDBS surfactant shows the best performance with the IFT value of 0.47 mN/m.

1 Introduction

Enhanced oil recovery (EOR) is a well-known technology that usually applied to improve oil production in the petroleum industry. EOR based on chemical compound called as surfactant (surface-active agent) exhibit numerous interesting properties that enable their use as additional component in mobilising of residual oil from capillary pore [1-2] Surfactants are used in various field due to their interesting physicochemical characteristics such as foaming, detergency, dispersion, and emulsification ability. It is an amphiphilic compound consists of non-polar lyophobic part called as tails group and polar lyophilic part called as head group. This amphiphilic structure is responsible for their role as a third component that adsorbs onto oil and water interface to reduce their interfacial tension. [3]
One type of surfactant that potential to develop is Sodium Lignosulphonate (SLS) which can be synthesized using lignin. Lignin is a compound that can be isolated from oil palm empty fruit bunches which is a waste or main byproduct of palm oil industries. This waste is not optimally used, and then it is possible to use it as a raw material in the synthesizing of SLS surfactant. This isolation process can be conducted using batch method with the highest yield of lignin in the amount of 14%. [4] Furthermore, the SLS surfactant can be resulted from the reaction between lignin as a precursor and sodium hydrogen bisulfite (NaHSO₃) as a sulfonating agent. The optimum condition on the synthesizing method of SLS surfactant has been previously reported, [5] hence is important to compare synthesized SLS surfactant with another surfactant, in order to observe their ability in reducing the surface tension of crude oil and formation water.

In this case, the SLS surfactant is can be compared with the commercial surfactant such as Sodium Dodecyl Benzene Sulfonate (SDBS) and Sodium p-Toluen Sulfonate (SpTS). SDBS is a famous surfactant that has been used in various field such as carbon nanotube dispersing agent [6] and heavy metal adsorption. [7] On the other hand, SpTS is a commercial surfactant that has similar structure with SDBS, but SpTS has shorter hydrophobic chains than SDBS. When compared to SLS surfactant, SDBS and SpTS have smaller hydrophobic chains. These structural differences are interesting to study, especially in their application for EOR technology.

Here, we report the initial comparison study of SLS surfactant with two commercially available surfactants including SDBS and SpTS. In the researcher knowledge, there is no reported study on the comparison of these three surfactants in EOR technology. This study is important to provide additional information about the suitable surfactant structure in EOR technology. The compatibility test, phase behaviour analysis, and interfacial tension (IFT) measurement were used to observe the surfactant ability in reducing interfacial tension of crude oil and formation water colloidal system.

2 Experimental

2.1 Material

The chemical used in this study were NaHSO₃ (Sigma Aldrich), NaOH (Sigma Aldrich), H₂SO₄ (Merck), and methanol. SDBS and SpTS were purchased from Sigma Aldrich and directly used without purification.

2.2 Synthesis of SLS Surfactant

Oil palm empty bunches were put into autoclave, which then added by the mixture of NaOH solution and ethanol with the ratio of 1:1. The system was heated at temperature of 170 °C (15 atm) for 5 hours. After filtration process, the resulted black liquor was acidified using H₂SO₄ 10% until pH 1. The mixture was then allowed to produce lignin precipitation for 8 hours. In addition, 0.1 M of dried lignin was sulfonated by NaHSO₃ solution (0.3 M) using reflux method for 4 hours at the temperature of 97 °C. The sulfonation product was then dried in the oven to produce brown powder of SLS surfactant.

2.3 Characterization

The SLS surfactant was characterized by Fourier Transform Infrared spectroscopy using KBr pellet technique (FTIR, Shimadzu Prestige-21). Furthermore, the performance of all surfactant in reducing interfacial tension of crude oil and formation water were analyzed by using compatibility test, phase behaviour analysis, and interfacial tension measurement (IFT meter TX500D).
3 Result and Discussion

3.1 FTIR Analysis

FTIR spectroscopy was used to understand the substitution of hydroxyl group (OH) by sulphonate group (-SO₃⁻) in the benzylic carbon of lignin structure. As can be seen in Figure 1, this substitution can be observed by the presence of FTIR absorption peak at 1465 cm⁻¹ corresponds to SO₂⁻ bending vibration. In addition, it is also can be identified by the band at 1118, 1026, and 826 cm⁻¹ which are resulted from S=O asymmetric stretch, S-O stretch (1), and S-O stretch (2), respectively, indicates that this compound is sodium lignosulfonate.

3.2 Compatibility Test

This test was performed to observe the compatibility of surfactant and formation water in a reservoir. It is expected that the formed mixture is a perfect solution or colloid. The suspension is not allowed due to it can be a barrier when the surfactant solution injected into the rock.[8] As can be seen in Figure 2, the SDBS and SLS surfactants produced a perfect solution, while SpTS surfactant generates a fine solution with small amount of un-soluble surfactant residue. Hence, it can be identified that SLS, SDBS, and SpTS surfactants were compatible with formation water.
3.3 Phase Behaviour Analysis

Figure 3. Phase behaviour analysis of crude oil/formation water with (a) no surfactant, (b) SDBS 0.5%, (c) SBDS 0.75%, (d) SDBS 1.0 %, (e) SLS 0.5%, (f) SLS 0.75%, (g) SLS 1.0%, (h) SpTS 0.5%, (i) SpTS 0.75%, and (j) SpTS 1.0%.

The phase behaviour analysis of SLS, SDBS, and SpTS in the crude oil and formation water colloidal system were shown in Figure 3. The concentration of SLS, SDBS, and SpTS surfactants were varied in 0.5; 0.75; and 1.0%. It is known that SLS surfactant was better than SpTS surfactant, while SDBS surfactant generates the highest performance proved by the best microemulsion formation. Furthermore, the optimum concentration of SLS, SDBS, and SpTS surfactants is 1.0%.

3.4 Interfacial Tension (IFT) Measurement

The interfacial tension (IFT) measurement is an important method to identify the effect of surfactant in the reducing interfacial tension of crude oil and formation water colloidal system. In this respect, the presences of surfactants have a vital role to reduce the interfacial tension between crude oil and formation water. The surfactant concentration used in this measurement was 1%. As can be seen in Table 1, the result shows that the performance of SLS surfactant was better than SpTS surfactant with the value of 1.67 and 3.59 mN/m, respectively. Meanwhile, SDBS surfactant shows the highest performance with the IFT value of 0.47 mN/m.

| No. | Surfactant Name | Surfactant Concentration (%) | Surfactant Density (g/cm³) | IFT (mN/m) |
|-----|----------------|-------------------------------|---------------------------|------------|
| 1   | SLS            | 1                             | 1.0076                    | 1.67       |
| 2   | SDBS           | 1                             | 1.0075                    | 0.47       |
| 3   | SpTS           | 1                             | 1.0005                    | 3.59       |
4 Conclusion
In conclusion, SLS surfactant was successfully synthesized by applying batch method using lignin from oil palm empty fruit bunches as a precursor. Its performance in reducing interfacial tension of crude oil and formation water colloidal system was analyzed by using compatibility test, phase behaviour analysis, and interfacial tension measurement, which then compared with two commercial surfactants called as Sodium Dodecyl Benzene Sulfonate (SDBS) and Sodium p-Toluene Sulfonate (SpTS). It is observed that the ability of that surfactants in reducing interfacial tension of crude oil and formation water follows the order of SDBS > SLS > SpTS.

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