

# An experimental study on ASP process using a new polymeric surfactant

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**Abstract** This paper presents an alternative chemical formulation using a new polymeric surfactant to improve the conventional alkali/surfactant/polymer (ASP) flooding. It is a one-component system for interfacial tension reduction and viscosity control. To simulate the conventional ASP flooding, the performance of the polymeric surfactant was studied in the absence and presence of sodium carbonate. The most outstanding feature of the new polymeric surfactant lies in its viscosity insensitivity towards an increasing alkali concentration up to 1.2 wt%. This feature makes the new formula superior to the conventional ASP process. A combination of alkali and surfactant with a concentration of 0.8 and 0.4 wt% was found to significantly reduce the interfacial tension while maintaining the desired solution viscosity. The optimal polymeric surfactant concentration was then validated in coreflood experiments using different surfactant concentrations. Using the optimum surfactant and alkali concentrations, tertiary oil recovery could reach 16.3 % of the original oil in place by injecting a 0.5 pore volume of the formulated slug. This makes the new polymeric surfactant promising because it has structural feature that can be modified to give a width range of interfacial tension reduction and viscosity control to suit reservoir conditions.

**Keywords** Enhanced oil recovery · ASP flooding · Interfacial tension · Mobility control

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## Introduction

The alkali-surfactant-polymer (ASP) flooding is an important method for chemical enhanced oil recovery. In the ASP process, the alkali reacts with the organic acids present in the crude oil to form an in situ surfactant. The formed in situ surfactant combines with the injected surfactant to produce synergistic mixtures at the oil/brine interface (Elraies et al. 2010a, b). The alkali is also claimed to raise the pH of the flooding material to reduce the surfactant adsorption onto the sand surface (Rudin et al. 1994; Touhami et al. 2001). This increases the electrostatic repulsion between the rock surface and the negatively charged surfactants.

The surfactant reduces the interfacial tension (IFT) between the brine and residual oil causing capillary number to increase. The capillary number is a ratio of viscous forces to forces arising out of IFT. The use of proper surfactant can effectively lower the IFT resulting in a corresponding increase in the capillary number (Berger and Lee 2006). A useful technique for increasing the oil recovery by chemical flooding is adding polymer to the flood water to reduce the mobility of the aqueous phase, thus improving the sweep efficiency. A polymer also increases the capillary number, by increasing the viscosity of the displacing phase (Gan-Zuo et al. 2000). The benefits of ASP flooding are both to effectively mobilize the residual oil and economically increase the recovery factor from a reservoir.

ASP flooding has been proven to increase oil recovery in the field with great success. Daqing oil field in China is one of the earliest and successful fields to apply ASP on an extended field scale with an increase in oil recovery of 18–23 % OOIP (Wang Fenglan et al. 2008). The department of energy project in the Sho-Vel-Tom field in Oklahoma reported that the application of the ASP process

reduced the oil saturation from 35 to <5 % (French 1996). However, even with these advantages and the success of other ASP projects, the process is not without some disadvantages (Wang Demin et al. 1999).

An earlier paper written by Jirui et al. (2001) addresses the corrosion and scale problems that occurred during the ASP flood in Daqing field. A strong alkali has a detrimental effect on polymer performance, and in many cases additional polymer is required to achieve the desired viscosity (Wang et al. 2006). Nasr-El-Din et al. (1992) conducted an experimental study to examine the effectiveness of alkali concentration in ASP performance. Their experiments also confirmed an exponential decrease in viscosity of the combined ASP slug with the increase in alkali concentration. A process that reduces some of the above problems is needed and this paper is proposing such a process.

In this paper, the performance of a new polymeric surfactant for enhanced oil recovery application has been evaluated. The aim of the polymeric surfactant is to overcome some of existing problems associated with the conventional ASP flooding without compromising the efficiency of the latter. A series of experiments were conducted to evaluate this surfactant in the absence and presence of sodium carbonate as an alkaline agent.

