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Thermal Stability Test and Formulation of Sodium Lignosulfonate with Isoamyl Alcohol as EOR Surfactant

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Abstract

Sodium lignosulfonate (SLS) is a promising low-cost surfactant that can be prepared from biomass. There has been large interest to utilize SLS as a chemical Enhanced Oil Recovery (EOR) surfactant. For that purpose, SLS is often mixed with other chemicals such as alcohols. The aim of this study was to find the best formulation of mixed-surfactant and to perform its thermal stability. The resulting mixed-surfactant was then characterized with variety of tests: aqueous stability, phase behavior, and IFT values. We found that a mixture that consists of 50 wt.% SLS, 30 wt.% Isoamyl Alcohol, and 20 wt.% of Palm Fatty Acid Distillate (PFAD) soap gave ultralow IFT at 1.864 × 10^{-3} mN/m. Phase behavior test shows that 1 wt% of mixed-surfactant formed a Winsor Type III. Subsequently, thermal stability test was conducted at 70°C for 90 days. The results showed that the IFT value fluctuates within the range of 10^{-3} mN/m for the first three weeks. After three weeks, the IFT values tend to increase to 10^{-2} mN/m until the end of the test. Hence, although ultralow IFT was achieved in the beginning of the test, further study is needed to improve the long-term stability of the present mixed-surfactant.

Keywords: *EOR; SLS; formulation; iso-amyl alcohol; thermal stability.*

Introduction

Surfactant injection is one of promising technique to improve oil production. When water was added to a low concentration of surfactants, commonly referred to as detergent injection or micro-emulsion, the interfacial tension between the surface characteristics of the rock and the oil-water mixture was reduced. Sulfonate-based surfactants were one of the many varieties of surfactants that were available and were frequently utilized for Enhanced Oil Recovery (EOR). Sodium lignosulfonate (SLS), which can be produced from lignin, is one of sulfonate-based surfactant that has attracted large interest. Due to the presence of a negative charge on its hydrophilic component, SLS was classified as an anionic surfactant. SLS was water soluble surfactant due to the presence of sulfonate (SO^{3-}) and salt ($NaSO^{3-}$) groups which act as the head and the rest of hydrocarbon groups as tail (Azis, et.al., 2017). For EOR application, SLS surfactants have been shown to lower the interfacial tension between the two liquid phases.

Low IFT values must be maintained by surfactants under a variety of reservoir conditions and oil properties. Therefore, obtaining surfactants with acceptable capabilities for EOR applications required suitable formulation. There are several methods to improve performance of EOR surfactants, for instance, alkyl polyglucoside (APG) cosurfactants have been reported to be added to alkyl ether carboxylate (AEC) surfactants, several alcohols were also added to petroleum sulfonates surfactant solution, and recently silica nanoparticles have also been mixed with sodium lignosulfonate surfactant to improve the surfactant ability (Azis, et.al., 2021; Borthakur, et.al., 1996; Wei, et.al., 2018; Zulkifli, et.al., 2020).

Wei, et. al (2018) showed that addition of isoamyl alcohol can reduce the value of IFT, while also changing the adsorption behavior of surfactant solutions. Several tests must be carried out to evaluate the suitability of surfactant formulation that gave the best performance. The solubility test was the first screening test to see if a type of surfactant was compatible with the formation water of a reservoir. The single phase or absence of precipitation in the surfactant solution that passes the test was one of important characteristic of the surfactant solution. The phase behavior test was also an important consideration when determining if a surfactant could be used in surfactant injection technology. The phase behaviour test goal was to quickly choose different ratios and concentrations of surfactants to identify the ideal formulation or combination of surfactants to create the middle phase type. The IFT test was carried out to test the surfactant's ability to transport oil through the pores of rock. A surfactant solution with an IFT value of 10^{-3} mN/m was the surfactant solution that passed this test (Anas, et.al., 2018).

Thermal stability of surfactants shows the long term stability of EOR surfactant as full scale EOR injection may take up to several months of operation. According to Handy, et. al. (1982), there are two important factors to take into account for surfactants in reservoir with elevated temperature. One of these is the impact of temperature on surfactant

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adsorption, and the other is the impact of heat on the stability of the surfactants. Despite of numerous publication on the influence of alcohol as cosurfactants, there is still little information on how alcohol may affect the long term stability of mixed surfactant. In specific, the influence of isoamyl alcohol addition to SLS is yet reported in the current literature. The aim of this paper is to enhance the performance of SLS as EOR surfactant through formulation with isoamyl alcohol. In this study, Isoamyl alcohol and PFAD soap were used as cosurfactants in the formulation of SLS. The main focus of the present work was to find the right formulation as well as to evaluate the the impact of isoamyl alcohol addition on the thermal stability of mixed surfactant. In addition, a number of tests were also conducted such as aqueous stability test, phase behaviour, and IFT test.

