STUDY OF POLYMER-SURFACTANT INTERACTIONS FOR CHEMICAL ENHANCED OIL RECOVERY IN CARBONATE RESERVOIRS

BY

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A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

DECEMBER, 2013

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

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TO MY BELOVED PARENTS

MR. OMAR AL-AMODI

&

MS. SHEFA'A BATOOK

TO MY BELOVED BROTHERS & SISTERS

EMAD, ABEER, HUSSEIN, AMANI, ABDULLAH

& ABDULLAZIZ

ACKNOWLEDGMENTS

First, praise and thank to Allah “The God” for blessing my actions. Thanks to Allah for every success I achieved, for every gift I got and for every step I made. Without your will and mercifulness, this work will never complete.

I would like to thank my parents for their support, encouragement and kindness. Thanks to my brothers, sisters and every member of my family.

I would like to appreciate and thank my thesis advisor Dr. Usamah A. Al-Mubaiyedh for his total cooperation, help, encouragement and supervision during the research work. Appreciations and thanks to Prof. Ibnelwaleed Ali Hussein for all of his excellent cooperation and advices on every part of the research work. I would like also to thank Dr. Abdullah S. Sultan for his gentle cooperation and the unique help through the research work.

I like to express my thanks to Saudi ARAMCO for funding and supporting this research work under the project No. CPM-2297. I thank King Abdullaziz City Science and Technology (KACST) for funding Core Flooding equipment. Special appreciations to King Fahd University of Petroleum & Minerals (KFUPM) for providing me the opportunity to join their MS and BS programs

Thanks to the faculty and staff members of Chemical Engineering Department, Petroleum Engineering Department, Center of Petroleum & Minerals, Chemistry Department and Earth Sciences Department for their effort and cooperation.

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LIST OF ABBREVIATIONS

EOR	:	Enhanced Oil Recovery
CEOR	:	Chemical Enhanced Oil Recovery
SP	:	Surfactant-Polymer
CMC	:	Critical Micelle Concentration
IFT	:	Interfacial Tension
PAM	:	Polyacrylamide
HPAM	:	Hydrolyzed Polyacrylamide
FT-IR	:	Fourier Transform Infrared Spectroscopy
TGA	:	Thermogravimetric Analysis
UV-vis	:	Ultraviolet-visible Spectroscopy
IC	:	Ion Chromatography

ABSTRACT

Full Name : ADEL OMAR HUSSEIN AL-AMODI
Thesis Title : STUDY OF POLYMER-SURFACTANT INTERACTION FOR CHEMICAL ENHANCED OIL RECOVERY IN CARBONATE RESERVOIRS
Major Field : MASTER OF SCIENCE IN CHEMICAL ENGINEERING
Date of Degree : DECEMBER, 2013

The global demand for oil has increased while the number of newly discovered oil reservoirs has decreased. Only one third of the oil in the existing oil fields is economically recoverable with primary and secondary recovery methods. The objective of this work is to study and investigate the interactions between polymer and fluoro-surfactants for their use in enhanced oil recovery applications in carbonate reservoirs. The rheological properties of surfactant-polymer solutions are studied. Fluoro-surfactant FS-61 showed relatively small effect on both the viscosity and the elasticity of the polymer solution while surfactant FS-50 showed no effect. Salts caused major reduction in the polymer viscosity. Both fluoro-surfactants showed good thermal stability at temperature higher than 150°C during short and long period tests. Adsorption experiments showed that sulfate ions in brine have major adsorption on the precipitated calcium carbonate. Surfactant FS-50 showed low adsorption density. Fluoro-surfactants showed slightly high interfacial tension and ultralow IFT values were measured when co-surfactants were added. Phase behavior experiments showed the inability of fluoro-surfactants in forming microemulsions. Core flooding experiment was performed for one SP solution of 0.25 wt% HPAM and 0.1 wt% of FS-50 at 90°C. After brine flooding, oil recovery was 44% and it was improved to 86.5% after SP flooding.

ملخص الرسالة

الاسم الكامل: عادل عمر حسين العمودي

عنوان الرسالة: دراسة تأثير البوليمرات و خوافض التوتر السطحي على تعزيز إستخراج النفط

التخصص: هندسة كيميائية

تاريخ الدرجة العلمية: ديسيمبر 2013

يعتبر النفط المصدر الأساسي للطاقة حول العالم متفوقا بذالك على العديد من مصادر الطاقة الأخرى. تتبقى كميات هائلة من النفط بعد عمليات استخراج النفط الاولية حيث يصعب إستخراجها. تستخدم تقنيات متقدمة تساعد في إستخراج النفط المتبقي. احد هذه التقنيات تعرف بأستخلاص النفط المعزز بواسطة المواد الكيميائية كالبوليمرات و خوافض التوتر السطحي. تعمل البوليمرات على زيادة لزوجة الماء المستخدم في عمليات استخراج النفط بينما تعمل خوافض التوتر السطحي على خفض طاقة التوتر السطحي بين الماء و النفط. يهدف هذا البحث على دراسة خوافض التوتر السطحي الفلورية و بولي اكريل أمايد كمواد تساعد في تعزيز إستخراج النفط. تعتبر الخصائص الريولوجية و بالاخص لزوجة الماء المستخدم في استخراج النفط عامل مهم جدا حيث تم دراسة مدى تأثير كلا من درجة الملوحة و درجات الحرارة العالية و تركيز خوافض التوتر السطحي الفلورية على مدى لزوجة محلول البوليمر. تم كذالك دراسة مدى إستقرار خوافض التوتر السطحي الفلورية عند درجات الحرارة العالية حيث لوحظ إستقرارها عند درجات حرارة عالية تبلغ 150 درجة مئوية. يعتبر إستقرار الخوافض عند درجات حرارة عالية ملائما لأبار النفط بالمملكة العربية السعودية حيث تبلغ درجات الحرارة حوالي 120 درجة مئوية. احد العوامل المهمة عند استخدام المواد الكيميائية في عمليات إستخراج النفط هو مدى إمتزاز أو إدمصاص هذة المواد و عدم القدرة على إعادة إستخدامها من جديد. لوحظ عند دراسة إمتزاز خوافض التوتر السطحي الفلورية على رواسب كربونات الكالسيوم أن إمتزازها يتم بشكل منخفض حيث تعتبر هذه الخاصية ملائمة في عمليات إستخراج النفط. تم كذلك قياس التوتر السطحي بين محاليل خوافض التوتر السطحي الفلورية و النفط و مدى تاثير درجة الملوحة و تركيز الخوافض و درجة الحرارة و الخوافض المساعدة على كفاءة الخوافض الفلورية. حيث لوحظ ان الخوافض الفلورية تعمل على خفض طاقة التوتر الى قيم منخفضة جدا عند وجود خوافض مساعدة لها. لدراسة مدى كفاءة محلول البوليمر و خافض التوتر السحي الفلورية تم تطبيق تجربة إستخراج النفط من تكوين الكربونات بواسطة محلول مائي ذو ملوحة عالية و اتباعه بمحلول البوليمر و خافض التوتر السطحي الفلوري ذو درجة ملوحة مطابقة. بعد استخدام الماء ذو الملوحة العالية وجد أن كفاءة استخراج النفط زادت إلى 44 % بينما ارتفعت كفاءة إستخراج النفط إلى 86.5 % بعد إستخدام محلول البوليمر و خافض التوتر الفلوري.

CHAPTER 1

INTRODUCTION

Enhanced oil recovery (EOR) is a technique where external sources of energy or materials are injected in oil reservoir to recover residual oil. The primary production is simply the use of the natural reservoir pressure. The reservoir will start draining the oil as the reservoir pressure decreases with time. Secondary methods are the injection of gas or water to repressurize the reservoir. The injected gas is natural gas which is released from the same reservoir. After primary and secondary methods, large amount of residual oil still in place and new techniques are performed to recover that oil. The remaining 70% of the oil in place is considered as a difficult target for oil industry (Hirasaki et al. 2008). The low prices of oil during 1980s, limited the development of new techniques that can improve the overall oil recovery especially chemical enhanced oil recovery (cEOR) which showed notable cost. Nowadays, oil prices have shown major increase that leads to more interest in new efficient technologies for mature oil fields.

1.1 Enhanced Oil Recovery (EOR) Techniques

EOR is mainly classified into three main methods; namely, thermal, chemical and gas methods (Manrique et al. 2010). Thermal methods help by reducing the oil viscosity by increasing the reservoir temperature and it is used widely for the production of heavy oil in sandstone reservoirs. Temperature is raised through three main mechanisms. They are mainly steam cycling, steam drive and combustion. Steam cycling is the injection of steam in the reservoir for weeks and it is followed by shutting down the reservoir. The production starts usually after a week. Raising the reservoir temperature will reduce the oil viscosity and will ease its flow to the production well. The cycle is then repeated. Steam drive process is similar to water flooding where steam is injected into the injection wells while the oil is produced in the production wells. In situ combustion is a process where air is injected after igniting oil in the reservoir. Most of thermal EOR methods are adopted in Canada, Russia, Venezuela, China and United States. However, it is not applicable for the production of deep oil reservoirs. Other problems in thermal methods are loss of heat to oil poor zones in the reservoir and low sweep efficiency of the injected steam. Also, corrosion of pipes is an operation problem associated with thermal methods. Gas EOR methods are used for light, condensate and volatile oil reservoirs (Manrique et al. 2010). It includes the injection of N_2, hydrocarbon gases and CO_2. Carbon dioxide injection is considered as the mostly used method among other gases injections but it is limited due to the availability of CO_2.

1.2 Chemical Enhanced Oil Recovery (cEOR)

Chemical enhanced oil recovery (cEOR) methods are widely used in sandstone reservoirs with polymer injection as the most popular method. cEOR methods are considered promising for sandstone reservoirs during the 1980s, however, the low oil prices and the high cost of chemicals prevented or limited its use. cEOR includes the injection of polymer, surfactant-polymer and alkali-surfactant-polymer. Polymers have large molecular weight and when they are added to the injected water, they increase the solution viscosity. Increasing the viscosity of the injected fluid will improve mobility ratio and will increase the sweep efficiency. The high viscosity of the injected water will displace oil to the production wells. Surfactants are surface active agents and they can lower the interfacial energy between two immiscible phases. They have a hydrophobic tail and a hydrophilic head. They are classified according to their dissociation in water to anionic surfactants, cationic surfactant, nonionic surfactants and zwitterionic surfactants. Surfactants can reduce interfacial tension between oil and water to 10^{-3} dyn/cm. Surfactants concentration is in the range of 0.1 wt% to 5 wt%. The reduction in interfacial tension will allow more displacement of the trapped oil in the rocks pores. Increasing surfactants concentration above their critical micelles concentration (CMC), micelles will start to form and they can form different shapes. Spherical micelles have size of 10^{-6} to 10^{-4} mm.

Polymer and some surfactants have viscoelastic properties. The word viscoelastic refers to those viscous fluids that have elastic properties so they return to their original form when the applied stress is removed. The addition of viscoelastic surfactants (VES) to fluids leads to an increase in the viscosity due to the formation of worm like micelles that entangle to form structure with higher viscosity. Also, when these VES are added, they reduce the recovery time. Alkaline materials are injected in reservoir to react with acid oil and form surfactants which will lower the interfacial tension. Sodium hydroxide, sodium carbonate and ammonium hydroxide are examples of alkaline injection in cEOR. The main problem in applying cEOR is chemicals limitation. Both high temperature and high salinity will lower the chemicals stability. Additional problems are mixing the chemicals with water, plugging the reservoir formation with polymers and chemicals lost due to adsorption or degradation. Lots of projects were conducted with cEOR for sandstone formations. Half of the world's oil fields are carbonate reservoirs (Seethepalli et al. 2004). Most of the reservoirs in the Kingdom of Saudi Arabia are carbonate reservoirs with light oil production. Carbonate formation reservoirs show difficulty for EOR applications. This difficulty is due to the nature of these reservoirs which includes low porosity, low permeability, fracturing and heterogeneity.

Several cEOR methods were applied for carbonate reservoirs in the United States (Manrique et al. 2010). In China, the recovery in Bohai Bay was about 13.5% with water flooding. Polymer flooding was started by the China National Offshore Oil Company and water cut was reduced from 95% to 54% with increase of 157,250 bbl for oil. The reservoir has temperature of 65^{o}C with depth equal to 1600 m (Gao 2011). In Oman, polymer flooding was used in the Marmul Field where the recovery was about 12% after water flooding. The reservoir has temperature of 46^{o}C and depth of 2,000 ft. It has oil with viscosity of 110 cP. Polyacrylamide (PAM) solution was injected with concentration of 1,000 ppm. The injection flow rate was 3,145 bbl/day. The polymer solution has a viscosity of 15 cP at 46^{o}C before injection. The recovery increased to be 46% after polymer flooding (Gao 2011). In Turkey, Bati Raman has 1.5% initial recovery and it was increased to 5% after CO_2 flooding. Polymer injection was started to enhance sweep efficiency and an increased production in 16 production wells was observed after three months. Polymer injection cost was estimated to be around 445,000 USD (Gao 2011). In Canada, East Bodo reservoir has oil with high viscosity which is in the range of 600 cP to 2,000 cP. Polymer injection was started with 10 cP viscosity of the polymer solution. The polymer concentration was 1,500 ppm. The injection flow rate was 1258 bbl/day. The wellhead pressure was about 870 psi (Gao 2011). In Suriname, the Tambaredjo reservoir has sandstone formation with depth of 1,270 ft. Oil viscosity is 400 cP with reservoir temperature of $36^{o}C$. Polymer solution was injected with concentration of 1,000 ppm. The polymer solution viscosity was about 60 cP and injection flow rate was 200 bbl/day. About 40% viscosity lost was observed in the polymer solution before reaching the formation rocks (Gao 2011).

1.3 Fluoro-Surfactants

Fluoro-surfactants are similar to hydrocarbon surfactants but they include the presence of fluorine atoms. Fluorine atoms replace part of the hydrogen atoms or the entire hydrogen atoms on the hydrophobic tail of the surfactant structure. Fluorine atom has higher electronegativity and larger volume compared to hydrogen atom. The carbon-fluorine bond is considered as very stable bond which is the reason for fluoro-surfactant to be thermally and chemically stable. Fluorine atoms also shield the carbon atom and because of their larger volume, the fluorine atoms prevent any carbon-carbon rotation. As a result, the tail of the fluoro-surfactants tends to form linear arrangements with minimum curvature. The presence of fluorine atoms on the hydrocarbon tail of the surfactants reduces the hydrophobicity of the tail due to the larger volume of fluorine atoms compared to hydrogen atoms which prevents or minimizes the interactions between the hydrocarbon tail and the oil phase. Fluoro-surfactants are considered more effective surface agents compared with hydrocarbon surfactants. Only small concentration can reduce the surface tension. Fluor-surfactants are also more chemically stable and they are applicable at high temperatures and pH. There was no deep investigation regarding fluoro-surfactants application for EOR. A study by Murphy and Hewet (2008) showed the potential of fluoro-surfactants for EOR. Nonionic fluoro-surfactants showed oil recovery between 10% and 87% while hydrocarbon surfactants showed only oil recovery between 8% and 52%. Cationic fluoro-surfactants can improve the stability of foaming when they are combined with cationic hydrocarbon surfactants. In thermal EOR, nonionic or anionic fluoro-surfactants can help when they condense in the steam phase and lower the surface tension at pH lower than 11. In the case of foam injection in EOR, fluoro-surfactants can form stable foams. Betaine fluoro-surfactants are able to form stable foam. Also, the addition of betaine fluoro-surfactants to both anionic and amphoteric hydrocarbon foaming enhances its stability. In sandstone formation, core tests showed that the treatment of silica (500 micron diameter glass balls) with fluoro-surfactants improved oil recovery compared to nitrogen gas purging and sodium benzene sulfonate foam. Lower pressure drop and more brine removal across the formation structure were observed which is due to the reduction in the capillary pressure in the small pores. These fluoro-surfactants also reduced water blocking in the pores. Pore blocking will lower the formation permeability and oil recovery will decrease.

1.4 Research Objectives

In this work, surfactant-polymer solutions (SP) are studied for EOR applications. Different tests were performed on SP formulations to investigate their potential in EOR. Rheology tests were performed to examine the influence of different parameters on the polymer viscosity. Thermally stability tests are performed to study the potential and the stability of fluoro-surfactants for high temperature reservoirs. Adsorption experiments of surfactant FS-50 in carbonate formation were conducted. Interfacial tension measurements for both fluoro-surfactants were performed. The ability of fluoro-surfactants in forming microemulations was tested in phase behavior experiments. Core flooding test was performed on selected SP formulation at high temperature and pressure. The objectives are as follow:

1. Study the rheological properties of polymer and polymer-surfactant solutions.
2. Study the effect of salinity, temperature, shear and surfactant concentration on the rheological properties.
3. Measure the interfacial tension IFT between surfactant solutions and oil where the effect of several parameters on IFT such as salinity, temperature, time and co-surfactants are tested.
4. Study the adsorption of surfactant FS-50 and ions in carbonate reservoirs.
5. Study the influence of the presence of oil and temperature on the adsorption of surfactant FS-50 and ions in carbonate formations.
6. Study the thermal stability of polymer and surfactants for short and long periods.
7. Study the phase behavior for fluoro-surfactants and determine the phase change.
8. Achieve the best SP formulation which has the ability to improve sweep efficiency and lower IFT between oil and SP solution.
9. Perform core flooding experiment using one selected SP system in carbonate formation and measure oil recovery percent.

CHAPTER 2

LITERATURE REVIEW

This chapter will discuss several concepts related to chemical enhanced oil recovery (cEOR). These concepts will give clear understanding on different difficulties in cEOR. Chemicals are injected in oil reservoir. Oil reservoirs have different environment and conditions compared to surface conditions. Reservoir conditions will cause several changes on the fluid properties. Rheological properties of the injected fluid will be affected by temperature, salinity and shear. Reuse of injected fluids will be affected by adsorption in the reservoir. Interfacial tension between oil and the injected fluid will be affected by surfactants, temperature and salinity. High temperature in oil reservoirs can cause thermal degradation to chemicals. All of these concepts must be investigated to test chemical EOR potential in actual fields.

2.1 Carbonate reservoirs

Carbonate reservoirs show low porosity and permeability and they are sometimes fractured. These properties cause lower oil recovery compared to sandstone reservoirs. Certain EOR methods show their ability to improve oil recovery from carbonate reservoirs. Based on a total of 1,507 projects, both gas and chemical EOR showed their ability for enhanced oil recovery in carbonate reservoirs while both thermal and chemical EOR in sandstone reservoirs as Figure (2.1) shows, Alvarado and Manrique (2010). Although carbonate reservoirs represents lower percentage compared to sandstone reservoirs, about 60% of the global oil is in carbonate reservoirs, Tabary et al. (2009). Chemical EOR includes mainly the injection of polymer with about 290 filed projects in literature. Most of these polymers are water soluble polyacrylamides (PAM) and xthan gum. However, for the case of carbonate reservoirs, most of the literature showed the injection of polyacrylamides. Chemical enhanced oil recovery is promising technique especially if they can be used with lower concentration to overcome the economic reasons. One example of carbonate fields where cEOR was used is the Eliasvilla field in the US. The Eliasvilla field has a depth of 40 ft. In 1980, polymer flooding was started using hydrolyzed polyacrylamide (HPAM) to raise the viscosity of the flooding water. Injection period lasted 34 months with polymer viscosity reduction from 40 cP to 5 cP at the end of the injection process. The oil production showed an improvement from 375 BOPD “Barrels of Oil Per day” to 1,622 BOPD.

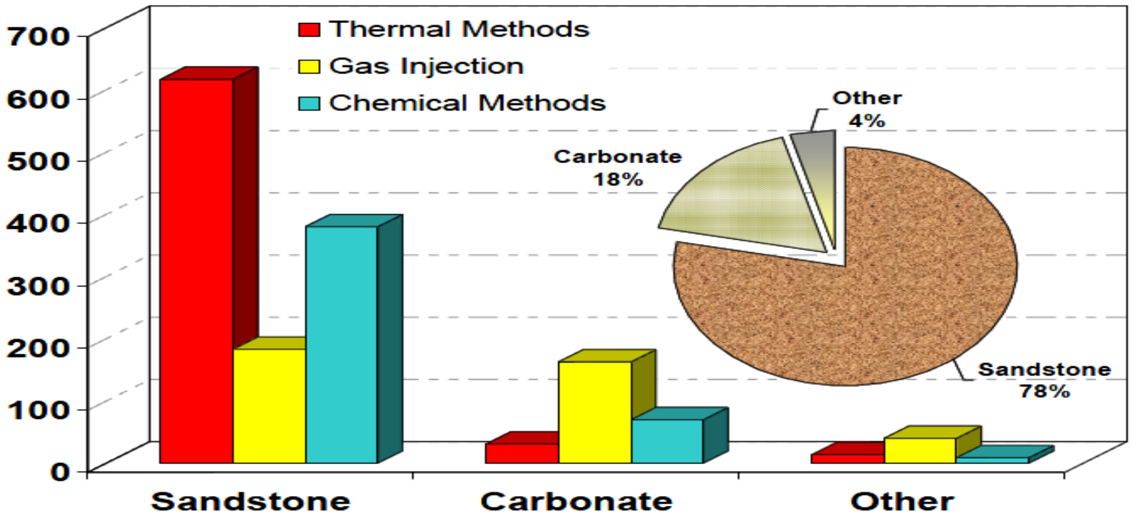


Figure 2. 1: EOR methods for both carbonate and sandstone reservoirs (Alvarado and Manrique, 2010).

2.2 Rheology of Surfactants and Polymers in EOR

Studying the rheological properties of surfactant-polymer solutions for EOR is very critical issue. It is mainly the measuring of the solution viscosity and elasticity at reservoir conditions. Since polymer is added to increase the injected fluid viscosity, it is very important to ensure that solution viscosity still high compared to sea water. Several parameters can lead to reduction in the solution viscosity and they need to be investigated. These parameters include reservoir temperature, brine solution salinity, surfactant concentration and shear due to injection. The reservoir average shear rate is 10 s^{-1} (Da Silva et al. 2010).

Bataweel et al. (2012) studied the rheological properties of surfactant-polymer and alkali-surfactant-polymer solutions for EOR applications. The effect of salts type and concentration, temperature, and surfactant type and concentration on the polymer solution was investigated. Two types of polymers were used; namely, HPAM with molecular weight of 18 million and a copolymer of acrylamide and 2-acrylamido 2-methy propane sulfate (AMPS) with molecular weight of 6 million. Three types of surfactants were used with two betaine-based amphoteric surfactants and an anionic surfactant of Alpha-olefin sulfonate. The effect of adding surfactant was tested at 6 wt% NaCl concentration. Amphoteric surfactant (SS-885) was added at different concentrations (0.1, 0.3, 1 and 3 wt%). It was observed that the solution viscosity increased with increasing the surfactant concentrations. The effect of adding brine was tested with a solution of 3,000 ppm HPAM concentration and 0.3 wt% amphoteric surfactant concentration. The brine salinity was varied by increasing NaCl concentration. The solution viscosity drops with increasing the salinity of the brine which is due to the charge shielding mechanism. The positive charge of the cations shielded the negative charges on HPAM chains. As a result, the polymer chains collapsed and viscosity decreased. The effect of cation type was also examined where different cations were added to a solution of 3,000 ppm HPAM concentration. The solutions were prepared in deionized water, 0.1 wt% $CaCl_2$ and 1 wt% NaCl. A shear thinning behavior was observed for the 0.1 wt% $CaCl_2$ solution along most of the shear rate range. However, for the case of 1 wt% NaCl, it showed lower shear thinning behavior. The effect of amphoteric surfactant was tested for solutions prepared with deionized water, 1 wt% and 6 wt% NaCl. For the case of deionized water, it was observed that there is no change in the solution viscosity when surfactant concentration was increased. When NaCl was added to the polymeric solution, an increase in viscosity was observed when surfactant concentration was increased. To examine the effect of the surfactant type on AMPS polymer solution, two different surfactants were used. The amphoteric surfactant showed no change in the solution viscosity. However, for the case of the anionic surfactant, solution viscosity decreased. Viscoelastic properties were examined at a strain value of 50 % which is in the linear region of viscoelastic behavior. The effect of seawater on the viscoelastic properties was examined and it was noticed that both elastic modulus and viscous modulus were reduced. The effect of the polymer type was also tested on the viscoelastic properties of the SP solution and it was observed that HPAM has higher viscoelastic properties compared to AMPS.

Han et al. (2012) studied the injectivity of sulfonated polymer solutions in carbonate reservoir rocks under reservoir conditions. Both resistance factor and residual resistance were obtained. The resistance factor is a measure of the mobility reduction during polymer propagation while residual resistance represents a measure of the permeability reduction after polymer treatment. In their experiments, seawater was used with total dissolved solids of 57,670 ppm. The solution has a viscosity of 0.28 mPa.s and density of 1.0099 g/cc at 100°C. The polymer is sulfonated polyacrylamides which is a copolymer of acrylamide and acrylamido tert-butyl sulfonate. It has a molecular weight of 12 million g/mole. The viscosity measurements were obtained for shear rates in the range of 0.001 s^{-1} to 3,000 s^{-1} at high temperature and pressure. Core flooding tests were applied with four core plugs with a plug diameter range of 3.7 to 3.8 cm and length range of 3.9 to 4.6 cm. Polyacrylamides polymer in water shows different viscosity shear relationships. It has a Newtonian behavior at low shear rate followed by a power law behavior at high shear rate and finally a shear thickening at higher values. The viscosity of the polymer solution as a function of shear rates was shown at a temperature of 98°C for different polymer concentrations. It was observed that the relaxation times at which critical shear rates were observed are 0.025 and 0.067 seconds for polymer concentrations of 0.2 and 0.5 wt% respectively. For polymer concentration of 0.1 wt%, critical shear rate was not observed. When the shear rate was increased further, the viscosity showed a decreasing behavior similar to a power law model. Finally, shear thickening was observed at higher shear rates. The Newtonian viscosity as a function of polymer concentration was also obtained. It was observed that the concentration at which there is sharp increase in viscosity is about 0.09 wt% while all polymer concentrations that were prepared in their work were above this critical concentration.

