

# A novel Surfactant Polymer (SP)/Alkaline-Surfactant-Polymer (ASP) formulation for enhanced oil recovery (EOR) processes

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## Abstract

An extensive investigation on the applicability of Polyvinyl Alcohol (PVA, a polymer) and its synergy with Rhamonolipid (a surfactant active agent) and/or alkaline (NaOH) was carried out to evaluate and define the best fluid formulation for enhanced oil recovery (EOR) processes. First, the effect of molecular weight, concentration, and temperature of PVA solution on surface tension (ST), interfacial tension (IFT), shear viscosity and thermodynamic stability was established. Then, a systematic formulation of PVA combined with Rhamonolipid and NaOH in reconstructed brine from Angolan offshore field was developed. The IFT experiment were carried out on crude oil samples obtained from Block T of Angolan offshore field. The combined PVA-Rhamonolipid (SP) and NaOH-Rhamonolipid-PVA (ASP) in saline medium reduced the ST and IFT to values below 30 mN/m and 1mN/m respectively. This provides an opportunity to use this new synergistic formulation in EOR processes particularly in offshore Angolan oilfields.

*Keywords:* Enhanced oil recovery (EOR), hydrolysed, polyacrylamide (HPAM), rhamnolipid, polyvinyl alcohol (PAV)

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## 1. Introduction

Polymer flooding has been widely used as an EOR techniques since early 1960s [1]. Its implementation can improve the mobility ratio between oil and

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water allowing an increase in sweep efficiency by reducing permeability con-  
trasts, thus, an increase the oil recovery [2, 3, 4, 5]. Hydrolysed polyacrylamide  
5 (HPAM) is the most frequently used polymer in water treatment as well as in  
EOR applications [6, 7, 8]. HPAM acts as an anionic coagulant which allows the  
modification of the water/oil mobility ratio and hence improve sweep efficiency  
[9, 5]. However, thermodynamic stability is usually a problem during the HPAM  
10 flooding process [10]. Specifically these problems are associated with mechani-  
cal degradation, salinity, temperature as well as non-degradability nature [11].  
High temperatures (i.e. temperature greater than 149 °C) cause HPAM degra-  
dation by radical scission and decomposition [11, 10, 12, 7, 13]. Further, high  
salt concentration decreases the efficiency of HPAM solution [14, 11, 7]. These  
15 therefore limits the applicability of HPAM in EOR processes. It is therefore  
crucial to identify a polymer that will be soluble in brine, biodegradable and  
suitable for high temperature and salinity.

### *1.1. Polyvinyl alcohol*

Polyvinyl alcohol (PVA) polymer is a water-soluble and biodegradable syn-  
20 thetic polymer obtained by alcoholysis of polyvinyl acetate [15]. PVA was up to  
the year 1999, one of the first synthetic polymer to be produced on a large scale  
commercially [16]. This type of polymer has been used in various industrial ap-  
plications such as emulsifier, stabiliser for colloid suspensions, sizing agent and  
coating in the textile and paper industries, etc [17]. Two types of this polymer  
25 has been reported: the fully and partial hydrolysed PVA. The solubility of PVA  
in water is primarily determined by the degree of hydrolysis. Thus, in order  
to fully hydrolyse (i.e. hydrolyse  $\geq 98\%$ ), elevated temperature of greater than  
80°C will be required [16]. Not much information regarding the application of  
PVA at elevated temperature is available in the literature [18]. However, some  
30 works in other fields have been reported on the rheological properties of PVA  
[15, 16, 19].

Lazareva and Shinkareva [19] studied the rheological and electro-physical  
characteristics of solutions of PVA and observed that the structure of aqueous

PVA solutions depends on the polymer concentration due to the network bonds  
35 formed with increasing concentration causing intermolecular interactions. Ku  
et al. [15] observed an increase on temperature in non-Newtonian index, there-  
fore the shear rate dependence of the blend viscosity decreased with a rise in  
temperature. The rheological properties of PVA of water and crude oil in EOR  
processes were investigated by Rezaian et al. [18]. It was observed an increase  
40 in viscosity of water-PVA solution from 1 to 28 cp. The increase in water viscos-  
ity, decrease its mobility and increase oil mobility, hence improving oil recovery.  
It was also reported that addition of PVA to crude oil resulted in viscosity  
reduction [18].

An investigation conducted in 2012 by Arjmand [7] observed that PVA is  
45 stable at high salinity and also decreases the IFT between oil and aqueous so-  
lution. The thermostability of PVA was proved in their research and reported  
that it can be used in reservoirs temperature greater than 250°C. Arjmand et  
al. [7], reported a reduction in IFT between oil and aqueous solution using  
PVA with improved oil recovery compared to HAPM. Further IFT reduction  
50 can be achieved by combining polymer and chemical surfactant than applying  
individual alone. However, chemically generated surfactants constitute an en-  
vironmental threat due to their toxicity and nondegradability nature. Hence,  
biologically produced surfactants have been identified as a good substitute for  
chemical surfactant flooding in EOR. Biosurfactants have variety of advantages  
55 over chemical/synthetic surfactants, such as high biodegradability, lower tox-  
icity, high selectivity and high environmental compatibility [20, 21], pH levels  
and salinity [22].

### *1.2. Rhamnolipid*

Rhamnolipid is one of emerging bio-surfactant (BS) that can be used in the  
60 oil industry for ST and oil/brine IFT reduction. They are reported to have a  
hydrophilic and hydrophobic in molecular structure and increase the solubility  
and biodegradability of insoluble compounds like hydrocarbons [21, 23].

The hydrophilic and hydrophobic present in rhamnolipid are able to display

a variety of surface activities that, among other roles, help solubilise hydrophobic substrates [24, 25]. These surface active properties lead to the reduction of surface tension (ST) and interfacial tension (IFT) [20]. Besides the aforementioned features, diverse functional properties can be accomplished by using rhamnolipid. These include emulsification, wetting, foaming, cleaning, phase separation, surface activity and reduction in viscosity of crude oil [26].

Several IFT and ST investigations have been carried out by using rhamnolipid [27, 28, 29, 30, 31, 32, 33]. The results showed that ST was reduced to the values below to 30 mN/m and IFT below to 1 mN/m. In contrast to the results observed by Lee et. al [34] where the results are not below 30 mN/m. However, the results are within the range of the surface tension of biosurfactants at the critical micelles concentrations (CMCs) of various purified biosurfactants that have been reported to range from about 27 - 35 mN/m [33].

The results of the investigation reported show that both PVA and rhamnolipid can be used to remove the mechanical degradation, toxicity, high temperature, ultra IFT reduction, and non-degradability observed in EOR flooding process by using HPAM or chemical surfactant flooding. The underlying mechanism of EOR application of bio-surfactant is not fully understood and the potential of combining controlled PVA with bio-surfactant have not yet been explored. Therefore, the SP flooding solution (PVA and rhamnolipid) is investigated in this paper to find the best fluid formulation for EOR processes.

## 2. Experimental description

### 2.1. Materials

Rhamonolipid, polymer alcohol (PVA), sodium hydroxide (NaOH), oil sample A and B and brine its primary materials used in this investigation. See Table 1 for the details of specification of the materials. The Rhamonolipid was supplied by Sigma Aldrich. It has molecular weight of 516 g/mol and purity of 96%. The PVA with degree of hydrolysis of 99% was supplied by Fisher Scientific. It has two molecular weights of 146,000 and 186,000 g/mol respectively.

