

CO-SURFACTANT POLYETHYLENE GLYCOL MONO-OLEATE IN THE FORMULATION OF NATURAL BASED-SURFACTANT FOR CHEMICAL EOR

SURFAKTAN PENDAMPING POLIETILEN GLIKOL MONO-OLEAT PADA FORMULASI SURFAKTAN BERBASIS NABATI UNTUK INJEKSI KIMIA EOR

Yani Faozani Alli¹⁾, Letty Brioletty¹⁾, Hestuti Eni¹⁾, and Yan Irawan²⁾

“LEMIGAS” R & D Centre for Oil and Gas Technology
Jl. Ciledug Raya, Kav. 109, Cipulir, Kebayoran Lama, P.O. Box 1089/JKT, Jakarta Selatan 12230 INDONESIA
Tromol Pos: 6022/KBYB-Jakarta 12120, Telephone: 62-21-7394422, Faxesimile: 62-21-7246150
Email: faozani@lemigas.esdm.go.id; E-mail: lettyb@lemigas.esdm.go.id;
E-mail: hestuti@lemigas.esdm.go.id;

²⁾ Pusat Penelitian Kimia LIPI
Kawasan PUSPIPTEK Serpong, Tangerang – Banten, 15314
Telephone : 021 – 7560929, Fax : 021 – 7560549

First Registered on November 17th 2016; Received after Correction on December 9th 2016

Publication Approval on: April 28th 2017

ABSTRAK

Surfaktan berbasis nabati seperti surfaktan metil ester sulfonat (MES) dari bahan minyak kelapa sawit telah menjadi fokus penelitian selama satu dekade terakhir untuk meningkatkan perolehan minyak, mengingat ketersediaan bahan baku kelapa sawit yang melimpah di Indonesia serta kebutuhan akan minyak sebagai sumber energi yang terus meningkat. Pengembangan surfaktan MES agar sesuai dengan karakteristik fluida reservoir lapangan target juga telah berhasil dilakukan dalam skala laboratorium dan skala lapangan. Pada penelitian ini, pengaruh penambahan surfaktan pendamping polietilen glikol mono-oleat (PMO) untuk meningkatkan kemampuan surfaktan dalam meningkatkan produksi minyak pada lapangan “L” di Jawa Tengah dalam skala laboratorium dilakukan melalui uji kompatibilitas, uji tegangan antarmuka (IFT), uji kestabilan termal dan uji core flooding. Hasil penelitian menunjukkan bahwa penambahan PMO sebagai surfaktan pendamping MES dapat meningkatkan kelarutan surfaktan di dalam air formasi terkait dengan keberadaan gugus etoksi yang mempunyai sifat antarmuka di dalam struktur molekul PMO. Penurunan IFT sebagai faktor penentu dalam injeksi surfaktan juga dapat dicapai hingga 10^{-3} dyne/cm, dan dapat bertahan hingga dua bulan pada suhu reservoir. Adapun pengujian kemampuan surfaktan dalam meningkatkan perolehan minyak melalui uji core flooding menunjukkan bahwa campuran surfaktan MES dan PMO dapat meningkatkan produksi minyak hingga 55.35% Sor dan berpotensi untuk dijadikan bahan injeksi kimia di lapangan target.

Kata Kunci : *injeksi kimia, surfaktan nabati, surfaktan pendamping, polietilen glikol mono-oleat, MES, EOR*

ABSTRACT

Natural-based surfactant such as methyl ester sulfonate, which is derived from palm oil, has increasingly become the focus of study for the last decade to improve oil recovery due to the abundant raw materials availability and the need for oil as a source of energy. Surfactant MES development with the targeted fluid reservoir characteristic has been conducted in the laboratory scale as well as in the field scale. In this study, the addition of polyethylene glycol mono-oleate as co-surfactant to enhanced oil recovery in the “L” oilfield in Central Java was investigated in the laboratory scale through compatibility

observation, IFT measurement, thermal stability and core flooding tests. The results showed that the presence of PMO improved the solubility of surfactant mixture in the water which formed one phase milky solution. Decreasing IFT as the crucial factor for surfactant flooding was also achieved until 10^{-3} dyne/cm and thermally stable for two months. Furthermore, core flooding experiments to study the performance of surfactant to recover oil production showed that the mixture of MES and PMO are able to enhance oil recovery until 55.35% S_{or} and have potential to be used as chemicals for chemical flooding in the targeted oilfield.

