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Kamal Elyasi Gomari, Sina Rezaei Gomari, Meez Islam, David Hughes

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Studying the Effect of Acidic and Basic Species on the Physiochemical Properties of Polymer and Biopolymer at Different Operational Conditions

Kamal Elyasi Gomari, Sina Rezaei Gomari^{*}, Meez Islam, David Hughes

School of Computing, Engineering & Digital Technologies, Teesside University, UK

Abstract

This paper describes an investigation and analysis of the physiochemical properties of polymer and biopolymer, namely interfacial tension (IFT) and viscosity, at elevated temperature and salinity. The methodology applied entails the testing and evaluation of the two surface-active components stearic acid and quinoline, which represent acidic and basic components respectively, in n-decane as a model oil in contact with polymeric solutions. The polymeric solutions contain Polyacrylamide (PAM) or Xanthan Gum (XG) in water at different saline levels. The results indicate that the effectiveness of polymer and biopolymer were significantly affected by the acidic or basic medium. Acidic systems have been found to be more active than basic systems in the reduction of IFT at room temperature. It is also noted that changing the water base from distilled water to seawater had no significant impact on IFT impact. Furthermore, an analysis at temperatures of $80\pm5^{\circ}$ c was conducted which indicated that there is an increase in IFT for all systems compared to at low temperature for both polymer and biopolymer systems. In respect to the effect of ageing time at high temperature, IFT increased slightly in the presence of polymer systems. However, in the case of biopolymer, IFT decreased with time at high temperature.

A study of rheological properties of these systems shows that the viscosity of polymer or biopolymer solutions decreased, with a subsequent increase in shear rates. Average values of viscosity of 45-100 cP at a low shear rate of 3 rpm and 5-9 cP at the high shear rate of 600 rpm were observed for both polymer and biopolymer systems. Acidic and basic components do not affect the viscosity of the solutions at ambient temperature, whereas the addition of seawater results in a slight decrease in viscosity. On the other hand, the application of higher temperature leads to a significant decrease in viscosity. As such, the highest reduction in viscosity was observed over time when surface-active components and seawater were used.

Keyword: Polymeric solutions; Polyacrylamide (PAM); Xanthan Gum (XG); Rheological behaviour; IFT; Acidic and basic oil

1. Introduction

^{*} Corresponding author's email: <u>s.rezaei-gomari@tees.ac.uk</u>

Despite significant increases in energy generation from renewable resources, fossil fuel is still one of the most important energy sources for our societies [1-2]. Mature reservoirs play an important role in the world's daily oil production. However, the main concern for the oil industry is how the production of oil from such reservoirs can be enriched. Therefore, employing efficient enhanced oil recovery (EOR) approaches could be effective in increasing the recovery of oil from mature reservoirs in the future [3].

The rate of success or failure of an EOR process can be determined in terms of its microscopic/macroscopic displacement efficiency in porous media. Over the last few decades, various methods have been adopted to improve microscopic and macroscopic displacement efficiency via the reduction of IFT at the oil-water interface and the mobility ratio of moving phases respectively. Surfactant and polymer flooding or newly developed bio-surfactant/bio-polymer flooding methods are considered to be effective in reducing the IFT between oil and water and in enhancing fluid mobility if they employed appropriately in hydrocarbon reservoirs [4]. In the first instance, the levels of oil and water composition are important parameters which influence the effectiveness of such methods. The composition of crude oil refers to the surface-active (polar) components, which have been mainly categorised as acidic, basic, or other components [5-8]. It has been proven that carboxylic acids (naphthenic acids) and nitrogen derivatives representing acidic and basic components respectively are vital in crude oil, which can strongly interact with water-additives hence affecting the interfacial properties of oil/water [9-11]. It should be noted that polymers can also influence interfacial tension. SiTu et al. [12] and Ma et al. [13] have both found that IFT increases with polymer concentration.

Although polar components in crude oil reduce interfacial tension, the presence of salts and changes in temperature have also been proposed by several authors as factors affecting interfacial properties. For instance, Lashkarbolooki et al. [14] examined the effect of salts on the interfacial activity of asphaltenic crude oil and the results indicated that MgSO4 can reduce the IFT to a lesser extent than other salts such as MgCl2.

The effect of temperature on the IFT at the crude oil-brine interface under anaerobic and aerobic conditions was studied by Hielmeland and Larrondo. Their results revealed that as temperature increases IFT also increases in anaerobic conditions, whereas in aerobic conditions IFT decreases with temperature [15]. The oil and water composition as well as temperature not only affect the interfacial activities of oil/water, but also they influence the rheological properties of water additives [16-18]. Lewandowska [19] examined the influence of salinity and temperature on the rheological properties of PAM and HPAM and the results

indicated that salinity and temperature have a drastic impact on the viscosity of polymer solutions. Similar observations were reported for changes in viscosity when biopolymer (xanthan gum) was used [20, 21]. Despite the above research performed on this topic, there is still some uncertainties about the impact of acidic and basic components on polymer/biopolymer and surfactant/bio-surfactant performance at reservoir conditions.

