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Master of Science in Petroleum and Mining Engineering

Stabilization of CO₂ Foam with nanoparticles and polymers for Enhanced Oil Recovery applications

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Abstract

Foam Flooding is a promising Enhanced Oil Recovery technique dedicated for maximizing oil recovery by altering the wettability in favorable conditions and more importantly to improve the mobility ratio. Also foam flooding significantly can improve the macroscopic sweep efficiency by lowering the gas mobility. Limited stability of conventional surfactants for foam generation is one of the reasons why foam is not being widely used as a common EOR technique. Some of the anticipated approaches for foam stabilization is the addition of polymers, so called polymer enhanced foam and nanoparticles.

The oil recovery by foam flooding mainly depends on the stability of the foam. At severe reservoir conditions, CO₂ foam becomes more unstable due to water drainage and gas diffusion through the lamella. The petroleum industry is using several foaming agents to produce and stabilize the CO₂ foams. These are mainly water-soluble surfactants, CO₂ soluble surfactants, nanoparticles, and water-soluble polymers. The objective of this thesis is to analyze the synergic effect of surfactants, polymers and nanoparticles on foam stability.

In this work, the CO₂ foam stability was assessed using several novel polymers and nanoparticles. The foam was generated using alpha olefin sulfonate surfactant initially at different concentration and salinity to obtain optimum surfactant concentration. Later on, 8 different polymers were used at different concentration to analyze their effect on stability of foam. Foam stability was assessed by analyzing the half-life and texture of the foam during its life. Foam decay was studied to compare the destructive mechanisms between surfactant and polymer foam. These polymers were mainly acrylamide-based sulfonated and associative polymers that contain thermally stable monomers that increase the salt tolerance and thermal stability. In the last, nanoparticles were used to get the synergic effect of polymers and nanoparticles on foam stability at different concentrations. The foamability, foam stability, foam diameter, bubble count per unit area of the different foaming system was measured using dynamic foam analyzer.

Results showed that the addition of polymers increases the viscosity of the foam which reduces the coalescence phenomena and film thinning however, the liquid drainage was not much

controlled by polymer addition. Nanoparticles performed the best job in controlling the liquid drainage and enhanced the foam stability up to large extent when used in combination of polymers. The novel sulfonated polymers showed much better performance compared to the conventional partially hydrolyzed polyacrylamide (HPAM) polymer. For HPAM, the viscosity of the solution reduced at high temperature in presence of salts. However, associative polymers maintained a reasonable high viscosity in presence of salts that resulted in less film thinning so will play key role in refining mobility ratio. Hence foam stability could be enhanced up to large extent if a proper combination of surfactant, polymer and nanoparticles are used. The foam stability is also assessed using foam structure analysis and effect of salinity on CMC of surfactant is also investigated. This study helps in understanding the role of polymer molecular structure, molecular weight, degree of hydrolysis, and addition of nanoparticles on stabilization of surfactant foam for CO₂ EOR.

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Introduction

1.1 Overview

Most of the world's discovered oil fields are in declining phase and the discovery rate of conventional oil fields is reducing with time. In contrary, the demand of oil and energy consumption is increasing day by day. The average conventional recovery factor of world's oil production is 35% which shows that almost twice of oil remained unproduced due to oil trapping and loss of system energy (Babadagli, 2007). To fill this gap between supply and demand of oil it is essential to recover maximum oil from existing oil reservoirs using enhanced oil recovery (EOR) methods. Gas injection as a miscible oil displacement is one of the major techniques used worldwide under the scope of EOR. CO₂ is the most widely used gas and it is estimated by Annual Energy Outlook 2014 that the oil production from the CO₂ projects will be doubled by 2030 (Lee *et al.*, 2015). CO₂ become supercritical at reservoir condition due to elevated pressure and act as a miscible fluid (except with heavy oils) and this interaction could result some favorable conditions such as reduction of the capillary forces and oil swelling leading to better recovery of oil.

However, the gas injection is widely used as one of the EOR technique but there are some problems which results in poor recovery of this technique. Due to high contrast in viscosity and density of injected gas and residing fluid (oil), gas injection consequence in channeling, viscous fingering and gravity segregation leading to poor sweep efficiency (Måløy, Feder and Jøssang, 1985; Yaghoobi, 2007). Due to poor volumetric sweep efficiency, gas could not contact with the large portion of oil resulting in low recovery factor. Channeling results due to flow of gas in high permeability zones particularly in heterogeneous and fractured reservoirs and gravity override occurs due to large density difference between oil and gas. In order to overcome the challenges associated with CO₂-EOR, several techniques have been proposed. Water alternating gas (WAG) injection, surfactant alternating gas (SAG) injection, combination of chemical EOR and CO₂ EOR methods such as addition of CO₂ thickeners and mobility control using foam are popular methods

to improve the mobility control in CO₂ flooding. Use of foam can give better recovery factors by improving areal and vertical sweep, reducing viscous fingering and by diverting gas from high permeable and previously swept zone (Li *et al.*, 2008; Thesis *et al.*, 2016). In foam flooding, the flow of gas is hindered by the foam generated using surfactant. Due to the hindrance, the gas can reach to the pores which have not been contacted before. Process of foam injection for CO₂ EOR was proposed in 1950s and since then lot of study and pilot tests has been done all around the world with promising results reviewed in literature (Bond and Holbrook, 1958; Al, 1967; Al-mossawy, Demiral and Raja, 2011).

Foam could be define as gas bubbles separated by films of liquid which are stabilized by surface acting particles (surfactants) or in a bookish language foam is defined as gas bubbles dispersed in a continuous liquid phase (Klempner and Frisch, 1991; Weaire, Hutzler and de Gennes, 2001). The foam using surfactant could be generated either by co-injection of liquid (surfactant solution) and gas or by surfactant alternating gas injection (SAG). But in either method the efficiency of foam injection is dependent on many factors out of which stability of foam is most important one. Film thinning, surfactant adsorption on rocks, film elasticity, gas diffusion, coalescence and liquid drainage due to gravity are the key parameters that determine the stability of a foam (Weaire, Hutzler and de Gennes, 2001; Cantat *et al.*, 2013). Liquid drainage due the gravity is the most important subject of study since it affects most of the aforementioned destabilizing factors (Langevin, 2017). A good surfactant should generate plenty of stable foam so that it can displace required distance without breakthrough of driving fluid. Adsorption of surfactant molecules on reservoir rock reduces surfactant concentration and limits foam generation, which in turn decreases the propagation distance within a reservoir (Prieditis and Paulett, 1992).

Although surfactant foams are good in improving oil recoveries but their short life in porous media is not efficient for long time treatments. To obtain the long-term stability, surfactant foam is stabilize by addition of polymers (Huh and Rossen, 2008; Zhao *et al.*, 2015) called as Polymer Enhanced Foam (PEF) and nanoparticles. PEF with nanoparticles (NPEF) is a convectional surfactant foam in which polymers and nanoparticles are added in aqueous phase which overcome the shortcomings of typical surfactant foam. Surfactant helps in reducing the surface

tension between the fluids and alter the wettability of reservoir rock. Addition of polymers hinder the desorption of surfactant molecules from the foam film (lamella) and increase the viscosity of foams which reduces coalesce phenomena and nanoparticles reduces the liquid drainage and hence increase the foam stability (Sydansk, 1994a; Sun *et al.*, 2014). NPEF flow into high permeability streaks and block the dominant channels hence improve the swept volume by making the piston like displacement of displacing fluid. PEFs and NPEFs have become the important technique of petroleum industry in many fields of application such as: selective acidizing, blocking of high permeable zones, improving sweep efficiencies, stabilizing surfactant foam in high salinity, high temperature and oil saturated zone, mobility control and conformance-improvement treatments specially for fractured and heterogeneous reservoirs (Sydansk, 1994a, 1994b; Huh and Rossen, 2008; Sun *et al.*, 2015; Zhao *et al.*, 2015; Reza Etminan, Goldman and Wassmuth, 2016; Li *et al.*, 2018).

1.2 Objective

The objective of this study was to get the most stable foam considering the high salinity conditions of reservoir environment by analyzing combine effect of surfactant, polymers and nanoparticles on a bulk foam generated at ambient conditions. Before getting the synergic effect of all additives (surfactant, polymers and nanoparticles), experiments were performed to compare the contribution and importance of each additive in foam generation and stabilization. The focus of study was to get an optimum concentration for each case to obtain the most stable foam also considering the economic feasibility especially in case of polymer enhanced foam. For PEF, experiments were conducted on eight different polymers to get the effect of polymer concentration, molecular weight and the degree of hydrolysis on factors effecting foam stability such as coalescence, diffusion and liquid drainage. Silicon dioxide (SiO_2) with particle size ranging 10 to 20 nanometers (nm) were used as nanoparticles for preparing nanoparticle-polymer enhanced foam (NPEF) and experiments were conducted at various polymer and NPs concentrations.

1.3 Chapter distribution

This thesis is divided into six main sections (Chapters). Chapter 1 (Introduction) was about relevant background theory which provide the overview of this study, importance of foam flooding over gas flooding and objective of this research.

Chapter 2 (Literature review) contains the theory related to the classification of foam, different properties of foam and their importance in foaming procedure.

Chapter 3 (Experimentation setup) describes the experimental procedure and setup used in this study for foaming.

Chapter 4 (Surfactant foam) explains the effect of surfactant concentration on foam generation ability and foam stability. The effect of addition of salt on performance of foam is also discussed in detail.

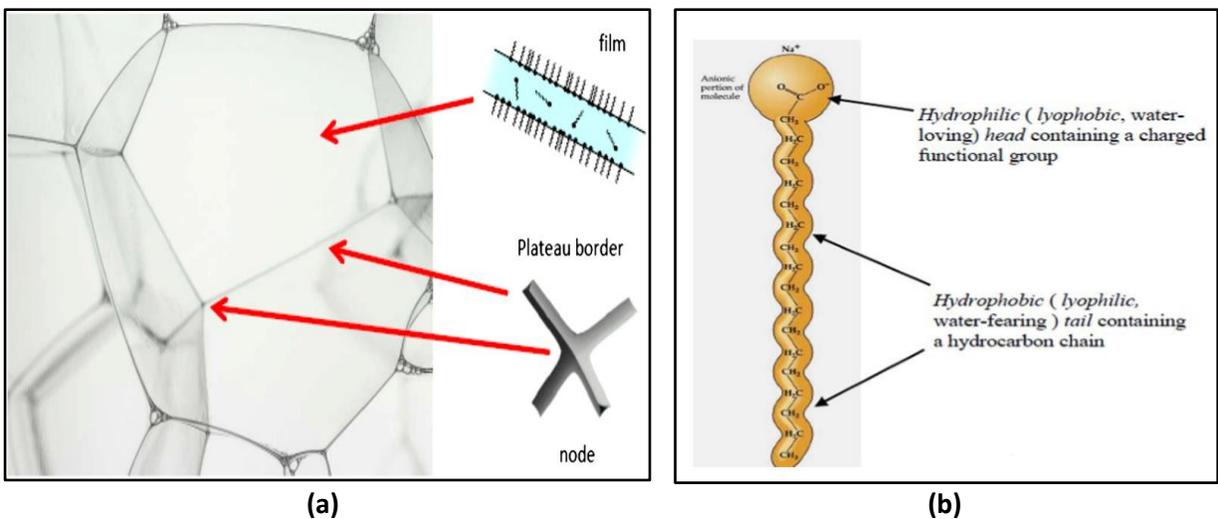
Chapter 5 (Polymer Enhanced Foam) describe the influence of polymer addition in surfactant foam and effects of polymer molecular weight and degree of hydrolysis on foam stability in a bulk foam. A comparison between a surfactant and polymer foam is studied.

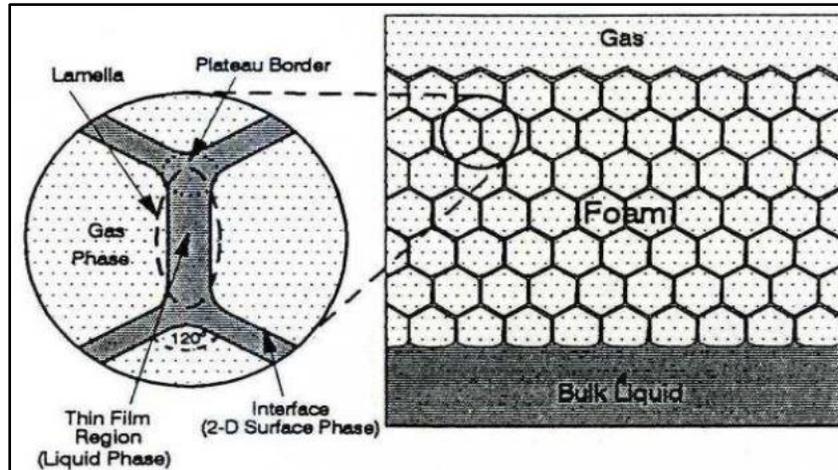
Chapter 6 (Synergic effect of polymers and nanoparticles) demonstrates the effect of addition of nanoparticles in PEF with varying concentration of NPs and finally the overall summary of the research.

2 Literature Review

2.1 Foam

Foam is defined as the gas bubbles dispersed in a continuous liquid phase (Weaire, Hutzler and de Gennes, 2001). The gas phase (dispersed) is preferred as discontinuous phase (internal phase) whereas the liquid phase is continuous and known as external phase. The contact between the bubbles in a continuous liquid phase occurs through the thin films called as lamellae. The thickness of these films ranges from a few nanometers to a few centimeters and these continuous films provide the connection between plateau border (Farajzadeh *et al.*, 2012). Plateau border is the line of junction of three lamellae as illustrated in Figure 1a. These thin films contain surfactant molecules to stabilize them. Surfactants are compounds that are used to reduce interfacial tension between water/oil or water/gas interphase (Bureiko *et al.*, 2015). They consist of hydrophilic and hydrophobic part. Typical structure is shown in Figure 1b. Four major types of surfactants are available based on head group (hydrophilic part). These are cationic, anionic, non-ionic and zwitterionic. Surfactant performance depends mainly on type of surfactant, charge on the surfactant and charge on the rock surface. Figure 1c shows the schematics of foam system generated in a bulk solution.





(c)

Figure 1: Plateau border and lamella representation (a), Surfactant structure (b) and generalized foam structure (c) (Shosa and Schramm, 2001)

2.2 Foam classification

Based on foam generation procedure, foam is classified into two main types that are: Bulk foam and foam in porous media.

2.2.1 Bulk Foam

Bulk foam is defined as a single homogenous mixture of a gas and liquid in which liquid is in a continuous phase. In bulk foam the liquid and gas velocities are considered to be the same as the gas bubbles are fully trapped in the liquid films and there no continuous channel for the gas to flow, because of this, such foam is also called as discontinuous gas foam. Foam height or foam volume and half-life of foam are the parameters to measure the foamability and stability of bulk foam. In petroleum industry, bulk foam is used in formation fracturing techniques, cementing and also in drilling operations.

2.2.1.1 Bulk foam generation

In early and late 90s, bulk foam was usually generated by stirring or shaking the surfactant containing solution with high speed and then the generated foam was transferred to a transparent graduated column or cylinder to measure its volume or stability manually. With the advancement of technology, nowadays foam is generated using automatic apparatuses by

passing the gas through the surfactant solution or even by stirring and then the connected software automatically starts to calculate the foam volume and stability just after the flow of gas is stopped. Figure 2 shows the bulk foam generated using dynamic foam analyzer.



Figure 2: Bulk foam generated by passing a gas through surfactant solution using foam analyzer

2.2.2 Foam in porous media

Foam in porous media is complex and different with respect to bulk foam. In porous network foam is defined as: “dispersion of a gas in a liquid such that the liquid phase is continuous, and at least some part of the gas is made discontinuous by thin liquid films called lamellae” (Hirasaki, 1989). Foam in porous network depends upon the pore size and pore throat distribution. The liquid film can stretch over the pore channel and a single bubble can occupy number of pores. Also the lamella interact with rock (pore wall) which effect the flow behavior of foam in porous media and influence the foam properties (Ransohoff and Radke, 1988).

