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## DIFFERENT APPROACH TO SURFACTANT SCREENING METHODS FOR ASP FLOODING

Darko Popić<sup>1</sup>, Jasna Pantić<sup>1</sup>, Milos Tripković<sup>1</sup>, Bojan Martinović<sup>1</sup>,  
Andrej Antropov<sup>1</sup>, Miroslav Crnogorac<sup>2</sup>

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### **Abstract:**

Selection of adequate surfactant is one of the most important steps in preparation for ASP EOR. There are many parameters to be taken in considerations in this process but different authors are prioritizing different parameters. Shown here is comparative analysis of two surfactants chosen according difference set of priorities, in one low IFT and stability and type of created microemulsion was priority (Surfactant A) and in another mobility of created microemulsion (Surfactant B). Bottle test was done with both surfactants to assess the stability of microemulsion at formation temperature, and coreflood test to assess ability of surfactant to mobilize trapped oil. During first round of tests Surfactant A gave better results, very low IFT and stabile Windsor type III microemulsion while Surfactant B gave higher IFT and Windsor type I microemulsion. During coreflood test Surfactant B performed better in terms of oil recovery factor (ORF) and injection pressures. Apparently, stabile Windsor type III microemulsion that is considered desirable in ASP injection and widely prioritized in surfactant selection process can cause decrease in permeability and injectivity issues. Good results can be obtained with IFT in “moderately” low range and stability of microemulsion is not critical in terms of oil recovery factor.

**Keywords:** Chemical EOR; Surfactant selection; Ultra low IFT; Coreflood testing

## 1 INTRODUCTION

Being that primary and secondary methods of oil production can extract only limited part of original oil in place (OOIP), and with most of the big oilfields being in late phase of production, there is higher demand to increase oil recovery from oilfields already in production. Conventional oil production methods leave large amounts of oil in reservoir, so there is a need for cost efficient methods to boost production. This goal is achieved by chemical enhanced oil recovery (cEOR) methods – injecting alkali, surfactant and

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<sup>1</sup> NTC NIS Naftagas doo, Narodnog fronta 12, 21000 Novi Sad

<sup>2</sup> University of Belgrade - Faculty of Mining and Geology, Đušina 7, 11000 Belgrade

E-mails: [darko.popic@nis.rs](mailto:darko.popic@nis.rs); [jasna.pantic@nis.rs](mailto:jasna.pantic@nis.rs); [milos.tripkovic@nis.rs](mailto:milos.tripkovic@nis.rs);

[bojan.martinovic@nis.rs](mailto:bojan.martinovic@nis.rs); [antropov.av@nis.rs](mailto:antropov.av@nis.rs); [miroslav.crnogorac@rgf.bg.ac.rs](mailto:miroslav.crnogorac@rgf.bg.ac.rs)

polymer separately or in mixture (ASP) in to reservoir to mobilize oil that couldn't be extracted by conventional production methods.

Chemical EOR / ASP methods are studied and implemented for decades in various condition all over the world. In this period significant progress was made in terms of developing products that can be used in harsh reservoir conditions (heavy oil, high temperature and salinity) but overall principle stayed the same. Alkali is reacting with organic acids that are occurring in oil naturally to form soap (Gao et al., 1995; Mahdavi & Zebarjad, 2018). This newly formed soap together with injected surfactant have a task to decrease interphase tension (IFT) between water and oil, change wettability of porous environment and create mobile microemulsion that will be produced with help of viscous polymer front arriving after surfactant (Mohyaldinn et al., 2019; Wang et al., 2007).

Surfactants are surface-active substances with polar (or hydrophilic) head and a nonpolar (hydrophobic) tail, this allows them to have affinity to aqueous and non-aqueous phase due to the amphiphilic nature. Generally speaking all surfactant types can reduce the IFT between the aqueous and oil phase and change environment wettability to more water-wet conditions, but selecting the suitable type of surfactant is very crucial in terms of solubility, thermal and chemical stability, and adsorption of the surfactant under harsh reservoir conditions (Borchardt et al., 1985; Eftekhari et al., 2015). Generally, surfactants are classified into main four groups: anionic, cationic, and non-ionic and zwitterionic (also known as amphoteric) (Gupta et al., 2020; Mahboob et al., 2022; Bera & Mandal, 2015).

