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Experimental Assessment of emulsification stability during Enhanced oil recovery in the presence of Polymer (PMMA) and nanoparticles (ZnO)

MSc (50/50) RESEARCH THESIS

Prepared by

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Submitted to

The School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, South Africa

Supervisor: Prof Jean Mulopo

June, 2018

Declaration

I declare that this thesis is my own unaided work. It is being submitted for the degree of Master of Science in Engineering at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at another university.

Emmanuel Muzang

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Abstract

Among several methods proposed as secondary or tertiary recovery techniques, water flooding has proven to be less costly in terms of operating costs but often results in lower recovery value and sweep efficiency. Water flooding may be preferred when limited economic resources exist and/or for the displacement of oils with similar mobility to water. In heavy oil reservoirs the low mobility of the oil makes this method inefficient as water mobility is much greater than the oil leading to unfavorable mobility ratio, large viscosity difference which may cause channeling or fingering in the reservoir sweep and an early water breakthrough. Surfactant injection has been considered as an attractive alternative in order to attain higher oil recovery volumes. For instance when a stable oil-in-water emulsion is injected in a reservoir after a secondary recovery with water flooding, it tend to flow through the same high permeable water-wet zone previously covered by water flooding and the oil droplets get trapped in the pore throats changing the wettability of the rock surface and decreasing the permeability of the invaded zone. As a result water injected afterwards is forced to flow through less permeable zones that were not swept previously and lead to an oil recovery increase. Often surfactant injection is useful for improving the sweep in the reservoir.

It has been found that polymer injection may decrease further water mobility, thus contributing to a favorable mobility ratio and optimized volumetric sweep efficiency. Though injection of polymer may not reduce the residual oil saturation in the reservoir, it results in an improvement of displacing front stability and better oil recovery compared to other techniques such as water flooding. Polyacrylamide copolymers or hydrolyzed polyacrylamide (HPAM) polymers are by

far the most widely used polymer for EOR but they are still expensive. Poly (methyl methacrylate) or PMMA was considered for this work since it's relatively cheaper and readily available. On the other hand emulsions can be typically stabilized by the use of emulsifiers that are usually added in volumes (up to less than 1%wt) in order to lower the operational cost of the recovery process. In particular, emulsions stabilized by solid particles (nanoparticles) have become recently an attractive alternative that provides stabilization in oil-in-water and water-in-oil emulsions by reducing the interfacial tension and the capillary pressure, but are still relatively less covered in open literature. Therefore this dissertation considers oil-in-water/water-in-oil emulsions stabilized by nanoparticles and polymers to extent knowledge in this area. Therefore; this study investigates the stability of crude oil/water emulsions in the presence and absence of polymer and nanoparticles using crude oil blend received from NATREF with average API gravity of 35 and in particular assess the influences of the temperatures, brine concentration, polymer/nanoparticle concentration, oil/water ratio and stirring mechanism. It further investigates whether or not the combination of polymers and nanoparticle can provide a more stable emulsion than polymers only. Poly (methyl methacrylate) or PMMA polymer and zinc oxide (ZnO) nanoparticle were used. Furthermore droplet size distribution was analyzed using a microscope to see how tight the emulsions are and the droplets distribution.

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1. INTRODUCTION

1.1. Oil Supply and Recovery

Edwin Drake drilled the first commercial oil in northwestern Pennsylvania in 1859 [1]. Oil has remained as the world's main energy source since then and the demand for this energy source is still increasing. Looking at the outlook for long term oil demand published in 2012 by the Organization of Petroleum Exporting Countries (OPEC), the need for oil will increase to 107 million barrel per day in 2035, from the current value of about 90 million barrel per day [2].

The ultimate recoverable oil reserves should be increased in order to meet the continuously increasing oil demand and keep sustainable oil supply. This could be achieved by replacing the produced oil by new reserves from new discoveries as well as applying enhanced/improved oil recovery (EOR/IOR) methods to maximize oil recovery from current mature oil fields by minimizing the trapped oil left behind in the reservoirs. Exploration and development of new oil reserves is cost and energy intensive and requires new installations and infrastructure. There are also only few number of large scale oil discoveries in past recent years compared to the past. In contrast, EOR/IOR methods are utilizing existing installations and facilities of the developed oil reservoirs. These methods are more energy efficient and are expected to play a major role in future oil supply [3].

In mature oil fields, after primary and secondary oil recoveries which are mostly governed by the reservoir original pressure, pressure maintenance schemes and water flooding, considerable amount of oil is trapped in the pore networks of the porous media by capillary forces exist in pore scale. To achieve maximized oil recovery in these fields, the capillary forces responsible for oil entrapment must be overcome. During the last 4-5 decades different EOR/IOR methods have been designed and implemented in order to efficiently recover oil left in the reservoir after water flooding projects. These methods include verity of physical, chemical, and technical processes and procedures which lead to increased final oil recovery and accelerated rate of oil recovery from the reservoirs [2].

It's important for us to differentiate between EOR and IOR methods. The IOR methods include all processes and procedures that affect economically increased oil recovery and cover primary, secondary, and tertiary stages of oil recovery. These recovery methods deal with both mobile and immobile oil left in the reservoir. The EOR methods mostly refer to tertiary oil recovery methods which could mobilize the immobile oil trapped in pore structure of the porous media. The most commonly applied EOR methods include but not limited to water based processes (polymer flooding, surfactant flooding, alkali/surfactant/polymer flooding), gas based processes (miscible gas injection, nitrogen (N_2) and CO_2 injection), thermal processes (in-situ combustion), and combination of these processes (water alternating gas (WAG), hot water injection, steam injection, foam injection) [3].

1.2. Motivation of the study

As energy crisis are getting worse, enhance oil recovery (EOR) methods are getting more attention and much study is been done on them. In fact, when a new oil reservoir is drilled, the oil amount obtained from it is about 20-40% of the potential, and hence there is still 60-80% oil left in the reservoir [4]. Applications of EOR technology gives an additional chance to get out more oil from the reservoir, possibly about another 5-30%. Generally, EOR technology is urgently required due to several reasons; declining oil production since 1995, non-productive primary and secondary recovery, high crude oil price, increasing energy demand of approximately 1.5% per year [4], and significant oil remaining after secondary recovery (~60% of original oil in place, OOIP). In enhanced oil recovery, chemicals such as surfactants, polymers and nanoparticles are injected to improve recovery. These chemicals help improve properties of the injected fluid and its interactions with the rocks. Polymers are chemicals characterized by large molecules which, when injected into water, add bulk to the water. The water is thickened and is able to sweep or wash the hydrocarbons from the pores within the reservoir [3].

Polyacrylamide copolymers or hydrolyzed polyacrylamide (HPAM) polymers are by far the most widely used polymer for EOR [4], but the polymers are still expensive costing on average USD2.5-USD3 [5] per kilogram even with the increase in oil prices, the price is not very competitive. Poly (methyl methacrylate) or PMMA on the other hand which was used as the polymer in this work cost on average USD0.7-USD1.2 per kilogram [5].Also HPAM its very sensitive to the brine salinity, hardness and presence of surfactants or other chemicals. This makes it very ineffective in reservoirs containing salts [6]. Moreover, addition of nanoparticle is said to further reduce interfacial tension between water and oil and help reduce the capillary pressure. Surfactants are frequently used to lower the IFT and to alter the wettability [7], but

chemical processes are often limited by the high cost of chemicals, possible formation damages, and losses of chemicals [8].Therefore, less expensive, more efficient, and environmentally friendly EOR methods are greatly needed. Nanoparticles have been utilized in subsurface applications due to their ability to alter certain properties in the formation [9]. Nanoparticles exhibit exceptional properties owing to the small size and large surface area [10]. Therefore, Nanoparticles are usually treated to avoid interparticles interactions. Owing to their small size (1–100 nm), Nanoparticles can be propagated through the formation using a stable aqueous dispersion.

The crude oil sample used in this research was obtained from NATREF (refinery tank F29107) and it is a blend of different crude oils from Nigeria, Angola and Saudi Arabia. A crude oil blend is a mixture of crude oils blended in the pipeline to create crude with specific physical properties. This is because heavy and extra-heavy crudes or bitumen cannot flow from the field to the refinery in their original state and at normal surface temperatures. They are thus blended with lighter crude oils primarily to reduce viscosity, thereby enabling transportation to a refinery. A secondary objective may be to provide a blended crude oil that has significantly higher value than the raw heavy crude. The blend is usually constructed so that the value of the overall blended volume is greater than the summed value of the initial volumes of individual heavy and light crudes [11].

Emulsion is an important part of the oil and gas industry and can be encountered at different stages while drilling, production, storage, transportation and processing of crude oil [12]. Efforts are put in to produce crude oil alone but it is generally combined with water. This water or the formation water causes problems and influence the production. It also usually increases the unit cost of production. The produced water must be separated from the oil, treated and disposed of

properly because the crude oil as selling product must not have more than 1% of water and sediments. The presence of water is also unwanted because of its contents of inorganic salts, which could provoke corrosion and there by cause damages to the refining and transport installations [13].

Produced water can be in the form “free water” which will settle out rapidly, or in the form of an emulsion. Regular oilfield emulsions are a dispersion of water droplets in oil. Emulsions are generally difficult to treat and may cause several operational problems in wet-crude handling facilities and gas/oil separating plants. They can also lead to high-pressure drops in flow lines, and cause an increase in demulsifier use. This problem is usually worst during the winter because of lower surface temperatures [14].

It is therefore very important to limit the formation of stable emulsions in the desalting unit or at least to ensure a fast and effective breaking of the formed emulsion. The formation of emulsions (stable or unstable) is a major preoccupation for oil production and refining ,this is the motivation behind this work; to assess stabilization of polymer and nanoparticle based emulsions using real crude oils systems in order to find out if the mixture of polymer with crude oil would give more stable emulsion over time and if the emulsion could be separated easily by using different temperatures and different concentrations but also to find out if the addition of nanoparticles to aqueous polymer solution would give more stable emulsion compared to the use of polymers alone.

1.3. Objective of the study

One of the most commonly used enhanced-oil recovery (EOR) methods is polymer flooding which also lead to the formation of water-in-crude oil emulsions during oil production. The pros and cons of emulsion formation have motivated significant research in the oil industry in the last few decades. Therefore, the objective of this study is to contribute to the understanding of water-in-crude oil emulsions stabilizing mechanisms in the presence of polymer and to investigate the emulsion stability when nanoparticle is added.

The various tasks of the project can be classified into:

1) To study the effect of oil-water proportions on oil-water mixture/ emulsion as a baseline scenario.
2) To investigate the effect of emulsion stability on oil-water mixture in the presence of Polymer (PMMA),by investigating the effect of polymer concentrations at different temperatures.
3) To investigate the effect of emulsion stability on oil-water mixture in the presence of nanoparticles (ZnO nanoparticles) by investigating the effect of different nanoparticles types at different temperatures.
4) To investigate the effect of emulsion stability on oil-water mixture in the presence of polymer (PMMA) and nanoparticles (ZnO nanoparticles). Different polymer (PMMA) and nanoparticles (ZnO nanoparticles) concentrations were investigated.
5) To investigate the effect of emulsion stability on oil-water mixture at different concentrations of brine in the presence of polymer (PMMA) and nanoparticles (ZnO nanoparticles) at different temperatures.

2. LITERATURE REVIEW

2.1. Oil Migration and Accumulation

An oil reservoir broadly consists of: a) a source rock where the oil is generated, b) a reservoir rock where the oil is accumulated, and c) an impervious trap called cap rock, which works as a barrier to prevent escape of oil from the reservoir [3]. After generation of oil through conversion of the organic material under catagenesis reaction in dominantly sedimentary rocks (source rock), due to the pressure gradients mainly governed by overburden compaction of the sediments, oil moves to and is accumulated in the reservoir rock.

The process of oil movement from the source rock to the reservoir rock is called primary migration. The reservoir rock must be porous and permeable in order to be a good candidate for oil accumulation. The movement of oil within the reservoir after accumulation is referred to as secondary migration. The main contributor to the secondary migration is buoyancy which is the result of density difference between gas, oil and water. The distinction between primary and secondary migration processes is based on petroleum migration through different pore sizes and lithology as well as the difference in state of petroleum distribution [15]. Figure 2.1 illustrates a typical anticlinal reservoir with gas cap at the top, oil at the middle and water at the bottom of the reservoir

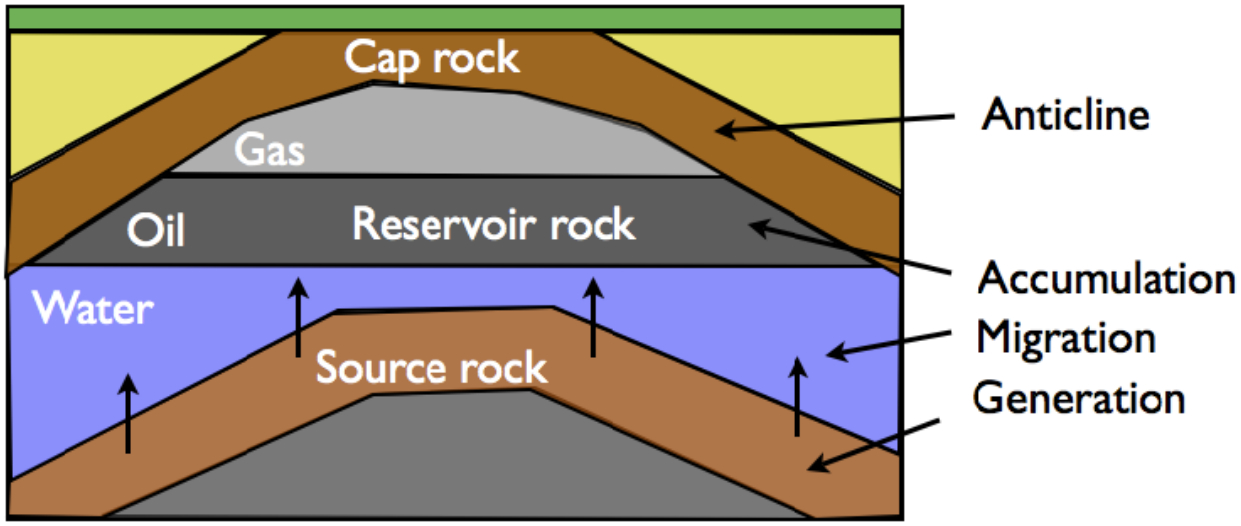


Figure 2.1: Oil generation, migration, and accumulation [48].

Most of the oil reservoirs are in sedimentary rocks. Sandstones, carbonates and shales are the sedimentary rock types. The reservoir rocks are dominantly in sandstones and carbonates (limestone, dolomite), while the shales normally behave as cap rocks in the reservoir. About 60% of world oil reserves are trapped in carbonate reservoirs and the remaining 40 percent are in sandstones. Compared to sandstone reservoirs which are highly homogeneous, the carbonate reservoirs are significantly heterogeneous and naturally fractured, and therefore the prediction of the behavior of such reservoirs is extremely challenging [16].

2.2. Mechanisms of Oil Recovery

Oil is normally produced from the reservoir through three different stages, known as primary recovery, secondary recovery and tertiary recovery. Depending on the characteristics of the reservoir and its physical and chemical properties as well as recovery potential at each recovery stage, in some reservoirs, tertiary recovery techniques could be implemented right after the primary oil recovery. In some cases, especially for the extra heavy oil reservoirs, the primary

and/or secondary recovery stages would be skipped because of the low recovery potential of such reservoirs in these stages. In such cases, the tertiary recovery stage is the first and possibly the only stage for economical oil recovery [17].

2.3. Primary Oil Recovery

In the primary oil recovery stage, oil is produced from the reservoir by the natural displacement energy that exists in the reservoir. The source of this natural energy comes from different driving forces depending on the characteristics of the oil reservoir. These driving forces include depletion drive, rock and fluid expansion drive, water drive (aquifer drive), gas cap drive, gravity drainage drive, and combinations of these driving mechanisms [18]. These mechanisms will be described in following subsections.

Early identification of the responsible drive mechanism(s) of the reservoir is crucial in order to determine the primary recovery potential of the reservoir and deploy a suitable plan for further development of the reservoir in secondary and tertiary recovery stages.

2.3.1. Depletion Drive

Depletion drive mechanism which is also referred to as solution gas, dissolved gas or internal gas drive, is the dominant mechanism with the liberation and expansion of gas as a consequence of oil production and pressure decline is the main source of energy in the reservoir [2].

2.3.2. Rock and Fluid Expansion Drive

In reservoirs with a pressure above bubble point pressure, the main drive mechanism is the expansion of rock and fluids (water and oil) due to their compressibility. These reservoirs which

are also called under-saturated reservoirs, experience a rapid pressure decline because the compressibility of oil/water and rock is fairly low. This is also the reason for poor efficiency and low primary recovery factor in the reservoirs with this drive mechanism [2].

2.3.3. Water Drive

In reservoirs with water drive as principal driving mechanism, the source of driving energy is acquired from the aquifers that bound the reservoir from the bottom (bottom drive) or laterally (edge water drive). In such reservoirs water fills the pore spaces initially filled with oil, and displace oil upwards to production wells. Depending on the characteristics of the reservoir, water drive mechanism could result in very high oil recovery with very low pressure decline during the life time of the reservoir. These reservoirs are also subjected to higher water production which depend on production water/oil ratio (WOR), could affect the reservoir economic limits [2].