2.2.2.1 Foam generation in porous media

Foam in porous media can be generated by either co-injection of gas and surfactant or surfactant alternating gas (SAG) method. In co-injection, a specific surfactant and gas ratio is required while in SAG, surfactant solution is followed by the gas to generate the foam in porous media. Generation of foam in a porous media is a dynamic process, foam is continuously generated and destroyed with the flow of solution in pore network. On pore level foam is generated by following

three fundamental processes: snap-off, lamella division and leave behind. Once the foam is created by these mechanisms, then the flow of generated foam in a porous media leads to further foam generation

2.2.2.1.1 Snap-off

Snap-off phenomena take place when a multiphase flow occurs in a porous media. Presence of surfactant solution is not the necessary condition for the occurrence of the snap-off phenomena. However, the presence of the surfactant solution is one of the supporting conditions for making this phenomenon more dominant. It takes place when a non-wetting phase (gas bubble) enters the pores through the pore-throat due to capillary pressure. After passing the pore-neck, bubble start to expand in new pore decreasing the capillary pressure which allow the movement of liquid phase towards pore-neck. With time, enough liquid accumulates in pore-neck which make the color unstable and as a result bubble snap-off. It is the most responsible phenomena for foam generation in porous media and this process take place continuously as the foam propagate in the reservoir (Shah *et al.*, 2018). Snap-off mechanism make the foam discontinuous within the reservoir and the produced foam either flow or block the gas path hence the relative permeability of gas reduces up to much extent. Figure 3 is a pore-scale illustration of snap-off phenomena.

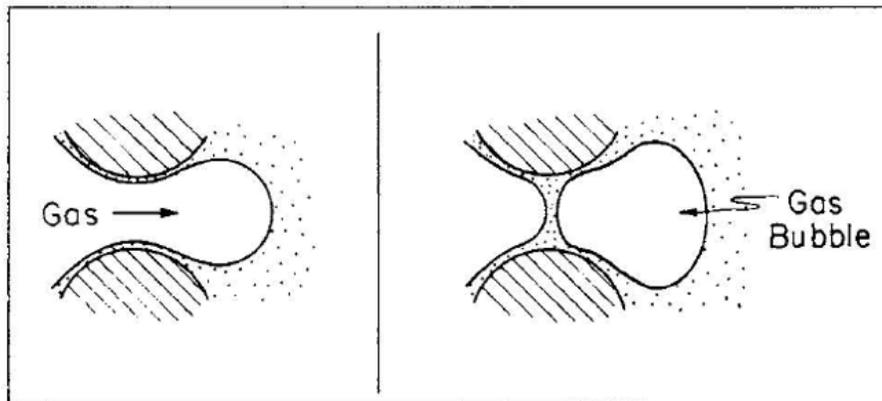


Figure 3: Schematic of snap-off phenomena in porous media

2.2.2.1.2 Lamella division

Lamella division takes place when a moving lamella splits into two, in other words when a moving bubble divides into two or more bubbles on approaching the branch point in porous media as illustrated in Figure 4. Like snap-off, lamella division keep on generating repeatedly within reservoir (Ransohoff and Radke, 1988). One can mix snap-off phenomena with lamella division

however at pore scale both are totally different. Lamella division is the secondary process of foam generation as pre-generated foam is required for this process. The division of lamella depends few conditions. According to Chambers (1990), lamella division is not possible if the size of bubble is smaller than the size of pore body. It means that the bubble size should be greater than pore body size when approaches the branch point. Also, the probability of lamella division reduces when the pores surrounded by branch point is already filled by foam or lamella. The presence of stationary bubbles decreases the branch points and act as elastic pore wall which divert the splitting of lamella into two or more bubbles (Rossen, 1988).

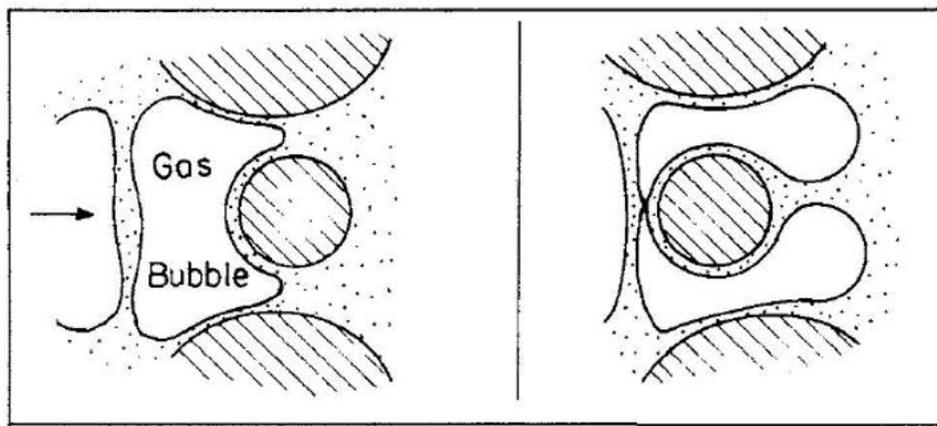


Figure 4: Lamella division process within pore network

2.2.2.1.3 Leave behind

The leave-behind mechanism, as shown in Figure 5, occurs when two gas fronts invade a liquid saturated pore space from different directions and the liquid is pushed into a lamella by the two fronts (Ransohoff and Radke, 1988). This mechanism generates lamellae that are parallel to the flow direction (NGUYEN, Q. P., 2000). In a porous body, leave-behind happens relatively often resulting in a large number of lamellae. The lamellae reduce the relative permeability to gas by blocking flow paths (Ransohoff and Radke, 1988). The leave-behind mechanism occur as the saturated pore space is drained by gas generating relatively weak foam, due to a moderate increase in resistance to gas flow (Ransohoff and Radke, 1988). If leave-behind is the only mechanism generating lamellae, the result is continuous- gas foam and low reduction in mobility (Yu, Rossen and Vincent-Bonnieu, 2019).

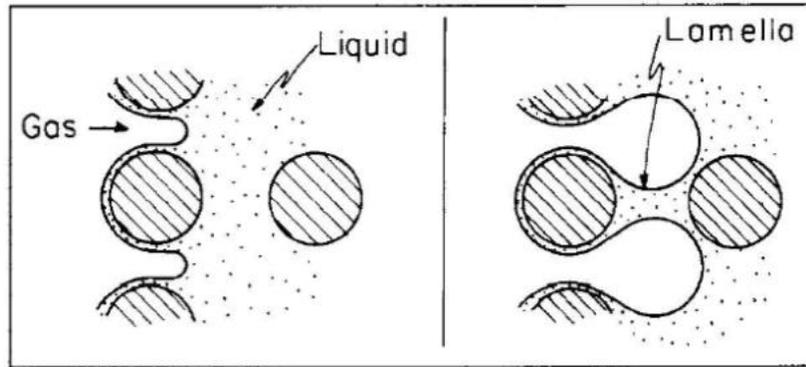


Figure 5: Schematic of leave-behind phenomena in porous media

2.3 Foam Characteristics

Foam can be described by foam quality and foam texture with the range of bubble sizes.

2.3.1 Foam Quality

Foam quality represents the percentage or fraction of gas in foam and can be fairly high, potentially reaching 97 %. The foam quality, f_g , can be defined as (Farajzadeh *et al.*, 2012):

$$f_g = \frac{q_g}{q_g + q_{liq}}$$

where the gas flow rate is q_g and the liquid flow rate is q_{liq} . Foam quality can represent gas fractional flow in porous network studies. At low gas fractional flow, the gas bubbles are widely spaced, separated by thick wetting liquid lenses or bridges, whereas at high gas fractional flow gas bubbles are in direct contact, separated by lamellae. In enhanced oil recovery high gas fractional flow is most used.

2.3.2 Foam Texture

Foam texture is the average bubble size. The bubble size can range from 0.01 μm up to macro emulsions (LAKE, 2010). David and Marsden Jr (1969) studied bubble size and bubble size distribution in a porous media. They were able to measure bubble diameter ranging between 0.20 mm to 0.60 mm in porous media. Foam texture is closely linked to foam quality. Foam will become unstable if the bubble size becomes greater, hence lower foam quality. Foams with a wide range of bubble sizes are expected to be unstable (LAKE, 2010). The flow properties of foam in a permeable medium are depend on foam texture. Foam will flow as dispersed bubbles if the

average bubble size is smaller than the pore diameter. Opposite, if the average bubble size is greater than the pore diameter foam will flow as a development of lamellae (LAKE, 2010). Foam texture determines the pressure drop/flow-rate relationship of foam in a porous network. In turn, foam texture in porous network is decided by pore-level mechanisms that generate and destroy which are dependent on the ratio between pore-body and pore-throat size. Foam will obtain a new texture when advancing through a porous network, regardless of whether the foam is generated externally or in situ, because the porous medium will model and reshape the foam (NGUYEN, Q. P., 2000). The processes that generate and destroy foam defines the foam texture.

2.4 Foam States and Foam Flow Regimes

No foam, weak foam or strong foam are three states that can occur when foam flow through a porous network, Figure 6. The first state (see Figure 6A) occurs when originally no lamellae are present due high capillary pressure, high oil saturation or that the porous network is oil wet. These mention properties can destroy or destabilize lamellae. Consequently, conventional gas flooding occurs leading to high water saturation in the smallest pores in the porous network. The second state is weak foam (see Figure 6B). Weak foam is generated by a moderate increase in the effective foam viscosity that causes a moderate increase in the pressure gradient or reduced water saturation in the porous network. The third state is strong foam (see Figure 6C) that is fine textured foams which consist of many lamellae. A significantly increasing pressure gradient or reduced water saturation is caused by the ability strong foam must increase the effective foam viscosity (or decrease the mobility of the gas phase) (Kam, 2013)

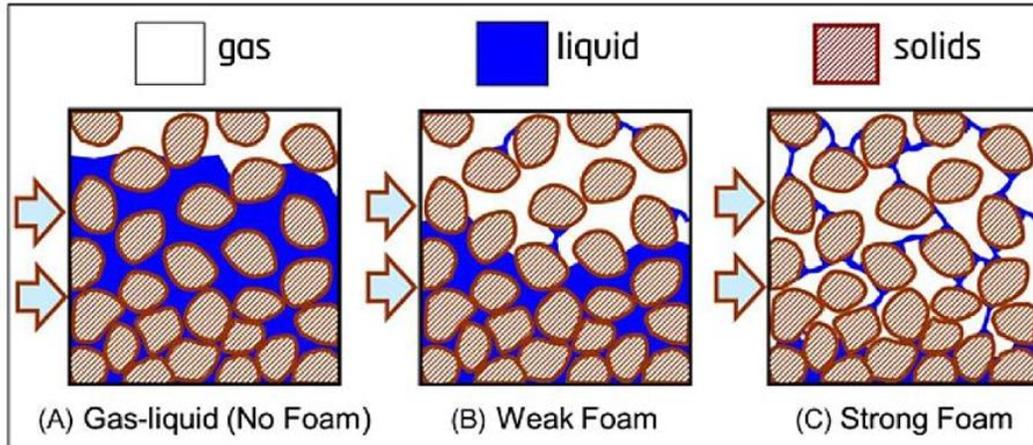


Figure 6: Schematics of states of foam. (A) no foam, (B) weak foam and (C) strong foam are three states of foam that can occur when foam flow in porous media (Kam, 2013).

In strong foam two flow regimes can be classified based on the gas fractional flow, f_g :

- High-quality regime
- Low-quality regime

In the high-quality regime, the pressure gradient is independent of gas flow rate and dependent on liquid fluid flow rate, whereas in the low-quality regime the pressure gradient is independent of liquid flow rate and dependent on gas flow rate. Between the two flow regimes, there is a transition zone, which occur at of $f_g^* = 0.94$ and this value corresponds to when the critical capillary pressure is reached (Osterloh and Jante, 1992).

2.5 Foam stability and Surfactant

The effect of surfactants, capillary suction, bubble size distribution, liquid drainage and diffusion of gas on foam stability is presented in this section. Wettability, pressure and temperature are other factors that influence the foam stability (Shen, 2013), but will not be further discussed in this thesis as these factors are not considered during the experimental work.

A vital criterion for achieving successful foam flooding is foam stability. Foam stability is the ability foam has to resist bubble collapse or coalescence. Foam is not thermodynamically stable, meaning it will break down over time. The stability of single foam films decides the longevity of foam. The stability of these films is in turn dependent on physiochemical properties and process

like surfactant concentration, salt concentration, adsorption, liquid drainage, gas diffusion, surface forces, capillary pressure and mechanical fluctuations (Weaire, Hutzler and de Gennes, 2001; Farajzadeh *et al.*, 2012; Cantat *et al.*, 2013).

Foam stability can be quantified by measuring its half-life cycle (Shen, 2013). This method is used in the experimental work of this thesis by using dynamic foam analyzer. The longevity of foam includes stability against film thinning and coalescence. Film thinning, two or more bubbles converge and the liquid film separating them becomes thinner. Coalescence, thin liquid films between bubbles breach and merge into one larger bubble.

2.5.1 Surfactants

A foaming agent acts like a surface-active substance. A foaming agent is vital to enable stable lamellae and generate foam. The most common foaming agent, surfactant, consist of a non-polar lipophilic tail and a polar hydrophilic head. Surfactants can dissolve in solvents and spontaneous adsorb on interfaces, which reduces the interfacial energy, due to their amphiphilic properties. Foam generation from a surfactant solution can be divided into 3 steps:

1. As gas is injected into the surfactant solutions bubbles are generated. Surfactant molecules cover the created gas-liquid interface.
2. Increased bubble volume fraction and contacting bubbles with surfactant layer causes formation of foam films.
3. The amount of bubbles rises, and foam is generated.

Figure 7 shows the key steps for generation of surfactant layer in a lamella. On the left hand-side foam is stabilized by surfactant. On the righthand-side enlarged area of foam film which illustrates surfactant layers at the gas-liquid interface. The surfactants accumulate at the interface with its polar parts in contact with water, whereas the non-polar parts are in contact with air. Surfactant molecules are also present inside the liquid film.

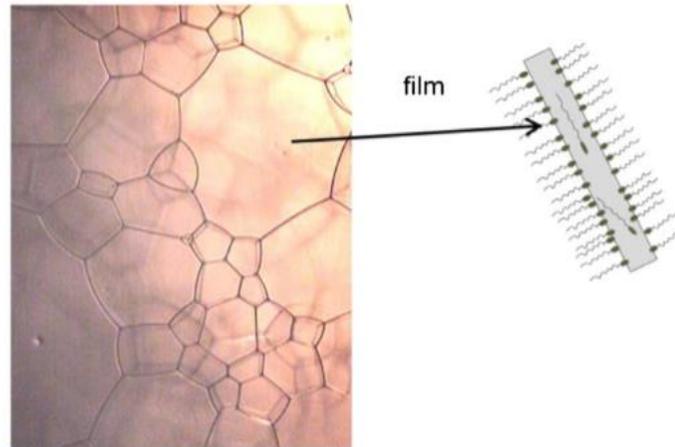


Figure 7: Key steps for generation of surfactant layer in a lamella

Micelle is an aggregate of surfactant molecules. Micelles form spontaneously at high surfactant concentrations and the lipophilic parts of the surfactant molecule are oriented inwards and hydrophilic parts outwards. Critical micelle concentration (CMC) is the surfactant concentration at which micelle formation becomes dominant. At or above CMC of surfactants the best possible foaming ability is reached (Yekeen *et al.*, 2017). Polymers together with surfactant in a water solution can also be used as a method to stabilize foam.

2.5.2 Capillary Suction

Lamellae rupture initiated by capillary suction can be explained by the disjoining pressure (Bertin, Quintard and Castanier, 1998). The disjoining pressure is an additional pressure within liquid films which supports or stabilizes the film. It depends on the film thickness, h . The disjoining pressure function, indicated by $\Pi(h)$, is the sum of repulsive forces and attractive forces acting between two interfaces (Skauge *et al.*, 2007). A positive disjoining pressure indicates repulsive forces between film interfaces and the film is stable. A negative disjoining pressure implies attractive forces between the two interfaces and the film is unstable. The disjoining pressure increases when the film thickness decreases until Π_{max} is reached. Π_{max} is equivalent to the critical capillary pressure (P_c^*) for film rupture. The film becomes unstable and break once the capillary pressure exceeds the critical pressure (Skauge *et al.*, 2007). Above P_c^* longevity of lamellae and bulk foam is reduced because at sufficiently high capillary suction pressure (higher than Π_{max}) macroscopic disturbance can start film breaking (Farajzadeh *et al.*, 2012). Adsorption of surfactant molecules at each gas-liquid interface of the film leads to extra repulsive forces (Shen,

2013). The disjoining pressure varies with surfactant type, surfactant concentration and salinity (Farajzadeh *et al.*, 2012).

