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# Insight into hydrophobic interactions between methyl ester sulfonate (MES) and polyacrylamide in alkaline-surfactant-polymer (ASP) flooding

**Saiful Hafiz Habib*, Dina Kania**, Robiah Yunus**,****,†, Badrul Hisham Mohamad Jan***, Dayang Radiah Awang Biak****, and Rabitah Zakaria*****

*Institute of Advanced Technology, UPM 43400 Serdang, Malaysia
**Institute of Plantation Studies, UPM 43400 Serdang, Malaysia
***Chemical Engineering Department, Faculty of Engineering, University Malaya, 506300, Kuala Lumpur, Malaysia
****Chemical and Environmental Engineering Department, Faculty of Engineering, UPM Serdang, 43400, Malaysia
*****Process and Food Engineering Department, Faculty of Engineering, UPM Serdang, 43400, Malaysia

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**Abstract**−The interaction between methyl ester sulfonate (MES) surfactant and polyacrylamide (PAM) polymer in alkaline-surfactant-polymer (ASP) flooding due to electrostatic charges and hydrophobicity of both elements at the interface was investigated. In the ASP flooding, sodium hydroxide (NaOH) and sodium carbonate ($Na_2CO_3$) were used as alkali. At high PAM concentrations, the strong hydrophobic interaction between the PAM backbone and the carbon chain of MES destabilizes surfactant packing at the interface, increasing interfacial tension (IFT). The higher conductivity value of the ASP slug (15 mS/cm) compared to the alkali-surfactant (AS) slug (7 mS/cm) indicates a strong electrostatic interaction caused by the rapid mobilization of free surfactant molecules across the PAM backbone at the water–oil interface. The lowest IFT value for ASP flooding was 0.28 mN/m. Sand pack flooding tests showed that the optimum PAM concentration in ASP flooding was 1,000 ppm, resulting in a 20-35% oil recovery. A negative effect of PAM on the oil recovery was observed at a higher PAM concentration of 9,000 ppm. IFT and mobility ratios were irregularly related to the oil recovery. At 1,000 ppm PAM, the oil recovery for ASP slug with MES and commercial surfactant sodium dodecyl sulfate (SDS) was 25% and 20%, respectively, indicating that MES is superior to SDS.

Keywords: Applications, Oil and Gas, Surfactants, Surface and Interfaces, Hydrophobic Polyacrylamide

## INTRODUCTION

Alkaline-surfactant-polymer (ASP) flooding has been known as a highly efficient method for chemical enhanced oil recovery (EOR) [1,2]. Surfactants are used to lower the interfacial tension (IFT) between the trapped oil and injected brine [3-5], whereas alkali reacts with organic acids in crude oil to produce *in situ* soaps that can synergistically reduce IFT even further [6-8]. Meanwhile, the role of polymer is to increase the viscosity of the displacing fluid, thereby improving the water-oil mobility ratio and reducing the fingering effect [7,8]. Therefore, the combination of these chemicals in ASP flooding can enhance the oil recovery by increasing both sweep and displacement efficiency [2,9-11]. Their effects occur simultaneously in the reservoir [12].

Mobility ratio, M, indicates the efficiency with which oil can be displaced by another immiscible fluid [13], where a value less than 1 is desired. The fingering effect occurs as a result of less viscous displacing fluid bypassing the formation, creating multiple breakthroughs, particularly in high permeability zones, and leaving large amount of oil behind. These multiple breakthroughs, denoted by an asterisk (*) in Fig. 1, lead to a high mobility ratio. Adding polymer increases the displacing fluid viscosity and produces a uniform breakthrough. M can be calculated using the following equation:

$$M=\frac{\frac{k_w}{\lambda_w}}{\frac{k_o}{\lambda_o}} \tag{1}$$

where $k_w$: relative permeability of water, $\lambda_w$: viscosity of water, $k_o$: relative permeability of oil and $\lambda_o$ is the viscosity of oil [13,14].

Polymer and surfactant interactions were reported to occur as a result of the electrostatic charges and hydrophobicity of both elements at the interface [15]. The interactions are quantified by the balance between hydrophobic forces and electrostatic interaction [16]. The synergy of these interactions comes from the electrostatic and hydrophobic forces of surfactant-polymer binding [15,16]. At the interface, anionic surfactants such as MES create vacancies between surfactant molecules due to electrostatic interaction between its headgruops. Introducing polymer into the solution will make these sites vacant and form a compact layer of polymer-surfactant, influencing the molecular arrangement at interface, hence reducing the IFT [19]. Experimentally, it has been proven that reducing the IFT increases the oil recovery. Meanwhile, Guzmán et al. [20] reported that adding polymeric chains to a surfactant solution induces surfactant micellization due to the rapid binding of surfactant on the polymer chain and lowers the critical micelles concentration

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[†] To whom correspondence should be addressed.
E-mail: robiah@upm.edu.my

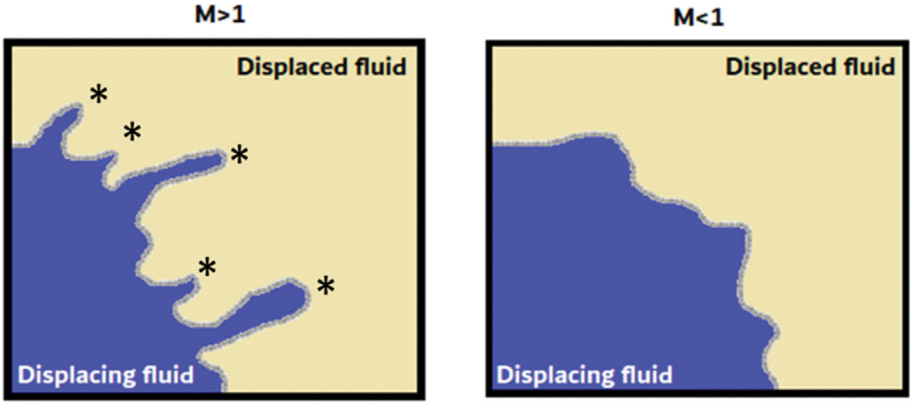

**Fig. 1. Fingering effect during oil recovery.**

(CMC) of the surfactant. Moreover, the hydrophobic interaction between the surfactant and the polymer balances the entropy associated with surfactant micellization.

Sun et al. and Xuan et al. [18,19] reviewed the literature and concluded that the synergy between surfactant and polymer during chemical flooding is critical for incremental oil recovery. Samanta et al. [23] reported that the combination of surfactant and polymer successfully increased the oil recovery by 2.8% when compared to surfactant flooding alone. Yin and Zhao [9] demonstrated that surfactant-polymer flooding increased oil recovery by 7-10% when compared to single surfactant and single polymer flooding. Other studies [21-23] also disucessed the effect of surfactant concentration on the surfactant polymer binding mechanism. In the multi complex aqueous solution of ASP slug, surfactant molecules interact with the polymer at a concentration below critical aggregation concentration (CAC) [26]. By increasing the surfactant concentration, the polymer chain becomes saturated with surfactant molecules, resulting in the formation of surfactant micelles on the polymer backbone. This interaction is highly dependent on the hydrophobicity of polymer and surfactant [27]. However, the effect of polymer concentration on the surfactant polymer interaction that contributes to the oil recovery factor has not been extensively studied.

