IATMI22-114

Experimental Studies on the Performance of Palm-Oil and Petroleum Based Surfactant in High Salinity Reservoir

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Abstract. The use of surfactant in tertiary oil recovery is very promising effort to mobilize the remaining oil by its ability to influence the properties of fluid and rock. Surfactants are injected to maximize the performance by lowering the interfacial tension between water and oil in the reservoir. Different types of surfactants have been evaluated and selected after series of evaluation steps. In this paper, the performance of palm-oil based surfactant (methyl ester sulfonated) in comparison to petroleum-based surfactant was investigated through screening of enhanced oil recovery (EOR) methods including interfacial tension (IFT) measurement, aqueous stability, filterability ratio (FR), thermal stability, phase behavior, dynamic adsorption, and tertiary oil recovery test. These measurements were conducted in order to make a comparative analysis determining the best surfactant in the presence of high salinity brine (~ 16,000 mg/L) and reservoir temperature at 60 °C. The findings showed both of palm-oil based and petroleum-based surfactant were compatible with the high salinity brine. Additionally, the aqueous stability of palm-oil based surfactant did not indicate a clear solution while petroleum-based surfactant presented otherwise at room temperature and at 60 °C. The IFT measurement for both palm-oil based and petroleum-based surfactant demonstrated the optimum concentration 8000 mg/L with low IFT. In the next stage of FR test results, the palm-oil based surfactant had tendency to plug porous media as the value was above 1.2 while the petroleum-based surfactant met the criteria of FR <1.2 as the value was 1.04. The results of thermal stability test, the IFT value of the palm-oil based surfactant was decreasing while petroleum-based surfactant was relatively constant. In the phase behavior test, both of surfactant formed a Winsor type III. The result of the dynamic adsorption of palm-oil based surfactant did not show the lowest-standard limit of adsorption value < 400 µg/gr, but petroleum-based surfactant presented 358 µg/g. Surfactant flooding were conducted in rock core with permeability of 63 mD. The petroleum-based surfactant demonstrated an oil recovery factor (RF) of 54.2% OOIP. This current surfactant screening test indicated that the palm-oil based surfactant was not well adapted to EOR methods. Overall, the main objective of this laboratory case study provides an evaluation of an alternative surfactant for EOR implementation in high salinity reservoir.

Keyword(s): Enhanced oil recovery; Surfactant screening; High salinity

1 Introduction

Several methods have emerged for Enhanced Oil Recovery (EOR) to recover the remaining entrapped oil as tertiary oil recovery. One of the methods is by injecting surfactant into the reservoir which has role to change the capillary force. This capillary force of oil and brine plays a prominent role and hence it needs to be reduced which results in an improving displacement efficiency. The designed EOR surfactants should meet the criteria for technical and economic reasons. Thus, it is necessary to assure the main parameters of surfactant applied in EOR.

The classification of chemical surfactants depends on the charge existing on the hydrophilic head, including the non-ionic, anionic, cationic, and zwitterionic (1). Nowadays. there has been a considerable attention related to the anionic surfactant for EOR application. One of the remarkable characteristics of anionic surfactant is because of their low tendency to adsorb on the negatively charged rock surface. Alkyl ethoxy carboxylate (AEC) was studied to investigate the performance its adsorption (2). Anionic surfactant derived rapeseed oil was introduced and applied into carbonate/sandstone reservoirs (3). Palm-oil and petroleum-based surfactant are the most anionic surfactant widely used in sandstone reservoir. Palm-oil based surfactant is produced by mixture various fatty acid ethyl esters (4). Petroleum-based surfactant is synthesized by sulfonation of fraction of the crude oil using either sulfuric acid or oleum (5).

The present work comes to highlight the potential in determining of palm-oil based and petroleum-based surfactant for EOR through chemical screening test.