The aim of this study is to determine the effect of acidic and basic components in crude oil on the physiochemical properties of water additives which can be used to control the mobility ratio of moving phases in the reservoirs. The selected water additives are Polyacrylamide (PAM), and Xanthan Gum (XG) as a polymer and biopolymer respectively. Experiments were performed at both ambient and $80\pm5^{\circ}$ C temperatures on model oil consisting of ndecane with stearic acid and quinoline as acidic and basic oil respectively and seawater or deionised water as the aqueous phase.

2. Materials and methods

2.1 Materials

In this work, two types of water-soluble polymers were used: Polyacrylamide (PAM), and Xanthan Gum (XG). Stearic acid and quinoline were used to represent acidic and basic components in oil respectively. n-decane was used to represent the oil. The acidic and basic components were then mixed into n-decane to create a model oil resembling crude oil. The source, purity, molecular weight and structural formula of the chemicals used in this work are listed in **Table 1**. The seawater was prepared based on Kester's recipe as presented in **Table 2** in terms of both gravimetric and volumetric salts. In addition, the crude oil was also used in this work to validate the results. The crude oil was supplied by Equinor (Norway) and the source of the crude oil is the North Sea. The crude oil has an API gravity of 37.50° with acid number of 0.3 mg KOH/g.

Material	Supplier	Purity	Molecular weight	Structural formula
Polyacrylamide (polymer)	Sigma-Aldrich	-	2 million g/mol	$(C_3H_5NO)_n$
Xanthan gum (biopolymer)	Sigma-Aldrich	-	5-6 ×10 ⁶ g/mol	$(C_{35}H_{49}O_{29})n$
Stearic acid (acid)	Sigma-Aldrich	≥98.5 %	284.48 g/mol	C ₁₈ H ₃₆ O ₂
Quinoline (base)	Sigma-Aldrich	≥97 %	129.16 g/mol	C ₉ H ₇ N
n-decane	Sigma-Aldrich	≥94 %	142.28 g/mol	CH ₃ (CH ₂) ₈ CH ₃

Table 1. Chemicals and surface-active components used for experiments

Table 2. Gravimetric and Volumetric salts [22]

Salt	Molecular weight	g/l solution
Sodium chloride (NaCl)	58.44	23.926
Sodium sulfate (Na ₂ SO ₄)	142.04	4.008
Potassium chloride (KCl)	74.56	0.677
Sodium bicarbonate (NaHCO ₃)	84.00	0.196
Magnesium chloride (MgCl ₂ .6H ₂ O)	203.33	10.831
Calcium chloride (CaCl ₂ .2H ₂ O)	147.03	1.5199

2.2 Methods

2.2.1 Solution preparation and mixing procedure

PAM and XG in powder form were first added to distilled water (DW) or seawater and mixed using a mixer at a speed of 1000 rpm for 1.5 hours at room temperature to acquire a homogeneous solution. Subsequently, the prepared solution was then added to the model oil and mixed for 1 hour. In this study, concentrations of 5000 and 1500 ppm were used for the polymer and biopolymer respectively. The reason for selecting these concentrations was related to the time separation of the two phases (n-decane/DW), where for higher concentrations a longer separation time would be required. Figure 1 shows the phase separation time for DW and model oil at ambient conditions. As can be seen from the figure, with concentrations above 5000 ppm for PAM and 1500 ppm for XG in water, the phase separation time increases, especially for the biopolymer, which makes IFT measurements extremely difficult.



Figure 1: Phase separation time (Distilled water/n-decane) @ 25±2°C

For the polymer systems, 10 min was enough to separate the n-decane from the DW, while approximately 180 min was taken for the biopolymer systems. Despite these different separation times for polymer and biopolymer systems, all measurements were taken 4 hours after preparing the solutions. The measurements were performed at room temperature conditions $(20\pm2^{\circ}C)$ and at $80\pm5^{\circ}C$ for different ageing times of 0, 1, 10, and 20 days. **Table 3** lists all of the polymer/biopolymer solutions used in this work.

Polymer/n-decane solution	Biopolymer/n-decane solution
PAM + DW/n-decane	XG + DW/n-decane
PAM + DW/Acidic n-decane	XG+ DW/Acidic n-decane
PAM + DW/Basic n-decane	XG+ DW/Basic n-decane
PAM + Seawater/Acidic n-decane	XG+ Seawater/Acidic n-decane
PAM + Seawater/Basic n-decane	XG+ Seawater/Basic n-decane

Table 3. Polymer and biopolymer/n-decane solutions

2.2.2 Interfacial tension (IFT) measurements

Measurements of interfacial tension (IFT) were conducted using a Kruss Digital Tensometer model K9. Initially, 25 ml of oil sample and 75 ml of either polymer or biopolymer solution were prepared in a small beaker. After suitable times for mixing and phase separation, the beaker was placed into a plastic holder within the IFT device. Subsequently, a platinum circle ring was used to measure the IFT between the two liquid phases (n-decane and DW). This procedure was repeated three times for each sample to ensure the accuracy of the results, and the average was then assigned as the IFT measurement.