Numerous studies have tried to determine whether methyl ester sulfonates (MES) derived from renewable feedstocks can be used as an environmentally friendly surfactant in EOR flooding [28,29]. MES is an oleo-chemical anionic surfactant with a long hydrocarbon chain that has an excellent IFT reduction, emulsifying ability, detergency performance, stability in hard water and is relatively inexpensive [25-28]. Pal et al. [32] reported the formation of a stable emulsion (ultra-low IFT) from coconut oil MES and crude oil over a wide salinity range. Kipkemboi and Rop [33] found that MES has a lower hydrophile-lipophile balance (HLB) and a lower CMC value than the conventional surfactant sodium dodecyl sulfate (SDS), indicating it may perform better. However, current EOR studies mainly use MES for surfactant flooding or alkaline-surfactant (AS) flooding [29,30,32,33], with limited use of MES for ASP flooding. Combining polymer with MES and alkaline may increase the ASP flooding viscosity and efficiently reduces the mobility ratio of oil to water and sweeps the oil to production well.

In this study, the feasibility of developing a high-performance ASP slug containing polyacrylamide (PAM) polymer and a plant oil-based methyl ester sulfonate (MES) surfactant was investigated. NaOH and $Na_2CO_3$ were selected as alkali due to their dissociative ability to form free ions in water. The effects of PAM concentration on IFT, conductivity, and reduction of mobility ratio were measured as the basis of the assessment. These properties give insights on the synergy between each component in the ASP slug, particularly the surfactant-polymer interaction, prior to field injection [31-34]. The effects of increasing PAM concentrations on the IFT, conductivity, mobility ratio of ASP flooding were determined and discussed based on the oil recovery percentage from the sand pack experiment. Sand pack data ultimately validated the theory of IFT, conductivity and mobility ratio facilitate the ASP flooding at high PAM concentration. All results were compared to formulations containing the commonly used surfactant sodium dodecyl sulfate (SDS).

## EXPERIMETAL

### 1. Materials

Polyacrylamide (PAM), >99%, sodium hydroxide (NaOH); >97%; and sodium carbonate ($Na_2CO_3$); 99.6%, and sodium dodecyl sulfate (SDS) $[CH_3(CH_2)_{10}CH_2OSO_2Na]$, 99% were purchased from Fisher Scientific Sdn. Bhd. Palm based methyl ester sulfonates (MES) $[CH_3(CH_2)_{13}CO(CH_3)SO_3Na]$, >95% were purchased from Lion Chemicals Sdn. Bhd. N-decane, >99% was purchased from Sigma Aldrich Sdn. Bhd.

### 2. IFT Measurement of ASP Slug Solution

IFT of all ASP formulations with n-decane was measured with SVT 15N spinning drop tension meter at 45 °C and 7,000 rpm until it reached equilibrium. Four types of ASP slug were prepared: MOHP (MES/NaOH/PAM), MCOP (MES/$Na_2CO_3$/PAM), SOHP (SDS/NaOH/PAM), and SCOP (SDS/$Na_2CO_3$/PAM).

### 3. Conductivity Measurement

Conductivity measurements were done to investigate the surfactant-polymer interaction in ASP slug solution. SevenCompact S230 Conductivity meter was used for the measurement. The probe was calibrated at 84 μS/cm, 1,413 μS/cm and 12.88 mS/cm before samples were tested. 20 mL sample was placed in the beaker with the probe immersed in the sample. The reading was taken after the value was stable. 0.2%-2.0% MES and SDS were dissolved in 4.5% NaCl and 5.0% NaCl solutions, respectively.

### 4. Viscosity Measurement

The viscosity of flooding slug solutions was measured to calculate the oil mobility ratio. HAAKE Viscotester 550 was used to measure the viscosity of all slug samples. Prior to measurement, the sensor was secured to the rotor to establish a zero point. The samples were filled in the cup and placed in the temperature control vessel. The temperature vessel was connected to the oil bath. The oil bath temperatrure was set at 45 °C for the analysis. The spindle was then immersed in the vessel until it was parallel to the rotor sensor. The desired speed was selected and reading was taken after the reading was stable. The experiments were done in triplicate.

### 5. Sand Pack Flooding Experiments

Sand composed of $SiO_2$ and CaO with a particle size of 100 mesh or 0.150 mm was used in these experiments. The sand was packed vertically in a jacketed glass sand pack holder of 32 cm in length and 3.0 cm in diameter, as shown in Fig. 2. Both sides of sand pack were equipped with stainless steel sieves with the size of 300 mesh per inch with sieve opening of 0.053 mm to prevent sand flow. The porosity and permeability were calculated at 31% and 9.2 Darcy, respectively.

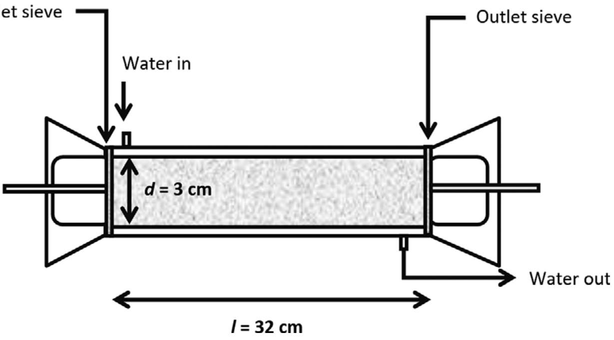

**Fig. 2. Cross sectional area of the sand pack.**

Fig. 3 shows the experimental setup of the flooding system. Two peristaltic pumps were used to drive the low and high viscous feed into the sand pack. A pulse dampener was used immediately after each pump to provide a constant flow rate for the injection fluid. A low flow transmitter was used to record the pressure drop within the sand pack. To prepare the sand pack for flooding test, 4.5% and 5.0% NaCl brine was injected for about three pore volumes (PV), followed by 3 PV of n-decane to reach the connate water saturation at atmospheric pressure and room temperature.

Then, for the secondary oil recovery, 3 PV of brine (water-flooding) was injected and the n-decane recovery was collected at the collection tube after each of 0.5 PV. Centrifugal process was done to separate the effluent from the collection tube to obtain the oil recovery percentage. Then for the tertiary oil recovery, the sand pack was continuously flooded with 1 PV of a prepared ASP slug solution. The process ended with 4 PV chase water. The flow rates of the injections were kept constant at 0.4 cc/min, or about 2 ft/day frontal advance rate to mimic real field injection velocities [38,39].

## RESULTS AND DISCUSSION

### 1. Critical Micelle Concentation (CMC) of MES and SDS

In EOR studies, the CMC values for surfactants are commonly determined using the conductivity method, surface tension method, or interfacial tension (IFT) method [40-42]. Conductivity method reveals the mobility of free surfactants in a solution, with higher conductivity indicating a higher mobilization of the surfactants. The CMC is determined from an abrupt change in conductivity slopes in response to the changes in the surfactant concentration. This explanation coincides with the theory of Schramm and Marangoni [43], where the conductivity properties change dramatically due to a highly cooperative association taking place at the interface hence reduce the solution electrostatic forces.

