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THE EFFECT OF ANIONIC AND NONIONIC CO-SURFACTANT FOR IMPROVING SOLUBILITY OF POLYOXY-BASED SURFACTANT FOR CHEMICAL FLOODING

PENGARUH SURFAKTAN PENDAMPING ANIONIK DAN NON-IONIK UNTUK MENINGKATKAN KELARUTAN SURFAKTAN BERBASIS POLIOKSIDA UNTUK INJEKSI KIMIA EOR

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ABSTRAK

Surfaktan merupakan salah satu komponen yang penting dalam teknologi injeksi kimia untuk memproduksi minyak tahap tersier pada lapangan dengan perolehan minyak minyak yang masih rendah dari produksi primer dan sekunder. Mekanisme yang terjadi adalah penurunan tegangan antarmuka antara minyak dan air yang akan memperbaiki efisiensi pendesakan secara mikroskopis. Studi ini mempelajari pengaruh surfaktan nonionik dan anionik Tergitol, Teepol, Merpol, dan SDS terhadap kelarutan surfaktan berbasis polioksida POS melalui analisa kompatibilitas, perhitungan rasio filtrasi, dan pengukuran IFT. Walaupun penambahan Teepol dan Merpol tidak merubah kelarutan awal dari POS pada setiap konsentrasi, penambahan Tergitol dan SDS mampu merubah kelarutan POS menjadi jernih dan transparan. Namun, sifat utama dari surfaktan untuk menurunkan IFT juga berubah, tidak mampu lagi melepaskan minyak yang terikat di dalam batuan reservoir. Paparan panas terhadap campuran surfaktan juga telah merubah penampakan visual larutan surfaktan menjadi keruh, sebagai indikasi terjadinya degradasi termal. Hasil pengujian menunjukkan bahwa penambahan surfaktan pendamping anionik dan nonionik meningkatkan kelarutan POS, namun meningkatkan pula IFT. Dari studi ini dapat disimpulkan bahwa kompatibilitas POS dalam air formasi dapat diperoleh dengan menambahkan surfaktan pendamping yang tepat. Pemilihan surfaktan pendamping yang lain diperlukan untuk memperoleh kelarutan surfaktan yang homogen sekaligus dapat mempertahankan IFT pada level yang sangat rendah.

Kata Kunci: *surfaktan berbasis polioksida; enhanced oil recovery; injeksi kimia; kelarutan; surfaktan pendamping*

ABSTRACT

Surfactant is one of the crucial components for chemical flooding to recover oil production in the tertiary stage of the low primary and secondary recovery oil field. The mechanism is performed by decreasing the interfacial tension of oil and water which enhancing microscopic displacement efficiency. The present study showed the effect of commercial nonionic and anionic co-surfactant Tergitol, Teepol, Merpol, and SDS on the solubility of polyoxy based-surfactant (POS) through compatibility analysis, filtration ratio analysis, and IFT measurement. Whereas the presence of Teepol and Merpol did not change the original compatibility of POS in all concentrations, the addition of co-surfactant Tergitol and SDS were able to alter the solubility of POS from milky solution into a clear transparent solution. However, the most important characteristic of surfactant for reducing the IFT of oil-water was affected by the addition of co-surfactant which does not have sufficient IFT to release the trapped oil in the reservoir. Thus, exposing the mixture of surfactant and co-surfactant for a few days at the reservoir temperature has changed the visual appearance of solution from a clear transparent solution into a milky suspension, indicating the occurrence of thermal degradation. These results suggest that the addition of anionic and nonionic co-surfactant improved the solubility of POS, but increased the IFT. It can be concluded that the compatibility of POS in the brine can then be achieved by mixing it with suitable co-surfactant. Screening the other co-surfactant is required to obtain the one that enhances the compatibility as well as maintaining the ultralow IFT of POS.