2.2.3 Viscosity measurements

All viscosity measurements were carried out using a Fann model 35 viscometer with the rotor-bob-torsion spring combination of R1-B1-F1. For the measurements, 250 ml of oil sample and 750 ml of either polymer and biopolymer solutions were prepared. After observing the two separated phases, 350 ml of the polymer or biopolymer solution was collected in a syringe and deposited into a cup, which was then placed on the viscometer. **Figure 2** presents the details of the applied procedure for IFT and viscosity measurements in this study.



Figure 2: Schematic of applied procedure for viscosity and IFT measurements

The viscosity of various solutions (see **Table 3**) as a function of shear rate were measured over the range of 5.109 to 1021.8 s^{-1} .

3. Results and Discussion

3.1 Interfacial tension (IFT) measurements for reference point

Table 4 shows the results of IFT measurements for the reference point of pure n-decane with distilled water and IFT measurements for both DW and seawater with n-decane in the presence of acidic and basic components.

Solution	IFT (mN/m)
DW + n-decane	38.2
DW+ Acidic n-decane	12.5
DW+ Basic n-decane	26.4
Seawater + n-decane	22.2
Seawater + Acidic n-decane	11.5
Seawater + Basic n-decane	21

Table 4. IFT measurements for reference solutions

As can be seen from this table, the presence of acidic and basic components in model oil results in IFT reduction. This reduction is more pronounced for acidic components than basic components. Moreover, a higher degree of reduction was observed in the presence of salts where, for instance, the IFT between DW/basic n-decane at 26.4 mN/m was reduced to 21.0 when the water phase was changed from distilled water to seawater. Similar observations with regards to the impact of polar components in the oil phase as well as water phase composition on IFT have been reported [23–25]. Rudin and Wasan [23] studied the effect of acid concentration on IFT and the results indicated that it was reduced to 11 and 24 mN/m

respectively when using concentrations of acid of 10^1 and 10^2 mol/m³. Standal et al. [24] examined the effect of the three surface-active components quinoline, 5-indanol and 1-naphtoic acid on the IFT between oil and water solutions. They concluded that 1-naphtoic acid had no effect on IFT, whereas a 5-indanol/oil/water solution caused a reduction. In addition, use of the quinoline/oil/water system leads to slight reductions in interfacial tension compared to 5-indanol/oil/water.

3.1.1 Effect of acidic/basic components and salinity on IFT between polymeric solution and model oil

Usually the acidity and basicity of crude oil are identified by acid and base numbers. If the acid number of crude oil is higher than its base number this means the oil is more acidic and vice versa [26, 27]. Acid and base components are always present in oil and so it is important to understand their impact when brought into contact with other solutions. **Figure 3** shows the effectiveness of the acidic and basic components on IFT with polymeric solution (PAM or XG) and distilled water at ambient temperature.



Figure 3. Effect of acidic/basic components and salinity on IFT by adding polymer and biopolymer @ 20 ± 2 °C.

With comparison to the reference point, it can be seen that PAM led to a significantly higher reduction in IFT compared to XG. In fact, by adding PAM to the distilled water there was a significant drop of 34.2 mN/m in IFT, while there was a reduction of only 15 mN/m when adding XG. This difference in IFT for PAM and XG can be attributed to their hydrolysis in water which leads to an increase of carboxylic molecules in the solution [28]. **Figure 4** presents the molecular structures of PAM (Figure 4a) and XG (Figure 4b) and their interactions with water. As can be seen in this figure, the amide group in the PAM structure releases the carboxylic group (RCOOH) through chemical transformation between RCOO-from PAM and H+ from water when dissolved in water. The formation of carboxylic molecules (in situ surfactant formation) and their affinity towards interface causes a significant drop in IFT for PAM solution. In contrast to PAM solution, XG with tri-

saccharide side acid chain attached to glucose backbone produces carboxylic acid (pyruvic acid) when associated in water. The latter acid has high solubility in water and less affinity towards interface, hence the IFT reduction is lower than that of PAM.



a: Interaction of Polyacrylamide (PAM) with water and release of carboxylate ions



b: Interaction of Xanthan gum (XG) with water and release of Pyruvate ion (carboxylate ion type)



d: Interaction of quinoline with water

Figure 4: Structure of PAM (a), XG (b), stearic acid (c), quinoline (d) and their interaction with water.

The addition of basic and acidic components to the n-decane resulted in further reductions in IFT where, for instance, including stearic acid into the system reduced the IFT to 1 mN/m for PAM solution and to 11.9 mN/m for XG solution which is equivalent to 75% and 48% reduction, respectively. The lesser reduction of IFT for XG can be ascribed to the presence