The key to successful cEOR is selecting right surfactant or alkali surfactant mixture that will effectively mobilize trapped oil held in small pores by capillary forces. It is achieved through decrease of IFT to a point of forming microemulsion and changing reservoir rock wettability. In surfactant selection process one of the main criteria is type of microemulsion formed with oil and its stability (Bera & Mandal, 2015; Guo et al., 2012; Salager et al., 2013) – Winsor type III microemulsion that is stabile in time at reservoir condition. Some authors suggest that most important criteria is mobility of formed microemulsion (Puskas et al., 2017, 2018). Stable Winsor type III emulsion can be achieved only with very low IFT values (order of 10<sup>-3</sup> mN/m or lower) but mobile microemulsion can be achieved with higher IFT values (order of 10<sup>-2</sup> mN/m).

In this paper are presented two different surfactants chosen by these two criteria for same reservoir, using two mentioned principles. Since different guiding principles were used in these two cases it was impossible to compare these surfactants except to test their performance with bottle test, emulsion stability and core flood experiments.

All experiments mentioned in this paper were done as a part of preparation for chemical EOR project on oilfield in northern part of Serbia. Reservoir rock is upper Miocene sandstone, medium to coarse grained, carbonaceous in parts, loose to moderately well

cemented with siliceous and calcareous cement. Entire reservoir is generally high permeable, with permeability ranging from 1 to 6 Darcy.

## 2 METHODS AND MATERIALS

Reservoir conditions and oil characteristics, main criteria for surfactant selection, were shared with surfactant manufacturers. Of all samples received, the two most promising were selected: 1st for its low IFT value and 2nd for high oil displacement efficiency determined by thin layer chromatography. For both surfactants optimal concentration is set to 0,5%. Characteristics of tested surfactants are shown in table 1.

**Table 1** Main characteristics of surfactants used in experiments

Product name	Composition	Measured IFT	pH of aqueous solution
<b>Surfactant A</b>	mixture of mono and diesters of phosphoric acid and ethoxylated C12-C15 alcohols with isobutanol	IFT: $1,9-2,1 \cdot 10^{-4}$ mN/m (in 0,5% solution)	5,93
<b>Surfactant B</b>	Sulfonic acid derivative and fatty acid methylester derivative in 2-butoxyethanol solvent	IFT: 0,0078 mN/m (in 0,5% solution)	7,5 - 9,5

Reservoir oil has total acid number (TAN) ranging from 0,7 - 2,0 mg KOH/g usage of alkalis is recommended (Sheng, 2015; Chang et al., 2006). Surfactant A has a low pH value so it is combined with 1% of  $\text{Na}_2\text{CO}_3$  to boost oil displacement. Addition of alkali will boost oil displacement through saponification process that occurs when alkali comes in contact with naphthenic acids in oil (Gbadamosi et al., 2019), and also to decrease adsorption of surfactant to rock surface (Zhong et al., 2020). Surfactant B has pH around 8,5 so adding alkali in mixture wouldn't increase efficiency of oil displacement – what was the intention of manufacturer.

Since salinity and TDS of formation water is not high (11 g/l of NaCl equivalent and 13,9 g/l TDS) and very low iron content (below 2 mg/l) it was decided that formation water separated at gathering station will be used for preparation of ASP / SP mixture during field operations. For purpose of laboratory testing all ASP/SP mixtures were prepared with modelled formation water, recipe is shown in table 2.