Talwar et al. (2008) studied the effect of binary surfactant mixtures on the rheology of associative polymer solutions. The association polymer is hydrophobically modified alkali-soluble emulsion polymer (HASE). This kind of polymer is considered as hydrophilic polymer that has hydrophobic groups which have multiple uses in EOR. Adding surfactants has an influence on the rheological properties of HASE which may lead to increase in the solution viscosity. The first surfactant that was examined is nonylphenol polyethoxylate (NPe) which is nonionic surfactant where (e) is the length of the hydrophilic ethoxylate chain (e=6, 8, 12 and 15). In the case of adding NP8, NP12 and NP15, the solution showed a maximum in zero shear viscosity as function of surfactant concentration. However, in the case of NP6, viscosity showed continuous increasing behavior as function of surfactant concentration. The reason is that NP8, NP12 and NP15 form micelles which circulate the hydrophobes groups of the polymer and reduce the polymer viscosity. Mixtures of surfactants were also tested to maintain the effect of binary surfactants on the solution properties. All samples were tested at pH=9 and temperature of 25^{o}C. Also, a pre shearing was applied with shear of 5 s^{-1} for 180 seconds to clear structure history. A mixture of NP4 and NP12 combined with 0.5 wt % HASE was tested and compared with NP8 so the two solutions have similar EO chain length. It was observed that the mixture had similar viscosity behavior to NP8. It showed a maximum in viscosity and then it followed by a decrease as concentration was increased. However, the NP4-NP12 solution had the maximum at higher surfactant concentration. Another observation noticed after the maximum value, the mixture showed higher viscosity compared to NP8 by an order of magnitude while they showed similar trends at low surfactant concentration. Dynamic tests were also applied on the samples where storage and loss moduli were plotted as function of angular frequency. From the plot, both G_{∞} and T_r were found. T_r represents longest relaxation time and it is the inverse of the frequency at the intersection of $G^{'}$ and $G^{''}$ curves. It provides the lifetime of the hydrophobic junctions. G_{∞} is considered as $G^{'}$ at high frequency (25 rad/s) and it represents the density of hydrophobic junctions. It was observed that the two solutions had similar behavior regarding G_{∞} across different surfactant concentration while NP4-NP12 showed higher T_r than NP8 at high surfactant concentrations. Also, it was noticed that the intersection for the mixture happens at lower frequency compared to the NP8 solution. It means higher life time for the mixture. It showed that the hydrophobic junctions are connected and held tighter for the case of the surfactant mixture leading to stronger viscoelastic response while NP8 solution showed lower response. Also, this result was confirmed using Arrhenius plot to calculate the activation energy which was higher in the case of the mixture. Another surfactant mixture combination (NP6 and NP12) was tested at different surfactant ratios. Low shear viscosity was obtained as function of surfactant concentration for different NP6:NP12 molar ratios (1:0, 6:1, 3:1, 2:1, 1:1, 0:1) in 0.5 wt% polymer solution. It was observed that the viscosity increase with raising the NP6 content in the mixture. NP12 solution showed an increase in the viscosity to a maximum. This behavior was also noticed for surfactant concentrations (3:1, 2:1, 1:1). However, for NP6 solution, the viscosity increased without reaching a maximum and the same happened for the (6:1) mixture. Dynamic test showed that G_{∞} and T_r also increased with increasing the NP6 content. It was explained that adding NP6 surfactant to the solution will lead to transfer of the micelles from the spherical shape to the cylindrical shape which exhibit higher network junction life.

Mandal et al. (2008) studied different conditions of alkali, surfactant and polymer to produce optimum formulations in particular, the desirable rheological properties and interfacial tension for EOR. They studied the effect of salts, alkali and surfactant on the polymer solution. Also, the reduction in surface tension was studied for different surfactant and alkali concentrations. Polyacrylamide was used as polymer for increasing sweep efficiency and Sodium hydroxide was used as alkali which helps by altering the rock wettability to water-wet and reacting with acids to produce in situ surfactants. Surfactants that were used include two anionic surfactants; namely, Sodium Dodecyl Sulfate (SDS) and Sodium dodecylbenzene sulfonate (SDBS). Different concentrations of polymer, surfactant and alkali were prepared for rheological and surface tension studies. The stirring process was made with low agitation speed to avoid mechanical degradation for 8 to 10 hours. Rheological properties were obtained using Brookfield cone and plate viscometer while surface tension was studied using the ring method of Auto tensiometer with platinum ring. NaCl and Na_2CO_3 were used as salts. It was observed that the apparent viscosity of all solutions decreased with increasing the shear rate which is a result of the alignment of polymer chains. The viscosity-shear relation followed a power law model at low shear rates. At higher shear rate, shear thinning behavior was observed. The solution viscosity showed a reduction as temperature was increased. Also, a reduction was observed in the solutions viscosity as the sodium chloride concentration was increased. This reduction in solution viscosity is due to the reduction in the repulsion forces within the polymer chains. It is known that polyacrylamide chains stretch in deionized water due to the repulsive forces between the negative charges within the polymer chains. As a result of increasing salt concentration, the hydraulic radius of the polymer chain will decrease. The viscosity behavior was also compared with the addition of calcium chloride. The calcium ions have higher positive charge compared to the sodium ions which leads to lower viscosity. Adding alkali to the polymer solution affects the solution viscosity in two ways. One way is that alkali provides positive ions into the solution which reduce the viscosity by shielding the negative charge on the polymer chains. The other way is that the alkali can hydrolyze the amide group which leads to an increase in the viscosity. The solution viscosity was measured at different alkali concentration to examine the effect of alkali on the rheological properties. The viscosity shear relation was obtained at different sodium hydroxide and sodium carbonate concentrations. It was observed with sodium hydroxide that as the time increased after mixing, the solution viscosity increased. This can be explained due to the hydrolysis of polyacrylamide in the presence of strong alkali which leads to more carboxylate groups that have negative charges. More carboxylate groups will increase the negative charge and the hydraulic radius. As a result, higher viscosity of polyacrylamide solution in deionized water was observed. The effect of adding surfactant SDS was tested and it was observed that as the surfactant concentration increased, the viscosity was reduced. It was a result of charge shielding mechanism. Further investigation was obtained on the effect of adding both surfactant and alkali together on the solution viscosity. For a solution of 0.5 % SDS and 5,000 ppm polymer solution, the viscosity decreased with increasing sodium hydroxide concentration.

Kjoniksen et al. (2008) tested modified polysaccharides for the use in EOR. Three types were used which are commercial hydroxyethylcellulose (HEC) “ nonionic hydrophilic polysaccharide”, synthesized and modified hydrophobically HEC (HM-HEC) and an anionic sample of (HM-HEC(-)). The rheological properties of each polymer were examined by applying steady shear experiments in the presence of anionic surfactants sodium dodecyl sulfate (SDS) or hydroxypropyl-β-cyclodextrin (HP-β-CD). Enhancement in viscosity was observed for the synthesized HM-HEC(-) as the concentration increased compared with commercial HEC. Also, HM-HEC(-) showed shear thickening at medium shear rates followed by shear thinning at higher shear rates. This thickening behavior is due to chain alignments while the thinning behavior is due breaking of network structure. The zero shear rate viscosity (η_o) was also measured for the three polymer solutions at different polymer concentrations. HM-HEC(-) showed major viscosity enhancement even for low concentrations. Polymer solution with concentration of 0.5 %, HM-HEC(-) showed higher zero shear rate viscosity than both HEC and HM-HEC solutions. The reason for that is the effect of the electrostatic forces. These forces increase the volume of the network and increase the solution viscosity. The effect of adding surfactants SDS and HP-β-CD was examined on the polymer solution of HM-HEC(-) with concentration of 0.2 wt% at different temperatures. In the case of SDS, there was a maximum in viscosity and then it followed by relative viscosity reduction as function of surfactant concentration. The maximum viscosity value decreased with increasing solution temperature. Viscosity maximums were tested with surfactant concentration of 2 mmolal. The maximum value for viscosity was related to the forming of cross links between the polymer and SDS. In the case of adding HP-β-CD, the solution viscosity decreased as surfactant concentration was increased.

Seright et al. (2011) investigated a new polymer for the use in EOR and compared it with commercial HPAM. The polymer is hydrophobic associated polymer “an anionic-polyacrylamide-based tetra-polymer”. It has molecular weight of 12-17 million g/mol and 15-25 mol% anionic content including sulfonic monomer. The comparison was made with commercial HPAM with molecular weight 18-20 million g/mol and 35-40 mol% anionic content. Both polymers were examined in brine with 2.52% total dissolved solids (TDS). The rheological behavior of both polymers was tested. For different polymers concentrations, the viscosity was plotted versus shear rate and both polymers showed similar results. Also, elastic modulus, loss modulus and complex viscosity were plotted. The associated polymer (AP) had similar rheological behavior with commercial HPAM. It was also shown that both polymers do not cause any face plugging in cores with multiple sections in both Berea sandstones and porous polyethylene. The results of core flooding for both polymers were close. There was 0-8 % viscosity loss when they were subjected to pressure gradient of 235 psi/ft. However, for a pressure gradient of 2,500 psi/ft, the associated polymer showed 19-35 % viscosity loss whereas HPAM showed 5-17 %.

Veerabhadreppa et al. (2011) studied the rheological behavior of HPAM and polyoxyethylene (PEO) for application in EOR. Different grades of HPAM were selected that have the same shear viscosity but different elastic properties. HAPM-1, HPAM-2, HPAM-3 and HPAM-4 have the same molecular weight. HPAM-4 has the highest polydispersity index while HPAM-1 has the lowest. HPAM-5 and HPAM-6 have higher molecular weight with HPAM-6 having the highest polydispersity index compared to HPAM-5. A plot of viscosity versus shear rate for HPAM-1 to HPAM-4 was plotted. The viscosities of the samples were similar to each other. For the frequency sweep test, the four samples HPAM-1 to HPAM-4 were subjected to the same shear stress with frequency range from 0.01 Hz to 1 Hz. The viscose modulus was the same for all polymer samples; whereas, the elastic modulus was different for the different samples with HPAM-4 having the highest elasticity.

Wu et al. (2012) introduced new classes of improved polymers that showed better properties under high temperature and high salinity conditions. Polyacrylamide loses its viscosity due to two main reasons. It loses its molecular weight by hydrolysis and mechanical degradation in the injection process. Also, the interactions with other ions lead to the change in macromolecular conformation. So, polymers should stand well under high salinity where ions can interact with the injected polymer. The polymers used in their study were prepared by the polymerization of acrylamide with one or more monomers such as sodium 2-acrylamido-2-ethyl sulfonate (Na-AMPS), N-vinyl pyrrolidone (N-VP), sodium 3-acrylamide 3-methyl butyrate (Na-AMP) and N-vinyl amide (N-VAM). The brine has two values of total dissolved solids. They are 34,655 ppm which is low value and the other is 180,000 ppm which is considered as high TDS value. The polymers viscosity were plotted versus aging time at two temperature (90^oC and 120^oC) in both low and high TDS. It was observed that polymer A has a stable structure when tested for 180 days. Also, the change was relatively low for other samples but they showed lower viscosity values. At higher salinity, it was observed a reduction in the polymer viscosity for all samples. Polymer A showed the highest viscosity. The increase of temperature leads to reduction in the stability of the polymer solutions.

Siggel et al. (2012) studied a new class of viscoelastic surfactants for EOR. Triphenoxymethane (TPM) showed viscoelastic behavior at low concentration (lower than 1 wt%). Dynamic experiments were applied with small amplitude. The time sweep was started immediately at constant angular frequency of ω=10 rad/sec and constant strain amplitude of γ=100%. It was observed for 0.1 wt% solution of TPM, the complex viscosity increased to reach a steady value of 12.7 mPa.sec after two hours. Within a period of 30 minutes, the loss modules was dominant leading to viscose behavior while after 30 minutes, there was a crossover and loss modules was no longer dominant and the elastic behavior will response to the deformation. Frequency sweep test was performed to observe the effect of time on both viscose and elastic properties. It was observed that both storage and loss moduli have a slop of about 0.5 while the slop of complex viscosity is -0.5. This behavior is related to partially cross linked temporary structures.

2.3 Interfacial Tension and Wettability Alteration in EOR

Surfactants are injected in oil reservoir to lower interfacial tension between the injected fluid and oil. Low IFT values will enhance oil recovery. Several parameters have influence on surfactant functionality. Higher temperature can cause surfactant degradation. Co-surfactants, salts and alkali are also used to help lowering IFT. Polymer concentration can also have influence on IFT. In general, IFT changes significantly with surfactant concentration before critical micelle concentrations (CMC). After reaching CMC, surfactants start to form micelles and IFT remains constant. Surfactants can also change the reservoir wettability. Oil-wet reservoirs have low permeability to oil and high permeability to brine solution. Surfactants can change the reservoirs wettability to water-wet where oil permeability is increased.

Mandal et al. (2008) studied also surface tension for their surfactants. As surfactant concentration was increased, the surface tension decreased until it reached a plateau at surfactant concentration of 0.1 %. Surfactant SDBS showed lower values compared to surfactant SDS. The influence of adding polymer with different concentration was tested with surfactant SDS. It was observed that the presence of polyacrylamide increase surface tension of the surfactant solution. The same influence was observed when polyacrylamide was added to SDBS surfactant solution. The influence of alkali on surface tension was studied. NaOH was used as alkali in SDS solution and SDS-polyacrylamide solution. Surface tension reached minimum and then increased as alkali concentration was increased in the surfactant solution. The lower surface tension values were obtained at surfactant concentration of 0.1 %. Polymer influence was tested with surfactant concentration of 0.1 % and it showed negligible effect on surface tension as NaOH concentration was increased.

Wang et al. (2010) optimized surfactant interfacial tension and polymer viscosity in EOR. Two surfactants were tested which are DEA and Petroleum Sulfonate (PS). HPAM with molecular weight of 18 million Dalton was used. All IFT experiments were performed at 30^{o}C using spinning drop tensiometer. Several surfactant and polymer combinations were tested. Surfactant PS with concentration of 200 mg/L showed IFT value around 4 mN/m with different polymer concentrations. As surfactant concentration was increased to 1,000 mg/L, IFT decreased to about 0.2 mN/m with different polymer concentrations. Surfactant DEA with concentration of 3,000 mg/L lowered IFT to 0.018 mN/m with different polymer concentrations. Ultralow IFT value was observed with solution of 1,000 mg/L of PS and 2,000 mg/L of DEA. Polymer concentration showed again no influence on IFT values. Concentration of 4,000 mg/L of PS and DEA showed also ultralow IFT results. In general, HPAM showed negligible effect on IFT.

Sharma et al. (2011) studied changing the wettability for non-fractured carbonate reservoir from mixed-wet to water-wet at high temperature and salinity (temperature of 100^{o}C and salinity of 50,000 ppm). They used three types of surfactants with concentration less than 0.2 wt%. Contact angle experiments were applied to these surfactants as well as core flooding experiments. Also, dual surfactants were tested where an improvement in oil recovery was observed. Carbonate reservoirs are normally mixed-wet. For water-wet reservoirs, the oil permeability is high while it is low for water. This will delay water breakthrough. The wettability can alternate through two mechanisms. The first mechanism is due to the change in the brine ionic composition. The second mechanism is through surfactants that lead to altering the wettability of the rocks. In their work, they used different commercial non-ionic surfactants with cloud point above 100^{o}C. Non-ionic surfactant include the homologous series of NP ethoxylates, the homologous series of 15-S-ethoxylates and TDA 30EO. Also, two anionic surfactants which are ethoxylated sulfonates AV-70 and AV-150 were used. Cationic surfactants are CTAB, DTAB, Arquad C-50 and Arquad T-50. Brine contains 150.6 g of NaCl, 70 g $CaCl_2.2H_2O$, 20.6 g $MgCl_2.6H_2O$ and 0.5 g Na_2SO_4. For aqueous stability test of non-ionic surfactants, the surfactants have the form R-EO$_x$ where R is hydrocarbon chain and is attached to multiple of different EO (ethoxy group). These surfactants have cloud point. Cloud point is defined as a temperature above which they do not give a clear solution in brine and it is a function of the surfactant molecular structure and the brine ionic composition. In this test, the surfactants are mixed with deionized water and brine. It was observed that the cloud point increased with increasing the number of the ethoxy group until finally it reached a constant value. However, as salinity was increased, the cloud point decreased due to the presence of electrolytes in the solution. For the case of anionic surfactants, they contain hydrocarbon chain and sulfates groups. These sulfates groups show hydrolysis at high temperature. Cationic surfactants were tested which are ammonium salts of hydrocarbon chain. Surfactant solutions were tested for their interfacial tension when injected with brine. They have concentration of 0.2 wt% with oil to brine ratio of about 100 at temperature of 25^{o}C. The lowest IFT was 0.4 dynes/cm with surfactant NP-10 while the highest IFT was 10.9 dynes/cm with surfactant NP-70. Dual systems of anionic or cationic surfactant to aqueous solution of non-ionic surfactants were also tested and their IFT were between 1 dynes/cm and 5 dynes/cm. The addition leads to an increase in the cloud point of the non-ionic surfactant. The dual systems showed cloud point above 100^{o}C. Contact angle measurements were performed for the surfactant to alter rocks wettability. In the case of the non-ionic surfactant, the experiments were applied at 80^{o}C with surfactant concentration of 0.2 wt%. It was observed that the wettability alteration decreased as the number of the EO groups increased for the homologous series of NP-ethoxylate. The same was observed for the homologous series of 15-S-ethoxylates. These two series can alter the rocks wettability to intermediate-wet. In the case of anionic surfactants, they were tested with concentration of 0.1 wt% and both AV-70 and AV-150 showed intermediate-wet wettability alteration. DTAB which is a cationic surfactant was prepared with brine to have concentration of 0.1 wt% and it showed wettability alteration to intermediate-wet. CTAB wasn’t stable at 100^{o}C and was excluded. Both Arquad C-50 and T-50 did not show wettability alteration. In the case of dual surfactant system, both 0.2 wt% NP + 0.1 wt% DTAB and 0.2 wt% 15-S + 0.1 wt% DTAB showed wettability alteration from oil-wet to intermediate-wet.

Further, spontaneous imbibition was conducted to ensure the wettability alteration. Different systems were tested and recovery was measured. It was observed that the dual system of 0.2 wt% NP + 0.2 wt% DTAB gave a recovery of 81 % OIP. Some of the solutions which showed good wettability alteration in contact angle experiments did not show high recovery. Due to its high recovery value in spontaneous imbibition, core flooding was performed on this system.

Seethepalli et al. (2004) investigated wettability alteration for surfactant flooding in carbonate reservoirs. They investigated the interactions of dilute alkaline anionic surfactant solutions with crude oil. Several experiments were conducted including wettability, phase behavior, interfacial tension and adsorption. In their work, ten surfactants were tested. Surfactants 4-22, 5-166 and S-6566 are alkyl aryl sulphonates. Alfoterra series are alkyl propoxylated sulfates. DTAB surfactant is dodecyl trimethyl ammonium bromide which is cationic surfactant and it was used as reference. In phase behavior study, dilute solutions of surfactant were prepared with different concentrations of sodium carbonate. In interfacial tension study, IFT was measured with the use of spinning drop tensiometer. In wettability test, contact angles measurements were performed with the help of a Kruss goniometer. It was observed that anionic surfactants (SS-6656, Alfoterra 35, 38, 63, 65, 68) have the potential for changing the wettability to intermediate water-wet with performance better than cationic surfactant DTAB. Sulphonate surfactant of 0.05 wt% lowered IFT to 10^{-2} mN/m. The lowest IFT for surfactant Alfoterra was 10^{-3} mN/m. In the case of DTAB, minimum IFT was 0.04 mN/m but with higher surfactant concentration at 2 wt%.

2.4 Surfactants Adsorption in EOR

Surfactants adsorption is considered an important issue in EOR due to economic reasons. High adsorption will cause surfactant loss during injection of surfactant solution. As a result, the injected surfactants can’t be reused again. Surfactants with low adsorption are considered excellent candidate for EOR application.

Hunky et al. (2010) studied adsorption of surfactants in ultra-shallow heavy oil reservoirs. Igepal CO-530 surfactant adsorption was tested on silica and kaolinite powders. Different surfactants solutions of Igepal CO-530 were prepared. The absorbance of these solutions was measured with UV-visible to construct the calibration curve of absorbance versus surfactant concentration. Both silica and kaolinite powders are dried at 100^{o}C to remove all moistures. Ten grams of surfactant solution was added into test tube and followed by the addition of 0.5 grams of the silica powder. All the tubes of different surfactant concentration were shaken at room temperature for 24 hours to reach equilibrium. The samples were centrifuged and the surfactant adsorption was measure using UV-visible and the calibration curve. The same procedure was performed with kaolinite. It was observed that surfactant Igepal CO-530 has higher adsorption on kaolinite than silica. Surfactant Igepal CO-530 showed maximum adsorption density of 22.13 (mg/g) on kaolinite formation while it showed maximum adsorption density of 6.9 (mg/g) on silica. As surfactant concentration was increased, the adsorption density showed a plateau in the case of silica. However, in the case of kaolinite, adsorption density increased and then decreased. The reason for lower adsorption on silica is due to the weak interactions between the surfactant and silica powder.

Gao and Sharma (2013) studied static adsorption for anionic surfactants for EOR applications. Gemini surfactants were investigated in their work. Static adsorption experiments were performed to measure surfactants adsorption. Particles disaggregated from Berea sandstone were used as adsorbents. Total-organic-carbon analysis was used to measure surfactant concentration after adsorption experiments. Surfactants solutions were prepared in brine of 10,000 mg/L NaCl concentration. The surfactant solution was agitated with Berea solids for one day at 25^{o}C. It was observed that the adsorption density increased as surfactants concentration was increased. At 1,000 ppm surfactant concentration, adsorption density reached a plateau of 5 mg/g. The solid sites are filled with surfactant ions and adsorption density is no longer a function of surfactant concentration. The influence of salinity on adsorption was also investigated. It was observed that as the salinity was increased, the adsorption density increased. Surfactant solubility was reduced as salinity was increased and more surfactants ions are adsorbed on the solid. The effect of the tail length on adsorption was observed and it was found an increase in adsorption as the tail length was increased.

Seethepalli et al. (2004) investigated adsorption of anionic surfactants in carbonate reservoirs. Three sulphonates surfactants from Oil Chem were tested to study their adsorption on calcite powder in the presence and the absence of Na_2CO_3. The surfactant solution and the calcite powder were added into vials. The equilibrium period was 48 hours. UV-visible was used to measure surfactant concentration after adsorption experiments. In the absence of Na_2CO_3, adsorption was low at lower surfactant concentration followed by an increase as surfactant concentration is increased. Above CMC, the adsorption reached a plateau. The plateau value is 3.5 mg/m^2 for surfactant 5-

166, 0.9 mg/m^2 for surfactant 4.22 and 1.3 mg/m^2 for surfactant SS-6566. In the presence of Na_2CO_3, adsorption showed major decrease. It was about 0.15 mg/m^2 for surfactant 5-166. The adsorption of the other surfactants was very low. The presence of Na_2CO_3 caused an increase in the pH of the solution. It was 10.3 whereas the point of zero charge of calcite is 8.2 which caused the surface to have negative charge. The negative charge on the surface will repel anionic surfactants and low adsorption is taking place.

2.5 Core Flooding and Oil Recovery in EOR

Core flooding experiments are performed to test the actual potential of chemical EOR at reservoir conditions. Core samples are used to represent reservoir. Different formulations such as carbonate and sandstone are used depending on the research objective. The core samples are saturated with known volume of oil inside the pores of the core sample. After running the core flooding experiments, the total oil recovery % is calculated to indicate chemical EOR performance.

Veerabhadreppa et al. (2011) studied also HPAM flooding. The core sample was saturated with mineral oil and oil volume was also measured. Constant flow rate of polymer solution was injected with flow rate of 4 ml/min. It was observed the most elastic HPAM solution has the highest oil recovery compared to other HPAM solutions with lower elasticity. It was also observed that both polymer molecular weight and polydispersity index have clear influence on oil recovery. Higher molecular weight will increase oil recovery and higher polydispersity index will increase oil recovery. Polymer degradation due to shear was tested by measuring both viscous modulus and storage modulus. Lower oil recovery was observed with samples that showed larger reduction in polymer elasticity. The lowest reduction in elasticity was observed for the polymer solution of the highest polydispersity index.

Han et al. (2012) investigated the influence of their sulfonated polymer and the rock properties on the loss of injectivity with core flooding system. Polymer concentration was 0.1 wt% and it was mixed with sea water. Polymer solution was injected into carbonate core sample where an increase in differential pressure was observed. The resistance factor (RF) which is the ratio of the differential pressure for polymer injection to the differential pressure for water injection was calculated. At low shear rate, RF was affected mainly by polymer concentration while at high shear rate, RF was high and it was affected by the permeability of the core sample. Core plugging was not observed after polymer injection.

Sharma et al. (2011) studied also the performance of their surfactant by performing core flooding experiments. Five pore volumes of brine flooding were initially injected at flow rate of 0.06 ml/min. The flow rate was then increased to 1 ml/min where another five PV were injected. The flow rate was again increased to 10 ml/min with 10 PV injections. The core was then saturated with crude oil and examined to calculate oil recovery. The surfactant-brine solution was injected at flow rate of 0.06 ml/min for 1 PV and then it was followed by brine injection at the same flow rate for four PV. The flow rate was then increased to 1 ml/min and 10 ml/min. The surfactant formulation used in core flooding experiment was 0.2 wt% NP + 0.2 wt% DTAB. The recovery of brine solution at flow rate of 0.06 ml/min was 29% while surfactant-brine injection showed higher recovery of 40%. In the second 5 PV where higher flow rate was used, brine flooding showed 25% recovery while surfactant-brine showed recovery of 15%. The last 10 PV where the flow rate was 10 ml/min, brine recovery was 3% while surfactant-brine recovery was 6%. The total recovery after brine flooding was 57% while higher recovery percent was observed after surfactant-brine flooding with recovery of 61%.