## Materials and methods

### Material description

Crude oil collected from Angsi I-68 reservoir, offshore Trengganu, Malaysia was used throughout this study. The total acid number was 0.478 mg KOH/g and the live oil had a viscosity of 0.3 cp. The API gravity of the dead oil used in this study was 40.1°, and the kinematic viscosity was 1.456 mm<sup>2</sup>/s at test temperature of 90 °C.

The alkali used was analytical grade sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>). The surfactant used in this paper was polymeric sodium methyl ester sulfonate (PMES). A single step route similar to Ye et al. (2004) was used to produce the new polymeric surfactant via polymerization process. The purpose of this process is to graft the sulfonated group to the hydrophobic groups that are grafted to the polymer backbone. Therefore, the polymerization was conducted with an excess of different surfactant to acrylamide ratios for IFT reduction and viscosity control. More details about the surfactant synthesis and performance can be found (Elraies et al. 2010a, b).

Softened water was used as injection water, and the synthetic brine similar to the formation water was blended to saturate the core sample prior to coreflood test. The compositions of the softened water and synthetic brine are given in Table 1.

**Table 1** Softened water and synthetic brine compositions

	Softened water	Synthetic brine
Total salinity (ppm)	107	9,990
Sodium (ppm)	43.9	3,810
Chloride (ppm)	48	6,070
Calcium (ppm)	0.9	30
Magnesium (ppm)	13.6	25
Potassium (ppm)	0.6	55

### Apparatus and methods

The kinematic viscosity of various polymeric surfactant solutions was measured using Tamson viscometer model TVB44 at 90 °C. Interfacial tensions between different polymeric surfactant solutions and Angsi crude oil were measured with spinning drop method. Model SVT 20 spinning drop tensiometer equipped with video camera was used to determine the IFT at ambient temperature. For each sample, the fluids whose IFT was to be measured were introduced into a capillary tube. The tube was first filled with the denser fluid and then closed with teflon cap having a rubber septum. Then, a drop of the less dense fluid (oil) was injected into the tube through the rubber septum using a syringe. The tube-cap assembly was inserted into the tensiometer slot and screwed firmly in place. Appropriate rotation speed was then adjusted, so that the oil droplet can be suitably elongated. Lastly, the IFT between the two fluids were calculated using a built-in software system.

The static surfactant adsorption was measured in the absence and presence of different alkali concentrations. The adsorption tests were performed by adding the alkali-polymeric surfactant solutions to sandstone samples at a solid to liquid ratio of 1 % (mass/volume ratio). The solutions were prepared using softened water and then mixed with the sandstone by a magnetic stirrer for 1 h. Consequently, the samples were closed with phenolic screw caps to limit the evaporation during the equilibration period of 5 days at 90 °C. After the equilibrium time, the surfactant concentration in each sample was determined by comparing the refractive index values after equilibrium with the initially plotted calibration curves.

Oil recovery was determined using linear Berea sandstone core samples. A series of coreflood tests were conducted horizontally to define the optimum surfactant concentration. In a typical test, core sample was saturated with synthetic brine followed by oil until an immobile water saturation condition is achieved. The core was then flooded to the residual oil saturation or the remaining oil saturation as designed. At the residual oil saturation, the core was flooded with 0.5 PV of APS slug using an injection rate of 0.5 ml/min. Once the entire APS slug has

been injected, extended water flood was initiated until the oil production became negligible. For all runs, synthetic brine similar to Angsi formation water was used to displace Angsi crude oil before and after the APS flood was initiated. The APS slug was prepared using softened water.