Materials and Methods

Materials. Commercial technical grade of sodium lignosulfonate (SLS) as main raw material was purchased from Sweden. The SLS powder is directly used as received without further purification. Figure 1 shows the photograph of commercial SLS powder. A number of chemicals, such as isoamyl alcohol from Merck and palm fatty acid soap for formulations were obtained from Coal, Gas and Petroleum Technology Lab UGM. Crude oil with specific gravity of 42°API and saline water (from the same field) were also obtained from this lab for the IFT measurement.

Figure 1. Raw material of sodium lignosulfonate commercial.

Experimental Setup

Preparation of surfactant solutions. SLS surfactant solutions were prepared by mixing it with brine on a magnetic stirrer at 70°C for 2 hours (Figure 2). Subsequently, the solution was filtered to remove solid impurities. The solutions was prepared based on mass basis. The amount of PFAD soap and isoamyl alcohol were added in a mass ratio of 50% SLS, 20% PFAD soap, and 30% isoamyl alcohol %w/v.

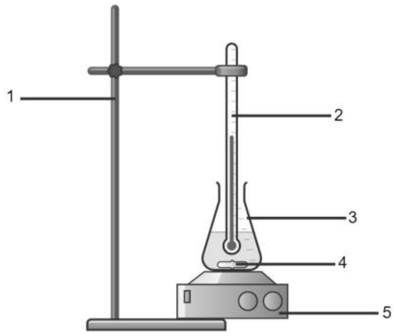

Figure 2. Preparation surfactant solution with and without formulation. *Note:* 1 = Stative; 2 = Thermometer; 3 = Erlenmeyer; 4 = Magnetic stirrer; 5 = Hot plate.

Table 1 and 2 showed the amount of SLS and composition of formulations for surfactant solution.

Table 1. The composition for SLS surfactant solution in 30 ml brine (without formulation)

Concentration (%)	Mass of SLS (gr)
0.50%	0.15
1%	0.3
2%	0.6
3%	0.9
4%	1.2

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Table 2. The composition for surfactant solution with formulations in 30 ml brine

Concentration (%)	SLS, 50% (gr)	PFAD soap, 20% (gr)	Isoamyl Alcohol, 30% (gr)
0.50%	0.0375	0.015	0.0225
1%	0.0375	0.03	0.045
2%	0.0375	0.06	0.09
3%	0.0375	0.12	0.18
4%	0.0375	0.18	0.27

Aqueous Stability Test. Aqueous stability tests were conducted for each surfactant solutions with and without formulations. The samples were aged for a few days while the turbidity and type of phase separation were periodically recorded.
Phase Behaviour Test. Phase behavior test was conducted in 10-mL graduated cylinder, surfactant solution and crude oil were put inside the cylinder consecutively using syringes before the tops were sealed and left to dry at room temperature. Then, the samples were put into a hot plate and stirred for up to 15 minutes at 60°C and later stored at room temperature.
Thermal Stability Test. For the purpose of performing thermal stability test, the best sample formulation was heated in an oven for a certain period of time.In this study, thermal stability test was conducted at 70°C. The temperature was selected to mimic the real reservoir temperature of 70°C at Tempino field. Typical crude oil characteristics for that particular temperature of 70°C can be seen at Table 3 below.

Table 3. Characteristics of oil from Tempino field (Swadesi, et. al., 2015)

The characteristics of oil from Tempino Field	Tempino (TPN) oil value
SARA:	
Saturated	71.60%
Aromatics	25.49%
Resins	2.14%
Asphaltenes	0.78%
EACN (Equivalent Alkane Carbon Number)	8.29
TAN (Total Acid Number)	-
Viscosity	0.90 cP (66°C)
API Gravity	42

IFT Measurements. Interfacial tension (IFT) was measured using a TX-500 Spinning Drop Tensiometer at the Department of Chemical Engineering, UGM with every sample was tested in duplo. A capillary pipe was filled with the SLS solution and then sealed. As much as 2 µL of crude oil was injected into a capillary pipe using a micrometer. The IFT value was recorded after the capillary tube had been rotating at 3000 rpm for at least 30 minutes at a temperature of 60 °C.