2 Research Methodology

2.1 Materials

The following materials were used, brine water, palm-oil based surfactant (methyl ester sulfonated), petroleum-based surfactant, crude oil, native core sample. Total dissolved solids (TDS) of brine water composition were measured 13,000 – 20,000 mg/L with the amount of dissolved calcium and magnesium (hardness) is generally considered as soft; 62 - 100 mg/L. Palm-oil based surfactant has acidic in pH (3.3), only 20% of anionic content, and molecular weight of 400 g/mol. Petroleum-based surfactant has the highest molecular weight of 985 g/mol. The crude oil properties have °API gravity value 50.81, wax content 0.06 %wt, total acid number (TAN) 0.08 mg KOH/g, viscosity 0.63 cSt, and its hydrocarbon composition is dominated by $C_{14}H_{10}$ – $C_{17}H_{36}$. Native core samples have permeability 63 - 758 mD.

2.2 Methodology

2.2.1 Aqueous Stability

The first approach of screening test is to see whether surfactant candidate is compatible with 16,000 mg/L salinity brine in various concentrations of surfactant. This test was carried out to observe the suitability of surfactant in brine which the good performance is indicated by no precipitation and sediment as one of the criteria of EOR. Intensive observation periods were carried out in sealed tube from day 1 to day 7 and subjected to both room and reservoir (60°C) temperature.

2.2.2 Interfacial Tension

Determination of the optimum surfactant concentration in reducing interfacial tension to the lowest level were conducted through IFT measurement using Spinning Drop Tensiometer TX-500 C/D at reservoir (60°C) temperature. The reduction in IFT should be in the range of up to ultra-low 10^{-03} dyne/cm under reservoir conditions to significantly overcome the force to release the trapped oil.

2.2.3 Filterability Ratio

The experimental modelling of filtration represents how the effectiveness of the surfactant onto native core when applied in reservoir condition. The flow rate of surfactants was observed by passing the solution at constant pressure of 20 psi through filter membrane of 0.45 µm pore sizes using filtration tool and recorded the time per 50 gr. It is expected the solution would not precipitate and has no aggregates as the requirement filterability value < 1.2.

2.2.4 Thermal Stability

Test was performed during 7 months of aging period at 60°C in depth of crude oil reservoirs. Each of surfactant with certain concentration was prepared as final aqueous solution into sealed glass ampoules in oxygen-free environment.

2.2.5 Phase behavior

In phase behavior stage, crude oil and surfactants are mixed with 1:1 ratio in emulsions under certain conditions over 7 months. The volume of surfactant solution as aqueous phase and oil phase performed using 5 mL graduated pipette, thus water and oil solubilization ratios can be analyzed. This test was examined to understand the long-term stability of the compatible surfactant to form Winsor Type III as microemulsion is desirable in EOR.

2.2.6 Adsorption

The sandstone cores were used in dynamic adsorption experiment which have the permeability ranges 174 – 758 mD. This parameter of the test is conducted to identify the characteristic on both surfactant and native core, hence the injection strategy in surfactant flooding could be analyzed after the highest reduction of surfactant retention in porous media. The decrease of surfactant concentration indicates the loss of a valuable chemical component and is affected by complex reservoir conditions. The absorbance and the calibration curves values were measured before and after the experiment using coreflooding unit. The measurement of adsorption test is using two-phase titration method.

2.2.7 Tertiary Oil Recovery

The core was firstly prepared in the following sequence by drying into the desiccator under vacuum within 8 hours and saturated with brine over 12 hours as primary imbibition process. The initial mass before and after of the core were measured as determine the pore volume (PV). The core was set into core-holder in coreflooding unit with 500 psi confining pressure and 100 psi backpressure. The system was injected with produced water of the brine to measure effective permeability of water (Kw). The OOIP was obtained by injecting crude oil until displacing brine was no longer produced and after some time the core was aged for 13 hours at 60°C. Residual oil saturation was achieved by waterflooding as secondary imbibition and incremental oil recovery was done by injecting surfactant slug with the injection rates of 0.1 cc/min.