### Results and discussion

#### Polymeric surfactant performance

The viscosity and IFT performances of the polymeric surfactant were investigated using different PMES. Figure 1 shows that the viscosity of the solution significantly increases as PMES concentration increases. The viscosity of the solution was approximately 1.75 mm<sup>2</sup>/s for a 0.2 wt% PMES solution concentration, 2.533 mm<sup>2</sup>/s for 0.4 wt% concentration, and 5.124 mm<sup>2</sup>/s with the highest PMES solution concentration (0.7 wt%). The latter solution viscosity is very high as compared to the viscosity of the crude oil (1.654 mm<sup>2</sup>/s). So in order to design a cost-effective polymeric surfactant slug that offers a favorable mobility ratio, a polymeric surfactant concentration of 0.4 wt% was chosen as the optimum concentration for the chemical flooding displacement of the crude oil used in this work. The determination of cost-effect was based on the viscosity and IFT performance of the surfactant.

The IFT between Angsi crude oil and various surfactant concentrations are also shown in Fig. 1. The polymeric surfactant showed good results in term of IFT reduction, where the IFT between the crude oil and surfactant solution could be reduced from 13.6 mN/m to 0.323 mN/m using 0.2 wt% surfactant concentration. As seen in Fig. 1, the IFT reduced drastically upon the addition of surfactant concentration which explains the surface adsorption and

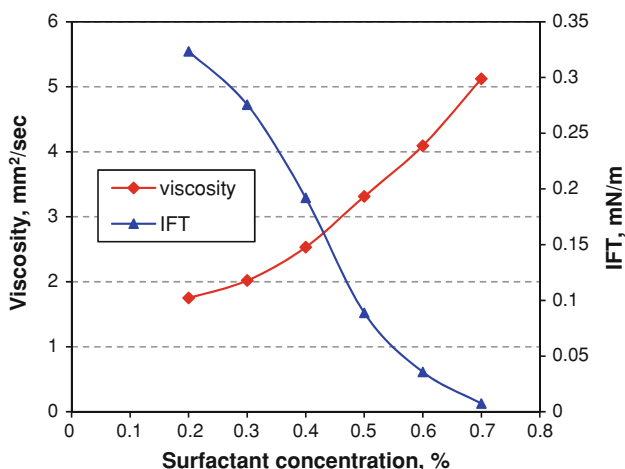


Fig. 1 IFT and viscosity performance of various surfactant concentrations

aggregative properties of the surfactant. As the surfactant concentration increase, more surfactant molecules will be aggregated at the oil/water interface to form micelle solution. Using the selected surfactant concentration of 0.4 wt%, the IFT decreased to 0.192 mN/m where the IFT was stabilized.

#### Viscosity and IFT in the presence of alkali

Since alkali has a significant impact on ASP flooding performance, the effect of alkali on the performance of the PMES was investigated using different sodium carbonate concentrations and 0.4 wt% of polymeric surfactant concentration. The purpose of these measurements was not only to study the effect of the alkali on the IFT reduction, but also to determine if the presence of sodium carbonate in the system would affect the viscosity of the polymeric surfactant. Figure 2 shows the viscosity performance in the absence and presence of sodium carbonate at 90 °C. The presence of alkali at concentrations ranging from 0.2 to 1 wt% does not affect the viscosity of the system; the viscosity of the polymeric surfactant remains constant at 2.533 mm<sup>2</sup>/s. This shows the stability of the viscosity of the new polymeric surfactant in the presence of sodium carbonate, if compared to the conventional ASP formula where its viscosity is greatly affected by the added alkali (Nasr-El-Din et al. 1992).

Figure 2 shows also the IFT between the crude oil and different alkali concentrations in the presence of 0.4 wt% surfactant. As seen in Fig. 2, the IFT decreased significantly due to the addition of alkali concentration and reached 0.024 mN/m at 0.8 wt% alkali. When the alkali concentration was 0.2 wt%, IFT did not change much.