2.3.4. Gas Cap Drive

The driving energy in the gas cap drive reservoirs is provided by the expansion of the gas gap that exists above the oil column in the reservoir. The gas cap itself could exist as primary or secondary gas cap. The expansion of gas cap results in displacing the oil downwards to production wells. The efficiency of the gas cap drive mechanism depends mainly on the size of the gas cap. The reservoirs with gas cap drive are subjected to high produced gas/oil ratio (GOR) [4].

2.3.5. Gravity Drainage Drive

Gravity drainage or gravity segregation drive mechanism is a driving force for primary oil recovery caused by density differences between gas, oil, and water present in the reservoir. This drive mechanism is very slow since the long period of time is needed for segregation of fluids

and obtaining equilibrium state in the reservoir. Therefore this mechanism results in high oil recovery in long term periods [4].

2.3.6. Combination of Drive Mechanisms

In many reservoirs it is possible to observe more than one responsible drive mechanism. For example, the reservoir with gas cap and aquifer is benefited from both gas cap drive and water drive mechanisms [19].

2.4. Secondary Oil Recovery

Secondary oil recovery processes are the starting point of intervention in the reservoir by applying external energies and forces in order to increase oil recovery. These processes include injection of water into the aquifer and/or injection of gas into the gas cap to maintain the original reservoir pressure or prevent rapid pressure decline and thereby supporting the water drive and/or gas drive mechanisms in the reservoir. It is highly recommended to start the pressure maintenance processes (water and gas injection) during the early production life of the reservoir to increase the recovery efficiency and prevent oil entrapment in water and gas invaded zones [20].

When water is injected into the oil column in the reservoir, to physically push and displace oil towards the production wells, the process is called water flooding. Water flooding is by far the most extensively applied method to maximize oil production from the oil reservoirs. Due to the vast application of water flooding during the secondary oil recovery stage, the term secondary recovery is almost synonymous with water flooding. Similar to water flooding, immiscible injection of gas into the oil column to displace oil to the production wells without resulting in oil

swelling, oil viscosity reduction or favorable phase behavior, falls in the category of secondary oil recovery processes [21].

2.5. Tertiary Oil Recovery

After primary and secondary stages of oil recovery, the reservoir drive mechanisms are no longer strong enough. At this stage, physical displacement of oil with water and gas injection ends up with high water oil ratio (WOR) and/or gas oil ratio (GOR) in production well, and the reservoir enters to its depleted phase of lifetime and further oil production would be uneconomical. In such a condition significant amount of oil still remains in the reservoir. Depending on the rock-fluid properties of the reservoir (rock type, permeability, oil viscosity, etc.) and involved drive mechanisms, usually one-third to more than-two third of oil remains trapped in oil reservoirs after primary and secondary recovery stages. The current average global oil recovery factor (RF) is estimated to be around 35% [22]. Increasing the recovery factor from current level of 35% to 45% would result in the addition of about one trillion barrel to world's oil reserve [23].

The key solution and an important tool to extend the economic life time of oil reservoirs, is the application of tertiary oil recovery methods. Tertiary recovery methods, sometimes, are synonymously used with enhanced oil recovery (EOR) processes, however based on definition by Lake [17]; EOR processes are not necessarily restricted to tertiary recovery. Figure 2.3 schematically presents the manner that application of EOR methods would increase the oil production rate as well as extend the economic life time of the reservoirs.

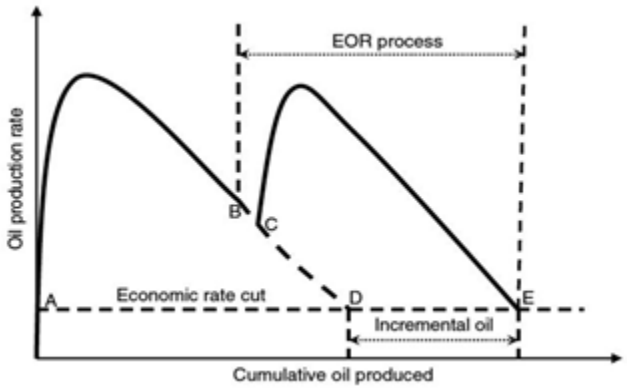


Figure 2.2: Schematic of incremental oil recovery from an EOR process [24].

In the tertiary recovery stage (EOR), it is possible to recovery almost 30-60% of the field's OOIP (original oil in place) which is high compare to primary and secondary recovery methods where recovery factor is equal to 20-40% [25].The main types of EOR are:

- Thermal recovery
- Gas flooding
- Chemical flooding

2.5.1. Thermal recovery

Enhanced oil recovery method where steam or air is injected to the heavy oil reservoirs to decrease the viscosity of oil. During this process the mobility ratio decreases and oil flows towards production wells. This EOR method is widely used in unconventional oil fields of Venezuela and Canada [25].

2.5.2 Gas flooding

In gas injection process the interfacial tension between water and oil reduces and this leads to better displacement efficiency. Carbon dioxide is main injection fluid for this method due to its low cost and because it decreases oil viscosity [25].

2.5.3. Chemical flooding

Chemical flooding consists of two processes: polymer flooding and surfactant-polymer flooding [24]. To produce oil that is trapped in reservoir, surfactants are injected and then polymer to decrease the mobility ratio of oil and water which gives favorable volumetric sweep efficiency.

2.6. Polymer Flooding

Polymer flooding has been used for more than 40 years to effectively recover the remaining oil from the reservoir, up to 30% of the original oil in place. Because of decreased water production and enhanced oil production, the total cost of using the polymer flooding technique is less than that of water flooding. The polymer flooding efficiency ranges from 0.7 to 1.75 lbs. of polymer per barrel of incremental oil production [26].Polymers added to water increase its viscosity and reduces water permeability due to mechanical entrapment, thus decreasing its mobility [4]. The process usually starts with pumping water containing surfactants to reduce the interfacial tension between the oil and water phases and to alter the wettability of the reservoir rock to improve the oil recovery. Polymer is then mixed with water and injected continuously for an extended period of time (can take several years). When about 30% to 50% of the reservoir pore volume in the project area has been injected, the addition of polymer stops and the drive water is pumped into the injection well to drive the polymer slug and the oil bank in front of it toward the production wells (Fig.2.3).

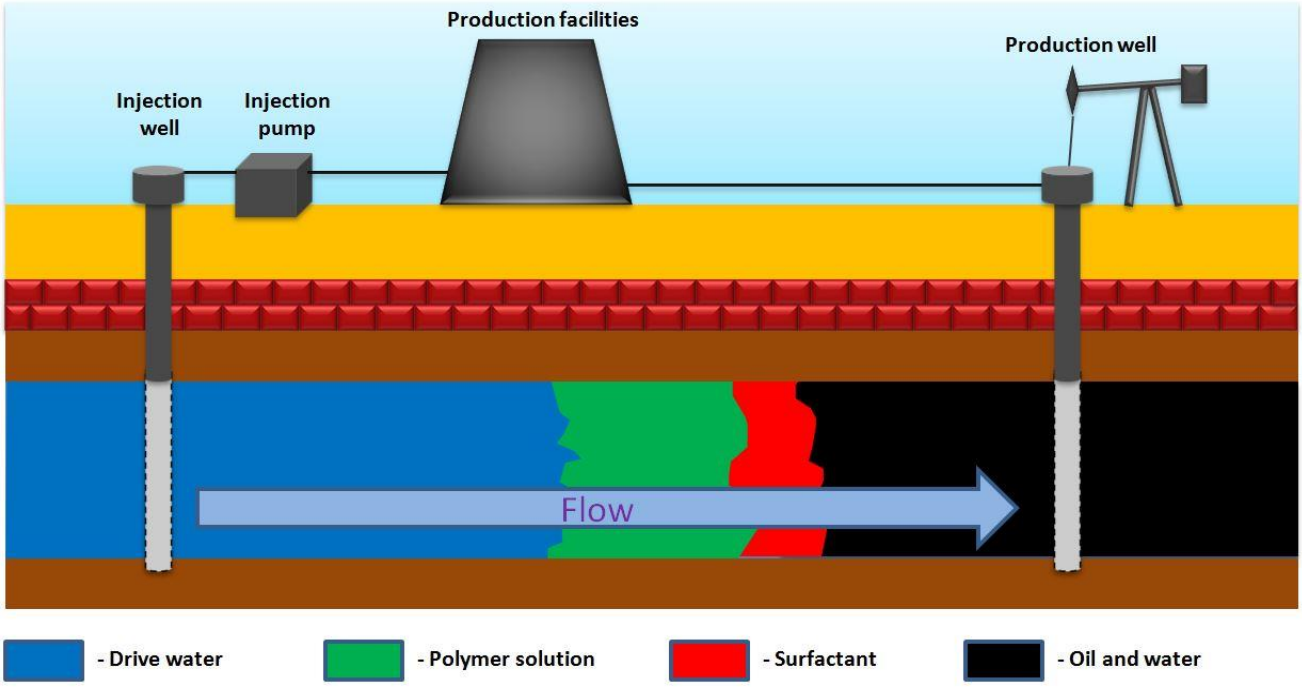


Fig. 2.3: Polymer flooding [26].

Polymer flooding is one of the chemical enhanced oil recovery methods was introduced in late 1960s. In this chemical EOR method, polymer is added to the injected water in order to increase injected fluid viscosity and to improve oil displacement in the reservoirs.

According to reports, the first commercially success was gained in Daqing oil field of China where oil recovery factor increased up to 20% after applying polymer flooding technique [27]. After some successful projects, it is currently believed that polymer flooding can be profitable EOR technique.

2.6.1. Mechanics of Polymer Flooding

The main purpose of polymer flooding is improving sweep efficiency and consequently enhanced oil recovery which is gained due to the following:

- Increase in viscosity of injected fluid
- Decrease in water and oil mobility ratio
- Decrease in a volume of capillary trapped oil

Figure 2.3 above demonstrates an overview of the mechanics of polymer flooding.

2.6.2. Type of Polymers

Polymers used in enhanced oil recovery methods are divided into two groups: synthetic polymers and biopolymers.

a) Synthetic polymers

This type of polymers are produced synthetically and polyacrylamide - water soluble polymers are the one of the widely used synthetic polymers for EOR. Polyacrylamides can be in various forms: in liquid phase, gels, powder and so on.

b) Biopolymers

Biopolymers are formed by living organisms. The molecular weight and structure of biopolymers are smaller than synthetic polymers. Therefore it gives hardness that causes a good viscosifying effect in salinity water and a bad viscosifying effect in fresh water [26].

2.6.3. Poly (methyl methacrylate) PMMA

Poly (methyl methacrylate) (Figure 2.4), which is commonly referred to as PMMA is commonly called by its trade mark name PLEXIGLAS™. In the chemical literature, it could also be listed as "2-propenoic acid, 2-methyl-, esters, methylester, and homopolymer" or under the Chemical Abstract Number CAS [9011-14-7].

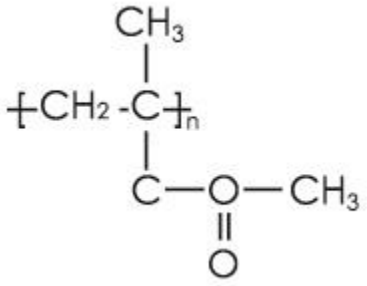


Figure 2.4: Poly (methyl methacrylate) PMMA [28]

As mentioned above, PMMA is a polymer and therefore has undergone a polymerization process. In this particular case no cross-linking exists between long chain molecules therefore can be considered a thermoplastic. PMMA is a vinyl polymer therefore it is composed of vinyl monomers; that is, molecules containing carbon-carbon double bonds. PMMA is thus the product of the polymerization of free vinyl radicals called methyl methacrylate (Figure 2.5).



Figure 2.5: PMMA polymerization [28]

PMMA is a member of a family of polymers which chemists call acrylates, or better known under the name acrylics. The general properties of PMMA are provided in table 2.1 below;

Table 2.1: poly (methyl methacrylate) at a glance [29]

Poly(methyl methacrylate)	
Type	Thermoplastics
Monomer:	Methyl methacrylate
Polymerization:	Free radical vinyl polymerization
Morphology:	Amorphous
Glass transition temperature:	105 °C

PMMA belongs to a subset of polymers referred to as amorphous. This group of polymers does not crystallize during the cooling process because they have semi-flexible or rigid backbone structures. The most important thermal transition in an amorphous polymer is the glass-rubber transition (Tg). The Tg is the narrow temperature range over which the amorphous polymer changes from the hard glassy state to the soft rubbery state. It is usually possible to assign Tg to a specific temperature using mechanical storage modulus, tanα or the loss modulus. Polymers in

the glassy domain, where the temperature of the surroundings is less than Tg, tend to be stiff and potentially brittle while polymers in the rubbery domain are softer and more flexible [29].

2.6.4. Criteria for Polymer Flooding

Kaminsky et al [30] proposed the schematic of processes for the appraisal and development of polymer flood projects (Figure 2.6).

The first step is the screening of reservoir where reservoir geometry and fluid, rock features are studied due to the passing criteria. If the properties of suggested reservoir are matched with the screening criteria, further deep investigations like modeling, laboratory works, and reservoir specification can be considered. Eventually these phases result in a technical-economical evaluation.

The next phase is to determine targets and structure the pilot test. After successful study on pilot test, the profitable scenario is developed and improved; this involves field scale modeling and an operation strategy that examines realization, observation and operations.

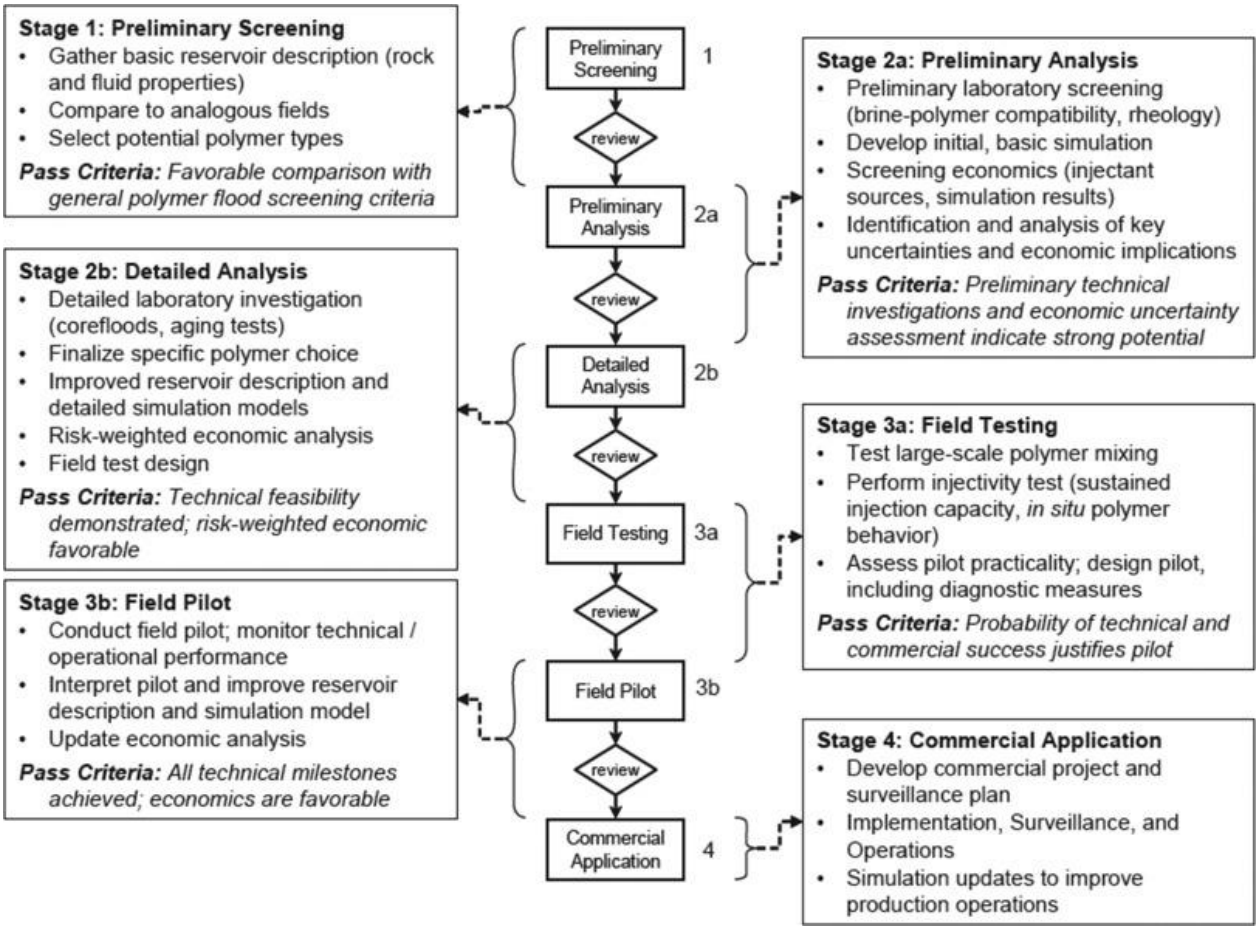


Figure 2.6: Polymer Flood Project Evaluation and Development Process [30].

Based on the literature, there are two fundamental arguments for employing the selection rules [31]:

- Find reservoirs with high mobility ratio and poor volumetric sweep efficiency
- Define if the properties of reservoir meet the screening criteria for polymer flooding.