Keywords: chemical flooding, natural-base surfactant, co-surfactant, polyethylene glycol mono-oleate, MES, EOR

I. INTRODUCTION

Currently, there has been considerable progress globally made on surfactant flooding either in laboratory studies or in pilot scale. However, in Indonesia, that really only began in the last decade, as indicated by several studies that has been reported relating to the invention of local surfactant in the laboratory scale. Among the three pilot projects involving chemical injection in Indonesia that have been performed, only one was in Kalimantan using local chemicals (Bou et al. 2000; Wibiwo et al. 2007; Rilian et al. 2010; Zulfikar et al. 2014). It showed that the chance to develop surfactant to be applied in Indonesian mature oil fields is still possible.

Chemical flooding is one of the enhanced oil recovery (EOR) methods which involves the injection of surfactant to mobilize oil saturation, polymer to improve volumetric sweep efficiency, and alkaline to minimize the adsorption of chemicals into the reservoir rock (Samantha et al. 2012; Bera et al. 2014; Zhu et al. 2014; Battistuta et al. 2015). Surfactant is an amphiphilic molecule which consist of hydrophilic and hydrophobic groups. However, a specific surfactant characteristic is required for chemical flooding due to the different nature of reservoir fluids in each reservoir (Adkins et al. 2010). It has to be able to obtain ultralow interfacial tension (IFT), and be thermally stable, compatible, saline resistant, and hardness resistant (Adkins et al. 2012).

Surfactant for EOR is usually derived from petroleum, such as sodium alkylarylsulfonates, sodium alkyl benzene sulfonates and sodium alkyl sulfonates (Marhaendrajana et al. 2016), although the study to use natural based-surfactant has arisen recently due to its renewable and environmentally friendly features (Phan et al. 2010; Hambali et al. 2012; Jeirani et al. 2013; Song et al. 2016). One of the potential crops to be used as surfactant raw material is palm oil (Hidayati et al. 2012; Sugihardjo, 2013; Bantacut & Darmanto, 2014). As the biggest

producing country of palm oil, its availability in Indonesia will not be an issue for upscaling surfactant production.

Recently, Jin et al. (2016) reported the utilization of palm oil as a raw material of anionic surfactant methyl ester sulfonate (MES). They produced MES from esterification and sulfonation of waste cooking oil. Application of MES has been commercially used as an active cleaning ingredient in laundry detergent, substituting to the current surfactant workhouse, Linear Alkyl Benzene Sulfonates. It gives excellent bio-degradability, improved calcium hardness tolerance during washing process, and superior detergency (Ivanova et al. 2016). On the other hand, the application of MES as a surfactant for EOR was reported by several researchers (Hidayati et al. 2012; Sugihardjo 2013; Sugihardjo & Eni 2014).

Polyethylene glycol mono-oleate (PMO) is a lipophilic non-ionic surfactant (O/W) derived from natural oils which consists of several ethoxy groups and is utilized as emulsifiers, viscosity modifier, emollient and a processing aid in the textile industry. The mono of polyethylene glycol 200 and 300 are the most important for these properties. PMO is generated from esterification of polyethylene glycol with oleic acid, followed by washing, purification and product finishing (Irawan & Ika 2015).

In this study, we attempt to investigate the effect of PMO as co-surfactant to improve the compatibility of MES as chemical injection in the "L" oilfield, as well as to reduce the IFT of oil and water. The other EOR tests including the filtration test, phase behaviour analysis, and the core flooding test were also analyzed.

II. METHODOLOGY

Palm oil-based surfactant MES and PMO were used as the main surfactant and co-surfactant, respectively. The surfactants were synthesized and developed in the Research Centre of Chemistry, Tangerang, Indonesia. Polymer with concentration in the range of 750-1500 ppm was used for core flooding experiments for improving macroscopic sweep efficiency. Anionic surfactant CS II was used

to compare the performance of targeted surfactant to enhanced oil recovery through the core flooding test. Ethylene glycol butyl ether (EGBE) was used as a solvent. Analytical grade of sodium carbonate (Na_2CO_3) was used as alkaline. Formation water and crude oil were obtained from “L” oilfield in the Centre of Java.

A. Compatibility Test

A single surfactant MES or surfactant mixture were mixed with formation water in the presence of EGBE as a solvent. The solubility of single surfactant MES and the mixture of MES-PMO were visually observed at room temperature to study the effect of PMO on MES solubilization. The phase formation, colour changing, and precipitation were recorded to investigate the compatibility of surfactant formulation with the reservoir fluid.