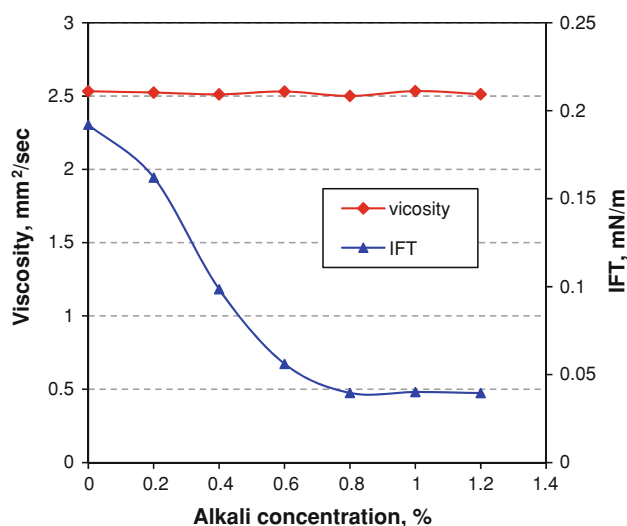
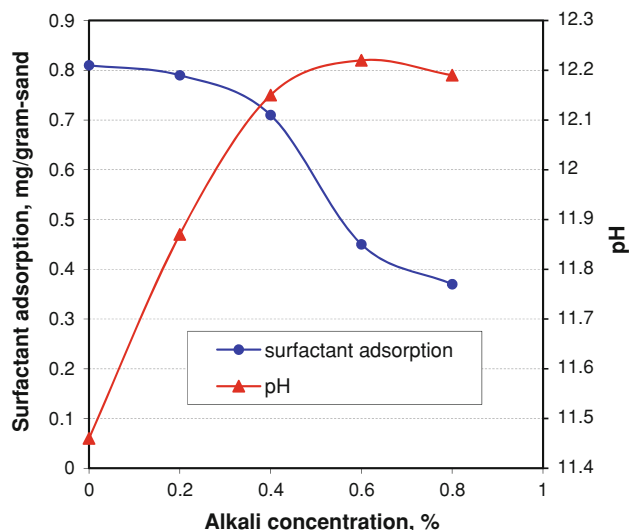


Fig. 2 Viscosity and IFT performance in the absence and presence of various alkali concentrations



**Fig. 3** The effect of different alkali concentrations on surfactant adsorption isotherms

However, significant decreases were observed when the alkali concentration was as high as 0.2–0.8 wt%. This rapid decrease in the IFT can be explained by the production of in situ surfactants with the added surfactant to produce synergistic mixtures at the oil/brine interface. This was caused by the reaction between the acids and esters present in the crude oil and alkali. As a result, 0.8 wt% alkali concentration was selected as the optimum concentration in the presence of 0.4 wt% surfactant concentration.

#### Static surfactant adsorption

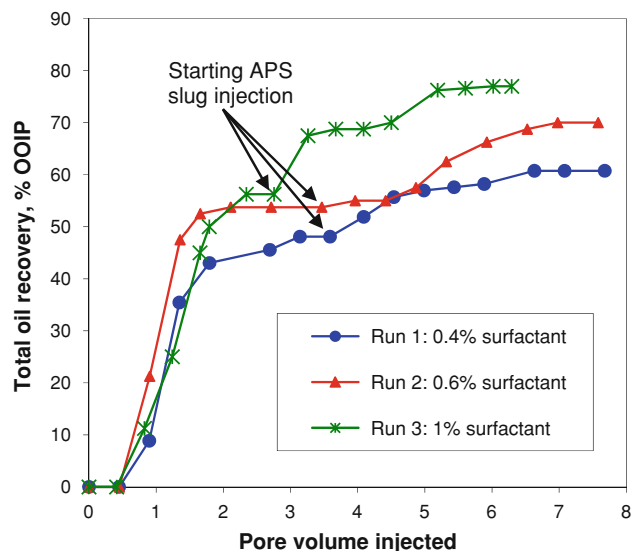
Figure 3 shows the surfactant adsorption isotherm with the corresponding pH in the absence and presence of different alkali concentrations at 90 °C. The surfactant adsorption decreased considerably with the addition of alkali to the surfactant solution. This is because high pH makes the sand surface more negative, and the electrostatic repulsive force drives more surfactant to solution. When the alkali was introduced to the system, the surfactant adsorption was reduced from 1.21 mg/g-sand to 0.79 mg/g-sand due to the introduction of 0.2 wt% alkali. When the alkali concentration was over 0.6 wt%, the saturation adsorption of the surfactant on sand was optimal, as shown by the adsorption isotherm. The saturation adsorption was estimated to be about 0.4 mg/g-sand.