of Na⁺/K⁺ ions in the side chain structure of XG molecule which can be dissociated and in turn interacted with the carboxylate ions (RCOO-) in water solution. The latter interaction produces sodium/potassium acetate which results in reduction of available carboxylic acids at interface, therefore a lesser reduction in IFT was observed for XG. The interaction between acid/base components with water are also presented in Figure 4c and Figure 4d. The interfacial activities of produced molecules (carboxylic and amino acids) and ionic species (carboxylate and amino) show that the added natural surfactant (stearic acid) or in situ formation of surfactant from PAM/XG solution in water dominating the IFT reduction. In general, surfactants are amphiphilic molecules containing both hydrophobic chain and hydrophilic head that have the ability to adsorb to the oil and water interface [30]. Depending on the length of hydrophobic chain the concentration of surfactant at interface changes where the longer length results in higher adsorption hence higher reduction in IFT. It is clear that when polymer is mixed with water, the process of hydrolysis can be happened which activate the functional groups. The released functional group of RCOO- interacts with H+ creating the carboxylic acid (in situ surfactant formation). This process can happened for XG as well but the generated carboxylic acid (Pyruvic acid, see figure 4b) has higher affinity towards water which results in lesser concentration at interface. Moreover, it should be noted that minimization of interfacial energy by the surfactant is functional in holding the polymer at oil-aqueous interface [31]. The obtained IFT results in Figure 3 reflect clearly the difference between these two polymers.

Similar results were observed when basic components were used but these were not as effective as the acidic system. The nitrogen in quinoline reacts with a hydrogen in water to form a covalent bond with nitrogen and hydrogen which leaves a charged R-(NH+) group known as amino acid. The decrease in IFT is mainly due to presence of amino group (NH+) but due to lack of significant carboxylic group (COOH) in the solution, this reduction is not significant as stearic acid. In fact, stearic acid can act as surfactant and reduce IFT significantly [32] which is not the case for quinoline.

Additionally, it can been seen from **Figure 3** that the change in IFT was almost constant when salt was added to the systems. The present results are in line with those of previous studies [33-34] on the effect of organic acids and salinity on the interfacial tension of n-decane/water systems, in which the addition carboxylic acids was found to reduce the IFT by up to 22–26 mN/m compared to the pure water system. In addition, their conclusions confirmed that salinity did not significantly affect IFT measurements.

3.1.2 Effect of temperature on IFT

Figure 5 shows the effect of temperature on IFT with different systems for PAM (**Figure 5a**) and XG (**Figure 5b**). Based on these results, as temperature increases IFT also increases. For both polymer and biopolymer, minimal values of IFT of 1 and 11.9 mN/m were achieved at $20\pm2^{\circ}$ C in the system of acidic n-decane, which increased to 8.7 and 17.8 mN/m respectively at $80\pm5^{\circ}$ C. Ye et al. [35] studied the influence of temperature on the IFT at the crude oil-gemini surfactant interface. Their results indicated that, by increasing the temperature up to 70°C, the IFT gradually declined. However, further increases in temperature increased the IFT. The critical temperature in this effect was called the phase inversion temperature (PIT). The adsorption of surfactant at the interface increased before the PIT, resulting in a decrease in IFT, while after the PIT an inverse effect was observed in which the desorption of surfactant from the interface into the oil phase led to increased IFT.



Figure 5. Effect of temperature on IFT (a) polymer (b) biopolymer's solutions

To shed more light on the effect of temperature on IFT between model oil and polymeric solutions, the IFT measurements were conducted for more temperature points between 25° C to 80° C and results are presented in **Figure 6**.



Figure 6: Identification of Phase Inversion Temperature (PIT) for PAM and XG solutions.

As can be seen in this figure, the phase inversion temperature (PIT) for XG and PAM solutions were found to be around 50°C and 40°C, respectively. The observed IFT trend for both polymeric solutions are in-line with hydrolysis of polymer against temperature reported by recent study by Godwin Uranta et al. [29] where they reported that higher temperature was favourable for more hydrolysis of polymers in water which in turn was favourable for more carboxylic acid formation (surfactant) in the solutions. Due to increase in formation of surfactant into the solution, the IFT reduces with the temperature, however as temperature exceeded the PIT, the solubility of surfactant in water increases which results in reduction of adsorbed surfactant at interface hence the IFT increases[36].

Another study by Rezaei Gomari et al. revealed that, by increasing temperature from 25° C to 50° C, the value of IFT dropped from 4.7 mN/m to 2.8 mN/m, while it increased to 4.1 mN/m by increasing the temperature further to 70° C [37]. It is noticed that by increasing temperature to $80\pm5^{\circ}$ C, the increase in IFT in the PAM/n-decane was much higher than that of XG/n-decane. For instance, the IFT increased by 13.9 mN/m in the system of polymer/seawater/acidic n-decane, whereas there was a rise of only 6.1 mN/m in the XG/seawater/acidic n-decane system.

3.1.3 Effect of aging time on IFT

Figure 7 illustrates the effect of ageing time on IFT for different systems at temperatures of $20\pm2^{\circ}$ C (Figure 7a) and $80\pm5^{\circ}$ C (Figure 7b). It can be seen from Figure 7a that there is a direct link between time and increasing IFT. In fact, as time goes on, the IFT increases. During the period covered in Figure 7a, there was a slight rise in IFT for the systems of acidic n-decane. However, the IFT increased significantly over the period without and with basic n-decane systems. For example, from 0 to 20 days, there was a rise of 2.3 mN/m in IFT

from 1 to 3.3 mN/m for the PAM/acidic n-decane system. Meanwhile the IFT increased up to 9.4 mN/m and 11.3 mN/m in the PAM/basic n-decane and PAM/n-decane systems respectively. It is known that the reduction in IFT occurs due to the adsorption and accumulation of surface- active components at the oil-water interface; however according to Saha et al. [38], the increase in IFT over time could be due to a reduction in levels of surface- active components at the oil-water by the development of a higher concentration gradient. Another study by Okasha [39] on the effect of temperature and pressure on IFT, where they observed that IFT increased significantly over time, supports the present results.