In Fig. 4, the changes in conductivity slope indicate that the CMC

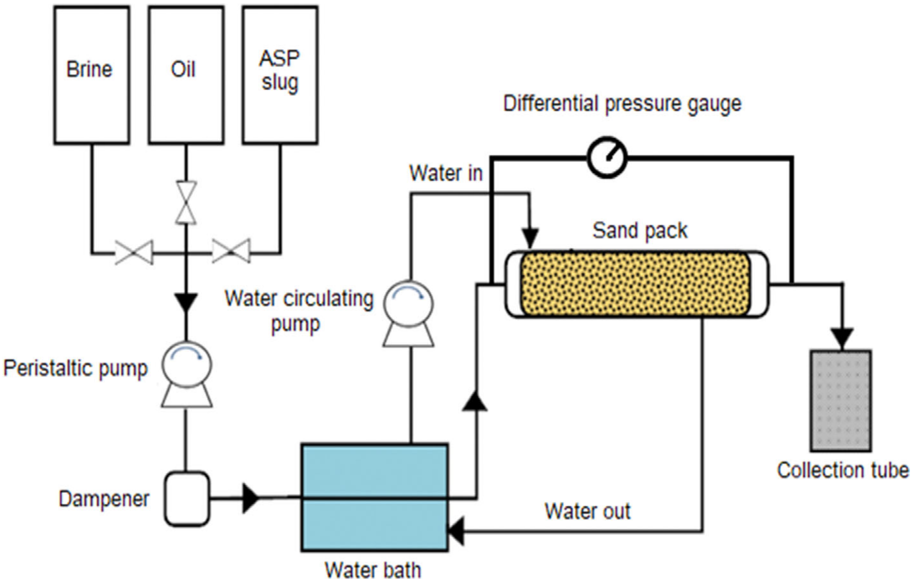

**Fig. 3. The schematic diagram of sand pack flooding setup.**

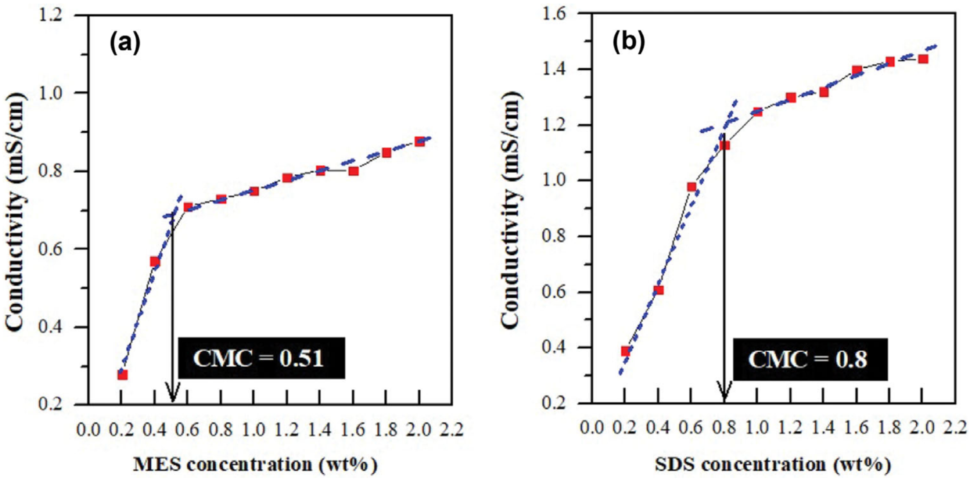

**Fig. 4. CMC determination by conductivity method for (a) MES and (b) SDS in NaCl solution.**

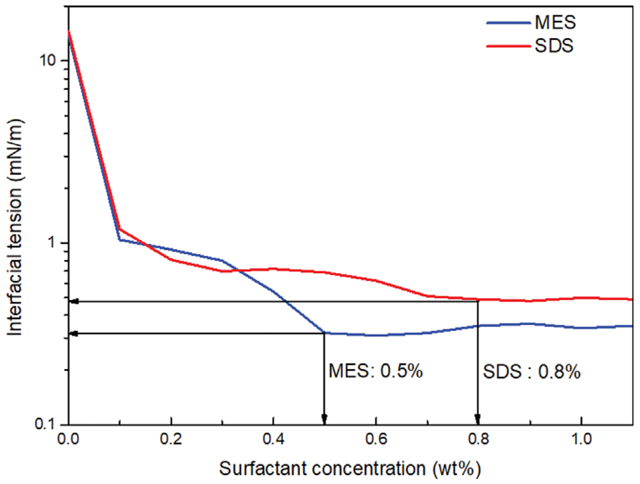

**Fig. 5. CMC determination for MES and SDS in NaCl solution using IFT method.**

for MES and SDS in a NaCl solution are at a surfactant concentration of 0.51 wt% and 0.8 wt%, respectively. Similarly, the IFT slope in Fig. 5 shows that the first points with the minimum IFT value are at MES and SDS concentrations of 0.5 wt% and 0.8 wt%, respectively, which are attributed to CMC. Beyond this point, the IFT does not change significantly. From this data, a good agreement was observed between these two methods. The lower CMC for MES is due to the stronger hydrophobic properties attributed from its higher carbon number [44]. The results show that less surfactant concentration is required for MES to form micelles, which contributes to the reduction of interfacial free energy in the mechanism of IFT reduction. This demonstrates that MES has a high potential to be a superior surfactant to SDS in EOR.

To compare with another EOR study, Ahmadi et al. [40] investigated the potential for surfactant flooding by measuring the CMC of saponin natural surfactant in a brine solution and obtained a higher CMC. They also found that the CMC for the surfactant values differed slightly when measured by conductivity and IFT, which are about 3.4 and 3.0 wt%, respectively. In another study, Babu et al. [45] synthesized the MES surfactant for surfactant flooding and obtained 0.45 wt% CMC value for the pure surfactant solution. The CMC value gradually decreased after the MES was dissolved in increasing brine solution. Meanwhile, Hazarika and Gogoi [46] reported CMC value of 0.4 wt% for SDS in brine solution using IFT analysis. This shows that CMCs of various surfactants in brine solutions vary significantly in EOR application. For pure MES surfactant (without brine solution), Saxena et al. [47] and Soy et al. [48] obtained lower CMC values. However, the comparison with previous studies is inadequate due to the differences in the method and the surfactant solution content. Nonetheless, the purpose of the surfactant CMC screening in the current study was to determine the appropriate concentrations of MES and SDS to use in the ASP formulations for the subsequent experiments.

### 2. Effect of Polymer on Viscosity and Interfacial Tension (IFT) of ASP Slug

The formulations of ASP slug, presented in Table 1, were obtained through a screening process. MOHP and MCOP were formulated using MES surfactant, while SOHP and SCOP contained SDS surfactant. The effect of polyacrylamide (PAM) polymer con-

**Table 1. ASP slug formulation**

| Sample | Formulation | Surfactant conc. (wt%) | Alkali conc. (wt%) | PAM conc. (ppm) |
|---|---|---|---|---|
| MOHP | MES/NaOH/PAM | 0.5 | 0.5 | 2,000, 4,000,<br>6,000 & 8,000 |
| MCOP | MES/$Na_2CO_3$/PAM | 0.5 | 0.5 | |
| SOHP | SDS/NaOH/PAM | 0.8 | 0.3 | |
| SCOP | SDS/$Na_2CO_3$/PAM | 0.8 | 0.3 | |

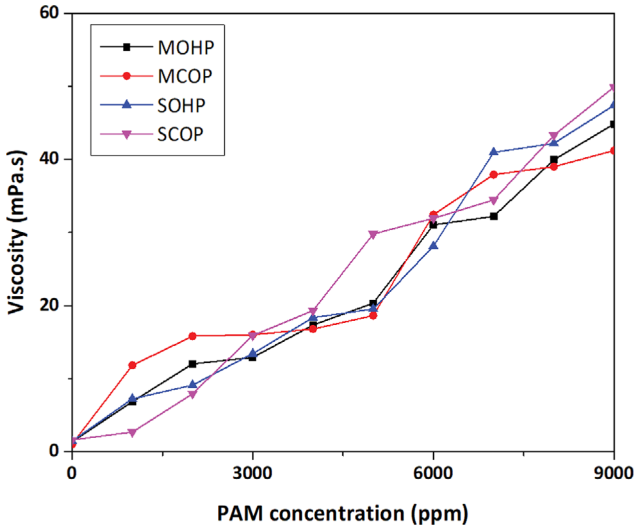

Fig. 6. Effect of polymer concentration on ASP slug viscosity.