Keywords: polyoxy-based surfactant; enhanced oil recovery; chemical flooding; solubility; co-surfactant

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I. INTRODUCTION

The use of surfactant for chemical flooding has been recognized to be effective to increase the displacement efficiency of oil in a mature oilfield by decreasing interfacial tension (IFT), increasing the capillary number, as well as enhancing the microscopic displacement efficiency (Ahmadi et al., 2014; Bera et al. 2014). As one of the best methods in enhanced oil recovery (EOR) technologies, chemical flooding is then expected to recover the remaining oil that cannot be produced by primary and secondary recovery which yield only 20-40% of the OOIP (original oil in place). Along with surfactant, the other substances with different roles, such as polymer as well as alkaline, were used as injected materials into the reservoir (Olajire 2014; Fletcher et al. 2015). While polymer was used for increasing the mobility control (Pingping et al. 2009; Crespo et al. 2014), alkaline was injected as a sacrificing agent to minimize the adsorption effect of surfactant into the core (Seng et al. 2011; Hirasaki et al. 2011).

Surfactant for chemical flooding application has unique and tailor-made properties associated with different reservoir fluid characteristics (Babu et al. 2016). The chemical is required to be salinity resistant and hardness resistant due to the high saline and high cationic divalent of formation water (Guo et al. 2015; Yuan et al. 2015; Song et al. 2016). Thus, in order to reduce the IFT between oil and water, the surfactant has to be optimized to adjust to the targeted crude oil properties. Usually, two or three kinds of surfactant consisting of main surfactant and co-surfactant were formulated for generating the sufficient surfactant for chemical flooding (Li et al. 2017). However, both chemicals have the characteristic as surfactant by the presence of hydrophilic and hydrophobic at the end of the molecule. Four types of surfactant were classified based on the ionic charge of the molecule, cationic, anionic, nonionic and zwitterionic surfactant. Commercially surfactant that is available in the market includes teepol, merpol, and tergitol which are identified as nonionic surfactant, and sodium dodecyl benzene sulfate (SDS) which is identified as an anionic surfactant.

Teepol, merpol, tergitol, and SDS are market brand surfactant that usually is used for household applications, such as detergent, personal care, cleanings and food processing (Adeniyi et al. 2015). The study of utilizing brand market surfactant for surfactant flooding has been reported on recently. Taiwo et al. (2016) investigated the use of Teepol for recovering light oil, the addition of Tergitol and SDS for lowering the adsorption (Bera et al. 2013) and wettability alteration (Bera et al. 2015).

Previously, we investigated the effect of polyoxy groups of sulfonated natural oil-based surfactant for chemical flooding application. It showed that the presence of polyoxy groups are able to reduce the IFT of oil and water in a targeted oilfield to the level of 10^{-3} dyne/cm as required for chemical injection. However, sulfonated surfactant consisting of polyoxy groups formed a whitish solution with precipitation indication. This phenomenon is not expected due to the possibilities of chemicals to plug in the reservoir pore throat. In the present study, the effect of the addition of Teepol, Merpol, Tergitol and SDS was analyzed as co-surfactant to improve the aqueous stability of POS for chemical flooding.

III. Methodology

POS as the main surfactant was synthesized and developed in the Research Centre of Chemistry, Tangerang, Indonesia. Nonionic surfactant Teepol, Merpol, and Tergitol as well as anionic surfactant SDS were used as co-surfactant. Crude oil was collected from "X" Oil Field (South of Sumatera) with a viscosity of 3.16 cP at reservoir temperature (60°C), and oil gravity of 34.39°API. Brine was synthetically formulated based on formation water composition from "X" Oil Field (Table 1) to ensure the similar component of water during the experiments. POS at various concentrations was mixed with synthetic water in the presence of various co-surfactants at different concentrations. The effect of the addition of co-surfactant was investigated on the presence and absence of co-surfactant through the EOR analysis.