2.7. Overview of Nanotechnology used for EOR

In recent years nanotechnology has gained vast interest in the petroleum industry through the use of nanoparticles particularly in the drilling, completion and production operations, this has enhanced the rheological properties of fluids at favorable and elevated temperatures [32]. Nanotechnology deals with the application, design, characterization and production of materials and devices based on nanometer scale. Nanoparticles have distinctive properties due to their small sizes and greater surface area per unit volume; they have dimensions in the order of 1-100nm [10]. For EOR, nanotechnology has become the cutting-edge technology, adding nanoparticles to fluids can benefit EOR significantly and improve well drilling by changing fluid properties, wettability alteration of rocks, interfacial tension reduction, mobility increase of capillary-trapped oil and drag reduction. According to Zhang [33] nanoparticles are used to stabilize emulsion droplets which are small enough to pass typical pores, flow through the reservoir rock without much retention and also remain stable under hard conditions in the reservoir due to irreversible adsorption of the nanoparticles on their droplet surface. Nanoparticles that are less than 30nm in diameter can be either hydrophilic or hydrophobic.

2.7.1. Commonly used Nanoparticles for EOR

Cheraghiam and Hendraningrat [32], investigated, commonly used nanoparticles from the metal oxide group: Silicon dioxide (SiO_2), Aluminum oxide (Al_2O_3), Nickel Oxide (Ni_2O_3) and Iron Oxides (Fe_2O_3). The metal oxides are popular and considered as polar molecules or hydrophilic. They are known to significantly reduce the viscosity of the crude oil when dispersed in brine solution. Studies by Negin et al., [34] summarizes the application of nanotechnology and classifies the most commonly used nanoparticles for EOR. In listing the dominant mechanism of

surfactants which leads to EOR, nanoparticles CuO, Al_2O_3, Ni_2O_3 and Fe_2O_3 are best for viscosity reduction. When needing to effectively reduce the IFT, then SiO_2 and Polymer coated nanoparticles are best. SiO_2 has another advantage/dominant mechanism to alter wettability of the formation rock.

Zinc Oxide (ZnO) is another nanoparticle known in the industry but not much work has been done on them. This nanoparticle can have a polar and non-polar structure therefore can be hydrophilic or hydrophobic. Studies done by Ogolo et al., [35] looked at ZnO as EOR agent in sandstones, they found that when injected it negatively affected the permeability of samples used. Furthermore, their study saw an additional decrease in permeability when brine was used. Ogolo et al., [35] argued that the injection of ZnO could lower the overall oil recovery factor.

Negin et al., [34] made a recommendation for further investigation into ZnO nanoparticles. For this reason, this research paper focuses on the application of ZnO nanoparticle with polymer (PMMA) to stabilize crude oil emulsion.

Cheraghian and Hendraningratgave, showed evidence that nanoparticles enhances the stimulation fluids due to easy access of the nanoparticles into the o/w interface to reduce the IFT [36] between the oil and water and enhance the oil production [32].

Experimental studies by Le et al., using different types of surfactants with nanoparticle SiO_2 showed great potential for EOR application on rock surfaces as this displayed a resistance to adsorption [37]. Further research work took surfactant solutions and investigated the effects of adding nanoparticles on IFT and found that the presence of nanoparticles changed the rheological properties [38].

2.7.2. Effects of nanoparticles on Interfacial tension (IFT) reduction

Studies done by Suleimaniv et al, show that surfactant contribute to the stability of nanoparticles and emulsions to decrease IFT, these two emulsifiers complement each other [39].

2.8. Oil Droplet Measurement

Droplet Size distribution (DSD) in an emulsion depends on several factors such as IFT, emulsifying agents, bulk properties of oil and water, presence of solids and shear. DSD of an emulsion should be taken into consideration as it determines the stability of the emulsion Emulsions generally look dark and less bright when they have large diameter droplets (low total interfacial surface area) [40]. As a rule of thumb, the smaller the average size of the dispersed water droplets, the tighter the emulsion. Emulsions that have smaller size droplets (≤10 micron) will generally be more stable, see figure 2.8 below. The droplet size distribution affects emulsion viscosity because it is higher when droplets are smaller. Mixing using Ultrasonic stirrer also affects the droplet sizes formed.

There are different methods used to determine DSD for oilfield emulsions and they are:

- Physical separation

- Scattering techniques such as X-ray and light scattering, these technique measures droplet sized 0.4nm to > 100μm

- Microscopy and image analysis.

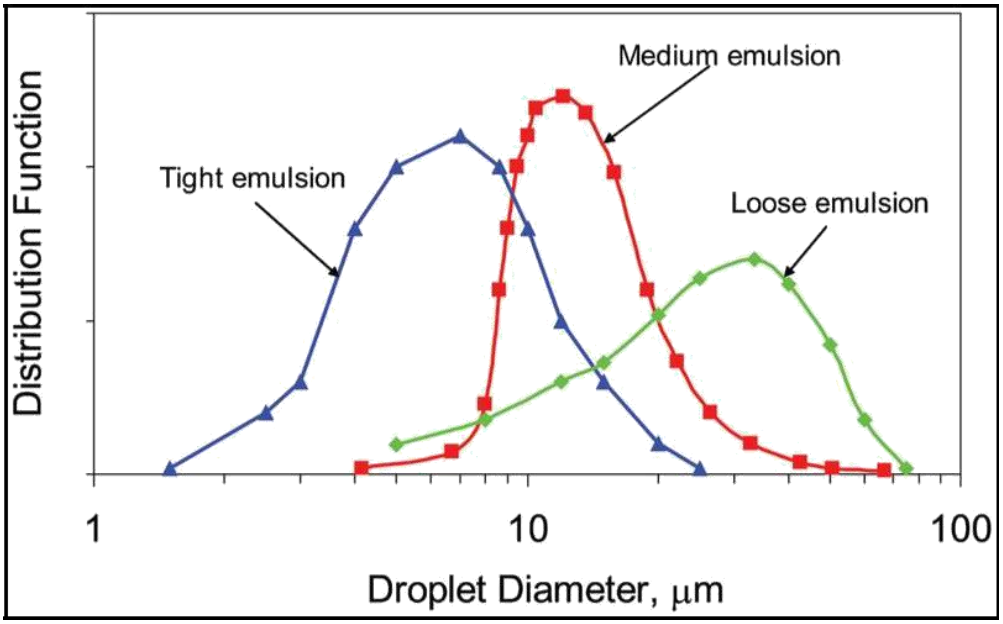


Figure 2.8: Droplet-size distribution of petroleum emulsions [40].

2.9. Problems associated with Heavy Crude Oil production

Although polymers and surfactants play a large role in heavy oil production, these emulsifiers do not provide long term stability of emulsion. Commonly used polymers such as HPAM and PAM have poor shear resistance and therefore don't have high tolerance to temperatures, salinity and don't possess tremendous viscosifying ability [32]. During production the polymer molecular chains tends to be cut off when polymer solution passes through the porous medium, perforations, pipeline and the pump at high speed. This leads to the reduction in viscosity of polymer solution. Crude oil is not produced alone, it is comingled with water, and the water creates (and) usually increases the unit cost of oil production. The produced water must be separated from the oil, treated and dispose-off properly. Heavy oil production can cause problems in both upstream and downstream. For upstream operations, figure 2.9, issues such as wax precipitation, viscous emulsion, corrosion, hydrate formation, asphaltene precipitation and emulsion breaking can occur in pipelines and production tubes disturbing

flow [41]. In downstream operations the process of upgrading heavy oil or residual can be expensive especially when looking at processes such as hydrogen addition or carbon injection.

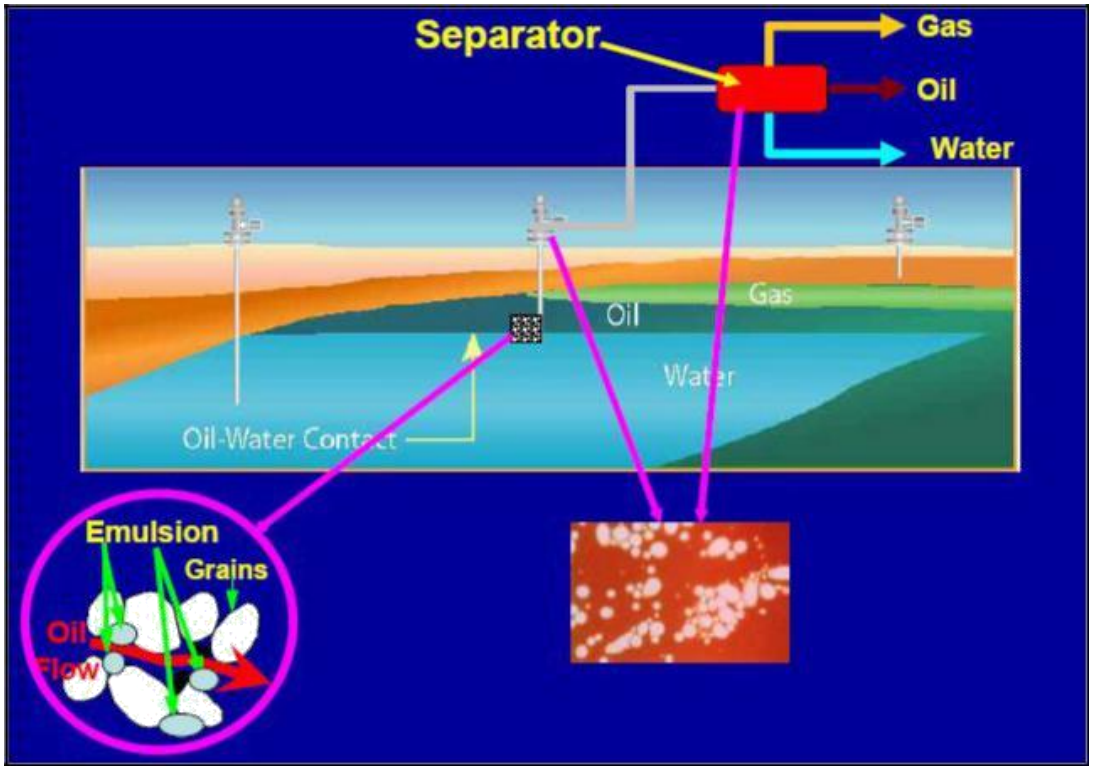


Figure 2.9: Occurrence of emulsions during production in the reservoir and separator [40].

2.10. Origin of Crude oil Sample

The crude oil sample used in this study was obtained from NATREF (refinery tank F29107) .It is a blend of different crude oils from Nigeria, Angola and Saudi Arabia (table 1). These crude oils have different properties due to the different origins and consequently their formation brines differ as well. Table 2.2 lists the crude oil blend properties including and their American Petroleum Institute (API) gravity values.

2.10.1. Nigeria Crude Oil

Nigeria produces high value low sulfur content and light crude oils and they include the 1)Brass River Blend,(2)Bonny Light, (3) Escravos, (4)Forcados, (5)Qua Iboe and (6) Erha crude oil., these crude oil have different API° gravity specifications ranging from 30-36. (Eastern Union energy). Out of the crude oil blend received from NATREF, 60.79% of the crude is of Nigerian origin, with average API° gravity of 35.

Table 2.2: Crude oil Sample: Crude oil Blend from NATREF (refinery Tank F29107)

Crude feed	Country of origin	Mass	Mol wt%	API°	
BONNY LIGHT (BLT)	Nigeria	32.37	5.15	34.6	
ESCRAVOS (EST)	Nigeria	240.04	38.10	33.7	
FORCADOS (FBT)	Nigeria	1	0.11	30	
QUA IBOE (QIT)	Nigeria	1	0.15	36	
ERHA (ERT)	Nigeria	12	1.94		
BRASS RIVER (BRT)	Nigeria	97	15.34	38	
NEMBA (NET)	Angola	7	1.09	38.6	60.79%
ARAB EXTRA LIGHT (AET)	PG-Saud Arabia	15.67	2.49	30	
ARAB LIGHT (ALT)	PG-Saud Arabia	88.36	14.03	39	
ARAB MEDIUM (AMT)	PG-Saud Arabia	70.84	11.24	20	38.13%
ARAB HEAVY (AHT)	PG-Saud Arabia	65	10.37	10	
Total Feed		**630.00**	**100**		

2.10.2. Angola Crude Oil

Angola has different types of crude oil from heavy to light crudes. Heavy crude is known as Kuito (very viscous crude with medium sulphur content with API values of 19° and 0.66° respectively). The Nemba crude oil is a light crude oil with API gravity of 38° and makes up only 1% of the crude oil blend provided for this research (Sunga Energy). Due to the existence at this low percentage, the crude oil will not be discussed further as it has very insignificant effects to the blend.

2.10.3. Saudi Arabia Crude Oil

The Saudi Arabian crude oil is very diverse, from the Saudi oilfields there are five types of crude oil produced; namely Arabian (1)Heavy, (2)Medium, (3) light, (4)extra light and (5) super light crude oil. Arabian heavy and medium crude oil are produced offshore and have API gravity that range from 6° -10° for heavy crude and 10° -21° for medium crude oil. The light, extra light and super light crude oil are produced onshore from different field; their API gravity range from 21-30, 30-39 and 39-50 respectively.

Saudi Arabia crude oil makes up 38.13% of the crude blend provided for this research, this in essence makes the blend light with an average API gravity of approximately 35.

2.11. Stability of Crude oil emulsions

From a purely thermodynamic point of view, an emulsion is an unstable system because there is a natural tendency for a liquid/liquid system to separate and reduce its interfacial area and, hence, its interfacial energy. However, most emulsions demonstrate kinetic stability (i.e., they are stable over a period of time) [14].

Produced oilfield emulsions are classified on the basis of their degree of kinetic stability.

- Loose emulsions separate in a few minutes, and the separated water is free water
- Medium emulsions separate in tens of minutes
- Tight emulsions separate (sometimes only partially) in hours or even days

2.11.1. Factors affecting crude oil emulsion stability

Since interfacial films are primarily responsible for emulsion stability, it is important to understand factors that affect interfacial films. Important factors are [14];

- Heavy polar fractions in the crude oil
- Solids, including organic (asphaltenes, waxes) and inorganic (clays, scales, corrosion products, etc.) materials
- Temperature
- Droplet size and droplet-size distribution
- pH of the brine; and brine composition

2.11.2. Emulsion Stability Mechanisms

An emulsion is a heterogeneous liquid system that consists of two immiscible liquids with one of the liquids dispersed in another. It has an external (continuous) phase with an internal (dispersed) phase with small portion of droplets. Crude oil and water emulsions can be classified into one of the following [12]:

- Water-in-oil (W/O) emulsions consist of water droplets in a continuous oil phase.
- Oil-in-water (O/W) emulsions consist of oil droplets in a continuous water phase.
- Multiple emulsion (W/O/W) or (O/W/O), consists of tiny droplets suspended in bigger droplets that are suspended in a continuous phase.

Produced oilfield emulsions are classified on the basis of their degree of kinetic stability.

- Loose emulsions separate in a few minutes, and the separated water is free water.
- Medium emulsions separate in tens of minutes.
- Tight emulsions separate (sometimes only partially) in hours or even days.

Whereas, forming stable emulsion is a very interesting subject, demulsification is another topic that oil producers worry about. Demulsification is the process of breaking crude oil emulsion into oil and water phases. The mechanisms that are involved in breaking emulsions can be classified into the following three processes:

- **Flocculation (aggregation):** the droplets clump together and may get close to each other during flocculation, even touching at certain points without losing their properties. The rate of flocculation depends on the water cut, temperature, oil viscosity, and the density difference between the oil and water. In flocculation, the van der Waals attraction is weak.

- **Coalescence:** the droplets fuse together to form a large drop during coalescence. This irreversible process leads to a reduction in the number of water droplets and leads to complete demulsification. Coalescence is enhanced by a high rate of flocculation, the absence of strong films, high interfacial tensions, low oil and interfacial viscosity, a high water cut, and a high temperature [42].

- **Creaming and Sedimentation:** This process is produced by external forces (typically gravitational or centrifugal). When such forces exceed the thermal motion(kinetic theory) of the droplets (Brownian motion), a concentration gradient builds up in the system with the larger droplets moving faster to the top (if their density is lower than that of the medium) or to the bottom (if their density is larger than that of the medium) of the container [12].

3. EXPERIMENTAL WORK

3.1 MATERIALS

- ***Polymer:*** Poly(methyl methacrylate) (PMMA), also known as acrylic or acrylic glass.

- ***Nanoparticles*****:** ZnO nanoparticles were selected, supplied by Sigma Aldridge. This was in a white powder form with formula weight of 81.39g/mol and particle size <10nm. Properties are summarized in Table 3.2.

- ***Brine*****:** NaCl was dissolved in distilled water to prepare the brine solution. Polymer and nanoparticle aqueous solutions were prepared using brine solution.

- ***Test bottles*****:** 60 poly vial test bottles were used to mix the crude oil and aqueous solutions.

- ***Crude Oil sample*****:** The crude oil sample used was collected from NATREF (refinery tank F29107), crude oil properties are summarized in Table 2.1 (in Chapter 2) its properties.

- ***A water bath***: A hot water bath (figure 3.1) was used to heat and maintain the system at a fixed (room) temperature. The temperature was increased to 50°C and 70°C measure the stability of emulsion under higher temperatures.



Figure 3.1: Water bath with thermometer and Controller.