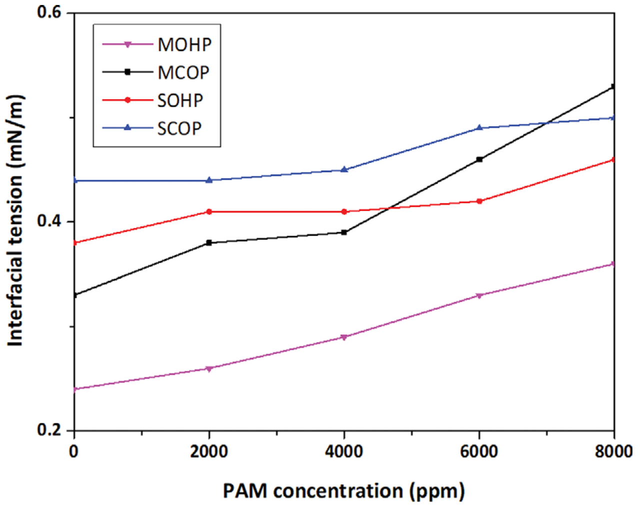

Fig. 7. Effect of PAM concentration on IFT of ASP/n-decane.

centration on viscosity of ASP slug is shown in Fig. 6. The results of ASP slug with SDS surfactant are also presented as a comparison. All formulations show that the viscosity increased as the PAM concentration in the ASP slug increased. Increases in PAM concentration result in an increase in the hydrodynamic radius of random coiled PAM and swollen macromolecules of PAM. The friction between the coiled and swollen PAM increases the viscosity of the solution [49].

The ASP slug viscosity was solely affected by the number of coiled PAM and its macromolecules when the salinity and surfactant concentrations were fixed. Thus, increasing the PAM concentration in ASP slug increases its viscosity explicitly. At 9,000 ppm PAM, SCOP and SOHP had a slightly higher viscosity than MOHP and MCOP. This may be due to the higher hydrophobic interaction between PAM backbones and MES compared to SDS, as MES has a longer hydrophobic tail. A stronger hydrophobic interaction between MES and PAM induced the coiling of the PAM backbone, reducing the ASP slug viscosity due to lower PAM elongation. The viscosity of all ASP slugs with MES was comparable with the viscosity of ASP slug with SDS.

Fig. 7 shows the effect of PAM polymer concentration on the IFT of ASP/n-decane. The IFT values for all formulations were increased as PAM concentration increased. This could be because the addition of hydrophobic group of PAM interacts with the hydrophobic tail of MES/SDS and induced the surfactant rearrangement at water/n-decane interface. Below the CMC value, the hydrophobic interaction promotes surfactant binding to the polymer chain, induces micelle formation and adsorption of surfatant at interface, hence decreases the IFT of ASP slug/n-decane [42,43]. However, in this study, increasing the PAM concentration in the solution increased the hydrophobic sites and the strength between surfactant and PAM backbone, as also reported by Guzmán et al. [20]. As a result, this hydrophobic interaction reduced the solubilty of surfactant hydrophilic head in the water and significantly increased the IFT [52]. Ma et al. [53] reported similar results, stating that increasing the hydrophobic strength of the polymer backbone at the oil-water interface disrupted the surfactant arrangement at the interface and disturbed the adsorption-desorption of surfatant. The optimum surfactant micellization occurs at the critical micelle concentration (CMC), above which further surfactant addition does not reduce the IFT. Hence, the addition of high concentration PAM into the surfactant solution at CMC value may increase the surfactant-polymer critical aggregation concentration (CAC).

Guzman et al. [20] reported that the optimum interaction between surfactant and polymer at the interface can be achieved when the CMC value is higher than the CAC value. A higher surfactant concentration is essential to obtain a stable surfactant-polymer interaction at the interface. Rosen and Kunjappu [54] stated that the tendency of the surfactant to adsorb at the oil-water interface was higher than its tendency to form micelles. The surfactant would adsorb at the interface and lower its free energy, which led to a reduction of IFT. Continuous addition of surfactant increases the number of surfactant at the interface, consequently inducing surfactant micellization. Upon reaching this point, no significant changes of free energy of the interface occurred, hence the IFT remained unchanged [55]. This indicates that the mechanism of IFT reduction is majorly affected by the adsorption of surfactant at the interface, while surfactant micellization indicates the starting point of a stable IFT.

In this particular study, the surfactant-polymer interaction at surfactant concentrations below the CMC value exhibited higher surfactant-polymer interfacial stability due to the adsorption of free surfactant molecules at interface [56]. Therefore, increasing the PAM concentration in ASP slugs increased the surfactant-polymer CAC value where surfactant molecules became aggregates within the polymer macromolecules. Consequently, less surfactant adsorbed at interface. As a result, the IFT increased. The observations also agree with the findings reported by Dey et al. [57] and Azum et al. [16], who found that the hydrophobicity of the solution increased as polymer concentration increased and therefore the hydrophobic binding sites increased. Surfactant hydrophobic parts are prone to bind to the polymeric chain, reducing the surfactant adsorption in water phase and ultimately increasing the IFT.

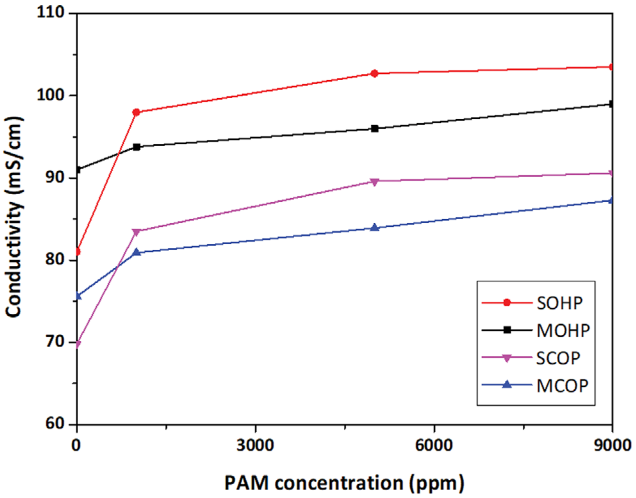

**Fig. 8. Electrical conductivity value for ASP formulation with various PAM concentrations.**

## 3. Conductivity of ASP Slug

Conductivity represents the electrostatic behavior of the dissociative ions from any surfactant at the interface as well as from the polymer backbone. In the context of this study, increased conductivity may indicate increased ion mobility along the polymer chain. Fig. 8 depicts the electrical conductivity profiles for various ASP formulations as a function of PAM concentration. It can be seen that the electrical conductivity of the solution increased significantly when PAM was added at 1,000 ppm to the formulations. This suggests that the presence and movement of ions in PAM affected the electrical conductivity of the solution.