B. IFT Measurement

The IFT of MES in the absence and presence of PMO were measured to compare the effect of co-surfactant PMO on reducing IFT. 2 μL crude oil was injected into the capillary tube filled with surfactant. The IFT value was measured using Spinning Drop Tensiometer TX-500C/D. The tube was spun at 6000 rpm under elevated reservoir temperature (60°C). Density difference between both liquids was used as an input to calculate IFT. Stable IFT after 10 minutes was then recorded.

C. Thermal Stability Investigation

A series of surfactant solutions were put into the oven at 60°C for several days. The IFT was then measured using a Spinning Drop Tensiometer TX-500C/D. The degree of thermal hydrolysis was then evaluated by comparing the IFT value before and after surfactant exposed with thermal.

D. Core Flooding Experiments

Several core flooding experiments were conducted on standard core Buff Berea. A high

pressure and high temperature chemical flooding system was used for core flooding experiments. Routine core analysis was firstly conducted which included measuring the dimensions, permeability, and porosity. The petrophysical parameters are presented in Table 1. The oil displacement performance of the surfactant flooding system was tested. Core flooding experiment procedure was described as: vacuuming the weighing core at -1 atm for several hours, followed by saturation with formation water for 3 hours. Water pore volume was calculated by material balance. Wetted core was then weighed. Mass difference was determined as water pore volume. Core was put in core holder and injected with formation water, and water phase permeability was measured. The drainage process was started by injecting crude oil with gradient rate from 0.1 to 10 mL/min until no more brine was produced. The initial oil in place (S_{oi}) was calculated by using the material balance method. The core was placed in a 60°C oven for aging the interaction between crude oil and core for 3 days. Water flooding was conducted by injecting the crude oil-saturated core with injection water until water cut more than 98%. Then the chemical slug consisting of surfactant and polymer was injected as designed. Finally, subsequent water flooding was injected with injection water.

A core flooding experiment was conducted at reservoir temperature with a fluid injection rate at 0.1 mL/min, which simulated the displacement velocity of chemical flooding in an oil reservoir. During the experiments, the pressure drop, oil production and total fluid production were recorded on a timely basis in order to calculate the incremental oil recovery and water cut of flooding precisely.

Table 1
Standard routine core analysis for core flooding experiments

Core	Length (cm)	Dia (cm)	Ka (mD)	Por (%)	PV (cc)	S_{oi} (cc)
Buff Berea 1					70.54	42.55
Buff Berea 2	30.400	3.745	350 - 600	21.60	67.12	41.05
Buff Berea 3					66.43	42.10
Buff Berea 4					70.54	45.00

III. RESULTS AND DISCUSSIONS

A. Solubility improvement of PMO-contained surfactant

The compatibility of surfactant was first studied due to the surfactant's ability to produce homogeneous solution, which is essential to obtain clearly sufficient chemicals. As presented in Figure 1, the presence of PMO as co-surfactant, enhanced the solubility of the surfactant solution. Whereas increasing the concentration of single surfactant MES formed two phases, with the oil phase on the top layer (Figure 1a), but it was not the case for MES and PMO mixtures which formed one phase milky solution (Figure 1b). It indicated that the addition of PMO improved the solubility of the surfactant

due to the molecular groups of PMO which consist of ethoxy with interface affinity (Levitt et al. 2006), although optimization will be required to generate a transparent homogeneous solution.

B. The effect of PMO to generate ultralow IFT

The study to investigate the effect of PMO addition to the palm oil-based surfactant, MES, was conducted by measuring the IFT in the presence and absence of PMO. Co-surfactant PMO2, PMO3 and PMO4 indicated the different ratio of surfactant MES and co-surfactant PMO. The study showed that single surfactant MES gave an IFT value of around 10^{-1} dyne/cm, which is not enough to mobilize the oil, whereas in the addition of PMO at various ratios, the ultralow IFT at 10^{-3} dyne/cm IFT can be

