IATMI22-118

High Paraffinic-Naphthenic Oil Recovery Using Spacer-Assisted Surfactant on SP Chemical EOR Study

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Abstract. Chemical Enhanced Oil Recovery (EOR) has been stated as an efficient method to recover trapped residual oil in reservoir but it has many challenges on selecting and screening the chemical. Molecular phenomena should be reviewed due to complex interaction between chemical component in the system. Surfactant chemical structure corresponds to chemical interaction and EOR performance. This study evaluated the performance of spacer-assisted surfactant on preliminary screening and coreflooding test. Native crude oil 48.9ºAPI, native produced water 17571 ppm, 9 surfactants and HPAM polymer has been used. Gradual laboratory test has been conducted during preliminary screening consists of phase behavior test, IFT test, CMC test and thermal stability test. The best surfactant combined with polymer then tested on high pressure high temperature coreflooding to know its oil recovery. Preliminary screening exhibits spacer-assisted surfactant has better compatibility, lower IFT, and good thermal stability. The best surfactant, Surfactant SA2028, recovered 33.92% IOIP 68.16% ROIP during surfactant flooding and 47.17% IOIP 94.79% ROIP when combined with polymer injection. This study confirmed spacer-assisted surfactant is a new potential topic on EOR surfactant synthesis and formulation to get better performance.

Keyword(s): Spacer; Alkene Oxide; Light Oil; Paraffinic Oil; Naphthenic Oil; Chemical EOR.

1 Introduction

Surfactant flooding is one of the most promising techniques to Enhance Oil Recovery (EOR). The main mechanism of surfactant flooding is to reduce the interfacial tension (IFT) between the surfactant slug and crude oil that improves oil recovery by lowering the capillary forces (Elraies et al., 2009). Surfactants are classified according to ionic head group as nonionic, cationic, anionic and zwitterionic (Ottewill et al., 1984).

Nonionic surfactants primarily serve as cosurfactants to improve system phase behavior. Although they are more tolerant of high salinity, their function to reduce IFT is not as good as anionic surfactants. Cationic surfactants can strongly adsorb on negative surface of sandstone rock and it would be avoided. In reverse, anionic surfactants are most widely used and relatively cheaper (Sheng, 2010; Sekerbayeva et al. 2020). This class of surfactant bears a negative charge such as carboxylate (COO^-), sulphate (SO_2^{-4}), or sulphonate (SO^{-3}). The sulphate class has greater tolerance salinity (both monovalent and divalent cations) but decompose at high temperatures. On the other hand, sulphonate class is poor to high salinity and precipitates in the presence of divalent cation, but it can be used at higher temperature (Gbadamosi et al., 2019). Zwitterionic surfactant is relatively much more expensive although it has good performance (Varade & Ghosh, 2017).

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Surfactant development expand into extended surfactant such as alkoxide addition as spacer. Chen et al. (2020) has reported spacer assisted has good amphipathicity and theoretically has better performance than none spacer-assisted surfactant. This study would confirm the recovery performance this kind of surfactant on native oil, native brine and native pressure-temperature condition.

2 Experimental

2.1 Material

It is important to have a representative crude oil sample when designing an EOR process. Crude oil and brine were acquired from Sumatera, Indonesia. Commercial synthetic core and Pertamina's formulated surfactants also involved at this study.

2.1.1 Crude Oil

The crude oil is paraffinic oil with high naphthene content as shown at Table 1 and Figure 1. It has 0.788 cP viscosity and API 48.9°.

Table 1. Compositional Hydrocarbon of Crude Sample.

Hydrocarbon Type	%m/m
N-paraffins	18.89
Iso-paraffins	29.70
Naphthenes	31.04
Aromatics	9.86
Saturates c15+	4.87
Aromatics c15+	3.09
Non N-paraffin c20-c36	2.55
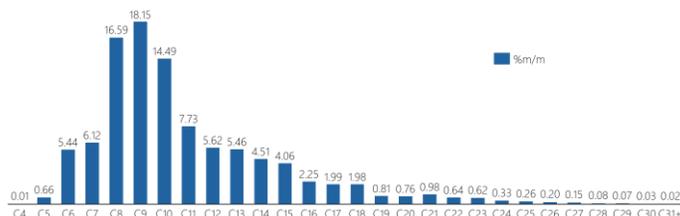
Figure 1. Carbon Distribution of Crude Sample.

2.1.2 Brine

Formation water salinity and divalent ions are critical to chemical EOR processes for both surfactants and polymers. Although chemical suppliers claim their products can be tolerant to high salinity, most of the chemical EOR processes have been applied in low-salinity reservoirs (Sheng, 2010). Aghaeifar et al. (2015) was reported low salinity EOR study using ~23000 ppm. Surfactant formulation was carried out using relatively lower sanility brine as listed at Table 2 including other properties.

