TEMPERATURE SENSITIVE SUPRAMOLECULAR ASSEMBLIES FOR ENHANCED OIL RECOVERY

A Thesis

by

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ABSTRACT

Worldwide energy consumption is increasing at a rapid rate. To meet this increasing demand, maximizing oil recovery from existing sources has become critical. For this purpose, Chemical Enhanced Oil Recovery techniques are being increasingly used and researchers are interested in the development of new materials for use in chemical flooding.

This work reports on a novel adaptable amphiphile formed by the supramolecular assembly of a complex formed by an amino-amide and citric acid to be used as a viscosity modifier in displacement fluids for oil recovery. The rheological behavior of the amphiphilic system in response to various parameters like shear, concentration, temperature and salinity is studied. Studies show that the developed adaptable amphiphile system can increase the viscosity of water 10^6 times by addition of only 5 wt% of the amphiphile. It is also noted that the changes in viscosity of the adaptable amphiphile system are reversible. The altered rheological properties are attributed to the formation of network-like entangled structures due to supramolecular assembly triggered by temperature. This research establishes some of the intriguing properties of temperature-responsive supramolecular assemblies which can prove to be highly beneficial in application to Enhanced Oil Recovery technologies.

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1. INTRODUCTION

1.1 Background of Oil Recovery

Worldwide energy consumption is increasing at a rapid rate and is set to increase 50% compared to the current level by 2030 (ShamsiJazeyi, H. et al, 2014). Although there is a strong and increasing demand for oil as a main energy resource, there has been a decline in the number of new oil fields discovered and the oil industry is facing challenges in increasing well productivity. It is estimated that even after all the conventionally applied methods have been exhausted, there would still be 2.0 x 10^{12} barrels of conventional oil and 5.0 x 10^{12} barrels of heavy oil remaining in the reservoirs throughout the world (Bera et al, 2015; Blaskovich et al.,2000; Li et al., 2009). Only 20-50% of total oil present in an oil reservoir may be extracted using primary and secondary recovery methods alone. The remaining 50-80% of oil remains adsorbed onto the surface of rocks thus resulting in oil entrapped within the rock pores (Chen et al. 2014). Enhanced oil recovery (EOR) or Tertiary recovery methods aim at recovering this remaining oil entrapped in the rock pores. Hence there has been a huge amount of interest in the development of new EOR techniques to recover as much oil as possible. The major EOR methods include gas injection, chemical injection and thermal injection. Chemical flooding has been increasingly used nowadays and researchers are showing interest in the developing new materials for use in chemical flooding.

At this point, it is very important to increase recovery efficiency of oilfields that are still under use. Enhanced oil recovery (EOR) targets at improving recovery efficiency of this huge amount of oil left in reservoirs after conventional methods. General principle of EOR is injection of displacing fluid into producing field and the function of this fluid is to sweep oil through the well (Morgan, McCormick et al., 1990). Chemical methods for EOR have become popular since the 1980s (Nilsson, Kulkarni et al. 2013). One approach of chemical EOR is the addition of modifying agents that reduce the interfacial tension between water and oil, increasing the effectiveness of the waterflooding process, thereby resulting in an increase in the total amount of oil recovered. This is a promising method and has undergone a tremendous growth in EOR. In this approach, viscosity modifying agents are added to water in order to bring the viscosity of injected fluid close to viscosity of oil in the reservoir. This water flooding based method enables the sweep of high amount of the displaced oil and reservoir even in micropores and cracks that cannot be otherwise recovered.

Some of the commonly used viscosity modifying agents in the industry are polymers such as polyacrylamide poly(acrylic acid), poly(vinyl alcohol) (Zhang, She et al. 2011), polysaccharides, cellulose and other poly(vinylpyrrolidine). Recent advances show that researchers have been showing high interest in the self-assembly of ionic surfactants into threadlike or wormlike micelles. Wormlike micelles are long, flexible, cylindrical chain like structures which form an entangled network that confers viscoelastic properties to the solution.

However, these chemical enhanced oil recovery processes have a few challenges. One of the large challenges is the characteristics of oil reservoirs vary vastly and this necessitates the tailoring of the chemistry specifically for any given reservoir. Another challenge observed is, the loss of effectiveness of the polymers or surfactants somewhere in the middle of the path while traversing through the field (Thomas et al. 2008). Another main challenge involved in the chemical methods used for EOR is the cost, which depend on factors like fluctuating cost of oil and production, which can cause a major hindrance to the widespread adoption of any new technology. To overcome these limitations there is a need to develop new materials and additives that have adjustable viscosity to overcome injection limitations are needed to make efficient EOR in challenging reservoirs or harsh environments.

1.2 Objectives Statement

As the global energy need is increasing at a rapid rate. It has become critical to maximize oil recovery from existing sources. Enhanced oil recovery (EOR) methods aim at recovering the remaining oil entrapped in the rock pores. Chemical flooding has been increasingly used nowadays and researchers are interested in the development of new materials for use in chemical flooding. In recent times, smart amphiphilic systems have received a lot of attention from researchers owing to their ability to respond to environmental stimuli like pH, temperature, light, etc.

In this research we study a smart material with adjustable viscosity for use in enhanced oil recovery. The underlying concept is that the amphiphilic system maintains low viscosity at the time of injection for ease of injectivity and pumping, thus saving energy and then the viscosity increases with the geothermal gradient, rendering high viscosities at the oil bed for efficient oil sweep. One of the challenges with surfactant flooding in oil reservoirs is that each oil reservoir varies in its characteristics such as temperature, porosity, type of crude oil present, etc. This requires that viscosity and interfacial tension be adjusted differently for each reservoir. The use of an adaptable amphiphilic system eliminates the need to develop a unique surfactant system for each type of reservoir. The goal is to develop the adaptable mechanism of the new system by evaluating rheological properties of the material such as viscosity at steady-shear and visco-elastic behavior as a function of the reservoir conditions. Laboratory experiments with several environmental conditions from oil fields such as concentrations, salinities and temperatures need to be considered for future pilot application.

2. BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

2.1.1 Oil Recovery

Crude oil recovery involves multiple phases. There are three processes involved in oil recovery are: Primary, secondary and tertiary (enhanced oil recovery EOR) processes (Green, Willhite, 1998).

In primary recovery driving mechanisms depend on the natural energy present in the reservoir. This natural energy is used to displace the oil to producing wells. The source for the natural drive are solution gas, water drive, fluid and rock expansion, gas cap, gravity drive or combination of two or more of the driving mechanism.

In secondary recovery water and gas are injected to increase the natural energy of the reservoir by either hydrocarbon displacement to producers or by increase of reservoir pressure to initial level by water injection and maintenance of pressure at these levels. Water flooding is the most commonly used form of secondary recovery as it is easily available and efficient in comparison gas injection.

Tertiary recovery or EOR is result of injection gas, chemical, hot water or steam to recovery oil that was not extracted during the previous recovery processes. The injected fluids during EOR operation interacts with the oil and rock in the reservoir thus creating suitable oil recovery conditions. As a result there is a reduction in interfacial tension (IFT), oil swelling, reduction of oil viscosity, alteration of wettability, mobility modification or favorable phase behavior.