2.5.3 Liquid Drainage

Liquid drainage by gravity is important to consider during the foam stability test done during the experimental work of this thesis. Liquid films residing in foam can become thinner due to gravity induced liquid drainage. Spherical gas bubbles will transform into polyhedral as liquid flow downwards through existing liquid films. Capillary forces compete with gravity forces during this transformation. Liquid drainage by gravity is shown in Figure 8. A gas/liquid interface is curved at the Plateau border generating low pressure (P_B), whereas at the flat interface along the thin film region the pressure (P_A) is high. Liquid residing in liquid films is forced to flow towards Plateau border due pressure differences at the interfaces. The process may lead to bubble coalescence due to thinning of the film and movement in the foam.

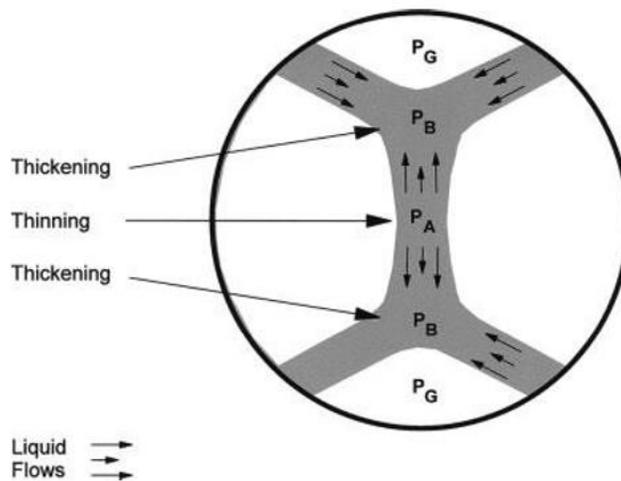


Figure 8: Schematic illustration of liquid drainage. Pressure in the thin film region is P_A , pressure in the Plateau border is P_B and pressure in the gas phase is denoted P_G

2.5.4 Bubble Size

Foam stability is not directly a function of bubble size, but there may be an ideal bubble size for the variety of individual foam types that are more stable than other sizes. Foam with a uniform bubble size distribution will act more stable than foam with non- uniform size distribution. Foam containing small sized bubbles are generally more stable than foam with large bubbles (Shen, 2013).

2.5.5 Diffusion of gas

Injection of gas through the surfactant solution results in the formation of foam with bubbles of various sizes. After the formation of foam, gas start to diffuse between the bubbles depending on the size and pressure between the adjacent bubbles. As the time passes bubbles become larger which reduces the thickness of the lamellae. This diffusion of the gas among the bubbles result in the coarsening and coalescence of bubbles which as a result make the foam unstable. The rate of the diffusion depends upon the thickness and elasticity of the bubble film. Figure 9 shows the schematic of gas diffusion between the bubbles for three different time.

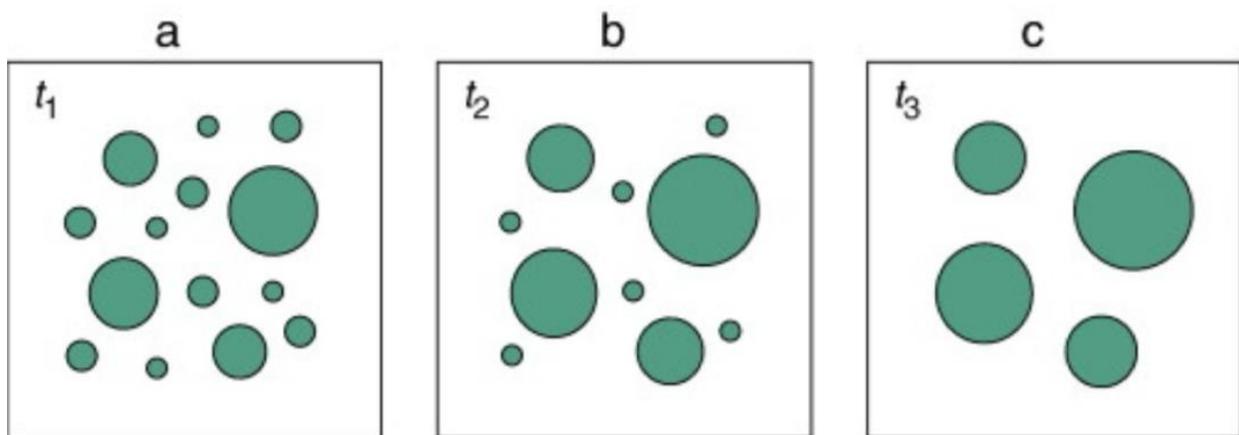


Figure 9: Schematic of gas diffusion among the bubbles

2.6 Polymer Foam

Polymer enhanced foam (PEF) is addition of a water-soluble polymer to a foam system (Sydansk, 1994a). Polymer enhanced foam can be generated by using the same type of gases and surfactants used in conventional foam. The addition of polymer increases the liquid phase viscosity hence improving the foam stability by adsorbing at the interface like surfactants (Sheng, 2013). The increased foam stability is caused by decreasing the rate of liquid drainage, reducing the rate of gas diffusion and reduce the gas permeability of the lamellae (Bureiko *et al.*, 2015). PEF can be utilized to control the mobility ratio and enhance the sweep efficiency in an oil reservoir. One can regulate the viscosity of the liquid phase in PEF by varying polymer concentration and molar mass. In addition, foam quality and foam texture will be affected by adding polymer to the aqueous foam. The choice of polymer type is based upon application,

sweep efficiency or blocking and diverting fluids, and environmental properties such as the temperature, salinity pH and shear conditions.

2.6.1 Polymers

A polymer added to the injection water is an EOR method referred to as polymer flooding. The purpose is to decrease the mobility of water. This leads to increased water viscosity and a reduction in the relative permeability to water (Huh and Rossen, 2008). The result is a lower mobility ratio, which is more favorable for oil recovery due to improved volumetric sweep efficiency. Application of polymers is advantageous in reservoirs where the oil viscosity is high or in heterogeneous reservoirs (LAKE, 2010). Polymer has a molecular weight in the million, hence only a small amount of polymer (0.1 to 1 ppm) added to the water will increase its viscosity significantly (LAKE, 2010). Polymer molecules are long chains of repeating organic molecular entities, referred to as monomers. The synthetic polymer hydrolyzed polyacrylamide (HPAM) and the biopolymer Xanthan are the most common used polymers in enhanced oil recovery (Sydansk, 1994a; LAKE, 2010)

In this thesis, partially hydrolyzed polyacrylamide (HPAM) and acrylamide/2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) copolymers with varying molecular weight and degree of hydrolysis are used to enhance foam flooding. HPAM is a polyacrylamide that has been partly hydrolyzed. HPAM's physical features are due to its negative charged molecule caused by hydrolysis. The synthetic polymer will not be soluble in the aqueous phase if the hydrolysis is too low. If the hydrolysis is too high, HPAM will be sensitive to salinity. HPAM have the ability to increase the water viscosity due its large molecular weight (LAKE, 2010). Figure 10 shows the molecular structures of HPAM and AMPS.

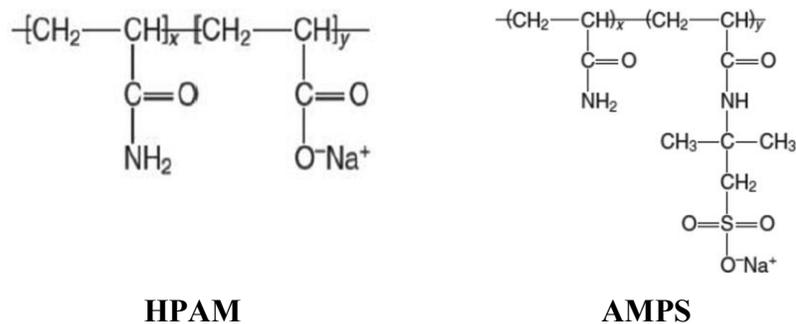


Figure 10: Molecular structure of HPAM and AMPS polymers

2.7 Foam Flooding in EOR

Carbon dioxide, nitrogen, steam, air and hydrocarbon gases are used in EOR (Farajzadeh *et al.*, 2012). A problem associated with gas injection is the poor sweep efficiency, which causes the overall oil recovery to be low since gas only contacts and sweep a small portion of the oil within the reservoir (Kovscek *et al.*, 1995; Li *et al.*, 2008; Farajzadeh *et al.*, 2012). Poor sweep efficiency is caused by (Farajzadeh *et al.*, 2012):

- Gas channels through high permeable zones in heterogeneous reservoir.
- Viscous fingering caused by differences in viscosity between gas and oil.
- Gas has lower density than brine and oil resulting in gravity overriding. Gas rises to the top of the reservoir and overrides the oil-rich zone.

Foaming of the injected gas phase will reduce the gas mobility within the porous network leading to piston like displacement of front which improve the sweep efficiency (Li *et al.*, 2008). The displacement fronts of gas and foam are illustrated in Figure 11. Foam flooding results in enhanced recovery due improved mobility ration as a result of increased viscosity of displacing fluid, blocking of high permeability zone and diversion of displacing fluid to un-swept zones.

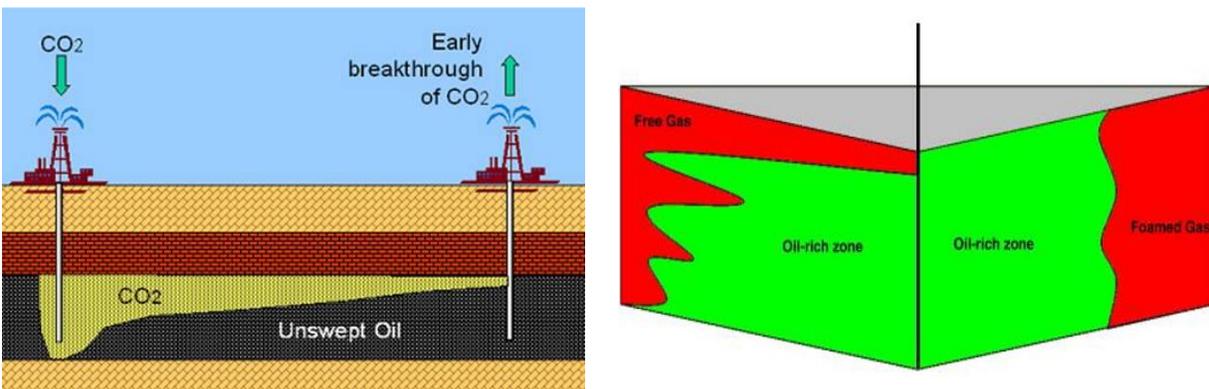


Figure 11: Displacement schematics of foam and gas flooding

3 Experimental Setup

3.1 Material

The surfactant used in this study is Alpha Olefin Sulfonate (AOS) which was purchased as an aqueous solution from Al Biariq Petrochemical Ind Co Ltd (Riyadh, K.S.A) having a minimum concentration of 35%. AOS is an anionic surfactant with industrial purity and was used as received. The sodium chloride (NaCl, >99%) was purchased from Ottoweg, Darmstadt, Germany. Partially hydrolyzed polyacrylamide (HPAM) and acrylamide/ 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) copolymers with varying molecular weight and degree of hydrolysis were supplied by SNF Floerger, France. The details of the polymers are given in Table 1. Deionized (DI) water from a Mili-Q purification system was used for preparation of all solutions. The resistivity of water was 18.2 MΩ.cm and its total organic content (TOC) was 3 ppb.

Table 1: Polymers used in this study, with molecular weights (million Daltons) and degree of hydrolysis (%)

Polymer type	Polymer	Molecular Weight	Anionicity
HPAM	P1	9	15
	P2	15	15
	P3	12	30
	P4	15	30
AMPS	P5	7	5
	P6	9	5
	P7	7	13
	P8	9	13

3.2 Sample Preparation

A batch solution of 1% v/v was prepared from the 35% AOS solution. Magnetic stirrer was used to make the homogenous solution by stirring at 600 rpm for two hours and then the solution was left overnight. Further samples of concentrations from 0.025% to 0.75% v/v were prepared by dilution of the 1% batch solution. Each sample was prepared 1 hour before the experiment time in order to keep consistency. Similarly, a 2 M batch solution of NaCl was prepared in DI water by mixing salt with magnetic stirrer. Stirring for 3 hours at room temperature was carried out to

ensure complete dissolution of the salt and later the filtration of solution was done to remove any undissolved particles. Further dilutions were performed according to required molar concentration in the 0.01M to 1M concentration range. Digital balance with closed environment condition having accuracy of 0.01 mg was used for weighing purpose.

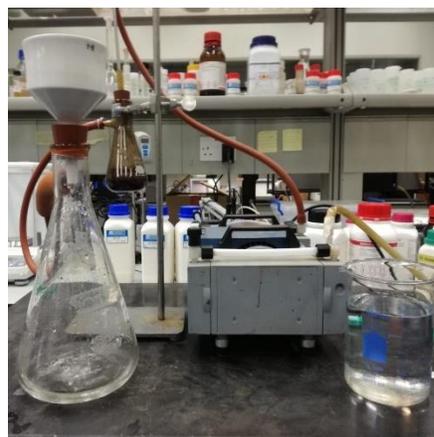
Preparation of polymer solution requires extra care to achieve proper mixing and hydration of solid polymer particles in aqueous solution. DI was set on stirrer on such speed that it makes a vortex in water up to 70 percent of its depth. Then the solid polymer was uniformly sprinkled on the shoulder of the vortex in 25 to 30 seconds. Dropping huge amount of polymer powder in water makes slugs (fish-eyes) and if the sprinkling is done in long time (more than 30 seconds), the already dissolve polymer increase the viscosity of solution which avoid the proper hydration of remaining polymer. After the polymer is transferred the stirrer was set on speed of 300 rpm for 2 hours. The lower rpm is selected to avoid any mechanical degradation of polymer and after stirring, each polymer solution was given the stabilization time of 18 hours before experimentation. For addition of nanoparticles in PEF, firstly NPs were dispersed in surfactant solution with the help of high-speed digital stirrer at speed of 7000 rpm for 15 minutes. The spinning head of stirrer should be completely immersed into the solution to avoid formation of any foam during dispersion of NPs. After addition of NPs, polymer solution was prepared as discussed above. Figure 12 shows the different setups for solution preparation.



High-Speed digital stirrer



Salt preparation (magnetic stirrer)



Filtration setup

Figure 12: Stirring and filtration setup for solution preparation

3.3 Surface tension and CMC

Surface tension was measured using Optical Interfacial tensiometer by applying pendant drop method. All measurements were performed at 23°C and a measuring time of 10 minutes to ensure that equilibrium was established. Calibration of apparatus was done using small metal bead of known diameter and surface tension of deionized water was measured which came out 72.95 dyne/cm, Same values with a minor differences could be found in literature (Harkins and Brown, 1919; Vargaftik, Volkov and Voljak, 1983). Measurements were conducted two times for each sample and reported as the average, all the measurements were within the spread of 0.45 dyne/cm. Density values, used in the calculation of the surface tension, for each sample was first calculated with densitometer (Anton parr DMA 4500) at 23°C. The critical micelle concentration (CMC) was determined by plotting surface tension measurements vs log of concentrations, the point at which the slope of isotherm changes abruptly (point of inflection of chart) correspond to CMC.

3.4 Foamability and Stability

Foamability and stability of samples were measured using Dynamic Foam Analyzer (DFA100) by KRUSS, Germany. All measurements were performed at 23°C and atmospheric pressure. The solution, 50 ml, is poured with help of syringe in a transparent measuring column which is located between a linear LED panel and a line sensor. Air is pumped into the liquid from bottom through a filter plate/paper to produce foaming. The air was injected for 20 seconds at flowrate of 0.2 L/min for all experiments. The line sensor measures the light transmitted through the measuring column over its full height. The gas phase above the foam and the liquid are permeable to light, while the foam column absorbs some of the emitted light. LED and sensor panels around the glass column measure the intensity of light passing through the column and the two phase boundaries, liquid/foam and foam/air, are detected using the measured differences in light intensity. Figure 13 shows a schematics and original setup of dynamic foam analyzer.