In respect to the effect of ageing time at high temperature (see **Figure 7b**), the same trends as with low temperature were observed for the PAM systems (except for the polymer/acidic system). Although the IFT increased slightly during the first 10 days, there was a minor drop in the IFT of up to 1.3 mN/m between days 10 and 20. However, in the case of the XG systems, the IFT increased marginally from 0 to 1 day, and after that it began to decrease between 1 and 20 days.





3.1.4 Examining the impact of polymeric solutions on IFT using crude oil

The impact of polymeric solutions in DW was also examined with crude oil and results are presented in **Figure 8**. As it is shown in this figure, the IFT between DW/Crude oil is reduced from 28.7 mN/m to 2.3 and 10.2 when PAM and XG were added to the solution, respectively. These results are in line with the observed results for model oil where significant reduction of IFT was recorded for PAM solution than that of XG solution. The impacts of aging time and temperature were also shown a similar results which confirm the findings of this research with the model oil.



Figure 8. Impact of polymeric solutions (PAM and XG) on IFT between polymeric solutions and crude oil with respect of ageing time and temperature @ 20±2°C and 80±5°C.

3.2 Rheological behaviour of polymeric solutions in acidic and basic oils

3.2.1 Effect of acidic/basic components and salinity on viscosity of polymeric solutions

Figure 9 shows the viscosity behaviour of PAM/XG systems under the effect of acidic/basic components and seawater. In general, it can be seen from the figure that the viscosity of all systems decreased with increasing shear rate, indicating that PAM and XG solutions are non-Newtonian fluids. The behaviour of this type of fluids can be characterised as pseudoplastic [40]. In order to analyse the results further, low and high shear rates were selected in **Figure 10**. The shear rates were selected in a way to resemble the flow regime of polymeric solutions near well bore (higher shear rate) and far from the well bore (reservoir with lower shear rate). The results show that the viscosity of both polymer and biopolymer are quite high and acceptable to displace the oil located far from the well bore. However, the lower viscosity at high shear rates presents a higher velocity flow regime around the well bore which is also favourable to the polymer's injectivity.

It is observed that the viscosity of XG is almost twice that of the PAM at the low shear rate (Figure 10a), while at the high shear rate the viscosity of the PAM is slightly higher than that of XG (Figure 10b).

The results show no changes in the viscosity of the solutions under the influence of acidic or basic components. However, the viscosity decreased slightly after the addition of seawater up to 10cP and 5cP at low shear rate and 1cP at high shear rate for both XG and PAM systems respectively. In the literature, the majority of water-soluble polymers are described as having an -OH group. Once the polymer is exposed to water molecules, hydrogen bonds are formed. As salt is introduced into the solution, the hydrogen bonds between the polymer and water molecules become weak so that the viscosity of the solution will decrease. In fact, the force between a water hydrogen atom and a polymer oxygen atom is dependent on the dielectric constant of the medium, where a higher constant means stronger bonding. The dielectric constant decreases by adding salts to the solution, thus reducing its viscosity [41]. Sveistrup et al. [42] studied the effect of salinity on XG at 25°C and the results revealed that the



viscosity of XG decreases as a result of the addition of salt to the system.



Figure 9. Effect of (a) acidic (b) basic components and seawater on viscosity with added polymer and biopolymer @ 20±2°C



Figure 10. Effect of (a) low and (b) high shear rates on viscosity with different solutions @ 20±2°C

3.2.2 Effect of temperature on viscosity of polymeric solutions in presence acidic and basic components

Figure 11 illustrates the effect of high temperature on the viscosity of PAM and XG systems under the influence of acidic/basic components and seawater. In general, viscosity decreases with increasing temperature from $20\pm2^{\circ}$ C (see Figure 9) to $80\pm5^{\circ}$ C for all systems. It is reported by Xiong et al. [43] and Godwin Uranta et al. [44] that the degradation of the polymer occurs when the amide groups present in the polymer structure are hydrolysed in aqueous solution. The degree of hydrolysis can rise by increasing temperature and aging time. The high degree of hydrolysis causes a change in the viscosity of the polymer gel which leads to a decline in its performance. It is stated by Kumar et al. [36] that, a higher movement of polymer molecules, a decrease in the inter-chain liaisons and an increase in polymer solubility are the main reasons of declining in polymer viscosity at higher temperature. Figure 12 shows images taken from polymeric solutions at low (Figure 12 a) and high (Figure 12b) temperatures with aging time, respectively. These images clarify the changes in polymer properties with changing the cloudiness of the polymer solutions where

the low temperature required longer time to become separated (transparent). Moreover, Mahdavi et al. [45] have observed a similar trend for viscosity and temperature and they attributed this to the increasing incidence of polymer chain collisions and reduced average intermolecular forces resulting in the reduction of the viscosity of the solution at high temperature.