Results and Discussion

Aqueous Stability

Figure 3 shows the results of the aqueous stability test. The aqueous stability test of SLS surfactant solutions without formulation was tested at various concentrations, and the result indicated that no phase separation occurred and all solutions were remain transparent. The result showed that SLS dissolved perfectly in brine water. Therefore, the SLS surfactant solution passed the aqueous stability test at all concentrations. However, the surfactant solution was rather thick at the concentrations of 2%, 3%, and 4%. As a result, the colour of the solution was rather dark. It is worthnoting that conducting IFT test would be challenging if the solution colour was too dark since it would be difficult to observe the oil in the surfactant solution.

When we added isoamyl alcohol and PFAD soap (after formulation), it appers that our results gave phase separation at various concentration. Hence, it could be infered that , based on the aqueous stability test, mixed surfactant solution with formulation did not pass the test. Since the surfactant solution will eventually be dispersed in the rock, good surfactant solubility in the formation of water was crucial. Thus, the surfactant's ability to help lowering the tension of the oil-water interface in the rock will be equal when the surfactant solution is injected. The main factor in determining the injectivity of hazy solutions is to ensure it is thermodynamically stable (equilibrated) systems that will maintain their micellar characteristics when injected (Sugihardjo, 2008). The test results revealed that some solutions were thoroughly dissolved while other solutions exhibited phase separation.

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(a) (b)

Figure 3. The results of aqueous stability test. Surfactant solutions (a) without formulation; (b) with formulation.

Phase Behaviour

Figure 4 and 5 show the result of phase behaviour tests. For EOR purposes, the favoured phase type is Type III, followed by Type I and Type II, according to Winsor (Sheng, 2011). Phase behaviour tests on an SLS surfactant solution showed that every sample generated Winsor Type I (Oil – Microemulsion). For surfactant solution with formulation at the concentration 0.25% and 0.5%, according to test results, formed Winsor Type I. Winsor Type III was formed at 1% concentration (Oil-Microemulsion-Water). Winsor Type II was created by 2% and 3% concentrations (Microemulsion-Water). The optimal concentration for the formulation of a surfactant solution, based on the results of the phase behaviour, was 1%, followed by concentrations of 0.25% and 0.5%, and then 2% and 3%. According to the results, adding isoamyl alcohol to SLS surfactant solutions could assist in the formation of microemulsions.

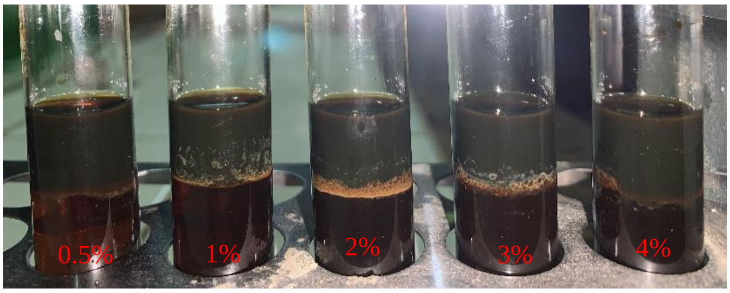

Figure 4. Phase behaviour test result for surfactant solution without formulation (only SLS)

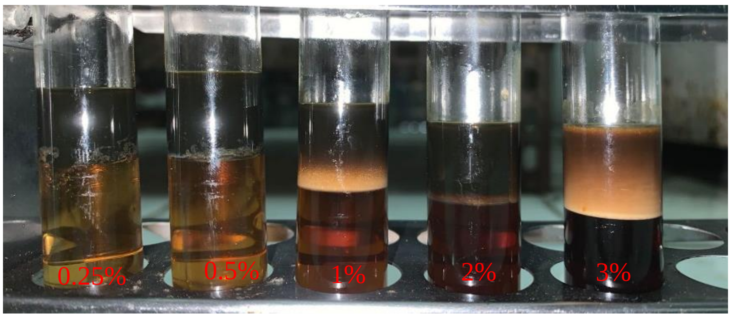

Figure 5. Phase behaviour test result for surfactant solution with formulation (mixed-surf)

IFT Measurements

The lowest IFT value for SLS surfactant solution alone was ca. 9.064×10^{-2} mN/m at a concentration of 0.5%. After formulation with isoamyl alcohol and PFAD soap, the mixed surfactant gave the lowest IFT value of 1.864×10^{-3} mN/m at 1% concentration. According to Wei, et.al. (2018), the addition of isoamyl alcohol can lower IFT values. It showed in Tables 4 and 5 belows, formulation of surfactant solutions with addition of isoamyl alcohol have the lowest IFT value than surfactant solution without alcohol. The IFT value of the proposed surfactant solution for the EOR should be less than 10^{-3} mN/m. Thus, the most suitable IFT value for EOR was obtained at variations in the formulation of surfactant solutions at a concentration of 1%.