3 Results and Discussion

3.1 Aqueous Stability

Surfactant compatibility has important role in screening phase as the test should pass over a specified time to achieve a high soluble and have no precipitation. This experiment was performed for a period of 7 days at room and 60°C temperature with the concentration of both palm-oil and petroleum-based surfactant are 1000 – 15,000 mg/L. The result of palm-oil based surfactant showed presence of the suspension when treated in 16,000 mg/L of brine. Each concentration of this surfactant formed cloudy solution which is not favorable. As can be seen in **Table 1**, palm-oil based surfactant was not completely dissolved in the brine solutions. Comparatively, the excellent solubility was achieved by all the concentrations of petroleum-based surfactant. The result showed this surfactant demonstrate a perfect solution.

Table 1. Aqueous stability.

Solutions	Concentration (mg/L)	Remarks
Palm-Oil based surfactant	1000	Hazy
	3000	Hazy
	5000	Hazy
	8000	Hazy
	10000	Hazy
	15000	Hazy
Petroleum based surfactant	1000	Clear
	3000	Clear
	5000	Clear
	8000	Clear
	10000	Clear Yellowish
	15000	Clear Yellowish

3.2 Interfacial Tension

Figure 1 shows the critical micelle concentration (CMC) of palm-oil and petroleum-based surfactant against concentration. CMC of palm-oil based surfactant was observed with IFT values in the range $1.0E^{01}$ – $8.2E^{-03}$ dyne/cm with the lowest value at 10,000 mg/L concentration. However, considering the cost and safety factor to require the best concentration applied in EOR, 8000 mg/L concentration of palm-oil based surfactant is more effective. Comparing the obtained results of CMC of petroleum-based surfactant, it was reported with the ultra-low IFT in a range of 5000 – 15,000 mg/L concentration which gives about 6.26E^{-03}, 4.88E^{-03}, 6.27E^{-03}, and 8.39E^{-03} dyne/cm, respectively. The lowest level of 8000 mg/L concentration was selected for the next screening tests by the same consideration to the safety factor. Both of palm-oil and petroleum-based surfactants represents non-significant difference on IFT in the range of 5000 – 15,000 mg/L concentration.

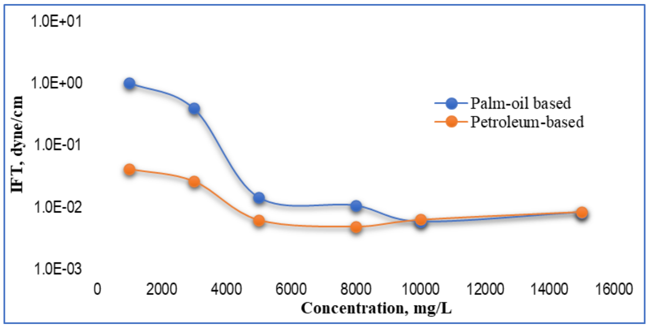

Figure 1. Interfacial tension (IFT) against concentration (mg/L)

3.3 Filterability Ratio

The filterability ratio informs palm-oil based surfactant with 8000 mg/L concentration which were previously selected has the value above > 1.2. This corresponds to a set of aggregates of solution which undissolved with the brine, thus the behavior of solution tends to pass the pore with greater difficulty and traps the space due to effect of debris. Palm-oil surfactant was not acceptable as it has tendency to not flow through the rock pores in the reservoir. The value of FR for petroleum-based surfactant with the same concentration as palm-oil based is 1.04. This petroleum-based surfactant flow through the 0.45 µm in less than 2 minutes with no issue. The flow rate was constant and contained no impurities.