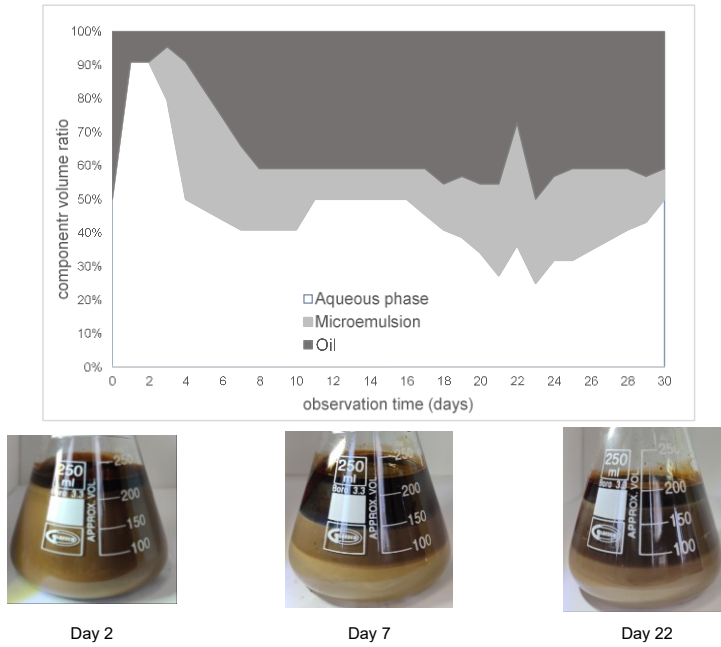
**Table 2** Salts used to prepare Main characteristics of surfactants used in experiments

Salts	concentration (g/l)
CaCl <sub>2</sub>	0,20
MgCl <sub>2</sub> ×6H <sub>2</sub> O	0,10
Na <sub>2</sub> SO <sub>4</sub>	0,05
NaHCO <sub>3</sub>	5,10
NaCl	7,50

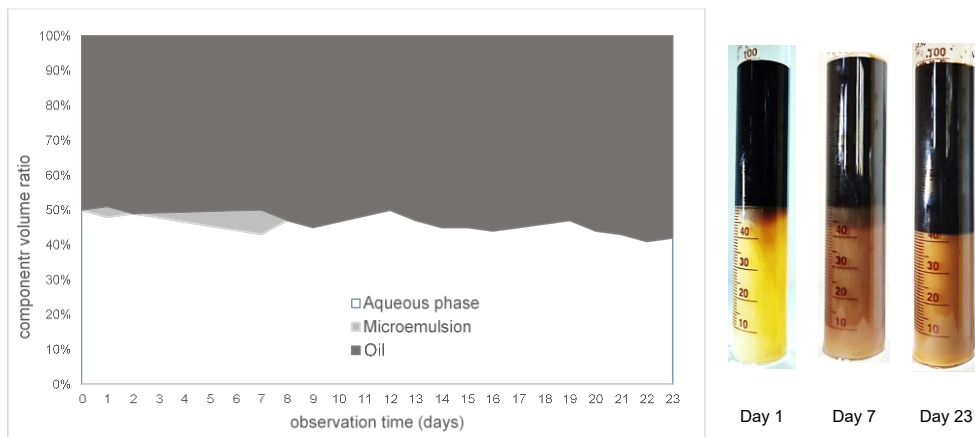
### 2.1 Bottle test

With both surfactants bottle test was performed to assess and compare ability to form microemulsion, quantity and stability of microemulsion. Bottle test was performed with reservoir oil, extracted from produced fluid only by heating without chemicals and with surfactant and alkali/surfactant mixture prepared with modelled formation water. Oil and alkali surfactant / surfactant solution were mixed in 1:1 ratio. After turning the bottle upside down continuously by hand for 2 minutes, samples were placed into a thermo regulated oven at 67°C (formation temperature) for a period of 30 and 23 days, respectively. Samples were taken out once per day to check for presence, type and quantity of microemulsion.

Results of bottle test with mixture 0,5% Surfactant A + 1% Na<sub>2</sub>CO<sub>3</sub> and 0,5% Surfactant B are shown in figures 1 and 2.