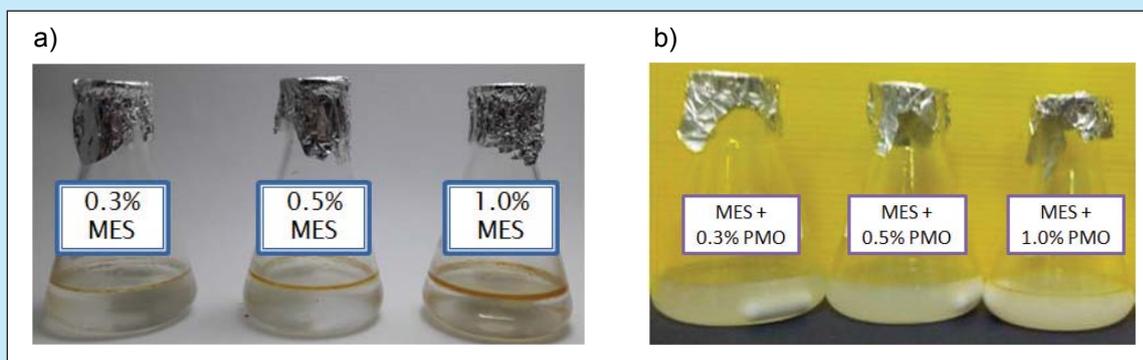


Figure 1
The effect of PMO on solubility of surfactant solution;
a) Single surfactant MES mixed with brine water formed two phase solutions;
b) In the presence of PMO, milky one phase solution were obtained.

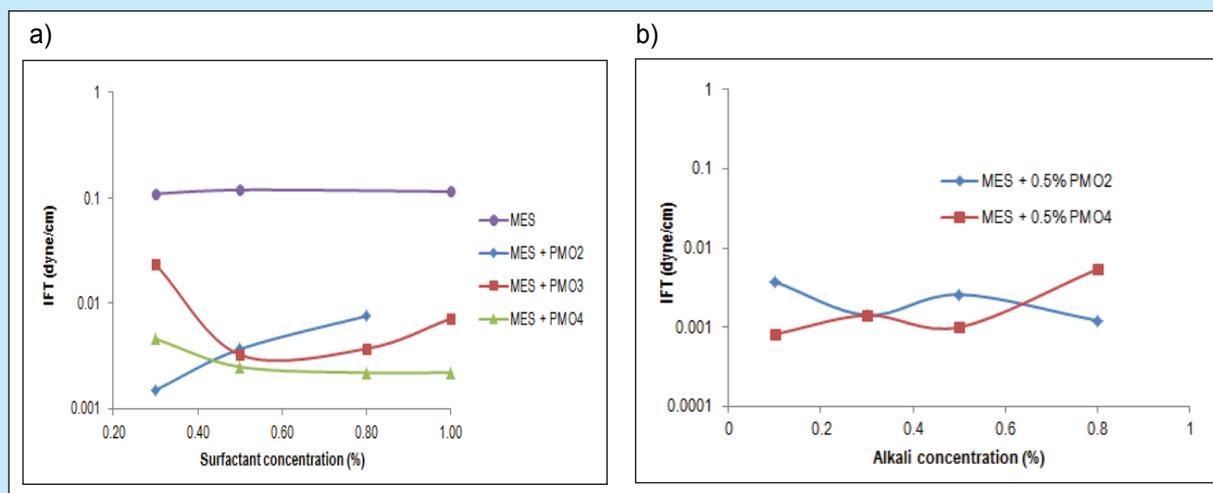


Figure 2
The effect of PMO on reducing IFT. a) In the presence of PMO, ultralow IFT were obtained from 0.3 – 1.0% of PMO, b) Different ratios of MES and PMO gave the similar level of IFT at 10^{-3} dyne/cm.