Table 2. Chemical and Physical Properties of Brine.

Parameter	Brine			
TDS, mg/L	17571			
pH	7.9			
Density, g/mL	1.0134			
Ion, mg/L				
	Na	6315.0	Sr	10.1
	K	54.3	Fe	13.1
	Ca	203.2	Cl	10068
	Mg	165.4	HCO3	737
	Ba	2.1	SO4	2
Total Cation, mg/L	6763			
Total Anion, mg/L	10807			
Resistivity 60 °F, Ω	0.47			

2.1.3 Injected Chemical

The tested surfactant samples are listed at Table 3 below supported with ion type and presence of spacer group.

Table 3. List of Tested Surfactant.

No.	Surfactant ID	Ion Type	Spacer Group
1	SA114	Non-ionic	Yes
2	SA115	Anionic	No
3	SA116	Non-ionic	No
4	SA117	Non-ionic	No
5	SA208	Anionic	No
6	SA202	Anionic	Yes
7	SA2026	Anionic	Yes
8	SA2022	Anionic	Yes
9	SA2028	Anionic	Yes

Polymer also involved on this study to observe sweeping phenomenon after surfactant flooding. The polymer is hydrolyzed polyacrylamide polymer with medium-high anionicity, high molecular weight, and good thermal stability up to 70 °C.

2.1.4 Core

Oil recovery test was conducted using synthetic sandstone core with 80-90 mD brine permeability, 6000-8000 US strength and 7.9 total clay content. The effective porosity of this core is 19.48%. Dried 1.5"-diameter 1 ft core was saturated with native brine using vacuum and purging method up to 2000 psi referred to API RP 40. Then the brine saturated core flooded by oil on 60 °C and 850 psi as reservoir temperature-pressure condition. Oil saturation followed by oil aging before starting the first recovery through waterflooding.

2.2 Compatibility Test and Phase Behavior

Interaction of brine and each surfactant was initially observed through visual tests. Surfactant solution divided into 0%, 0.5%, 1.0%, 1.5% and 2.0% w/w and stored at 20 mL vials. Adapted from API RP 63, visible changes in the solution (settling of suspended solids, scale formation, color change, gelation, phase separation, syneresis, etc.) would be considered as incompatibility. Crude oil : surfactant solution 1 : 1 ratio

with typical surfactant concentration mixed and rotated in 10 mL plugged measuring pipettes. Storage condition and duration of both tests were the same; at reservoir temperature along 2 weeks.

2.3 IFT and Thermal Stability Test

Parallel to visual tests, IFT measurement using spinning drop tensiometer at 60 °C 6000 rpm was performed to find out the lowest result. The selected surfactants then proposed to thermal stability test which had 8 weeks duration. IFT test conducted every week to monitor stability of the surfactant solution.

2.4 Coreflooding Test

Coreflooding apparatus has 1 L liquid accumulator capacity, core diameter 1" or 1.5", core length up 1 m, pressure capacity up to 10.000 psi, temperature condition up to 150 °C and injection system as low as 0.01 mL/min with 50 mL/min maximum rate. Produced oil automatically calculated through UHD camera system observing liquid level changes at sapphire window of high-pressure high-temperature (HPHT) separator.

Recovery test consisted of following sequence; first waterflooding (WF1) up to steady condition + 1 PV, surfactant flooding (SF), polymer flooding (PF) 1500 ppm 0.35 PV and second waterflooding (WF2) up to steady condition + 1 PV. Steady condition on waterflooding was achieved when there is no more oil recovery after 1 PV and then followed by 1 PV injection to ensure the stability. Surfactant injected volume varied into 2 schemes on this study. They were 2 PV injection and another is continuous injection until reached steady recovery (no oil recovered). Beside oil recovery parameter, pressure difference (dP) gradient is another constraint to define steady condition. The gradient should be less than 1% along the steady period.

3 Result & Discussion

3.1 Compatibility Test & Phase Behavior Test

Gbadamosi et al. (2019) reported anionic surfactant is susceptible to high salinity and Perez et al. (1995) found optimum salinity reduction as spacer increment means water-oil interaction are likely to increase which related to oil solubilization ratio and Winsor type III. Furthermore, surfactant compatibility and oil solubility can be adjusted by engineered the number of spacer group especially for anionic surfactant formulation. Table 4 and Figure 4 confirmed that spacer-assisted surfactants have better compatibility and tend to form microemulsion. SA114 whose spacer exhibited Winsor Type II, but no spacer-assisted SA116 & SA117 had not clear emulsion although they are at the same ionic group. Spacer reduced the turbidity of surfactant solution (Perez et al., 1995) and correlated with compatibility test result of SA208 become milky solution meanwhile other ionic surfactants assisted by spacer were clear.