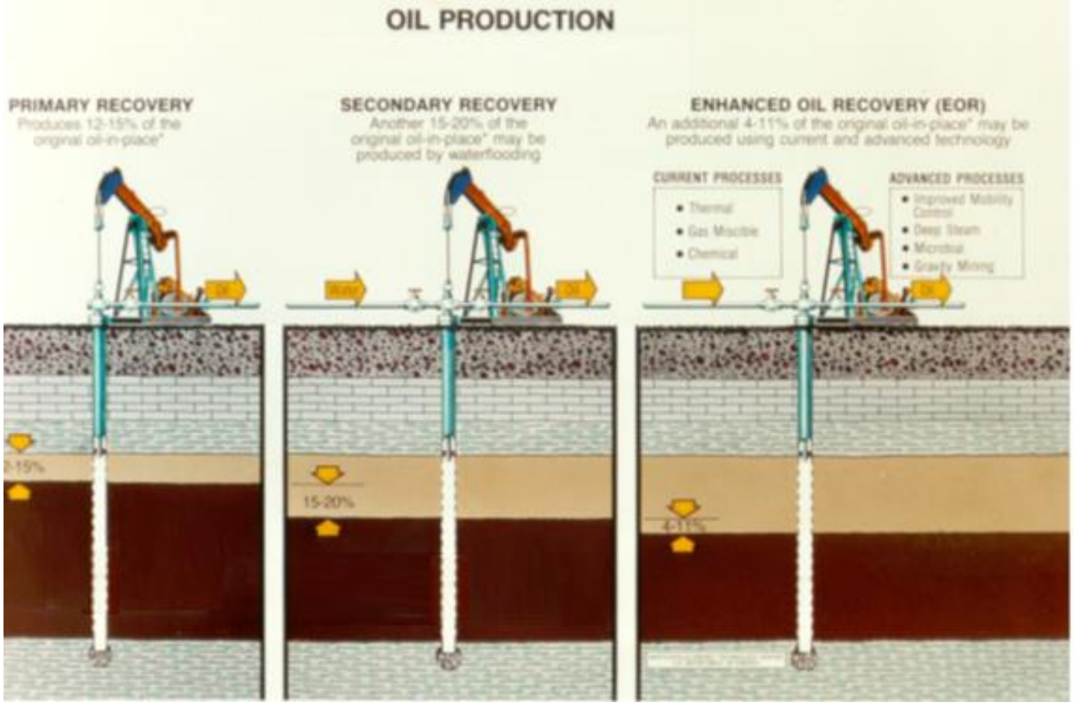

Figure 2-1 Different stages in oil recovery (Adapted from U.S. Department of Energy, EOR Process Drawings; Lindley, 2001)

2.1.2 Enhanced Oil Recovery

Enhanced Oil Recovery, or "EOR," encompasses the processes used to enhance oil displacement from a reservoir after the use of primary and secondary recovery methods. For effective recovery by any EOR method an efficient displacement need to be accomplished. The following equation gives the displacement efficiency:

$E = E_V \times E_D$

where E is displacement efficiency , E_D is microscopic displacement efficiency , and E_V is macroscopic (volumetric sweep) displacement efficiency.

E_D, microscopic displacement is related to mobilization of oil from the porous media on pore scale level. E_D measures the displacing fluid effectiveness in mobilizing oil contacted by injected fluid and lower residual oil saturation.

$E_{V,}$ macroscopic displacement is a measure of the displacing fluid effectiveness in sweeping the oil toward the production wells.

EOR aims to improve microscopic displacement efficiency by removing hydrocarbon stuck to the rock surface. Of the various EOR methods utilized since the inception of the idea in 1960s, chemical methods which involve polymers, surfactants, foams, alkali, etc. are important and attractive methods because even when used in small quantities they have the ability to effectively change the injecting fluid properties.

The two main factors influencing the effective recovery of remaining oil using chemical EOR methods are the relative mobilities of the displaced and the displacing fluids and maintenance of low interfacial tension during the flood (Green and Willhite 1998)

2.1.3 EOR Methods

There are many EOR methods that have been used in laboratory tests and field applications. The three main types of EOR methods used are: thermal methods, gas methods and chemical flooding (Taber et al.1997)

After the use of primary and secondary recovery methods, EOR methods are being employed in the industry to recover most of the oil leftover in the reservoir. Thermal methods are the most employed EOR methods, followed by gas methods and chemical methods still form a small percentage of the total EOR methods applied in fields worldwide.

Thermal methods are based on the principle of introduction of heat in forms such as steam injection to reduce the viscosity of oil resulting in its easier flow through the reservoir. This is one of the major type of EOR used in the fields currently.

Gas injection methods of EOR utilize the expansion of gases such as nitrogen, carbon dioxide, etc to drive more oil out of the reservoir. Some methods are based on gasses dissolving in oil, thereby increasing their mobility through the reservoir to the production well surface. This technology is being increasingly applied in the fields in recent years.

Chemical flooding methods involve the use of surfactants or polymers to increase oil recovery. The main principle lies in either reduction of interfacial tension between oil and water phases or increase in mobility of the oil by increasing the effectiveness of water floods. Chemical techniques do not have as wide application as the other techniques due to the some inherent limitations of the currently available materials for use in flooding.

2.2 Polymer Flooding

2.2.1 Mobility

Mobility of fluid is defined as a measure of the ease with which a fluid flows through porous media. Mobility ratio is by definition the ratio of mobility (λ) of displacing fluid to the mobility of the displaced fluid. When measuring a fluid's flow rate in porous media, mobility term and pressure drop term are combined in the equation known as Darcy's law.

$$\lambda = \frac{\kappa}{\mu}$$

$$M = \frac{\lambda_{displacing\ fluid}}{\lambda_{displaced\ fluid}} = \frac{\mu_{displaced}\kappa_{displacing}}{\mu_{displacing}\kappa_{displaced}}$$

$$\frac{q}{A} = v = \frac{k}{\mu}\frac{\Delta P}{L}$$

where λ is mobility of a fluid, μ is the viscosity of the fluid, κ is the effective permeability to the fluid, M is the mobility ratio, $\mu_{displaced}$ is the viscosity of the displaced fluid, $\mu_{displacing}$ is the viscosity of the displacing fluid, $\kappa_{displaced}$ is the effective permeability to displaced fluid, $\kappa_{displacing}$ is the effective permeability to displacing fluid, q is the volumetric rate, A is the cross section area, v is Darcy's velocity, ΔP pressure gradient in a distance L.