Two oil samples (A and B) obtained from Angolan offshore oilfield formations (Block T) were used. The two samples A and B are light crude with API of 32.13 and 31.41 respectively and supplied by BP Angola. The brine was formulated by replicating the brine configuration obtained from the same formations to the crude samples as depicted in Table 2.

### 2.2. Preparation of PVA, SP and ASP solutions

Deionised water or formulated brine were used in the preparation of the PVA solutions as well as surfactant-polymer (SP) or Alkaline-Surfactant-Polymer (ASP) under mixing conditions. PVA solutions with high degree of hydrolysis (99%) was heated to at least 80 °C for about 30 minutes to fully dissolve the sample. The concentrations of the polymer and NaOH solutions were calculated and reported as weight percentage of the formulation. The concentration in solution of SP and ASP were prepared in mass of 50 ml of stock solution of a 0.05 M by adding the volume of stock concentration of 0.5 ml and 1 ml, respectively.

### 2.3. Property measurements

The property measurement was performed on a rotational 8-speed viscometer. The viscometer uses a bob-and cup arrangement for rheological property determination. The liquid is placed inside the cup. The cup (outer cylinder) is rotated at a set speed (600, 300, 200, 100, 60, 30, 6, 3 RPM) that determines the shear rate. The liquid between the two cylinders exerts a drag force (torque) on the bob, which is measured and converted to a shear stress. The measured shear rate is calculated from set speed (in resolutions per minute) thus [35]:

$$\gamma = 1.72023 \times \Omega \quad (1)$$

and the shear stress from measurements at the set speed thus [35]:

$$\tau = \theta \times 5.107 \quad (2)$$

where  $\gamma$  is the shear rate in  $\text{s}^{-1}$ ,  $\Omega$  is the RPM or the revolutions per minute which is a measure of the frequency of rotation,  $\tau$  is the shear stress in  $\text{dyne}/\text{cm}^2$ , and  $\theta$  the readings at each speed. The effect of molecular weight, concentration, surfactant, alkaline, and temperature on PVA behaviour were investigated.

120 *2.4. ST and IFT measurements*

The surface tension (ST) and interfacial tension (IFT) measurement between aqueous solution and oil were performed by using ring-type attention tensiometer from Kruss. The apparatus was validated by using the ST measurements of water reported in the literature with different temperatures and the accuracy of  
 125 the calibration obtained was  $\pm 1.5$  %. ST and IFT measurements were carried out on the PVA and Rhamnolipid samples at varying temperature of 21.7, 30, 50, and 70 °C. Different ST and IFT aqueous solution and oil formulations were obtained by using the aforementioned rhamnolipid or their mixtures with PVA or NaOH.

130 *2.5. Thermodynamics and interfacial behaviour of Rhamnolipid*

The thermodynamic values of rhamnolipid were computed by using the Gibbs free energy (Eqs. 3 and 4). The CMC was obtained from the plots of surface tension or conductivity as function of logarithm of the concentration. The point where slop changes indicates the critical micelles concentration. The  
 135 right of this value, micelles is formed. Thus, no adsorption and process remains constant, which easily can be observed from the plot surface tension and logarithm of the concentration.

$$\Delta G_{misc}^{\circ} = (1 + \alpha) RT \ln X_{cmc} \quad (3)$$

$\alpha$  is calculated by using the following equation (Eq. 4):

$$\alpha = 1 - \beta = 1 - \frac{S_2}{S_1} \quad (4)$$

where  $\Delta G_{misc}^{\circ}$  is the Gibbs free energy in  $\text{KJmol}^{-1}$ ,  $X_{cmc}$  is critical micelles  
140 concentration in mol/l,  $\alpha$  is the degree of counter ion binding,  $\beta$  is degree of  
ionisation,  $S_1$  and  $S_2$  are slopes of conductivity concentration plot before after  
CMC,  $R$  is ideal constant in  $\text{JK}^{-1} \text{mol}^{-1}$  and  $T$  is temperature in K.

### 3. Results and discussion

#### 3.1. Rheological and solution characteristics

145 The shear-viscosity behaviour analysis, ST and thermal conductivity mea-  
surements, thermodynamic and interfacial behaviour measurements were carried  
out on the PVA, Rhamonolipid and or NaOH samples at varying temperatures  
and different molecular weights. Then, a comparative analysis to validate the  
results obtained from experimental studies with those reported from the litera-  
150 ture was performed.

##### 3.1.1. Shear-viscosity behaviour analysis

Shear behaviour of aqueous PVA solution with different Molecular weight  
(146,000 and 186,000 mol/g), polymer concentration (0.1wt% and 0.2wt%) at  
the same molecular weight, temperatures, effect of surfactant (rhamnolipid),  
155 alkaline (NaOH) were investigated at shear rates from  $5.16 \text{ s}^{-1}$  to  $1032.14 \text{ s}^{-1}$ .  
The shear-thinning behaviour and flow index smaller than one (1) were observed  
in all cases. This effect is significant from at lower shear rates ( $5.16 - 103.21 \text{ s}^{-1}$ )  
presenting the non-Newtonian behaviour. This non-Newtonian effect can be  
explained by alignment of the polymer molecules under the application of shear  
160 rate [36]. At higher shear rate the trends tend to Newtonian behaviour due to  
the curves start to level off. This means that viscosity for values of higher shear  
rates start to be independent of shear rate. This can be illustrated by the well  
known power law described in Eq. 5 [36]:

$$\mu = k \times \gamma^{(n-1)} \quad (5)$$

where  $\gamma$  is the shear rate,  $k$  is constant or consistency factor,  $n$  is the power  
165 law parameter or flow index, and  $\mu$  is the viscosity. For cases of  $n = 1$ , fluids  
behaves as Newtonian,  $n < 1$ , the fluid is shear-thinning whereas  $n > 1$ , fluid  
presents shear-thickening behavior [37, 36].

However, the shear-thinning effect on both PVA molecular weights presented  
the same behaviour on shear rates  $\leq 344.046 \text{ s}^{-1}$ , and then the apparent vis-  
170 cosity of PVA with lower molecular weight decreased in comparison with the  
one with higher molecular weight as illustrated in Fig. 1. The flow index is  
also greater on PVA with higher molecular weight in comparison with smaller  
molecular weight (Table 3).

It was observed on shear-viscosity behaviour of polymer concentrations (0.1wt%  
175 and 0.2wt%) that the value of flow index from 0.1 wt% concentration are smaller  
than the ones observed from 0.2 wt% concentration (Table 4) as indication of  
more shear-thinning behaviour (Fig. 2). The behaviour of shear rate versus  
viscosity, shows higher values of viscosity with increase of PVA concentration  
(Fig. 2).