3.2. Instruments

A hielscher UP200S Ultrasonic Processor (200 watts, 24kHz) was used to mix the aqueous solutions and the crude oil. An Ohaus Explorer EP413 milligram balance was used to weigh the chemicals in preparation of the aqueous solutions. Olympus BX 63 OFM microscope was used to analyze the samples with the most stable emulsions formed to determine the tightness of the emulsion by looking at the droplet size distribution of emulsions formed.





Figure 3.2: (a) Hielscher UP200S Ultrasonic Process (b) Olympus BX 63 OFM

Table 3.1: Properties of Polymer

Name of Polymer	Mw	Description	Supplier
Poly(methyl methacrylate)	~15,000	White Powder	Sigma Aldridge

Table 3.2: Properties of Nanoparticles

Type of nanoparticle	Particle size (nm)	Description	Supplier
Zinc Oxide (ZnO)	<10nm	White powder	Sigma Aldridge

3.3. Experimental Procedure

Three different experiments were conducted and four aqueous solutions were prepared as follows per experiment:

Experiment 1:Preparation of different solutions with 2% brine and 0.2g of polymer and 0.2g of nanoparticles

Four different solutions were prepared with 2g of NaCl, 0.2g of polymer (PMMA), 0.2g nanoparticle (ZnO) and labeled A1,B1,C1 and D1

A1…100g Distilled water + 2g NaCl

B1…100g Distilled water + 2g NaCl + 0.2g polymer (PMMA)

C1…100g Distilled water + 2g NaCl + 0.2g nanoparticle (ZnO)

D1….100g Distilled water + 2g NaCl + 0.2g Polymer + 0.2g nanoparticle composite

Experiment 2: Preparation of different solutions with 2% brine and 0.5g of polymer and 0.5g of nanoparticles

Four different solutions were prepared with 2g of NaCl, 0.5g of polymer (PMMA), 0.5g nanoparticle (ZnO) and labeled A2,B2,C2 and D2

A2…100g Distilled water + 2g NaCl

B2…100g Distilled water + 2g NaCl + 0.5g polymer (PMMA)

C2…100g Distilled water + 2g NaCl + 0.5g nanoparticle (ZnO)

D2.…100g Distilled water + 2g NaCl + 0.5g Polymer + 0.5g nanoparticle composite

Experiment 3: Preparation of different solutions with 10% brine and 0.2g of polymer and 0.2g of nanoparticles

Four different solutions were prepared with 10g of NaCl, 0.2g of polymer (PMMA), 0.2g nanoparticle (ZnO) and labeled A3, B3, C3 and D4

A3…100g Distilled water + 10g NaCl

B3…100g Distilled water + 10g NaCl + 0.2g polymer (PMMA)

C3…100g Distilled water + 10g NaCl + 0.2g nanoparticle (ZnO)

D3.…100g Distilled water + 10g NaCl + 0.2g Polymer + 0.2g nanoparticle composite

Preparing the aqueous solution mixtures with crude oil

Emulsification tests were conducted using poly vial bottles. In each set of tests, a group of bottles was used to contain different aqueous phases with the different chemicals and concentrations. In preparation of an emulsification bottle test, different ratios of aqueous phase were added to a test bottle first; see Table 3.3, 3.4 and 3.5 for ratios used. Then different ratios of crude oil were carefully added to the top of the aqueous phase with a syringe so that minimal mechanical disturbance occurs. An ultrasonic stirrer was then used to mix the crude oil and aqueous solutions.

Table 3.3: Water to Oil (W: O) ratios of samples prepared for Experiment 1

	A1	Oil		B1	Oil		C1	Oil		D1	Oil
1	9	1	6	9	1	11	9	1	16	9	1
2	7.5	2.5	7	7.5	2.5	12	7.5	2.5	17	7.5	2.5
3	5	5	8	5	5	13	5	5	18	5	5
4	2.5	7.5	9	2.5	7.5	14	2.5	7.5	19	2.5	7.5
5	1	9	10	1	9	15	1	9	20	1	9

Table 3.4: Water to Oil (W: O) ratios of samples prepared for Experiment 2

	A2	Oil		B2	Oil		C2	Oil		D2	Oil
21	9	1	26	9	1	31	9	1	36	9	1
22	7.5	2.5	27	7.5	2.5	32	7.5	2.5	37	7.5	2.5
23	5	5	28	5	5	33	5	5	38	5	5
24	2.5	7.5	29	2.5	7.5	34	2.5	7.5	39	2.5	7.5
25	1	9	30	1	9	35	1	9	40	1	9

Table 3.5: Water to Oil (W: O) ratios of samples prepared for Experiment 3

	A3	Oil		B3	Oil		C3	Oil		D3	Oil
41	9	1	46	9	1	51	9	1	56	9	1
42	7.5	2.5	47	7.5	2.5	52	7.5	2.5	57	7.5	2.5
43	5	5	48	5	5	53	5	5	58	5	5
44	2.5	7.5	49	2.5	7.5	54	2.5	7.5	59	2.5	7.5
45	1	9	50	1	9	55	1	9	60	1	9

3.4. Microscopic Observations

The droplet size distribution for oilfield emulsions is determined by several techniques, for this research microscopy and image analysis technique was used. The microscope used for this was the Olympus BX 63 OFM, figure 3.2. Thin section slides were prepared for samples with W: O ratios 5:5 for all four solution mixtures for all three experiments with brine and crude oil.

Preparing microscopy slides for the aqueous solution mixtures with crude oil

A pipette was used to collect aqueous solutions from test bottles. The thin section slides were used to place the solution drops of the emulsion formed (continuous phase) with a microscope slip placed on top of it to seal the aqueous solution in place. Pictures were taken for different samples and investigated for droplet size distribution.

4. RESULTS AND DISCUSSION

The use of surfactant is often considered appropriate for increasing oil recovery when dealing with difficult reservoir conditions such as thin reservoirs, high permeability, great depth, etc. Still the application of surfactants and other chemicals is often challenging in the cases of heavy oil reservoirs due to high viscosity which may lead to a low mobility of the fluid and possible inefficient sweep. In general oil displacement is more efficient when the mobility of the displacing fluid is less than the displaced fluid (oil). Therefore the challenge is to generate a low mobility drive fluid in a cost-effective manner.

Polymer injection has the potential to decrease water mobility and provide a favorable mobility ratio. In addition rock permeability can also has a great impact in oil recovery. Reservoir heterogeneity may lead to thief zones in which the displacing fluid tends to channel quickly due to higher permeability, thus low sweep efficiency may be obtained due to uncovered zones. Several methods have been used to reduce the permeability of high permeable zones. Injection of polymers followed by water flooding may be also used for the profile modification to reduce the permeability of high permeable zones.

Emulsions are generally unstable and the heavier liquid will settle to the bottom over time, in our case the lighter liquid will be the oil and the different solutions labeled A1,B1,C1,D1,A2,B2,C2,D2,A3,B3,C3 and D3 are the heavier liquids. Surfactants are usually used as stabilizing agents to keep the emulsion from separating. But in this research, we are investigating if polymers and nanoparticles often used to increase bulk and sweep efficiency can also be used as surfactants in enhanced oil recovery.

Polymers can absorb at the oil–water interface and thus enhance the stability of emulsions. Polymer concentration is the key factor to stabilize the synthetic W/O crude oil emulsion [39]. Nanoparticles stabilize emulsions droplets which are small enough to pass typical pores, and flow through the reservoir rock without much retention and also remain stable under hard conditions in the reservoirs due to irreversible adsorption of the nanoparticles on their droplet surface [24].

It is the objective of this study to compare emulsion stabilities of water/oil in the presence of different concentrations of polymer, nanoparticles and brine using three different experiments;

Experiment 1

Four different solutions were prepared with 2g of NaCl, 0.2g of polymer (PMMA), 0.2g nanoparticle (ZnO) and labeled A1,B1,C1 and D1.

Experiment 2

Four different solutions were prepared with 2g of NaCl, 0.5g of polymer (PMMA), 0.5g nanoparticle (ZnO) and labeled A2,B2,C2 and D2.

Experiment 3

Four different solutions were prepared with 10g of NaCl, 0.2g of polymer (PMMA), 0.2g nanoparticle (ZnO) and labeled A3, B3, C3 and D4.

Solutions A1,B1,C1,D1,A2,B2,C2,D2,A3,B3,C3 and D3 were placed in poly vial bottles with crude oil with water-to-oil ratios of 9:1, 7.5:2.5, 5:5, 2.5:7.5 and 1:9. When the aqueous solution was mixed with crude oil, a homogeneous solution formed within 2 minutes of stirring. The bottles were then placed in a water bath at various temperatures (25°C, 50°C and 70°C respectively) to assess the effect of temperature on the emulsion stability. Some amount of the

solution (~10%) was lost during re-emulsification process and was accounted for. Samples with water-to-oil ratio 1:9 and 2.5:7.5 displayed an oil continuous phase and those with 9:1 and 7.5:2.5 displayed a water continuous phase.

It is common knowledge that oil and water don't mix. If you try to mix them together they quickly separate, with the water sinking to the bottom and the oil floating on top. If you mix them very vigorously one of them will break up into droplets and disperse in the other. But even this dispersion won't last long and the two will soon separate as before. Vigorously mixing oil and water has two possible outcomes: In one, droplets of oil are dispersed in a continuous phase of water. In the other, droplets of water are dispersed in a continuous phase of oil. The first form is called an oil-in-water emulsion (oil droplets dispersed in water, or O/W emulsion for short), while the second form is called a water-in-oil emulsion (water droplets dispersed in oil, or W/O emulsion) [44].

In order to calculate the emulsion stability, the following equation was used:

Equation 1: $$Emulsion\ Stability\ (\%) = (Height_{max} - Height_{brine}) \div Height_{max}$$

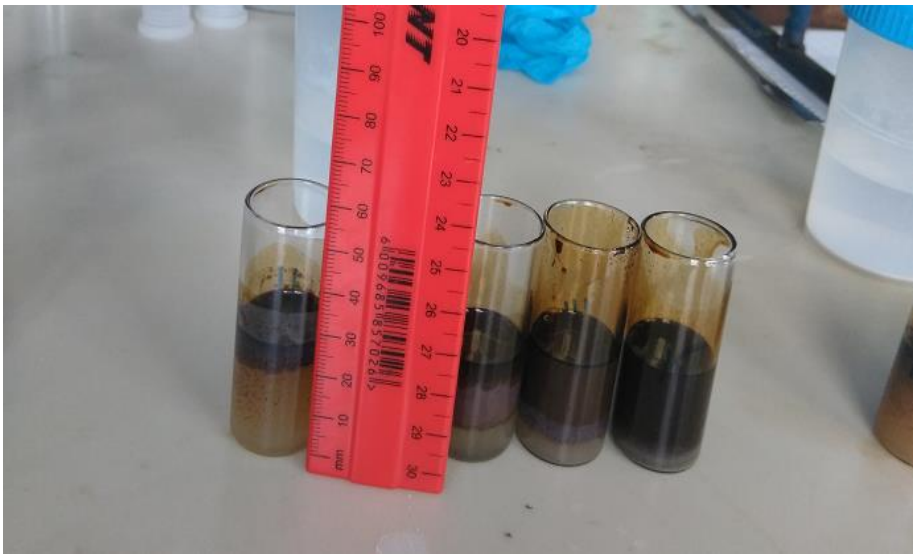


Figure 4.0 Emulsion stability measurement

4.1. Effects of temperature on emulsion stability Experiment 1

Four different solutions were prepared with 2g of NaCl, 0.2g of polymer (PMMA), 0.2g nanoparticle (ZnO) and labeled A1, B1, C1 and D1;

A 1…100g Distilled water + 2g NaCl
B 1…100g Distilled water + 2g NaCl + 0.2g polymer (PMMA)
C 1…100g Distilled water + 2g NaCl + 0.2g nanoparticle (ZnO)
D 1.…100g Distilled water + 2g NaCl + 0.2g Polymer + 0.2g nanoparticle composite

The above four solutions were mixed in poly vial bottles with crude oil with water-to-oil ratios of 9:1, 7.5:2.5, 5:5, 2.5:7.5 and 1:9 for each solution. Emulsion stability curves were plotted against time at temperatures 25°C, 50°C and 70°C.

4.1.1. The effects of temperature on emulsion stability of Solution A1 (2%wt Brine + crude oil)

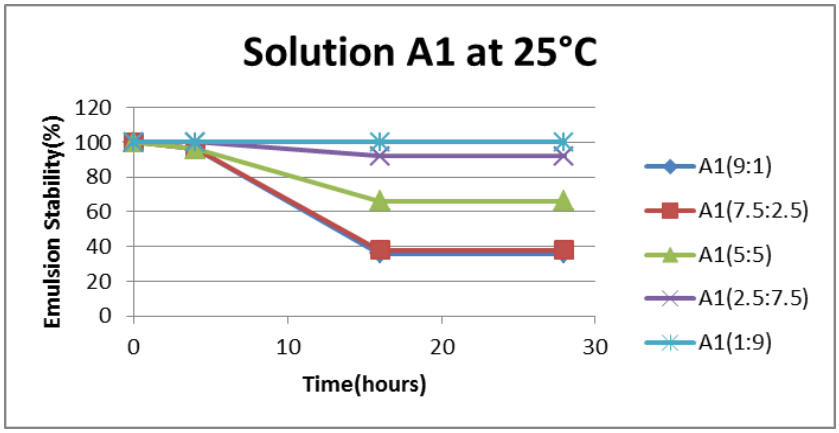


Figure 4.1: Stability of Solution A1 (W: O) at 25°C over 28hours

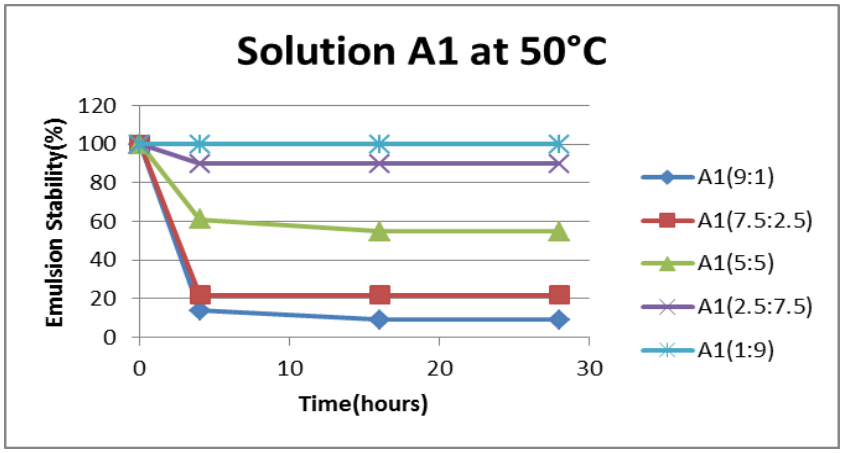


Figure 4.2: Stability of Solution A1 (W: O) at 50°C over 28hours

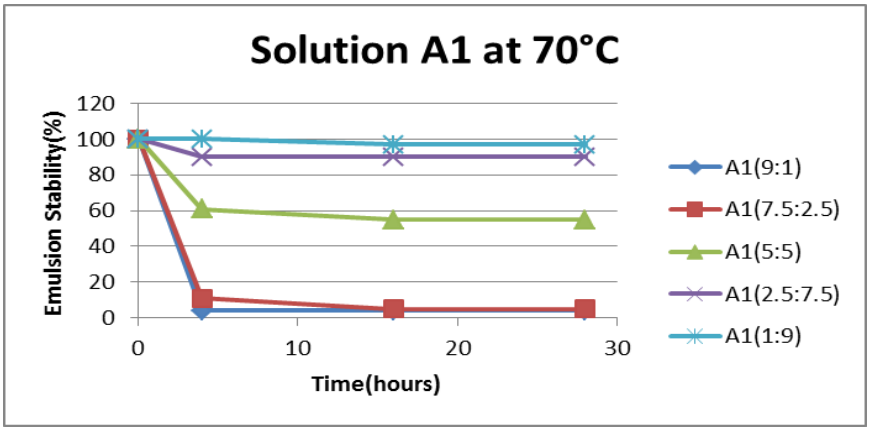


Figure 4.3: Stability of Solution A1 (W: O/) at 70°C over 28hours

At 25°C, sample with water-to-oil ratio of 5:5 had an emulsion stability of 96% after 4hrs (figure 4.1) and this reduced to 66% after 18 hours and remained constant thereafter. At 50°C, the emulsion stability was lower at 61% after 4hours and decreased to 55% after 18 hours and then remained constant thereafter (figure 4.2). When the temperature was increased to 70°C the stability was 61% after 4hours and decreased to 55% after 18 hours and then remained constant thereafter (figure 4.3).

At 25°C, sample with water-to-oil ratio 9:1 exhibited 96% emulsion stability after 4 hours and decreased to 39% after 16 hours and then remained constant thereafter (figure 4.1). At 50°C, emulsion stability was lower at 14% after 4hours and decreased to 9% after 16 hours and then remained constant thereafter (figure 4.2). When temperatures were increased to 70°C (figure 4.3) the stability decreased to 4% after 4hours and remained constant.

At 25°C, sample with water-to-oil 7.5:2.5 had had an emulsion stability of 96% after 4hrs (figure 4.1) and this reduced to 38% after 18 hours and remained constant thereafter However, under a much higher temperature of 50°C the samples' emulsion stability was 22% after 4 hours and remained constant thereafter (figure 4.2). At 70°C the emulsion stability was 11% after4hrs and reduced to 5% after 15 hours and there after remained constant.