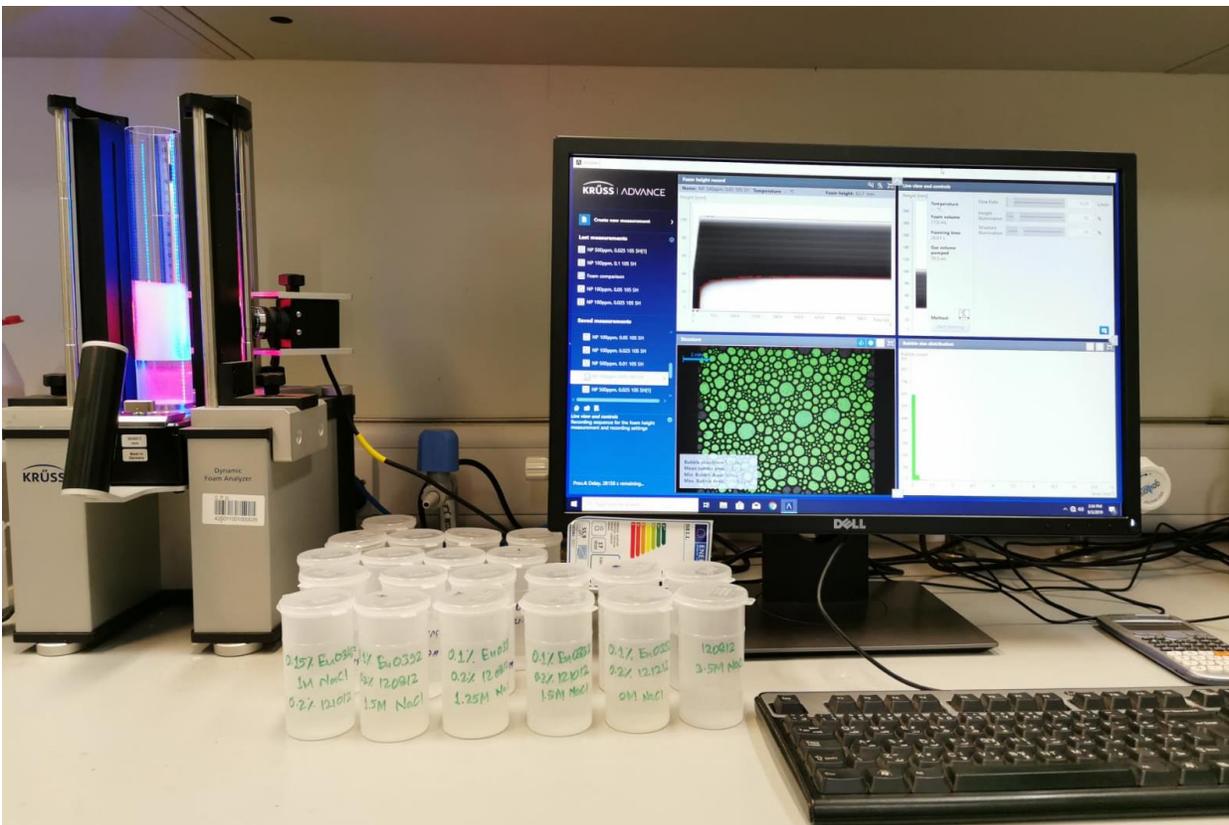
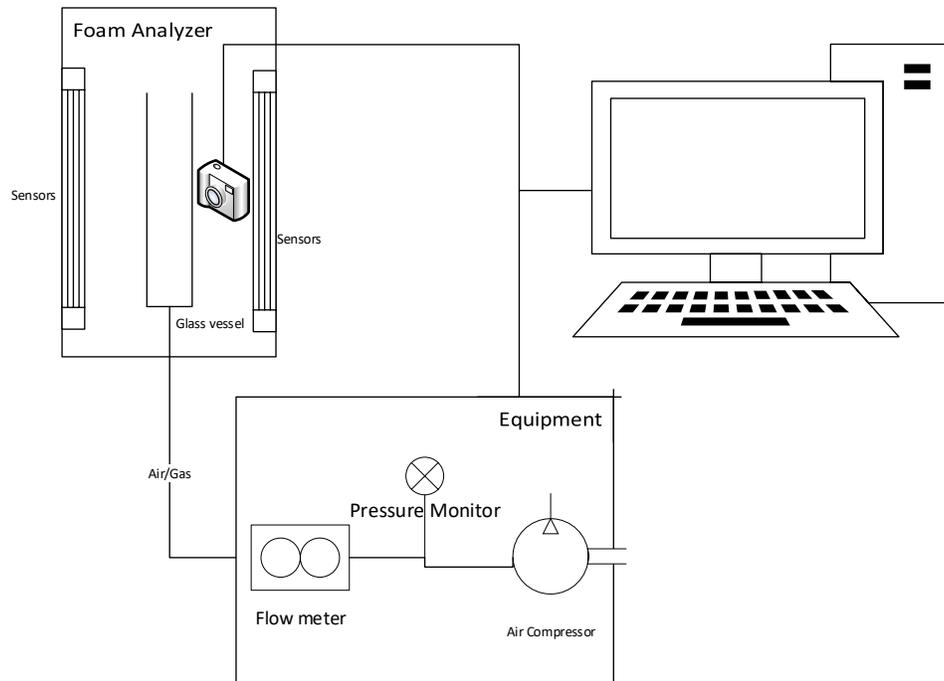


Figure 13: Schematic and experimental of a Dynamic Foam Analyzer

4 Surfactant Foam

Alpha Olefin Sulfonate (AOS) surfactant was used to generate the surfactant foam. Later, different molar salt solution was added in surfactant solution to see the effects of salinity on foam stability. AOS surfactant is best suited for harsh environments because of lesser adsorption on sandstones, good foamability in hard water and the ability to maintain a stable foam in the existence of oil (Farajzadeh, Krastev and Zitha, 2008). The finest advantage of olefin sulfonate surfactants on other surfactants is their good functioning under high saline and high temperature environment (Puerto *et al.*, 2012)

The foamability and stability of foam depend upon surfactant concentration, critical micelles concentration (CMC), formation of black films (common and Newton black films), electrolyte concentration and some other parameters (Apaydin and Kovscek, 2001). CMC is the most critical parameter in a surfactant containing solution. At CMC, surfactant molecules start to accumulate to form thermodynamically stable aggregates called micelles (Williams, 1961; Sperandio, 1965) due to which the properties of a foam vary evidently. Traditionally, a solution with concentration above CMC should be used to get maximum foaming properties (Xu *et al.*, 2009). However, the presence of salt reduces the CMC (Gurkov *et al.*, 2005; Farajzadeh, Krastev and Zitha, 2008) and hence affects the foam properties. The decrease in the CMC that is induced by salt is appreciated by industry because it reduces the amount of surfactant needed. Formation of Common and Newton black films (CBF, NBF) are other important factors which effect the stability of foam. The probability of formation of these films takes place when the film thickness reaches the range of nanometers (4 to 50 nm), particularly in the presence of electrolytes (Pugh, 1996). At this thin scale, in addition to van der Waals and electrostatic forces, third short range forces came into being for the formation of such metastable films (Ruckenstein and Manciu, 2002). However, the formation and thickness of these films depends on type and concentration of surfactants and electrolytes (Cohen *et al.*, 1991). Formation of Common or Newton film provides extra stability to foam by reducing the lamella rupturing (Ruckenstein and Manciu, 2002).

Several researchers have found in their experiments that the addition of salt increases the stability of foam (Xu *et al.*, 2009; Behera *et al.*, 2014; Varade and Ghosh, 2017) while others have

found that the salts increases the collapse rate so destabilizes the foam (Vikingstad, Aarra and Skauge, 2006; Filippov *et al.*, 2018) However, a clear understanding of the underlying mechanisms that determine the impact of salt on the formation and stabilization of foam is necessary. In this chapter, we have investigated the effect of surfactant concentration on foamability and foam stability below and above CMC with and without presence of salt.

4.1 Effect of AOS concentration on Surface tension and CMC determination

It was found that the surface tension of AOS solution decreases with increasing surfactant concentration, which reflects the increment in surface activity of AOS surfactant. With addition of surfactant in solution, adsorption of surfactant on air-liquid interface increases which reduces surface tension. After reaching the CMC, the surface tension does not decrease further with addition of surfactant. The CMC was determined by the abrupt change in slope of surface tension versus log of concentration isotherm. CMC represents the concentration at which the surfactant still exists as a monomer in solution; at larger concentrations the monomers aggregate to form micelles. This aggregation alters the physio-chemical properties of the surfactant solution below and above CMC, hence the properties of foam also show most variability away from CMC. The value of CMC obtained for our AOS solution was 0.07%.

4.2 Effect of AOS concentration on foamability and foam stability

Figure 14 shows the height of foam generated as a function of time for six different concentrations of AOS and thus represents the foamability as a function of concentration. The foam height is increasing by the increase of surfactant concentration and it can be seen that 1% gives rise to the highest initial foam column. AOS at 1% shows maximum height, while there is a sudden decrease in foam height after few seconds which indicates poor stability of foam that arise from AOS at 1%. The effect of the surfactant concentration on foam generating ability is inferred from the maximum foam height at a particular concentration, which increases as the surfactant concentration is increased. Due to increase of surfactant concentration, surfactant molecules increases in bulk solution which results in quicker rate of migration to the gas-liquid

interface (Yekeen *et al.*, 2017) and as fast is the migration rate of surfactant molecules towards interface, higher is the generation of foam (Karakashev and Manev, 2003; Bournival *et al.*, 2014). It is clear from the results that foam height is directly proportional to AOS concentration. Same trends could be found in literature for different type of surfactants (Xu *et al.*, 2009; Simjoo *et al.*, 2013; Yekeen *et al.*, 2017).

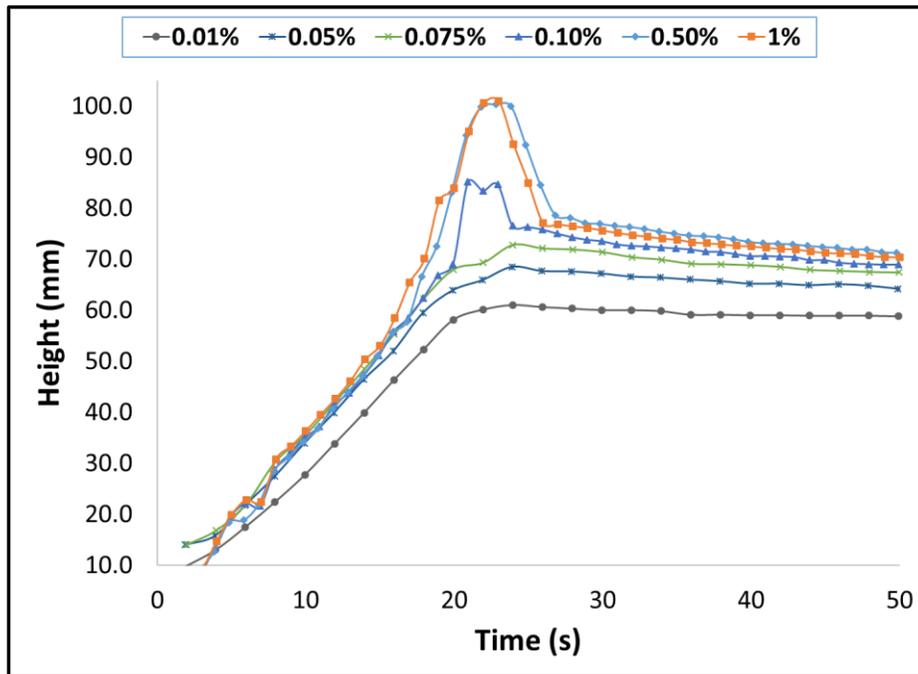


Figure 14: Initial foam height increases with increase in surfactant concentration

Figure 15 shows the foam volume stability (FVS) as a function of time. It can be easily noted that 0.075% AOS has maximum stability and 1% AOS has minimum stability while the trend is not linear throughout with concentration change. The AOS foam has shown maximum stability at 0.075%, which is just above the CMC value. This result is in an agreement to group of scholars (Yekeen *et al.*, 2017) who has found optimum value of concentration for maximum stability (as discussed below) rather than the simple direct relation of stability with concentration. Stability increases from 0.01% to maximum value at 0.075% and then again starts to decrease gradually and reach the constant lowest value beyond an AOS concentration of 0.5%. (Wang and Mulligan, 2004; Wang and Chen, 2013) related the decrease in stability of foam at surfactant concentration greater than CMC with increased weight (gravitational effect) of foam because of excess molecules of surfactant at the lamella. Due to excess of molecules of surfactant, the impact of

gravitational force on drainage of foam increases, which results in constant liquid drainage from the film formed between adjacent bubbles, eventually rupturing the foam film and bubble coalescence (Baz-Rodríguez *et al.*, 2014). According to (Pugh, 1996) the following equation of liquid flow between parallel plates could be used to describe the vertical drainage under the influence of gravitational force, where the drainage is expressed as an average vertical velocity (V_{av}):

$$V_{av} = \rho gh^2 / (8\eta)$$

Where η is liquid's bulk viscosity, ρ is the density of liquid present in the film, h is the thickness of film and g is gravitational constant. However, this vertical drainage is more important in reasonably thick films, i.e. concentrations greater than CMC. Also, the rupturing phenomena in thin layer (less than 100 nm) and in a thick layer (greater than 100 nm) are different which affect the stability of foam. Formation of common black film and Newton black film in thin films give extra stability to lamina as discussed above. So, there exist an optimum concentration which gives maximum stability and above that concentration the foam stability again start to decrease by these results, we can conclude that there is an optimum concentration for foam stability which comes out to be 0.075% in this case as deduced from experimental results.

(Behera *et al.*, 2014) suggested that the rate of collapse increase at higher concentration due to decrease in elasticity of lamella. Elasticity decreases with increase in surfactant concentration and leads to fast collapse of foam. Elasticity is the degree of the capacity of film to regulate its surface tension at the moment of stress. High elastic film has more stability than a low elastic film (Wang, 2018). Due to presence of excessive surfactant molecules in bulk solution at high concentration, the adsorption of surfactant molecules in thin liquid film increases. This results in low rate of film thinning and liquid drainage. Hence, bubble coalescence is reduced and interfacial elasticity of foam is increased due to stabilization of foam lamellae by surfactant molecules (Firouzi and Nguyen, 2013). But the increase in foam stability was found only up to a specific concentration of surfactant, after which increasing surfactant concentration increases the collapse rate of foam (Yekeen *et al.*, 2017).

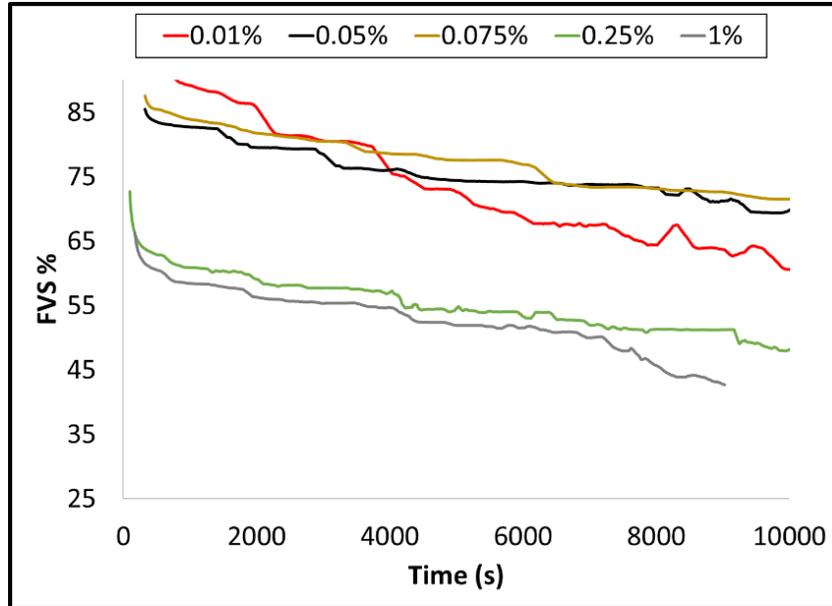


Figure 15: Foam volume stability with time for different AOS concentration. Stability increases up to 0.075 wt% and then again start to decrease onwards

Table 2 shows the comparison of half-life and maximum foam volume of all nine concentrations. Half-life results support the exact trend of foam stability as shown by FVS in Figure 15.

Table 2: Half-Life and Max. foam volume associated with different AOS concentrations

Concentration (%)	Half-life (hrs)	Max Foam Vol (ml)
0.01	3.58	73.8
0.025	7.08	76.1
0.05	8.35	83.0
0.075	8.71	88.0
0.1	4.74	103.0
0.25	2.39	117.0
0.5	1.81	121.3
0.75	1.82	121.6
1.0	1.89	122.2

Figure 16 shows graphical representations of half-life and maximum foam volume for a clear overview of how they change with concentration. From the results (a) it can be easily seen that

half-life has direct relationship with the AOS concentration till 0.075 wt% and then have an inverse relation with further increase in concentration. Figure 16 (b) shows that maximum foam volume is directly proportional to AOS concentration as also conclude from Figure 14 for foam height. This is confirmation of the trend discussed above. However, the effect is drastic at small concentrations and gradual after 0.1%.