Hongwei et al. (2011) studied the effect of surfactant concentration in low permeability core samples of Daqing oil field. SY surfactants were used with different concentrations. The highest surfactant concentration was 0.5% while 0.1% is the lowest. Oil recovery was 12.2% with surfactant concentration of 0.5%. The recovery at surfactant concentrations of 0.4% and 0.3% was 11.86% and 11.78%, respectively. At surfactant concentrations of 0.1% and 0.2%, the recovery was enhanced by 5.23% and 6.85% respectively. Reservoir simulation was also performed and it predicted that oil recovery can be improved by 3.5% within three years of flooding with surfactant concentration of 0.3%.

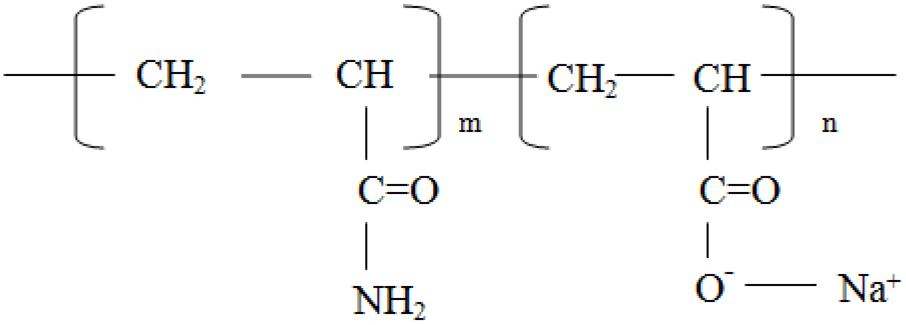
Kumar et al. (2011) studied chemical EOR in heavy oil reservoir. The recovery percent was calculated for both brine and alkaline-surfactants (AS) flooding. Three scenarios were performed. The first case was the injection of 20,000 ppm brine solution followed by AS flooding at the same salinity. The second case is the injection of 2,000 ppm brine solution followed by AS flooding at the same salinity. The third case is the injection of 20,000 ppm brine solution followed by AS flooding at 0 ppm salinity. For the first case, oil recovery was 35% after brine flooding while AS flooding showed an increase of 18%. For the second case, the recovery percent after brine flooding was 33% and it was increased to 40% after AS flooding. For the third case, AS flooding did not show any increase in oil recovery after brine injection.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Materials

In this work, we implemented one type of polymer and two types of fluoro-surfactants. HPAM from SNF was used as polymer with molecular weight of 16 million Dalton and 25-30 mol % hydrolysis. HPAM structure is shown in Figure (3.1). Fluoro-surfactants were supplied from DuPont. Capstone FS-61 is a phosphate base surfactant where the hydrocarbon chain is totally fluorinated and it is anionic. Capstone FS-61 has a composition of 15% surfactant and the other 85% is deionized water. The counter ions for surfactant FS-61 are ammonium salts. The other surfactant Capstone FS-50 is partially fluorinated betaine base surfactant and it is amphoteric. Capstone FS-50 has a composition of 27% surfactant and the other 73% is deionized water with small amount of ethanol. The two surfactants are shown in Figure (3.2). Both surfactants have low critical micelles concentration (CMC) with deionized water. More physical and chemical properties for both surfactants are shown in Table (3.1). The effect of salts was studied using a brine solution with salinity 57,000 ppm. Brine composition is shown in Table (3.2). Crude oil was used as the light phase in adsorption, IFT, phase behavior and core flooding experiments. Uthmaniyah light crude oil with API gravity equal to 30 has been used. It has a density 0.8757 g/cm^3 and whole oil molecular weight of 251 g/mol. The oil viscosity is 13.1 cp at room temperature. Oil composition is provided in Table (3.3).



$$-[CH_2-CH(C(=O)NH_2)]_m-[CH_2-CH(C(=O)O^-Na^+)]_n-$$

Figure 3.1: Molecular structure of HPAM

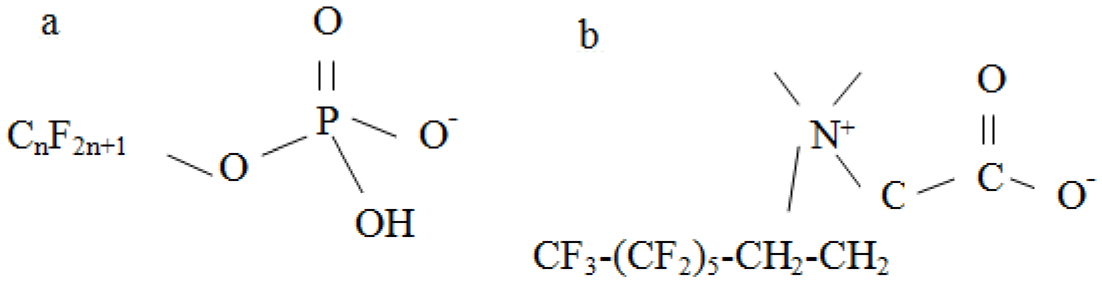


Figure 3.2: Molecular structure of fluoro-surfactant.

(a) FS-61, (b) FS-50

Table 3.1: Physical and chemical properties of surfactants FS-50 and FS-61

Property	**FS-61**	**FS-50**
Form	Viscous liquid	Liquid
Color	Amber	Amber, clear
pH	7-9	6.5
Boiling point	100°C	82°C
Vapor pressure	1.1 hPa	53 hPa at 20°C
Density	1.2 (g/cm^3)	1.03 (g/cm^3)
Composition	13-15 % solids in water	27% solids in water/ethanol
Water solubility	soluble	Completely soluble

Table 3. 2: Brine solution composition

Salt	**Concentration (g/L)**
$NaHCO_3$	0.1652
Na_2SO_4	6.3390
NaCl	41.1724
$CaCl_2$	1.8021
$MgCl_2$	8.1595
Total salinity (TDS)	57.64

Table 3. 3: Oil composition

Component	Moles	Mole %
C5	0.00216	1.23
C6	0.007434	4.23
C7	0.018767	10.67
C8	0.027806	15.81
C9	0.025519	14.51
C10	0.025371	14.43
C11	0.019607	11.15
C12+	0.049211	27.98
TOTAL	0.175876	100

3.2 Experimental Work

3.2.1 Rheology Experiments

Steady shear experiments were performed to observe the viscosity as a function of shear rate and to find the effect of the surfactants concentration on the polymer viscosity. The shear range was 0.01 s^{-1} to 2,500 s^{-1}. Viscosity was tested at low temperature of 50°C and at higher temperature of 90°C. A relation between solutions viscosity as a function of temperature was found using temperature ramp test. The thermal stability of the SP solutions was also tested during temperature ramp test. Shear rate of 1 s^{-1} and 1°C per minute temperature ramp were used. The effect of surfactant concentration on the viscoelastic properties of the polymer was investigated with frequency sweep test. The strain value was 20% which is within the linear region of a strain sweep test. Experiments were performed using TA Discovery Hybrid Rheometer (DHR) with peltier concentric cylinder system shown in Figure (3.3). It consists of a jacket, an inner cylinder (cup) and a rotor (bob). The cup diameter is 30.39 mm while the bob diameter is 27.97 mm and bob length is 41.90 mm. Both the cup and the bob are made from Aluminum. For each run, 22 ml of sample was used in the concentric cylinder geometry. The heating is through peltier elements and a circulating fluid is used as a heat sink. In all tests, the polymer concentration was kept constant at 0.25 wt%. The effect of different parameters will be tested such as the effect of salinity, surfactant concentration and temperature to observe their influence on the solution viscosity. Polymer surfactant solutions were prepared as follow:

1. 0.25 g of polymer powder was added to 100 ml beaker filled with 70 ml of water with continuous stirring.
2. Surfactants were added slowly to the polymer solution with continuous stirring.
3. Water was added slowly to the surfactant polymer solution to a total volume of 100 ml.
4. The solution was stirred for 4 hours to maintain good mixing between polymer, surfactant and water.
5. After that, stirring was stopped and the solution was allowed to equilibrate for 36 hours.
6. The sample was then tested with the required test.
7. Steady shear tests were performed to study the effect of shear on the solutions viscosity.
8. Strain sweep test was performed to locate the range of linear viscoelastic behavior at constant frequency of 1 Hz. Strain of 20% was selected from strain sweep test.
9. Frequency sweep tests were performed with strain of 20% to study the influence of temperature and surfactant concentration on the elastic modulus.
10. Temperature ramp tests were performed to study the solution thermal stability at shear rate of 1 s^{-1} and to find a relation between temperature and viscosity.

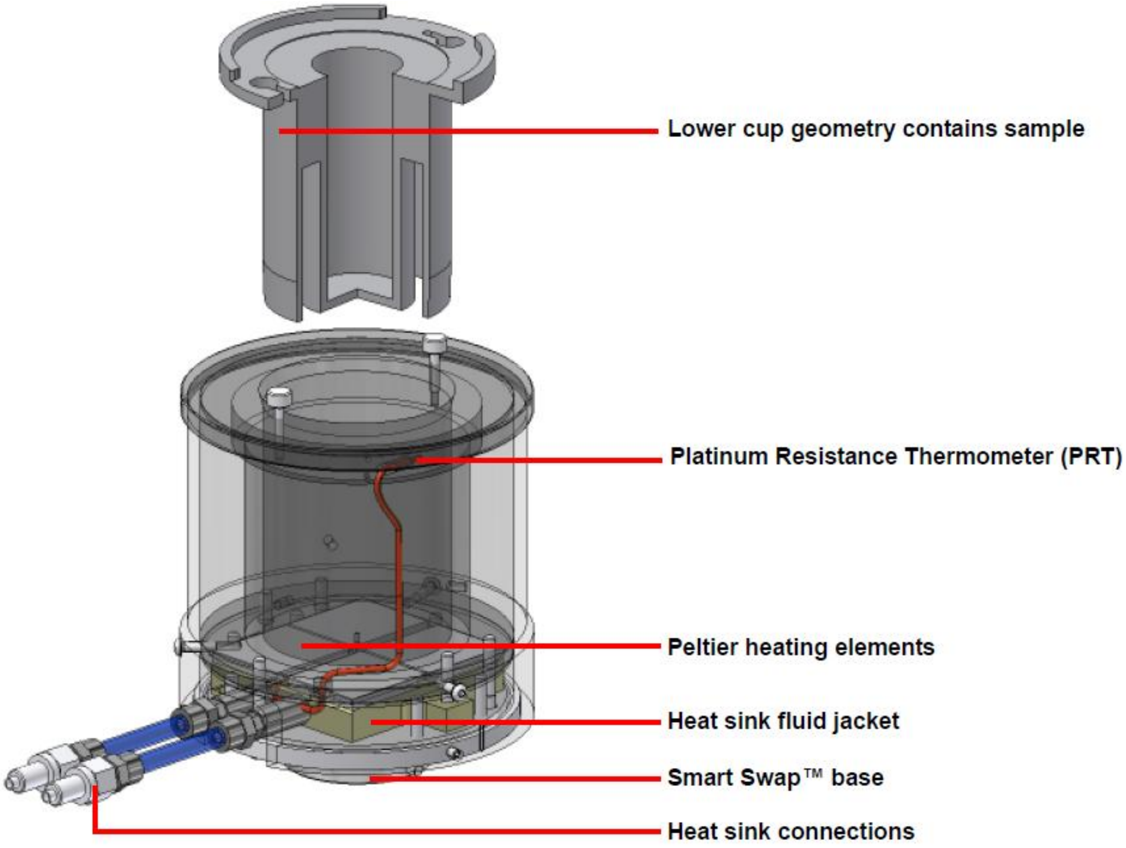


Figure 3.3: Peltier concentric cylinder geometry

3.2.2 Thermal Stability Experiments

The stability of surfactants was studied using thermogravimetric analysis (TA Instruments SDT-Q600 TGA). TGA method measures continuously the material weight while it is heated. Material components start degrading as temperature increases. The sample weight percent loss is plotted as a function of temperature to determine the temperature at which the sample starts to degrade. The derivatives of weigh percent loss can be plotted as a function of temperature to locate the points of inflection. Fourier Transform Infrared Spectroscopy (Thermo Scientific Nicolet 6700 FT-IR) was used to observe the effect of aging on the surfactant structure. FT-IR is used to get infrared spectrum of absorption and emission of solid and liquid samples. FT-IR measures how sample absorbs light at each wavelength. FT-IR was used to compare the spectrum for fresh sample with the spectrum for aged sample. If sample degrades, new peaks may appear or other peaks may disappear or absorbance is lowered when compared with fresh sample spectrum. Since the surfactants are in solution form with water, we have to use water as background for our measurements rather than air. Surfactants were aged for three weeks at 90^{o}C. Sample preparation was as follow:

1. A small volume from the surfactant solution was taken which contains both surfactant and water.
2. The solution was transferred to a small flat curved glass and put in oven at a temperature of 40^{o}C for drying until solid surfactant was formed.
3. The solid surfactant was taken from the oven and TGA analysis was applied. Degradation with nitrogen was performed.

4. In the case of FT-IR analysis, the surfactant solution is transferred into small closed vials and put into oven at 90^{o}C for about 20 days for aging.
5. Then, FT-IR analysis was applied on both aged and fresh surfactant solutions to check any difference in the spectra.

3.2.3 Static Adsorption Experiments

Static adsorption was performed to study surfactant, cations and anions adsorption in carbonate formation. Surfactants loss due to adsorption is considered as concern in EOR for economic reasons. Carbonate powder was used which has higher surface area compared to actual carbonate rocks. Surfactant, cations and anions adsorption was tested where the effect of the presence of oil and temperature were observed. The experiments were conducted at 25^{o}C and 90^{o}C. The experimental plan for static adsorption is shown in Table (3.4). Surfactant concentration was fixed at 0.3 wt% which is higher than CMC value. The test procedure is as follow:

1. Two grams of precipitated calcium carbonate ($CaCO_3$) was added to 40 ml vials.
2. The brine solution was added with a volume of 30 ml.
3. The closed vials were then shacked for 24 hours and after that it was left to equilibrate for another 24 hours.
4. The shacking process was performed in a water bath where the test temperature was set.
5. Sample of the brine was then filtered through 0.45 µm pore diameter filters. It was transferred to small vials for ions chromatography (IC) analysis to measure both the cations and anions concentrations.

6. Another sample of the brine solution was taken and filtered through the same process for UV-vis analysis to investigate surfactant and carbonate adsorption.
7. Samples from the initial brine were taken for IC and UV-vis analysis as references in adsorption experiments.
8. The brine solution showed no absorbance using UV-vis analysis.
9. The surfactant absorbance was calculated by taking the difference between the total absorbance and the absorbance of the carbonate in the brine solution.
10. The absorbance of sample (2) was subtracted by the absorbance of sample (1) to calculate surfactant absorbance in sample (2). Similar procedure was performed with the other samples.
11. A calibration curve was constructed by measuring the absorbance of samples with known surfactant concentration.
12. The calibration curve was used to calculate the surfactant concentration after adsorption experiments.
13. Adsorption density Γ (mg/g) was calculated to study ions and surfactant adsorption using the following equation:

$$\boldsymbol{\Gamma = \frac{(C_i - C)V}{M}} \qquad \boldsymbol{(3.1)}$$

C_i and C (ppm) are concentrations before and after the adsorption experiments respectively, V (L) is the solution volume and M (g) is the mass of adsorbent PCC.

Table 3.4: Adsorption test samples

Sample number	Test conditions
1	SW+PCC at 25^{o}C
2	SW+PCC+S at 25^{o}C
3	SW+PCC at 90^{o}C
4	SW+PCC+S at 90^{o}C
5	SW+PCC+Oil at 25^{o}C
6	SW+PCC+Oil+S at 25^{o}C
7	SW+PCC+Oil at 90^{o}C
8	SW+PCC+Oil+S at 90^{o}C

SW: Sea Water, **PCC**: Precipitated $CaCO_3$, **S**: Surfactant FS-50

3.2.4 Interfacial Tension Experiments

The SITE100 Spinning Drop Tensiometer was used to measure the interfacial tension between light phase (oil) and heavy phase (surfactant solution) and it is shown in Figure (3.4). This instrument can measure ultralow interfacial tension values in the range of (10^{-3} - 20) mN/m. Both heavy and light phases are injected into a rotating capillary made from glass. The drop radius is perpendicular to the rotation axis and it depends on the interfacial tension between the two phases (γ), the density difference between the two phases (ρ_H-ρ_L) and the rotation angular frequency (ω). According to Bernhard Vonnegut equation (1942), interfacial tension can be calculated using the following relation:

$$\boldsymbol{\gamma = \frac{1}{4}(\rho_H - \rho_L)\omega^2 R^3 \left(1 + \frac{2R}{3L}\right)} \qquad (3.2)$$

Where:

$(\rho_H - \rho_L)$ is the density difference between the heavy and the light phase, $\omega = 2\pi f$ is the angular velocity, R is the elongated drop radius and L is the elongated drop length.

When $L \gg R$, equation (3.2) can be approximated to be:

$$\boldsymbol{\gamma = \frac{1}{4}(\rho_H - \rho_L)\omega^2 R^3} \qquad (3.3)$$

A schematic of the rotating capillary is shown in Figure (3.5), the lighter phase (oil) was injected into a rotating capillary which is already filled with the heavy phase. A high speed rotation of the capillary will cause elongation of the light phase drop due to the centrifugal force. Parameters such as surfactant concentration, salinity, addition of co-surfactants and temperature will be examined. The measurement procedure is described below:

1. Oil circulation was started and temperature was set at $30^{o}C$.
2. The capillary was filled with the heavy phase which is surfactant solution.
3. Air bubbles were removed from the heavy phase.
4. Calibration was done by determining the scale factor using calibrating wire.
5. The capillary was rotated with initial speed of 1,000 rpm.
6. Both the densities of the heavy and the light phases were entered in the software.
7. A drop of the light phase which is oil was injected using a micro syringe.
8. The drop was placed so it can be seen in the camera window.
9. Illumination was adjusted.
10. Measurements were performed at different temperature values.

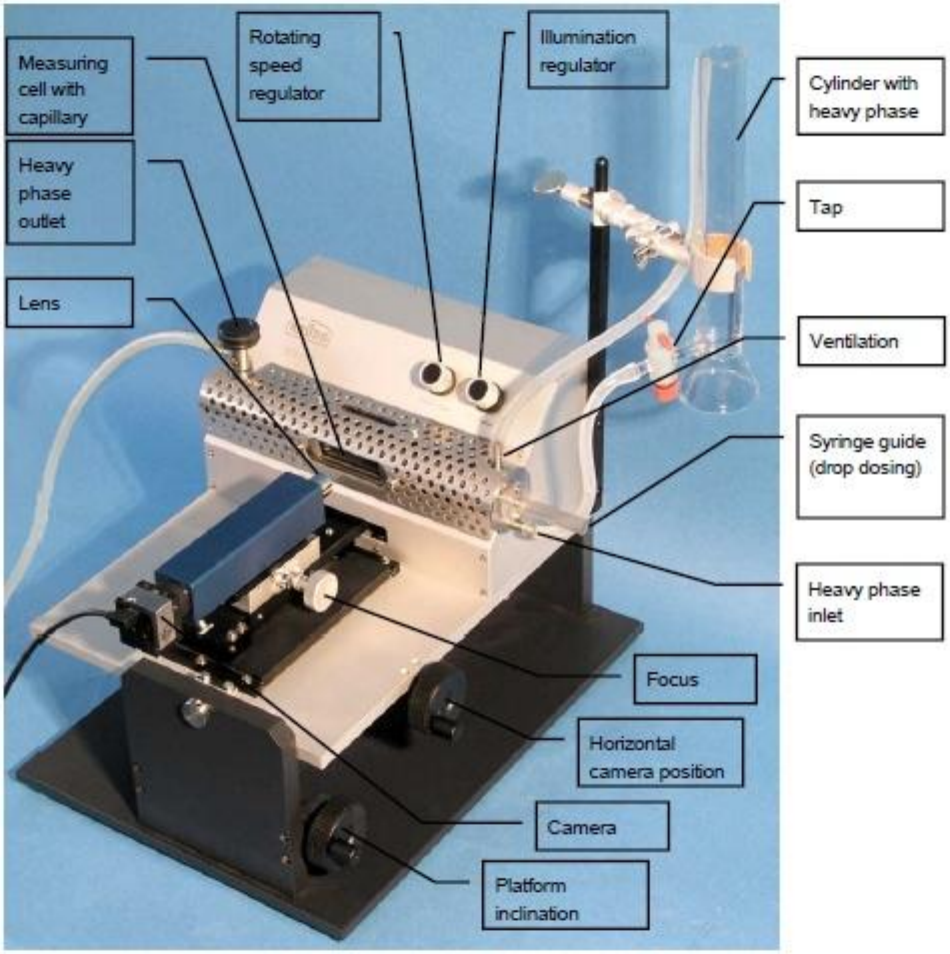


Figure 3. 4: SITE 100 Spinning Drop Tensiometer

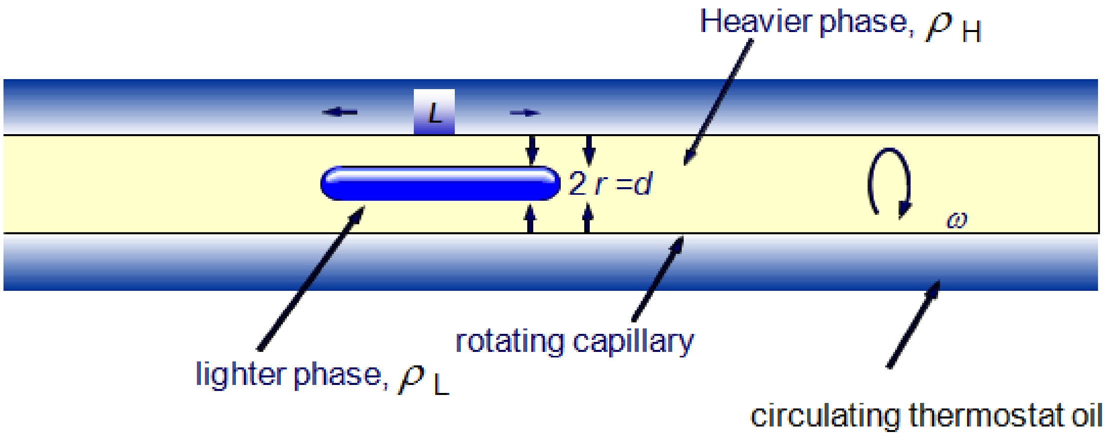


Figure 3.5: Instrument rotating capillary

3.2.5 Phase Behavior Experiments

Phase behavior experiments were used to evaluate the potential of surfactants for EOR. Mixing of oil, water and surfactant will separate into one of the three types of phases described by Winsor (1954). Type I microemulsion is oil into water, type II is water into oil and type III is middle phase microemulsions. Surfactants can solubilize more amount of oil and lower amount of water as salinity is increased. The salinity at which equal amount of oil and water are solubilized is known as the optimal salinity. Both oil and water solubilization ratios are equal $\sigma_o=\sigma_w$. Water solubility ratio is defined as the amount of water in microemulsion V_w per volume of surfactant V_s while oil solubility ratio is defined as the amount of oil in microemulsion V_o per volume of surfactant V_s. A salinity scan test was applied to monitor the formulation of middle phase microemulsion. The minimum IFT value is related to the solubilization ratios of oil and water at the optimal salinity. Since we know the minimum IFT value from IFT experiments, surfactant concentration was fixed at 0.1 wt% (the minimum IFT value of FS-50 in sea water) and salinity was changed from 0 ppm to 57,000 ppm. It is expected that surfactant phase behavior will change from type I to type III to type II as salinity is increased. The experimental procedure for FS-50 is as follow:

1. Five ml of surfactant brine solution (0.1 wt% surfactant concentration) was transferred into 15 ml graduated tubes.
2. Five ml of oil was transferred into the same graduated tube to have totally 10 ml of both oil and surfactant solution.

3. Totally nine tubes were prepared with different salinity concentrations (0 ppm, 7,125 ppm, 14,250 ppm, 21,375 ppm, 28,500 ppm, 35,625 ppm, 42,750 ppm, 49,875 ppm, 57,000 ppm)
4. The nine tubes were then rotated vertically with speed of 30 run per minute to mix the two phases.
5. Mixing was done at 25^{o}C for one day and after that the tubes were kept stand vertically for equilibrium.
6. Pictures were taken at different times to monitor the formation of type III phase.
7. Mixing was also done at 90^{o}C for one day with the same speed and after that the tubes were kept stand in oven at 90^{o}C for equilibrium.
8. Again pictures were taken to check formation of phases.
9. In the case of surfactant FS-61 which showed incompatibility with salts, phase behavior experiments were applied with deionized water with varying surfactant concentration (0.1, 0.3, 0.5, 0.7 and 1.0 wt%).

3.2.6 Core Flooding Experiments

Oil recovery experiments were conducted using Indiana limestone core plug (carbonate formation). It is 3.765 cm in diameter and 30.455 cm in length. The porosity is 17.39% and the pore volume is 58.96 cm^3. The measured permeability is 73.729 mD. CoreTest FDES-645 will be used for core flooding experiments. Figure (3.6) shows core flooding system. Core flooding experiment procedure is as follow:

1. The core sample was cleaned using toluene. Core was put into core cleaner where toluene was heated to about 80^{o}C. Toluene was evaporated and forced through the core to remove the fluid inside and then followed by condensation in closed core cleaner. The cleaning process lasts for one day.
2. The core was dried at about 75^{o}C for another day.
3. The dry weight of the core was taken.
4. The core was then vacuumed for about four hours to remove air in the pores.
5. The core was saturated in core holder with formation water (213,734 ppm) under confining pressure of 2,000 psi for one day. Then, the core was taken out and kept immersed in formation water for another two days for ions equilibrium at room temperature.
6. The wet weight of the core sample was taken and the pore volume (PV) was calculated as follow:

$$\mathbf{PV} = \frac{\mathbf{wet\ weight - dry\ weight}}{\mathbf{formation\ water\ density}} \qquad (\mathbf{3.4})$$

7. The core sample was then transferred into the core holder of the core system to measure permeability using formation water.
8. The core flooding system was designed by CoreTest to perform core flooding experiments for cores sample length up to 12 inches.
9. All accumulators of the system were filled with fluids (formation water, surfactant polymer solution, brine, oil).
10. After the core was placed in rubber sleeve inside the core holder, confining liquid was injected around the sleeve and the core holder was checked for leaks.