**Figure 1** Microemulsion stability during bottle test with Surfactant A. (a) day 2: Windsor type I microemulsion; (b) day 7: Windsor type III microemulsion, (c) day 22: Windsor type III microemulsion



**Figure 2** Microemulsion stability during bottle test with Surfactant B. (a) day 1: day 1: Windsor type III microemulsion, (b) day 7: Windsor type III / type I microemulsion; (c) day 23: Windsor type I microemulsion

With both surfactants bottle test was performed to assess and compare ability to form microemulsion, quantity and stability of microemulsion. Bottle test was performed with reservoir oil, extracted from produced fluid only by heating without chemicals and with surfactant and alkali/surfactant mixture prepared with modelled formation water. Oil and alkali surfactant / surfactant solution were mixed in 1:1 ratio. After turning the bottle upside down continuously by hand for 2 minutes, samples were placed into a thermo regulated oven at 67°C (formation temperature) for a period of 30 and 23 days, respectively. Samples were taken out once per day to check for presence, type and quantity of microemulsion.

With Surfactant A Winsor type I microemulsion was formed immediately after mixing when 80% of present oil was dispersed in water phase. Gradually, after 2 days Winsor type I microemulsion is starting to break apart with increase in free oil phase and forming of type III microemulsion. Aqueous phase is not clear, it contains lots of dispersed oil and it looks like aqueous phase in Winsor type I microemulsion. Microemulsion layer formed between aqueous and oil phase is relative stable and, with changes in volume, it exists during entire observation period of 30 days. With Surfactant B immediately after mixing small quantity of Winsor type III microemulsion is formed, with oil phase dispersed in aqueous phase so it resembles type I microemulsion. Winsor type III microemulsion is stable for 7 days and it is dispersed. After that mixture resembles Winsor type I microemulsion with oil in water emulsion but volume of oil phase is slowly increasing over observation period so part of water is dispersed in oil phase as well.