A favorable mobility ratio is maintained to avoid fingering of injected fluids. For an inefficient displacement where injecting fluids tend to bypass the oil, M is larger than 1

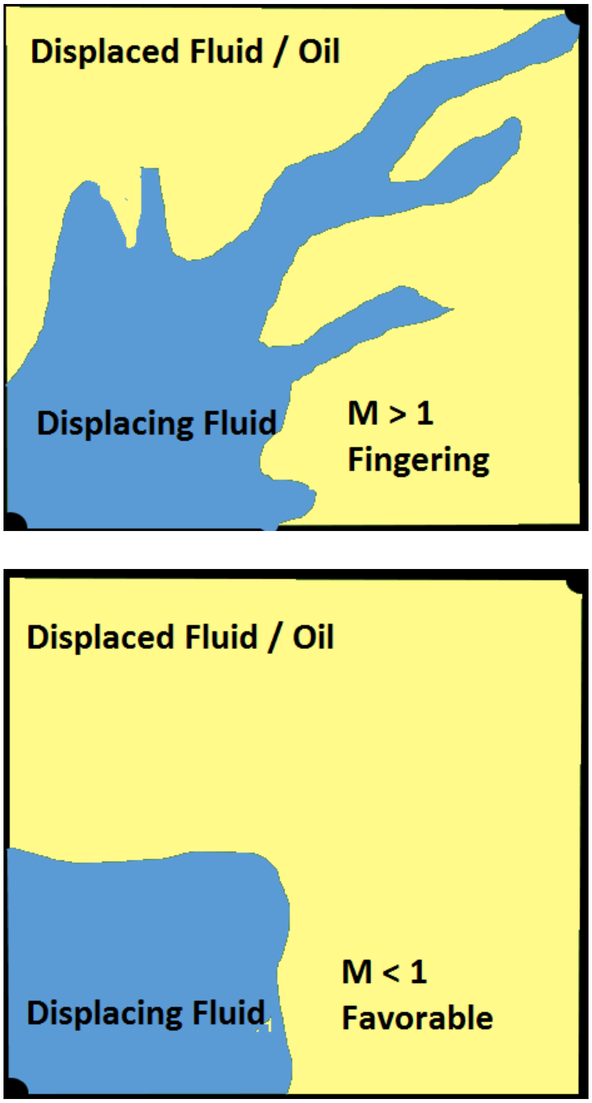

Figure 2-2 Viscous fingering of injected fluids

To obtain an effective recovery, the mobility of the displacing fluid must be equal or less than the mobility of the mobilized oil to prevent the injected fluid from bypassing the oil-water bank. The mobility of the mobilized oil is low due to relative permeability effects in the rock. Hence the viscosity of the displacing fluid usually must be higher than the mobilized oil so as to achieve lower or same mobility. Usually the viscosity of the displacing fluid is increased by addition of polymers.

Interfacial tension (IFT) between the oil and injecting fluid plays an influential role at the pore regions in reservoir. Strong interfacial tension will trap oil and cause relatively high residual oil saturation, in the same pore. One of the commonly used methods to obtain higher oil displacement efficiency is the reduction in IFT by adding chemicals like surfactants to oil.

Since 1980’s, there have been significant number of pilot plant tests for chemical EOR. Several field studies have been conducted by major oil firms in United States, China, Canada and many other countries in the world (Falls et al.,1994; Bragg et al., 1982; Jay et al.,2000; Shutang et al.,1996). In recent times there has been a surge in the number of projects involving chemical EOR due to its good results.

2.2.2 Polymer Flooding Process

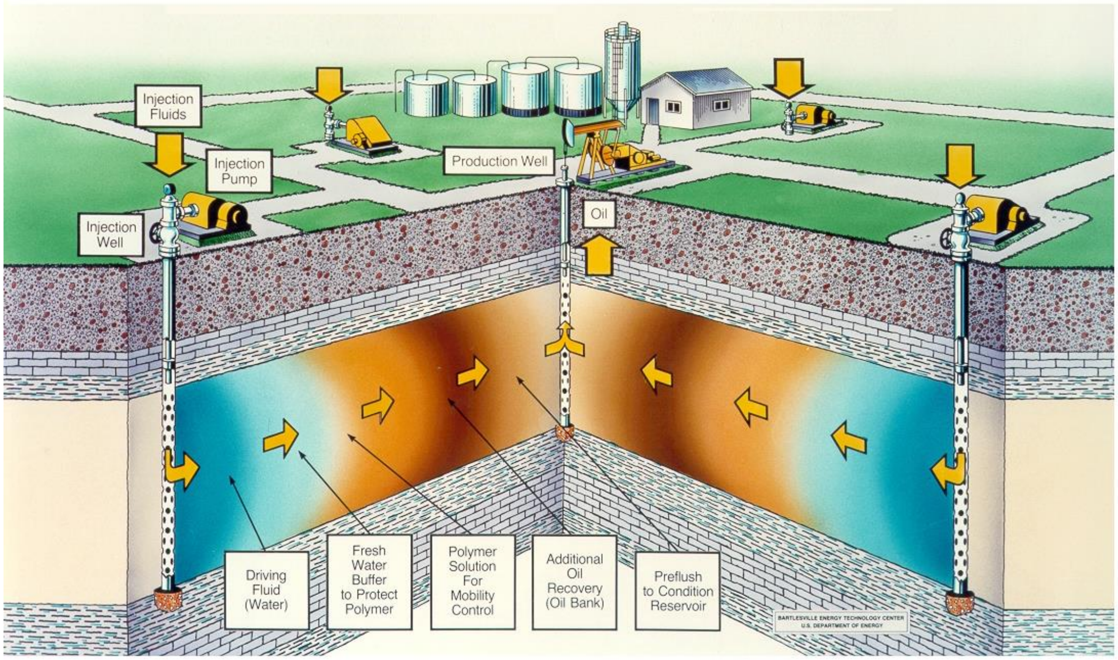

Figure 2-3 Polymer flooding process (Adapted from U.S. Department of Energy, EOR Process Drawings; Lindley, 2001)

Polymer flooding is one of the simplest and important methods to thicken the displacing fluids as addition of only a small amount could increase the volumetric displacement (Pope et al., 2011). The primary function is to reduce the mobility of water thus forcing water to flow through more channels in reservoirs. The less amount of the displacing fluid used in polymer process can also reduce the operational costs in handling disposal of produced water. Performance of polymer process is usually determined by resistance factor (RF). Resistance factor compares resistance to flow of the polymer solution through a porous media to the resistance to flow of water. It is defined as the ratio of water mobility to polymer solution mobility. Higher RF value indicates lower mobility in porous media which is a desirable feature for efficient oil sweep.

Successful field studies using polymer flooding processes have been reported in various places like Marmul (Oman) (Koning et al., 1988), Oerrel (Germany) (Maitin et al., 1992), Courtenay (France) (Putz et al., 1992), Daqing (China) (Wang et al., 2008) fields, etc. There are lot of field studies currently in progress as well. However, there are several critical factors that limit the use of polymer flooding process such as low values of pumping efficiency, polymer injectivity, loss of polymers due to degradation or retention. The costs from polymer consumption is a very important factor.

2.2.3 Types of Polymers

There are two types of polymers that are primarily used in Polymer Flooding: Synthetic polymers and Biopolymers. Most commonly used synthetic polymers are water soluble polymers like polyacrylamide, polysaccharide, poly(vinylpyrrolidone) and polyvinyl alcohol. Performance of polyacrylamide as a viscosity modifier depends on factors like degree of hydrolysis and molecular weight. Partially hydrolyzed polyacrylamide is commonly used in field applications of EOR. Even though commonly used in the field, polyacrylamide has its limitations such as loss of viscosity due to ionic shielding caused by salinity and shear degradation, thus resulting in reduced performance as the polymer advances through the oil field during flooding process. Despite these limitations, synthetic polymers do have certain advantages like high temperature tolerance and low cost.