11. If there is no leak, the confining pressure was set at 1,500 psi and the inlet and outlet pipes were connected.
12. The pore pressure was set by setting the back pressure at 500 psi. Again, leaks were checked.
13. Both the upstream and the dawn stream were purged with formation water to remove air from the piping system.
14. Permeability measurements were started by injecting formation water through the core with flow rate of 0.25 ml/min until pressure difference across the core was stabilized.
15. The flow rate was increased to 0.75 ml/min until the pressure was stabilized. The same procedure was done with flow rates of 1 ml/min and 1.25 ml/min.
16. Using Darcy's law for linear flow, the permeability was calculated:

$$\mathbf{K} = \frac{\mathbf{245\ Q\ \mu\ L}}{\mathbf{A\ \Delta P}} \tag{3.5}$$

    Where K (mD) is the core sample permeability, Q (ml/min) is the injected fluid flow rate, μ (cP) is the formation water viscosity, L (cm) is the core sample length, A (cm^2) is the core sample cross sectional area and ΔP (psi) is the pressure across the core sample.
17. The oven was monitored to set the reservoir temperature of 90^{o}C.
18. Oil was flashed through the core forward and backward for a period of two weeks to saturate the core with oil. The effluent was collected using 15 ml graduated cylinders until no more water is produced and the pressure drop was recorded.
19. The initial water saturation (S_{wi}) was calculated as follow:

$$\mathbf{Swi} = \frac{\mathbf{PV - volume\ of\ produced\ brine}}{\mathbf{PV}} \qquad (\mathbf{3.6})$$

20. The core was saturated with oil up to S_{wi} and oil recovery process was started by brine flooding with salinity concentration of 57,000 ppm at flow rate of 0.5 ml/min.
21. The effluent was collected using 15 ml graduated cylinders until no more oil was produced. Still residual oil was in the core.
22. The chemical flooding was started by injecting polymer surfactant solution through the core with flow rate of 0.5 ml/min and oil recovery percent was calculated.
23. The chemical solution has polymer concentration of 0.25 wt%, brine with salts concentration of 57,000 ppm and surfactant concentration of 0.1 wt%. The optimum surfactant concentration from IFT experiments was 0.1 wt%.

Figure 3.6: Core flooding system (CoreTest FDES-645)

CHAPTER 4

RESULTS AND DISSCUSIONS

4.1 RHEOLOGY

Rheology of the injected fluid is a critical issue in EOR. The injected fluid must have high viscosity to increase sweep efficiency. Several parameters were studied to determine their effects on the solution viscosity such as reservoir temperature and salt concentration because polymer will be injected with brine where salts have major effect on viscosity. Shearing due to injection of SP solution also causes a reduction in viscosity. Surfactant concentration can cause an increase or decrease in viscosity depending on the interactions with polymer molecules. Surfactant concentration may also has negligible influence on polymer solution viscosity. All of these parameters will be tested to come up with the polymer concentration suitable for EOR applications. Figure (4.1) shows the viscosity as function of shear rate for polymer solution and polymer-surfactant (FS-50) solutions in deionized water at 50^{o}C. Polymer concentration of 0.25 wt% was fixed for all solutions. HPAM solutions showed a typical non-Newtonian behavior with shear rate. The solutions viscosity is a function of shear rate and as the shear rate is increased the solution viscosity decreased due to shear thinning effect. At a typical shear rate in the reservoir (10 s^{-1} to 50 s^{-1}), HPAM solution has 20 times higher viscosity than that of water (0.001 Pa.s). When HPAM is added to water, repulsive forces are formed due to the negative charge on the carboxylate group. As a result, the solution viscosity increases. The influence of surfactant FS-50 concentration is presented in Figure (4.1). As the surfactant concentration is increased the solution viscosity showed no change. Similar behavior has been reported in deionized water with hydrocarbon betaine base surfactant by Bataweel et al. (2012). Figure (4.2) shows similar shear thinning behavior at 90°C. Solutions viscosity curves shifted down at higher temperature. About 37% reduction was observed in the viscosity at higher temperature at low shear rates while similar viscosity values were observed at typical reservoir shear rates (10 s^{-1} to 50 s^{-1}). It is well known that the viscosity is inversely related to temperature. The influence of surfactant FS-61 was also tested on HPAM solution. The viscosity decreased slightly as surfactant (FS-61) concentration is increased as shown in Figure (4.3) and (4.4) at 50°C and 90°C, respectively. Surfactant concentration of 0.2 wt% caused 40% reduction in the polymer viscosity. The reduction is observed only at low shear rates while at typical reservoir shear rates, the effect of surfactant concentration on viscosity is no longer observed. The presence of positive charge ammonium salts as counter ions in surfactant FS-61 shielded the negative charges on HPAM chains and caused small reduction in solution viscosity. Mandal et al. (2008) reported similar decrease in viscosity with SDS surfactant. A strain sweep test was performed as shown in Figure (4.5) to locate the range of linear viscoelastic behavior and a strain % of 20 was used for all frequency sweep tests. Both Figures (4.6) and (4.7) show the effect of surfactant FS-50 concentration on the elastic modulus of the polymer solution at 50°C and 90°C, respectively, using frequency sweep test. It was observed in the two cases that the surfactant caused 25% decrease in the elastic modulus of the polymer solution. However, increasing surfactant concentration did not show any further reduction. As the temperature is increased to 90°C, the solutions elastic modulus decreased. The decrease in polymer elasticity is about 42%. The reduction in the elastic modulus is between 35% and 44% for polymer-surfactant solutions. Figures (4.8) and (4.9) show the influence of surfactant FS-61 on the elastic modulus at 50^{o}C and 90^{o}C, respectively. As the concentration is increased the polymer elastic modulus decreased. It was observed that the elastic modulus of the polymer solution is decreased by 49% for a surfactant concentration of 0.2 wt% at 50^{o}C. As the temperature is increased to 90^{o}C, the reduction in elastic modulus of polymer-surfactant solutions was 35% to 45%. Thermal stability of the polymer-surfactant solutions is studied using temperature ramp tests. Figures (4.10) and (4.11) show Arrhenius plot of viscosity as a function of inverse temperature for polymer solution with surfactant FS-50 and FS-61, respectively. The relation was linear with no change in the slope within temperature range of 35^{o}C to 90^{o}C. It is shown that the polymer-surfactant solutions are stable within this range. A change in the slope would indicate a change in polymer morphology. Arrhenius relations for the different surfactant concentrations were fitted and presented in Table (4.1) where the values of both the flow activation energy and the pre exponential factor are summarized. It was observed that changing surfactants concentration caused a change in the pre exponential factor (A). The pre exponential factor is related to polymer molecular weight distribution and it is sensitive to any structural changes. The flow activation energy (E) showed relatively small change with surfactants concentration.

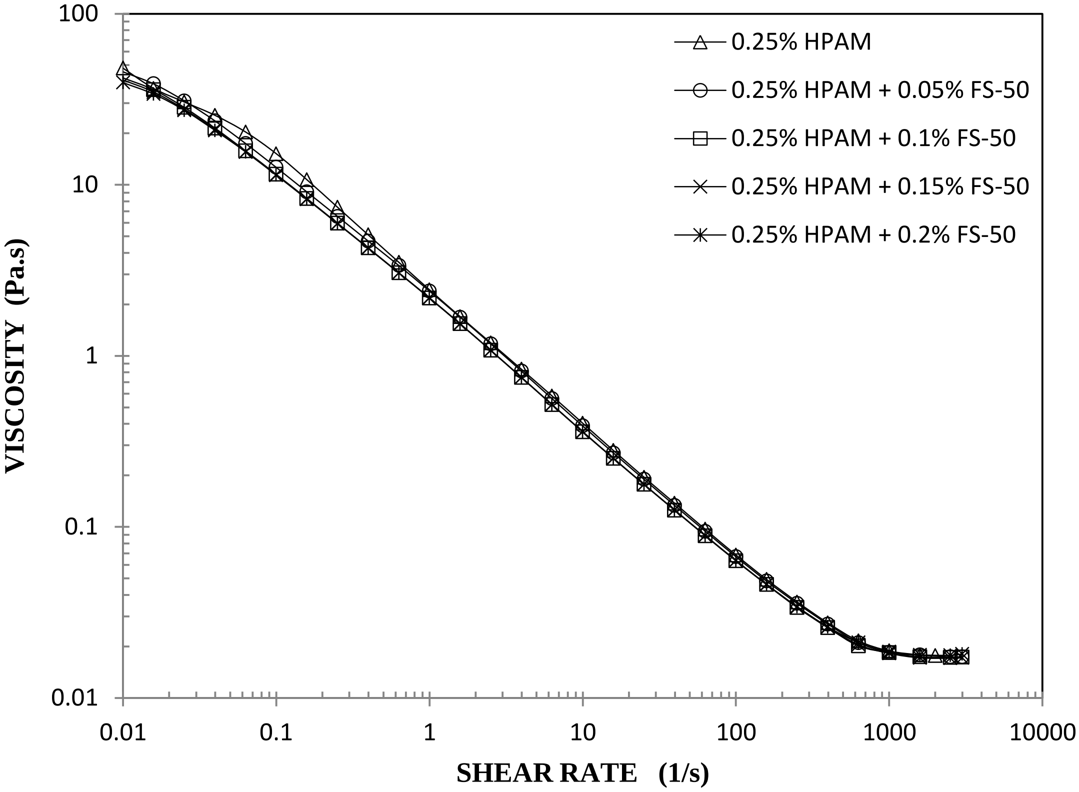


Figure 4. 1: Viscosity of HPAM solution with different FS-50 concentrations at 50^{o}C

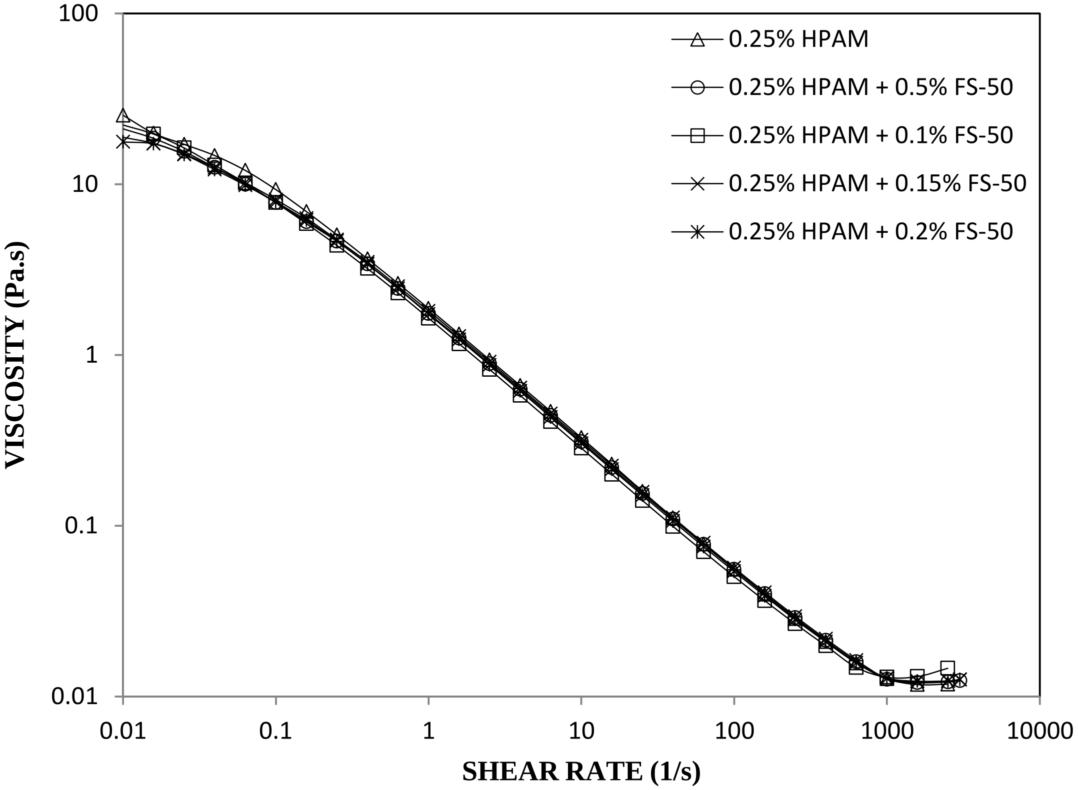


Figure 4. 2: Viscosity of HPAM solution with different FS-50 concentrations at 90^{o}C

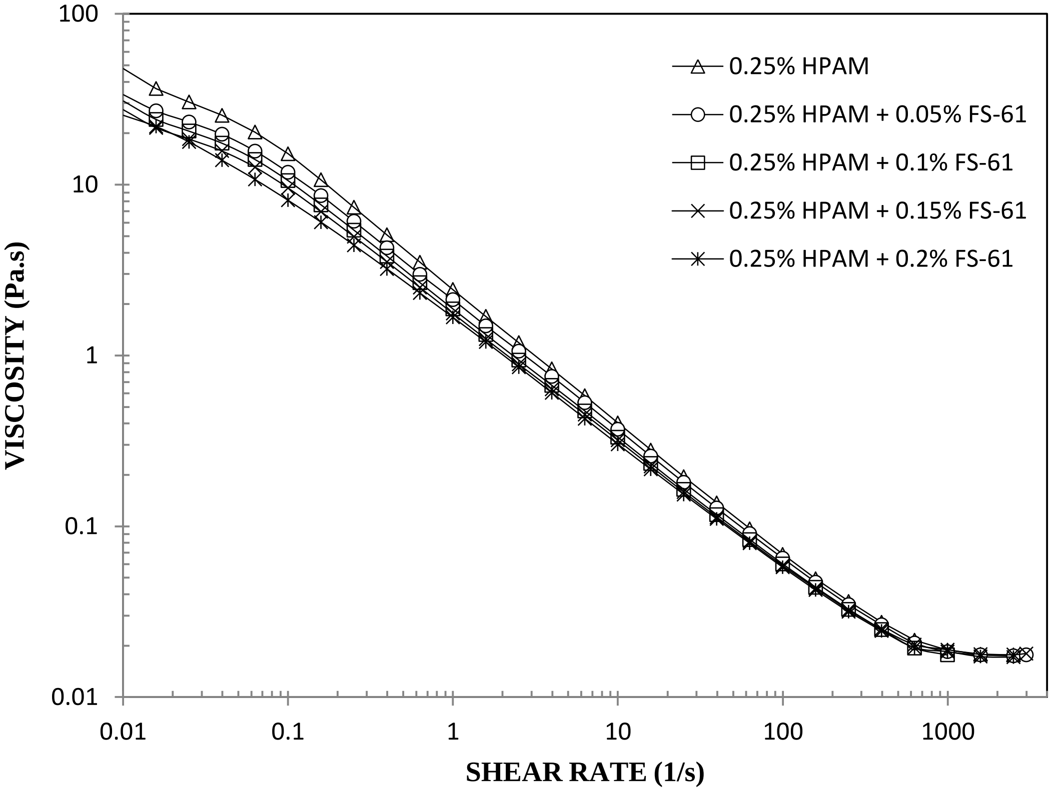


Figure 4. 3: Viscosity of HPAM solution with different FS-61 concentrations at 50^{o}C

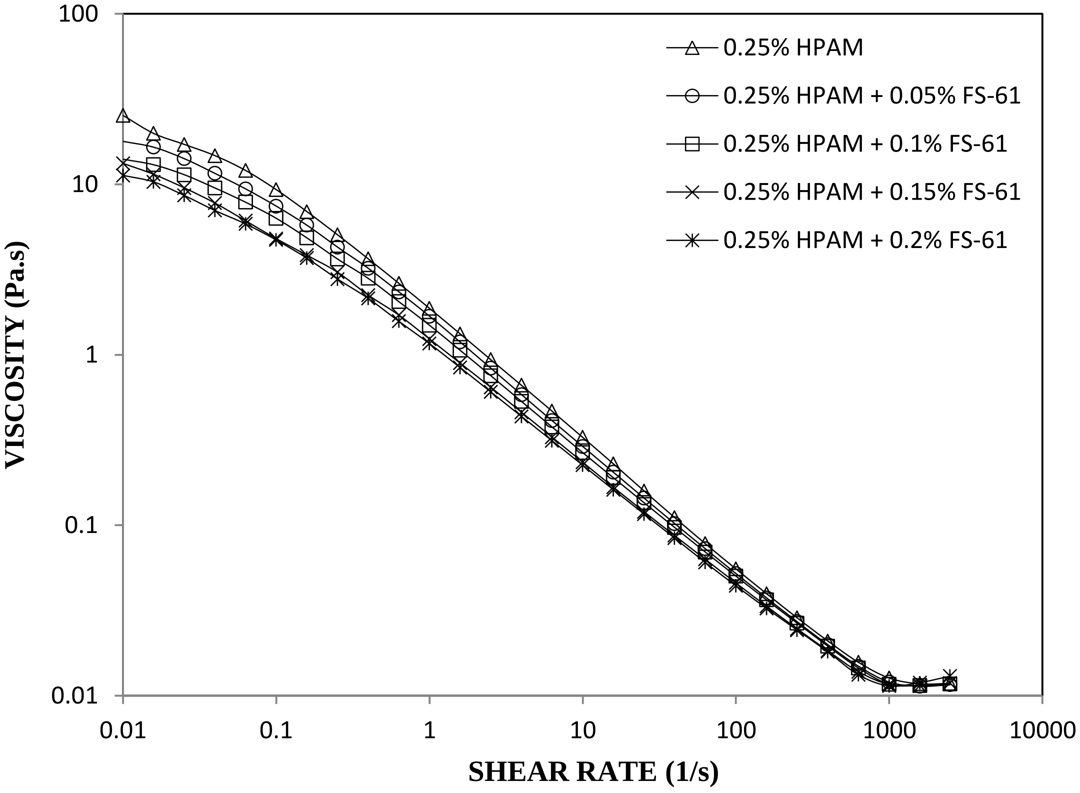


Figure 4. 4: Viscosity of HPAM solution with different FS-61 concentrations at 90^{o}C

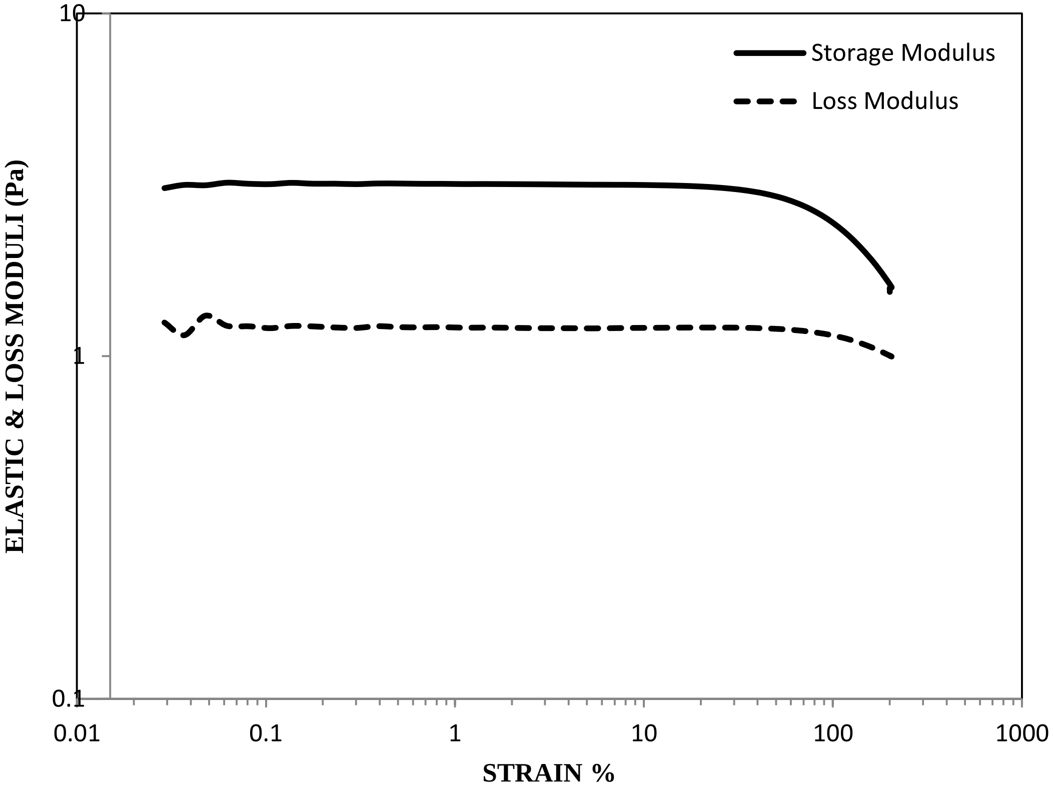


Figure 4. 5: Strain sweep test for 0.25 wt% HPAM solution.

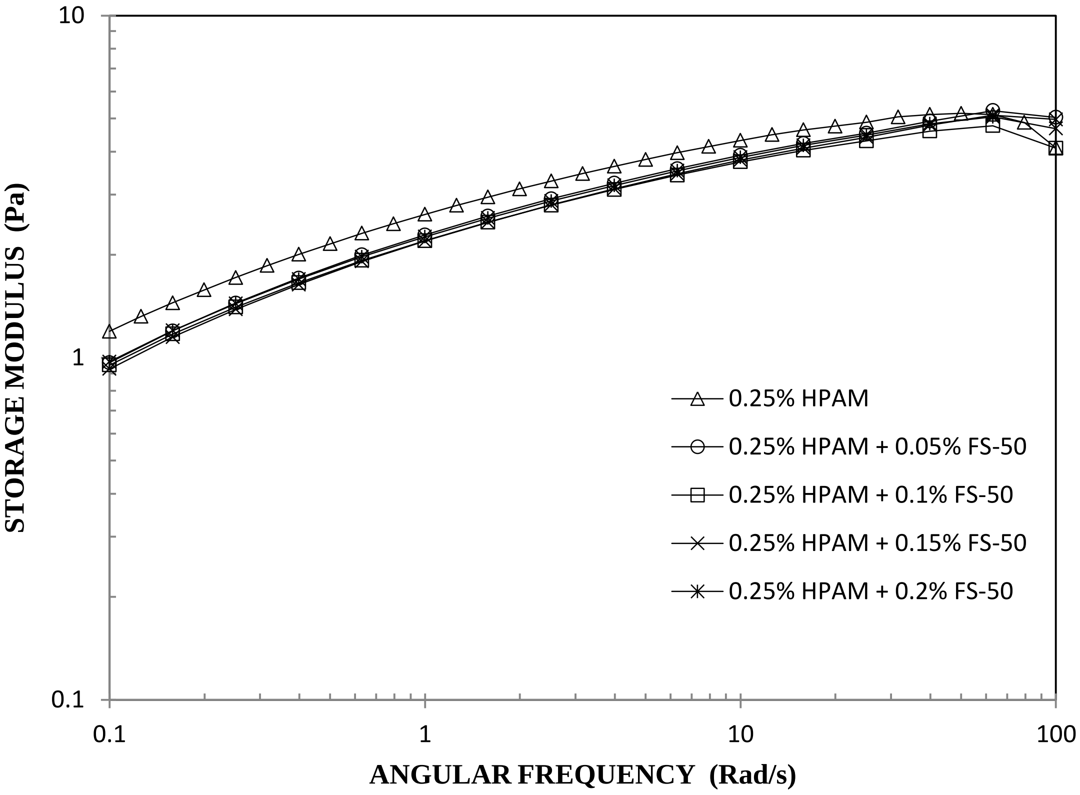


Figure 4. 6: Elastic modulus of HPAM solution for different FS-50 concentrations at 50°C

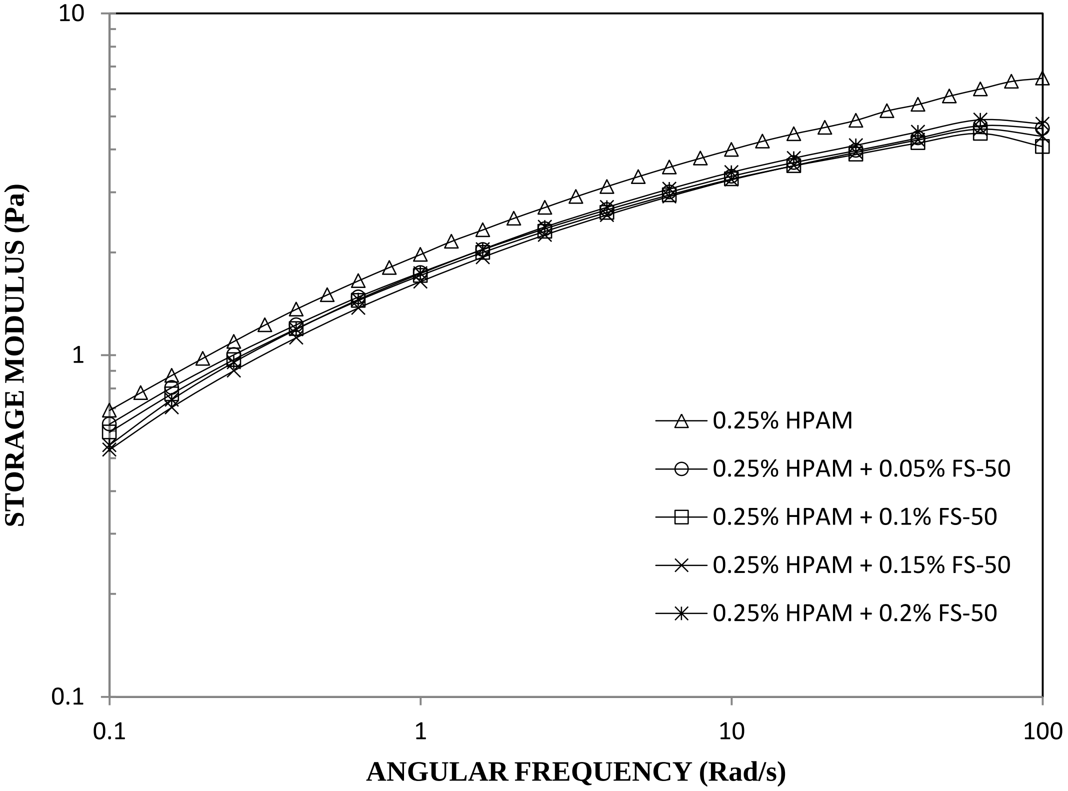


Figure 4. 7: Elastic modulus of HPAM solution for different FS-50 concentrations at 90^{o}C