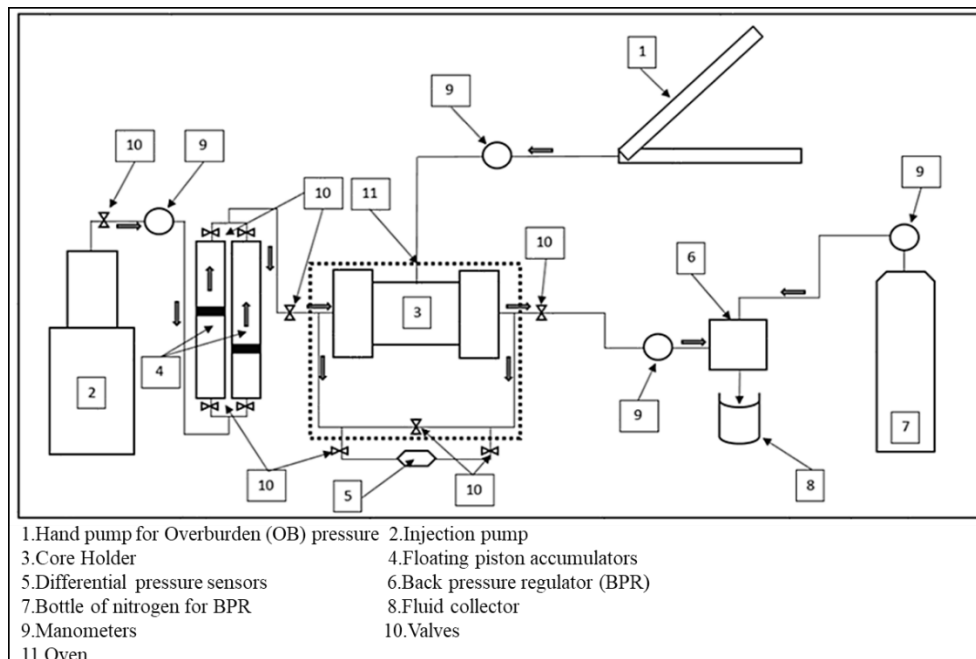
## 2.2 Coreflood test

To test ability of these surfactants to mobilize residual oil from porous rock sample coreflood tests were performed with ASP / SP mixtures prepared with Surfactant A (ASP mixture) and Surfactant B (SP mixture). As criteria to determine surfactant performance changes in oil recovery factor (ORF) were used. ORF represent decrease in residual oil saturation ( $S_{oi-Sor}$ ) divided by initial oil saturation ( $S_{oi}$ ). Test were performed on cylindrical samples formed from sand and poorly consolidated sandstone retrieved during coring operations. All rock samples undergo soxhlet extraction using toluene to remove any residual oil or contamination. After extraction sand was tightly packed in thermoresistant sleeves to form cylindrical samples 3,81cm (1,5 inch) in diameter and approximately 13,5 cm (5,3 inch) long. Sample characteristics are shown in table 3.

For preparation of ASP mixture (in case of Surfactant A) and SP mixture (Surfactant B) as polymer was used HPAM with high molecular weight (18-20 106 Da) in concentration sufficient to reach target mixture viscosity of 10 mPa\*s that was chosen according to oil viscosity and average reservoir permeability. As alkali 1% of Na<sub>2</sub>CO<sub>3</sub> was used. All mixtures were prepared with model formation water. For purpose of experiment reservoir oil, extracted from produced fluid only by heating without chemicals, was diluted with petroleum benzine (C7 n and iso alkanes with cyclic HC) to decrease its

viscosity to value at reservoir conditions. During experiment, two ASP/SP mixtures were used: first with surfactant concentration of 0,1% and second of 0,5% - to imitate dilution effect that will happen in reservoir.

Coreflood experiments were performed on “in house” coreflood system, with coreholder placed in thermo-regulated oven, with regulation of back-pressure (pore pressure), lateral pressure (overburden) and syringe pump for fluid injection. Setup of coreflood system is shown on figure 3. Coreflood test were performed at 67 °C reservoir temperature, with 140 Bar of overburden pressure and with 65 Bar of pore pressure (back pressure).



**Figure 3** Setup of coreflood system used in experiments

Coreflood experiment was done in as per following steps:

- Injecting the model formation water (MFW) at three flow rates until the differential pressure stabilizes (minimum 1 pore volume), goal is to determine linear permeability for MFW ( $K_w$ ).
- Injection of oil at a constant flow rate until the differential pressure stabilizes (minimum 3 pore volumes). Fluid at outlet is sampled and initial water saturation ( $S_{wi}$ ) is determined by measuring quantity of produced fluid.
- Partial isolation of the core sample on reservoir conditions (aging process) for a period of 72 h. Oil is periodically injected for six hours at a lowest possible flow rate.

- Oil injection at three flow rates until the differential pressure stabilizes (minimum 1 pore volume). Linear effective permeability for oil ( $K_{o@S_{wi}}$ ) is determined.
- Injecting MFW at constant flow rate until the differential pressure stabilizes (minimum 3 pore volumes). During injection, fluid at outlet is continuously sampled, the volume of displaced oil is monitored to determine change in oil recovery factor (ORF1). After stabilizing the differential pressure, the effective permeability for MFW ( $K_{w1@S_{or}}$ ) is determined. 2-3 pore volumes of MFW re injected at an increased flow rate to confirm ORF value.
- Injecting first ASP / SP composition (alkali + polymer + 0.1% surfactant concentration), total of 2 pore volumes at constant flow rate. Differential pressure is recorded and the fluid at the outlet is continuously sampled (every 0.2 pore volume). Volume of displaced oil is monitored to determine change in oil recovery factor (ORF2).
- Injecting second ASP / SP composition (alkali + polymer + 0.5% surfactant concentration), total of 2 pore volumes at constant flow rate. Differential pressure is recorded and the fluid at the outlet is continuously sampled (every 0.2 pore volume). Volume of displaced oil is monitored to determine change in oil recovery factor (ORF3).
- Injecting MFW at constant flow rate. The MFW is pressed until the differential pressure stabilizes (minimum 3 pore volumes). During indentation, the fluid at the outlet is continuously sampled every 0.5 pore volume. Volume of displaced oil is monitored to determine change in oil recovery factor (ORF4). After differential pressure is stabilized, the effective permeability for MFW ( $K_{w2@S_{or}}$ ) is determined.