According to Nizri et al. [58] and Winnik et al. [59], the increased conductivity of ASP solutions is due to the mobility of sodium ions across the PAM backbone where either free surfactant or its micelles are attached. This polymer-surfactant complex facilitates the movement of sodium ions between micelles. In addition, the higher conductivity solution purportedly proved that addition of PAM backbone in the solution increased the mobility of free surfactant and salts ions across the PAM backbone and suggested that the amount of micelles had reduced [60]. However, increases in PAM concentrations above 1,000 ppm did not cause a further significant increase in conductivity. The enhancement in conductivity was less than 5 mS/cm when the PAM concentration was increased from 1,000 to 9,000 ppm. The results suggest that a PAM concentration of 1,000 ppm may be sufficient to improve the oil recovery.

The data indicate that when an anionic MES or SDS surfactant is used in the ASP system, only a small amount of polymer is needed to alter its conductivity. Subsequently, similar ASP formulations were used in sand pack core-flood experiments to investigate further the effect of conductivity and viscosity of PAM on the oil recovery. This data can be used to predict the percentage of oil recovered from various formulations.

## 4. ASP Flooding

For chemical flooding, fixed concentrations of MES and alkali (i.e., 0.5%MES/0.5%NaOH and 0.5%MES/0.3%$Na_2CO_3$) were used for MOHP and MCOP, while PAM concentration was varied between 1,000, 5,000, and 9,000 ppm. Tests were also conducted using SDS surfactant as a comparison study with a fixed concentration of 1.1%SDS/0.3%NaOH and 0.9%SDS/0.3%$Na_2CO_3$ for SOHP and SCOP. The results of ASP flooding for each sample are presented in Table 2.

## 5. Oil Recovery

Fig. 9(a) and (b) shows the n-decane recovery by pore volume for systems containing MES surfactant, which are (a) MOHP and (b) MCOP flooding at different PAM concentrations. Prior to MOHP flooding, approximately 40% of n-decane was produced during the water flooding stage. At 2.5 PV, the oil recovery due to

**Table 2. ASP flooding results**

| ASP type | PAM conc. (ppm) | Viscosity (mPa·s) | Mobility ratio reduction (ΔM) | Oil recovery (%) | Total oil recovery (%) |
|---|---|---|---|---|---|
| MOHP | 0 | 1.35 | 0.216 | 27.8 | 79.2 |
| | 1,000 | 6.84 | 0.749 | 37.9 | 90.9 |
| | 5,000 | 20.34 | 0.756 | 31.4 | 80 |
| | 9,000 | 44.87 | 0.873 | 25.2 | 70.5 |
| MCOP | 0 | 1.04 | 0.254 | 24.9 | 79.5 |
| | 1,000 | 11.82 | 0.785 | 30.8 | 85.2 |
| | 5,000 | 18.62 | 0.846 | 32.4 | 84.5 |
| | 9,000 | 41.21 | 0.866 | 27 | 74.6 |
| SOHP | 0 | 1.43 | 0.243 | 28.2 | 82.3 |
| | 1,000 | 7.22 | 0.764 | 34.9 | 85.7 |
| | 5,000 | 19.54 | 0.814 | 35.8 | 86.4 |
| | 9,000 | 47.43 | 0.852 | 27.8 | 76 |
| SCOP | 0 | 1.59 | 0.328 | 23.2 | 75.8 |
| | 1,000 | 2.68 | 0.542 | 28.2 | 81.6 |
| | 5,000 | 29.8 | 0.861 | 31 | 84.3 |
| | 9,000 | 50 | 0.855 | 20.3 | 70.5 |

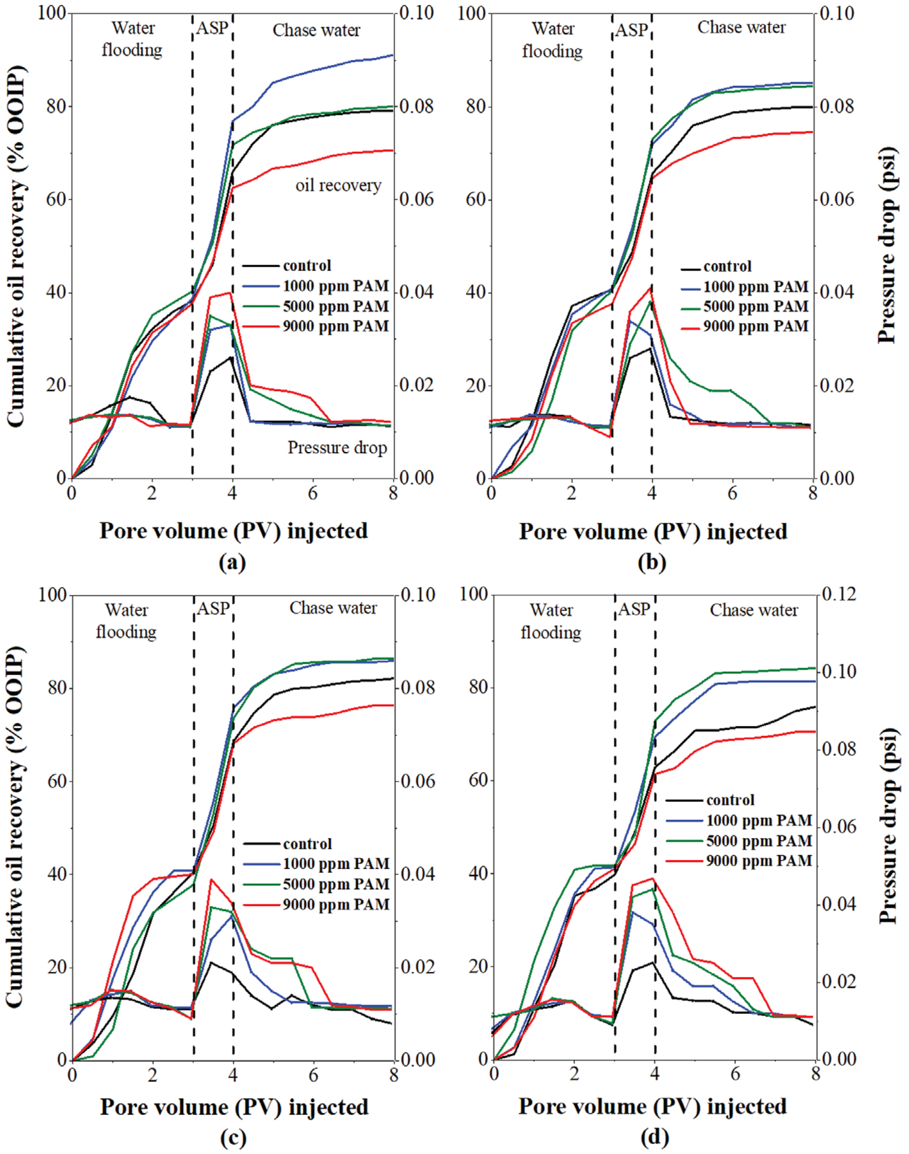

**Fig. 9. Oil recovery performance for ASP flooding at different PAM concentration: (a) MOHP flooding, (b) MCOP flooding, (c) SOHP flooding and (d) SCOP flooding.**

water flooding was observed to be reduced, implying the need for chemical flooding. MOHP flooding was then injected at 3.0 PV-4.0 PV. A significant recovery improvement was observed when PAM was added to the flooding. A similar oil recovery pattern was observed during MCOP flooding (Fig. 9(b)). The graph shows that 38-40% of n-decane was produced by water flooding. A significant improvement in oil recovery occurred after 1.0 PV of MCOP was injected.