Table 1
Synthetic water formulation of "X" oil field

Ionic	Conc. (mg/l)
Natrium (Na^+)	6649.14
Calcium (Ca^{2+})	240.00
Carbonate (CO_3^{2-})	243.20
Bicarbonate (HCO_3^-)	90.00
Sulfate (SO_4^{2-})	7.00
Chloride (Cl^-)	9762.50
Iron (Fe^{3+})	0.98

A. Compatibility Observation

The effect of co-surfactant on the compatibility of surfactant was analyzed by visual observation of surfactant solubilization in the absence and presence of co-surfactant at different concentrations. Compatibility of surfactant was performed at room temperature as well as at the reservoir temperature to study the effect of elevated temperature on the aqueous stability of surfactant formulation, the mixture of surfactant and co-surfactant.

B. IFT Measurement

In order to investigate the effect of co-surfactant on the IFT of the main surfactant, various concentrations of single POS and co-surfactant in the synthetic brine were measured and compared with the mixture of surfactant and co-surfactant. The IFT measurement was conducted by Spinning Drop Tensiometer TX500 C/D (Fig. 1). The capillary tube filled with surfactant solution was injected with 2 µl of crude oil "X", and put into the IFT unit. The tube was spun at 6000 rpm and 60 °C to adjust to the reservoir temperature of "X" Oil Field. Thermal stability of surfactant was also observed by putting the surfactant solution in the air bath for one month. The IFT was then measured and compared with the initial condition to identify its thermal stability characteristics.

Figure 1
Spinning drop tensiometer TX500 C/D for measuring IFT of oil and water.

C. Filtration Ratio Analysis

The addition of nonionic or anionic surfactant was believed to alter the solubility of POS. To quantify the precipitation indication, filtration ratio analysis was carried out on the absence and presence of various co-surfactant. The mixture of surfactant and co-surfactant was diluted in the synthetic brine and allowed to flow into the 0.45 µm filter paper under pressurized air 30 psi. The filtration ratio was then calculated by $F_R = (T_{500}-T_{400})/(T_{200}-T_{100})$, where T_x is the time to collect x ml of surfactant mixture.

III. RESULTS AND DISCUSSION

A. The Effect of Co-surfactant on the Solubility of POS

Compatibility of surfactant as an injected chemical is the most crucial parameter for chemical flooding. A homogeneous solution is required for the effectiveness of chemical performances in the targeted fluid reservoir. Previously, we found that POS from palm oil was able to reduce the IFT to the ultralow level. However, it formed a milky/whitish solution with the precipitation indication as the concentration was increased. The addition of co-surfactant is then expected to improve the solubility of POS for chemical flooding. The compatibility of surfactant on the presence of various co-surfactant at different concentrations of surfactant and co-surfactant is presented in Table 2.

As can be seen in Table 2, the addition of co-surfactant affects the solubility of POS. While the mixture of surfactant with non-ionic surfactant (either Merpol or Teepol) formed more whitish solution, the presence of nonionic co-surfactant Tergitol and anionic co-surfactant SDS improved the solubility of the targeted surfactant at the different concentrations. Clear mixture solution occurred with the addition of SDS in the range of 1.0 – 3.0%, whereas the addition of Tergitol produced a clear solution in the range of 0.5 – 2.0% and forming suspension again as the concentrations of the co-surfactant were increased. To analyze the solubility as a ratio POS function, the solubility of POS at 1.0% with the addition SDS and Tergitol was also observed, and indicated that higher concentrations of POS required more co-surfactant to dissolve POS to become a clear solution.

Identification of solubilization ability of the surfactant mixture with the synthetic formation water was performed by filtration analysis and the filtration ratio was calculated. The results showed that 0.5% POS in the presence of 1% Tergitol which produced a clear solution were having lower F_R at 1.00 than single surfactant 0.5% POS which generated F_R at 1.80 (Fig. 2), indicating the ability of Tergitol to dissolve the suspension of POS.