Table 4. Compatibility Test and Phase Behavior Test Result.

No	Sample ID	Surfactant Concentration (%w/w)	Compatibility	Winsor Type
1	Brine	0	Clear	II
2	SA114, SA115,	0.5	Clear	II
		1.0	Clear	II
		1.5	Clear	II
		2.0	Clear	II
3	SA202, SA2026,	0.5	Clear	III
		1.0	Clear	III

	SA2027,	1.5	Clear	III
	SA2028	2.0	Clear	III
4	SA116,	0.5	Clear	
	SA117	1.0	Clear	Not visually
		1.5	Clear	observed
		2.0	Clear	
5	SA208	0.5	Milky (+)	II
		1.0	Milky (+)	II
		1.5	Milky (++)	II
		2.0	Milky (++)	II

Epoxide spacer is part of the dense interphase area due to hydrocarbon bent formation by oxygen (Forgiarini et al., 2010; Chen et al., 2020). Higher surfactant concentration enhanced dense hydrophobic environment and lowered the middle phase volume with high emulsion density (Chen et al., 2019) as shown at Figure 5B.
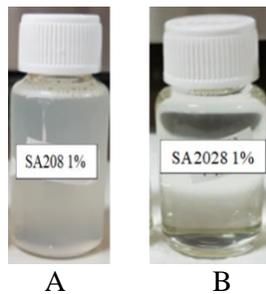
A B
Figure 4. Milky SA208 1.0% (A) and Clear SA2028 1.0% (B).
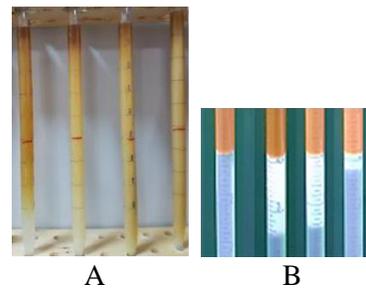
A B
Figure 5. Phase Behavior of Left-Right 0.5%, 1.0%, 1.5% & 2.0% SA2028 30 Minutes After; Mixing (A) and 7 Days (B).

3.2 *IFT & Thermal Stability Test*

He et al. (2019) and Lv et al. (2020) explained low IFT between the microemulsion phases would contribute to the ease of dispersion of one in the other. The particle size is predominantly in the order of 1 μm or below. The IFT between water and oil is low. When the particle size is about 0.1 μm, the IFT becomes ultralow for example in middle phase microemulsion, the particle size is in the order of nanometers (Sheng, 2010). IFT test result as shown at Figure 6 emphasizes the Winsor Type III surfactants at Table 4.
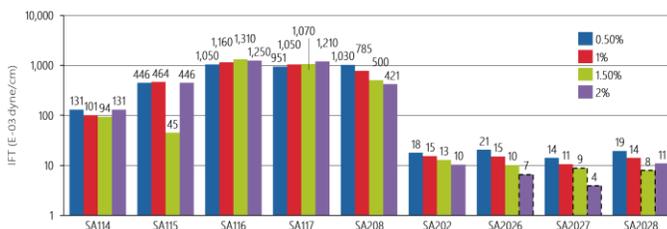
Figure 6. IFT Result of Surfactants Preliminary Screening.
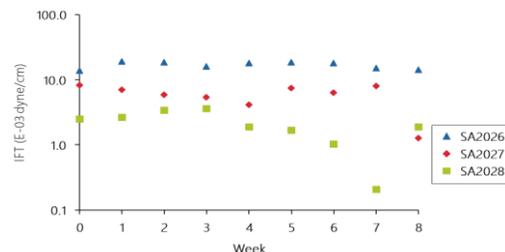
Figure 7. Thermal Stability Result of Selected Surfactants.

According to compatibility, Winsor Type III and lowest IFT parameter; SA2066, SA2067 and SA2028 passed the criteria and proposed to thermal stability test. The selected concentration for thermal stability test who has IFT lower than 10^{-2} dyne/cm as dashed line at Figure 6. SA 2028 1.5% who has epoxide spacer was the only one kept stable below 10^{-2} dyne/cm along 8 weeks. Epoxide spacer can improve dynamic molecular amphipathicity and rugby ball shape or truncated cone-shaped (Chen et al., 2019; Hussain et al. 2019). Both are contributed by the epoxide coil and lead to the good thermal hydrolysis stability as shown at Figure 7.