Examples of biopolymers used in polymer flooding processes are Xanthum gum, scleroglucan, hydroxyethylcellulose, etc. Biopolymers in contrast to synthetic polymers have a high tolerance to shear and salinity, making them preferable over synthetic polymers in that respect. However, biopolymers do not have a high temperature tolerance and are easily susceptible to microbial attack and degradation. Also, these are relatively more expensive than synthetic polymers.

2.2.4 Polymer Design

There are several challenges that need to be addressed to have a commercial application of polymer flooding process. Some of the critical challenges are the cost of pumping due to high injection pressure required of a highly viscous solution, injection well fractures, retention of polymer in pores and mechanical degradation of polymers due to high shear rates in porous media. Apart from these industry is focusing on environmentally friendly materials. There is a need to develop new materials addressing these challenges for increase in the commercial application of polymer flooding process.

To overcome the pumping and injectivity limitations, designing an adaptable system that maintains low mobility at injection well, and then increases mobility at the reservoir bed where it comes in contact with oil is desirable. In this design it is important that the system is shear tolerant to overcome the mechanical degradation limitation of existing polymers. High salinity and temperature tolerance are additional attributes of the new system that could prove extremely beneficial in application to varied types of oil reservoirs.

2.3 Amphiphiles and Supramolecular Assemblies

Amphiphiles are synthetic or natural molecules with the ability to self-assemble into a variety of structures like nanotubes, micelles, nanofibers, vesicles and lamellae. While amphiphile self-assembly has attracted considerable attention for a long time now, due to their vast applications in fields like material science, gene and drug delivery, recent developments in nanotechnology research have brought forth a combination of amphiphile assembly and supramolecular self-assembly processes for the development of more complex, hierarchical nanostructures. Introduction of stimulus responsive supramolecular amphiphile assembly-disassembly processes in particular, provides novel approaches for various applications.

Supramolecular gels have been receiving a lot of attention from researchers these days due to their unique structural configuration and the potential applications arising from their altered characteristics owing to the structural assembly. These have application to a variety of fields like food industry, medicine, oil extraction, etc. The noncovalent entanglement of fibers to form a three dimensional network is a characteristic most supramolecular gels consist of. The formation of these gels can be triggered or controlled by a range of external factors like temperature, pH, light, ionic strength, etc.

In this research we study a novel amphiphile system for flooding purpose with an adjustable property to overcome injectivity limitation and the potential to resolve degradation effect. The newly developed adaptable amphiphile system by the supramolecular assembly of a complex formed by a long chain amino-amide and citric acid and has the property of reversibly adjusting viscosities. This can enable us to overcome the injectivity limitation in flooding process. The reversible structure of the designed supramolecular assembly can solve the mechanical degradation limitation of polymers.

3. MATERIALS AND METHODS

We develop an adaptable amphiphilic system by complexing citric acid and a long chain amino amide. We then study its rheological behavior under various parameters like shear, concentration, salinity etc.

3.1 Materials

Citric acid (99%), Aluminum oxide (Al_2O_3, 150 mesh), hydrochloric acid (37%), stearic acid (95%), sodium hydroxide (≥97.0%) and sodium chloride, (NaCl, ≥98.0%), calcium chloride ($CaCl_2$), sodium fluoride (NaF, 99%) and N,N-dimethyl-1,3-propanediamine (DMPDA,>99%)

3.2 Synthesis of Supramolecular Assemblies

To synthesize the long chain amino amide, the protocol mentioned in Chen et al, 2014 was followed. N-(3-(dimethylamino)propyl)stearamide was formed by performing the condensation of DMPDA with stearic acid without any solvent in a reflux oil. The reaction was performed in an inert atmosphere (Ar) to prevent the formation of any undesired byproducts due to oxidation. In this reaction NaF served as the catalyst. Al_2O_3 was used for the absorption of water formed condensation reaction. Any excess amount of DMPDA left after the completion of the reaction, was washed off using cold acetone. The resulting product was then vacuum dried for 24 h at a temperature of 40°C. The obtained N-[3-

(dimethylamino)propyl]stearamide and citric acid were added into water and heated in a microwave oven for 10s and then for another 5s. Finally, the solution was heated to 90 °C in an oven for 2 h.

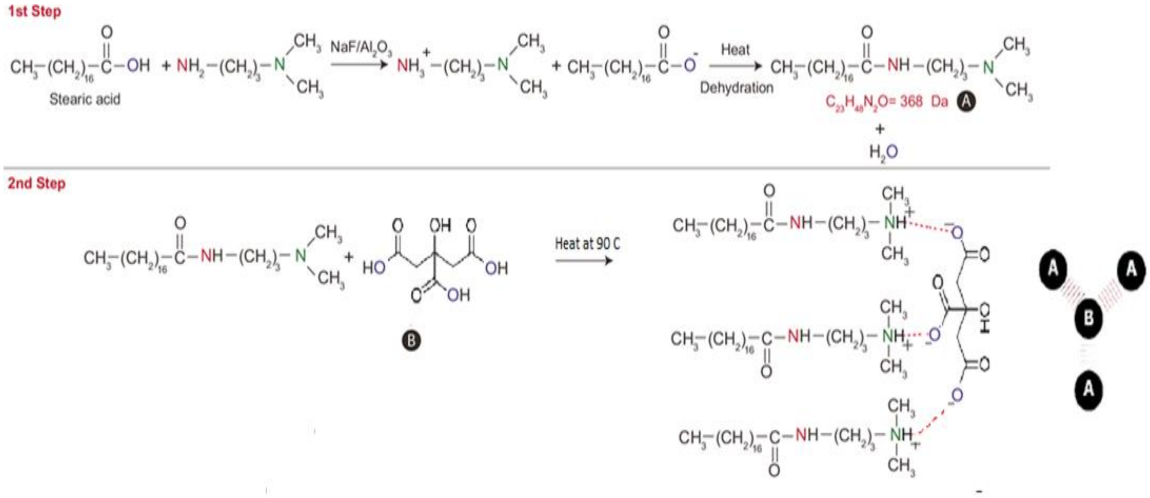

Figure 3-1 The two step method for synthesis of temperature sensitive adaptable amphiphile

3.3 Rheology Measurements

Steady and dynamic rheological experiments were performed with a rotational rheometer (HAAKE™ RheoStress™ 1, Thermo Electron GmbH, Karlsruhe, Germany) with a plate-and-plate sensor (diameter of 20 mm). And the gap between the two plates was set at 1 mm. The temperature was controlled by a refrigerated circulator (PolyScience, Niles, IL, USA) at desired temperature with ±0.1 °C. Dynamic viscosity measurements were performed over the shear rate range of 10^{-2} to 10^{3} s^{-1}. The complex shear modulus was measured over a frequency range from 0.01 to 100 Hz. Solution of different concentrations was characterized at temperature from 23 °C to 90 °C. Before measurement, the solution was equilibrated in a water bath of the same temperature to measure at for at least 30 min, making sure the solution obtained stable properties at the according temperature before the measurement. A solvent trap was put above the sensor plate in order to minimize evaporation of the sample during the measurements. Each experiment was repeated at least three times for statistical reliability.