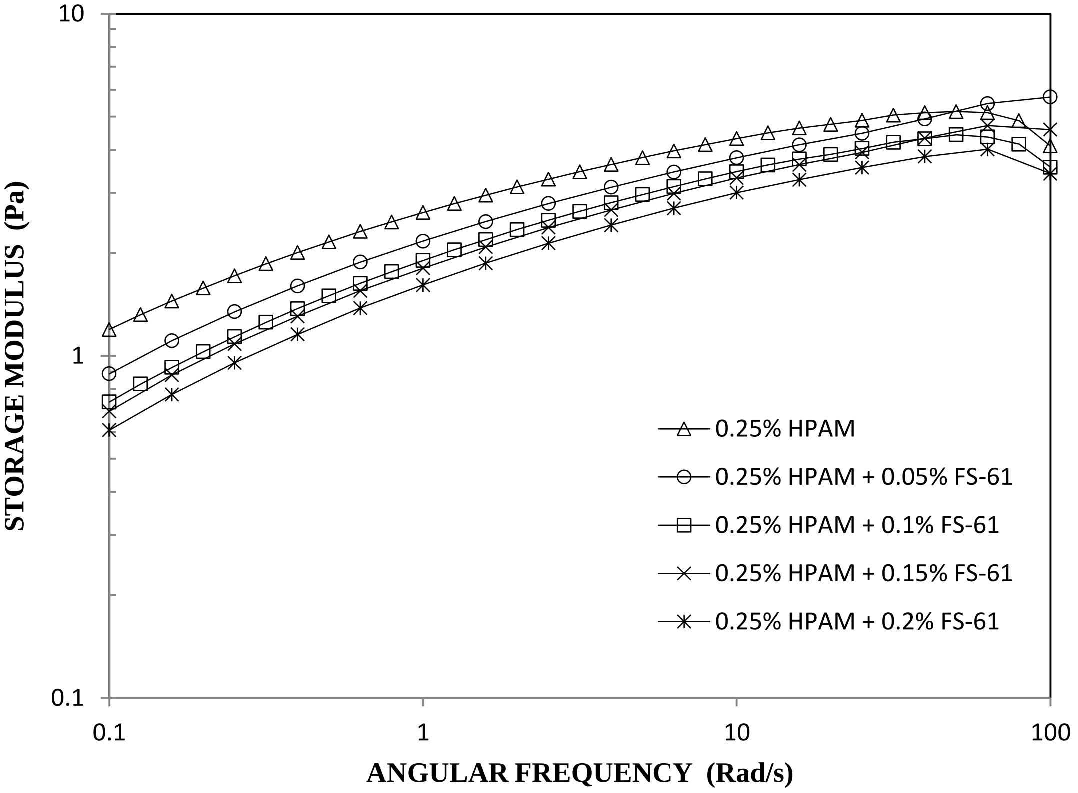


Figure 4. 8: Elastic modulus of HPAM solution for different FS-61 concentrations at 50^{o}C

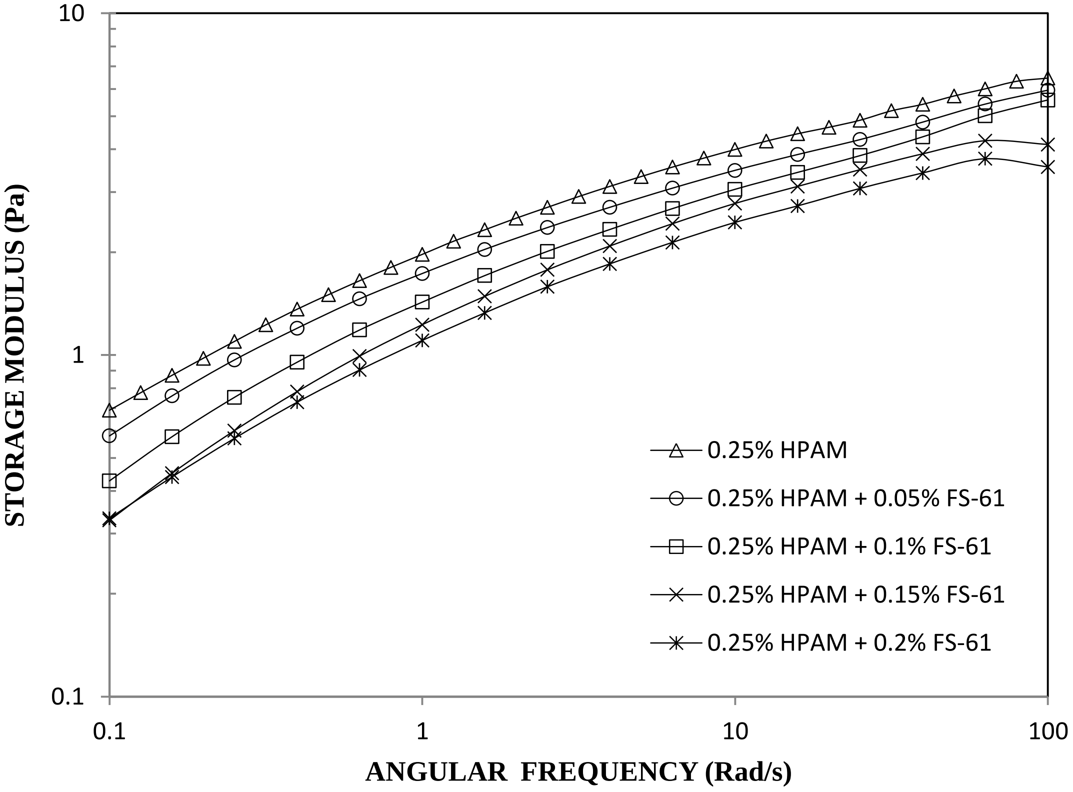


Figure 4. 9: Elastic modulus of HPAM solution for different FS-61 concentrations at 90°C

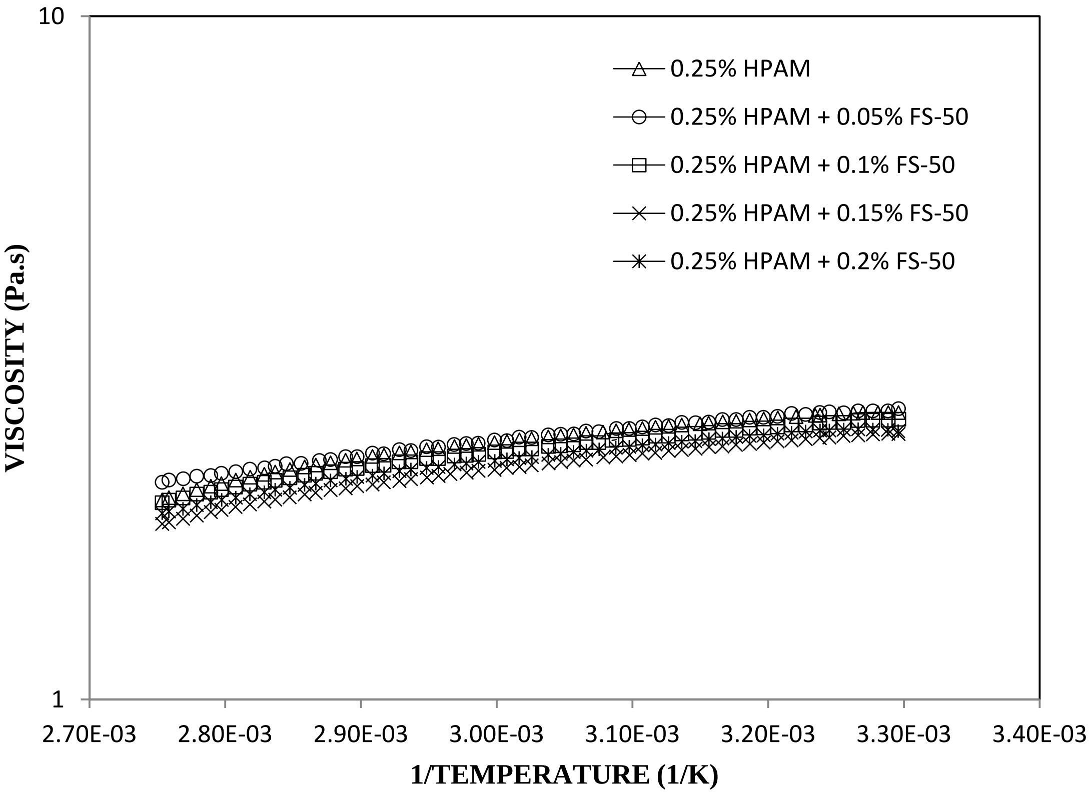


Figure 4. 10: Temperature ramp for HPAM solution with different FS-50 concentrations

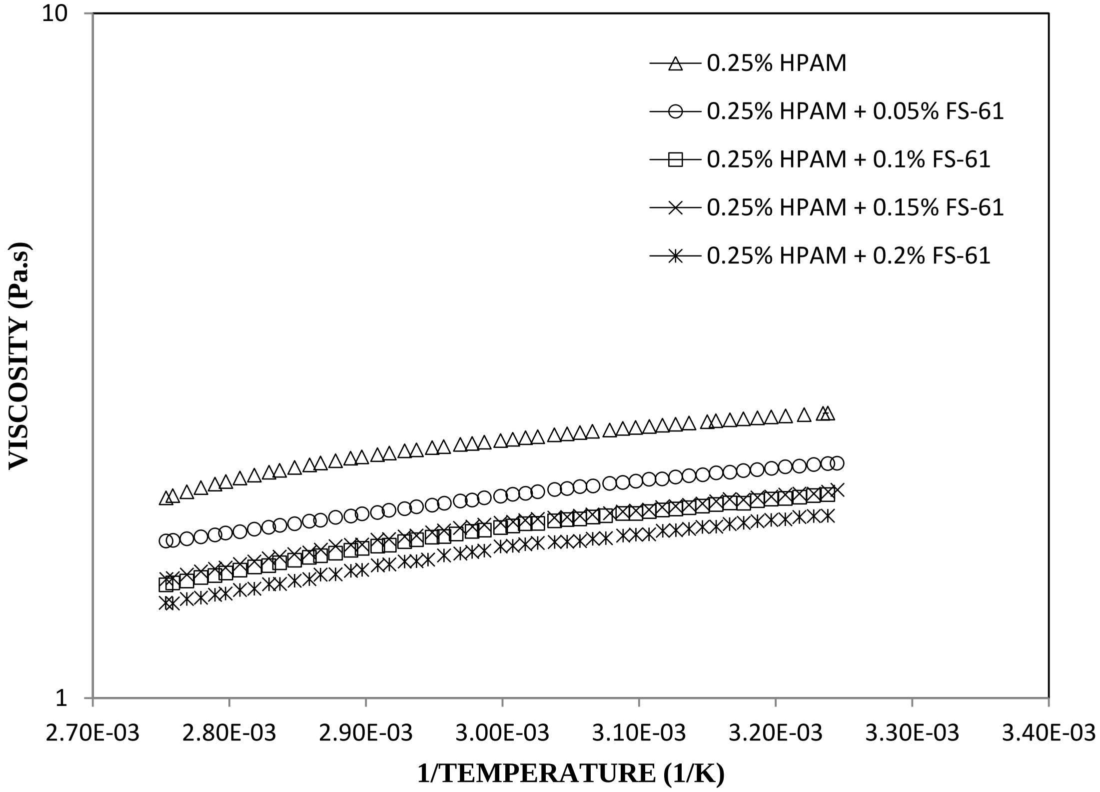


Figure 4. 11: Temperature ramp for HPAM solution with different FS-61 concentrations

Table 4. 1: Parameters of Arrhenius relation for HPAM solution with different surfactants concentrations

FS-50 concentration (wt%)	A (mPa.s)	E (kJ/mol)	FS-61 concentration (wt%)	A (mPa.s)	E (kJ/mol)
0.05	507.00	4.23	0.05	376	4.57
0.1	514.00	4.12	0.1	270	5.17
0.15	424.00	4.49	0.15	303	4.89
0.2	475.00	4.26	0.2	262	5.07

Preparing polymer solution in deionized water represents the ideal case due to the absence of salts. In actual reservoirs, the injected fluid is mixed with sea water and the reservoir itself has salts which can influence the injected fluid viscosity. Surfactant FS-61 is incompatible with salts by forming precipitations while surfactant FS-50 is compatible and can tolerate salts. Figure (4.12) shows the effect of salts on polymer and polymer-surfactant solutions at 90^oC. Salts caused significant reduction in polymer viscosity due to charge shielding effect. Both monovalent cations such as Na^+ and divalent cations such as Mg^{++} and Ca^{++} shield the negative charge of HPAM chains and cause shrinking in their volume and as a result, polymer viscosity is decreased. This behavior has been reported by Mandal et al. (2008) and Batweel et al. (2012). Four different salinity concentrations were tested with HPAM solution (14,250 ppm, 28,500 ppm, 57,000 ppm and 228,000 ppm) and all showed similar viscosity reduction compared with HPAM solution in deionized water. Although, viscosity reduction is large, it is still 10 times higher than water viscosity (0.001 Pa.s) at a typical shear rate values in actual reservoirs ($10\ s^{-1}$ to $50\ s^{-1}$). Adding surfactant FS-50 to polymer solution in sea water showed no influence on viscosity. Two different surfactant concentrations were tested (0.1 wt% and 0.2 wt%) in 57,000 ppm sea water. They showed no change in viscosity compared to polymer solution at the same salinity value. Interactions between surfactant molecules and salts ions have no influence on viscosity.

From rheology analysis, we have clear understanding on the influence of reservoir conditions on the viscosity of the injected fluid. At reservoir conditions ($T = 90^oC$, shear $= 10\ s^{-1}$, salinity = 57,000 ppm), a solution of 0.25 wt% HPAM concentration has viscosity of 0.01 Pa.s that is 10 times higher than that of water. Fluoro-surfactant FS-50 has negligible influence on the solution viscosity in the presence and the absence of salts. Fluor-surfactant FS-61 is incompatible with salts which is a major problem in EOR application and it is excluded from core flooding experiment. SP solution of 0.25 wt% HPAM concentration and X wt% FS-50 surfactant concentration will be used in core flooding experiment. Since surfactant FS-50 has no influence on the solution viscosity, the decision on the X value will be made after IFT measurements. The X value is the optimum surfactant concentration which gives lower IFT.

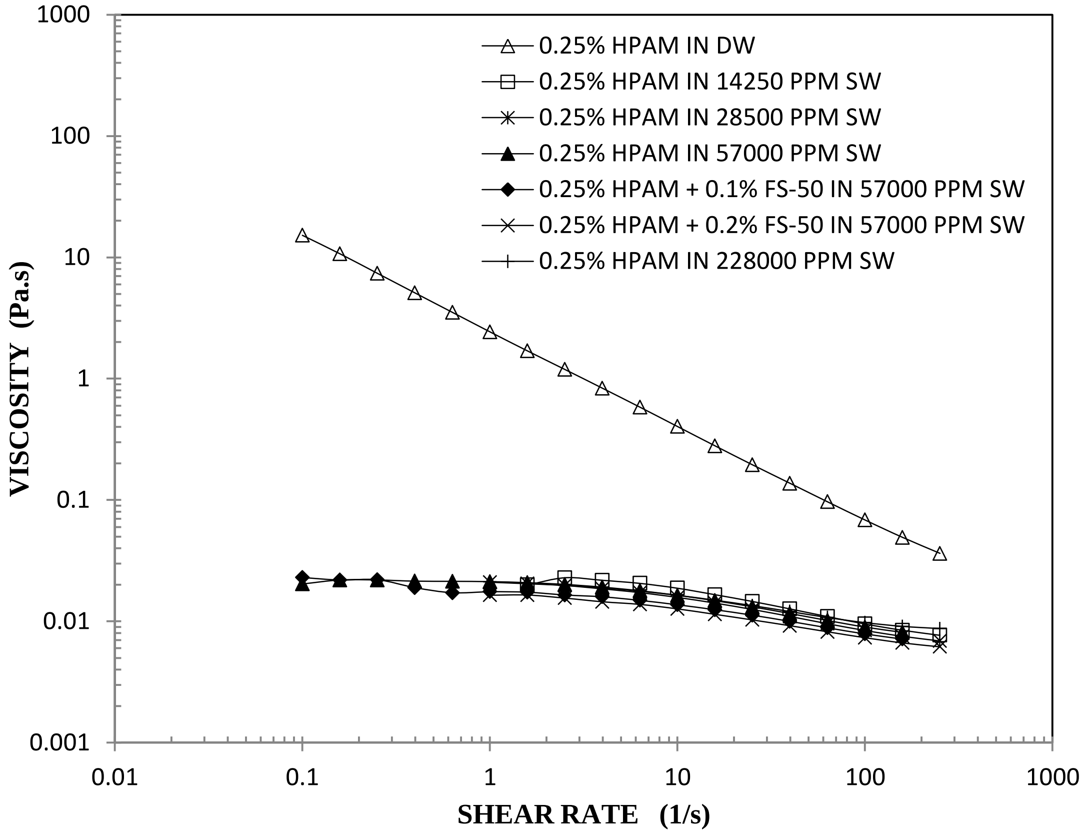


Figure 4. 12: Effect of salts on HPAM solution and HPAM solution with surfactant FS-50 at 90^{o}C

4.2 THERMAL STABILITY

4.2.1 Thermogravimetric Analysis (TGA)

Thermal stability of surfactants is a major concern in EOR. The high temperature in the reservoirs can cause surfactant thermal degradation. The thermal stability of fluoro-surfactant will be tested at 90^{o}C to check their stability for short and long periods at high temperatures. Figure (4.13) shows TGA analysis for both surfactants FS-50 and FS-61. It was observed that a small decrease in the sample weight below 150^{o}C which is due to the evaporation of water moisture. Samples were dried at 40^{o}C to form solid surfactant and some water moisture remained in the samples. At temperature of 230^{o}C, major change in weight loss was observed for surfactant FS-50. Surfactant FS-50 is considered thermally stable up to 230^{o}C while reservoir temperature is around 110^{o}C. Surfactant FS-61 is thermally stabile up to 160^{o}C where major change in weight loss was observed. The stability in fluoro-surfactants is due to the existing of fluorine atoms on the hydrocarbon chain of the surfactant. Fluorine-Carbon bonds in fluoro-surfactants are more stable compared to hydrogen-carbon bonds in hydrocarbon surfactants. Both fluoro-surfactants showed excellent thermal stability and can be considered as promising candidates for high temperature reservoirs. TGA analysis is a short period test. Samples are kept for short period of time at certain temperature. Another analysis must be used to determine the stability of fluoro-surfactants for long periods under high temperature.

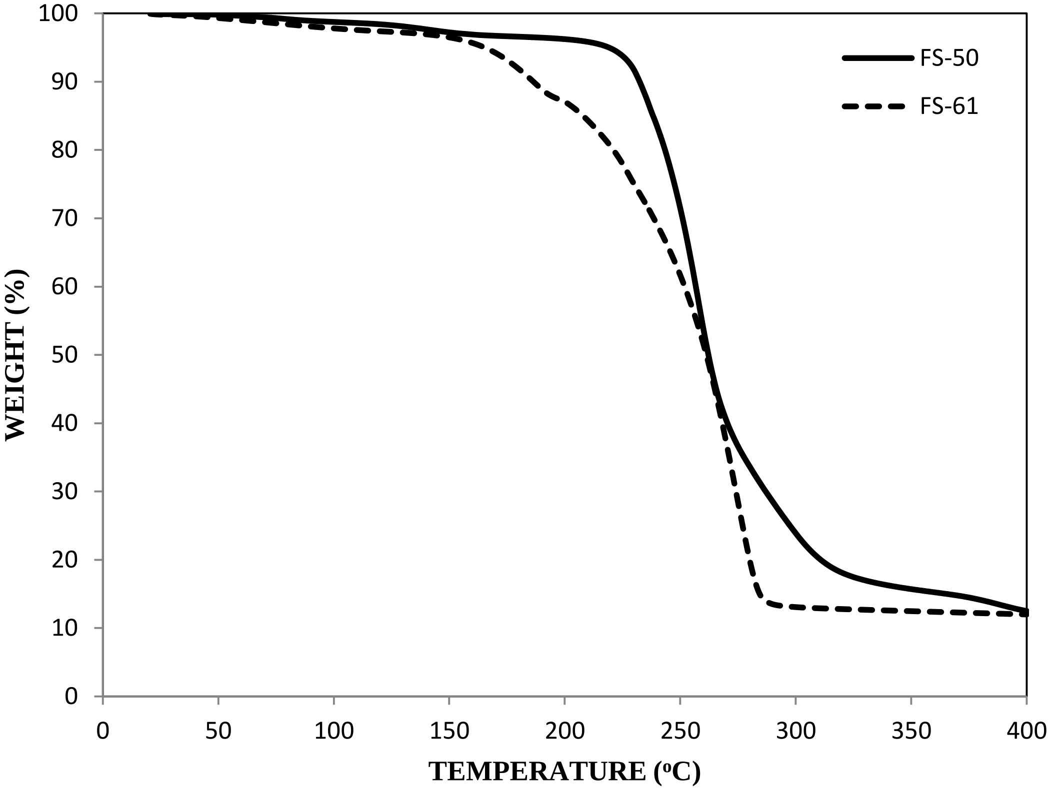


Figure 4. 13: TGA analysis for surfactant FS-50 and FS-61

4.2.2 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR was used for long period thermal stability tests where samples were aged for three weeks at 90^{o}C. Both the aged and the fresh samples of the surfactant were analyzed using FT-IR to investigate any changes in the structure. Water was used as background in FT-IR test rather than air to eliminate water absorbance in the surfactant solution. Figure (4.14) shows the spectrum for fresh and aged samples of surfactant FS-61. It was observed that both spectra are similar with relatively small difference. Figure (4.15) shows absorbance for surfactant FS-50 and again the same spectra were similar for fresh and aged samples. Similar peaks trend was observed in both surfactants which give an excellent indication about the structure stability of fluoro-surfactants at 90^{o}C for long time. Fluorine-Carbon bonds showed an excellent thermal stability even for long periods. Fluoro-surfactants showed good potential in EOR from thermal stability point of view. Similar thermal stability results were reported by Adkins et al. (2010) with ether sulfate surfactants while Siggel et al. (2012) reported thermally stable viscoelastic surfactants at 70^{o}C.

From thermal stability analysis, it can concluded that both fluoro-surfactants have excellent stability at typical reservoir temperature (T = 90^{o}C). Surfactants thermal degradation due to high temperature and long period of time of both fluoro-surfactants was not observed due to the strength and the stability of the fluorine-carbon bonds in surfactants FS-50 and FS-61.