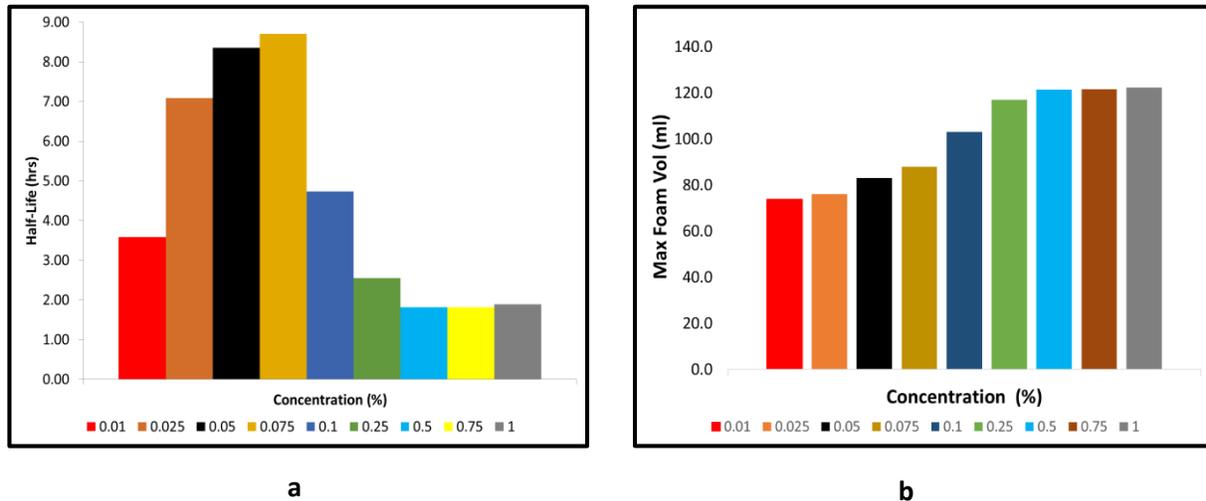
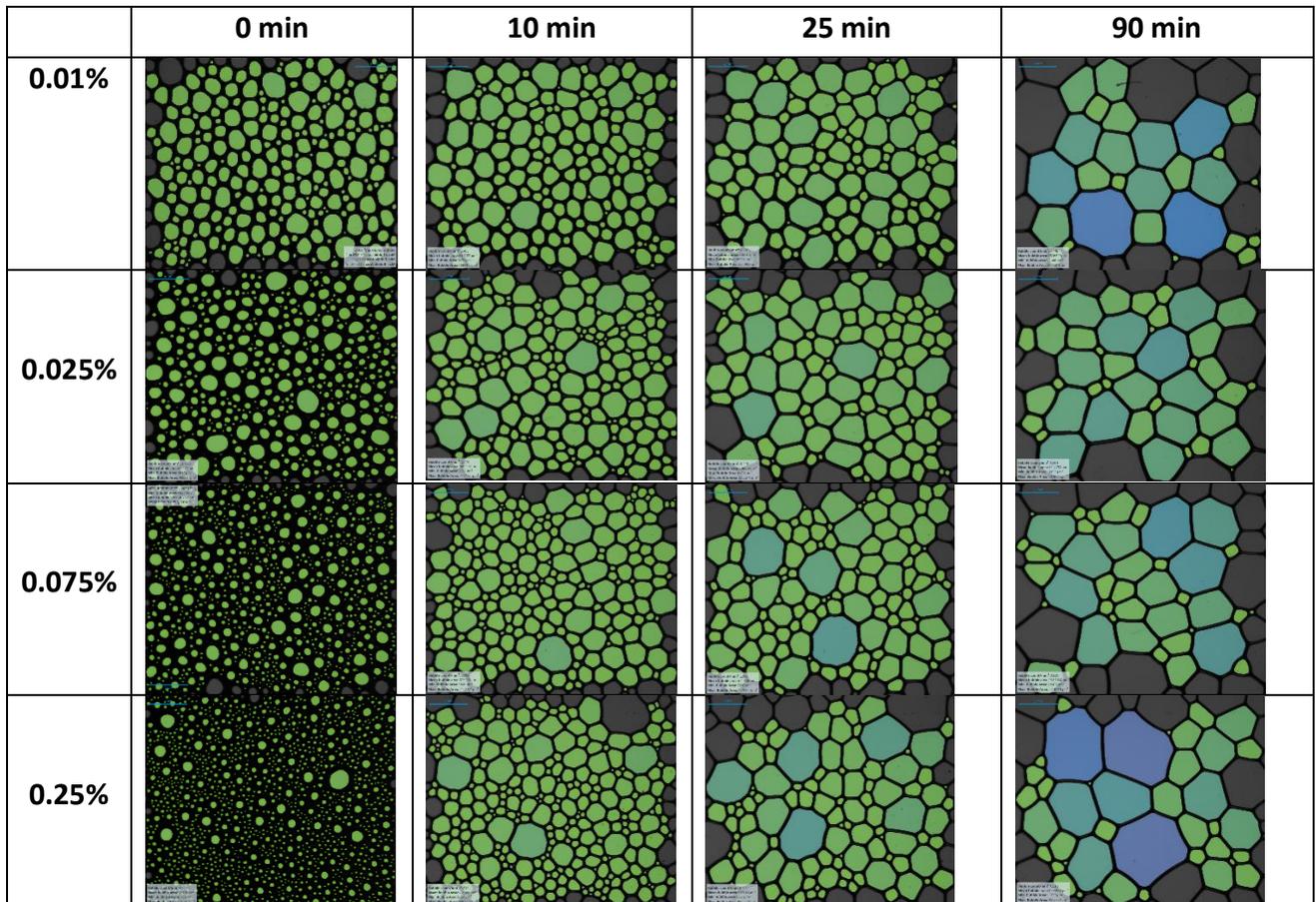


Figure 16: Half-life (a) and maximum foam volume (b) generated at each AOS concentrations

4.3 Foam structure with aging

Foam is comprised of bubbles of various sizes. With time, larger bubbles increase in size due to diffusion of gas from smaller adjacent bubbles and the bubbles become polyhedral from spherical shape. The bubble growth as a function of time is called Ostwald ripening (Stevenson, 2012). Figure 17(a) summarizes the effect of concentration on foamability and stability throughout the foam lifespan. It was observed that the size of bubbles at $t=0$ decreased as the concentration of surfactant increased from 0.01 % to 1%. This is in line with the result that the foam volume increases with surfactant concentration as discussed in section 4.2 hence the size of the bubble reduces to produce more bubbles (compact foam) in the same area. As time passes, diffusion of gas increases the size of larger bubbles and vanishes smaller bubbles which reduce the bubble count. Due to the increase in the size of bubbles, the film thickness reduces which further increase the rate of diffusion and coalescence to make the foam unstable. Therefore, just like foam height and half-life, bubble count and average bubble size are other parameters to asses

the foamability and foam stability, respectively. Figure 17(b) shows the bubble count with time and the results are in accordance with images i.e the bubble count increases as the concentration increases from 0.01% to 1%. Figure 17(c) shows the average bubble area of foam with time for the same five concentrations. Initially, 1% AOS foam shows the minimum and 0.01% shows the maximum bubble size but with time the increment in the size of bubbles is at a maximum (least stable foam) for 1% AOS foam and is minimum for 0.075% AOS foam. In Figure 17(c), it can be seen that 0.075% shows the minimum bubble area and 1% AOS solution shows the maximum bubble area. Hence, 0.075% AOS foam has maximum stability. All concentration curves are in accordance with the half-life results obtained above: stability increases from 0.01% to 0.075% and then again start to decrease and reach the minimum value at 1% AOS solution. Hence the change in bubble structure does not seem to agree with the conclusions that are reached based on foam half-life and volume.



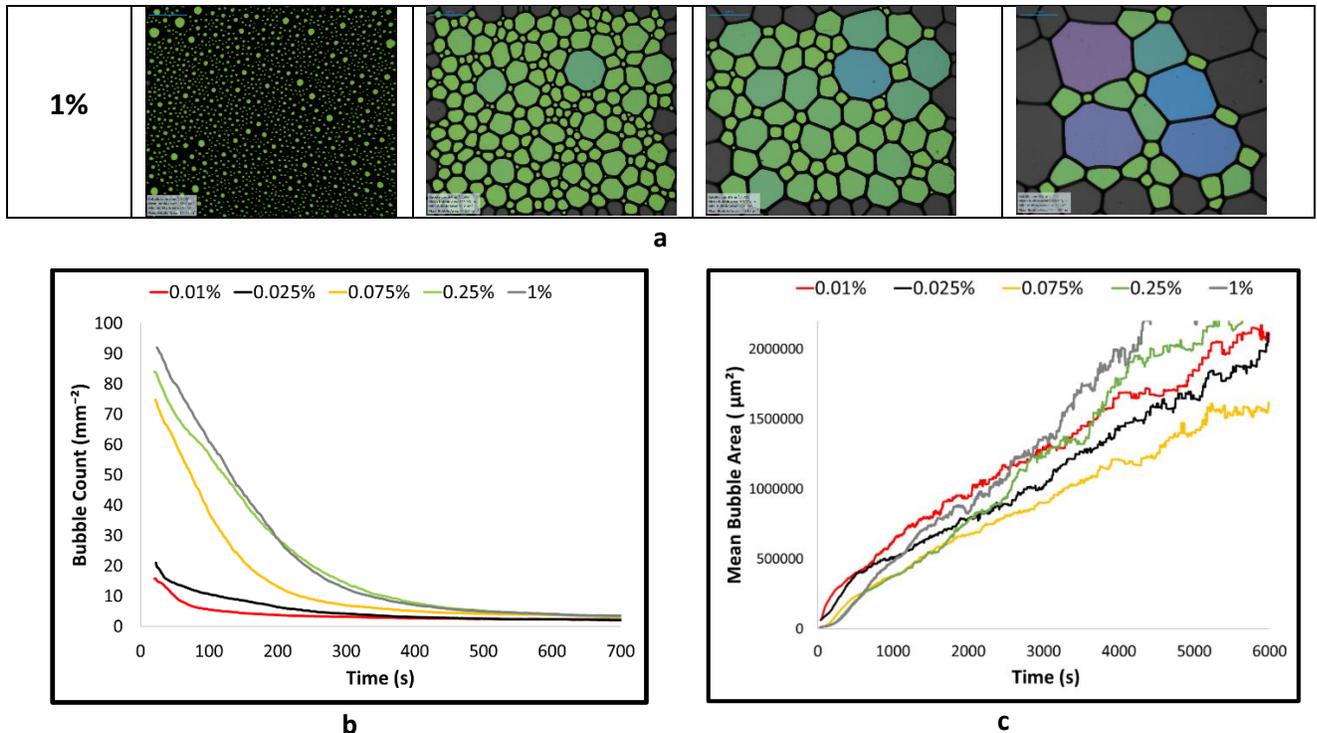


Figure 17: Foam stability at different surfactant AOS concentrations: (a) Images of bubbles and structure of foam, (b) bubble count, and (c) bubble area.

4.4 Surface tension and effect of salt concentration on CMC

The effect of salt concentration on surface tension in 0.01% AOS solution are shown in Table 3. Surface tension reduces with increase in salt concentration. Similarly, a reduction in CMC is observed with addition of salt in AOS solution. The value of CMC reduces from 0.07% to 0.0015% with addition of 1M NaCl salt. Figure 18 represents the surface tension isotherms for AOS and AOS plus 1M NaCl solution. (Farajzadeh, Krastev and Zitha, 2008) also study the change in CMC of AOS with change in NaCl conc. according to their finding the critical micelle concentration (CMC) decreases with increasing NaCl concentration. Similar results were obtained by (Yekeen *et al.*, 2017) which state that: A significant reduction in CMC and surface tension of SDS solution was observed with addition of NaCl in the bulk solution. They reported the reduction in CMC of SDS by order of one with addition of 1 weight percent NaCl to solution. As the amount of added salt increases, the surface tension reduces further resulting in lower CMC values.

Table 3: Effect of salt concentration on surface tension, surface tension decreases with addition of salt

Surface tension (mN/m)	Salt concentration (M)
56.0	0
32.7	0.25
30.3	0.5
29.1	0.75
28.0	1

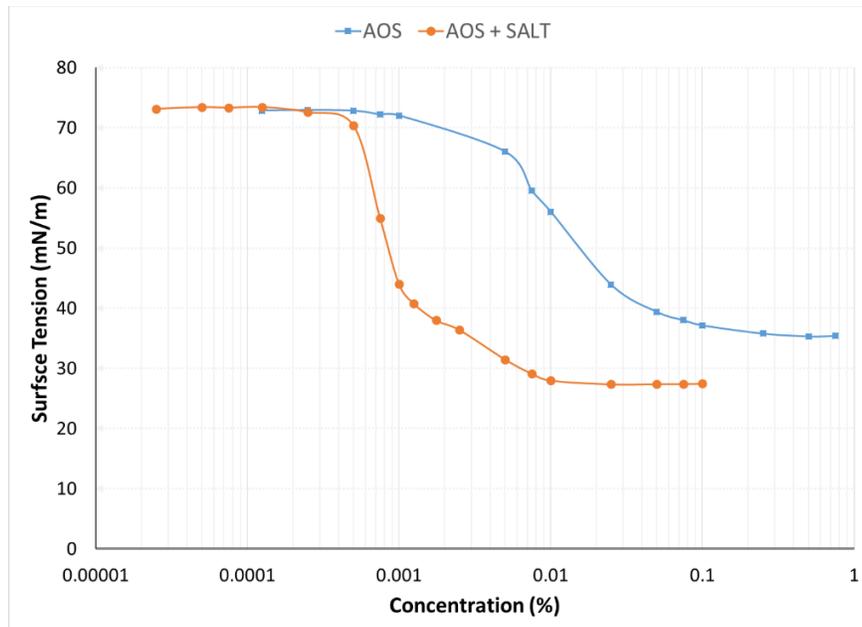


Figure 18: Surface tension of a 0.01 % AOS solution in deionized water and in 1 M salt solution.

Chattopadhyay et al. has related the decrease of CMC and surface-tension of surfactant solution to the fact that the salt favors the transition of molecules of surfactant towards the gas-liquid interface in order to reduce the electrostatic repulsion among the charged head of surfactant molecules (Chattopadhyay and Harikumar, 2003; Xu *et al.*, 2009). Such a shielding of repulsive force promotes the hydrophobic strength of surfactant monomers which results in the formation of micelles at lower surfactant concentration to consequently decrease the CMC (Muherei and Junin, 2007).

4.5 Effect of salt concentration on foam stability

Effects of salts on foamability and stability of foam are ambiguous. Some have found salts to have negative effects on stability as well as foam generation capability while others have found that salts stabilize foam or have a neutral impact. According to Behera and Varade et al. foam stability, as defined by the proportion of foam that has collapsed with time, increases with increase of salt concentration in solution (Behera *et al.*, 2014; Varade and Ghosh, 2017). Xu et al. studied the effect of NaCl as an electrolyte on the SDS surfactant solution below and above the CMC. Addition of NaCl to an SDS solution improve foamability and stability of foam to a certain extent. They noticed the decrease in surface tension and zeta-potential with increase of salt concentration, which as a result reduce the surface charge of SDS micelles. Hence, the results suggest that the stability of foam and foamability increase in the presence of salts (Xu *et al.*, 2009). Tan et al. studied the effect of NaCl, MgCl₂, and CaCl₂ on the foam generated using polypropylene glycol (PPG) (Tan *et al.*, 2005). They suggested that the valence of the ions has a greater effect on the foamability of PPG than salt type. According to Tan et al. less foamability and foam stability in the existence of salt are because of mitigation in electrostatic repulsion among the charged bubble surfaces. High salt concentration reduces electrostatic repulsion, and therefore foamability. Vikingstad et al. reported the effect of salt on AOS and FS500 in presence and absence of oil (Vikingstad, Aarra and Skauge, 2006). The brine concentration has little or no effect on the foam height in the absence of oil (Vikingstad, Aarra and Skauge, 2006). However, in the presence of oil, high ionic strength reduces the foam stability. Farajzadeh et al. (Farajzadeh, Krastev and Zitha, 2008) have also analyzed the effect of salt on AOS surfactant foam. They measured the foam film thickness as a function of NaCl and AOS concentrations. They have found a relation between the film thickness and the contact angle of the meniscus with the film. They found critical AOS concentration value for the formation of stable films and also for the formation of stable newton black films, the critical NaCl saturation value. Craig et al. (Craig, Ninham and Pashley, 1993) performed a series of experiments to demonstrate the effect of electrolytes on coalescence of foam bubbles. According to their observation, the effect on bubbles coalescence is not consistent for different type of electrolytes as some reduces the coalescence phenomena

while other others do not. Hence, hydrophobic interaction with electrolytes could be the reason for the change in coalescence phenomena due to presence of electrolytes.