3.3.1 Effect of Temperature

To study the effect of temperature on the viscosity of the supramolecular assemblies, 150mM samples were used for rheological experiments performed at temperatures 23 °C, 35 °C, 50 °C, 70 °C and 90 °C.

3.3.2 Effect of Concentration

To study the effect of concentration on the viscosity of the supramolecular solutions, samples at 4 different concentrations 150mM, 120mM, 100mM and 75mM were used for rheological experiments at two temperatures, 90°C and 50°C

3.3.3 Effect of Salinity

To study the effect of salinity on the supramolecular solution, two salts NaCl and $CaCl_2$ were added to 150mM supramolecular solution at two different concentrations, 3 wt% and 5 wt% and their rheological properties were measured at an optimum temperature set at 60°C

3.4 Characterization of Supramolecular Assemblies

An optical microscope with a heat stage was used to better understand the mechanism by which the supramolecular solution is sensitive to temperature. Since the maximum temperature for the heat stage was 50 °C, microscopy images were captured at 23°C, 35 °C and 50 °C. First the supramolecular solution was heated to desired temperature in an oven, and the temperature of the heat stage was set to that temperature. Then a drop of supramolecular solution was placed on a glass slide and covered with a cover slide for microscopy imaging.

4. RESULTS AND DISCUSSION

4.1 Adaptable Amphiphile Synthesis

The adaptable amphiphile system was successfully synthesized using the above mentioned method. Figure 4.1 shows the amphiphile at room temperature and 70°C. The same was observed both while heating the sample from 23°C to 70°C as well as cooling it back to 23°C.

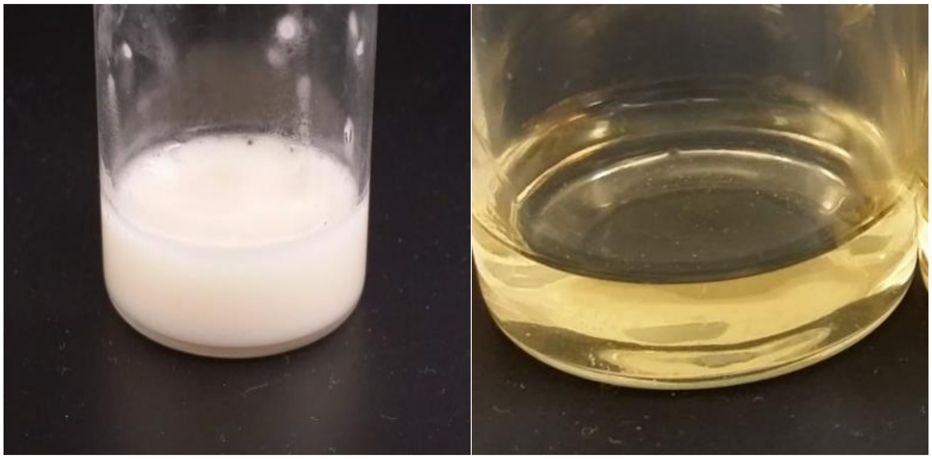

Figure 4-1 Optical pictures of ~10 wt% amphiphile solution at 23°C (left) and 70°C (right)

Rheological measurements were performed at different temperatures, amphiphile concentration, and salt concentration to observe the effect of these parameters on the viscosity of the developed adaptable amphiphile system.

4.2 Influence of Temperature on Viscosity

Figure 4.2 shows the plot of viscosity measured as a function of shear rate at 23°C, 35°C, 50°C, 70°C and 90°C of 150 mM amphiphile solution. At all these temperatures it was observed that the sample showed decrease in viscosity with increase in shear rate i.e the adaptable amphiphile has a shear-thinning nature. As temperature increased it was noted thatthe viscosity of the solution increased at any given concentration. The viscosity values in the temperature range of 50°C to 70°C remained nearly the same with no difference in the order of magnitude. At a temperature of 90°C, solution had the highest viscosity at low shear rates but dropped quickly below the viscosity range at 50°C to 70°C with increasing shear rate. In the temperature range of 50°C to 70°C the viscosity is higher than the values at other temperatures for a wider range of shear rates. At a temperature of 70°C, the amphiphile solution was about 10^6 times more viscous than water which has a viscosity value of 1 mPa·s. However, when the temperature was decreased to 23°C, the viscosity reduced to approximately the order of 10^4 mPa·s. The reversibility of the temperature specific amphiphile was confirmed when the viscosity increased to 10^6 mPa·s again when the temperature was increased to 70°C.

This rheological data suggests that there is a network like structure formation in the amphiphilic solution causing the altered rheological properties at different temperatures. The reversibility in viscosity indicates the breakage of the network structure and recombination with change in temperature.

It was observed that at low shear rates, the viscosity of the solution is significantly different at different temperatures. But at high shear rates, it is seen that the difference in viscosities is negligible for the temperature range 35°C to 90°C, yet considerably higher than the viscosity at 23°C. This suggests that there is a disruption of the supramolecular network structure under high shear. Figure 4.3 shows the measured viscosity as a function of shear rate studies conducted on 75mM sample. All readings are the average of three repeats.

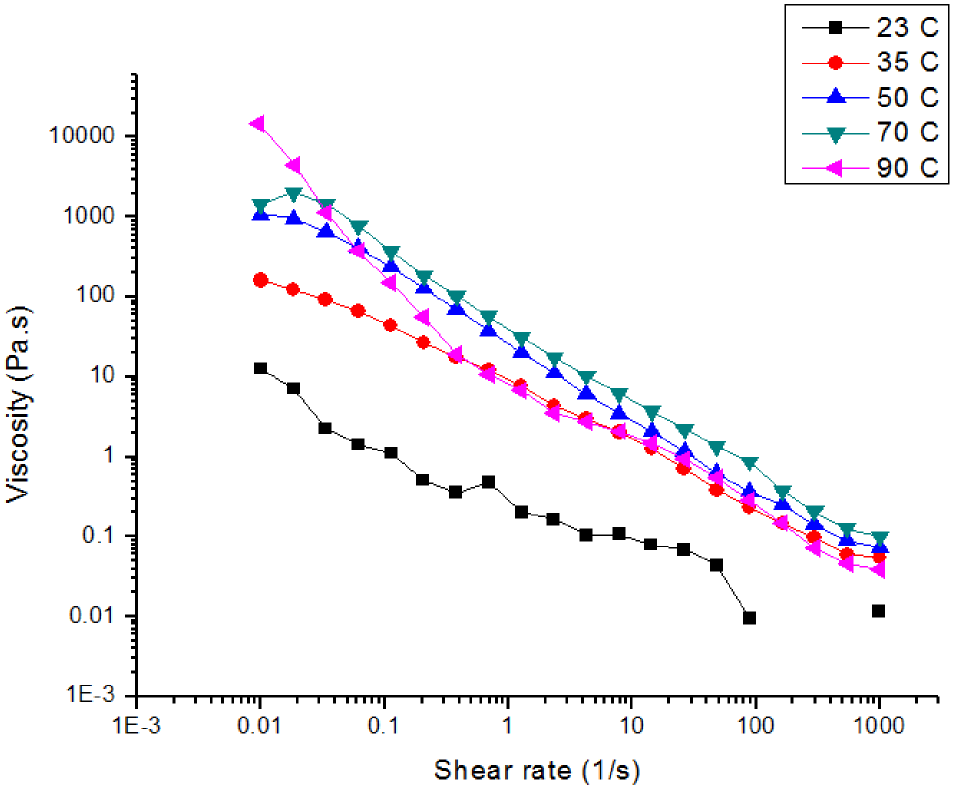

Figure 4-2 Viscosity vs shear rate of 150mM amphiphile solution at different temperatures