#### Coreflood test

To examine the performance of the new polymeric surfactant for enhanced oil recovery application, three coreflood tests were performed using different surfactant concentrations and 0.8 wt% alkali concentration. For all

**Table 2** Summary of core samples properties and coreflood tests

	Core 1	Core 2	Core 3
Length (cm)	7.6	7.5	7.5
Diameter (cm)	3.8	3.8	3.8
Permeability (md)	88.4	113	84.9
Porosity (%)	15.7	16.4	16.9
Pore volume (cc)	13.3	13.2	14.5
Surfactant concentrations (%)	0.4	0.6	1
Alkali concentrations (%)	0.8	0.8	0.8
Residual oil after water flooding (%)	51.9	46.3	43.8
Residual oil after APS and chase water (%)	39.3	30.1	23.1



**Fig. 4** Effect of various surfactant concentrations on oil recovery (Alkali 0.8 %)

coreflood experiments, the injection strategy started with the first water flooding, chemical slug injection and then the last step involves waterflooding as chase water. The actually injection velocity for all cases was about 0.279 cm/min. Table 2 summarises the physical core properties and coreflood results.

Figure 4 shows the oil recovery performance as a function of pore volume injected. The recovery increased significantly as the surfactant concentration was increased. Using 0.6 and 1 wt% surfactant concentration, 16.2 and 20.7 % OOIP were recovered when 0.5 PV of APS slug was injected and followed by chase water, respectively. This high oil recovery was due to the synergistic effect between surfactant and alkali to emulsify and mobilize the crude oil. This increases both the microscopic displacement efficiency and sweep efficiency. However, with 0.4 wt% surfactant, only 12.6 % OOIP was produced after the injection of 0.5 PV APS slug followed by extend waterflood. The low oil recovery from this test was only due to

the microscopic displacement efficiency as a result of the low IFT observed during IFT test. The surfactant viscosity was not sufficient to mobilize the emulsified crude oil. As a result, the selected surfactant concentration from the screening study conducted prior to the coreflood test was not effective. Therefore, in order to design a cost and effective slug, 0.6 wt% surfactant was selected as the optimum surfactant concentration for this study.

## Conclusion

1. A combination of the polymeric surfactant and alkali showed good results for IFT reduction and viscosity control when Angsi crude oil was used as the oil phase.
2. The viscosity of the system was not affected by the addition of the alkali. The major contribution of the new formula is its ability to maintain the desired slug viscosity when the alkali is added to the flooding material. The viscosity of the APS slug will not be reduced with the addition of alkali as seen in conventional ASP flooding process.
3. Based on a series of core flood tests, the final oil recovery was improved as the surfactant concentration was increased up to 0.6 wt%. Beyond this concentration, the increment in oil recovery was not significant as compared to 0.6 wt% surfactant, where it is almost double in the case of 1 wt% surfactant.
4. Studies of oil recovery by alkali-polymeric surfactant (APS) flooding showed that the 0.8 wt% alkali and 0.6 wt% surfactant had the best performance in recovering residual oil after waterflooding. Tertiary oil recovery of 16.2 % OOIP was recovered when 0.5 PV of the APS slug was followed by chase water.
5. Throughout this study, softened water was used to prepare the polymeric surfactant. The salinity of this softened water is very low as compared to field application. Thus, the performance of the polymeric surfactant should be investigated using high saline water. Having a salinity range, the optimal salinity and the desired microemulsion could be determined.

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