3.4 Thermal Stability

The thermal stability of surfactant was studied based on scoring of CMC measurement result which placed in both 8000 mg/L concentration of palm-oil based and petroleum-based surfactant. Both of surfactants are intended to assess of long-term stability in order to evaluate the thermal degradation at 60°C within period of 7 months. As described in **Figure 2**, palm-oil based surfactant remained at a constant IFT value during the period of 30 days and increased significantly after, up to 1.82E^{01} dyne/cm. As opposed to petroleum-based surfactant performed excellent thermally stable all over the long-term period in the range of IFT value 3.00E^{-02} – 6.00E^{-03} dyne/cm. The period of 30 and 60 days, petroleum-based surfactant showed increasing the number of IFT value due to crude oil droplet was not stable during the IFT measurement process and the values are likely to deviate. Thus, performing phase diagrams experiments through phase behavior to confirm the presence of microemulsion are recommended, and therefore the low IFT value as an equation developed by Huh which can be used to calculate IFT using the optimal solubilization ratio (6).

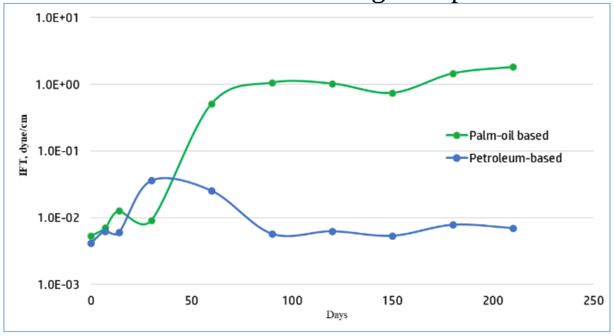

Figure 2. IFT thermal stability

3.5 Phase Behavior

To evaluate Winsor type III microemulsion in 16,000 mg/L salinity brine, phase behavior experiment was demonstrated. The phase volume ratios of a crude oil and surfactant mixture as presented in **Figure 3** and **4** were visually observed for 7 months. Palm-oil based surfactant formed Winsor type I in 2 and 24 hours. After 30 days aging at 60°C, the result of phase behavior switched to middle phase microemulsion (type III) and became stable then. The oil solubilization ratio of palm-oil surfactant result was demonstrated really slow in forming microemulsion which is not favorable due to ineffective for incremental recovery. In contrast to phase behavior of petroleum-based surfactant presented excellent result as the solution displayed Winsor type III in 2 hours.

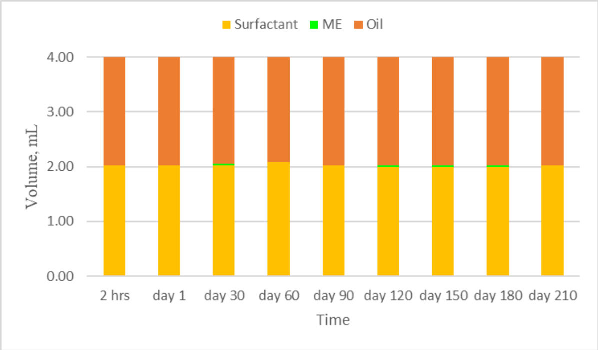

Figure 3. Phase behavior of palm-oil based surfactant

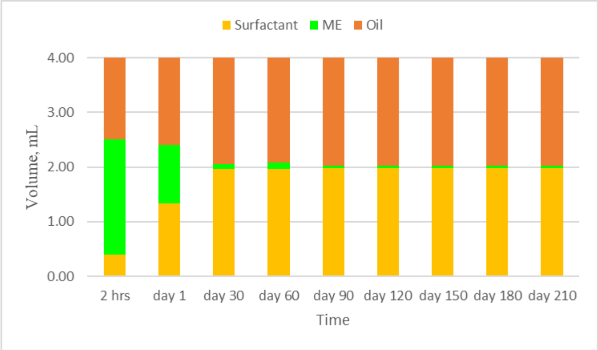

Figure 4. Phase behavior of petroleum-based surfactant

3.6 Adsorption

The dynamic adsorption experiment was using sandstone core from the depth 685.2 – 663.8 m. The adsorption of palm-oil based surfactant into the core was discovered to be 894 µg/g. Due to high amount of adsorption into the core, palm-oil based surfactant appeared not preferable as chemical EOR candidate since the lowest standard limit is < 400 µg/g. This high adsorption can substantially delay oil displacement and recovery during chemical flooding process. Comparatively, petroleum-based surfactant adsorbed less into the core with adsorption value was 358 µg/g.