Results of coreflood experiments were shown in figures 4 and 5 and in table 3. Amount of oil produced during coreflood test is expressed through Oil Recovery Factor (ORF): ratio between decrease in oil saturation of certain phase and initial oil saturation.

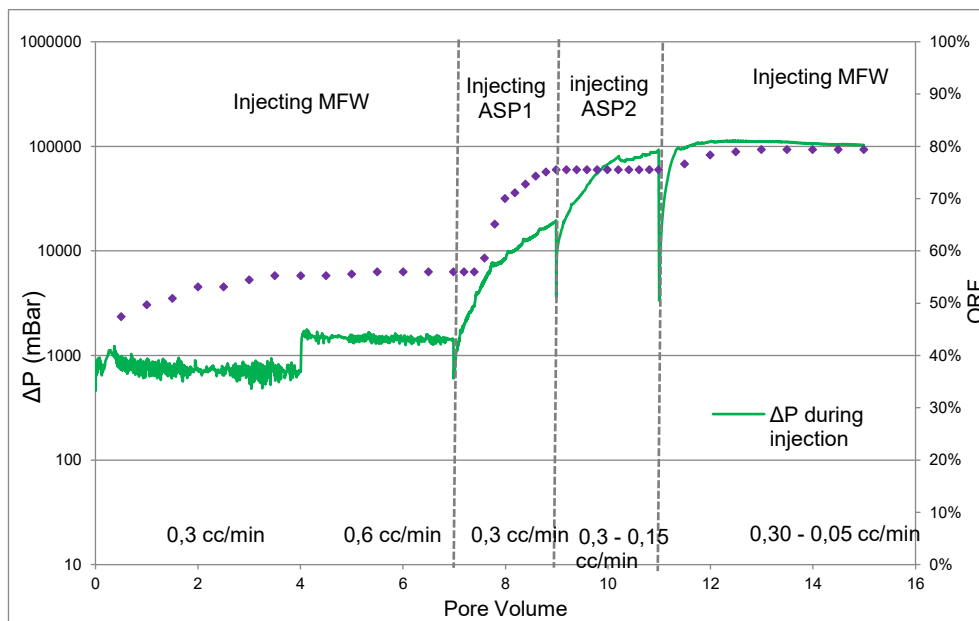
Changes in differential pressure during injections are also shown on figures 4 and 5 as indicators in changes in permeabilities during and after ASP / SP mixture injections: Resistivity modification and residual resistivity factor. Resistance modification ( $R_m$ ) (Ferreira & Moreno, 2019; Thomas, 2019) is calculated from differential pressure during water injection prior to ASP/SP injection and differential pressure during ASP/SP injection at same flow rate using equation 1.



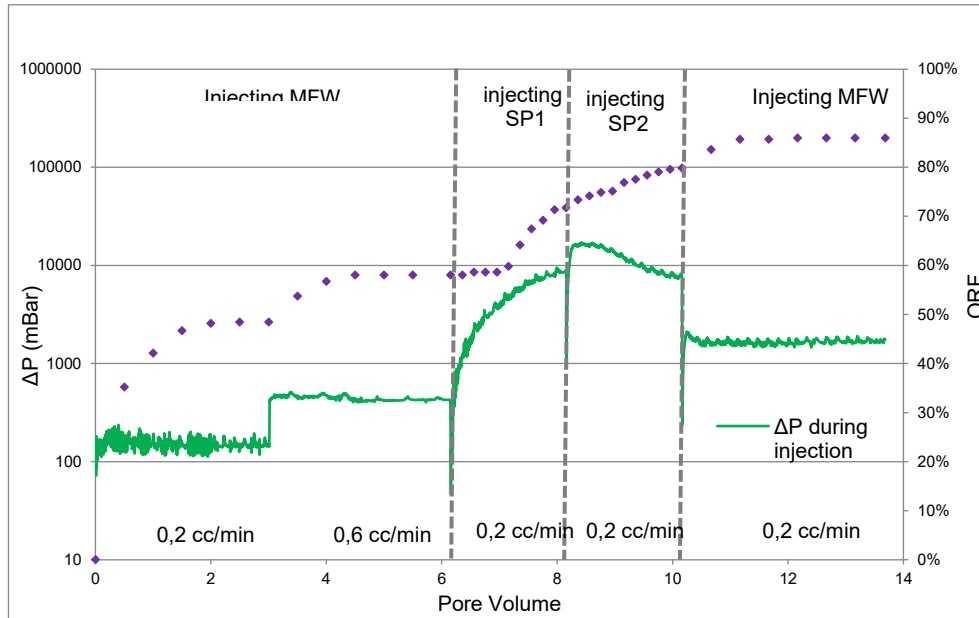
$$Rm = \frac{\Delta P_p}{\Delta P_w^{before}} \quad \begin{array}{l} \Delta P_p \text{ Differential pressure during ASP/SP} \\ \text{injection} \\ \Delta P_w^{before} \text{ Differential pressure during water injection} \\ \text{before ASP/SP mixture} \end{array} \quad (1)$$