The results indicate that the addition of 1,000 and 5,000 ppm PAM in both MOHP and MCOP recovered more n-decane than the control sample (without polymer), indicating a positive effect of PAM on oil production. 1,000 and 5,000 ppm PAM in MOHP recovered 31-38% of n-decane, while the control sample recovered 27.8%. This result is consistent with those reported by Jung et al. [49], who observed optimal oil recovery at 1,000-2,000 ppm PAM concentrations. However, at 9,000 ppm PAM, the n-decane recovery was found to be significantly lower at 25.2%. Similar findings have been reported by Zhang et al. [62], where increasing the PAM concentration at a certain point disturbed the OH- layers at the interface that support micelle stability, resulting in micelle breakage. Hence, it can be suggested that increasing the PAM concentration to 9,000 ppm is not beneficial.

Similarly to MCOP, 1,000 and 5,000 ppm PAM recovered 31-32% of n-decane, while the control sample recovered 24.9% (Fig. 9(b)). Moreover, the recovery of n-decane for 1,000 and 5,000 ppm PAM is comparable towards the end of chase water injection. Meanwhile, the control sample and the sample containing 9,000 ppm PAM have a similar pattern, indicating that no improvement in oil recovery has occurred. Based on MCOP data, an increase in PAM concentration after 1,000 ppm did not affect the n-decane recovery. The decreasing pattern of oil recovery by chase water further proves that a higher degree of adsorption took place in the core.

Wei [63] produced similar results, which revealed that higher polymer adsorption was observed at higher concentration.

As a comparison, the effect of PAM concentration on n-decane recovery for systems containing SDS surfactant (SOHP and SCOP) is shown in Fig. 9(c) and (d). For SOHP, 1,000 and 5,000 ppm PAM recovered 34.9% and 35.8% of n-decane, respectively, while the n-decane recovery for the control sample was 28.2%. Meanwhile, for SCOP, 5,000 ppm PAM produced the highest percentage of n-decane recovery of 31%. 9,000 ppm PAM recovered 20.3% of n-decane, which is less than the sample without PAM. Similar to previous ASP floodings, adding 1,000 ppm PAM or 5,000 ppm PAM showed a marginal improvement in n-decane recovery despite a significant increase in slug viscosity. Similar explanations as for MOHP and MCOP apply to SOHP containing 9,000 ppm PAM.

It can be seen for all ASP flooding, the recovery by chase water decreased as the PAM concentration increased. This could be because as the hydrodynamic radius of the ASP slug increases in proportion to the PAM, mechanical entrapment of the ASP slug occurs in the porous media [64]. The dilute chase water injected into the sand pack was unable to move the trapped ASP slug due to the viscosity issue, hence the flow of chase water was diverted to a region with less ASP slug accumulation and recovered a small percentage of oil.

## 6. Water to Oil Mobility Ratio

According to the mobility ratio principle, increasing the viscosity of the displacing fluid reduces the water-to-oil mobility ratio,

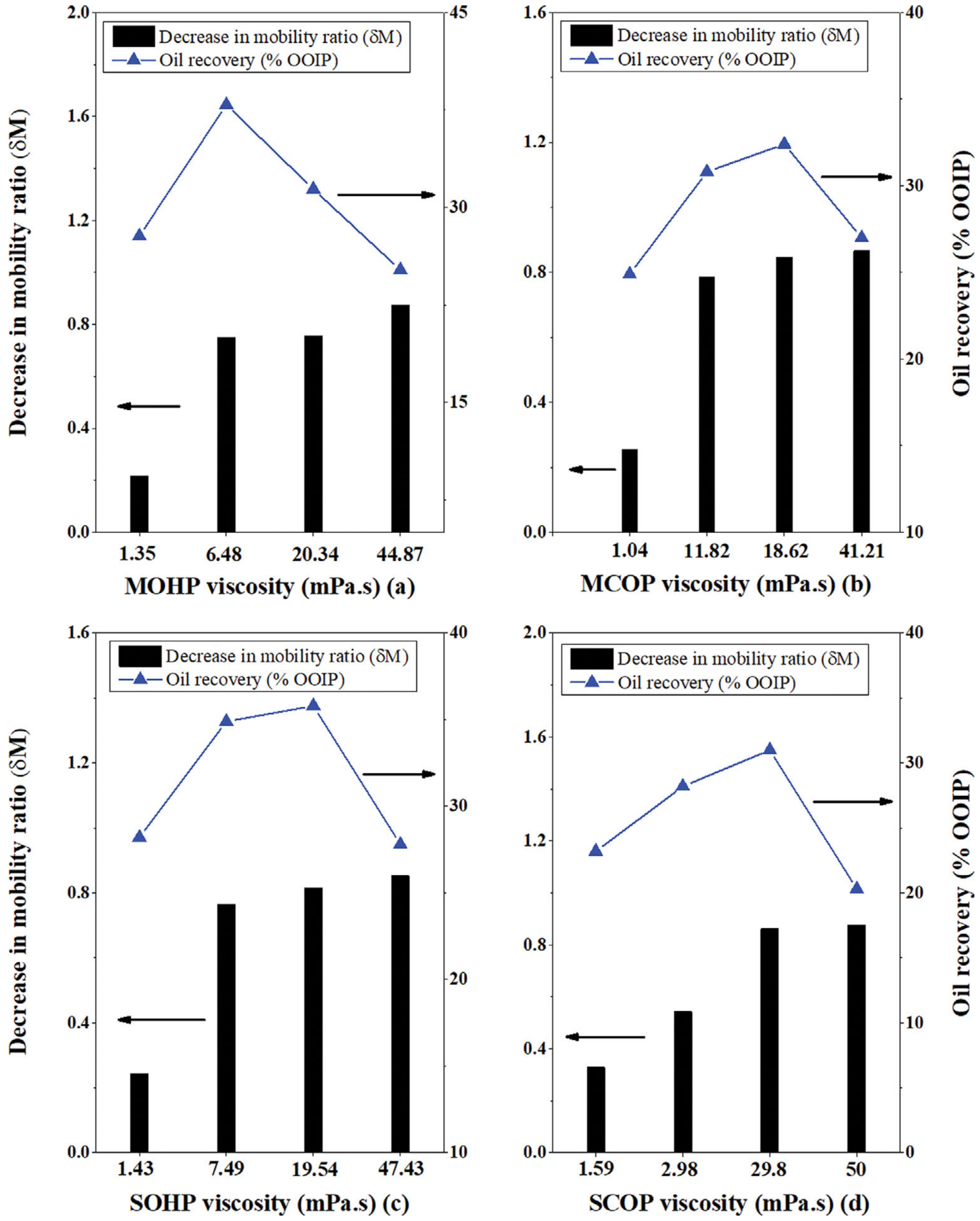

**Fig. 10.** **Correlation between oil recovery with viscosity and mobility ratio for (a) MOHP flooding, (b) MCOP flooding, (c) SOHP flooding and (d) SCOP flooding.**

which pushes the oil towards the production well. Polymer plays an important fundamental role in ASP flooding to increase the viscosity of ASP slug and mobilize the oil during EOR [65]. The correlation between oil recovery, viscosity and mobility ratio in Fig. 10 shows that the oil recovery increases when the viscosity of ASP slug reaches 20 mPa·s for most flooding types. Meanwhile, the mobility ratio decreased for all ASP flooding as the ASP slug viscosity increased. As the PAM concentration increased, the mobility ratio decreased as well, but the recovery factor dropped at slug viscosities of 20-40 mPa·s. At higher PAM concentrations, some PAM may have been trapped in the core during flooding, preventing the n-decane from coming out from the sand pack system. Ikeagwu and Samuel [66] also found that a high viscosity polymer flooding induced its retention in porous media, resulting in plugging.