The percentage changes in viscosity of PAM and XG between temperatures of $20\pm2^{\circ}$ C and $80\pm5^{\circ}$ C are shown in **Figure 13** for the two shear rates of 3 and 600rpm. According to **Figure 13a**, the seawater/acidic n-decane system exhibited the highest reductions in viscosity of 50% and 22.2% for XG and PAM respectively, while distilled water/basic n-decane system showed the lowest reductions in viscosity. It is noticed that the loss of viscosity in the case of the addition of polymer was approximately constant for all systems, whereas biopolymer solutions showed varying percentage reductions. In contrast, at the high shear rate (**Figure 13b**) similar results were observed, where seawater/acidic n-decane system had the highest reduction in viscosity. In addition, it was discerned that the percentage reduction in viscosity



Figure 11. Effect of acidic/basic components and seawater on viscosity with added polymer and biopolymer @ 80±5°C





Figure 12: Visual observation of changes in polymeric solutions @ 25°C (a) and 80°C (b) with aging time.



Figure 13. Effect of temperature on the reduction of viscoity from $20 \pm 2^{\circ}$ C to $80 \pm 5^{\circ}$ C at shear rates of 3 rpm (A) and 600 rpm (B)

3.2.3 Effect of aging time on viscosity of polymeric solutions in presence acidic and basic components

To investigate the influence of ageing time on viscosity, PAM and XG solutions at a shear rate of 600 rpm were tested at three time intervals of 1, 10, and 20 days. It should be noted that there were no changes in viscosity in the solutions at ambient temperature, and thus only the temperature of $80\pm5^{\circ}$ C is analysed here. **Tables 5 and 6** show the viscosity results for PAM and XG systems on day zero at high temperature.

Figures 14 and 15 illustrate the percentage change in viscosity of PAM and XG against ageing time at a temperature of $80\pm5^{\circ}$ C. In general, the viscosity decreased for all systems over time, which can be attributed to damage to the polymer chains [45]. It should be noted that the highest reduction in viscosity was observed when polar components were used in the systems. For instance, after 20 days of ageing, the highest reductions of viscosity were observed in the seawater/acidic n-decane system, at 64.7 % and 83.3 % for PAM and XG respectively. Whereas the loss in viscosity was 35% for PAM and 42.8 % for XG in the distilled water/n-decane system.

Table 5. Viscosity of polymer (PAM) @ 0 day

Solution	Viscosity(cP) @

	shear rate 600 rpm
Polymer+DW/n-decane	5
Polymer+DW/Acidic n-decane	5.5
Polymer+DW/Basic n-decane	6
Polymer+Seawater/Acidic n-decane	4.25
Polymer+Seawater/Basic n-decane	4.5

Table 6.	Viscosity	of biopolymer	(XG)	(a, 0)	day
	/		()	(/ -	/

Solution	Viscosity(Cp) @ shear rate 600 rpm		
Biopolymer+DW/n-decane	3.5		
Biopolymer+DW/Acidic n-decane	4.5		
Biopolymer+DW/Basic n-decane	4.75		
Biopolymer+Seawater/Acidic n-decane	3		
Biopolymer+Seawater/Basic n-decane	3.25		



Figure 14. Percentage loss of polymer (PAM) viscosity against ageing time at 80±5°C



Figure 15. Percentage loss of biopolymer (XG) viscosity against ageing time at 80±5°C

4. Conclusions

In the present study, experimental values of IFT for n-decane/distilled water systems and the effect of surface-active components and seawater on the rheological behaviour of a polymer

(PAM) and biopolymer (XG) have been reported. The results indicate that by adding polymer or biopolymer to the solutions, the IFT between n-decane and distilled water can be reduced. However, the effectiveness of polymer on the reduction in IFT was much higher than that of a biopolymer. The addition of basic and acidic components to the n-decane reduced the IFT between water and polymeric solutions further, and the highest reductions in IFT were observed for the acidic component. However, it would appear that seawater does not have a significant impact on IFT. A polymer and a biopolymer were used to increase the viscosity of the solution. The presence of acidic and basic components does not change the viscosity of solutions, while the presence of seawater leads to decreased viscosity. The results show that increased temperature had undesirable effects on viscosity over time, especially in the presence of acidic components. The same conclusion was observed for IFT at high temperature, while in the case of the biopolymer its value was reduced with ageing.

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References

[1] S. Sorrell, Reducing energy demand: A review of issues, challenges and approaches, Renewable and Sustainable Energy Reviews 47 (2015) 74-82.

[2] S. Shafiee, E. Topal, When will fossil fuel reserves be diminished? *Energy Policy* 37 (2009) 181-189.

[3] V. Alvarado, E. Manrique, Enhanced Oil Recovery: An Update Review, *Energies* 3 (2010) 1529-1575.