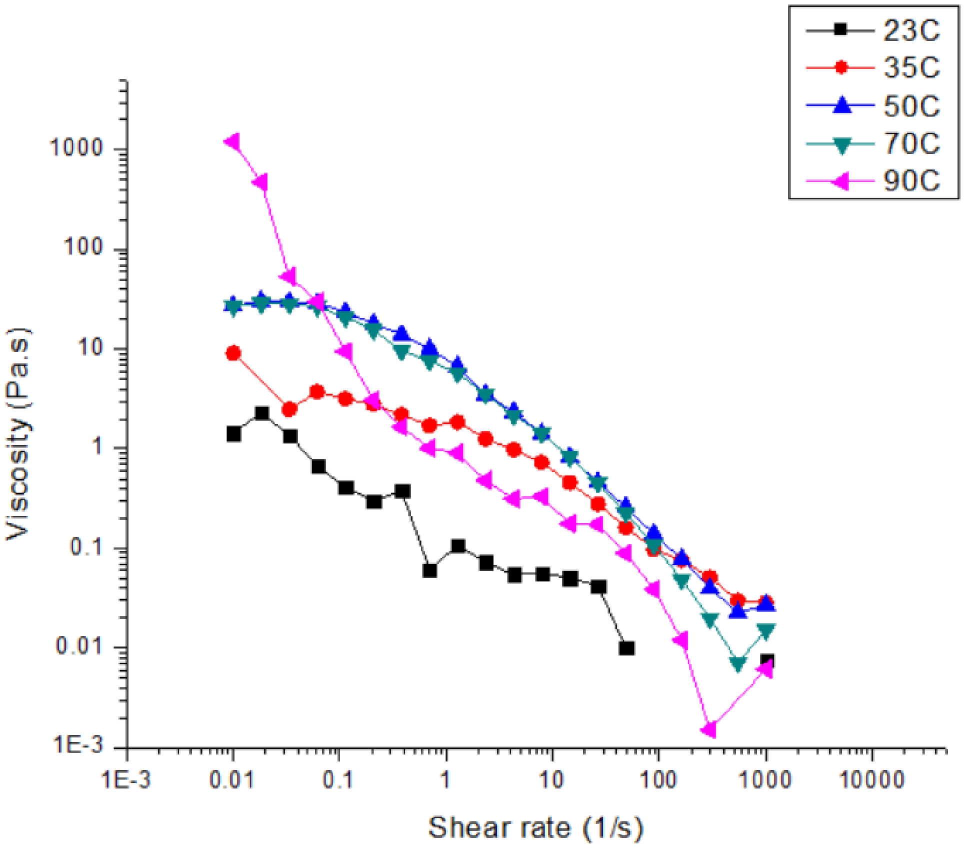

Figure 4-3 Viscosity vs shear rate of 75mM amphiphile solution at different temperatures

4.3 Influence of Concentration on Viscosity

Concentration of the adaptable amphiphile that is needed to be added to the injected fluid to get optimal extraction of oil is an important parameter to be considered while choosing materials to be used in chemical flooding for EOR. Rheological studies as a function of amphiphile concentrations were carried out at 50°C. Figure 4.4 displays the viscosity of the solution with respect to varying shear rate at concentrations of 75 mM , 100mM, 120mM and 150 mM (5 wt%). It was observed that the increase in viscosity at low shear rates was nearly two orders of magnitude with increase in concentration of solution from 75 mM to 150 mM. However, it was observed that the difference in the viscosities of the amphiphile solution at different concentrations was negligible at very high shear rates. This finding also indicates that extremely high shear rates disrupt the network structure of the amphiphilic solution.

The network structure of the amphiphile solution is formed due to the micellar self-assembly leading to entanglements forming a network like structure. An increase in concentration of the amphiphile increased this micelle counter length thus increasing the degree of entanglement which in turn lead to higher flow resistance i.e. viscosity

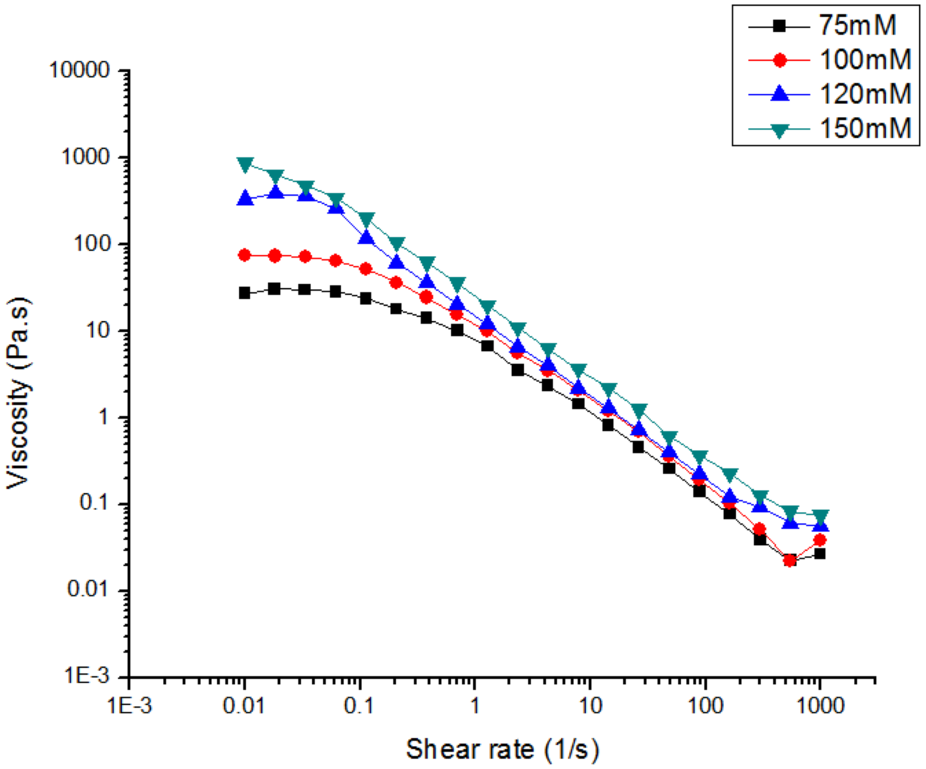

Figure 4-4 Viscosity vs. shear rate at different amphiphile concentrations at 50°C

4.4 Influence of Salinity on Viscosity

Most oil reservoirs contain some connate water containing high concentrations of divalent ions and sodium chloride. The presence of these salts are known to reduce the efficiency of chemical oil recovery of some of the currently used polymers. Therefore it becomes imperative that we study the effect of salinity on our adaptable amphiphile system to assert its potentiality for application in chemical enhanced oil recovery.