The performance of ASP slug at higher polymer concentration is supported by Sorbie [64] and Park et al. [67], who reported that at high polymer concentration, polymer can be mechanically trapped in narrow pore throats as well as hydrodynamically trapped in stagnant zones. Higher polymer concentration contains higher polymer chain. These polymer chains possess polar groups that can be adsorbed irreversibly to the polar point of rock surfaces and stop the oil mobilization towards production well [68]. Moreover, a higher degree of adsorption may take place in the sand pack due to its bigger porosity.

From Fig. 10, the optimum recovery for MOHP was obtained at slug viscosity of 6.48 mPa·s (1,000 ppm PAM). The oil recovery trend for MCOP, SOHP and SCOP was similar but the optimum recovery occurred at 18.62 mPa·s, 19.54 mPa·s, and 29.8 mPa·s, respectively, all at 5,000 ppm PAM. However, the recovery at 5,000 ppm PAM was marginal, indicating that the mobility ratio effect was negligible. In general, this oil recovery trend shows the limitations of mobility ratio control theory in explaining the oil recovery in sand pack flooding experiments. In theory, the increase in viscosity of SOHP samples, particularly from 7.49 mPa·s to 19.54 mPa·s, should result in increased n-decane recovery. Although these results correlated well with those of MCOP, higher n-decane recovery was achieved by MCOP flooding with a smaller gap in viscosity and a lower reduction of mobility ratio. For SCOP flooding, the correlation between viscosity and mobility ratio was unclear. According to Fig. 10(d), the viscosity for SCOP flooding was 2.98 mPa·s and 29.8 mPa·s at 1,000 ppm and 5,000 ppm PAM, respectively. Despite the significant difference in viscosity and mobility ratio reduction, these factors do not provide a positive effect on the n-decane recovery. This further proves that the principle relating polymer concentration to oil recovery has limitations.

In comparison to the earlier IFT results, the oil recovery data is consistent with the correlation of IFT and polymer concentration. Increasing PAM concentration in ASP slug increased the IFT of ASP slug/n-decane. As mentioned, the addition of hydrophobic properties in the ASP slug from the polymer backbone has an adverse effect on the micelle formation in a fixed surfactant concentration formulation. The increased number of hydrophobic sites in the ASP slug from the PAM induces a bridge-forming hydrophobic interaction with micelles, resulting in a flexible polymer chain wrapped around the bound micellar surface [69]. The increased hydrophobic interaction between surfactant and polymer destabilizes the micelles and surfactant at interface and gradually avoids direct contact with water molecules [60]. As a result, higher repulsive interactions between surfactant head groups in the micelle expand its core, allowing water to penetrate and producing a less dense packing of the micelle. Similar mechanism applied for surfactant packing at interface that would increase the IFT of the system [70]. SCOP flooding recovered the least amount of n-decane at all concentrations when compared to MOHP, SOHP, and MCOP flooding. Based on the percentage of oil recovered in the sand pack experiments, it can be concluded that SCOP flooding is the least advantageous ASP flooding method.

In summary, the low oil recovery of ASP slugs at high PAM concentrations is most likely due to the mechanical entrapment of the polymer in narrow porous media and hydrodynamic entrapment of the polymer in stagnant zones. Furthermore, as stated by Manichand and Seright [68], water soluble polymer such as PAM possesses polar groups that can be irreversibly adsorbed to the polar point of rock surfaces and stop the oil mobilization towards production well. However, since the retention of polymer through mechanical entrapment is small, it can be neglected in most practical cases. Additionally, it was determined that MOHP (MES/NaOH/PAM) or SOHP (SDS/NaOH/PAM) was the most effective flooding formulation, indicating that NaOH is the more suitable alkali than $Na_2CO_3$.

## 7. Correlation between IFT and ASP Flooding Recovery

Fig. 11 compares the IFT versus percentage of n-decane recovery for all ASP floodings to demonstrate their correlation. According to the graph, only MOHP floodings support the theory that lowering the IFT of ASP/oil improves oil recovery [71]. However, for MCOP, SOHP and SCOP floodings, this assumption is only fulfilled particularly at 5,000 ppm to 9,000 ppm PAM. On the other hand, the decrease in n-decane recovery from 5,000 ppm to 9,000 ppm was due to the polymer retention in porous media, as previously stated.

A similar finding was reported by Wu et al. [72], stating that ASP flooding performed well at low polymer concentration and high surfactant concentration. This is because at high polymer concentration, the IFT increases due to the polymer repulsion [73]. In addition, at higher polymer concentration, the critical displacement viscosity could be affected. Critical displacement viscosity is the minimum viscosity where the effect of IFT is the most effective. Hou et al. [74] concluded that the ASP slug viscosity must be kept at minimum to ensure the contribution of viscosity-mobility ratio and IFT during ASP flooding can be realized. Oladimenji et al. [75] stated that the critical displacement viscosity depends largely on the compatibility of the ASP constituents. It varies from one case to another. However, it is recommended that the ASP slug viscosity to be kept below 20 mPa·s to ensure that IFT has the maximum effect on oil recovery.

## 8. Comparison of Surfactant, Alkaline-surfactant and ASP Flooding Oil Recovery

Fig. 12 summarizes the oil recovery from water flooding (WF), single surfactant flooding (MES and SDS), alkaline-surfactant flooding (MOH, MCO, SOH and SCO) and ASP flooding (MOHP, MCOP, SOHP and SCOP). The addition of MES or SDS surfactant to the flooding increased the oil recovery by 14-15%. The findings