### 180 3.1.2. Surfactant-Polymer interaction in brine solution

Biosurfactant (rhamnolipid) - polymer (PVA) shear-viscosity showed that  
increasing the concentration of PVA at constant concentration of surfactant re-  
sults in increase in the viscosity of the solution. This is illustrated in the curves  
presented in Fig. 3(a) and 3(b). The viscosity increase is higher compared the  
185 case when polymer was added to Deionised water or brine. If polymer con-  
centration remains constant, then, changing the concentrations of Rhamnolipid  
does not significantly change the viscosity of the combined polymer-surfactant  
aqueous solutions (Fig. 4). This indicates that rhamnolipid does not inter-  
act physically or chemically with the polymer chain in the brine. To prove  
190 this, the wt% of rhamnolipid was increased to 100%. At lower concentration  
of Rhamnolipid, there was no significant difference in the physical or chemi-  
cal interaction with PVA. However, for higher concentrations, rhamnolipid is  
sensitive to salinity causing precipitation. The precipitation can be caused by



excessive concentrations of multivalent cations in range of 33% for hydrolysed  
195 polymers [38, 39, 40]. At high degree of hydrolysis, the precipitation is caused  
by site fixation phenomena and the low degree of hydrolysis the precipitation is  
caused by poor solvation [39, 40]. The power-law model parameters computed  
for curve fitting, are summarised in Table 5.

### 3.1.3. *Polymer-Alkaline interaction in brine solution*

200 The polymer-alkaline (AP) shear viscosity (Fig. 5) with two different molecu-  
lar weights (146,000 mol/g and 186,000 mol/g) in various concentrations at 21.7  
°C showed the same shear-thinning behaviour similar to the ones observed in  
previous analysis. This shear thinning behaviour may be cause by alignment of  
the highly anisotropic chains which results in decrease of viscosity. However, the  
205 flow indices,  $n$ , calculated are greater than the ones observed from Rhamnolipid-  
PVA interactions (Table 6). The values from the curves are higher compared  
when with those obtained from the mixture of deionised water and PVA, brine  
and PVA, Rhamnolipid and PVA. This can be explained by hydrolysis interac-  
tion as explained in the previous sections.

### 210 3.1.4. *Temperature effect on polymer, polymer/surfactant/alkaline interaction in brine solution*

The effect of the temperature on aqueous polymer and or surfactant solutions  
was investigated at different concentrations and molecular weight at different  
temperatures of 21.7, 30, 50, 70 °C. An extensive investigation was performed  
215 for solutions of PVA and deionised water, PVA with brine, PVA and surfactant  
(rhamnolipid) and brine with purpose to investigate the temperature tolerance  
and its impact on flooding process. In all cases, a steady decrease in viscosity  
with increase in temperature was observed. This decrease is more noticeable in  
solutions with higher concentration. This can be attributed to weaker hydrogen  
220 bonding and faster movement of the polymer chains at higher temperature [41].  
Or the liquid is structured, acquiring some plastic properties, as well as the  
capability of orientation ordering at certain share rates [19]. The power-law

parameters were calculated as shown in Tables 7, 8, and 9 and the results confirms that the shear thinning effect in which all power-law flow indices are smaller than one.

### *3.1.5. Implications of observation of the rheological properties of polymer/surfactant/alkaline interaction in brine solution*

The validation of this work will be performed by the few cases available in the literature. The plots of viscosity as a function of shear rate presented the thinning effect for the lower values of shear rate and deviated from this behaviour for high values of shear rate. This behaviour was observed and reported by Lazareva et. al [19] using PVA manufactured in Russia at 70°C. In the same work, different behaviour was reported from PVA manufactured from Japan which showed shear thickening behaviour from lower values and the deviated to Newtonian behaviour at higher shear rates at 30°C. PVA manufactured from Russia at 30 and 45°C presented Newtonian behaviour with different shear viscosities. The samples were tested at 16%wt in contrast with our samples that were tested at 0.1, 0.2, and 0.3%wt. These comparison should however be taken with caution as the molecular weight of the PVA used in these work were not stated.

An increase in apparent viscosity of PVA solution was observed in brine environment when compared with deionised water. This confirms the study performed by Arjmand et. al [7] that viscosity of PVA solution increases with high salinity and also can act as polymer gel in very high salinity. This is important factor that PVA could be used for polymer flooding in oil reservoirs with such an extreme conditions. Some polymers such as HPAM solution exhibit a viscosity decrease in high salinity environment due to the cationic concentration (i.e.  $\text{Na}^-$ ,  $\text{Ca}^-$ , and  $\text{Mg}^{2+}$ ) which have negative effect on HPAM.

The impact of shear viscosity with changes on temperatures were carried out during this study. Slight decrease was noticed in shear viscosity by increasing the temperature of the sample. From this test a statement can be raised that PVA is stable at high temperature. Hence, can be used in reservoirs with high

temperature. Although our test was limited up to 50°C, this was confirmed by [7]. In their work PVA was tested at high temperature and proved that PVA  
255 can be used in reservoirs at temperature above 248.89°C.

### 3.1.6. *Surface tension (ST) and thermal conductivity measurements*

The conductivity and surface tension of rhamnolipid has been investigated to evaluate the effect of ionic concentration of solute in solvent as well as the impact of changes in temperature. The results of conductivity and ST experi-  
260 ment carried out indicate an increase of conductivity and decrease on ST as the concentration of solute increased in solvent. The same effect was also noticeable in sensitivity analysis on temperature. A remarkable reduction of surface tension of water from  $\approx 72\text{mN/m}$  to values below  $30\text{mN/m}$  (Figs. 7 and 8) as was observed by experiments performed several authors [27, 31]. All values  
265 presented in this section are average values from several experimental trials.

The investigation was carried out on other temperatures 30°C, 50°C and 70°C and the results summarised in Table 10. Ambient temperature was taken as the reference. In order to further analyse the variations in the observed results were taken. This shows an increase on conductivity and decrease in ST.  
270 However, this decrease or increase is not significant.

### 3.1.7. *Thermodynamics of rhamnolipid*

0.5 ml and 1 ml incremental intervals were used in this study to investigate the degree of the system sensitivity to the process of micellisation. Depending on the incremental intervals chosen the CMC may vary slightly. However, a  
275 much smaller incremental interval is preferable to avoid missing the thermodynamic behaviour of the monomers when aggregating within the solution to form micelles. Further,, in cases where there are multiple dynamic points associated with physical reaction, the plots with more data points (i.e. smaller incremental intervals) will allow this process to be more visible.

280 The thermodynamic values of rhamnolipid were computed by using the Gibbs free energy (Eqs. 3 and 4). It is observed from Figs. 8(a) and 7(a)

that the slope changes from 0.98 mM which indicates that the critical micelle concentration occurs at this point. This illustrates that to the right of this value, micelles is formed. Thus, no adsorption and process remains constant, which easily can be observed from the plot surface tension and logarithm of the concentration (Figs. 8(b) and 7(b)). when  $\Delta G < 0$ , the reaction is favorable and there is a release of free energy, indicating a spontaneous reaction. Process endergonic is when  $\Delta G > 0$ , the reaction is unfavorable and energy is absorbed. The results are summarised in Tables 11 and 12

The CMC obtained from our investigation is  $0.98 \times 10^{-3}$  mol/l (Fig. 7 and 8). This illustrates what observed in ST investigation in which temperature has insignificant impact on ST or conductivity reduction. The results of CMC are greater than the ones reported by [42] from surface tension which are between  $1 \times 10^{-4}$  mol/l and  $4 \times 10^{-4}$ . The values of CMC obtained in our investigation are in the range of rhamnolipid CMC determined by other authors [43, 44, 45, 46] which is between 1 - 200 mg/dm<sup>3</sup> ( $2.56 \times 10^{-5}$  -  $5.115 \times 10^{-3}$  mol/l). [42] reported that the discrepancy of the CMC obtained by different authors may be caused by results from the various mixture of homologues where monorhamnolipid is a dominant form. According to their investigation, this discrepancy also suggest that CMC should not be treated as one point but treated as a range of concentration in which aggregates can be formed.