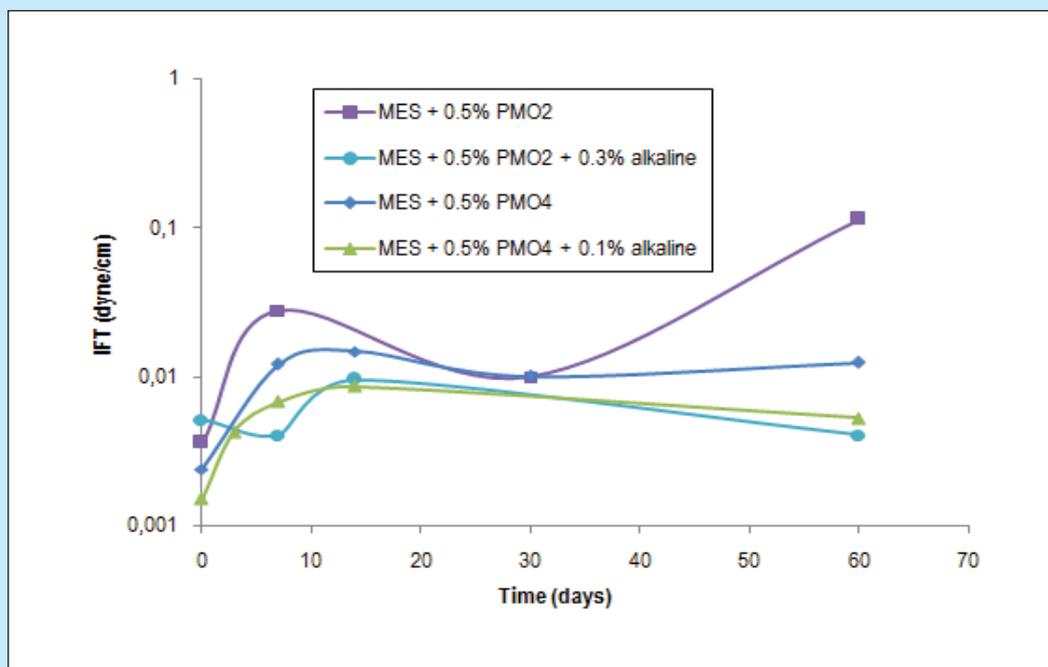


Figure 3
The effect of PMO to the IFT thermal stability. The IFT of PMO-contained surfactant tends to increase in the elevated temperature. The addition of alkaline minimize the effect of surfactant thermal hydrolysis.

reached in the range of 0.3 – 1.0% surfactant mixture concentration (Figure 2a). Furthermore, the effect of alkaline to the IFT at different ratios of MES to PMO was also investigated. As can be seen on the graph (Figure 2b), in all alkaline concentrations at different ratios of MES and PMO, ultralow IFT at 10^{-3} dyne/cm was obtained, suggesting alkaline compatibility with the surfactant mixture.

Decreasing IFT value from 10^{-1} dyne/cm to the level of 10^{-3} dyne/cm is the most important criteria to utilize surfactant as a chemical injection. Several studies reported that the mixture of two or more surfactants produced better performance chemicals rather than a single surfactant to mobilize oil recovery (Hirasaki et al. 2008; Adkins et al. 2012; Jang et al. 2014). This might be caused by the various components of crude oil. In the presence of a second surfactant, PMO, that consists of several ethoxy groups with interface affinity (Levitt et al. 2006), the surfactant mixture was then able to reduce the IFT to the ultralow level as required. The ultralow IFT at 10^{-3} dyne/cm is believed to recover oil production to be more than 90% of the original oil in place (OOIP) (Lake 1989).

C. The effect of PMO to the IFT thermal stability

The IFT thermal stability of surfactant mixture in the presence of PMO was analyzed to evaluate the possibilities of the surfactant's thermal degradation. This ability is crucial to ensure the performance of the surfactant under reservoir temperature during the flow between injection well to the production well which usually takes several days, even months. As presented in Figure 3, the IFT value of PMO-contained surfactant tend to be increasing above 10^{-3} dyne/cm at elevated temperature. However, the addition of alkaline, thermally stable surfactant mixture until 2 months was achieved, was associated with the increasing pH of surfactant solution. This result is in agreement with the previous study which showed that surfactant was thermally stable when the pH solution is maintained at pH 10-11. Whereas, the hydrolysis of surfactant occurs more rapidly when the pH solution is outside this range, especially at lower pH (Adkins et al. 2012).

D. The ability of MES-PMO surfactant to recover oil production

In order to investigate the performance of MES in the presence of PMO to enhance oil recovery,

Table 2
Oil recovery by chemical flooding at four different systems

Core number	Surfactant slug Component	Polymer slug		S_{or} after WF (% S_{oi})	Additional recovery		
		PV	Polymer		% S_{oi}	% S_{or}	
1	- 1% MES + PMO4 - 0.5% alkaline	1.0	--	--	59.69	17.27	28.94
2	- 1% MES + PMO4 - 1% MES + PMO4	0.3	750 ppm	0.5	62.48	8.04	12.87
3	- 0.5% alkaline - 500 ppm polymer	1.0	1250 ppm	1.0	56.65	31.35	55.35
4	- 0.5% CS II - 0.2% alkaline	1.0	1500 ppm	1.0	57.00	18.33	32.16