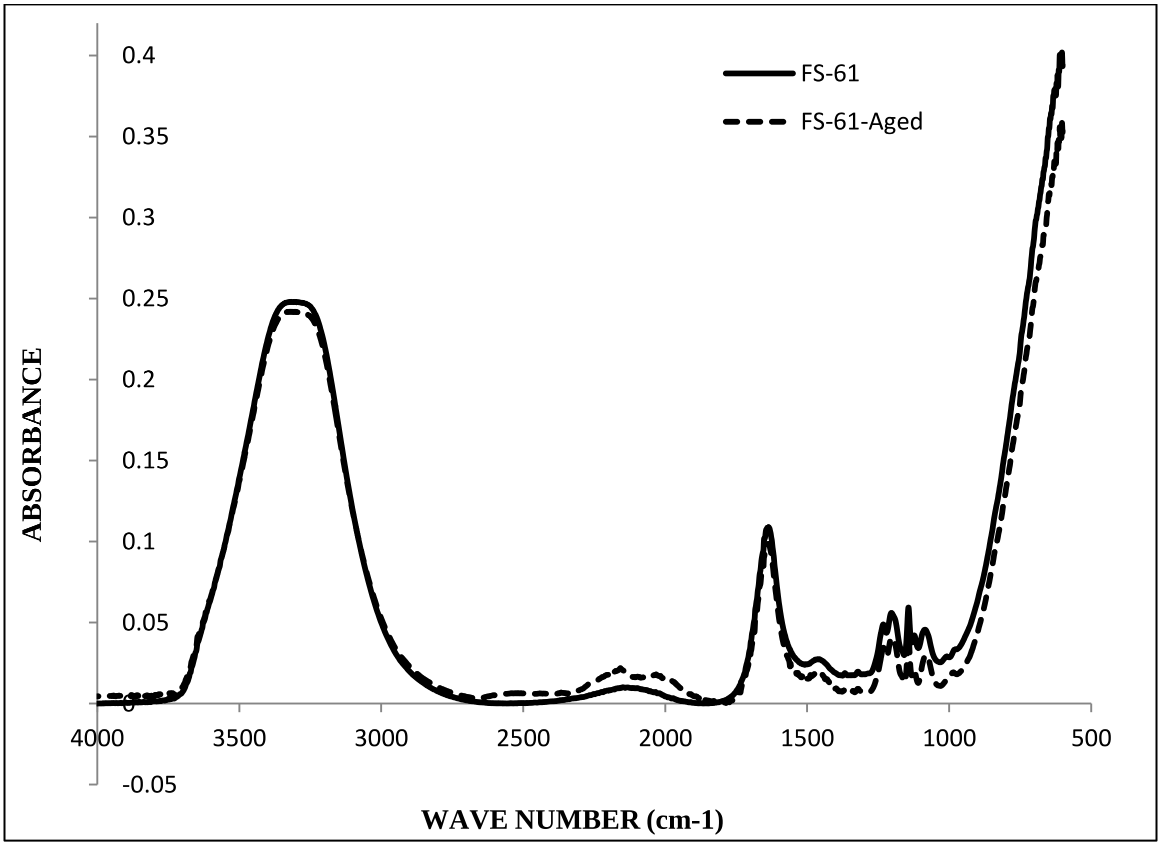


Figure 4. 14: FT-IR analysis for surfactant FS-61

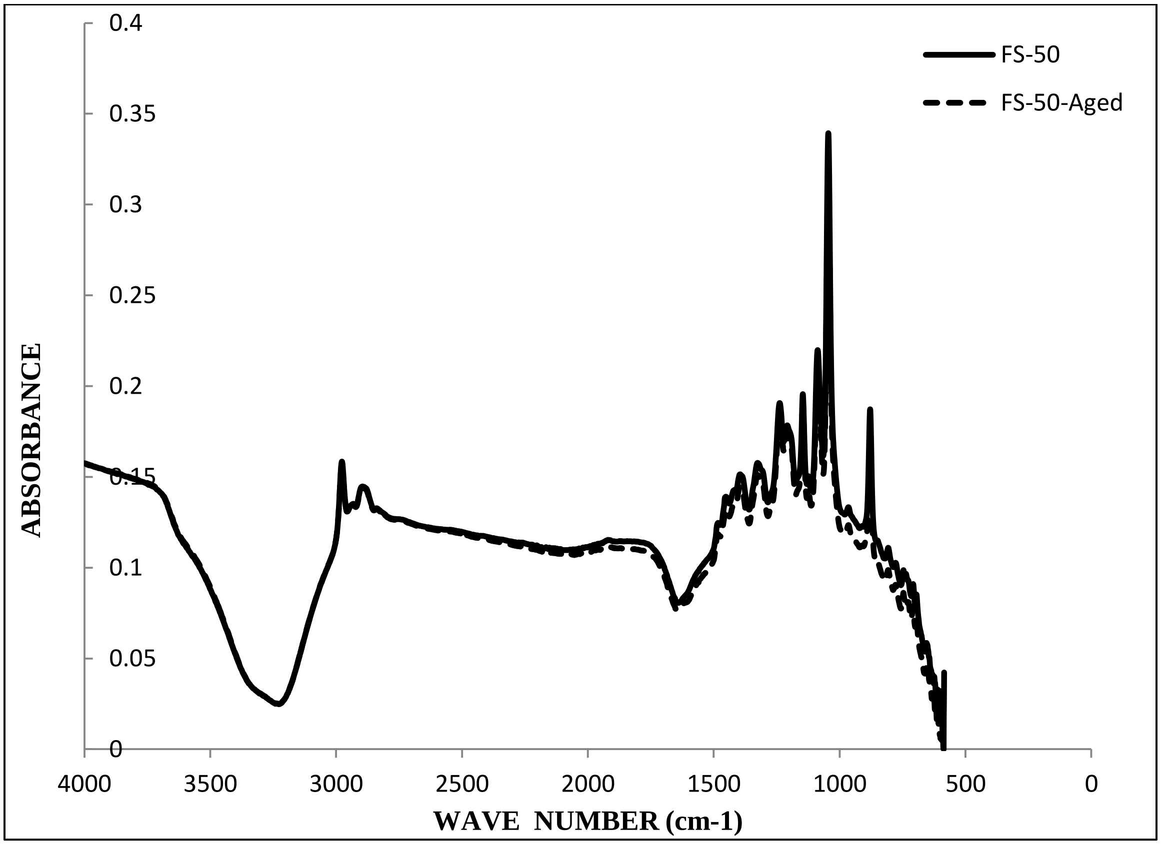


Figure 4. 15: FT-IR analysis for surfactant FS-50

4.3 ADSORPTION

Surfactants loss due to adsorption to the reservoir formation is considered as a major concern in EOR due to economic reasons. Loss of surfactants due to adsorption will limit their use again and additional fresh surfactants must be injected. Static adsorption was performed to study surfactants adsorption in carbonate formation. Precipitated calcium carbonate (PCC) in powder form was used as carbonate formation. Powder of PCC has higher surface area compared to actual carbonate rocks. Adsorption experiments lasted about three days to reach equilibrium. So, low adsorption in PCC indicates the good potential of surfactant in EOR from adsorption point of view. UV-vis was used to measure surfactant concentration in the samples after adsorption experiments. Eight samples were tested with different conditions as shown earlier in Table (3.4). Only four of the eight samples contain surfactant FS-50. Cations and anions adsorption was also investigated where IC was used to measure their concentrations. To check the accuracy of measuring salts concentration using IC, five samples from the same initial sea water were tested and all the samples showed similar results except in the case of Na^+ and Cl^- ions. This inaccuracy is due to their large concentration in sea water where error in dilution has major impact on measuring ions concentrations. However, Mg^{++}, Ca^{++}, and SO_4^{--} concentrations were similar in the five samples. Figure (4.16) shows adsorption density for cations and anions for the eight samples. Adsorption density is the amount of adsorbate per unit mass of adsorbent. It is the amount of surfactant or the amount of ions at the PCC solid surface. The positive values indicate adsorption of salt ions from the brine solution to the PCC while negative values indicate desorption from PCC to the brine solution.

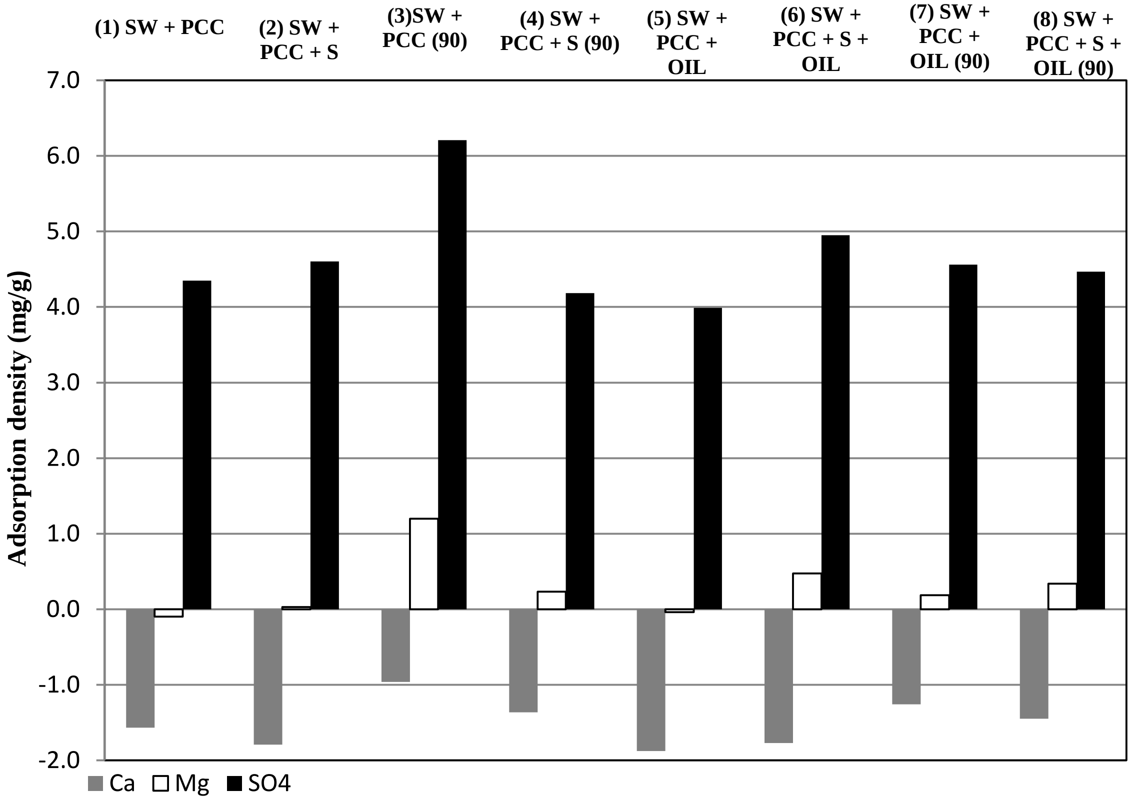


Figure 4. 16: Adsorption density for Magnesium, Calcium and Sulfate

4.3.1 Calcium Adsorption

Calcium ions are available in both brine solution and PCC formation. Both adsorption and desorption of calcium ions can take place. However, the net adsorption density will be measured. The first sample (SW+PCC at 25^{o}C) in Figure (4.16) shows desorption of calcium ions from PCC to the brine solution at 25^{o}C. Similar behavior was noticed in sample 2 (SW+PCC+S at 25^{o}C). Surfactant FS-50 showed small influence on adsorption of calcium ions at low temperature. Sample 3 (SW+PCC at 90^{o}C) and sample 4 (SW+PCC+S at 90^{o}C) were tested at higher temperature. It was noticed that higher temperature at 90^{o}C reduced desorption of calcium ions from the PCC to the brine solution. However, the presence of surfactant caused higher desorption of calcium to the brine solution. Sample 5 (SW+PCC+OIL at 25^{o}C) and sample 6 (SW+PCC+OIL+S at 25^{o}C) were tested in the presence of oil. The presence of oil increased slightly calcium desorption to the brine solution compared to sample 1 and sample 2. The influence of surfactant was very small in the presence of oil. At higher temperature, the presence of oil has no effect on calcium desorption as sample 7 (SW+PCC+OIL at 90^{o}C) and sample 8 (SW+PCC+OIL+S at 90^{o}C) showed. These samples had similar results compared to samples 3 and 4. However, as temperature is increased to 90^{o}C calcium desorption decreased.

4.3.2 Magnesium Adsorption

Magnesium ions will never show desorption process since PCC has no magnesium ions. Only adsorption of magnesium ions from the brine to the PCC can take place. The first two samples 1 (SW+PCC at 25^{o}C) and 2 (SW+PCC+S at 25^{o}C) showed no adsorption of magnesium ions from the brine solution to the PCC at 25°C. However, at higher temperature of 90°C, magnesium ions showed low adsorption process as samples 3 (SW+PCC at 90°C) and 4 (SW+PCC+S at 90°C) showed. The presence of surfactant FS-50 in sample 4 reduced adsorption of magnesium ions to the PCC. Sample 5 (SW+PCC+OIL at 25°C) and sample 6 (SW+PCC+OIL+S at 25°C) were tested with the presence of oil. Sample 5 showed no adsorption while sample 6 showed again low adsorption of magnesium in the present of surfactant FS-50. Sample 7 (SW+PCC+OIL at 90°C) was tested at higher temperature and no effect on magnesium adsorption was observed. Sample 8 (SW+PCC+OIL+S at 90°C) was tested at higher temperature with the presence of surfactant FS-50. It showed slightly low adsorption of magnesium ions from the brine solution to the PCC. The presence of oil at high temperature reduced magnesium adsorption compared to samples 3 and 4 which were tested with the absence of oil. Sakuma et al. (2013) reported similar adsorption of Mg^{++} ions at the surface of $CaCO_3$. They showed that surface Ca is replaced by Mg^{++} ions. Oil recovery is enhanced in carbonate reservoirs when both Mg^{++} and SO_4^{--} are present (Sakuma et al. 2013).

4.3.3 Sulfate Adsorption

Sulfate ions always show adsorption from the brine solution to the PCC. The first two samples 1 (SW+PCC at 25°C) and 2 (SW+PCC+S at 25°C) showed similar results of adsorption. The presence of surfactant in sample 2 showed no effect on adsorption process. Samples 3 (SW+PCC at 90°C) and 4 (SW+PCC+S at 90°C) were tested at higher temperatures. Higher temperature increased the adsorption of sulfate ions as samples 3 showed while the presence of surfactant FS-50 at higher temperature caused reduction in sulfate adsorption. Samples 5 (SW+PCC+OIL at 25^oC) and 6 (SW+PCC+OIL+S at 25^oC) included the presence of oil. It was noticed that oil has no effect on sulfate ions adsorption. At higher temperature, the presence of oil in sample 7 (SW+PCC+OIL at 90^oC) and sample 8 (SW+PCC+OIL+S at 90^oC) has again no effect on sulfate adsorption compared to samples 1 and 2. Sulfate ions showed major adsorption from brine solution to the PCC. Sulfate ions have higher ion strength with calcium compared to carbonate ions. Carbonate ions on the PCC were replaced by sulfate ions while carbonate ions were desorbed to the brine solution. UV-vis showed no absorbance when sea water was tested while a clear absorbance was observed when sea water with PCC was tested. It was a clear indication that carbonate ions desorbed to the brine solution and caused absorbance. Sulfate adsorption on the surface of $CaCO_3$ was also reported by Sakuma et at. (2013).

4.3.4 Surfactants FS-50 Adsorption

In adsorption experiments, only surfactant FS-50 was used due its ability to tolerate salts. Surfactant FS-61 was excluded because it precipitates in sea water. To measure adsorption of surfactant FS-50 in carbonate formation, UV-vis was used to measure the absorbance of surfactant in samples 2 (SW+PCC+S at 25^oC), 4 (SW+PCC+S at 90^oC), 6 (SW+PCC+OIL+S at 25^oC) and 8 (SW+PCC+OIL+S at 90^oC). First, calibration plot was constructed by measuring the absorbance of known surfactant FS-50 concentration. The plot is shown in Figure (4.16). Absorbance of PCC was also measured in UV-vis for samples 1 (SW+PCC at 25^oC), 3 (SW+PCC at 90^oC), 5 (SW+PCC+OIL at 25^oC) and 7 (SW+PCC+OIL at 90^oC). These samples contain no surfactant. Absorbance of PCC will be subtracted from the total absorbance of samples 2, 4, 6 and 8 which contain both surfactant and PCC. Absorbance of surfactant was used to recalculate surfactant concentration in samples 2, 4, 6 and 8 after adsorption experiments using the calibration curve in Figure (4.17). After getting surfactant concentration, adsorption density using equation (3.1) was calculated as shown in Table (4.2). The initial concentration of surfactant FS-50 in all samples was 0.3 wt% which is higher than CMC. Maximum adsorption density is achieved at surfactant concentration above CMC. Samples 2 and 4 showed lower adsorption density compared to samples 6 and 8. The presence of oil increased adsorption of surfactant FS-50. Similar adsorption density results have been reported by Luciani and Denoyel, (1996) with polydisperse surfactants (Triton). Gao et al. (2013) also reported similar adsorption density results with Gemini surfactants. Lower adsorption density results have been reported in their work.

From adsorption analysis, major sulfates adsorption was observed on the surface of solid PCC while carbonate ions were desorbed to the brine solution. Carbonate desorption was confirmed using UV-vis. Fluoro-surfactant FS-50 showed relatively low adsorption density on the surface of the solid PCC which is a requirement in EOR applications due to economic reasons. Fluoro-surfactant FS-61 was excluded due to its incompatibility with brine solution.

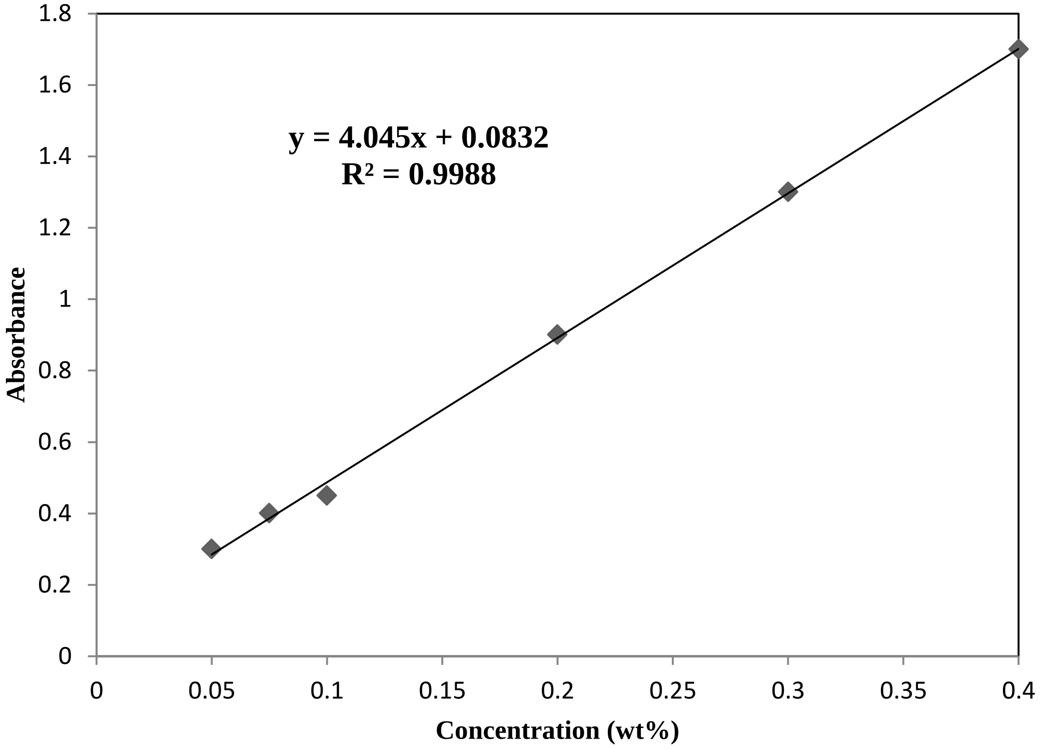


Figure 4. 17: Calibration curve for surfactant FS-50 using UV-vis

Table 4. 2: Adsorption results for surfactant FS-50

Sample	**Conditions**	**Absorbance**	**Concentration (wt%)**	**Γ(mg/g)**
2	SW+PCC+S at 25°C	0.4	0.261	5.856
4	SW+PCC+S at 90°C	0.4	0.261	5.856
6	SW+PCC+OIL+S at 90°C	0.35	0.22	12.02
8	SW+PCC+OIL+S at 25°C	0.35	0.21	12.03

SW: Sea water**, PCC**: Precipitated $CaCO_3$, **S**: Surfactant FS-50.

4.4 INTERFACIAL TENSION (IFT)

Surfactants are used in EOR to reduce the interfacial tension (IFT) between oil and the injected fluid. Decreasing IFT will cause an increase in capillary number and as a result oil recovery will increase. Figure (4.18) shows the effect of salts concentration on the interfacial tension between brine solution and oil. Three different salinity concentrations were tested (0 ppm, 28,500 ppm, 57,000 ppm). Deionized water with zero salts concentration gave high values of IFT which was 14.7 mN/m at 40^{o}C. As temperature is increased, IFT decreased and it reached its minimum value at about 75^{o}C where IFT was 9.4 mN/m. Increasing temperature caused 37% reduction in IFT in the case of deionized water. As salinity concentration is increased to 28,500 ppm IFT is reduced compared to deionized water. The reduction was about 42%. Salts have clear effect on IFT values. Increasing temperature in the presence of salts has no major effect on IFT. Minor change in IFT was observed with increasing temperature. Increasing salinity concentration further to 57,000 ppm showed lower IFT. The reduction was about 53% compared to deionized water at low temperature. Salts diffuse to the interface between oil and brine and reduce IFT. Figure (4.19) shows IFT values for solutions of deionized water with different FS-61 concentrations. In general, surfactant FS-61 showed relatively high IFT values compared to hydrocarbon surfactants. Ultra low IFT values have been reported by Wang et al. (2010) with Petroleum Sulfonate surfactants. However, Sharma et al. (2011) reported similar IFT values as fluoro-surfactants with NP ethoxylates surfactants. Four different surfactant FS-61 concentrations were used (0.1 wt%, 0.3 wt%, 0.5 wt% and 1 wt%). A temperature ramp test was performed for each surfactant concentration. 0.1 wt% surfactant concentration gave IFT value of 12.3 mN/m at 46^{o}C. As temperature is increased, IFT decreased slightly to reach a plateau of IFT equal to 11.5 mN/m. Although these values of IFT are lower than deionized water IFT values, it is relatively high for EOR applications. Increasing surfactant concentration to 0.3 wt% lowered IFT where it reached a value of 6.5 mN/m. As solution temperature is increased, no effect on IFT values was observed. Surfactant concentration of 0.5 wt% gave higher IFT compared to 0.3 wt%. It was about 10.2 mN/m at 50^oC and it decreased when temperature is increased to reach 8 mN/m at 80^oC. Further increase in surfactant concentration to 1 wt%, IFT was dropped. It showed a value of 5.6 mN/m up to 50^oC and then it decreased to about 2.6 mN/m up to 65^oC. After 65^oC, IFT showed a plateau of IFT equal to 2.6 mN/m. Surfactant FS-61 showed two concentrations where there is reduction in IFT which are 0.3 wt% and 1 wt%. The reason for this behavior is that surfactant FS-61 has two critical micelles concentrations (CMC) because surfactant FS-61 has a mixture of one fluorinated chain and two fluorinated chains on the phosphates group. The effect of salts on IFT in the presence of surfactant FS-61could not be tested due to the incompatibility of FS-61 with salts. Figure (4.20) shows IFT as a function of surfactant FS-61 concentration. It was observed that two minima at 0.3 wt% and 1 wt% surfactant concentration. Surfactant FS-61 was also tested in the presence of co-surfactants. Two co-surfactants were used which are Alfoterra 123-8s (anionic propoxylate surfactant from SASOL) and SS-885 (betain based amphoteric surfactant from Oil Chem). The effect of these two co-surfactants is shown in Figure (4.21) with 0.3 wt% FS-61 concentration and 0.1 wt% co-surfactant concentration. The reason for the chosen 0.3 wt% concentration of FS-61 is based on its IFT value. It was the second lowest IFT after surfactant concentration of 1 wt%. However, 1 wt% concentration is relatively high in EOR applications. The addition of SS-885 to surfactant FS-61 reduced IFT value compared to solution of FS-61 alone. The effect of temperature was almost the same but it was more noticeable in the case where co-surfactant was added. The reduction was about 23% at low temperature and it was 43% at high temperature. In the case of the other co-surfactant, the addition of Alfoterra showed exactly the same trend but it shifted IFT values from 6.5 mN/m to about 2 mN/m which is 69% reduction in IFT. Fluoro-surfactant FS-61 showed low potential with co-surfactants on IFT. The presence of Fluorine atoms on the hydrocarbon chain of FS-61 caused higher IFT. However, fluoro-surfactant FS-61 showed thermal stability at high temperatures. The reduction on IFT was not too much when it was compared with values at low temperatures. Surfactant FS-61 is not useful in EOR applications because it cannot tolerate salts.