The results obtained from Gibbs energy from conductivity approach are in the range from -71.719 to -44.593 KJmol<sup>-1</sup>. The only positive value obtained is 13.555 KJmol<sup>-1</sup> recorded in 50 °C which is the only ergonomic and spontaneous in the reverse direction. All others are exergonic (favorable reaction) and spontaneous forward direction. For surface tension, the calculated Gibbs energy are in the range from -108.430 to -98.822 KJmol<sup>-1</sup>. In contrast to the values of Gibbs energy reported by [42] that are in the range from -61.66 to -60.17 KJmol<sup>-1</sup>. The Gibbs energy obtained from this investigation are within the range of the ones reported by [47] which is  $-176.956 \pm 3.1$  KJmol<sup>-1</sup>; except the value obtained from conductivity at 50 °C. The observed values from our investigation as well as from other authors [42, 47] show the tendency of rha-

monolipid to absorb at the water-air interface and form micelles is higher than for the classical synthetic surfactants. This can be illustrated by the standard  
315 Gibbs free energy of adsorption and micellisation of rhamnolipid determined being considerable lower than those of the synthetic ones [42].

### 3.1.8. Interfacial tension reduction with PVA-brine aqueous phase for Angolan crude samples

The investigation in this section of our study focuses on evaluating the ef-  
320 fect of aqueous solution of formation brine mixed with PVA in IFT reduction. Fig. 9(a) shows IFT measurement of sample of aqueous phase composed of brine, 0.1 wt% PVA, and by changing NaOH concentration. The result shows an IFT reduction of aqueous solution and dead crude oil with increasing NaOH. This IFT reduction is generated by the reaction of NaOH with acidic component  
325 presents in the oil which create in situ surfactant. This reduction is more significant when rhamnolipid is added to the solution as illustrated in Fig. 9(b). However, this only works for lower concentration of rhamnolipid ( $\leq 0.98 \times 10^{-3}$  mol/l). Above this concentration the IFT remains constant. This shows that rhamnolipid at high concentration is sensitive to salinity.

330 The pH of different PVA molecular weight was also tested to check its impact by changing the NaOH concentration. The results from Fig. 10(a) shows that the values of pH for both polymer is the same. From Fig. 10(b) the IFT reduction is significant in PVA aqueous solution with brine by changing rhamnolipid concentration (C). However, the reduction is noticed in lower value of  
335 rhamnolipid concentration as was explained earlier. In contrast with experiment where with the same sample composition, the added chemical is the NaOH (B). The trend is the same however the samples with changing NaOH is above the other curve which shows the impact of surfactant in IFT reduction, compared to the in situ surfactant generated by alkaline (NaOH) with contact of acidic com-  
340 ponents present in the oil. The aqueous sample of PVA mixed with deionised water (A) which presents a continuous reduction in IFT. However, the values are still lower the ones obtained from sample (C). A decrease in IFT between

oil and aqueous was observed to values below 1 mN/m.

#### 4. Conclusions

345 An experimental investigation was conducted to examine the rheological and effects of NaOH, rhamnolipid, deionised water, and brine on the viscosity of dilute aqueous solutions of polyvinyl alcohol, a fully hydrolysed polymer over a wide range of parameters. The parameters investigated include concentration, temperature, shear rate and stress, and apparent viscosity. Based on the result  
350 of experimental investigation, the following conclusions can be drawn; The effect of molecular weight effect on the viscosity as a function of concentration in both cases, the viscosity of the polymer increase by increasing concentration. The effect of alkaline (NaOH) on the viscosity of polyvinyl alcohol (PVA) solutions as a function of temperature and concentration was complex as they  
355 affected the PVA chain both physically (charge shielding), chemically (hydrolysis) and no interaction in some cases. The combined PVA-Rhamnolipid-NaOH, PVA-Rhamnolipid-NaOH in brine solution reduced ST and IFT reduction to values below 30mN/m and 1mN/m respectively. This is due to the tendency of Rhamnolipid to adsorb at the water-air interface and water-oil interface to form  
360 the micelles is higher than for other conventional surfactants. This provides an opportunity to use this new and potential formulation in EOR processes in oilfield operations, particularly in offshore Angolan oilfields.

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#### Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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Table 1: Material used in the investigation

#		Material	Mw (g/mol)	API	Density (g/cm <sup>3</sup> )
1	Surfactant	Rhamnolipid	516		
2	Polymer	Poly(vinyl alcohol)	146,000		
3		Poly(vinyl alcohol)	186,000		
4	Alkaline	Sodium Hydroxide (NaOH)	40		
5	Oil	Oil A		32.13	0.8648
6		Oil B		31.41	0.8686
8	Brine				1.015

Table 2: Typical Angolan dead brine composition from field A formulated and used for the investigation

	Salt type	Concentration (mol/l)
Dead brine	Sodium chloride (NaCl)	0.23
	Calcium chloride (CaCl <sub>2</sub> )	0.26
	Barium chloride dehydrate (BaCl <sub>2</sub> .2H <sub>2</sub> O)	0.15
	Strontium chloride hexahydrate (SrCl <sub>2</sub> .6H <sub>2</sub> O)	0.15
	Potassium chloride (KCl)	0.08
	Magnesium chloride (MgCl <sub>2</sub> )	0.20
	Sodium bicarbonate (NaHCO <sub>3</sub> )	0.003
Total		1.073

Table 3: Power-law parameters of PVA at different molecular weight

	Polymer Mw, mol/g	k, cp	n	R <sup>2</sup>
P <sub>1</sub>	146000	181.27	0.335	0.950
P <sub>2</sub>	186000	184.44	0.358	0.920

Table 4: Power-law model parameters of PVA as a function of concentrations

	PVA Mw, mol/g	PVA wt%	k, cp	n	R <sup>2</sup>
P <sub>1</sub>	146,000	0.1	181.27	0.335	0.950
		0.2	71.35	0.567	0.926
P <sub>2</sub>	186,000	0.1	184.44	0.358	0.920
		0.2	148.42	0.506	0.888

Table 5: Power-law parameters of PVA Mw=146,000 mol/g for Mw= and rhamnolipid in brine solutions at different concentrations.

Group	PVA, wt%	Rlp, wt%	k, cp	n	R <sup>2</sup>
A	0.1	0.1	219.65	0.292	0.925
	0.1	0.2	218.26	0.315	0.943
	0.1	100	119.20	0.436	0.907
B	0.1	1	202.97	0.322	0.912
	0.2	1	65.218	0.593	0.875
	0.3	1	51.318	0.756	0.792
C	0.1	2	109.69	0.436	0.926
	0.2	2	168.19	0.412	0.888
	0.3	2	155.47	0.564	0.838

Table 6: Power-law parameters of PVA at different concentrations and molecular weight and NaOH mixed with brine.

	PVA Mw (mol/g)	PVA wt%	k, (cp)	n	R <sup>2</sup>
P <sub>1</sub>	146,000	0.1	208.91	0.312	0.917
		0.1	7.9282	0.917	0.309
P <sub>2</sub>	186000	0.2	162.63	0.530	0.947
		0.3	132.88	0.698	0.808

Table 7: Power-law parameters of 0.1wt% of PVA and rhamnolipid mixed with brine at different concentrations. PVA Mw=146,000 mol/g.