The plot shown in Figure 4.6 displays the change in the viscosity of the adaptable amphiphilic system with respect to shear rate at different salt concentrations. From the figure, it was observed that there was no significant difference in the viscosity at low shear rates on the addition of 3% NaCl, 3% $CaCl_2$ and 5% $CaCl_2$. However, in the presence 5% NaCl, the viscosity decreased by two fold as compared to the sample with no salt. However, it was noted that the effect of salinity on viscosity of the amphiphilic system at high shear rates was negligible. A possible explanation for this is that at very high shear rates, the network like entanglements imparting the viscosity are disrupted or reduced and thus, the presence of more salt does not influence the structure any further, resulting in no change in the viscosities.

Overall, the adaptable amphiphile system has highly adjustable viscosities and less sensitivity to salinity. The above experimental results strongly indicate the strong potential application of supramolecular assembly of amino-amide based amphiphiles as viscosity modifiers in chemically enhanced oil recovery.

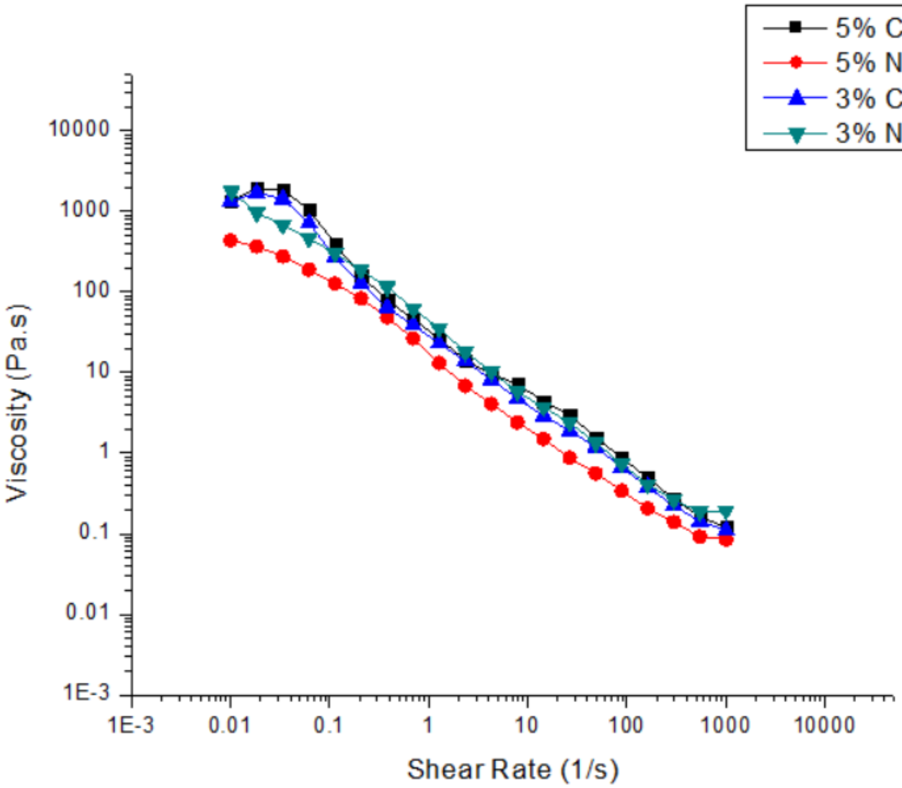

Figure 4-5 Viscosity vs. shear rate of 5% amphiphile solution with different concentrations of sodium chloride and calcium chloride

4.5 Dynamic Rheological Studies

Dynamic rheological spectra for the 150mM sample at temperatures 50°C and 90°C were measured. The elastic modulus G′ and the viscous modulus G″ are plotted as a function of frequency *f*. The plots show a crossover between elastic modulus G′ and the viscous modulus G″. This indicates that the sample has viscoelastic characteristics. It is observed that at low values of frequency *f* corresponding to short time scales, the elastic modulus G′ dominates over viscous modulus G″ indicating that the sample exhibits elastic behavior; while at high values of frequency *f* corresponding to long time scales, the viscous modulus G″ dominates over elastic modulus G′ indicating that the sample exhibits viscous behavior.