Visual observation showed faster demulsification within an hour for 70°C and 2 hours for 50°C, although all data was recorded after 4hours. Results also show that a much more stable emulsion is obtained with samples that have oil as the continuous phase compared to aqueous solution as the continuous phase. This may be due to the viscosity of the crude oil itself.

For instance samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions as phase separation occurred while samples 1:9, 2.5:7.5 showed more stable emulsions within 28hours for all

temperatures 25°C,50°C,70°C.But a slight decrease in emulsion stability of 92% was observed for sample 2.5:7.5 at 25°C within 16 hours. At 50°C and 70°C emulsion stability was further reduced to 90% after 4 hours. However; sample 1:9 showed full emulsion stability for all temperatures (>97%).

We know from Miller and Neogi, [45] that emulsions are dispersions of one liquid phase in the other. Thus, there is the dispersed phase and a dispersion medium called the continuous phase. The dispersion is called a macroemulsion if the dispersed phase is in form of droplets of the order of millimeters or less. Below 100 nm, the droplets are colloidal and show Brownian motion and diffusivity.

Kokal [40] has shown that the temperature influences the emulsion stability by affecting 1) the physical properties of the fluids that may lead to variation in interfacial film between immiscible fluids, and 2) the solubility of the oil in the continuous phase. Viscosity was identify as the single most important factor of emulsion instability as oil viscosity decrease when temperature increases. But also the increase in temperature increases the thermal energy of the droplets, thus increasing the dynamical interaction between droplets and eventually leading to a collision frequency increase. The collision frequency increase favors phase separation due to droplets merging. Despite the change in viscosity with temperature, it has been found that emulsions tend to have the viscosity of the continuous phase, thus if water is the aqueous phase the emulsion viscosities will tend to be around 1 cp even when using crude oils with higher viscosities. This characteristic allows the oil-in-water emulsion to be injected easily in the reservoir avoiding injectivity issues due to high viscosities (present in water-in-oil emulsions), additionally since emulsion purpose is to block high permeable zones then low viscosity lead to higher mobility and it is more likely for the emulsion to flood and decrease the permeability to

the water, forcing the water flooding to sweep less permeable zones. Additionally experiments have shown that below 50 percent of oil content the emulsion behaves as a Newtonian fluid; for a higher content of oil the emulsion changes and starts to behave as a pseudo non-Newtonian fluid that is a fluid which its flow varies with pressure and its viscosity lecture depends on the shear rate used to measure the viscosity [49].

Samples with water-to-oil ratio 1:9 and 2.5:7.5 displayed an oil continuous phase and those with 9:1 and 7.5:2.5 displayed a water continuous phase. From the stability graphs using solution A1 above, it was observed that, when water was the continuous phase in our experiments temperature had a greater influence on emulsion stability. Taking for instance water to oil ratio of 9:1 emulsion stability drops from 39% to 4% as temperature is increased from 25°C to 70°C.But for water to oil ratio of 1:9,emulsion stability remained constant at 97% as temperature was increased from 25°C to 70°C.

4.1.2. The effects of temperature on emulsion stability of Solution B1 (2%wt Brine + 0.2gPMMA+ crude oil)

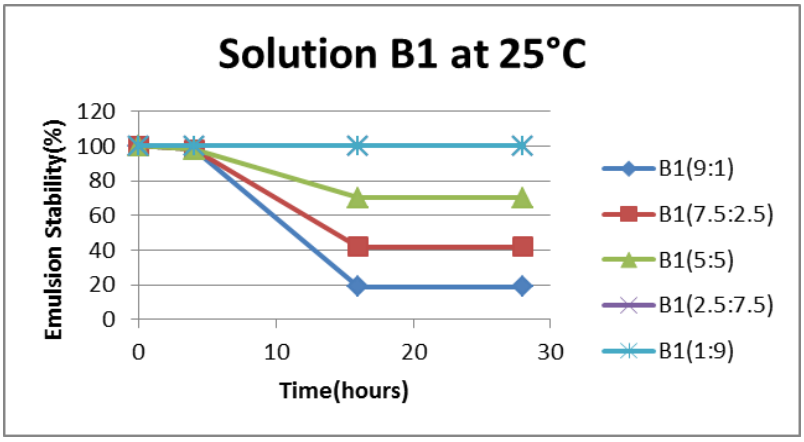


Figure 4.4: Stability of Solution B1 (W: O) at 25°C over 28hours

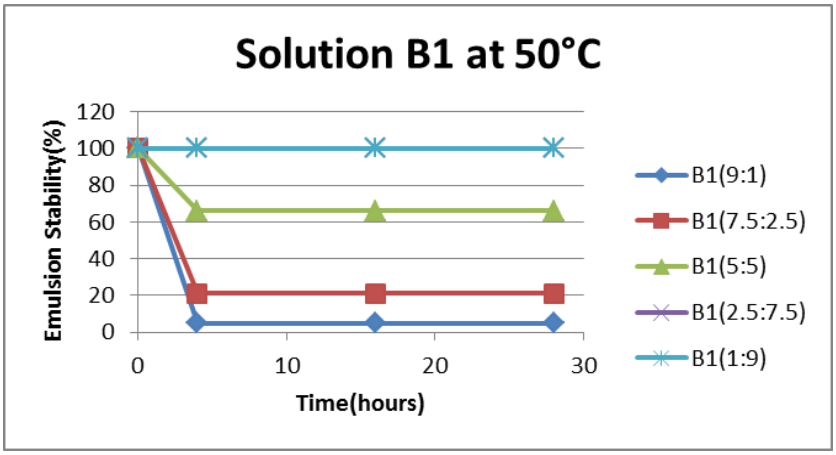


Figure 4.5: Stability of Solution B1 (W: O) at 50°C over 28hours

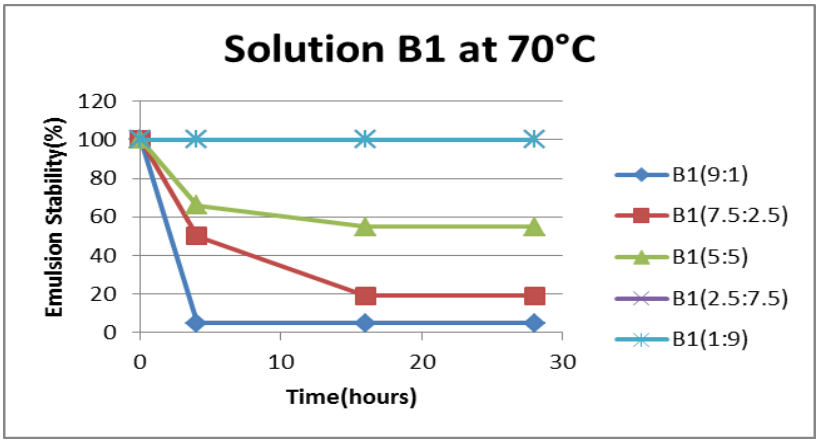


Figure 4.6: Stability of Solution B1 (W: O) at 70°C over 28hours

Using Solution B1 with 2% brine and 0.2g polymer, sample with water-to-oil ratio of 5:5 had emulsion stability of 98% under 25°C in 4hrs (figure 4.4), this reduced to 70% and remained constant over 28 hours. At 50°C, (figure 4.5), emulsion stability was lower at 66% after 4hours and remained constant for 28 hours. When temperatures were increased to 70°C (figure 4.6) the stability was 66% after 4hours and decreased to 55% then remained constant.

Sample with water-to-oil ratio 9:1 exhibited 98% emulsion stability under 25°C for 4 hours and remained constant at 19% for 28 hours. At 50°C, (figure 4.5), emulsion stability was lower at 5% after 4hours and remained constant for 28 hours. When temperatures were increased to 70°C (figure 4.6) the stability was 5% after 4hours and remained constant.

Sample with water-to-oil 7.5:2.5 had 98% emulsion stability under 25°C for 4 hours and remained constant at 42% for 28 hours. However, under a much higher temperature of 50°C the samples' emulsion stability was 21% in the first 4 hours and remained constant over 28 hours. Under 70°C the emulsion stability was 50% in 4hrs and reduced to 19% then remained constant.

Samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions as phase separation occurred for all temperatures 25°C,50°C,70°C and the emulsion stability graphs were very similar to solution A1 experiments. While samples 1:9, 2.5:7.5 showed more stable emulsions within 28hours for all temperatures 25°C, 50°C, 70°C. Samples with water-to-oil ratio 1:9 and 2.5:7.5 displayed an oil continuous phase and those with 9:1 and 7.5:2.5 displayed a water continuous phase. From the stability graphs using solution B1 above, it was observed that, when water was the continuous phase in our experiments temperature had a greater influence on emulsion stability.

This was not the case with solution A1 where no polymer was present as we recorded a slight decrease in emulsion stability as temperature was increased. Typically tertiary recovery techniques attempts to solve oil trapping by a combination of mobility control improvement, wettability changes and/or residual oil saturation reduction. In general polymers can stabilize an emulsion as they may be attracted to the oil-water interface with strong bonds by diffusion where they form films that may inhibit the coalescence of droplets. Polymers may also be charged which has the potential to enhance the stability of emulsions.

Adidin [43] has shown that the presence of polymer increased the emulsion stability since polymers added to water increases its viscosity. Furthermore Polymer is the material that plays an important role in the application of EOR technology, especially surfactant and hydrogel polymers. In the technology, surfactant polymer is injected to the reservoir to reduce an interfacial tension between oil and water and is able to wipe out the trapped oil from the reservoir rock and hence increase the oil production. While an injection of hydrogel polymer to the reservoir is to increase a viscosity of fluid containing water so that the fluid is more difficult to flow than the oil, and as a result, the oil production increases.

4.1.3. The effects of temperature on emulsion stability of Solution C1 (2%wt Brine + 0.2gZnO + crude oil)

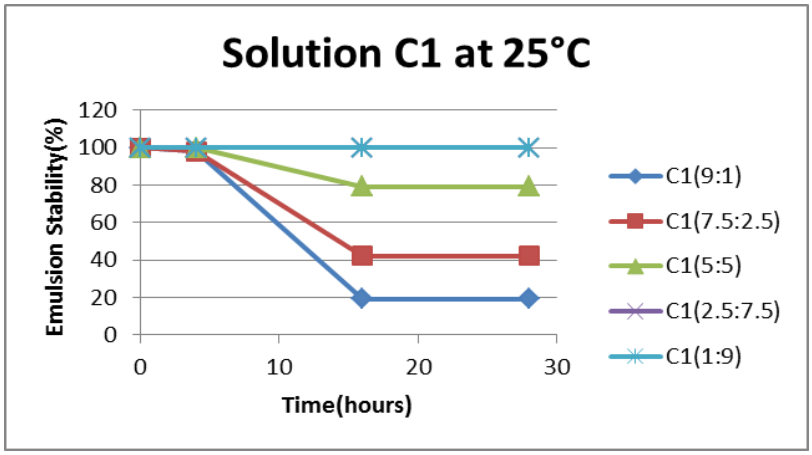


Figure 4.7: Stability of Solution C1 (W: O) at 25°C over 28hours

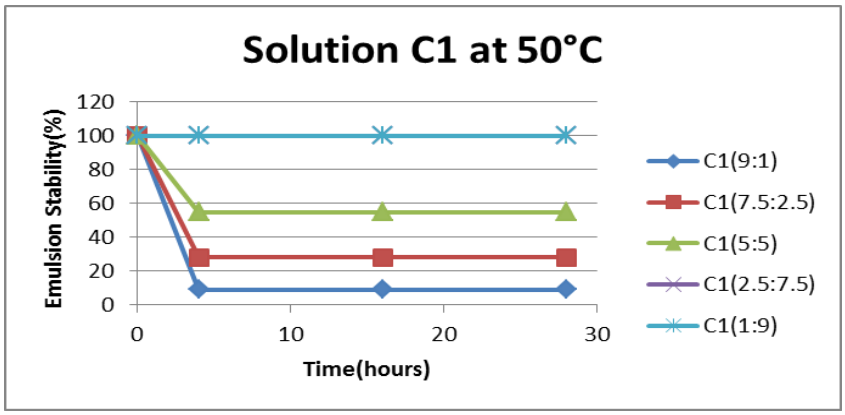


Figure 4.8: Stability of Solution C1 (W: O) at 50°C over 28hours

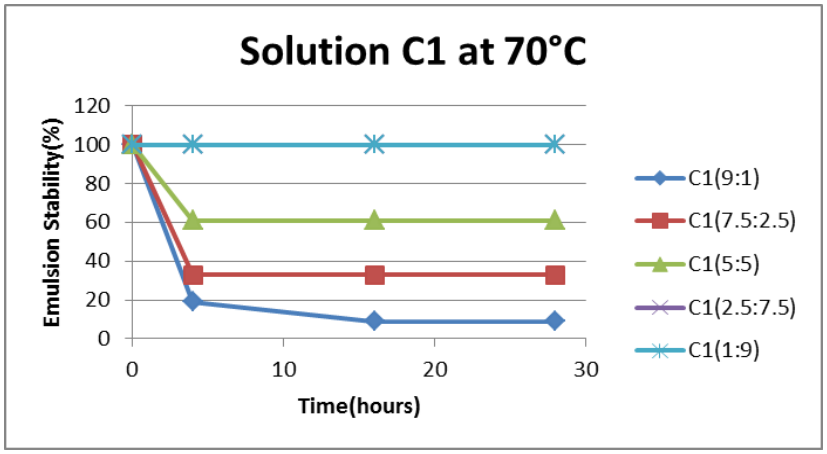


Figure 4.9: Stability of Solution C1 (W: O) at 70°C over 28hours

When solution C1 with 2%brine and 0.2g nanoparticle was mixed with different oil ratios, sample with water-to-oil ratio of 5:5 had more stable emulsions under 25°C in 4hrs (figure 4.7), this reduced to 79% and remained constant over 28 hours. At 50°C, (figure 4.8), emulsion stability was lower at 55% after 4hours and remained constant for 28 hours. When temperatures were increased to 70°C (figure 4.9) the stability was 61% after 4hours and then remained constant for 28 hours.

Sample with water-to-oil ratio 9:1 exhibited stable emulsions under 25°C for 4 hours and remained constant at 35% for 28 hours. At 50°C, (figure 4.8), emulsion stability was lower at 9% after 4hours and remained constant for 28 hours. When temperatures were increased to 70°C (figure 4.9) the stability was 9% after 4hours and remained constant for 28hours.

Sample with water-to-oil 7.5:2.5 had stable emulsions under 25°C for 4 hours and remained constant at 40% for 28 hours. However, under a much higher temperature of 50°C the emulsion stability was 28% in the first 4 hours and remained constant over 28 hours. Under 70°C the emulsion stability was 33% in 4hrs and then remained constant over 28hours.

Samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions and the emulsion stability curves were similar to solution A1 and Solution B1 but solution C1 showed slightly more stable emulsions when temperatures were increased compared to the other two solutions. Samples 1:9, 2.5:7.5 showed more stable emulsions within 28hours for all temperatures 25°C, 50°C, 70°C.

Using the water to oil ratio 7.5:2.5 as an example, we could observe a decrease in emulsion stability for solution C1 from 40% to 33% as temperature was increased from 25°C to

70°C.The decrease in emulsion stability is more higher for solution B1 from 42% to 19% and worst for solution A1 from 38% to 11% as temperatures were increased from 25°C to 70°C.

The increase in emulsion stability is due to the presence of the zinc oxide nanoparticles since according to Zhang [33], nanoparticles can be used to stabilize emulsion droplets which are small enough to pass typical pores. The nanoparticle stabilized emulsions droplets are small enough to pass typical pores, and flow through the reservoir rock without much retention. They also remain stable despite harsh conditions in reservoirs due to the irreversible adsorption of the nanoparticles on their droplet surface. In addition, the large viscosity of nanoparticle-stabilized emulsions can help to manage the mobility ratio during flooding, which provides a viable method to push highly viscous oil from the subsurface. Therefore, they have significant potential in reservoir engineering applications.

Bragg [50], has shown that tough nanoparticles may vary widely due to existence of different chemical composition, sizes and shapes, they should exhibit certain physical and chemical properties for use in EOR processes: 1) the solid particles should have at least some hydrophilic character for making an external emulsion as particles must be wetted by the external phase, 2) the solid particles must remain undissolved in the water phase under formation conditions, and have appropriate charge distribution for stabilizing an interfacial film between the internal droplet and the continuous phase. Third, the particle size should be sufficiently small to provide adequate surface area coverage of the internal phase. In some ways, the nanoparticles added to the emulsion act in the same way as an emulsifying agent, since solids are distributed in a certain way as a protection layer all along the oil/water interface to prevent coalescence. As a result emulsions prepared with nanoparticles may not be thermodynamically stable, but can have a metastable state for a long period of time. Bragg further indicates that emulsion stability

is achieved if nanomaterials used have high surface area/volume ratio, small mass and average size particle size of two microns or less, and have surface that is either attracted to oil phase by polar or asphaltenes hydrocarbons and surface partially or substantially hydrophilic to form an oil-in-water emulsion. It is important to point out that surface wettability of the solids may be modified from a natural hydrophilic to oleophilic, thus solids may be used to create either oil-external or water-external emulsions. Nanoparticles, because of their small size, are adequate to cover even the smallest oil droplets efficiently. This is particularly important when small pore throat diameter is present in the porous media the injectivity near to the wellbore is likely not to be affected. Oil-in-water emulsion stabilized by solid particles behaves differently than a typical emulsions. The stabilization process may be a combination of two phenomena that normally are negative for stabilization namely creaming and aggregation between particles which in most cases do not lead to coalescence due to well established protection. Aggregation appears during the steady conditions accompanied by a sort of creaming effect due to the effect of density difference based on to the amount of nanoparticles or oil used.