Residual resistance factor (RRF) (Ferreira & Moreno, 2019; Thomas, 2019) is calculated from differential pressure during water injection before and after ASP/SP mixture is injected through the sample using equation 2.

$$RRF = \frac{\Delta P_w^{after}}{\Delta P_w^{before}} \quad \begin{array}{l} \Delta P_w^{after} \text{ Differential pressure during water injection} \\ \text{after ASP/SP mixture} \\ \Delta P_w^{before} \text{ Differential pressure during water injection} \\ \text{before ASP/SP mixture} \end{array} \quad (2)$$



**Figure 4** Changes in differential pressure and ORF during injection of ASP mixtures prepared with Surfactant A. ASP1 – mixture prepared with 0,1% surfactant concentration, ASP2 – mixture prepared with 0,5% surfactant concentration



**Figure 5** Changes in differential pressure and ORF during injection of SP mixtures prepared with Surfactant B. SP1 – mixture prepared with 0,1% surfactant concentration, SP2 – mixture prepared with 0,5% surfactant concentration

**Table 3** Results obtained during coreflood tests with both surfactants, both tests performed in same way on similar samples.

Phase	Surfactant A		Surfactant B	
	Results	Calculated values	Results	Calculated values
Core sample characteristics	Length: 14,575 cm		Length: 13,705 cm	
	Porosity: 30,21%		Porosity: 32,7%	
	Pore volume: 44,94 ml		Pore volume: 49,73 ml	
	Kw: 182,29 mD		Kw: 165,64 mD	
Injecting oil / reaching Soi	ORF = 0 %		ORF = 0 %	
Injecting MFW (6 PV) to reach Sor	ORF1 = 56,25%		ORF1 = 58,05%	
	Kw1@Sor = 13,64 mD		Kw1@Sor = 12,24 mD	
Injecting first ASP / SP composition (2 PV)	1% Na <sub>2</sub> CO <sub>3</sub>		0,1% Surfactant B	
	0,1% Surfactant A		0,1% Polymer	
	0,1% Polymer		Rm1 = 62,52	
	Rm1 = 85,83			
Injecting second ASP / SP composition (2 PV)	ORF2 = 75,53 %		ORF2 = 71,72 %	
	1% Na <sub>2</sub> CO <sub>3</sub>		0,5% Surfactant B	
	0,5% Surfactant A		0,1% Polymer	
	0,1% Polymer		Rm2 = 53,69	
Injecting MFW (2 PV)	Rm2 = 816,4			
	ORF3 = 75,53 %		ORF3 = 79,84 %	
	ORF4 = 79,38 %		ORF4 = 85,92 %	
	Kw2@Sor = 0,005 mD		Kw2@Sor = 1,046 mD	
	RRF = 2718,3		RRF = 12,04	