[4] A. Mosayebi, M. Torabi Angaji, P. Khadiv-Parsib, P, The effect of temperature on the interfacial between crude oil and ethoxylated nonylphenols, *Petroleum Science and Technology* 34 (2016) 1315-1322.

[5] G.J. Hirasakl, Wettability: Fundamentals and Surface Forces, *Society of Petroleum Engineers* (1991) 217-226.

[6] W.K. Seifert, Effect of Phenols on the Interfacial Activity of Crude Oil (California) Carboxylic Acids and the Identification of Carbazoles and Indoles, *Anlytical Chemistry* 41 (1969) 554-568.

[7] J.G. Speight, The Chemistry and Technology of Petroleum, Fourth ed., Taylor and Francis Group, New York, 2007.

[8] S.J. Fathi, T. Austad, S. Strand, T. Puntervold, Wettability Alteration in Carbonates: The Effect of Water-Soluble Carboxylic Acids in Crude Oil, *Energy Fuels* 24 (2010) 2974-2979.

[9] M.Y. Jabbar, H.S. Al-Hashim, W. Abdallah, Effect of Brine Composition on Wettability Alteration of Carbonate Rocks in the Presence of Polar Compounds, *Society of Petroleum Engineers* (2013) 1-14.

[10] K.A. Rezaei Gomari, A.A. Hamouda, Effect of fatty acids, water composition and pH on the wettability alteration of calcite surface, *Petroleum Science and Engineering* 50 (2006) 140-150.

[11] M.J. Benedik, Ph.R. Gibbs, R.R. Riddle, R.C. Willson, Microbial denitrogenation of fossil fuels, *Trends in Biotechnology* 16 (1998) 390-395.

[12] W.X. SiTu, H.M. Lu, Ch.Y Ruan, L. Zhang, Y. Zhua, Effect of polymer on dynamic interfacial tensions of sulfobetaine solutions, *Colloids and Surfaces A* 533 (2017) 231-240.

[13] B. Ma, B. Gao, L. Zhang, Q. Gong, Zh. Jin, S. Zhao, Influence of Polymer on Dynamic Interfacial Tensions of EOR Surfactant Solutions, *Applied Polymer Science* 131 (2014) 1-5.

[14] M. Lashkarbolooki, Sh. Ayatollahi, M. Riazi, The Impacts of Aqueous Ions on Interfacial Tension and Wettability of an Asphaltenic–Acidic Crude Oil Reservoir during Smart Water Injection, *Chemical&Engineering Data* 59 (2014) 3624-3634.

[15] O.S. Hielmeland, L.E. Larrondo, Experimental Investigation of the Effects of Temperature, Pressure, and Crude Oil Composition on Interfacial Properties, *Society of Petroleum Engineers* 1 (1986) 321-328.

[16] A. Mandal, Chemical flood enhanced oil recovery:a review, *Oil Gas and Coal Technology* 9 (2015) 241-264.

[17] B.M. Das, S.B. Gogoi, D. Mech, Micellar-polymer for enhanced oil recovery for Upper Assam Basin, *Resource-Efficient Technologies* 3 (2017) 82-87.

[18] O.A. Omoniyi, F. Abdulmalik, A Review of Microbial Enhanced Oil Recovery: Current Development and Future Prospects, *International Journal of Scientific & Engineering Research* 6 (2015) 1378-1389.

[19] K. Lewandowska, Comparative Studies of Rheological Properties of Polyacrylamide and Partially Hydrolyzed Polyacrylamide Solutions, *Applied Polymer Science* 103 (2007) 2235-2241.

[20] H. Al-Sulaimani, S. Joshi, Y. Al-Wahaibi, S. Al-Bahry, A. Elshafie, A. Al-Bemani, Microbial biotechnology for enhancing oil recovery: Current developments and future prospects, *Society for Applied Biotechnology* 1 (2011) 147-158.

[21] A.A. Alquraishia, F.D. Alsewailemb, Xanthan and guar polymer solutions for water shut off in high salinity reservoirs, *Carbohydrate Polymers* 88 (2012) 859-863.

[22] D.R. Kester, I.W. Duedall, D.N. Connors, R.M. Pytkowicz, Preparation of Artificial Seawater, *Limnology and Oceanography* 12 (1967) 176-179.

[23] J. Rudin, D.T Wasan, Mechanisms for Lowering of Interfacial Tension in Alkali/Acidic Oil Systems: Effect of Added Surfactants, *American Chemical Society* 31 (1992) 1899-1906.

[24] S.H. Standal, A.M. Blokhus, J. Haavik, A. Skauge, T. Barth, Partition Coefficients and Interfacial Activity for Polar Components in Oil/Water Model Systems, *Colloid and Interface Science* 212 (1999) 33-41.

[25] K. Spildo, A.M. Blokhus, A. Andersson, Surface and Interfacial Properties of Octanoic Acid–Octylamine Mixtures in Isooctane–Water Systems: Influence of Acid:Amine Molar Ratio and Aqueous Phase Ph, *Colloid and Interface Science* 243 (2001) 483-490.