4.1.4. The effects of temperature on emulsion stability of Solution D1 (2%wt Brine + 0.2gZnO + 0.2gPMMA + crude oil)

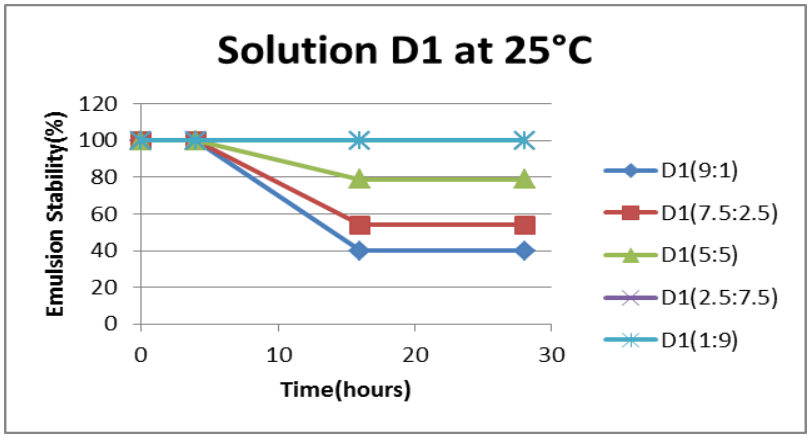


Figure 4.10: Stability of Solution D1 (W: O) at 25°C over 28hours

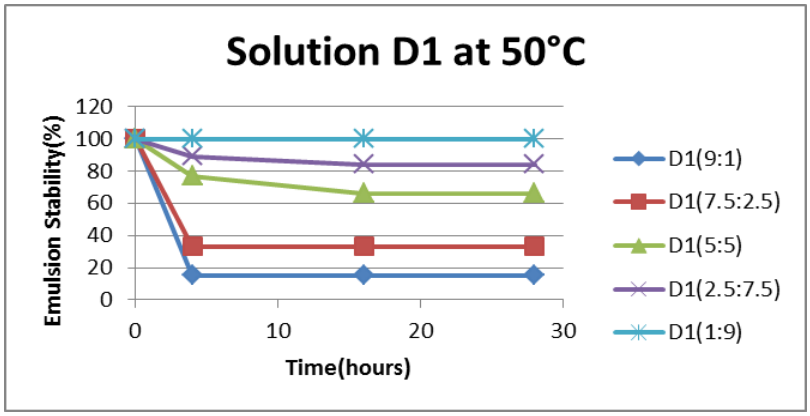


Figure 4.11: Stability of Solution D1 (W: O) at 50°C over 28hours

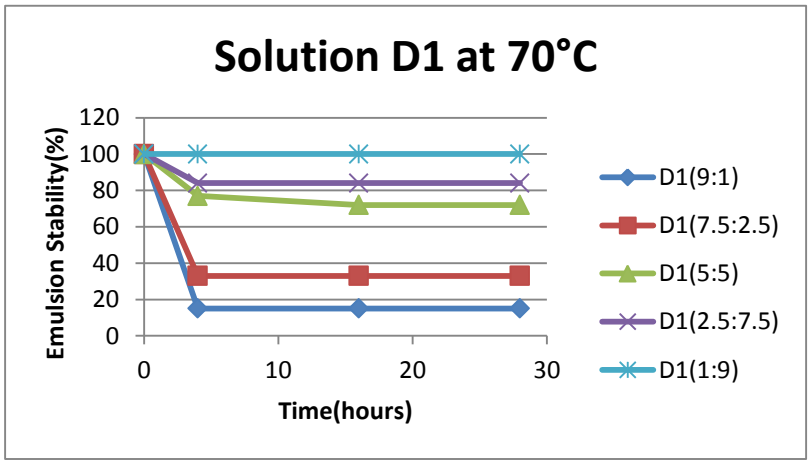


Figure 4.12: Stability of Solution D1 (W: O) at 70°C over 28hours

When solution D1 with 2%brine,0.2g nanoparticle and 0.2g polymer was mixed with different oil ratios, sample with water-to-oil ratio of 5:5 had stable emulsions under 25°C in 4hrs (figure 4.10) , this reduced to 79% and remained constant over 28 hours. At 50°C, (figure 4.11), emulsion stability was lower at 77% after 4hours and reduced to 66% and remained constant for 28 hours. When temperatures were increased to 70°C (figure 4.12) the stability was 77% after 4hours and reduced to 72% then remained constant for 28 hours.

Sample with water-to-oil ratio 9:1 showed stable emulsions under 25°C for 4 hours and remained constant at 40% for 28 hours. At 50°C, (figure 4.11), emulsion stability was lower at 15% after 4hours and remained constant for 28 hours. When temperatures were increased to 70°C (figure 4.12) the stability was 15% after 4hours and remained constant for 28hours.

Sample with water-to-oil 7.5:2.5 had stable emulsions under 25°C for 4 hours and remained constant at 54% for 28 hours. However, under a much higher temperature of 50°C the samples' emulsion stability was 33% in the first 4 hours and remained constant over 28 hours. Under 70°C the emulsion stability was 33% in 4hrs and then remained constant over 28hours.

Samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions as phase separation occurred while samples 1:9, 2.5:7.5 showed more stable emulsions within 28hours for all temperatures. But a slight decrease in emulsion stability of 84% was observed for sample 2.5:7.5 at 50°C and 70°C after 4hours and remained constant for 28hours.Sample 1:9 showed full emulsion stability for all temperatures within 28hours.At 25°C we recorded more stable emulsions for solution D1 compared to solutions A1, B1 and C1 due to the presence of both polymer and nanoparticle. As temperature is increased, a decrease of emulsion stability is observed in solution D1 compared

to solution B1 and C1 when oil is the continuous phase. But when water is the continuous phase, solution D1 showed slightly more stable emulsions compared to solutions A1,B1 and C1.

According to Garcia [46], degradation of the polymer PMMA occurs at higher temperature in the presence of nanoparticles because of the interaction between the two components. It is well-known that the properties of polymers under their Glass Transition Temperature (Tg) are dependent on their ‘‘preparation history’’. The same occurs with polymer-based Nano composites, not only because the organic matrix is amorphous but also because these systems are immiscible and biphasic. In the case of polymethacrylates, and more specifically of PMMA, according to the interaction between the organic and inorganic phases, two main types of composites exist: those in which there is a covalent linkage between the inorganic and organic and those in which there is not. Among the second, again, two types exist, according to the origin: those in which in situ polymerization is employed and those in which the polymeric matrix is previously synthesized and then mixed. Both the polymer and the nanoparticle polymer interface are strongly different in all these cases, and therefore caution has to be taken when comparing their properties. This is shown very clearly by the amount of apparently contradictory information regarding the properties of many Nano composite. This may be the reason why the decrease in emulsion stability is observed when temperature is increased since no covalent linkage exist between the nanoparticle and the polymer.

4.2. Effects of temperature on emulsion stability Experiment 2

Four different solutions were prepared with 2g of NaCl, 0.5g of polymer (PMMA), 0.5g nanoparticle (ZnO) and labeled A2, B2, C2 and D2;

A2…100g Distilled water + 2g NaCl

B2…100g Distilled water + 2g NaCl + 0.5g polymer (PMMA)

C2…100g Distilled water + 2g NaCl + 0.5g nanoparticle (ZnO)

D2.…100g Distilled water + 2g NaCl + 0.5g Polymer + 0.5g nanoparticle composite

The above four solutions were mixed in poly vial bottles with crude oil with water-to-oil ratios of 9:1, 7.5:2.5, 5:5, 2.5:7.5 and 1:9 for each solution. Emulsion stability curves were plotted against time at temperatures 25°C, 50°C and 70°C.

Note that in **Experiment 2** the concentration of polymer and nanoparticle were increased to 0.5g from 0.2g each, but the brine concentration was kept same as in **Experiment 1**.Thus these experiments will help us investigate the effects of increasing the concentrations of the chemicals on the emulsion stability as temperature is increased.

4.2.1. The effects of temperature on emulsion stability of Solution B2 (2%wt Brine + 0.5gPMMA+ crude oil)

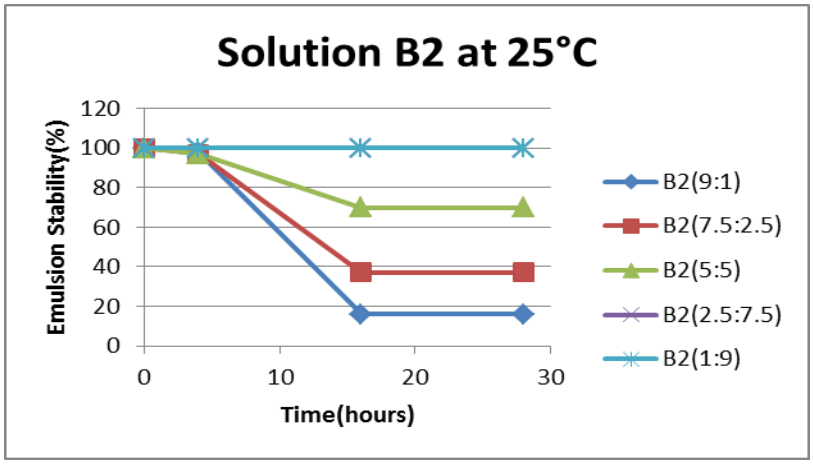


Figure 4.13: Stability of Solution B2 (W: O) at 25°C over 28hours

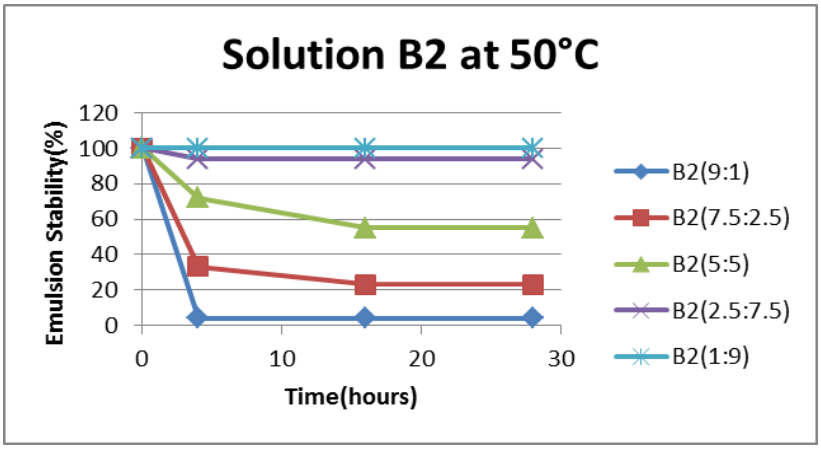


Figure 4.14: Stability of Solution B2 (W: O) at 50°C over 28hours

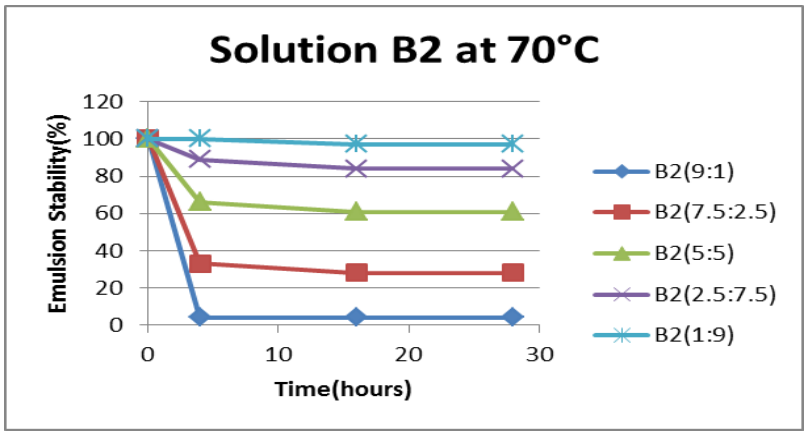


Figure 4.15: Stability of Solution B2 (W: O) at 70°C over 28hours

When polymer concentration is increased from 0.2g solution B1 to 0.5g solution B2,sample with water-to-oil ratio of 5:5 had emulsion stability of 97% under 25°C in 4hrs (figure 4.13) ,this reduced to 70% and remained constant. At 50°C, (figure 4.14), emulsion stability was 72% after 4hours and reduced to 55% then remained constant. When temperatures were increased to 70°C (figure 4.15) the stability was 66% after 4hours and decreased to 61% then remained constant.

Sample with water-to-oil ratio 9:1 exhibited 98% emulsion stability under 25°C for 4 hours and remained constant at 16% for 28 hours. At 50°C, (figure), emulsion stability was lower at 4% after 4hours and remain constant. When temperatures were increased to 70°C (figure 4.15) the stability was 4% after 4hours and remained constant.

Sample with water-to-oil 7.5:2.5 had 97% emulsion stability under 25°C for 4 hours and remained constant at 37% for 28 hours. However, under a much higher temperature of 50°C the samples' emulsion stability was 33% in the first 4 hours, decreased to 23% and remain constant over 28 hours. Under 70°C the emulsion stability was 33% in 4hrs and reduced to 28% then remained constant over 28hours.

Samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions and the emulsion stability curves were very similar to solution B1 in which only 0.2g of PMMA was used. Samples 1:9, 2.5:7.5 showed more stable emulsions within 28hours for all temperatures 25°C, 50°C, 70°C. But a slight decrease in emulsion stability of 94% was observed for sample 2.5:7.5 at 50°C.At 70°C emulsion stability was further reduced to 89%.

Sample 1:9 showed full emulsion stability for all temperatures within 28hours, but for a slight drop at 70°C to 97% after 16hours and remained constant for 28hours.Comparing this to solution B1 which had full emulsion stability for samples 1:9 and 2.5:7.5, it was observed that increasing the amount of polymer to 0.5g decreased the emulsion stability when temperature was increased. This may be attributed to the degradation of the polymer when temperature and polymer concentration are increased when oil is the continuous phase, since our polymer dissolves in oil and not brine.

Results tend to suggest that at higher polymer concentration the stability of the emulsion increases. This may be due to the decrease of droplet size distribution, thus strengthening the mobility control capability but ultimately affecting the oil viscosity reduction by dispersed oil and formation of oil mixing.

4.2.2. The effects of temperature on emulsion stability of Solution C2 (2%wt Brine + 0.5gZnO + crude oil)

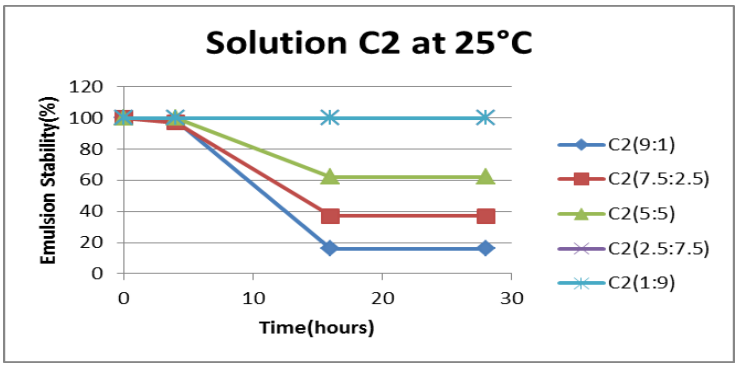


Figure 4.16: Stability of Solution C2 (W: O) at 25°C over 28hours

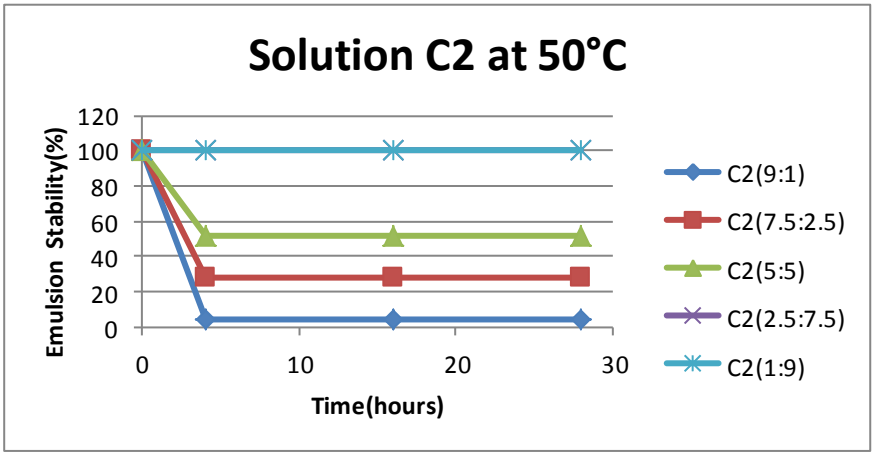


Figure 4.17: Stability of Solution C2 (W: O) at 50°C over 28hours

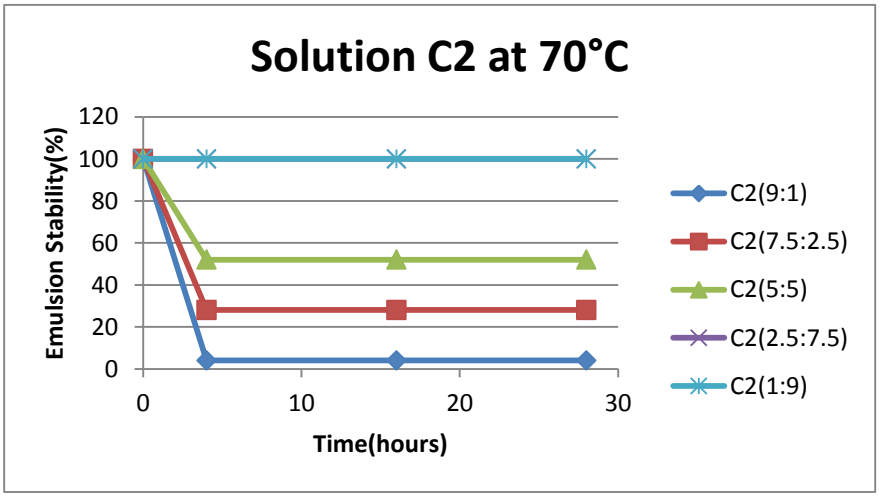


Figure 4.18: Stability of Solution C2 (W: O) at 70°C over 28hours

Also when nanoparticle concentration is increased from 0.2g solutionC1 to 0.5g solution C2,sample with water-to-oil ratio of 5:5 had full emulsion stability of 100% under 25°C in 4hrs (figure 4.16) , this reduced to 62% and remained constant over 28 hours. At 50°C, (figure 4.17), emulsion stability was 63% after 4hours and reduced to 52% then remained. When temperatures were increased to 70°C (figure 4.18) the stability was 52% after 4hours and then remained constant for over 28 hours.