3.7 Tertiary Oil Recovery

Considering the following result from the initial screening from the aqueous stability to adsorption test, petroleum-based surfactant was selected to the next phase of coreflooding experiment. Coreflooding aims to understand the performance of surfactant after series of evaluation steps. The experiment was conducted with the injection scenario of waterflood + surfactant flood + post flush using sandstone core. The core has permeability of 63 mD with pore volume (PV) of 65.3 cc. The fluid property of petroleum-based surfactant was measured at $3.01E^{-03}$ dyne/cm of IFT value. **Figure 5** reported the result of petroleum-based surfactant coreflooding experiment which gives the recovery factor (RF) 40.6% OOIP or 16 cc after waterflood. The highest oil recovery after surfactant flood and post flush was obtained RF of 54.2% or or 21.3 cc with total RF was reaching 94.8%. This outcome related to good phase behavior which mobilizes the remaining trapped oil (7).

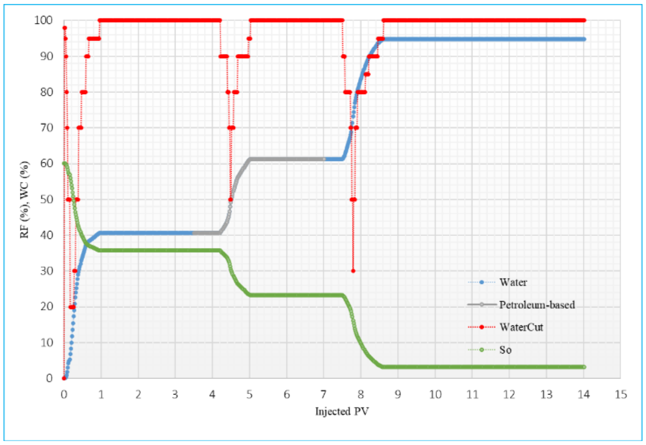

Figure 5. Plot of injected pore volume versus recovery factor

4 Conclusions

Considering the great performance of different surfactant types, petroleum-based surfactant is favorable for EOR. The compatibility, IFT, filterability ratio, thermal stability, phase behavior, adsorption, and coreflooding test of petroleum-based surfactant are already meet the criteria of surfactant screening as chemical EOR and it has potential to be implemented in high salinity reservoir.

Table 2. Chemical screening tests result.

Parameters	Palm-oil based	Petroleum based	Remarks
Aqueous Stability	Poor	Excellent	Clear
IFT	Excellent	Excellent	$10E^{-03}$ dyne/cm
FR	Poor	Excellent	< 1.2
Thermal Stability	Poor	Excellent	Stable at 60°C
Phase Behavior	Good	Excellent	Winsor type III
Adsorption	Poor	Excellent	< 400 μg/g
Coreflood	N/A	Excellent	RF > 50% OOIP

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Acknowledgments

The authors would really like to thank the Exploitation Department in Balai Besar Pengujian Minyak dan Gas Bumi "LEMIGAS" for the supports in this research.

Appendices

Tabel 1. Brine properties

Composition	Unit	Concentration
Anion		
Chloride	mg/L	6647 – 7356
Bicarbonate	mg/L	1647 – 1806
Sulfate	mg/L	0.06 – 0.09
Carbonate	mg/L	84
Hydroxide	Mg/L	0
Kation		
Natrium	mg/L	4964 – 5313
Calcium	mg/L	17 – 35
Magnesium	mg/L	27 – 65
Iron	mg/L	0
Barium	mg/L	0
Total Dissolve Solid	Mg/L	13565 – 20950
pH		8.21 – 8.36

Tabel 2. Crude oil properties

Determination	Unit	Result	Method
°API Gravity	-	50.81	ASTM D. 5002
Density at 15°C	g/cm^3	0.7754	ASTM D. 5002
Wax Content	%wt	0.06127	IFP-Alk. Eter