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Table 4. Surfactant solution without formulation

Sample No.	Concentration (% w/v)	Surfactant SLS (gr)	PFAD soap (gr)	Isoamyl Alcohol (gr)	Formation water/Brine (ml)	IFT (mN/m)	
						1	2
0	0 (brine)	0	0	0	30	1.299×10^{-1}	1.424×10^{-1}
1	0.5	0.15	0	0	30	1.015×10^{-1}	9.064×10^{-2}
2	1	0.3	0	0	30	9.806×10^{-2}	1.076×10^{-1}

Table 5. Surfactant solution with formulation

Sample No.	Concentration (% w/v)	Surfactant SLS (gr)	PFAD soap (gr)	Isoamyl Alcohol (gr)	Formation water/Brine (ml)	IFT (mN/m)	
						1	2
1	0.25	0.0375	0.015	0.0225	30	1.122×10^{-2}	1.185×10^{-1}
2	0.5	0.075	0.03	0.045	30	4.308×10^{-3}	4.998×10^{-3}
3	1	0.15	0.06	0.09	30	2.100×10^{-3}	1.864×10^{-3}

Thermal Stability

After the the aqueous stability test, phase behaviour test, and IFT test on surfactant solution, the thermal stability for the 1% surfactant solution formulation was further examined. Figure 6 shows the IFT results for 1 wt/% of mixed-surfactant after formulation for 13 weeks. As seen here, there was an increasing trend of IFT after 13 weeks of test. In the first week, the IFT value was 6.9 x 10^{-3} and remains stable until week two at the order of 10^{-3} mN/m. However, after week three, the IFT value increased to 10^{-2} until week 13. There was an outlier where in week nine the IFT value was decreased to 9.9 x 10^{-3}. To conclude, although the proposed formulation of SLS was successful in the beginning of the test to reach ultralow IFT in the order of 10^{-3} mN/m, the proposed formula was still not thermally stable. However, our study indicated that at least the proposed surfactant formulation already gave good thermal stability for the first three weeks.

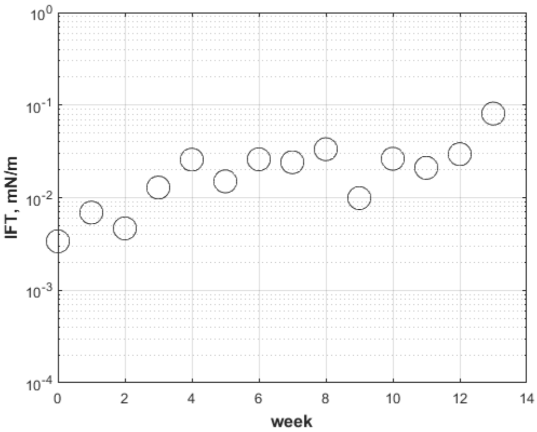

Figure 6. Results of IFT test on thermal stability. *Note:* ○ = Interfacial tension (IFT) value.

This study again revealed that for SLS, formulation with cosurfactant appeared to be an important step. The fluctuative values of IFT was not trivial to explain. It could probably due to the homogeneity issue of the mixture or probably due to any degradation of the surfactant. At high temperatures in both alkaline and acidic media, desulphonation occurs in sulfonate-based surfactants. In the absence of oxygen, desulphonation causes loss of surfactant activity only at very high temperatures. (Angstadt, 1987; Shupe and Baugh, 1991; Hocine et al., 2016). In this study, this was shown by the increase in the interfacial tension value with the length of time of storage in the oven compared to room temperature (week 0). In desulfonation, the release of acid sulfonic groups ($R{-}S(=O)_2{-}OH$) occurs. This study shows that the addition of isoamyl alcohol and PFAD soap were still insufficient to maintain this stability. So further research is required to test the influence of chemical additives which may improve the thermal stability of current formulations.

Conclusions

Formulation of SLS with isoamyl alcohols and PFAD soaps have been conducted in the persent work. Here, we found that 1 wt.% concentration of surfactant solution formulation with the composition of 50% SLS, 20% PFAD

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soap, and 30% isoamyl alcohol showed a promising result. Aqueous stability, phase behaviour, IFT, and thermal stability are some of the tests used to determine the compatibility of SLS surfactants and surfactant solution formulations. The results of the phase behaviour test showed the formation of a Type III (Oil-Microemulsion-Water) layer. Then, the IFT tests gave an ultralow IFT within the range of 10^{-3} mN/m. However, thermal stability test for 13 weeks still showed some instability results. Thus, it is important to conduct further study to find any potential chemical additives which in return may improve the thermal stability of the current formula.

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