Sample with water-to-oil ratio 9:1 exhibited 98% emulsion stability under 25°C for 4 hours and remained constant at 16%. At 50°C, (figure 4.17), emulsion stability was lower at 4% after 4hours and remained constant. When temperatures were increased to 70°C (figure 4.18) the stability was 4% after 4hours and remained constant for over 28hours.

Sample with water-to-oil 7.5:2.5 had 100% emulsion stability under 25°C for 4 hours and remained constant at 54% for over 28 hours. However, under a much higher temperature of 50°C the samples' emulsion stability remained at 28% for over 28 hours. Under 70°C the emulsion stability was also 28% in 4hrs and then remained constant over 28hours.

Samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions as phase separation occurred while samples 1:9, 2.5:7.5 showed more stable emulsions within 28 hours for all temperatures 25°C,50°C,70°C.This tells us that increasing the amount of nanoparticle to 0.5g had very negligible effects on the emulsion stability since the emulsion stability curves of solution C1 in which 0.2g of nanoparticle was used its very similar to solution C2 in which 0.5g of nanoparticle was used for all temperatures.

4.2.3. The effects of temperature on emulsion stability of Solution D2 (2%wt Brine + 0.5gZnO + 0.5gPMMA + crude oil)

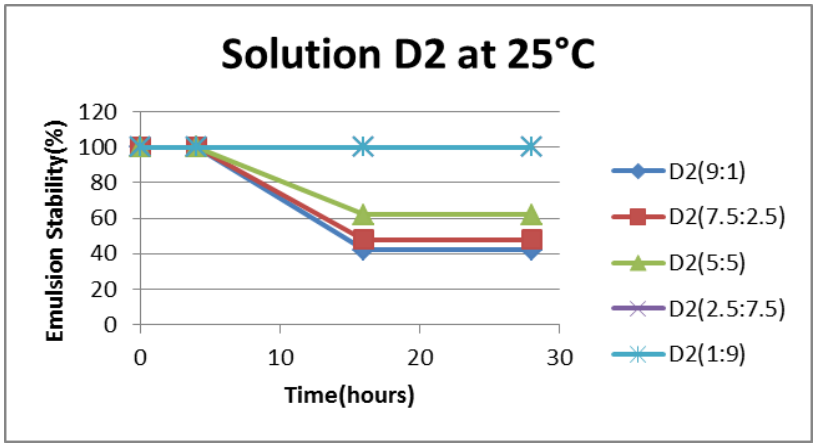


Figure 4.19: Stability of Solution D2 (W: O) at 25°C over 28hours

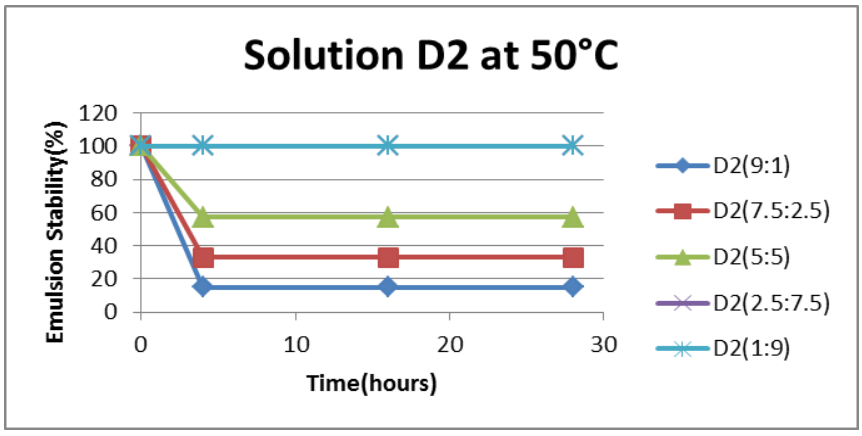


Figure 4.20: Stability of Solution D2 (W: O) at 50°C over 28hours

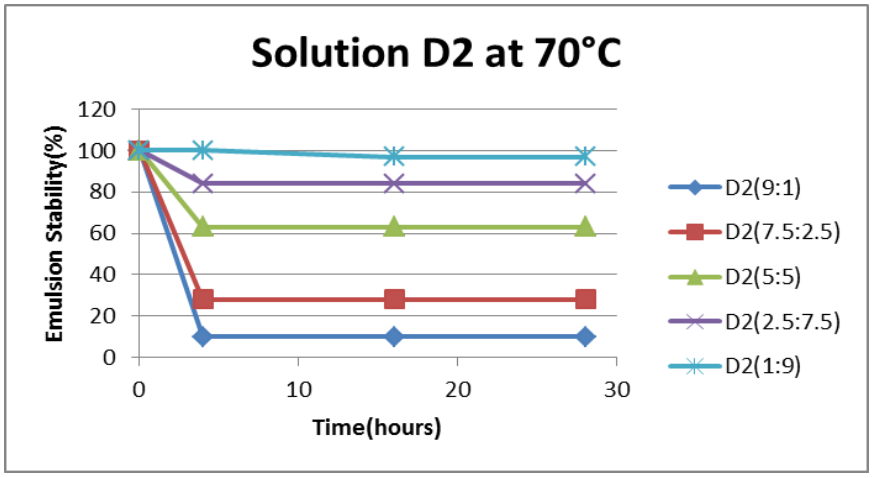


Figure 4.21: Stability of Solution D2 (W: O) at 70°C over 28hours

Using solution D2 with 0.5g of polymer and nanoparticle each, sample with water-to-oil ratio of 5:5 had full emulsion stability of 100% under 25°C in 4hrs (figure 4.19) , this reduced to 62% and remained constant over 28 hours. At 50°C, (figure 4.20), emulsion stability was lower at 57% after 4hours and remained constant for over 28 hours. When temperatures were increased to 70°C (figure 4.21) the stability was 63% after 4hours and remained constant over 28 hours. Sample with water-to-oil ratio 9:1 exhibited 100% emulsion stability under 25°C for 4 hours and remained constant at 42% over 28 hours. At 50°C, (figure 4.20), emulsion stability was lower at 15% after 4hours and remained constant for 28 hours. When temperatures were increased to 70°C (figure 4.21) the stability was 10% after 4hours and remained constant.

Sample with water-to-oil 7.5:2.5 had 100% emulsion stability under 25°C for 4 hours and remained constant at 48%.Under a much higher temperature of 50°C the samples' emulsion stability was 33% in the first 4 hours and remain constant over 28 hours. Under 70°C the emulsion stability was 28% in 4hrs and then remained constant over 28hours.

Samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions as phase separation occurred while samples 1:9, 2.5:7.5 showed more stable emulsions within 28hours for all temperatures. But a slight decrease in emulsion stability of 84% was observed for sample 2.5:7.5 at 70°C.The decrease in emulsion stability was also observed for solution D1, but at a lower temperature of 50°C.The increased amount of nanoparticle to 0.5g in solution D2 increased the emulsion stability at 50°C.Sample 1:9 showed full emulsion stability for all temperatures within 28hours except for 70°C where stability reduced to 97% after 16hours and remained constant for 28hours.

According to Garcia [46], the thermal degradation of the composites suffers strong changes as the amounts of nanoparticles are increased. Amounts of nanoparticles over 3% eliminate completely the initiation of degradation through labile chain ends, shifting by over 50°C the onset of thermal instability. It is proposed that at low nanoparticle ratio labile chain ends are trapped and stabilized at the interface with the nanoparticle; at high nanoparticle ratio, the interface is composed of a lesser concentration of labile chain ends and a higher concentration of normal repeat units and the formation of hydro peroxides at the backbone is promoted, which introduce labile sites and destabilize the polymer chain.

4.3. The effects of temperature on emulsion stability Experiment 3

Four different solutions were prepared with 10g of NaCl, 0.2g of polymer (PMMA), 0.2g nanoparticle (ZnO) and labeled A3,B3,C3 and D3;

A3…100g Distilled water + 10g NaCl

B3…100g Distilled water + 10g NaCl + 0.2g polymer (PMMA)

C3…100g Distilled water + 10g NaCl + 0.2g nanoparticle (ZnO)

D3….100g Distilled water + 10g NaCl + 0.2g Polymer + 0.2g nanoparticle composite

The above four solutions were mixed in poly vial bottles with crude oil with water-to-oil ratios of 9:1, 7.5:2.5, 5:5, 2.5:7.5 and 1:9 for each solution. Emulsion stability curves were plotted against time at temperatures 25°C, 50°C and 70°C.

Note that in **Experiment 3** the concentration of polymer and nanoparticle were kept same at 0.2g each as in **Experiment 1**, but the brine concentration was increased to 10%.Thus this experiments will help us investigate the effects of increasing the concentration of the brine on the emulsion stability as temperature is increased.

4.3.1. The effects of temperature on emulsion stability of Solution A3 (10%wt Brine + crude oil)

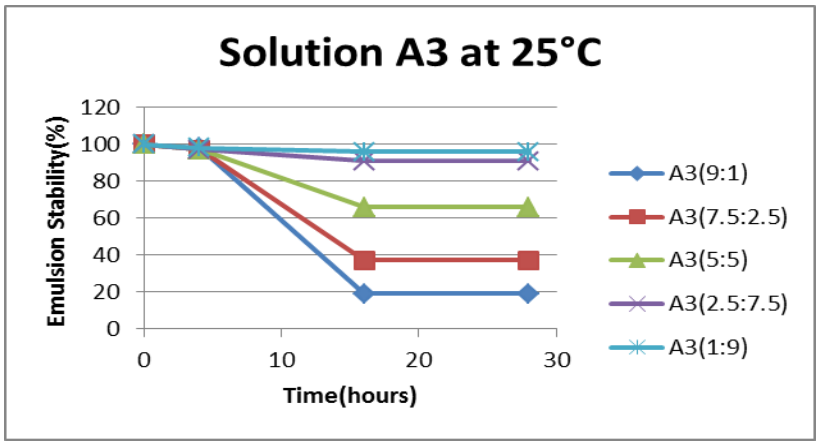


Figure 4.22: Stability of Solution A3 (W: O) at 25°C over 28hours

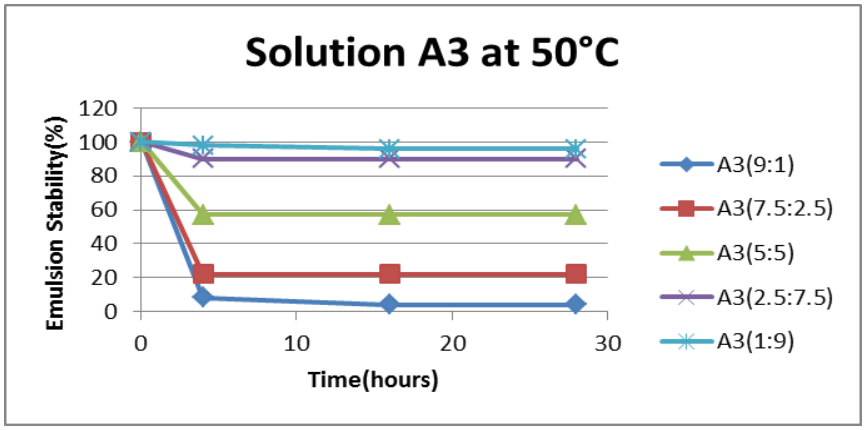


Figure 4.23: Stability of Solution A3 (W: O) at 50°C over 28hours

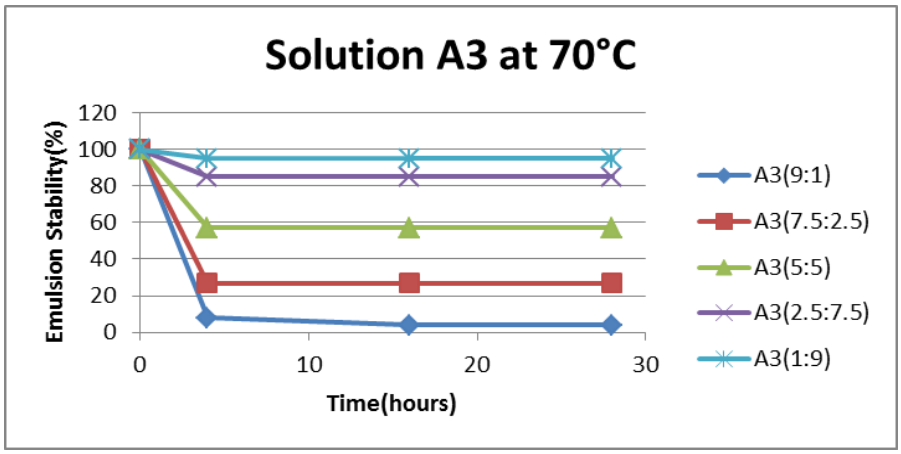


Figure 4.24: Stability of Solution A3 (W: O) at 70°C over 28hours

In solution A3 the brine concentration was increased to 10%. Sample with water-to-oil ratio of 5:5 had emulsion stability of 97% under 25°C in 4hrs (figure 4.22), this slightly reduced to 66% and remained constant over 28 hours. At 50°C, (figure 4.23), emulsion stability was lower at 57% after 4hours and remained constant for 28 hours. When temperatures were increased to 70°C (figure 4.24) the stability was 57% after 4hours and remained constant for 28 hours.

Sample with water-to-oil ratio 9:1 exhibited 98% emulsion stability under 25°C for 4 hours and remained constant at 19% for 28 hours. At 50°C, (figure 4.23), emulsion stability was lower at 8% after 4 hours and decreased to 4% remain constant for 28 hours. When temperatures were increased to 70°C (figure 4.24) the stability was 8 % after 4hours and decreased to 4% then remained constant for 28hours.

Sample with water-to-oil 7.5:2.5 had 97% emulsion stability under 25°C for 4 hours and remained constant at 37% for 28 hours. However, under a much higher temperature of 50°C the samples' emulsion stability was 22% in the first 4 hours and remained constant. Under 70°C the emulsion stability was 27% in 4hrs and then remained constant.

Samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions as phase separation occurred while samples 1:9, 2.5:7.5 showed more stable emulsions within 28hours for all temperatures 25°C,50°C,70°C.But a slight decrease in emulsion stability of 97% was observed for sample 2.5:7.5 at 25°C within 4 hours and later further decreased to 91% within 16hours and remained constant. At 50°C and 70°C emulsion stability was further reduced to 90% after 4hours and remained constant.

Sample 1:9 showed 96% emulsion stability at 25°C temperatures within 28hours,and further dropped to 95% at 50°C and 70°C after 16hours and remained constant for 28hours.When solutionA1 was used, Sample 1:9 showed full emulsion stability at 25°C(figure 4.1),which was not the case with solution A3.

The decrease in emulsion stability may be attributed to the increase in brine or salt concentration. Abouther Thalib [12], explained that emulsion stability decreases with increase in the salt concentration. High salinity increases the ionic force and reduces the thickness of the double layer and thus favors the agglomeration of drops. When the agglomeration of oil drops takes place, it leads to increase the separation of oil because increase of oil drop volume causes increases in the settling velocity according to Stock's Law.