To investigate the effect of salinity on foaming ability, a series of experiments were performed by keeping the AOS concentration constant (0.25%) while varying the salinity. Figure 19 shows the effect of varying salt concentration on the foamability of AOS. It can be easily noticed that the height of foam is increasing with the increase of molar concentration of salt. The experiments were only performed for one hour to screen for the effect on foamability.

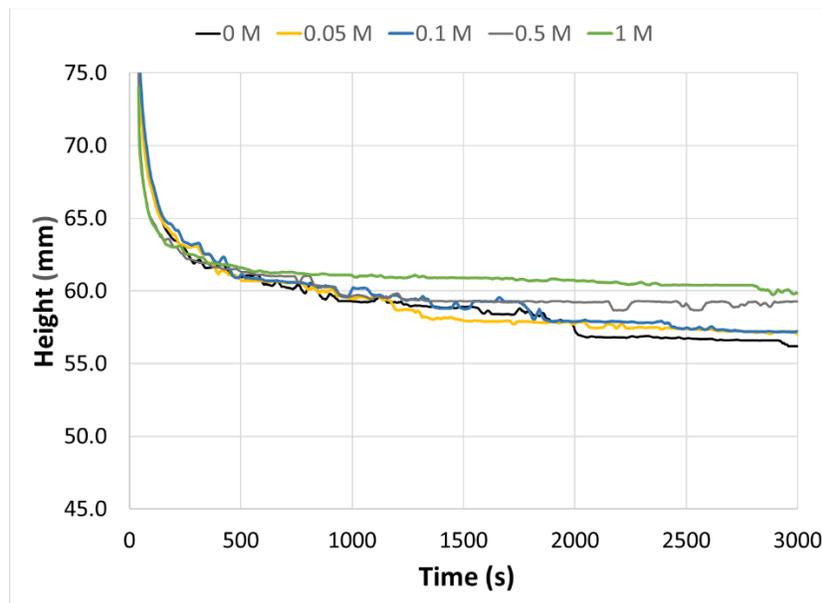


Figure 19: Foam height with time by increasing salinity of 0.25% AOS solution

To examine the effects of salinity on the foam stability, longer time-scale experiments were performed to ensure that all effects up until the half-life (using 1M NaCl and 0.25% surfactant solution) are captured. Surprisingly, the results show that the half-life was increased more than twofold. We propose that the presence of salt forms an electrostatic double layer (EDL) within the lamina and that the screening effect of this EDL is the main reason for the decreasing coalescence. This results in stabilizing the foam for an extended period of time because of formation of smaller and resistant bubbles which gives the tight packing of the liquid lamella among bubbles as also explained by Xu et al. (Xu *et al.*, 2009). The addition of NaCl salt decreases the gas solubility into the solution hence reduces the hydrophobic interaction which as a result

increase the foam stability by suppressing the coalescence rate of bubbles (Firouzi and Nguyen, 2014).

To assess the impact of surfactant concentration, a range of experiments were conducted where the salt concentration was kept constant at 1M and AOS concentration was varied. At 0.1% AOS and 1M NaCl solution, the results differ from the findings above in the sense that a lower half-life was observed for the saline solution, and this reduction in the stability becomes more prominent at AOS concentrations lower than 0.1 %. Figure 20 depicts the effect of salt addition at various AOS concentrations. From these results, it can be concluded that salts can stabilize or destabilize the foam depending on surfactant concentration in solution. Above a critical surfactant concentration, salt stabilizes the foam. However, at a lower concentration of surfactants, added salts result in destabilizing the foam.

We propose a mechanism to unify these apparently contradicting findings in Figure 21. When AOS is in demand to form the film, occupying surfactant molecules with electrolytes has a negative effect on film stability (left). Whereas when there is an AOS surplus, it was a positive effect to take the surfactants out of the equation and has a positive effect on film stability, because they will interfere with the (already appropriate amount of) surfactants at the interface of the film. At low concentrations, the AOS molecules are surrounded by electrolytes which result in a decreased film stability. However, at higher concentrations, the surplus surfactant molecules could improve film stability. In the case of higher surfactant concentrations and in the absence of electrolyte, low foam stability can be associated with high liquid drainage rate due to increased gravitational effect as explained above. In short, it is the balance between surfactant and electrolyte concentration that decides the film stability.

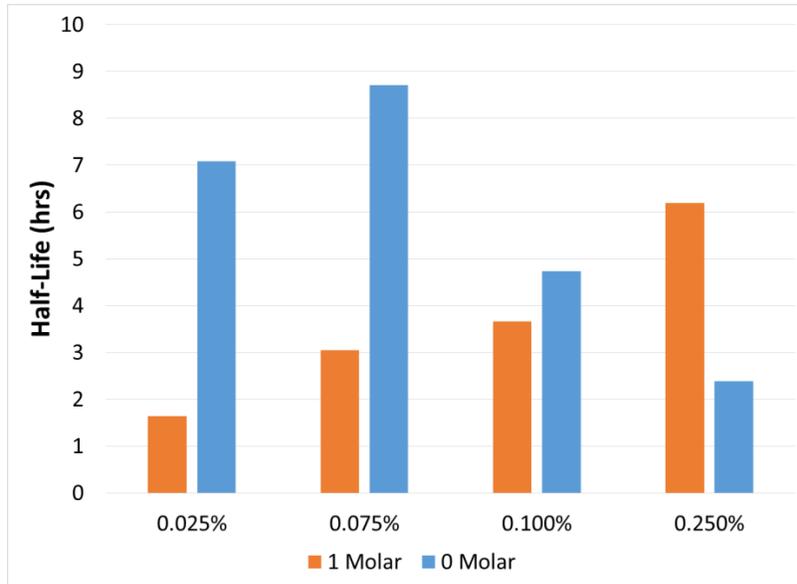


Figure 20: Comparison of the half-life of AOS foam in the absence and presence of salts at four different surfactant concentrations.

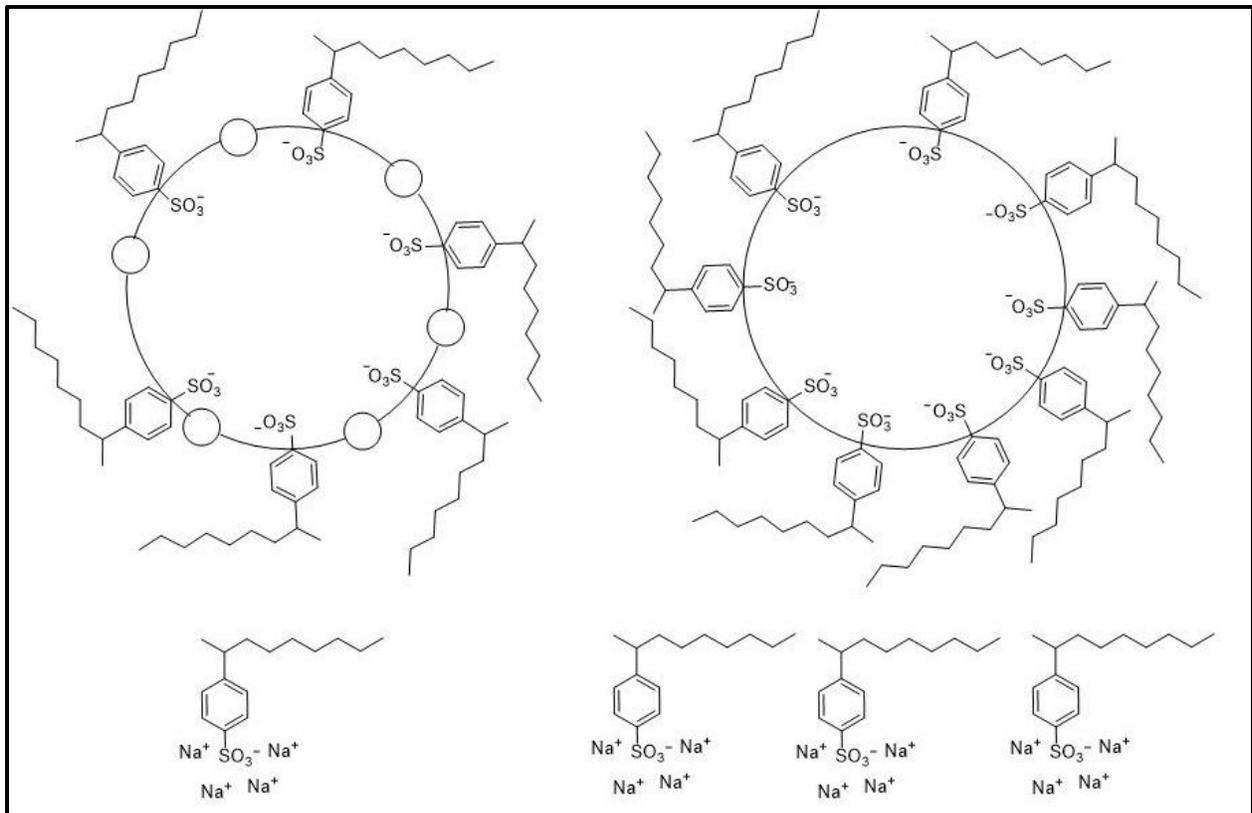


Figure 21: Proposed mechanism of the effect of salt addition on foaming properties

4.6 Summary of chapter

A systematic study was performed to examine the effect of surfactant concentration and presence of salt on the stability of surfactant foam. The key purpose of this chapter was to investigate the apparently contradicting findings that are presented in the literature on foaming characteristics in the presence of salt.

- Foamability increased with increasing AOS concentration. However, the effect is more dominant below CMC and not significant at higher concentrations (>CMC).
- In the absence of NaCl, an optimum surfactant concentration was found that maximize the stability of foam which was slightly higher than the CMC. The decrease in stability of foam at higher surfactant concentrations is due to the greater influence of gravitational forces.
- At constant salinity, the increase in AOS concentration improved foam stability. At some typical AOS concentration (0.25% in this case), the foam stability of AOS solution in presence of NaCl surpass the foam stability of AOS solution without NaCl.
- Salt can destabilize or stabilize the foam depending on the surfactant concentration; this apparently contradicting result is due to opposing effects of letting the electrolytes surround the AOS molecules at low vs high concentrations.
- When the AOS molecules are in excess, higher stability is achieved. However, when electrolytes are in excess, AOS molecules get completely surrounded by electrolytes which prevent them from entering the micellar structure that make up the foam lamellae.

5 Polymer Enhanced Foam

Enhanced oil recovery (EOR) processes using gas as a displacing fluid (miscible or immiscible) is applied in heterogeneous low-permeability oil reservoirs to reduce the viscosity (miscible injection) or to enhance sweep efficiency (immiscible displacement) (Hussain and Kamal, 2018). This technique, however, poses several challenges such as viscous fingering, gas riding, gravity segregation, poor mobility ratio and low sweep efficiency especially in heterogeneous and fractured oil reservoirs (Kamal *et al.*, 2018). The main reasons for these problems are the huge density and viscosity differences between injected gas and reservoir fluids (Yaghoobi, 2007). Foam or surfactant alternating gas (SAG) injection improves the sweep efficiency by hindering high permeability zones and diverting the fluid towards less permeable sections (Kovscek *et al.*, 1995; Li *et al.*, 2008). Also, the surfactant foams reduce the IFT between oil and water and improve the displacement efficiency (Burley, 1985). Surfactants can act as dispersants, wetting agents, demulsifiers, emulsifier, foaming agents and IFT reducers depending on the application and choice of surfactants (Hussain *et al.*, 2019).

Although surfactant foams are good in improving oil recoveries, their short life in porous media is not efficient for long term treatments. To obtain better stability, polymers are added in surfactant foams termed as Polymer enhanced foams (PEFs) (Huh & Rossen, 2008; Zhao *et al.*, 2015). Surfactant helps in reducing the surface tension between the fluids and alter the wettability of reservoir rock whereas polymers hinder the desorption of surfactant molecules from the foam film (lamellae) and increase the viscosity of foams which reduces the liquid drainage and coalesce phenomena hence increase the foam stability (Sydansk, 1994a). Polymer enhanced foam flow into high permeability streaks and block the dominant channels hence improve the swept volume by making a piston-like displacement of displacing fluid. The selected surfactant should be compatible with the applied polymer (Shakil Hussain, Kamal and Fogang, 2018). PEFs have become an important technique in petroleum industry in many fields of application: selective acidizing, blocking of high permeable zones, improving sweep efficiencies, stabilizing surfactant foam in high salinity, high temperature and oil-saturated zone, mobility control and conformance-improvement treatments especially for fractured and heterogenous

reservoirs (Sydansk, 1994b, 1994a; Huh and Rossen, 2008; Sun *et al.*, 2015; Zhao *et al.*, 2015; Li *et al.*, 2018; Shakil Hussain, Kamal and Fogang, 2018).

In this chapter, we have investigated the foamability and stability of polymer enhanced foam in comparison to surfactant foam. Furthermore, the effect of polymer's molecular weight and degree of hydrolysis on foam stability has been studied by investigating the bubble count, foam height, foam half-life and structure of the foam.

5.1 Effect of polymer addition to surfactant foam

Figure 22 shows the height of foams as a function of time. Surfactant foam was generated using 0.25% AOS and 0.5M NaCl solution while the PEF was generated using 0.25 % AOS, 0.5M NaCl solution and varying concentration of polymer. It was found that the volume of foam generated using surfactant solution was quite good but most of the foam was collapsed within few minutes which indicate the poor stability of surfactant foam. On the other hand, PEF generated less volume of foam as compared to AOS while the stability of PEF was much better than surfactant foam. It can be clearly seen in Figure 22 that the collapse of surfactant foam in early life is drastic in contrast to PEF which has shown vary less decrease in foam height. In AOS foam, the drainage of liquid makes the upper part of foam dry within few minutes and reduces the film thickness which increases the rate of diffusion of gas between the bubbles resulting in enlargement and collapse of bubbles. The diffusion of gas takes place from smaller bubbles to larger bubbles due to pressure difference which results in the elimination of smaller bubbles and enlargement of bigger bubbles (Stevenson, 2012).

The maximum volume of foam produced using surfactant solution was 117.7 ml on the contrary polymer solution generated only 83 ml of foam. But the interesting thing is that the half-life (time in which the volume of foam deteriorates to 50% of its initial volume) of PEF is much better than the surfactant foam. Surfactant foam has shown half-life of 2.6 hours while the PEF has 3.7 hours which is almost 1.5 times to that of surfactant foam life. The addition of polymer increases the viscosity of the foam. On the other side, this increment in viscosity makes the foam film thicker which reduces the film thinning and decrease the drainage of the liquid which as a result make

the foam more stable (Zhao *et al.*, 2015). High viscosity reduces the coalesce factor and diffusion on gas among bubbles while surfactant foam has more volume, but due to lower viscosity, bubbles easily merge into each other and, as a result, the foam collapses early as compared to PEF.