Rhamnolipid wt%	Temperature (°C)	k, cp	n	R <sup>2</sup>
0.1	21.7	219.65	0.292	0.925
	30	143.96	0.350	0.922
	50	303.93	0.169	0.962
0.2	21.7	218.26	0.315	0.943
	30	246.16	0.277	0.967
	50	276.03	0.202	0.951
100	21.7	119.2	0.436	0.907
	30	81.084	0.448	0.938
	50	256.44	0.232	0.962

Table 8: Power-law parameters of PVA and 1wt% of rhamnolipid mixed with brine at different concentrations. PVA Mw=146,000 mol/g.

PVA wt%	Temperature ( $^{\circ}$ C)	k, cp	n	$R^2$
0.1	21.7	202.97	0.322	0.912
	30	137.37	0.379	0.938
	50	278.28	0.211	0.962
0.2	21.7	65.218	0.593	0.875
	30	95.634	0.531	0.865
	50	208.04	0.311	0.910
0.3	21.7	51.318	0.756	0.792
	30	83.846	0.649	0.897
	50	59.94	0.636	0.851

Table 9: Power-law parameters of PVA - 2wt% of rhamnolipid mixed with brine at different concentrations. PVA Mw=146,000 mol/g.

PVA wt%	Temperature ( $^{\circ}$ C)	k, cp	n	$R^2$
0.1	21.7	109.69	0.436	0.926
	30	220.30	0.295	0.933
	50	258.54	0.241	0.962
0.2	21.7	168.19	0.412	0.888
	30	190.28	0.403	0.939
	50	86.442	0.472	0.935
0.3	21.7	155.47	0.564	0.838
	30	130.57	0.568	0.858
	50	162.24	0.468	0.906

Table 10: Impact of temperature on ST or conductivity. Ambient temperature is the reference temperature.

$\Delta$ Concentration	Surface tension (mN/m)			Conductivity (ms)	
	30 $^{\circ}$ C	50 $^{\circ}$ C	70 $^{\circ}$ C	30 $^{\circ}$ C	50 $^{\circ}$ C
$0.98 \times 10^{-3}$ mol/l	+0.63	+1.37	+3.22	-1.00	-3.67
$1.92 \times 10^{-3}$ mol/l	+0.64	+1.44	+2.82	-0.37	-3.70

Table 11: Conductivity with volume of stock added to solution  $V_1=0.5$  ml. mM stands for  $10^{-3}$  mol/l. A stand for exergonic and spontaneous forward, and B endergonic and spontaneous backward.

T, $^{\circ}$ C	$\beta$	$\alpha$	R, JK $^{-1}$ mol $^{-1}$	$X_{cmc}$ , mol/l	$\Delta G_{misc}^{\circ}$ , KJmol $^{-1}$	Description
21.7	1.060	-0.060	8.314	0.980	-46.562	A
30	1.124	-0.124	8.314	0.980	-44.593	A
50	2.249	-1.249	8.314	0.980	13.555	B

Table 12: Surface tension with volume of stock added to solution  $V_1=0.5$  ml. A stand for exergonic and spontaneous forward.

T, $^{\circ}$ C	$\beta$	$\alpha$	R, JK $^{-1}$ mol $^{-1}$	$X_{cmc}$ , mol/l	$\Delta G_{misc}^{\circ}$ , KJmol $^{-1}$	Description
21.7	0.002	0.980	8.314	0.980	-98.932	A
30	0.003	0.997	8.314	0.980	-101.680	A
50	0.002	0.998	8.314	0.980	-108.430	A
70	0.003	0.997	8.314	0.980	-115.106	A

Table 13: IFT reduction by using rhamnolipid, dead crude oil and brine

Concentration, $10^{-3}$ mol/l	Brine in solution		
	100%	50%	10%
0.00	22.49	20.36	20.40
0.98	0.88	0.74	0.89
2.83	0.82	0.79	0.74
4.55	0.74	0.79	0.73

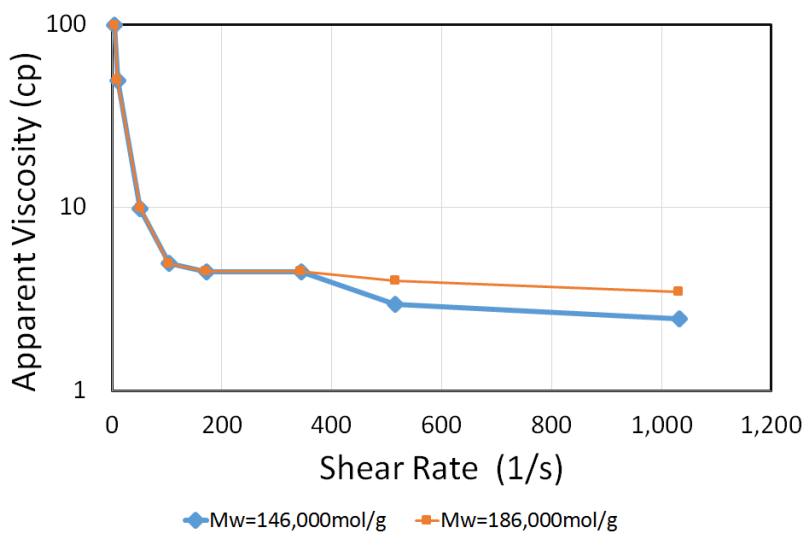
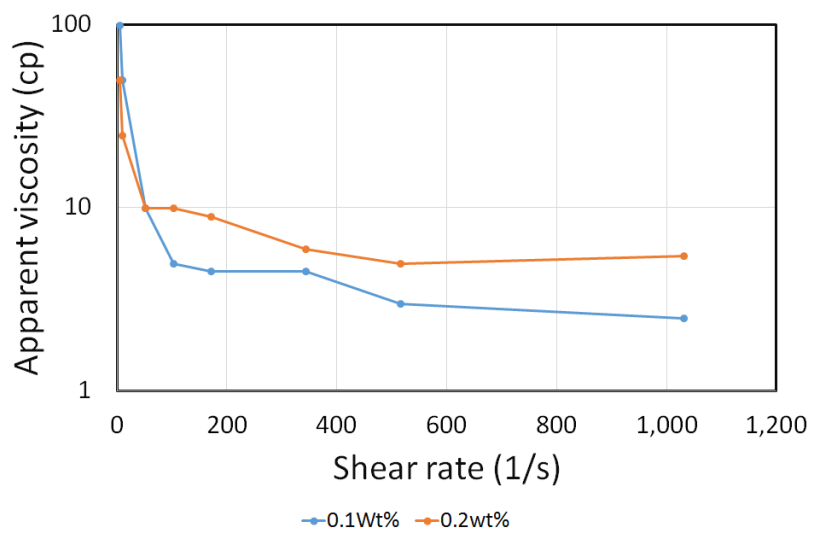
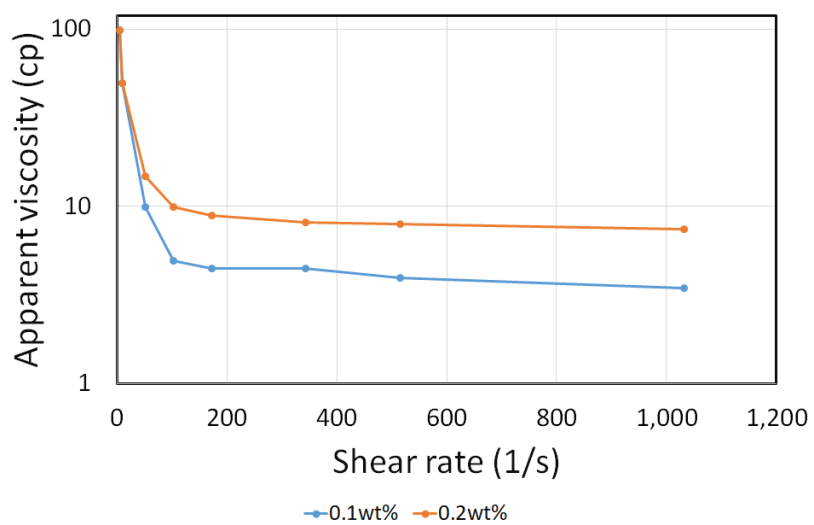


Figure 1: Shear-viscosity behaviour of PVA with different molecular weight at 21.7 °C.