### 3 RESULTS

#### 3.1 Bottle test results

Tested surfactants react differently with oil. Surfactant A in combination with alkali ( $\text{Na}_2\text{CO}_3$ ) is decreasing IFT to a value low enough to allow forming of stabile Windsor type III microemulsion, this kind of microemulsion is desirable in chemical EOR (Ahmed & Elraies, 2018) because it better mobilize trapped oil. After initial mixing, it took 2 days for Windsor type III microemulsion to form but it was stabile without mixing for 28 days after that. Surfactant B is forming Windsor type I microemulsion, oil is dispersed in water phase with smaller part of water dispersed in oil phase as well. Clearly, IFT is significantly reduced to allow mixing oil and water but not enough to allow forming of stabile Windsor type III microemulsion. Certain quantity of Windsor type III microemulsion formed after mixing but until 7-8 days it all disappeared.

If only criteria of quantity, stability, and type of microemulsion is taken in account, Surfactant A is giving much better results. With Surfactant B, Windsor type III microemulsion is present only in short period after mixing but mixing process is taking place in porous environment in reservoir during ASP/SP mixture injection (Bob, 2016; Villermaux, 2012). Because of that stability of microemulsion cannot be considered as excluding criteria in surfactant selection process.

#### 3.2 Coreflood test results

If we compare results of coreflood tests by oil recovery factor (ORF) value it is visible that both surfactants are able to mobilize big part of oil trapped after water sweep, with Surfactant B performing slightly better in overall results (A with ORF 79%, B with ORF 85%). From that perspective it looks like that type and quantity of microemulsion formed is not excluding criteria when it comes to surfactant selection – Surfactant B during bottle test formed very small amount of Windsor type III microemulsion, while most of the water phase looked like type I microemulsion.

From the curve shown on figure 4 it is visible that Surfactant A is mobilizing residual oil immediately after injection, even in 0,1% concentration. With increase in surfactant concentration there is no increase in oil production and there is just slight increase in oil production in post flush phase when water is injected through the sample. From Surfactant B performance, shown on figure 5, it is visible that mobilization of residual oil is not that fast and that efficient in low concentration as with Surfactant A. With increase in surfactant concentration ORF is increasing as well and there is moderate increase in oil recovery during post flush period. For both surfactants speed of reaction to surfactant and oil recovery during post flush stage is happening because of adsorption / desorption process during different stages of coreflood experiment (Gogoi, 2011; Liu et al., 2004). Significant difference between this two coreflood experiments is in differential pressure during injection stages. With Surfactant A there is big increase in

differential pressure during transitioning from lower to higher surfactant concentration and no pressure decrease during post flush phase. With Surfactant B there is a slight pressure increase when mixture with higher surfactant concentration is injected and there is pressure drop during post flush phase when water is injected. This is clearly visible in changes in Resistance modification ( $R_m$ ) and Residual resistance factor (RFF) values shown in table 3. This difference in injection pressures between two coreflood experiments cannot be caused by polymer retention since the same polymer is used in same concentration on very similar rock sample in both experiments.

#### 4 CONCLUSION

It seems that difference in injection pressures between two coreflood experiments is caused by significant quantity of stabile Windsor type III microemulsion because only difference between experiments is surfactant used and its way of interaction with oil. Stabile microemulsions can have high viscosity and cause flow restriction that can cause injection problems, especially with single surfactant system.

- From performance of Surfactant B, it is visible that absence of stabile Windsor type III microemulsion is not disadvantage during chemical EOR operations.
- Even with IFT value in “moderately” low range, good results on terms of ORF value can be obtained.
- Initial screening criteria that IFT value for oil / surfactant solution has to be as low as possible and that microemulsion has to be stabile Windsor type III is not valid.
- With surfactant that decrease IFT to “moderately” low value there is less risk that highly viscous microemulsions will form and cause flow problems in reservoir.
- If microemulsions are only stabile during, and shortly after mixing, there is less chance that chemical EOR operations can cause problems during oil preparation process in gathering stations, after oil is produced. If oil with traces of surfactant reaches production wells it is better that microemulsion lose stability immediately after “mixing” in porous environment stops and starts to dissolve to separate phases: oil and formation water. In this way impact on produced fluid is minimized.

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