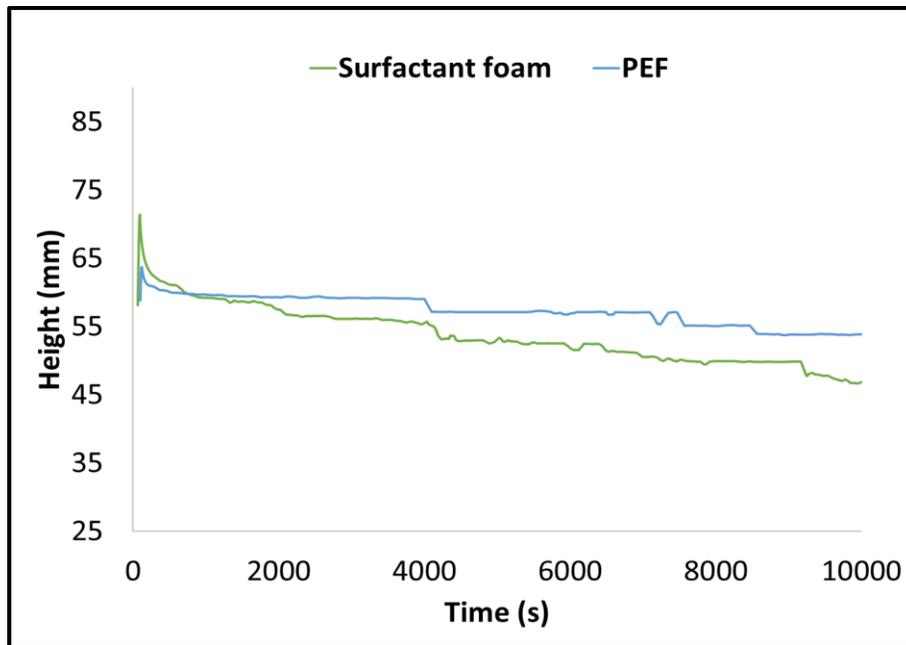


Figure 22: Height of surfactant foam and PEF as a function of time. Surfactant foam: 0.25% AOS +0.5M NaCl solution, PEF: 0.25% AOS + 0.01 Polymer-3 + 0.5M NaCl solution

5.2 Effect of polymer's concentration and molecular weight on foam stability

The PEF was tested over a wide range of concentration starting from 0.01% to 0.25 %. Several different polymers with different molecular weights and different anionicity were tested at different concentrations to get the clear impact of the aforementioned factors on foam stability. Figure 23 shows the effect of polymer concentration and molecular weight on the half-life of PEF. The results are of two polymers (P-5 and P-6) having molecular weights of 7 and 9 million Daltons, respectively. It was found that the half-life increases (by increasing the polymer concentration from 0.01 to 0.025 from 3.71 to 3.92 and 2.60 to 2.70 hrs. for P-5 and P-6 respectively). However, with a further increase in polymer concentration half-life start to decrease. So, an optimum

concentration to produce stable PEF was achieved. Same trends were observed for other sets of polymers tested having same degree of hydrolysis and different molecular weights. The increase in viscosity of solution with increasing polymer concentration and its effect on reduction in coalescence can still be observed from the structure of foam, which is discussed in the later section. However, the decrease in stability of foam after optimum concentration is due to the enhanced effect of gravity on the dense liquid of higher polymer concentration solution. It was also found that the polymer foam with a higher molecular weight shows lesser half-life than the polymer foam with lower molecular weight. The head retention value (HRV) is higher for P-5 than the P-6 (36s and 23s respectively), which shows the faster drainage of higher molecular weight polymer foam e.g. P-6. HRV is the time in which 25% of the liquid is drained out from the foam. Hence, the less half-life at higher concentration and faster drainage of higher MW foam could be correlated to gravity effects. Literature (Wang and Mulligan, 2004; Wang and Chen, 2013) discussed the same reason for the reduced stability of surfactant foam at higher concentration.

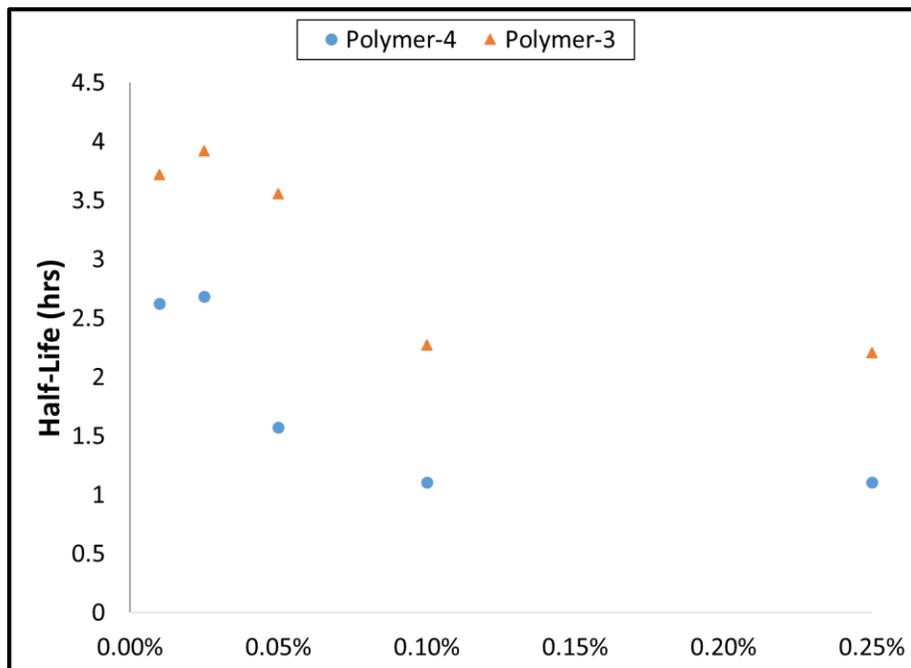


Figure 23: Half-life as a function of polymer concentration and molecular weight. Polymer-3 and Polymer-4 having a molecular weight of 7 and 9 million Daltons respectively.

5.3 Effect of degree of hydrolysis on foam stability

To check the effect of solely the anionicity on foam stability, results of polymers having the same molecular weight but different degree of hydrolysis (DH) were compared at different concentrations. Figure 24 shows the half-life of two polymers (P-2 and P-4) having MW of 15 million Dalton and DH 15 and 30, respectively. It was found that the PEF having higher DH shows higher stability throughout the concentration range tested. The influence of polymer concentration was the same as discussed above. However, the difference between the half-life of two polymers decreases as the concentration is increased.

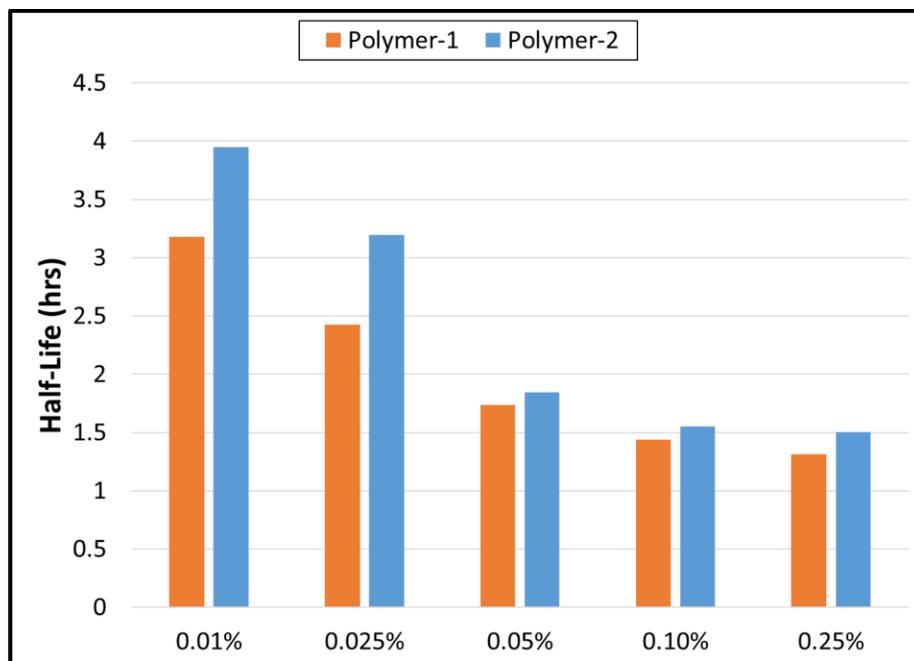


Figure 24: Half-life as a function of polymer concentration and degree of hydrolysis. HPAM 1630 and HPAM 3530 having a molecular weight of 15 million Daltons and DH 15 and 30 respectively.

5.4 Effect of temperature on polymer's viscosity

To assess the temperature tolerance, viscosity was measured at different temperature starting from 25°C to 80°C. Results show that the sulfonated polymers (AMPS) perform better at every temperate. However, the difference was minimum at low temperature. At high temperature, reduction in viscosity of sulfonated polymers was much lower than conventional HPAM polymers. Novel sulfonated polymers showed much better performance compared to the

conventional HPAM polymer. For HPAM, the viscosity of the solution reduced at high temperature in the presence of salts whereas sulfonated polymers maintained a high viscosity in the presence of salts that resulted in less liquid drainage and enhanced foam stability. Table 4 shows the viscosity comparison and percentage decrease in viscosity for conventional HPAM (P-1) and sulfonated (P-6) polymer at 25°C and 80°C.

Table 4: Viscosity reduction comparison of HPAM and AMPS at 25°C and 80°C

Temperature (°C)	Estimated zero shear viscosity (Pa.s)		Percentage decrease HPAM	Percentage decrease AMPS
	HPAM	AMPS		
25	8.30623	8.57243	80.5	46
80	1.62114	4.63218		

5.5 Effect of viscosity on gas diffusion through lamella

Due to stable viscosity of AMPS, film elasticity is maintained which reduces the gas diffusion between bubbles resulting in better stability of the foam. Reduction in liquid drainage rate was much higher for sulfonated polymer compared to the conventional HPAM due to viscosity of the foaming solutions. As a result, AMPS solution shows higher half-life than HPAM. Just like foam half-life, mean bubble area is another parameter to assess the stability of the foam. Increase in mean bubble area (bubble size) with time indicates less stability of the foam. Initially, foam comprises of bubbles of various sizes. With time, larger bubbles increase in size due to diffusion of gas from smaller adjacent bubbles and the shape of bubbles changes from spherical to polyhedral. This growth of the bubbles with time is known as Ostwald ripening (Stevenson, 2012). Figure 25 shows the increase of bubble size with time for 2 HPAM and 2 AMPS foams. The results show that the HPAM experience fast increase in bubble size with respect to AMPS. These results confirmed the increased viscosity effects of AMPS as discussed in the previous section. Also, the curve with higher polymer concentration experience less increase in sizes of bubbles as compared to lower concentration curve. Due to higher AMPS foam viscosity, the diffusion of gas through the bubbles films is reduced which slows down the Ostwald ripening process.

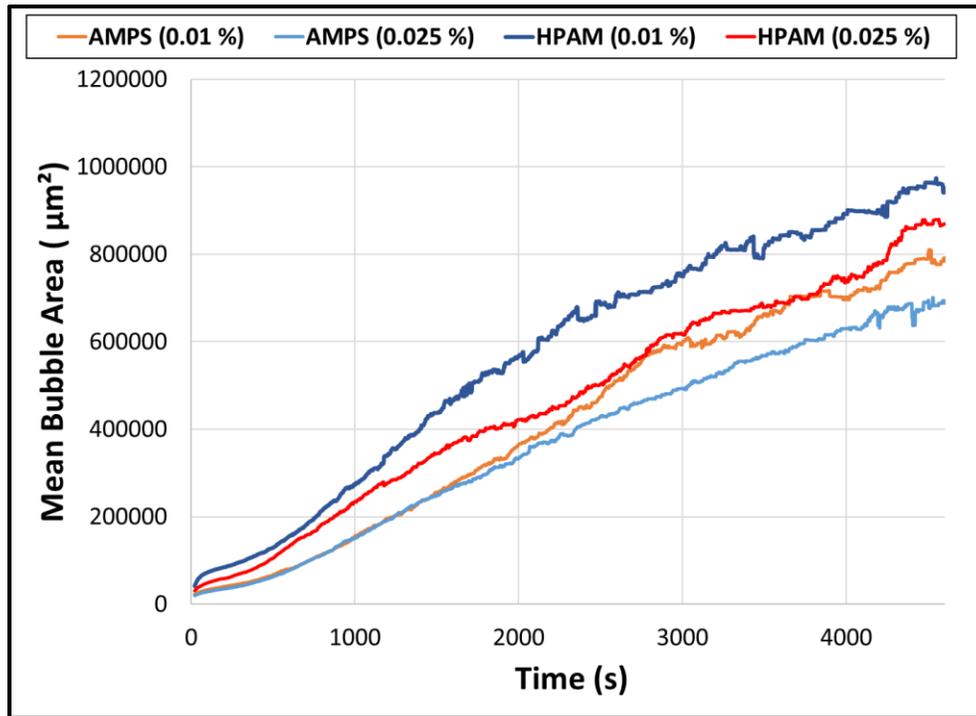


Figure 25: Comparison of Bubbles size of HPAM and AM-AMPS foams with time

5.6 PEF structure with aging

Figure 26 shows the images of foam captured by the camera, through the prism, attached at a height of 85 mm with a glass column. Time zero indicate the stabilization time of foam after injection of gas is stopped. Clear shift between the size and numbers of bubbles (bubble count) can be easily noticed from the images between the surfactant foam and PEF. AOS foam has much smaller and more bubbles at zero time which indicate the proper displacement of gas through the liquid due to lower viscosity of surfactant solution hence generating high foam volume. However, if we move across the time axis, the bubble size increases faster in surfactant foam indicating the higher diffusion of gas between the bubbles and greater coalesce factor. The number of bubbles at 150 minutes is much smaller in surfactant foam in comparison to PEF.

On making a comparison of the foam structure between the different concentration of PEFs which is shown in the lower three rows of Figure 26. It was found that with the increase in the concentration of polymer in PEF, the bubble count decreases and formation of boulder bubbles

with thick foam film was observed. While moving along the time axis, at higher concentration the fall of the foam (as a whole) under gravity is faster than at lower concentration. Absence of foam bubbles could be seen in the upper part of the image of 0.25% PEF at 150 mins. However, the size of bubbles in the same image is not that big as could be seen in AOS foam, this proves the above-stated justification that the collapse of PEF is due to the enhanced gravitational effect on dense foam.

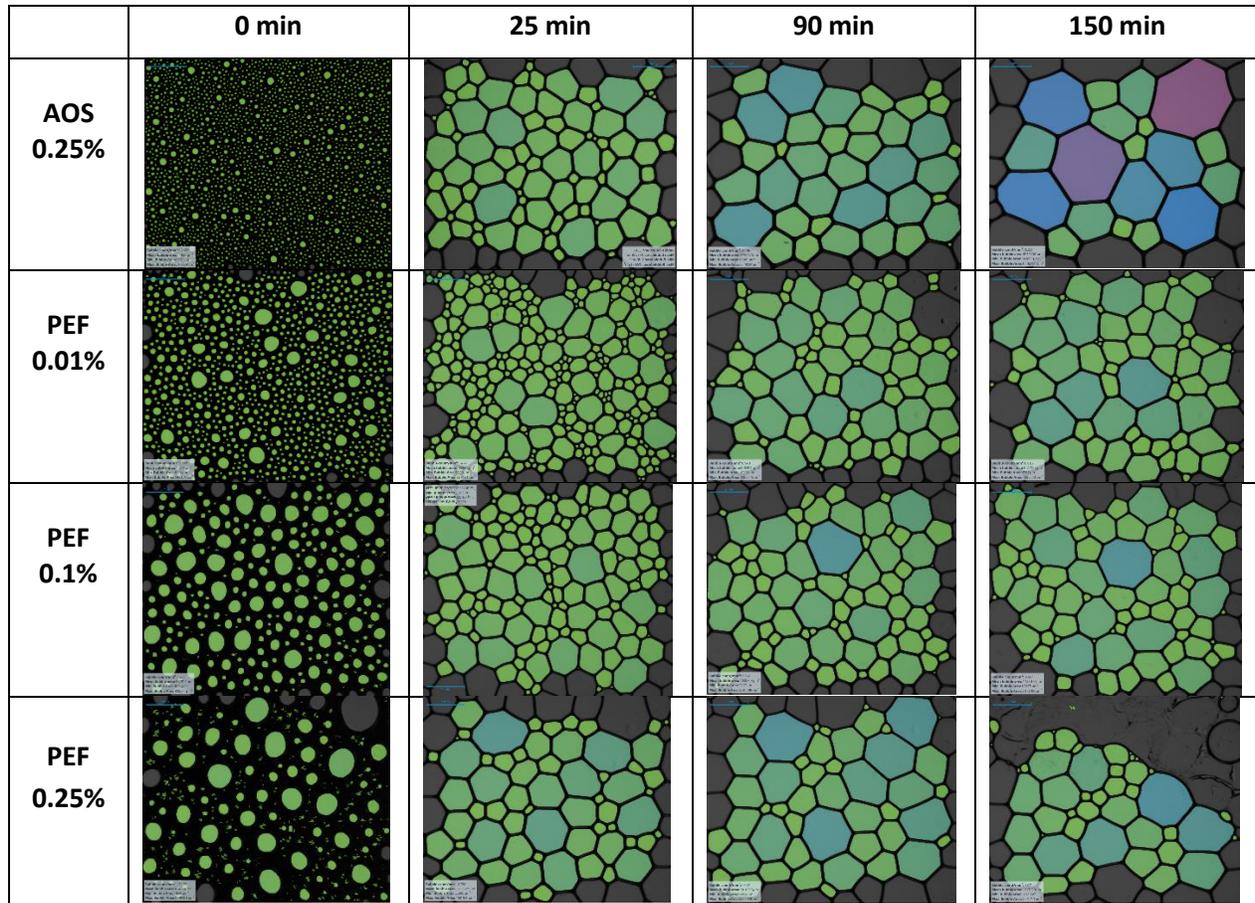


Figure 26: Images of foam structure for AOS and Polymer foam at different concentration and time

5.7 Summary of chapter

A systematic study was performed on the application of polymer enhanced foam by varying molecular weight and structure for CO₂ foam stabilization. The purpose of this study was to understand the influence of polymer molecular weight, polymer concentration and degree of

hydrolysis on foam stabilization for a foaming EOR process. Following conclusions have been made from the results obtained:

- Addition of polymer increases the foam stability by reducing the film thinning and coalesce factor. Increase in viscosity is the main reason for higher stability in PEFs. However, the foam volume is reduced with the addition of polymers.
- Optimum concentration was obtained for stable PEF after which the stability decreases with increasing the polymer concentration.
- Coalescence is reduced at high polymer concentration, but the half-life also reduces due to increased density of the liquid in bubbles films.
- Polymers with higher molecular weight generate less stable foam in comparison to lower MW polymer foam. But the polymers with a higher degree of hydrolysis generates more stable foam and vice versa.