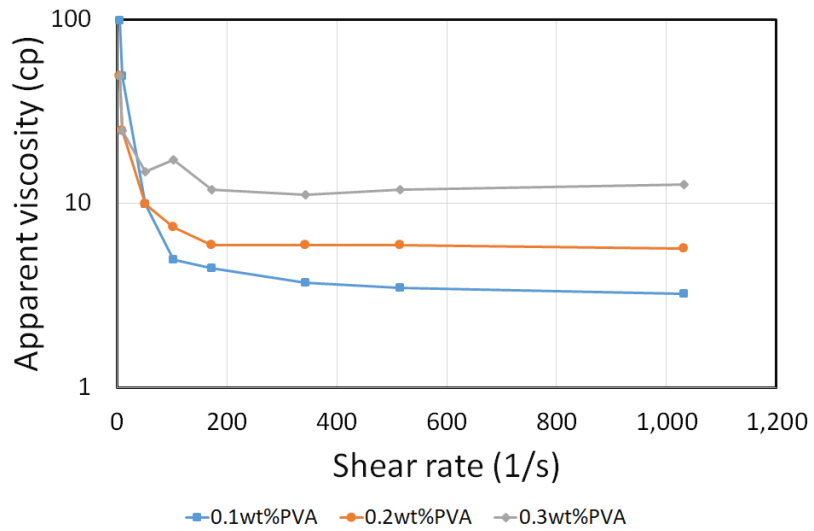
(a)



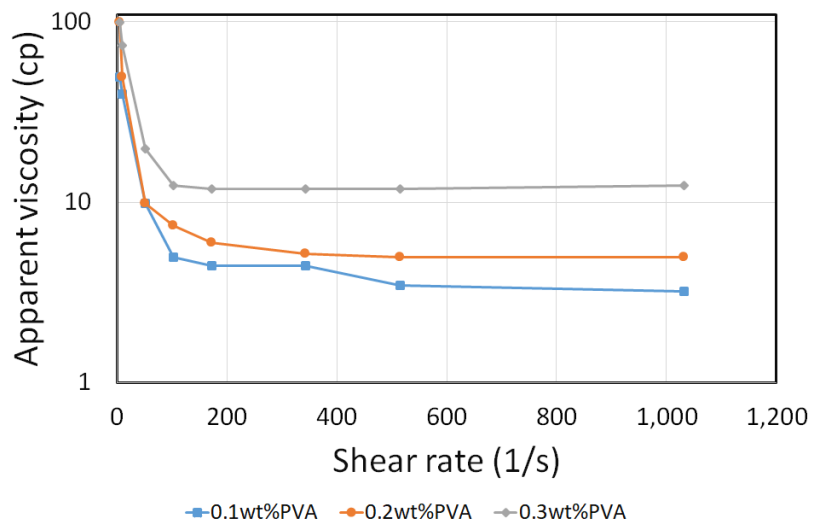
(b)

Figure 2: Shear rate versus shear stress for PVA solutions at 21.7 °C and different wt% concentration. (a) PVA with Mw=146000 mol/g, (b) PVA with Mw=186000 mol/g.





(a)



(b)

Figure 3: Shear-viscosity for PVA (M<sub>w</sub>=146,000 mol/g) and rhamnolipid (Rlp) mixed with brine at 21.7 °C. (a) PVA with different wt% and rhamnolipid with 1wt%, (b) PVA with different wt% and rhamnolipid with 2wt%.

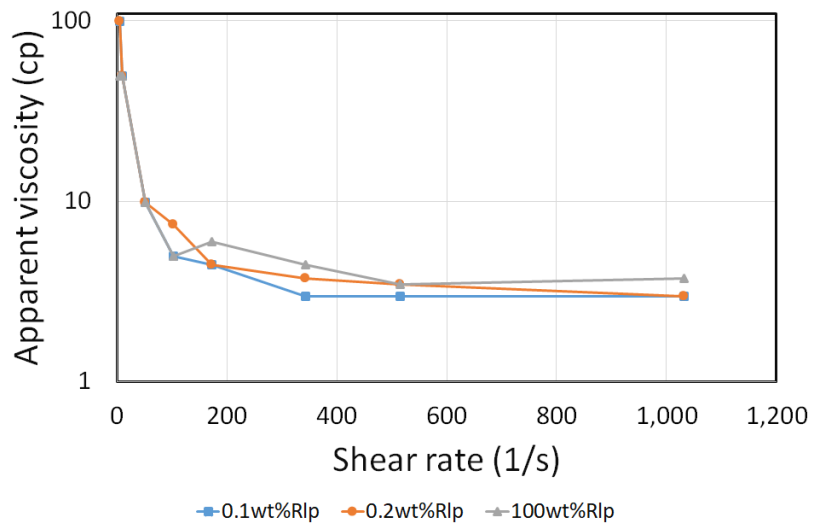


Figure 4: Shear-viscosity for 1 wt% PVA ( $M_w=146,000$  mol/g) and rhamnolipid (Rlp) with different wt% in brine solution at 21.7 °C.

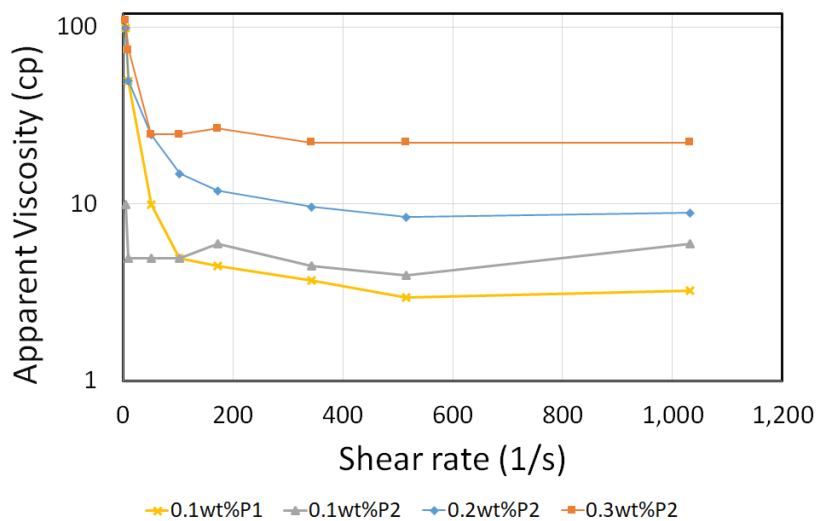


Figure 5: Shear viscosity versus shear rate for PVA solutions with brine mixed with NaOH with different concentrations at 21.7 °C. P1 is PVA with  $M_w=146,000$  mol/g and P2 is PVA with  $M_w=186,000$  mol/g.