B. The Effect of Co-surfactant on the IFT of POS

Aside from the effect of co-surfactant on the compatibility of surfactant, the influence of the second surfactant on the IFT of the main surfactant was also investigated to ensure the critical performance of surfactant as a displacing agent was not affected. IFT measurement was performed on the single POS and each co-surfactant as well as the mixture of surfactant and the co-surfactant solution. It was found that POS successfully reduced the IFT of oil and water to the level of 10^{-3} dyne/cm at 0.3

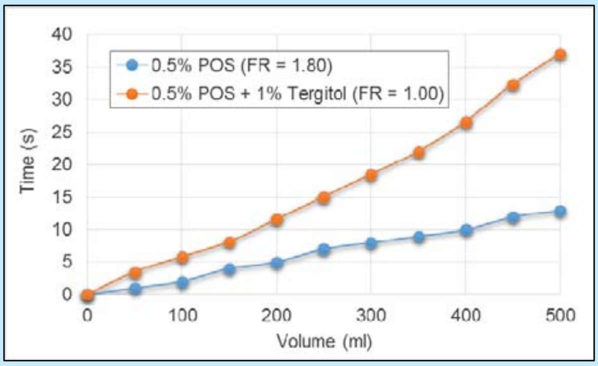

Figure 2
Filtration analysis of single surfactant 0.5% POS compared with the mixture of 0.5% POS and 1.0% tergitol.

Table 2
Compatibility of POS on the addition of various non-ionic and anionic co-surfactant at different concentrations of surfactant and co-surfactant

Conc. (%)	0.3% POS			1.0% POS		
	SDS	Tergitol	Merpol	Teepol	SDS	Tergitol
(-)	++	++	++	++	++	++
0.3	++	++	+++	+++	++	++
0.5	++	+	+++	+++	++	++
1.0	+	+	+++	+++	++	++
2.0	+	+	+++	+++	+	+
3.0	+	++	+++	+++	+	+