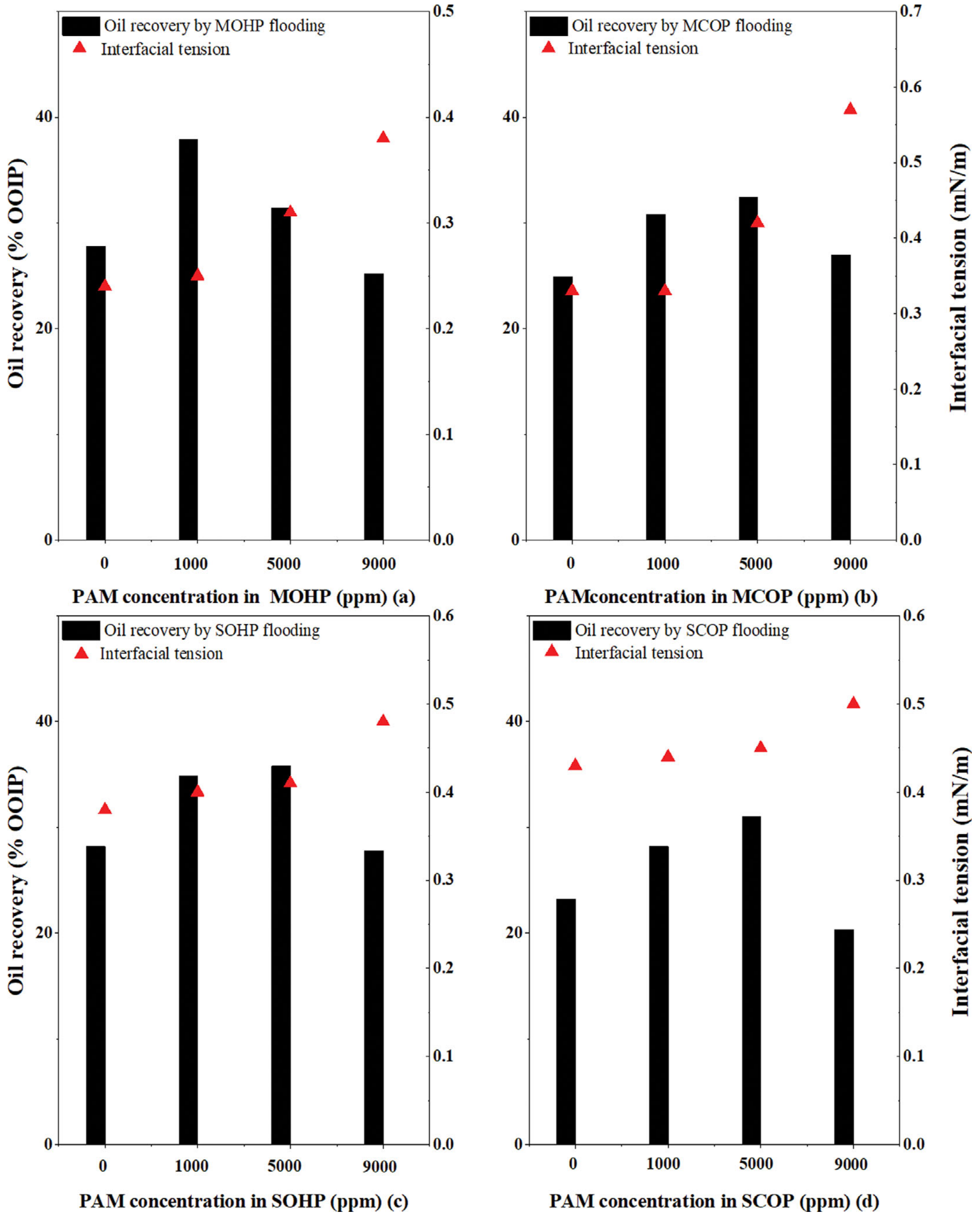

**Fig. 11. Correlation between oil recovery and IFT of ASP flooding at different PAM concentration for (a) MOHP flooding, (b) MCOP flooding, (c) SOHP flooding and (d) SCOP flooding.**

demonstrated that reducing the IFT between oil and water induced the oil recovery factor. The results also proved that adding alkali into surfactant flooding further increased the oil recovery, particularly for MOH and SOH flooding. The synergy between MES of SDS and NaOH was more effective than the synergy between $Na_2CO_3$ and MES or SDS. NaOH and $Na_2CO_3$ act as electrolytes at the ASP/decane interface, increasing the ionic strength of the aqueous phase and changing the structure and size of the electrical double layer (EDL) of the hydrophilic group of MES and SDS ($SO_4^{-2}$ and $SO_3^-$). $OH^-$ and $CO_3^{2-}$ anions of alkali are both kosmotropes that influence the structure of the EDL and the magnitude of the salting-out effect. $Na^+$ and $H^+$ have a higher surface affinity than $Cl^-$, $OH^-$ and $CO_3^{2-}$ which compose the outer layer of EDL. The $OH^-$ is more polarizable, whereas $CO_3^{2-}$ with double negative ions has a high hydrophilicity, resulting in a lower surface affinity towards hydrophobic interfaces [76]. Hence, the hydroxide ion of NaOH may promote better surfactant solubility at oil-water interface, resulting in a lower IFT value. The role of PAM in enhancing the oil recovery was evidenced in all MOHP, MCOP, SOHP and SCOP floodings. However, MOHP flooding is much supe-

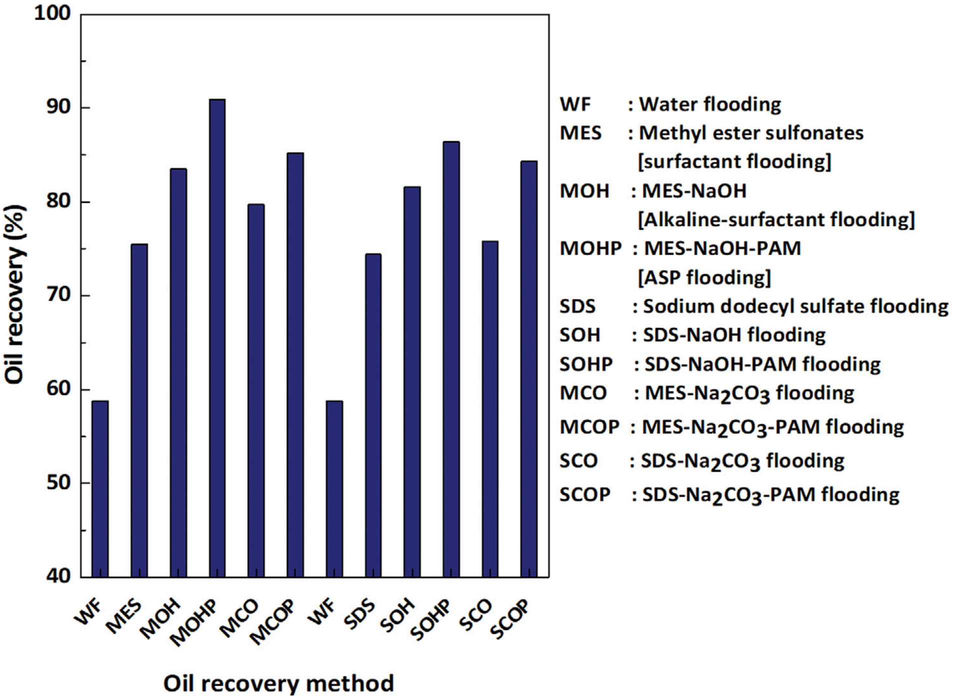

**Fig. 12. Comparison of surfactant, alkali-surfactant and ASP flooding oil recovery.**

rior compared to other ASP floodings with 7% more oil recovered. Based on these findings, it can be concluded that MES, NaOH, and PAM have a synergistic effect on oil recovery when compared to other ASP combinations.

## CONCLUSIONS

We found that new formulations of ASP slug containing alkali, a plant oil-based methyl ester sulfonates (MES) surfactant, and polyacrylamide (PAM) polymer had a comparable performance with ASP slug formulated with a commercial surfactant SDS. Increasing PAM concentration in ASP slug increased the IFT of ASP slug/n-decane due to the destabilization of micelles on PAM backbone. The role of polymer in increasing the oil recovery by reducing the mobility ratio was limited at high PAM concentration. We also concluded that the IFT and conductivity measurements are suitable tools for evaluating the performance of new ASP slug formulations prior to field application. At high polymer concentration, no linear correlation was observed between IFT in ASP flooding, conductivity of the ASP slug, and mobility ratio and oil recovery percentage. Among all ASP floodings, MOHP sucsessfully recovered the highest amount of OOIP at 90.9%. It is suggested that future research examine the contact angle of ASP containing MES surfactant, as well as the emulsification and adsorption behavior of MES at the oil-water interface.

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