[26] P. Zhange, T. Austad, The Relative Effects of Acid Number and Temperature on Chalk Wettability, *Society of Petroleum Engineers* (2005) 1-7.

[27] X. Quan, H. Shunli, P. Wanfeng, The effects of temperature and acid number of crude oil on the wettability of acid volcanic reservoir rock from the Hailar Oilfield, *Petroleum Science* 7 (2010) 93-99.

[28] Ch. Xiong, F. Wei, W, Li, Mechanism of Polyacrylamide Hydrogel Instability on High-Temperature Conditions, *ACS Omega* 3 (2018) 10716–10724.

[29] K. Godwin Uranta, S. Rezaei Gomari, P. Russell, F. Hamad, Studying the Effectiveness of Polyacrylamide (PAM) Application in Hydrocarbon Reservoirs at Different Conditions, *Energies* 11 (2018) 1-17.

[30] N. Pal, M. Vajpayee, A. Mandal, Cationic/Nonionic Mixed Surfactants as Enhanced Oil Recovery Fluids: Influence of Mixed Micellization and Polymer Association on Interfacial, Rheology, and Rock-Wetting Characteristics, *Energy & Fuels* 33 (2019) 6048-6059.

[31] N. Pal, N. Kumar, A. Mandal, Stabilization of Dispersed Oil Droplets in Nanoemulsions by Synergistic Effect of the Gemini Surfactant, PHPA Polymer, and Silica Nanoparticle, Langmuir, *Langmuir* 35 (2019) 2655-2667.

[32] D. Al Husseini, Effects of Anions and Amino acids on Surface Tension of Water, *Senior Honors Projects* 2010-current 67. https://commons.lib.jmu.edu/honors201019/67

[33] A. Bertheussen, S. Simon, J. Sjöblom, Equilibrium partitioning of naphthenic acids and bases and their consequences on interfacial properties, *Colloids and Surfaces A 529* (2017) 45-56.

[34] A.M. Sayed, K.B Olesen, A.S. Alkahala, T.I Sølling, N. Alyafei, The effect of organic acids and salinity on the interfacial tension of n-decane/water systems, *Petroleum Science and Engineering* 173 (2019) 1047-1052.

[35] Z. Ye, F. Zhang, L. Han, P. Luo, J. Yang, H. Chan, The effect of temperature on the interfacial tension between crude oil and gemini surfactant solution, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 322 (2008) 138-141.

[36] S. Kumar, N. Saxena, A. Mandal, Synthesis and evaluation of physicochemical properties of anionic polymeric surfactant derived from Jatropha oil for application in enhanced oil recovery, Journal of Industrial and Engineering Chemistry 43 (2016) 106–116.

[37] S. Rezaei Gomari, K. Elyasi Gomari, M. Islam, D. Hughes, New Insight into the Influence of Rhamnolipid Bio-Surfactant on the Carbonate Rock/Water/Oil Interaction at Elevated Temperature, *resources* 7 (2018) 1-12.

[38] R. Saha, R.V.S. Uppaluri, P. Tiwari, Effects of interfacial tension, oil layer break time, emulsification and wettability alteration on oil recovery for carbonate reservoirs, *Colloids and Surfaces A* 559 (2018) 92-103.

[39] T. Okasha, Investigation of the effect of temperature and pressure on interfacial tension and wettability. *International Symposium of the Society of Core Analysts held in* Trondheim, Norway. (2018)

[40] A.Z. Abidina, T. Puspasaria, W.A. Nugrohoa, Polymers for Enhanced Oil Recovery Technology, *Procedia Chemistry* 4 (2012) 11-16.

[41] P. Das, S. Konale, R. Kothamasu, Effect of salt concentration on base-gel viscosity of different polymers used in stimulation fluid systems, *Society of Petroleum Engineers* (2014) 1-9.

[42] M. Sveistrup, F. Mastrigt, J. Norrman, F. Picchioni, K. Paso, Viability of Biopolymers for Enhanced Oil Recovery, *Dispersion Science and Technology* 37 (2016) 1160-1169.

[43] B. Xiong, R. Dettam Loss, D. Shields, Polyacrylamide degradation and its implications in environmental systems, *npj Clean Water* 17 (2018) 1-9.

[44] K. Godwin Uranta, S. Rezaei Gomari, P. Russell, F. Hamad, Application of polymer integration technique for enhancing polyacrylamide (PAM) performance in high temperature and high salinity reservoirs, *Heliyon* 5 (2019) 1-14.

[45] S.Z. Mahdavi, J. Aalaie, T. Miri, S.M.R. Razavi, M.R. Rahmani, Study of polyacrylamide-surfactant system on the water–oil interface properties and rheological properties for EOR, *Arabian Journal of Chemistry* 10 (2017) 1136-1146.

HIGHLIGHTS

- Impacts of acidic/basic species on physiochemical properties of polymeric solutions.
- Acidic species showed a greater impact on rheological properties of PAM and XG.
- The effectiveness of PAM on the reduction in IFT was much higher than XG.
- Temperature showed undesirable effect on rheological properties of PAM/XG over time.
- More reduction in viscosity observed with acidic species at elevated temperatures.