+ : clear; ++ : light milky; +++ milky

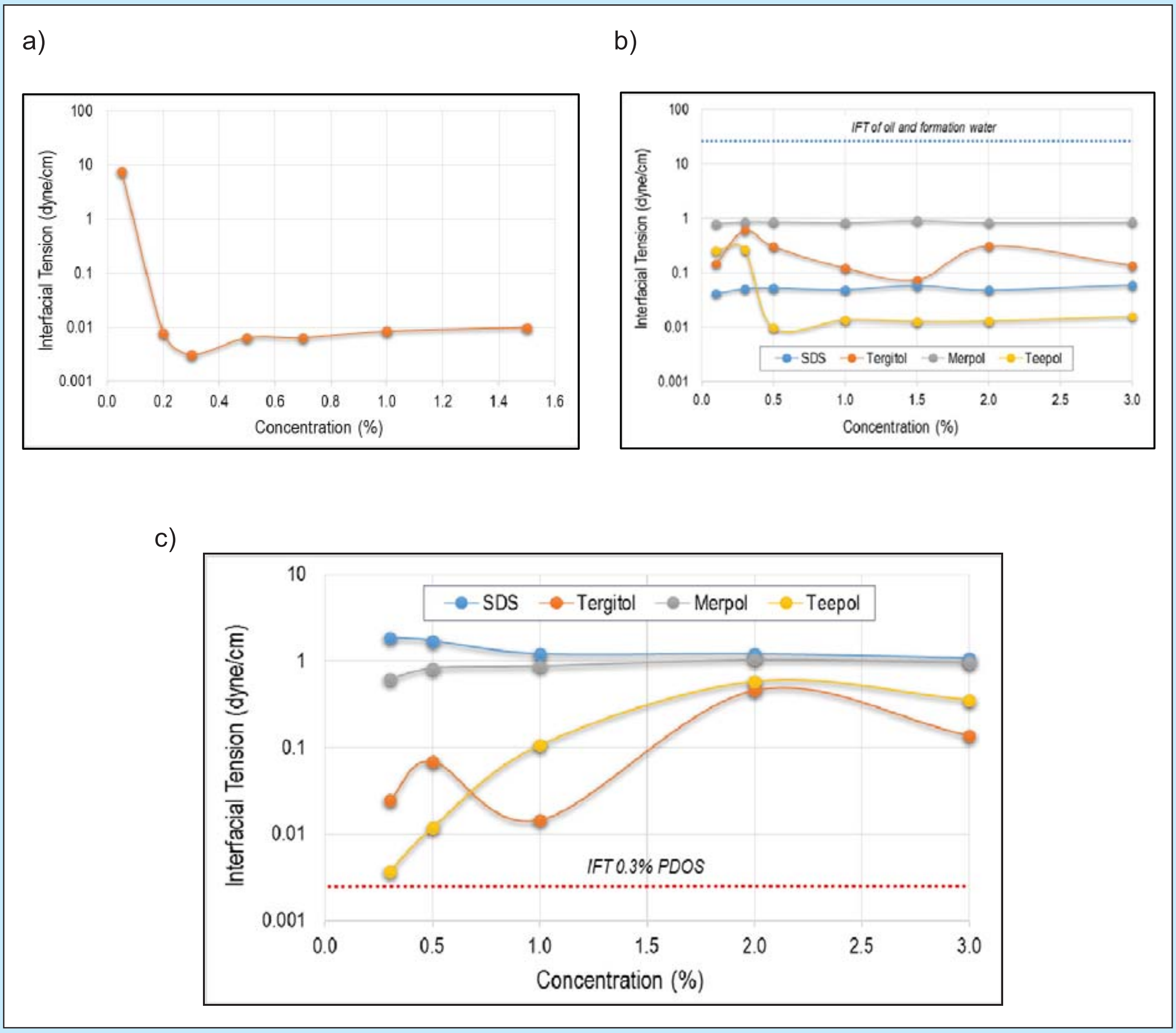

Figure 3
Results of IFT measurement of a) single POS; b) single anionic and nonionic co-surfactant; c) mixture of 0.3% POS and various concentrations of each co-surfactant.

Table 3
Compatibility of POS on the addition of various non-ionic and anionic co-surfactants at different concentrations of surfactant and co-surfactant

Time (days)	0.3% POS		1.0% POS	
	SDS	Tergitol	SDS	Tergitol
0	+	+	+	+
1	+	+	++	++
3	++	++	++	++
7	++	++	++	++
14	++	++	++	++
30	++	++	++	++

and 0.5% surfactant, as required (Fig. 3a), whereas the addition of single co-surfactant SDS, Tergitol, Merpol, and Teepol can only decrease IFT from original oil-water 39 dyne/cm, to the range of 10^{-1} - 10^{-2} dyne/cm (Fig. 3b). The IFT of surfactant solution in the presence of co-surfactant was also measured and presented in Figure 2c. As shown in the figure, the addition of various co-surfactant increased the IFT of POS, suggesting the higher influences of co-surfactant IFT's rather than POS itself.

C. Aqueous Stability of the Mixture of POS and Co-surfactant at Elevated Temperature

To simulate the aqueous stability of POS at the reservoir temperature, the solubility of surfactant was observed after being exposed to heating for several days. The mixture of surfactant in the presence of SDS and Tergitol which generated a clear solution were put in the oven for days. It was found that the mixture of 0.5% POS and 1% of SDS as well as 0.5% POS and 0.5% Tergitol formed a whitish/ milky solution after being stored in the oven after 3 days (Table 3), which suggested that co-surfactant SDS and Tergitol were sensitive to being heated, and were unlikely to be used as chemicals for chemical injection.

IV. CONCLUSIONS

The presence of non-ionic surfactant Merpol and Teepol in the POS solution has been shown as not having a great impact on the solubility of POS, but they did lead to an increasing IFT of the POS solution. Whereas the addition of SDS and Tergitol were identified as improving the appearance of the POS solution from milky suspension to transparent and clear. These results were confirmed by the filtration analysis that produced lower F_R than a single POS. On the other hand, the addition of SDS and Tergitol affected the IFT of POS as the main characteristic of surfactant to be higher and generated a hazy solution at the reservoir temperature. It can be concluded that the use of co-surfactant has the potential to improve the solubility of the main surfactant. However, a study to screen the other co-surfactant which improves the solubility of POS at room temperature as well as at reservoir temperature without an increase in the IFT is required.

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