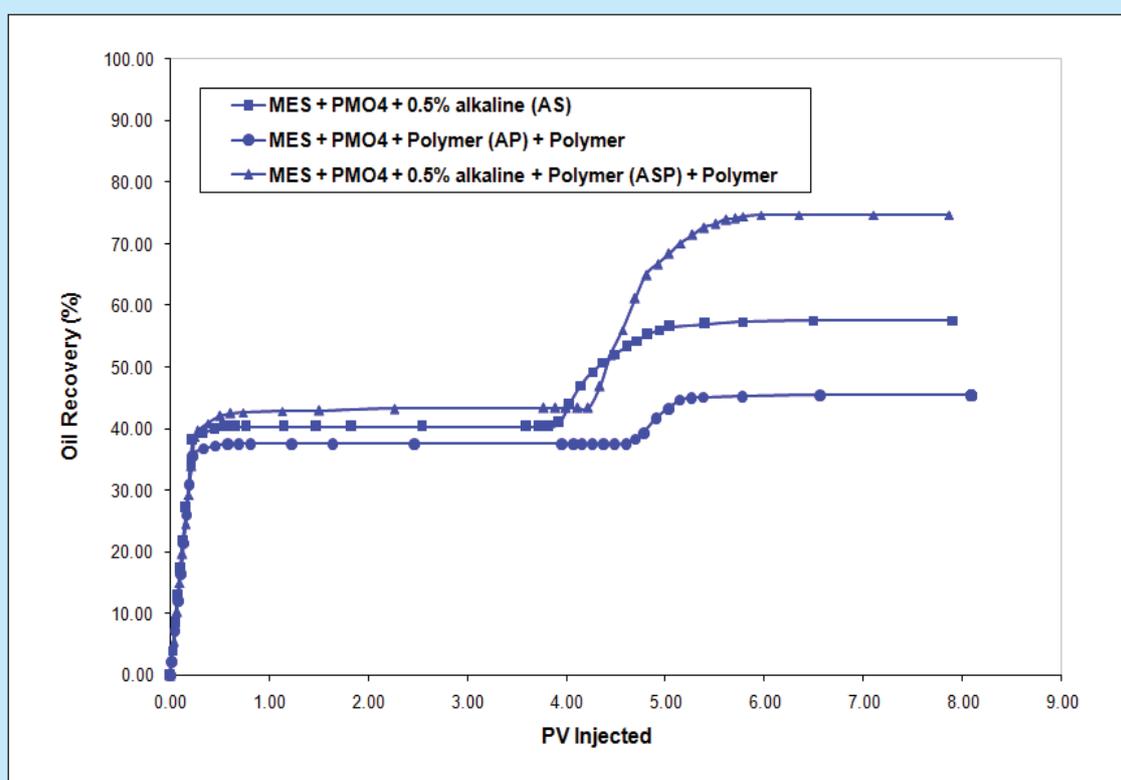


Figure 4
Cumulative oil recovery of chemical flooding in the presence of co-surfactant PMO.

several core flooding experiments were conducted. The addition of polymer to the slug design was intended to improve the displacement process as well as to lower the mobility ratio. All of displacement tests were performed under the same conditions of porosity and permeability using standard core Buff Berea. All chemical solutions were freshly prepared just before being used so as to avoid any effect of air exposure, which may alter the characteristics of

chemicals. A summary of displacement results is shown in Table 2.

The addition of PMO in surfactant MES proved to be able to enhance oil recovery. As described in Table 2, for 1.0 PV surfactant slug contains the mixture of 1.0% MES and PMO in the presence of alkaline and can recover oil production until 28.94%. However, the injection of 0.3 PV surfactant may not be effective to improve oil recovery as that

only obtained additional recovery at 12.87% S_{or} , although slug polymer was added for improving volumetric sweep efficiency. The highest recovery factor was achieved by the injection of slug design 3 consisting of alkaline, surfactant and polymer with additional recovery of 55.35% S_{or} . Chemical flooding containing surfactant, alkaline and polymer as the first slug followed by single polymer as the second slug was considered the most effective slug design for chemical injection. The different role of each chemical is crucial at providing the optimum performance of chemical design. Surfactant for microscopic sweep efficiency and polymer for macroscopic sweep efficiency in the presence of alkaline for hydrolytic stability has been proved to be effective to increase recovery factor.

IV. CONCLUSIONS

The presence of co-surfactant PMO in the surfactant mixture has a great influence on the solubility of surfactant in the targeted-fluid reservoir. One milky phase solution was observed in the addition of PMO associated with the ethoxy groups in the molecular structure of PMO. The addition of PMO into the surfactant solution was also shown to be effective in decreasing the IFT from 10^{-1} dyne/cm to the ultralow level and can be maintained under elevated temperature for two months. Core flooding experiments to investigate the performance of surfactant indicated that slug design with surfactant polymer in the presence of PMO followed by polymer drive is the most effective slug design to recover oil production with additional recovery at 55.35% S_{or} .

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