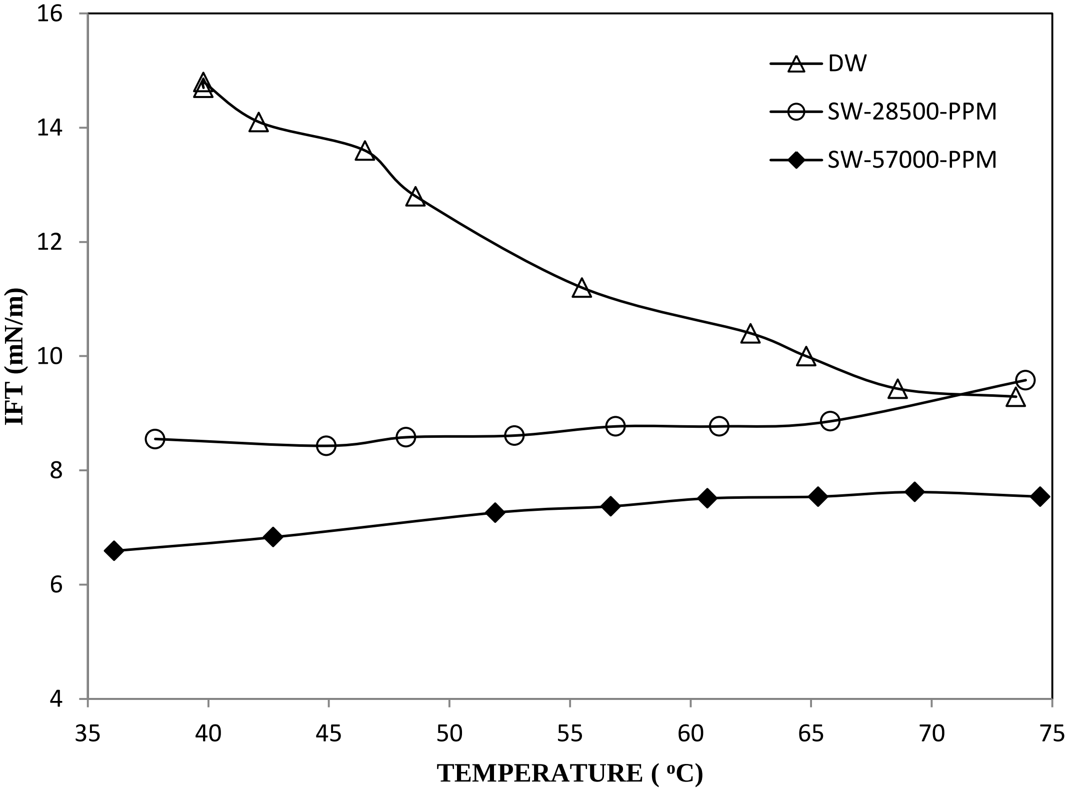


Figure 4. 18: Effect of salinity on IFT

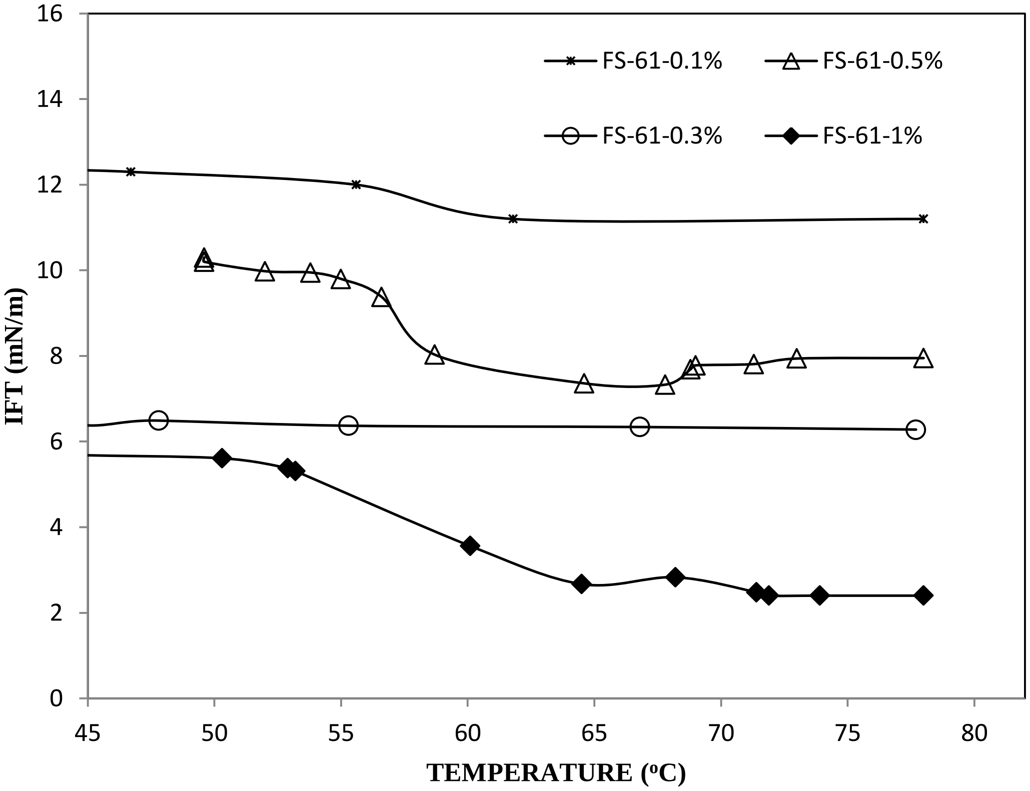


Figure 4. 19: Effect of surfactant FS-61 concentration on IFT in deionized water

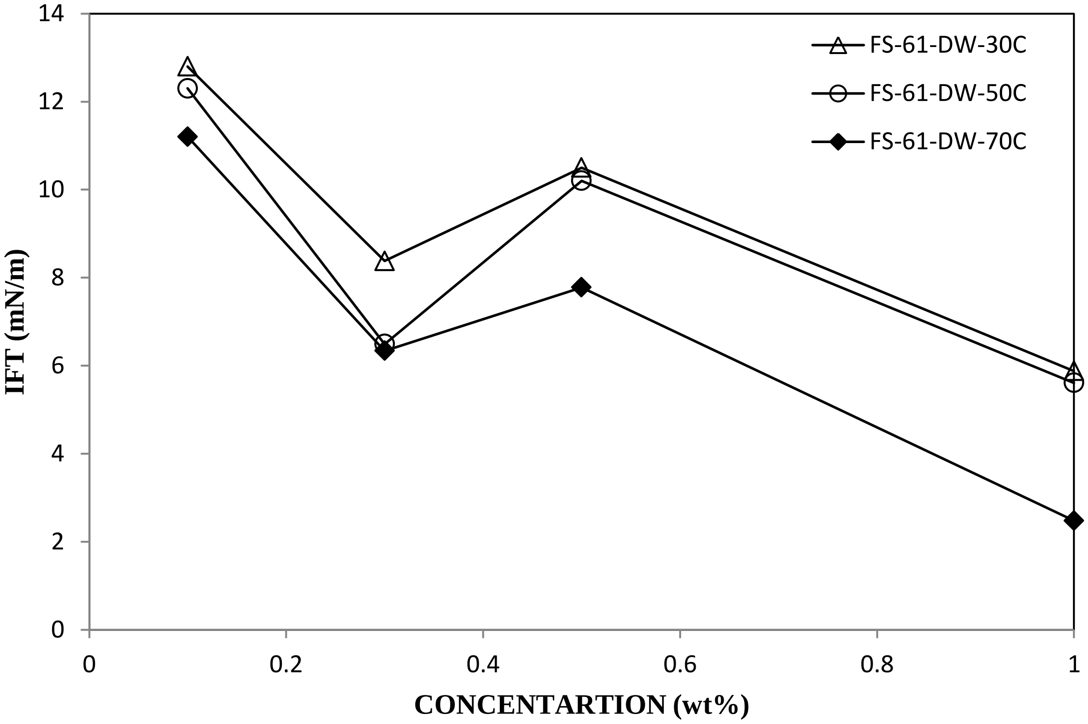


Figure 4. 20: IFT as a function of surfactant FS-61 concentration

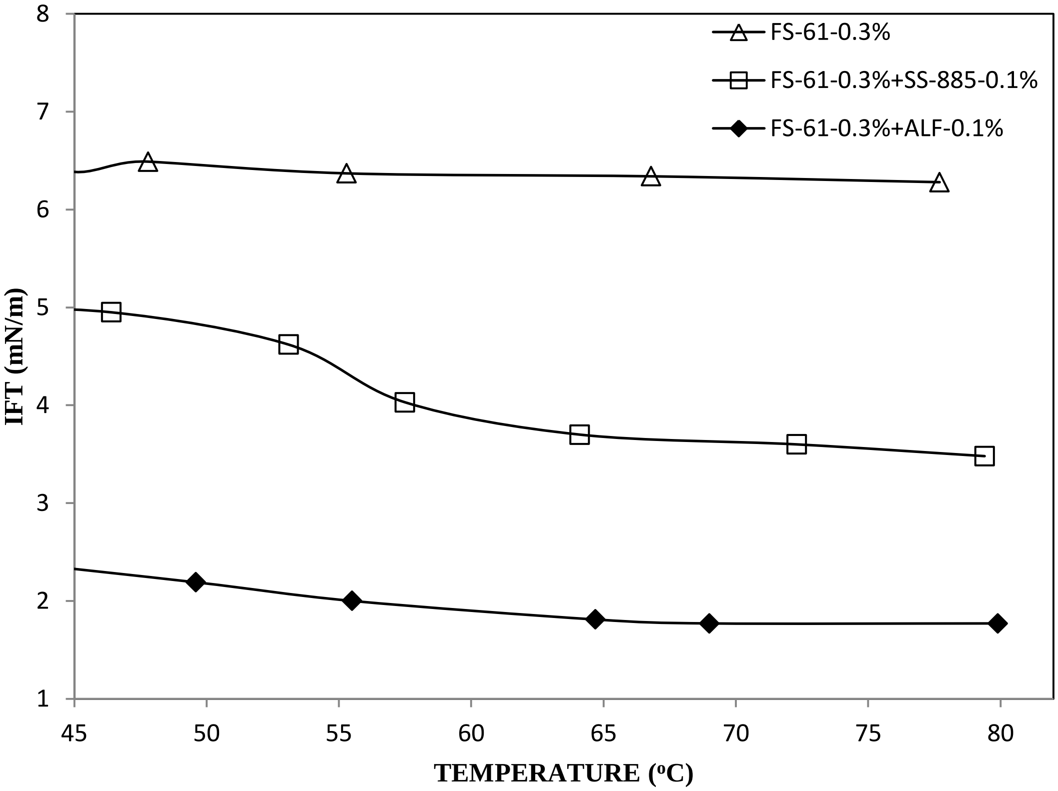


Figure 4. 21: Effect of co-surfactants on IFT in the presence of FS-61 in deionized water

Fluoro-surfactant FS-50 showed good compatibility with salts and it also showed lower IFT values in the presence of salts or the presence of co-surfactants since it is partially fluorinated. Figure (4.22) shows IFT results of FS-50 in deionized water. It gave lower IFT than surfactant FS-61. It was noticed that lower surfactant concentrations were able to reduce IFT compared to higher concentrations. Both surfactant concentrations of 0.05 wt% and 0.1 wt% gave IFT value of 3.2 mN/m within temperature range of 30^{o}C to 80^{o}C. Although these IFT values are not ultralow IFT, surfactant FS-50 showed good stability with temperature which is due to the presence of Fluorine atoms on the hydrocarbon chain of the surfactant. Increasing surfactant concentration to 0.2 wt%, 0.3 wt% and 1 wt% showed higher IFT values. So, surfactant FS-50 has very low critical micelles concentration (CMC) which is considered as a positive sign since low concentration of chemicals is required to minimize the cost of these chemicals. Figure (4.23) shows IFT results for FS-50 in the presence of salts. The concentration of salts in sea water was 57,000 ppm. Surfactant concentration of 0.05 wt% gave value of IFT equal to 1.72 mN/m at 30^{o}C and it showed a reduction in IFT as temperature was increased to reach 1.4 mN/m at 80^{o}C. Higher concentration of 0.1 wt% reduces IFT to 0.95 mN/m at 30^{o}C. However, increasing temperature showed no effect and IFT stayed almost constant up to temperature of 80^{o}C. Surfactant concentration of 0.1 wt% is the optimum concentration because increasing surfactant concentration to 0.2 wt% showed an increase in IFT. Figure (4.24) shows IFT as a function of surfactant FS-50 concentration in deionized and sea water. Optimum concentration was 0.1 wt% which is good for EOR. Similar IFT results have been reported by Santa et al. (2011) with APG surfactants. Emulsions are formed at the optimum surfactant concentration. Concentration of 0.1 wt% will be tested in phase behavior experiments to indicate if surfactant FS-50 is able to form emulsions. Lower values of IFT were observed with the addition of co-surfactants. Figure (4.25) shows a comparison between the optimum surfactant FS-50 concentration which is 0.1 wt% and 0.1 wt% of FS-50 with 0.05 wt% concentration of co-surfactant SS-885. The addition of co-surfactant reduced IFT to ultralow values. IFT decreased from 0.95 mN/m to 0.00798 mN/m at 30°C. Then, IFT increased as temperature is increased which is due the instability of the combination at high temperature. This caused lower functionality of the surfactants combination which increased slightly IFT to reach a maximum of 0.12 mN/m at 80°C. Another co-surfactant was also tested with FS-50 which is Alfoterre 123-8s. The surfactant solution has FS-50 with concentration of 0.1 wt% and co-surfactant concentration of 0.05 wt%. The solution showed dynamic IFT behavior as shown in Figure (4.26) where IFT changed with time at fixed temperature. It was noticed that higher temperature caused higher IFT values. At 70°C, IFT was 0.511 mN/m and it reached a plateau of IFT equal to 0.295 after 420 seconds. Lower temperature of 50°C showed IFT of 0.231 mN/m initially and it reached a plateau of 0.087 mN/m after 520 seconds. At temperature of 30°C, IFT was initially 0.179 mN/m and it reached a plateau of IFT equal to 0.00337 mN/m after 520 seconds which is ultralow value of IFT. Co-surfactant Alfoterra 123-8s is not stable at high temperatures which explain the increasing in IFT with increasing temperature. The co-surfactant starts to degrade and IFT increases at higher temperatures. However, up to 70°C the solution showed promising results of IFT. Wang et al. (2010) reported similar ultralow IFT values with the addition of co-surfactants.

From IFT measurements, fluoro-surfactant FS-61 did not show ultralow IFT values even with the presence of co-surfactant in deionized water. On the other hand, fluoro-surfactant FS-50 showed IFT of 0.9 mN/m in the presence of salts. This value was measured at surfactant concentration of 0.1 wt% which is considered as low concentration in EOR applications. Ultralow IFT values were only measured with the presence of co-surfactants. Fluorine atoms reduce the hydrophobicity of the surfactant tail and lower its interactions with oil. Surfactant FS-61 was excluded from core flooding experiments due to incompatibility with salts. Surfactant FS-50 will be tested in core flooding experiments with the optimum concentration of 0.1 wt% to measure oil recovery.

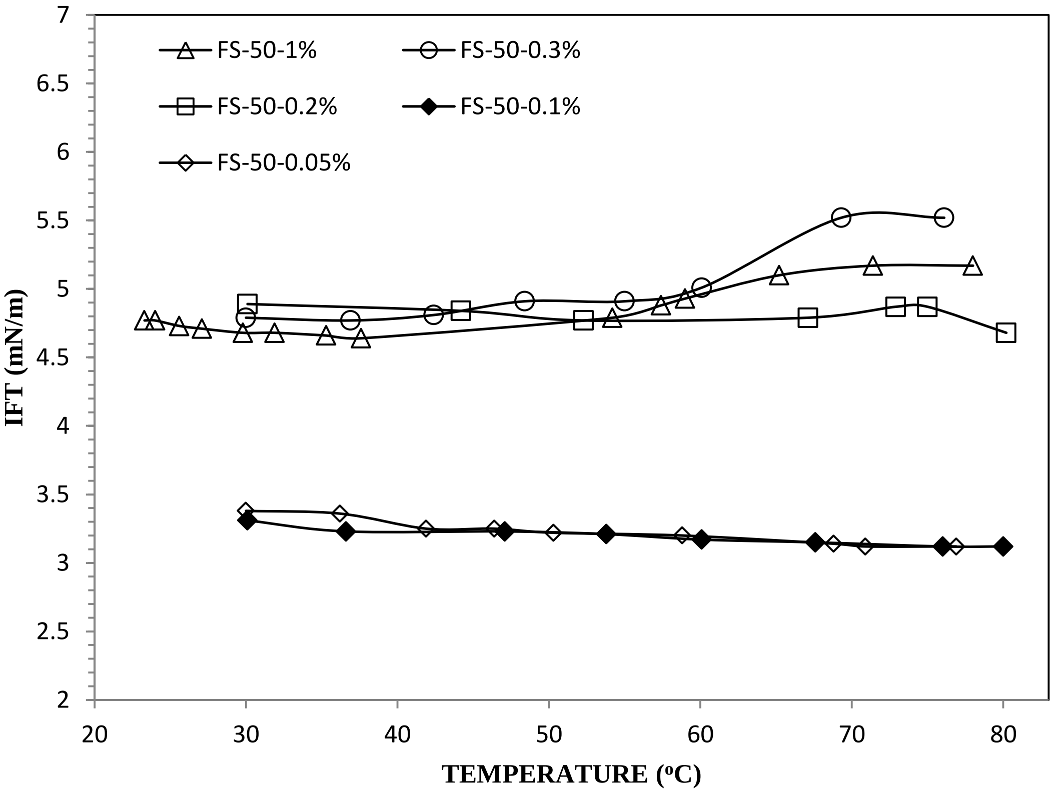


Figure 4. 22: Effect of surfactant FS-50 concentration on IFT in deionized water

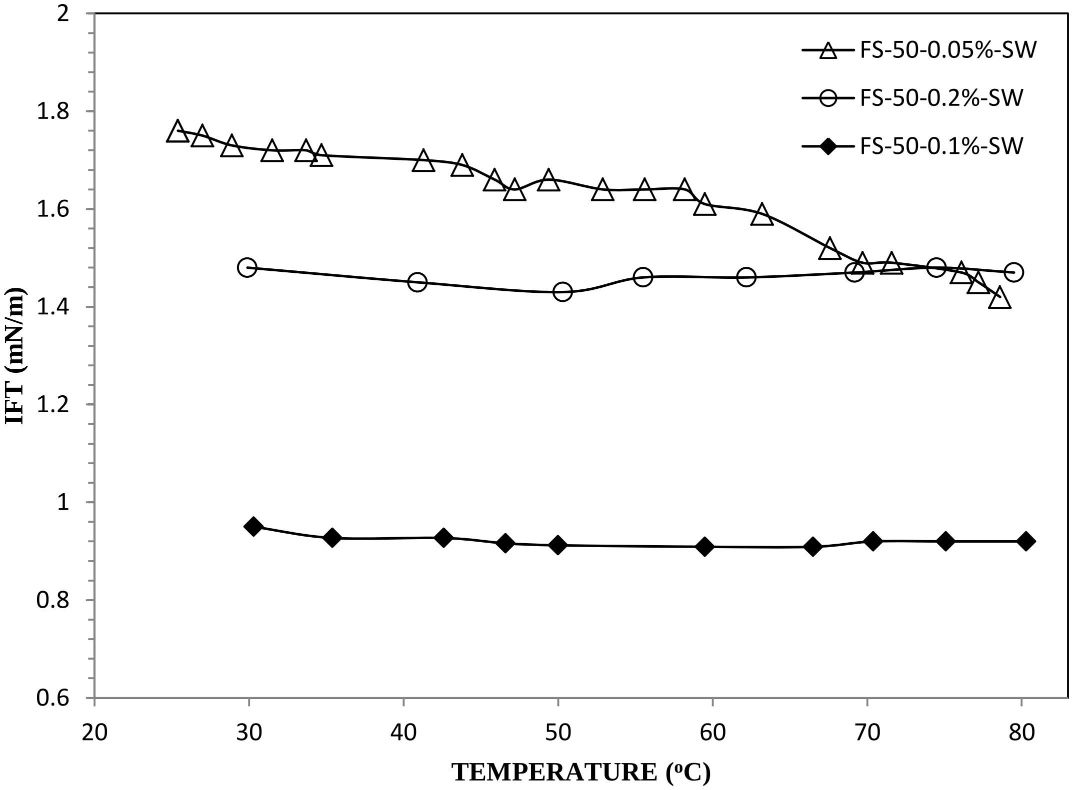


Figure 4. 23: Effect of surfactant FS-50 concentration on IFT in sea water

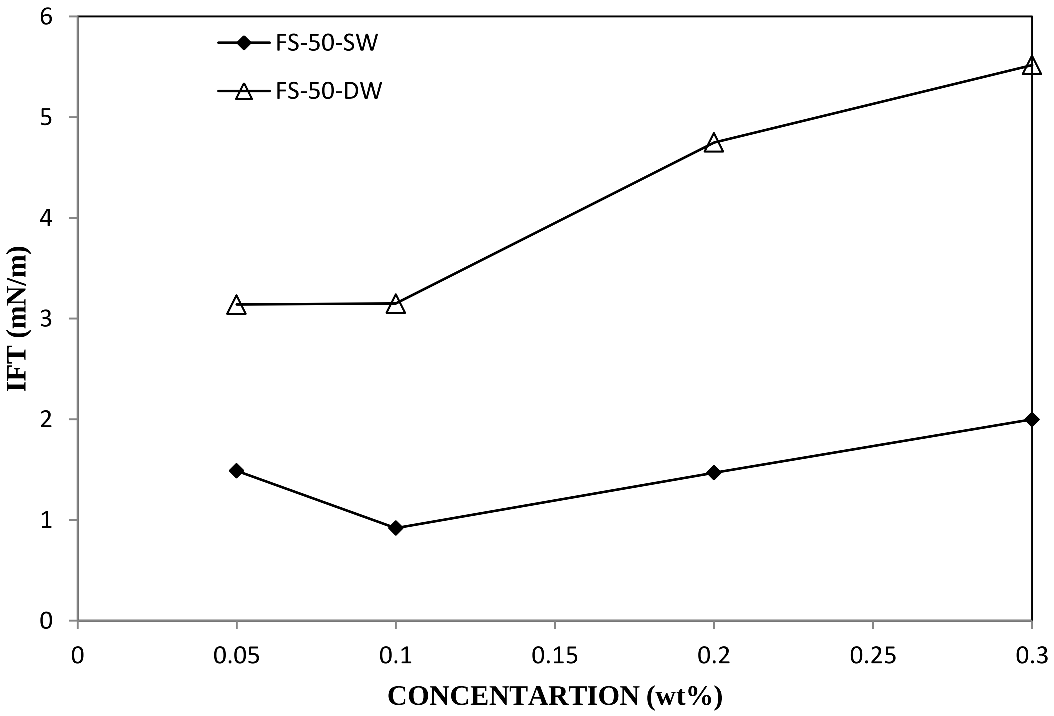


Figure 4. 24: IFT as a function of surfactant FS-50 concentration in deionized and sea water

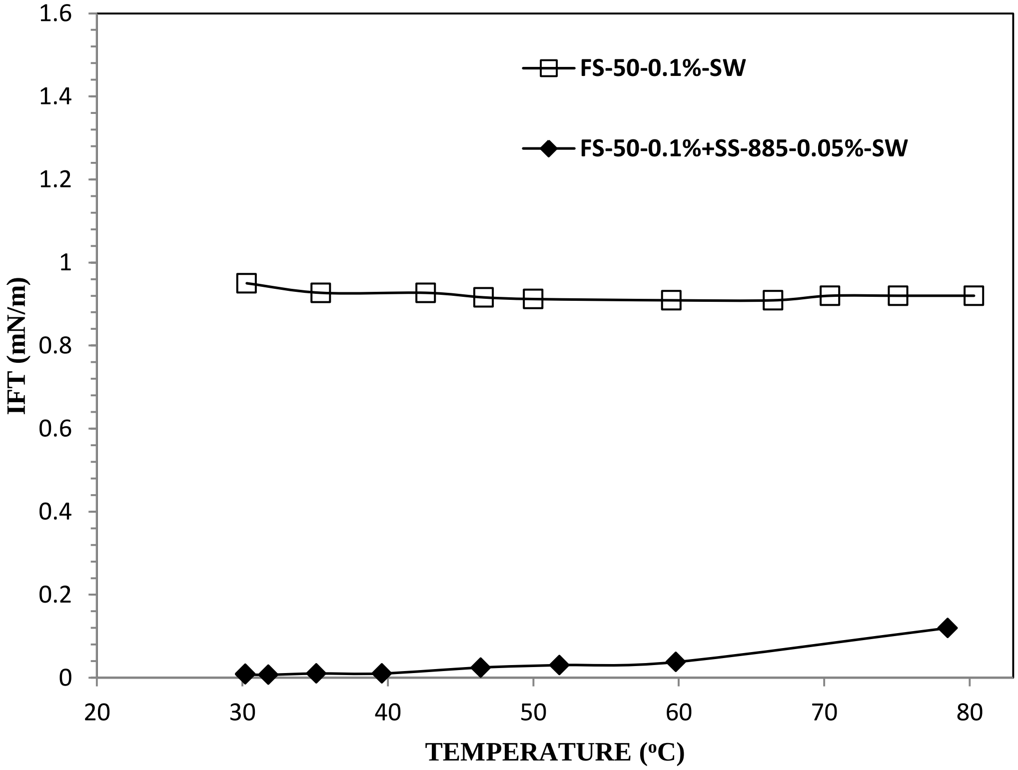


Figure 4. 25: Effect of adding co-surfactant SS-885 on IFT for FS-50 in sea water

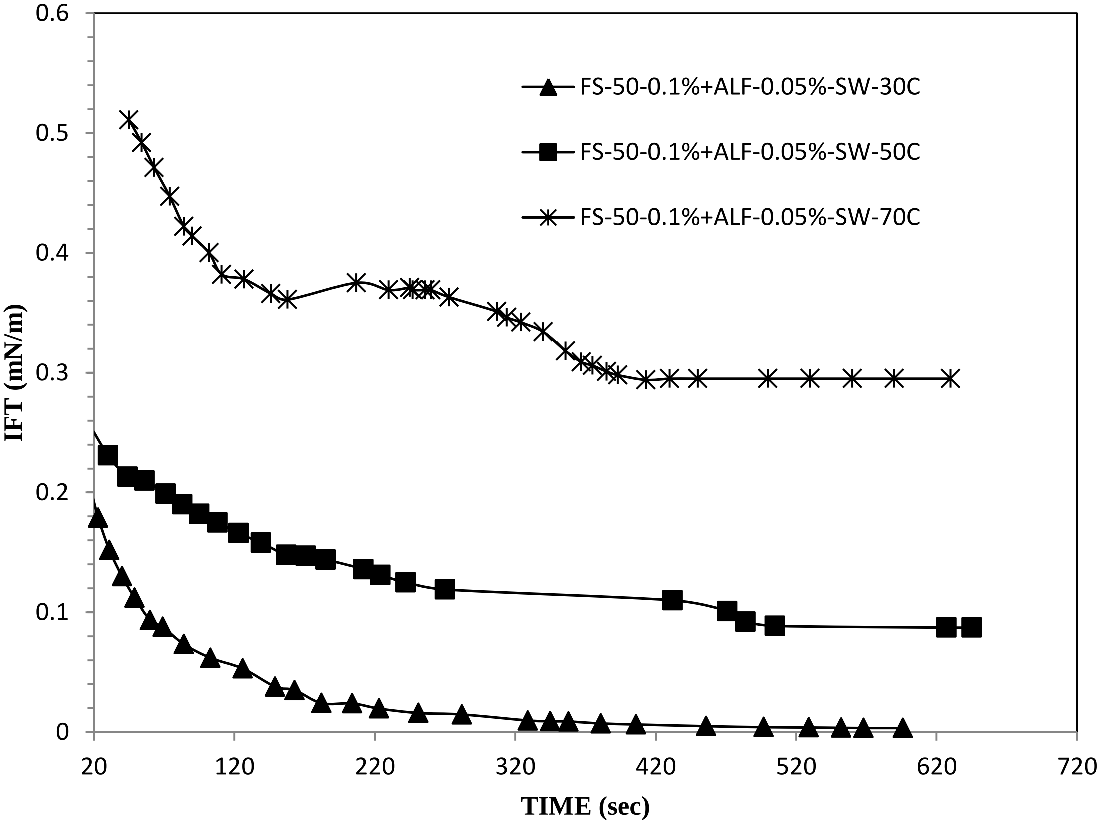


Figure 4. 26: Effect of adding co-surfactant Alfoterra on IFT for FS-50 in sea water

4.5 PHASE BEHAVIOR

Phase behavior experiments were performed to monitor Winsor phase behavior (type I, type II, type III). Three phase behaviors can be formed for oil, water and surfactant system. In Winsor type I system, surfactant forms oil in water microemulsion while in Winsor type II system, surfactant forms water in oil microemulsion. In Winsor type III system, surfactant forms separate microemulsion phase between both the oil and the water phases. The separated middle phase contains water, surfactant and oil. Winsor type III system is favorable for EOR and ultralow IFT can be achieved while Winsor type II is unfavorable for EOR. Ultralow IFT cannot be achieved with Winsor type I system. Surfactants with the ability to form phase III microemulsions are considered as good candidates for EOR applications. It shows the ability of the surfactant to interact well with both brine solution and oil. Phase behavior experiments can show the ability of certain surfactant in reducing IFT to ultralow values. A salinity scan test was performed to locate the salinity level where microemulsions are formed which is known as the optimal salinity. At the optimal salinity, equilibrium is between the microemulsions, the excess oil and the excess water phases. Correlations can be used to estimate IFT value using solubilization parameters at the optimum salinity. In general, fluoro-surfactants FS-61 and FS-50 are not capable to form microemulsions at different salinity levels. It is due to the existence of Fluorine atoms on the hydrocarbon chain of the surfactant. In the case of hydrocarbon surfactants, the hydrophilic head group can easily form interactions with the brine solution while the hydrophobic tail can form interactions with oil and it will modify the interfacial tension between the two liquids. However in the case of fluoro-surfactants where Fluorine atoms are on the hydrocarbon chain, Fluorine atoms occupy larger volume and prevent any interaction of carbon atoms with oil. Fluorine atoms reduce the hydrophobic property of the tail which will lower interactions with oil. As a result, it is difficult to form microemulsions with fluoro-surfactants. Equal volume of both oil and brine solutions was added into graduated tubes. The total volume was 10 ml and the initial interface was at 5 ml. Figure (4.27) shows pictures of phase behavior for surfactant FS-61 solution at 25^{o}C after 30 days where different surfactant concentrations were used in deionized water since it is incompatible with salts. Six samples were prepared with surfactant concentration of 0 wt%, 0.1 wt%, 0.3 wt%, 0.5 wt%, 0.7 wt% and 1 wt%. Type II phase was observed in all cases where oil phase was increased. A clear separation was observed only for 0 wt% and 0.1 wt% surfactant concentrations. The same concentrations were also tested at 90^{o}C. Figure (4.28) shows the phases at 90^{o}C after 15 days while Figure (4.29) shows the results after one month. Again type II phase was observed after 15 days however it was noticed that the volume of the oil phase was increased with increasing the surfactant concentration after 0.3 wt%. A clear separation was observed between the oil and the brine phases. After 30 days at temperature of 90^{o}C, the separation is clearer and the interface level is almost equal for all surfactant concentrations. The interface between the two phases is below 5 ml which means we have increasing in the volume of oil phase.