An optimum value of polymer concentration, molecular weight, and degree of hydrolysis is required in order to achieve the maximum foam stability.

6 Synergic effect of Polymers and Nanoparticles

The improvement in sweep efficiency, mobility ratio and increment in oil recovery using foam instead of water and gas injection is discussed in detail in literature and has been proved on lab scale as well as on reservoir scale specially in China (Li *et al.*, 2008; Sheng, 2013; Hosseini and Foroozesh, 2019). However, the overall efficiency of foam flooding mainly dependent on the life of stable foam. The short life of unstable foam could make the project unsuccessful at very early stage. Addition of polymers and nanoparticles in surfactant foam are playing a vital role to achieve stable foam at harsh reservoir conditions (Zhao *et al.*, 2015). Polymers mainly increase the viscosity of the foam and hence reduce the coalescence phenomena and improve the mobility ratio, nanoparticles adsorb at the lamella which increase the viscoelasticity of the thin film and mainly control the drainage of the liquid (Moradi-Araghi, 2000; Sun *et al.*, 2014). Apart from stabilizing foam, NPs hinders the fluid flow and are very effective in blocking high permeability streaks and are widely used in fracturing fluids (Lv *et al.*, 2015). Previous studies have reported use of NPs in controlling water production and enhancing the stability of foam (Sun *et al.*, 2014).

6.1 Effect of NPs concentration on foam stability

In this chapter fine SiO₂ is used as nanoparticles in polymer enhanced foam to get the synergic effect of polymers and NPs on foam stability. The nanoparticles (purity > 99 wt %) were supplied by Wacker Chemical co. Ltd. Germany. The diameter ranges from 11 to 14 nm with spherical shape. Nanoparticles concentration of 100, 250 and 500ppm were tested in (0.05% polymer + 0.25 AOS and 0.5M NaCl) solution. Later NPs concentration were kept constant (500ppm) and polymer concentration were varied to check the effect of polymer variation in presence of NPs. Addition of NPs increase the stability of foam drastically. None of the test reach half-life in test duration of 8 hours. Figure 27 shows the height of foam in presence of NPs with changing concentration. The height of foam remains almost constant for all three concentration for the whole length of experiment however, for highest concentration of NPs (500ppm), small decrease in foam height could be observed in second half of test. This shows that even small amount

(100ppm) of NPs can stabilize the foam effectively and higher concentration make the foam dense which will have worse effect on foam stability.

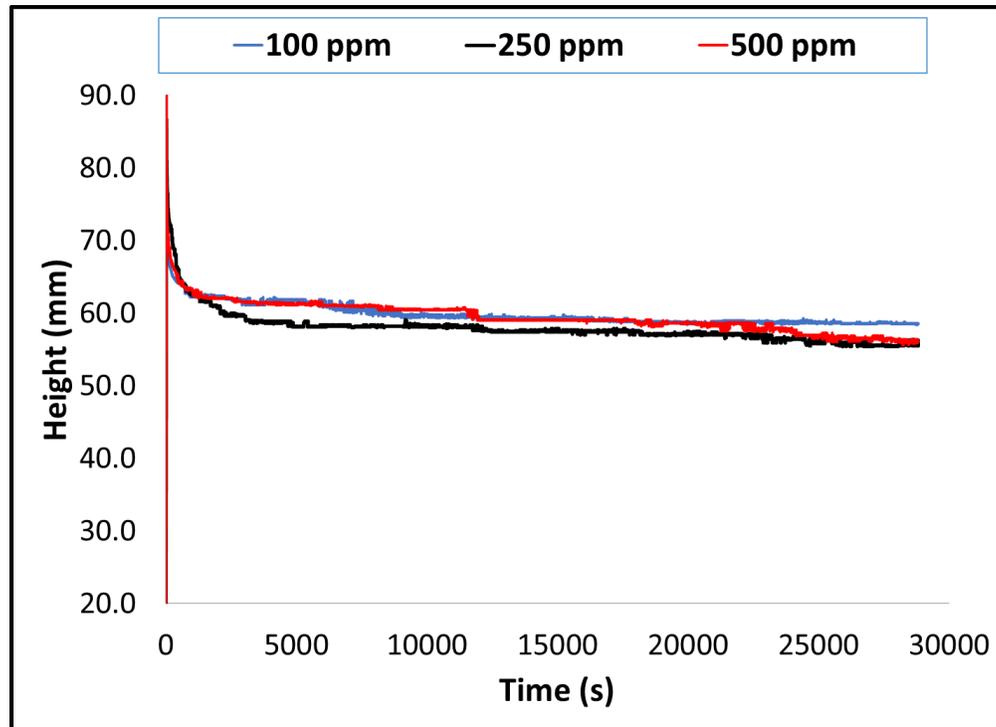


Figure 27: NPEF height with varying NPs concentration

6.2 Effect of polymer concentration on stability and stability of NPEF

To analyze the effect of polymer concentration in the presence of NPs, tests were performed by keeping the NPs concentration constant and polymer concentration were varied (0.05%, 0.1% and 0.25%). The worst NPs concentration (500ppm) was chosen in order to check if half-life could be obtained during the 8 hours test time. None of foam reached its half-life however, the effect of polymer concentration can easily be observed in Figure 28a. The curves have steeper trend of height with time for higher concentration foam. The results are in comparison with the trends obtained for PEF in previous chapter. Also, the foam volume decreases (but slightly) with increasing the polymer concentration as shown in Figure 28b. The foam volumes obtained were 93.1 ml, 91.4 ml and 89 ml for 0.05%, 0.15% and 0.25% polymer concentration foam respectively. From these results, it could be deduced that lower or optimum concentration of NPs and polymer are favorable to achieve the most stable foam.

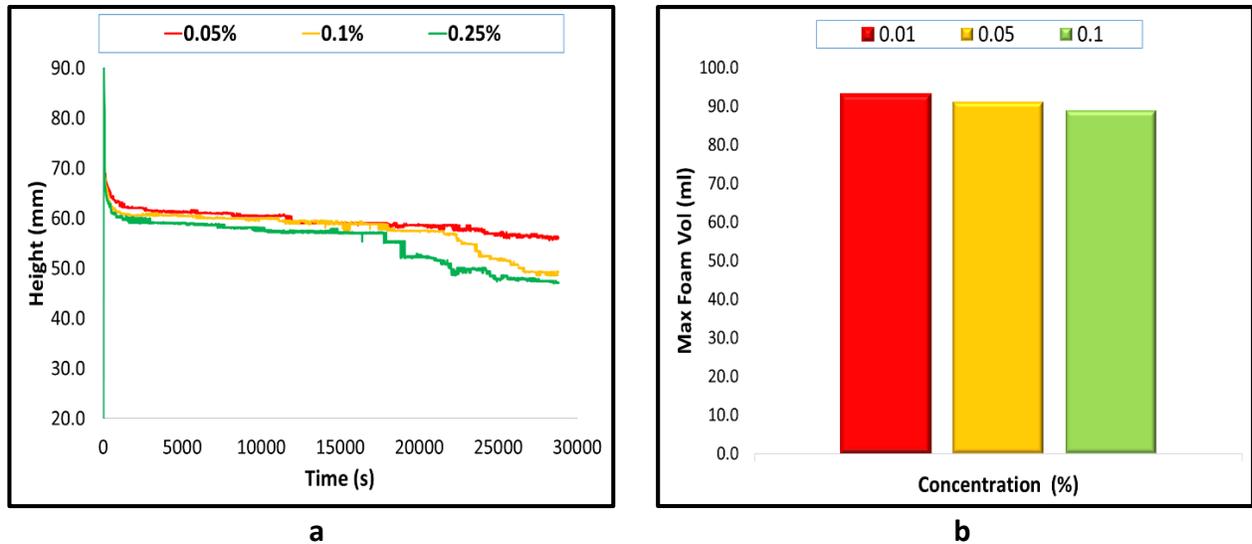


Figure 28: Foam height (a) and foam volume (b) for with changing polymer concentration for NPEF

6.3 NPEF structure with aging

Figure 29 shows the images of foam captured by the camera, through the prism, attached at a height of 85 mm with a glass column. Time zero indicate the stabilization time of foam after injection of gas is stopped. Clear shift between the structure of foam and numbers of bubbles (bubble count) can be easily noticed from the images between the surfactant foam and PEF and NPEF. The difference between the PEF and surfactant foam is already discussed in previous chapter. Both the PEF and NPEF contain the 0.25% of polymer concentration. The problem faced in PEF at higher concentration (greater than optimum concentration) was the excessive drainage of dense liquid which resulted in fast collapse of foam without reaching the maximum bubble size. The addition of NPs in PEF mitigates the liquid drainage by adsorbing at the liquid gas interface which can also be observed in images of bubbles for NPEF. The adsorption of NPs on liquid gas interface strengthen the film and increase the elasticity of lamella. Also, the difference in bubbles size for NPEF is less as compared to PEF which indicate the stable foam. Higher the difference between the sizes of bubbles more is the pressure gradient between the bubble which result in fatter diffusion of gas from smaller to larger bubbles. The size of the bubbles at 150 min also indicate that the NPs helps in reducing the diffusion of the gas between the bubbles which

is because of better elasticity of thin films of bubbles in presence of NPs as discussed by (Sun *et al.*, 2014).

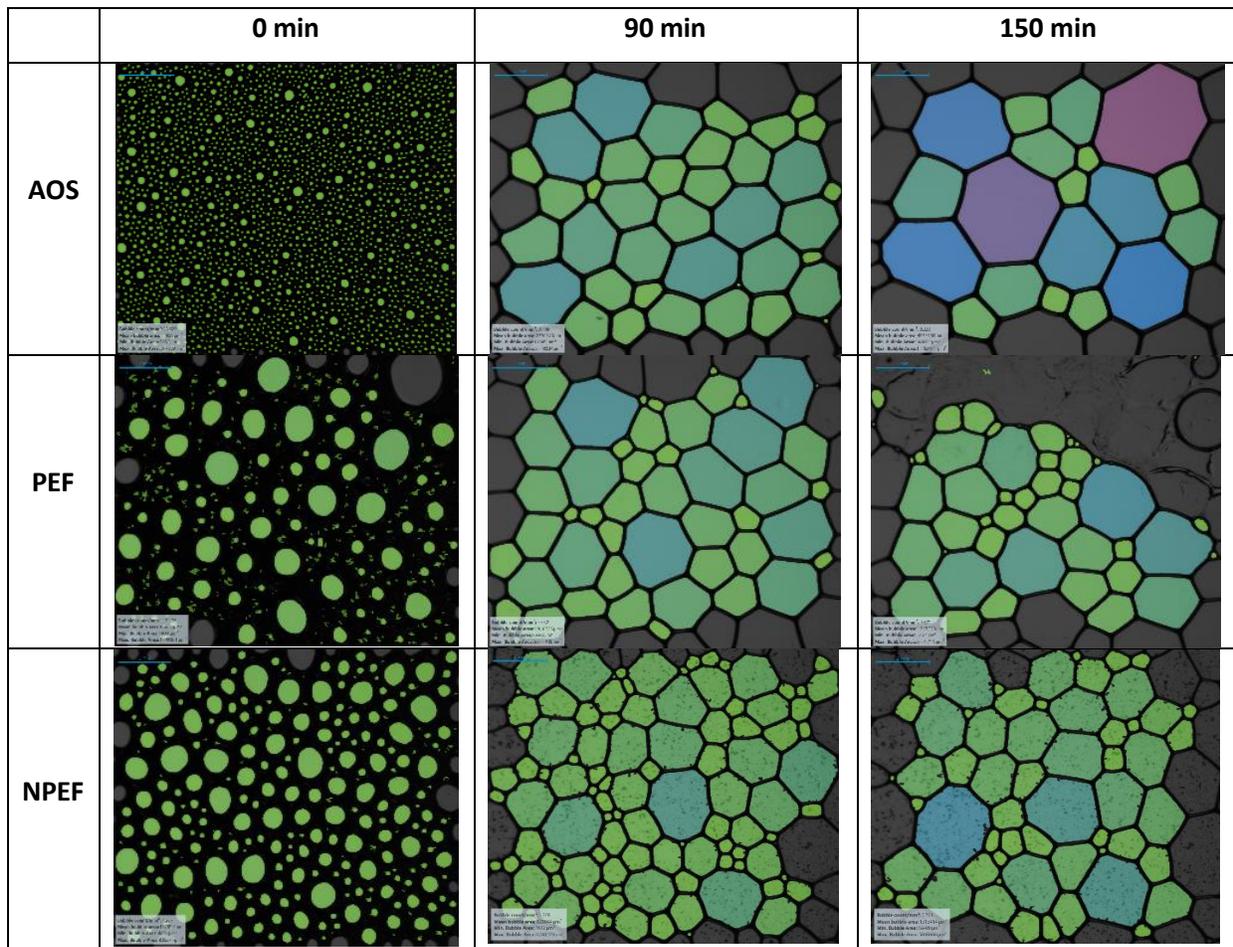


Figure 29: Foam images for AOS, PEF and NPEF at different time of experiment

7 Conclusions

A systematic study is done to get stabilized CO₂ foam using surfactants, polymers and nanoparticles. The step wise addition and effects of surfactant, salt, polymers and nanoparticles is done to get the clear understanding of effect of each component on foam stability. Following conclusion are drawn from this research study:

- Foamability increased with increasing AOS concentration. However, the effect is more dominant below CMC and not significant at higher concentrations (>CMC).
- In the absence of NaCl, an optimum surfactant concentration was found that maximize the stability of foam which was slightly higher than the CMC. The decrease in stability of foam at higher surfactant concentrations is due to the greater influence of gravitational forces.
- At constant salinity, the increase in AOS concentration improved foam stability. At some typical AOS concentration (0.25% in this case), the foam stability of AOS solution in presence of NaCl surpass the foam stability of AOS solution without NaCl.
- Salt can destabilize or stabilize the foam depending on the surfactant concentration; this apparently contradicting result is due to opposing effects of letting the electrolytes surround the AOS molecules at low vs high concentrations.
- When the AOS molecules are in excess, higher stability is achieved. However, when electrolytes are in excess, AOS molecules get completely surrounded by electrolytes which prevent them from entering the micellar structure that make up the foam lamellae
- Addition of polymer increases the foam stability by reducing the film thinning and coalesce factor. Increase in viscosity is the main reason for higher stability in PEFs. However, the foam volume is reduced with the addition of polymers.
- Optimum concentration was obtained for stable PEF after which the stability decreases with increasing the polymer concentration.
- Coalescence is reduced at high polymer concentration, but the half-life also reduces due to increased density of the liquid in bubbles films.

- Polymers with higher molecular weight generate less stable foam in comparison to lower MW polymer foam. But the polymers with a higher degree of hydrolysis generates more stable foam and vice versa.
- An optimum value of polymer concentration, molecular weight, and degree of hydrolysis is required in order to achieve the maximum foam stability.
- Addition of nanoparticles increase the stability drastically for PEF
- Nanoparticles adsorb at the liquid gas interface and reduce the liquid drainage and gas diffusion between the bubbles which make the foam more stable.
- Optimum concentration of NPs and Polymers are more effective as higher concentrations shows negative effect on foam stability.

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