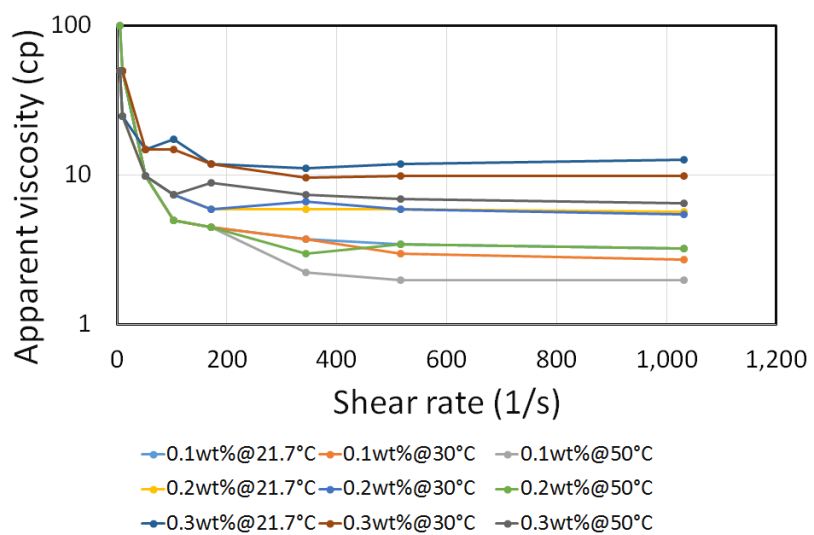
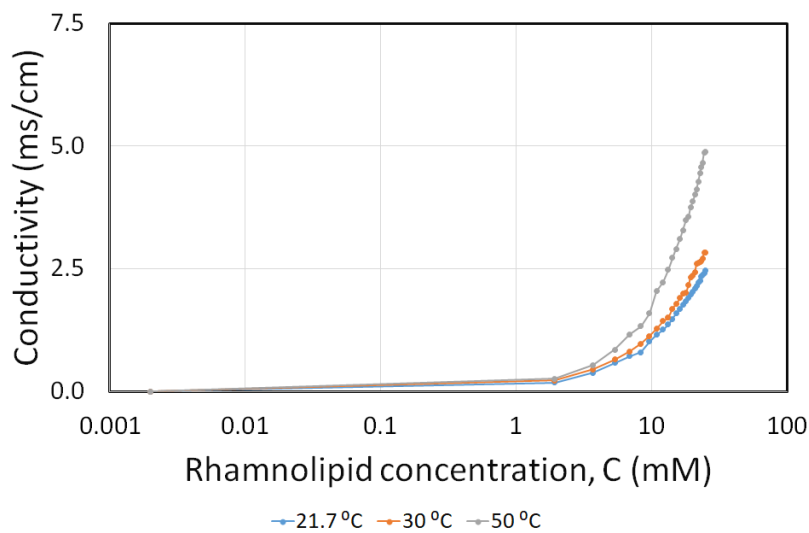
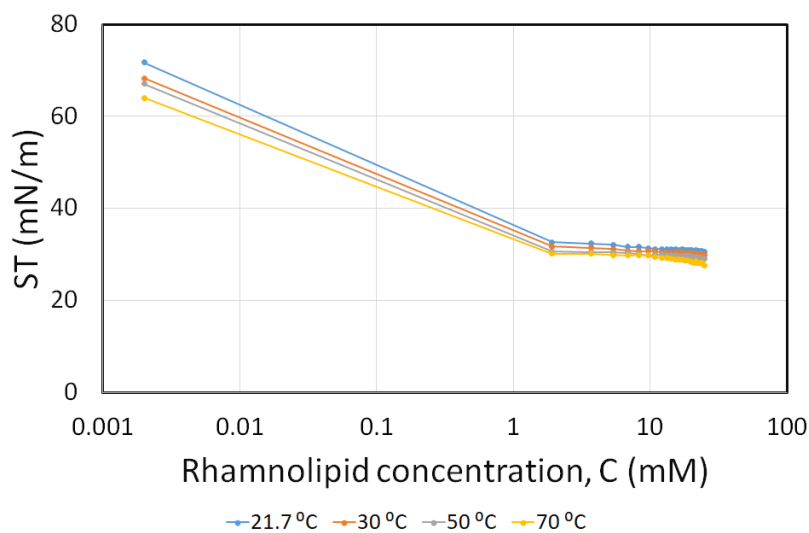


Figure 6: Shear-viscosity for PVA ( $M_w=146000$  mol/g) solutions with brine mixed with rhamnolipid at different temperatures and concentrations.

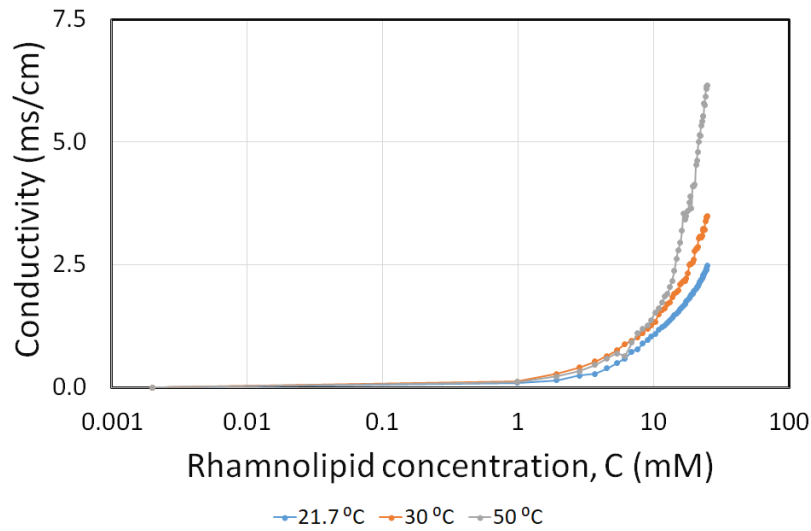


(a)

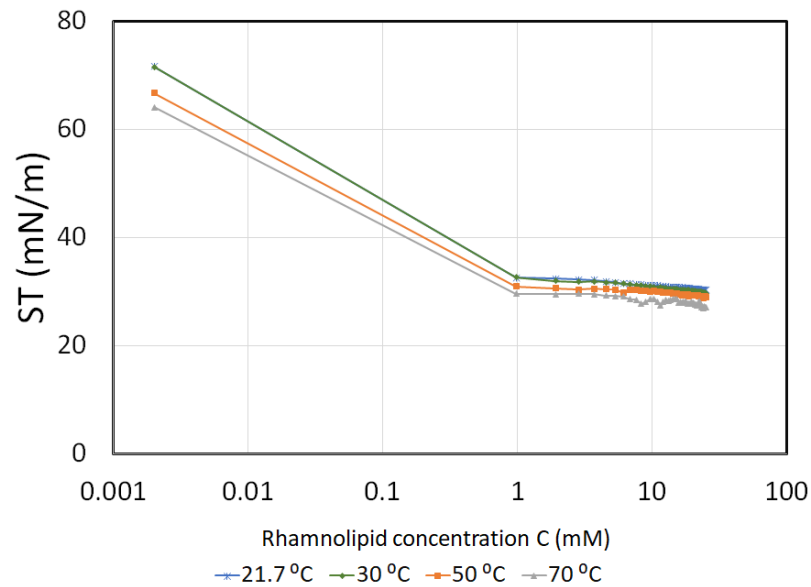


(b)

Figure 7: Rhamnolipid CMC calculation as a function of logarithm of the concentration. 1 ml volume of stock solution of rhamnolipid added at ambient temperature. (a) conductivity, (b) surface tension. mM stands for  $10^{-3}$  mol/l.