Figure (4.30) shows the results for surfactant FS-50 with concentration of 0.1 wt% and salinity scan from 0 ppm to 57,000 ppm at temperature of 25^{o}C after 30 days. No emulsions were formed with surfactant FS-50 at different salinities. It was observed that separation between the two phases at a level similar to the initial interface level as salinity increased. However, at salinity of 57,000 ppm, the oil phase volume was increased more. Figure (4.31) shows the results at 90^{o}C and all the samples showed almost the same trend with separation similar to the initial interface. No emulsions were formed. Surfactants FS-61 and FS-50 are not good in forming microemulsions which is due to the existence of Fluorine atoms on the hydrophobic part of the surfactant. Fluorine atoms act as layer between the oil and the hydrocarbon tail of the surfactant which will cause minimum interactions. It will be difficult to form emulsions since the hydrophobicity of the surfactant tail is low. Similar behavior was reported by Gao and Sharma, (2013) with Gemini surfactants where their surfactants were unable to form type III phase.

From phase behavior experiments, type III microemulsions were not observed using fluoro-surfactants FS-61 and FS-50. Type III microemulsions are favorable for EOR applications followed by type I system while type II system is unfavorable for EOR applications. Fluoro-surfactant FS-61 showed type II system at low temperatures while at high temperatures, a clear separation between the oil phase and the aqueous phase was formed. Fluoro-surfactant FS-50 also showed clear separation between the two phases at high temperatures.

Figure 4. 27: Phase behavior for surfactant FS-61in deionized water at 25^{o}C after 30 days

Figure 4. 28: Phase behavior for surfactant FS-61 in deionized water at 90°C after 15 days

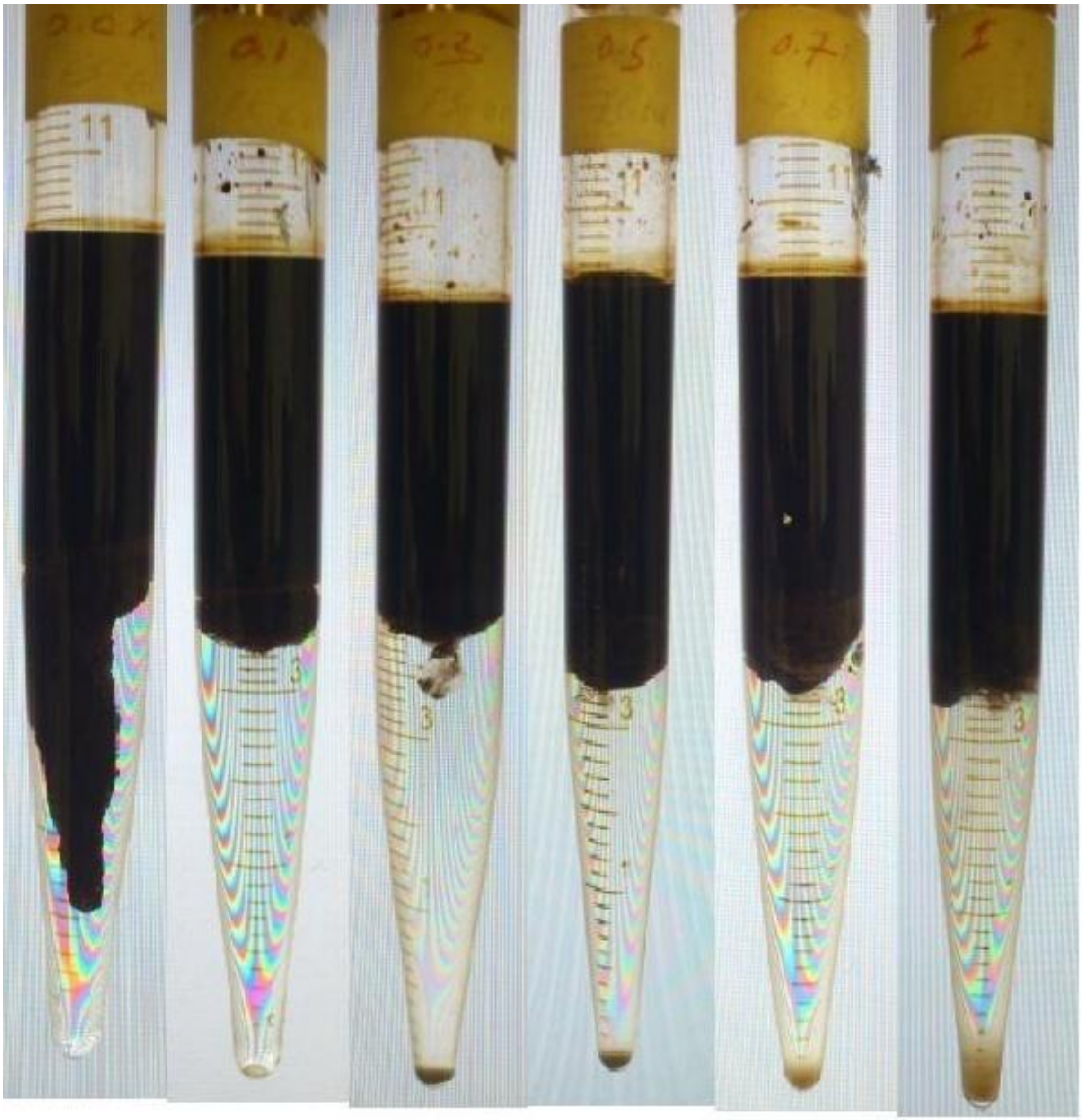


Figure 4. 29: Phase behavior for FS-61 in deionized water at 90°C after 30 days

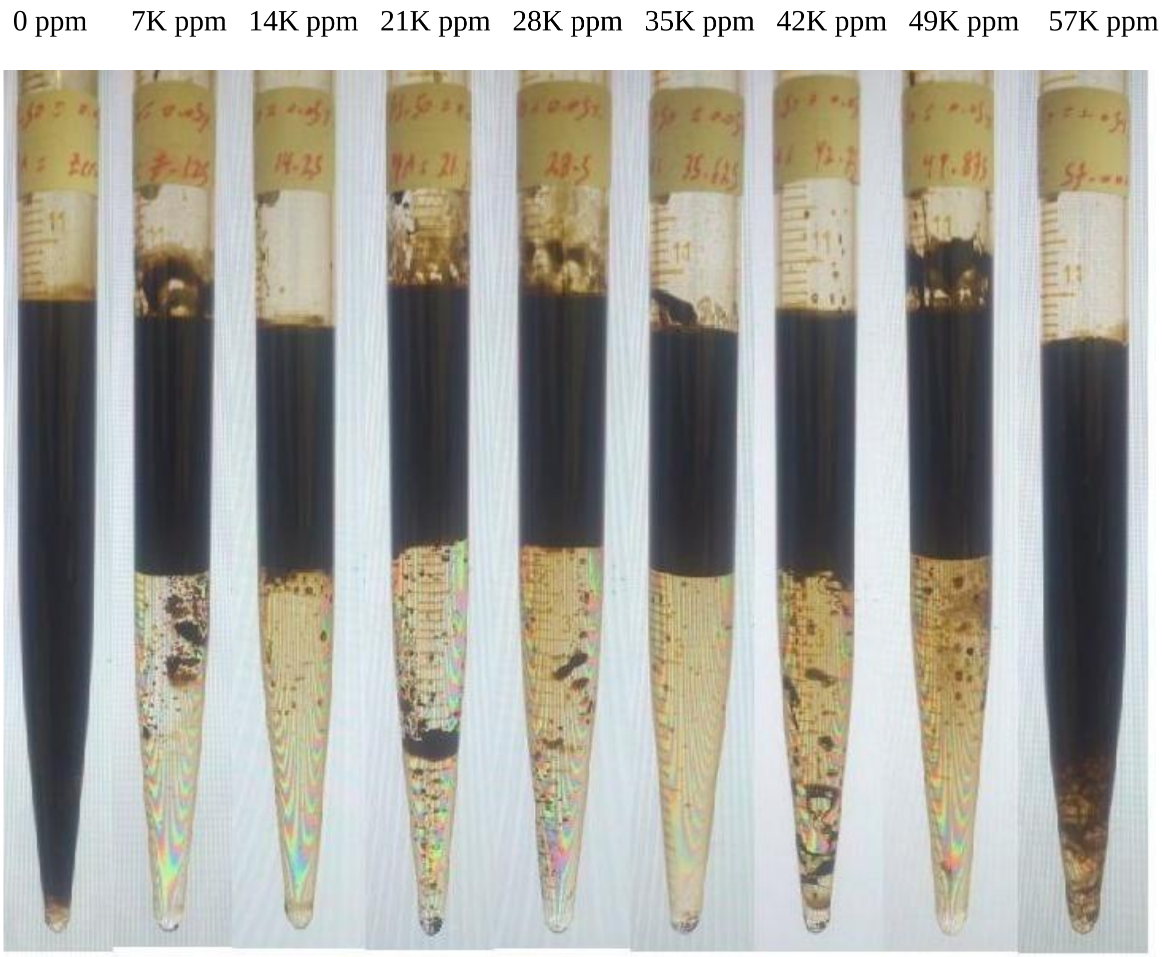


Figure 4. 30: Phase behavior for FS-50 (0.1 wt%) at 25^{o}C after 30 days

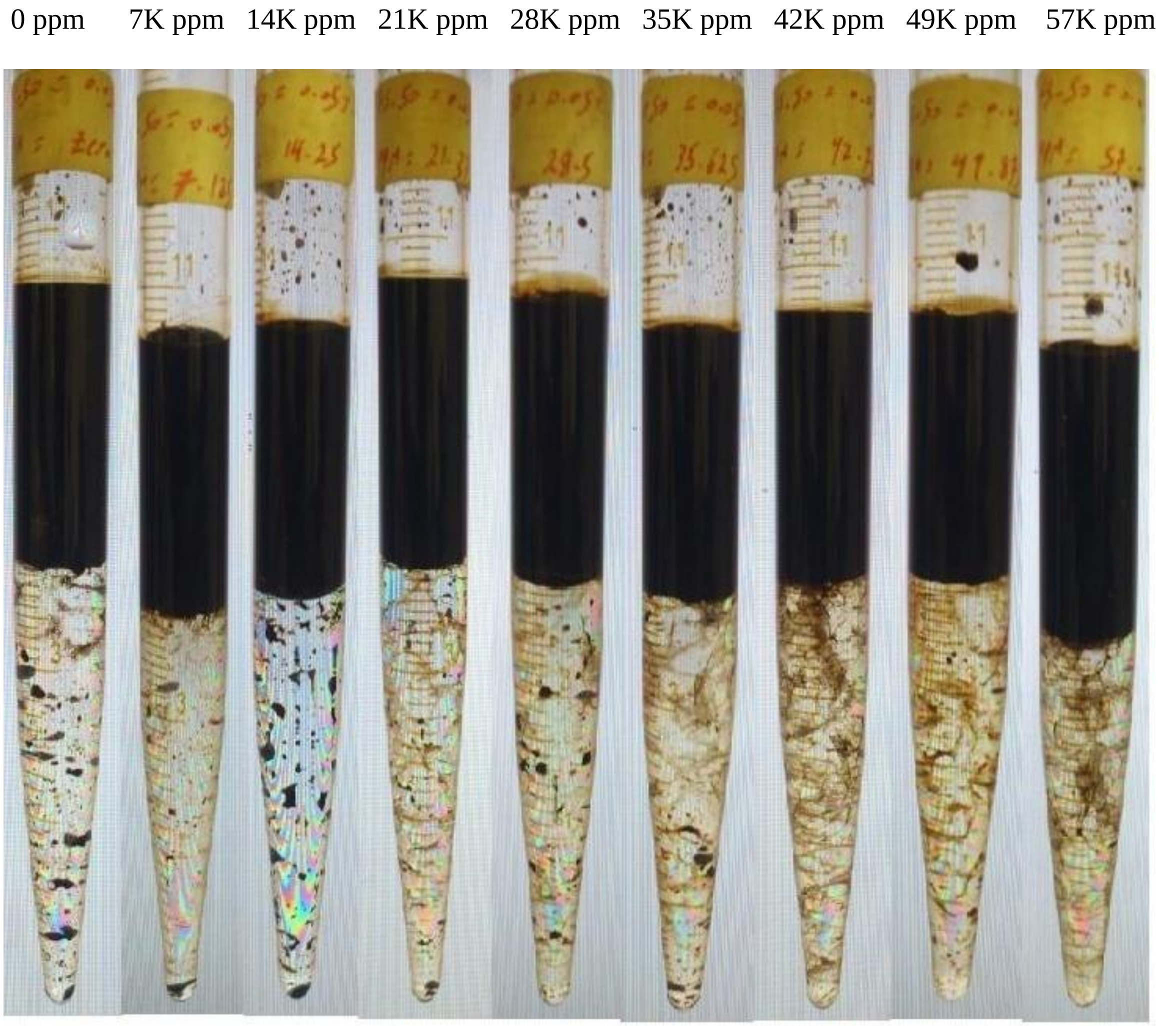


Figure 4. 31: Phase behavior for FS-50 (0.1 wt%) at 90^{o}C after 30 days

4.6 CORE FLOODING

Core flooding experiments were performed to investigate the potential of surfactant-polymer solution in EOR. Indiana limestone core sample was used. It is 3.654 cm in diameter and 30.455 cm in length. The porosity of the core sample is 0.174. The core sample has pore volume equal to 58 cc. It was calculated based on the difference between the dry and the wet weights of the core sample over formation water density. The permeability of the carbonate core sample was measured with formation water. The pressure drop across the core sample was measured at different flow rates of formation water as shown in Figure (4.32). Using Dracy's law for linear flow in equation (3.5), the core permeability was calculated and found to be 73.7 mD. It is low permeability value and the injected fluids must be treated well so pores won't be plugged. Oil must be filtered to remove particles that may cause pore plugging. The surfactant-polymer formulation must also have suitable viscosity at the test conditions so polymer chains won't plug the pores. After saturating the core sample with formation water, oil was injected to displace formation water. S_{wi} was calculated using equation (3.6) and found to be 23%. It shows that 23% of the pore volume is occupied by formation water. The other 77% of the pore volume is occupied by crude oil. Total oil volume in the core sample was around 45 cc. The core sample was aged for 15 days at 90^{o}C with oil to maintain equilibrium. Oil recovery process was started by flooding brine solution through the core to recover oil. Brine flow rate is 0.5 ml/min. The salinity of the brine solution was 57,000 ppm. The confining pressure was set at 2,000 psi. Confining pressure represents reservoir pressure which is the overbuilding pressure created by reservoir rocks. The pore pressure was set at 550 psi which is the pressure across the core sample. Temperature was set at

90^{o}C. About 2.3 pore volume of brine was injected and oil recovery was 44% as shown in Figure (4.33). Brine flooding was able to recover only 20 cc of the oil in the core pores. Brine flooding was stopped when no more oil was produced. Kumar et al. (2011) reported 35% oil recovery with brine solution of 20,000 ppm salinity concentration. Surfactant-polymer flooding was then started with polymer concentration of 0.25 wt% and surfactant FS-50 concentration of 0.1 wt%. Surfactant concentration of the SP solution was selected based on IFT experiments. The optimum surfactant concentration was 0.1 wt%. The SP solution has viscosity of 0.01 Pa.s at core flooding experiment conditions. After injection surfactant polymer solution, the recovery was increased. Table (4.3) shows oil recovery for different pore volume injections of SP solution. After four pore volume, the recovery was 42.5% and no more oil was produced. The SP flooding was able to increase oil recovery to about 86.5%. The remaining amount of oil was about 5 cc. Wang et al. (2010) reported lower oil recovery with formulations that were able to reduce IFT to ultralow values. They used lower polymer concentration in their work. The surfactant-polymer combination in this study showed excellent potential in EOR. The concentrations of both polymer and surfactant were small. About 232 ml of SP solution was injected which contains 0.58 g of polymer and 0.23 g of surfactant FS-50. However, their impact was clear and promised in EOR.

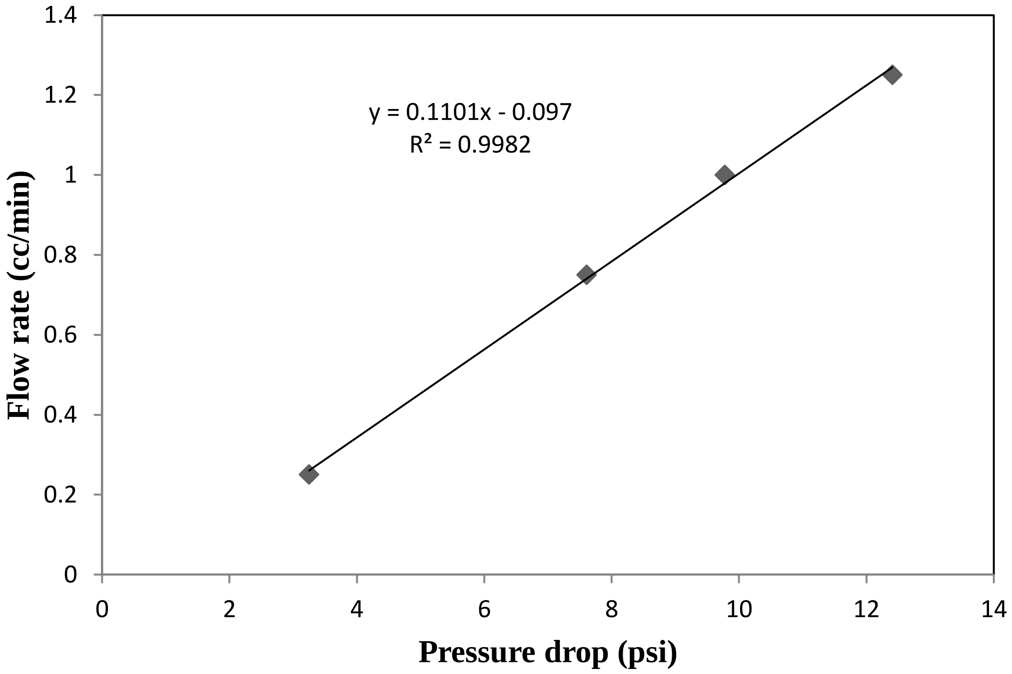


Figure 4. 32: Formation water flow rate versus pressure drop for permeability measurements

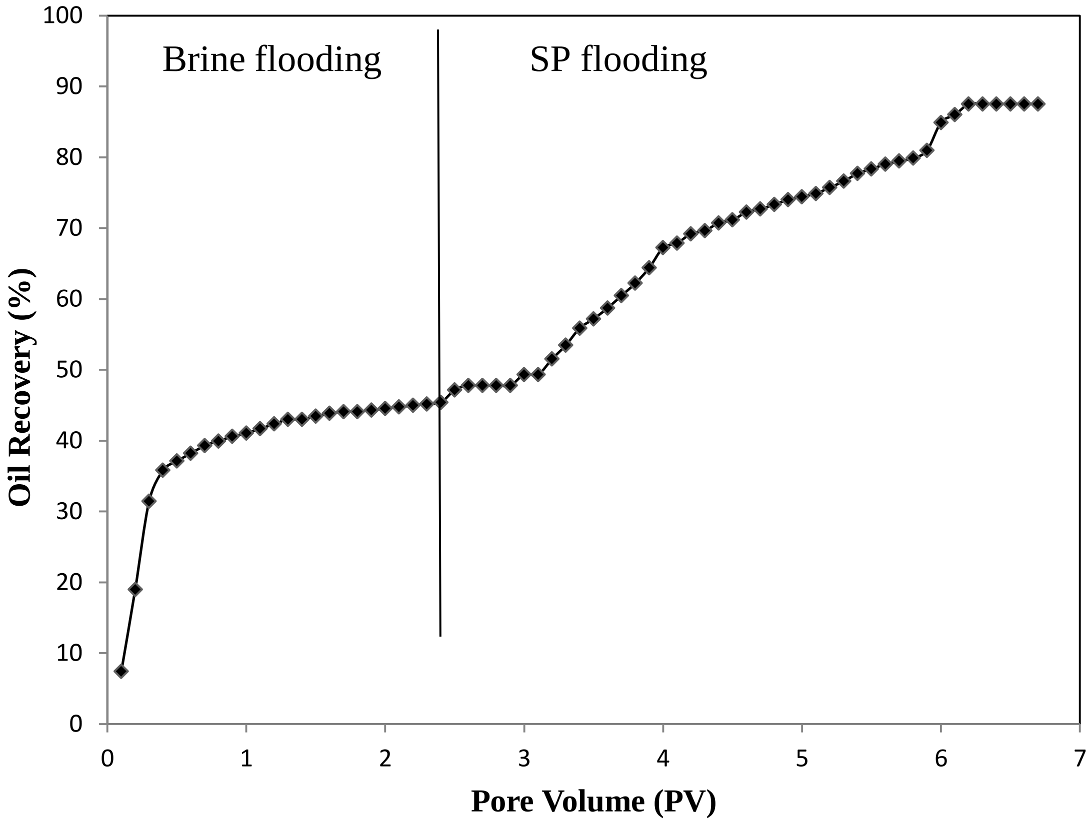


Figure 4. 33: Oil recovery % after brine and SP flooding.

Table 4. 3: Oil recovery % for different pore volume injections of SP

SP Flooding	
Pore Volume (cc)	**Oil Recovery (%)**
0.5	2.8
1	6.5
1.5	15.5
2	24.3
2.5	27.7
3	30.7
3.5	34.5
4	42.5
4.5	42.5

CONCLUSION

Surfactant-polymer formulation showed promising potential for cEOR application in carbonate reservoirs. Fluoro-surfactants and HPAM formulations (SP) were examined to test their performance for cEOR applications. The addition of HPAM to deionized water caused an increase in the solution viscosity. The repulsive forces between the polymer chains increase the solution viscosity. Increasing the water viscosity will improve the sweep efficiency of the injected fluid and increase oil recovery. Fluoro-surfactant FS-61 showed relatively small effect on the viscosity of the HPAM solution while fluoro-surfactant FS-50 has no effect on viscosity. The decrease in the solution viscosity is due to the presence of ammonium salts as counter ions for surfactant FS-61. A decrease in the storage modulus as function of surfactant concentration was also observed in the case of surfactant FS-61. Surfactant FS-50 caused a small decrease in the storage modulus. SP formulations were also tested in the presence of salts. The polymer viscosity decreased due to the charge shielding effect. Cations reduce the repulsive forces between the polymer chains and reduce the solution viscosity. Fluoro-surfactant FS-61 is incompatible with salts while fluoro-surfactant FS-50 works well with salts. At reservoir conditions where temperature is 90^{o}C and shear rate is 10 s^{-1}, a solution of 0.25 wt% HAPM and fluoro-surfactant FS-50 has ten times higher viscosity than that of water. This viscosity value is considered good for EOR applications. Both fluoro-surfactants FS-61 and FS-50 have an excellent thermal stability due to the strength of the fluorine-carbon bonds. Fluoro-surfactant FS-61 is thermally stable up to 160^{o}C while fluoro-surfactant FS-50 is stable up to 230^{o}C for short period of test. The two surfactants were also tested at 90^{o}C for three weeks and again they both showed an excellent thermal stability. The fresh and the aged samples have similar spectra which indicate similar structure. Fluoro-surfactants are applicable for high temperature reservoirs where temperature is about 120^{o}C. Adsorption tests were performed and adsorption density of ions and fluoro-surfactant FS-50 was calculated on precipitated calcium carbonate PCC. Major adsorption of sulfate ions on the surface of the precipitated calcium carbonate was observed while the carbonate ions were desorbed to the brine solution. The desorption of carbonate ions was confirmed by UV-vis. The initial brine solution showed no absorbance whereas the brine solution after adsorption test showed absorbance due to the presence of carbonate ions. Fluoro-surfactant FS-50 showed relatively low adsorption density on the surface of the precipitated calcium carbonate PCC which is favorable for EOR applications due to economic reasons. Surfactants are used to lower the interfacial tension between the oil and the brine phases. The presence of fluorine atoms in surfactants FS-61 and FS-50 reduces the hydrophobicity of the surfactant tail. They occupy larger volume compared to hydrogen atoms and prevent interactions with oil phase. Fluoro-surfactant FS-61 showed high IFT values even in the presence of co-surfactants. Fluoro-surfactant FS-50 has lower IFT values than fluoro-surfactant FS-61. The lowest IFT value was 0.9 mN/m at concentration of 0.1 wt% in brine solution. Ultralow IFT values were measured in the presence of co-surfactants. Phase behavior experiments showed that both fluoro-surfactants are unable to form type III microemulsions. A clear separation between the oil and the aqueous phases was observed at 90^{o}C. Core flooding experiment was performed with one potential SP solution of 0.25 wt% HPAM and 0.1 wt% FS-50 at 90^{o}C and 2000 psi confining pressure. The SP solution has viscosity of 0.01 Pa.s and IFT value of 0.9 mN/m. Indiana limestone core plug with permeability of 73 mD was used. It has length of 30.5 cm and diameter of 3.77 cm. After 2.4 pore volumes of brine flooding, the oil recovery was 44% and it was enhanced to 86.5% after 4 pore volumes of surfactant-polymer flooding. The concentrations of both polymer and surfactant were small. About 232 ml of SP solution was injected at 0.5 cc/min which contains 0.58 g of polymer and 0.23 g of surfactant FS-50. The SP formulation showed promising potential for EOR application.

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