3.3   Coreflooding Test

SA 2028 1.5% then proceeded onto oil recovery test at reservoir condition. There were 2 schemes of injected surfactant volume implemented between waterflood 1 (pre-flush) and waterflood 2 (post flush). First, 2 pore volume (PV) surfactant followed by 0.35 PV 1500 ppm polymer. Another scheme is maximum injection of surfactant until no oil recovered. Polymer is injected behind surfactant to avoid chase water fingering in the surfactant slug (Sheng, 2010). Sometimes when polymer is not injected with surfactant in the same slug, they will be mixed at their interface because of dispersion and diffusion. Polymer may also mix with surfactant owing to the inaccessible pore volume phenomenon when it is injected behind surfactant. Sheng (2010) referred to these phenomena as surfactant-polymer interaction (SPI). It optimizes sweep efficiency to get post-flush recovery 13.98% at Run I and get total RF 97.41% of initial oil in place (IOIP) at Run II as shown at Table 5. Oil recovery along polymer flooding almost reproducible between both schemes. Run II shows SA 2028 itself has good capability to recover oil up to 33.92 %IOIP or 83.43 %ROIP along surfactant flooding even though after more than 50% IOIP has been recovered.

Table 5. Coreflooding Result of 2 Schemes PV Injected

Run	PV (mL)	IOIP (mL)	Soi (%PV)	Oil Recovery					
				Unit	WF1	SF	PF	WF2	SF+PF+WF2	Total
I	65.73	36.37	55.33	mL	13.16	4.97	3.38	5.09	13.44	26.60
				%IOIP	36.19	13.66	9.30	13.98	36.95	73.14
II	65.61	32.37	49.88	mL	16.26	10.98	3.30	0.99	15.27	31.53
				%IOIP	50.23	33.92	10.19	3.06	47.17	97.41
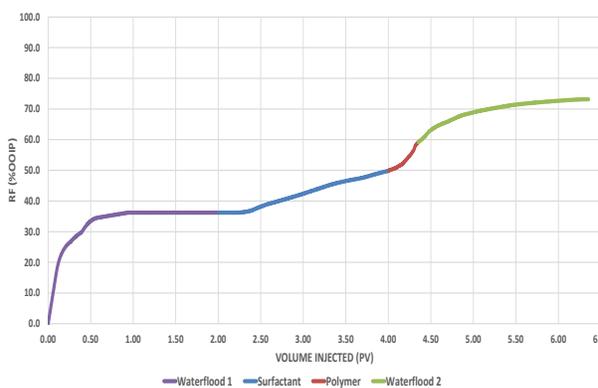
Figure 8. Injection of 2 PV SA2028 and Followed by 0.35 PV Polymer
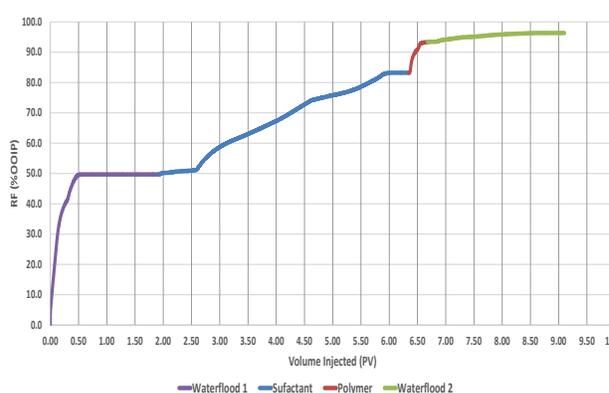
Figure 9. Injection of SA2028 up to Steady Recovery and Followed by 0.35 PV Polymer

4   Conclusion

A multi parameters surfactant screening at reservoir condition has been conducted. Based on the results from the present work, the following main conclusions can be drawn:

1. 3 of 9 surfactants passed the compatibility, Winsor Type III and IFT $< 10^{-2}$ dyne/cm criteria; SA2066, SA2067 and SA2028. They are spacer-assisted surfactants.
2. SA2028 was the only surfactant whose IFT value less than $< 10^{-2}$ dyne/cm along 8 weeks.
3. SA 2028 1.5% recovered 33.92% IOIP 68.16% ROIP during surfactant flooding and 47.17% IOIP 94.79% ROIP combined with polymer injection even though after more than 50% IOIP has been recovered. It recovered about twice of waterflood recovery and almost all oil in the core.
4. Based on this study, spacer-assisted anionic surfactant might be right choice to get good EOR performance for typical condition.

Further flooding design could be optimized to find out the most profitable injection scheme.

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