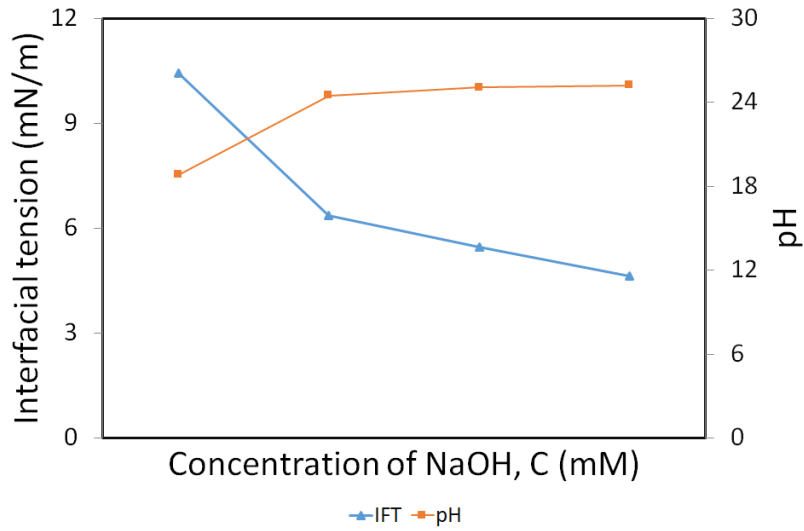


(a)

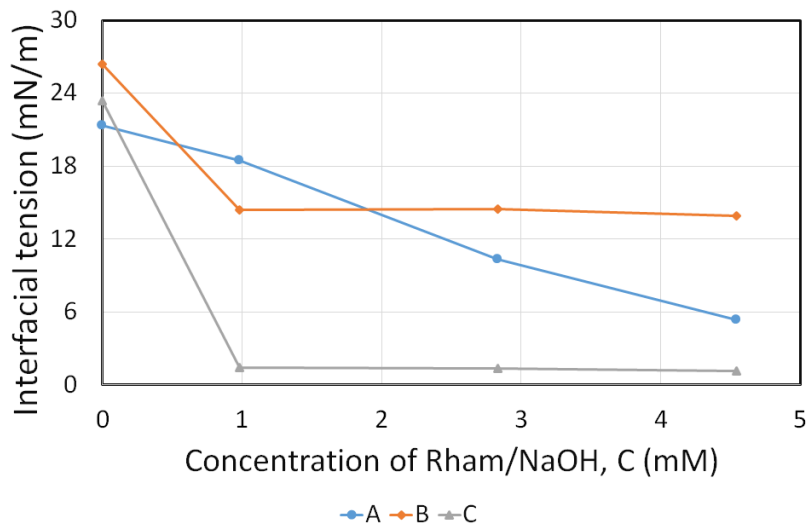


(b)

Figure 8: CMC calculation using conductivity and ST as a function of logarithm of the concentration. 0.5 ml volume of stock solution of rhamnolipid added,  $V_1$ . mM stands for  $10^{-3}$  mol/l. (a) conductivity; (b) surface tension

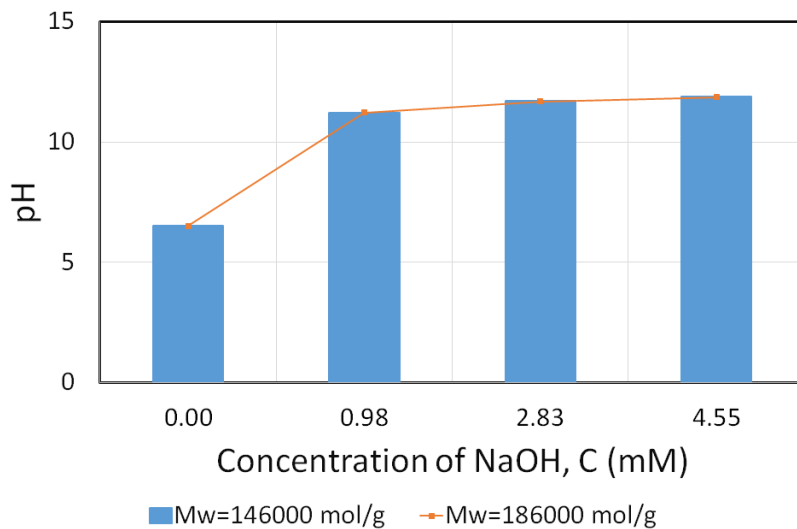


(a)

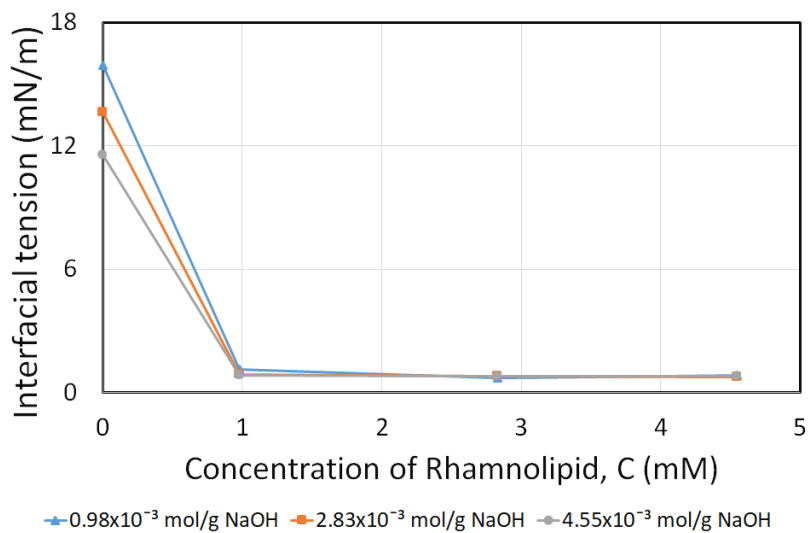


(b)

Figure 9: (a) pH and IFT measurement for oil with different 0.1wt% PVA ( $M_w=146,000$  mol/l) and brine as function of NaOH. mM stands for  $10^{-3}$  mol/l; (b) IFT measurement for oil with different 0.1 wt% PVA ( $M_w=146,000$  mol/l) and brine as function of rhamnolipid. mM stands for  $10^{-3}$  mol/l.



(a)



(b)

Figure 10: pH and IFT measurement. (a) pH comparison between 0.1 wt% PVA with  $M_w=146,000$  mol/l and  $M_w=186,000$  mol/l by changing NaOH concentration, (b) IFT measurement for oil with 0.1 wt% PVA ( $M_w=186,000$  mol/l). A: dead Oil, 0.1wt% PVA, NaOH mixed with deionised water by changing NaOH concentration; B: dead Oil, brine, 0.1wt%PVA, NaOH by changing NaOH concentration; C: dead Oil, brine, 0.1wt%PVA, rhamnolipid by changing rhamnolipid concentration.