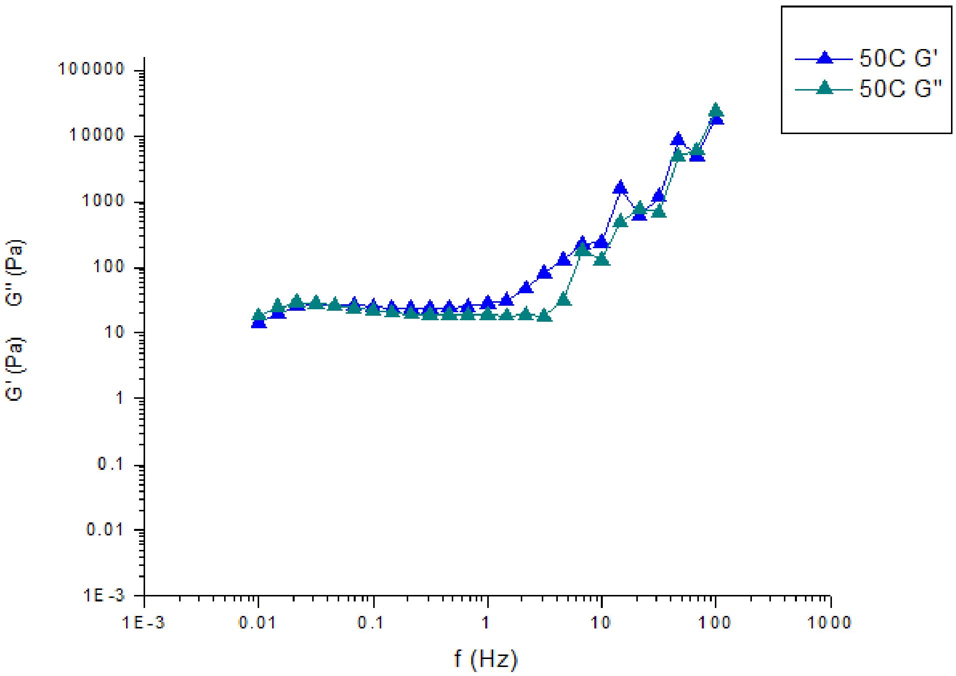

Figure 4-6 Dynamic rheology data of 150mM amphiphile solution at 50°C

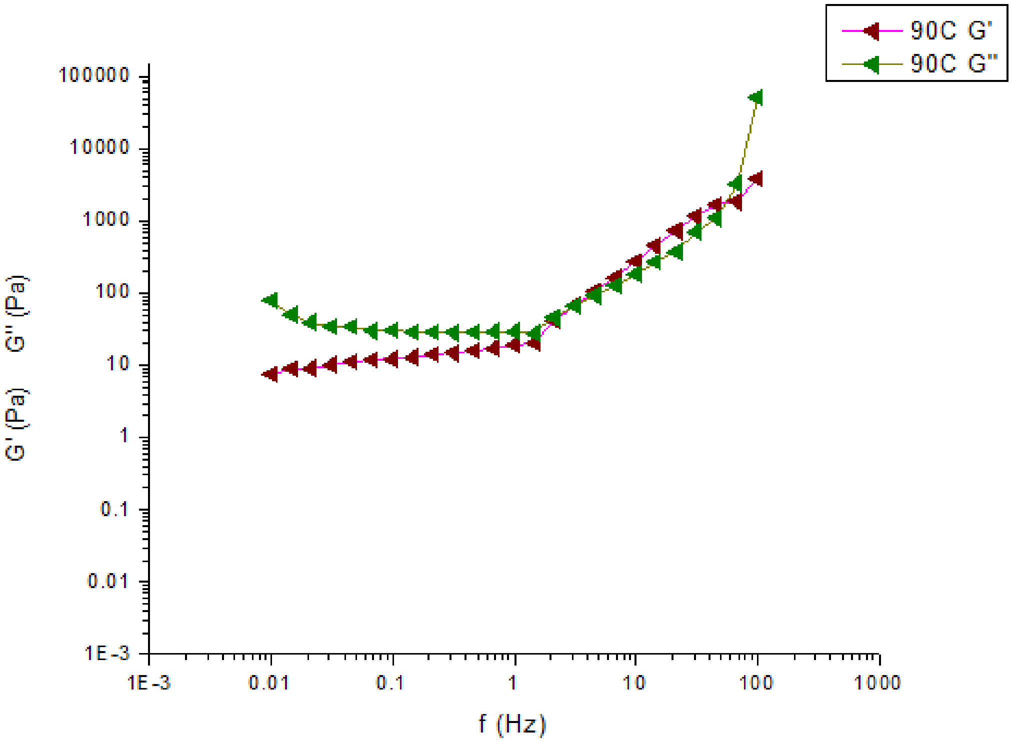

Figure 4-7 Dynamic rheology data of 150mM amphiphile solution at 90°C

4.6 Optical Microscopy Imaging

Optical microscopy images of the sample at temperatures 23°C, 35°C and 50°C were taken to better understand the structural changes involved in the change of viscosity behavior with temperature. At a temperature of 23°C, small, plate-like structures were observed while cylindrical rod like structures were detected at temperatures 35°C and 50°C.

From the optical microscopy image taken at 50°C it was observed that the cylindrical rod like structures entangle to form a network like structure as compared to the image taken at 23°C which shows loose plate like structures without any entanglements.

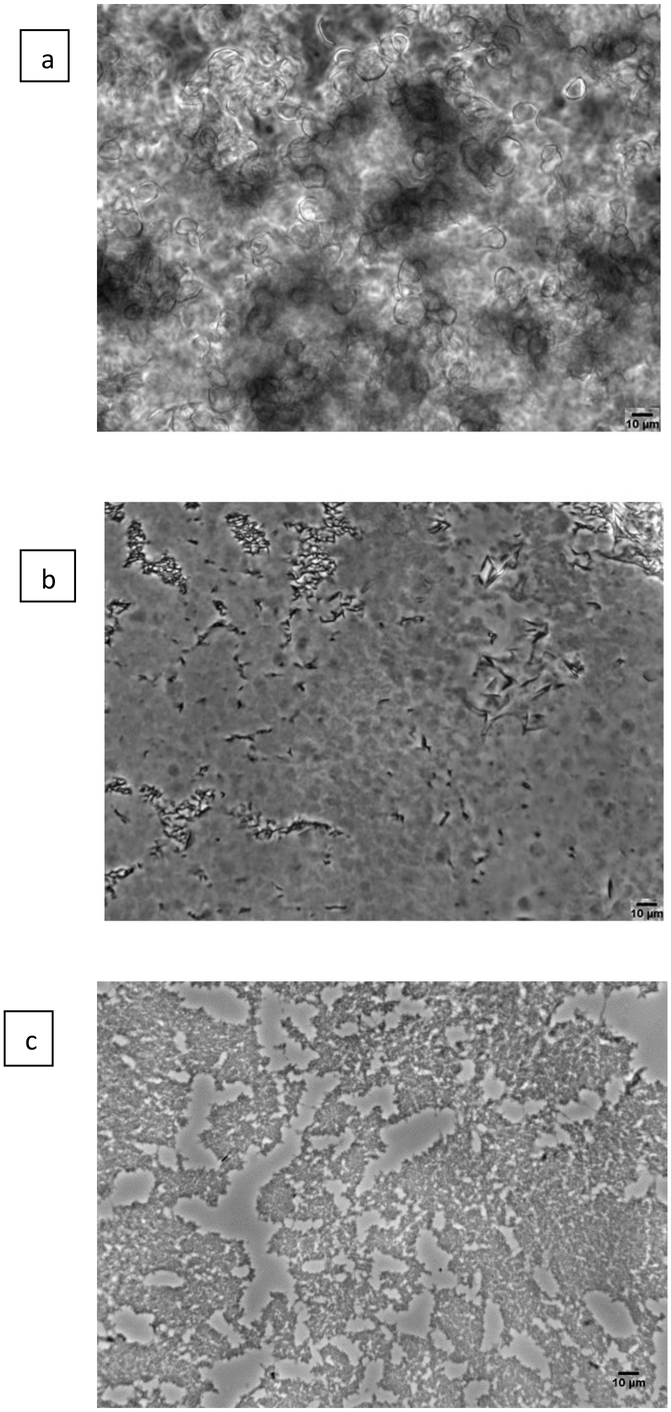

Figure 4-8 Optical microscopy images of 5% amphiphile solution at temperatures (a) 23°C (b) 35°C (c) 50°C

5. CONCLUSIONS AND FUTURE WORK

Our results indicate that we successfully synthesized a temperature responsive adaptable amphiphile system that displays intriguing adjustable rheological properties. Our system has a wide range of viscosities with a maximum of 10^6 times that of water. The tolerance to salinity displayed by the system asserts that it could have strong potential application as an EOR viscosity modifier. The reversibly adjustable viscosities would prove beneficial in eliminating the injectivity limitation in oil recovery as the amphiphile would have low viscosities during injection and pumping out stages, thus saving a lot of cost and energy required for pumping. This altered rheological behavior is attributed to the structural change into cylindrical structures forming a network at high temperatures. As oil reservoirs show wide variations in their characteristics, even within a single reservoir, the use of temperature adjustable viscosity can reduce the need for using different displacement fluids in different zones of reservoirs.

Future work may involve sand column displacement studies with the developed supramolecular solution at various temperatures to measure the oil recovery efficiency in comparison with traditionally used chemical EOR polymers like Polyacrylamide solution, etc. This would serve as a proof-of-concept for the usage of this amphiphilic system for enhanced oil recovery application in the oil fields in the future. The use of amphiphilic systems for conformance control in oil fields may also be evaluated.

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