4.3.2. The effects of temperature on emulsion stability of Solution B3 (10%wt Brine + 0.2gPMMA+ crude oil)

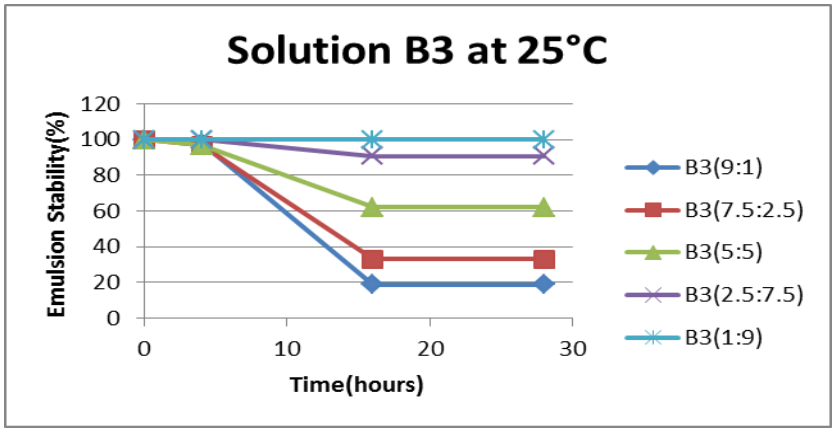


Figure 4.25: Stability of Solution B3 (W: O) at 25°C over 28hours

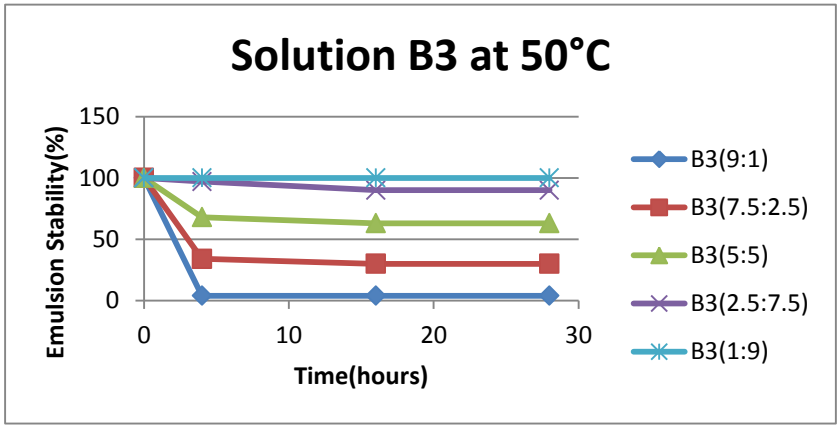


Figure 4.26: Stability of Solution B3 (W: O) at 50°C over 28hours

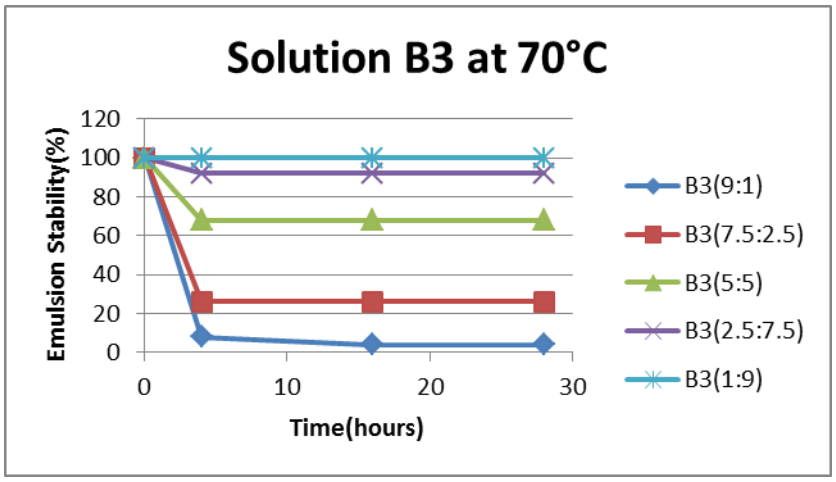


Figure 4.27: Stability of Solution B3 (W: O) at 70°C over 28hours

Solution B3 has same components as solutionB1,but the brine concentration in B1 was 2% while in B3 was 10%.From the graphs above, sample with water-to-oil ratio of 5:5 had emulsion stability of 97% under 25°C in 4hrs (figure 4.25) , this reduced to 62% and remained constant over 28 hours. At 50°C, (figure 4.26), emulsion stability was lower at 68% after 4hours and decreased to 63% after 16hours then remained constant for 28 hours. When temperatures were increased to 70°C (figure 4.27) the stability was 68% after 4hours and remained constant.

Sample with water-to-oil ratio 9:1 exhibited 98% emulsion stability under 25°C for 4 hours and remained constant at 19%. At 50°C, (figure 4.26), emulsion stability was lower at 4% after 4hours and remained constant for 28 hours. When temperatures were increased to 70°C (figure 4.27) the stability was 8% after 4hours and decreased to 4% after 16hours then remained constant.

Sample with water-to-oil 7.5:2.5 had 97% emulsion stability under 25°C for 4 hours and remained constant at 33% for 28 hours. However, under a much higher temperature of 50°C the samples' emulsion stability was 34% in the first 4 hours and decreased to 30% after 16hours then remain constant over 28 hours. Under 70°C the emulsion stability was 26% in 4hrs and remained constant over 28hours.

Samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions as phase separation occurred while samples 1:9, 2.5:7.5 showed more stable emulsions within 28hours for all temperatures 25°C, 50°C, 70°C. But a slight decrease in emulsion stability of 97% was observed for sample 2.5:7.5 at 25°C within 16 hours and remained constant. At 50°C emulsion stability was further reduced to 97% after 4hours and decreased to 90% in 16 hours and remained constant. When

temperature was further increased to 70°C emulsion stability was 92% after 4hours and remained constant.

The decrease in emulsion stability observed for sample 2.5:7.5 at 25°C, 50°C,70°C may be associated with the increase in salinity since brine concentration in B3 is higher than in B1. The stability of emulsions decreases with increase in the salinity concentration and at high concentration of salt, rapid aggregation occurs as a consequence of Van der Waals attractive, AL-qamshouai [47].

4.3.3. The effects of temperature on emulsion stability of Solution C3 (10%wt Brine + 0.2gZnO + crude oil)

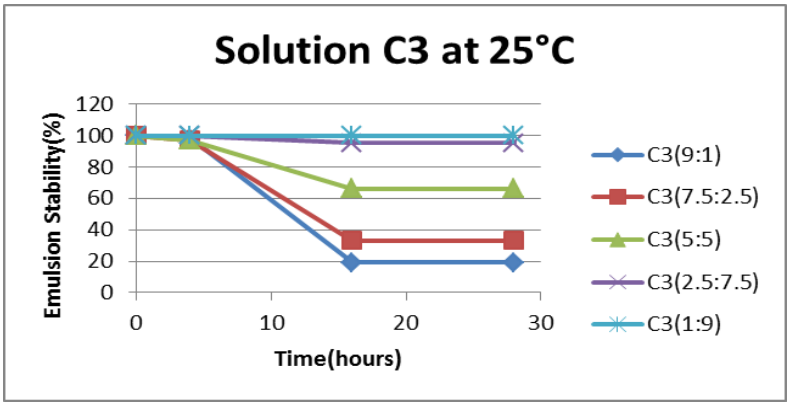


Figure 4.28: Stability of Solution C3 (W: O) at 25°C over 28hours

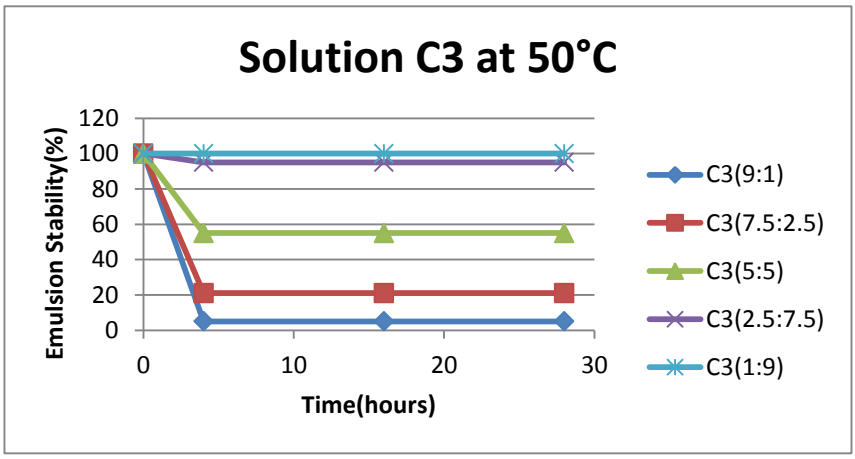


Figure 4.29: Stability of Solution C3 (W: O) at 50°C over 28hours

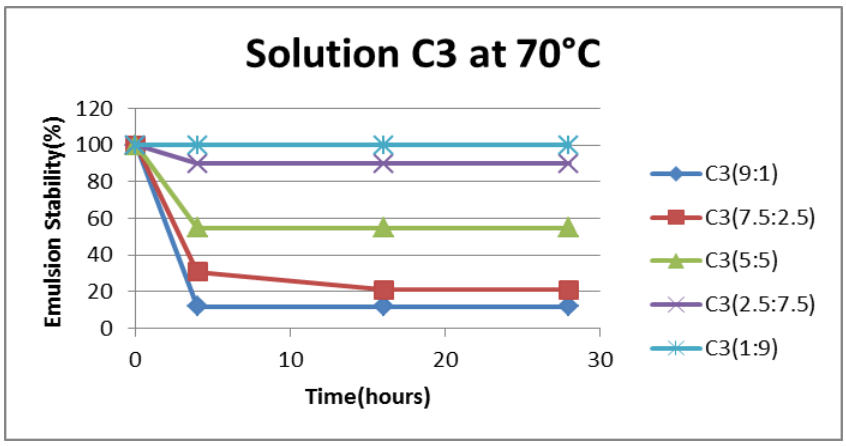


Figure 4.30: Stability of Solution C3 (W: O) at 70°C over 28hours

Solution C3 and solution C1 have same concentrations of ZnO nanoparticles, but the brine concentrations are 2% and 10% respectively. From the graphs above, ample with water-to-oil ratio of 5:5 had full emulsion stability of 97% under 25°C in 4hrs (figure 4.28) , this reduced to 66% and remained constant over 28 hours. At 50°C, (figure 4.29), emulsion stability was lower at 55% after 4hours and remained constant. When temperatures were increased to 70°C (figure 4.30) the stability was 55% after 4hours and then remained constant.

Sample with water-to-oil ratio 9:1 exhibited 100% emulsion stability under 25°C for 4 hours and remained constant at 23%. At 50°C, (figure 4.29), emulsion stability was lower at 5% after 4hours and remained constant. When temperatures were increased to 70°C (figure 4.30) the stability was 12% after 4hours and remained constant.

Sample with water-to-oil 7.5:2.5 had 100% emulsion stability under 25°C for 4 hours and remained constant at 44% for 28 hours. However, under a much higher temperature of 50°C the samples' emulsion stability was 21% in the first 4 hours and remains constant. Under 70°C the emulsion stability was 31% in 4hrs and decreased to 21% within 16hours and remained constant over 28hours.

Samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions as phase separation occurred while samples 1:9, 2.5:7.5 showed more stable emulsions within 28hours for all temperatures 25°C, 50°C, 70°C. But a slight decrease in emulsion stability of 95% was observed for sample 2.5:7.5 at 25°C.At 50°C emulsion stability was 95%.When temperature was further increased to 70°C emulsion stability was 90% .The decrease in emulsion stability observed for sample 2.5:7.5 at 25°C, 50°C, 70°C may be associated with the increase in salinity since brine concentration in C3 is higher than in C1

4.3.4. The effects of temperature on emulsion stability of Solution D3 (10%wt Brine + 0.2gZnO + 0.2gPMMA + crude oil)

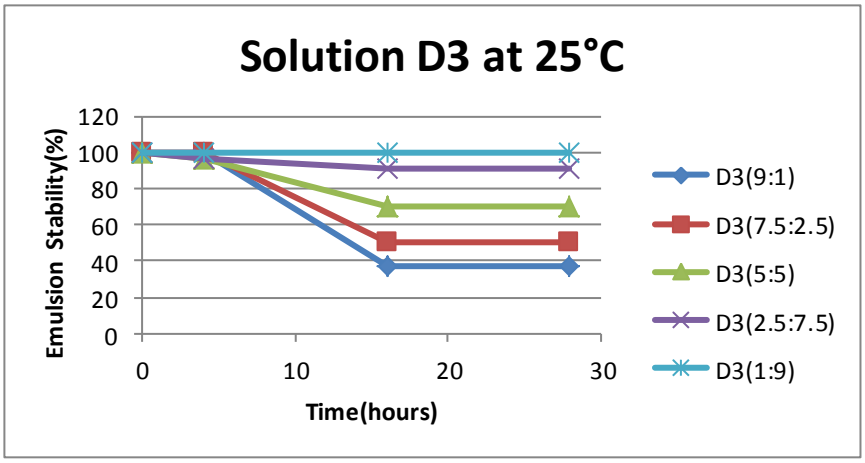


Figure 4.31: Stability of Solution D3 (W: O) at 25°C over 28hours

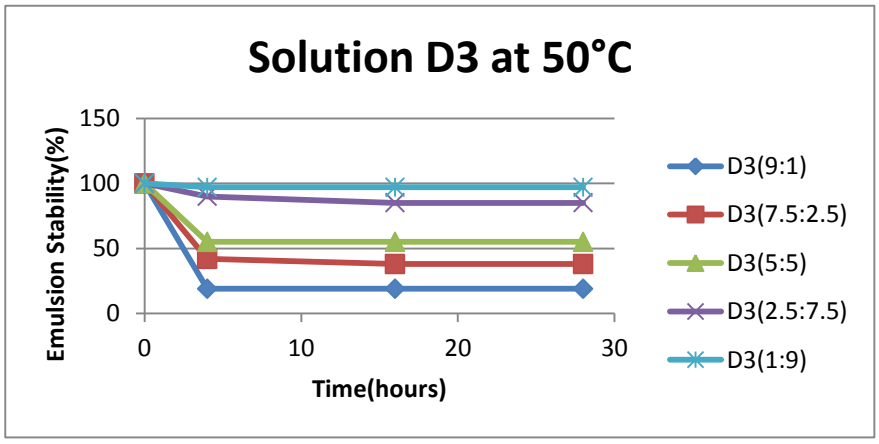


Figure 4.32: Stability of Solution D3 (W: O) at 50°C over 28hours

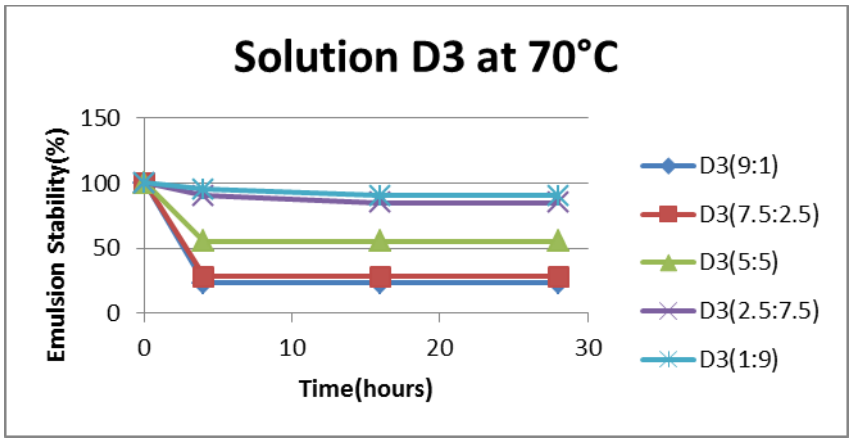


Figure 4.33: Stability of Solution D3 (W: O) at 70°C over 28hours

Sample with water-to-oil ratio of 5:5 had full emulsion stability of 97% under 25°C in 4hrs (figure 4.31) ,this reduced to 70% and remained constant over 28 hours. At 50°C, (figure 4.32), emulsion stability was lower at 55% after 4hours and remained constant for 28 hours. When temperatures were increased to 70°C (figure 4.33) the stability was 55% after 4hours and remained constant for 28 hours.

Sample with water-to-oil ratio 9:1 exhibited 100% emulsion stability under 25°C for 4 hours and remained constant at 37%. At 50°C, (figure 4.32), emulsion stability was lower at 19% after 4hours and remains constant. When temperatures were increased to 70°C (figure 4.33) the stability was 23% after 4hours and remained constant.

Sample with water-to-oil 7.5:2.5 had 100% emulsion stability under 25°C for 4 hours and remained constant at 50% for 28 hours. However, under a much higher temperature of 50°C the samples' emulsion stability was 42% in the first 4 hours and reduced to 38% within 16hours then remain constant over 28 hours. Under 70°C the emulsion stability was 28% in 4hrs and then remained constant over 28hours.

Samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions as phase separation occurred while samples 1:9, 2.5:7.5 showed more stable emulsions within 28hours for all temperatures. But a slight decrease in emulsion stability of 97% was observed for sample 2.5:7.5 at 25°C within 4 hours and later decreased to 91% and remained constant. At 50°C and 70°C emulsion stability was further reduced to 90% after 4hours and reduced to 85% within 16hours then remained constant.

Sample 1:9 showed 97% emulsion stability at 50°C within 4hours and remained constant. At 70°C emulsion stability was further reduced to 95% after 4hours and reduced to 90% within 16hours then remained constant. The decrease in emulsion stability observed for sample 1:9 at 50°C, 70°C may be associated with the increase in salinity since brine concentration in D3 is higher than in D1.

4.4. Effects of phase ratios on Emulsion Stability Before mixing

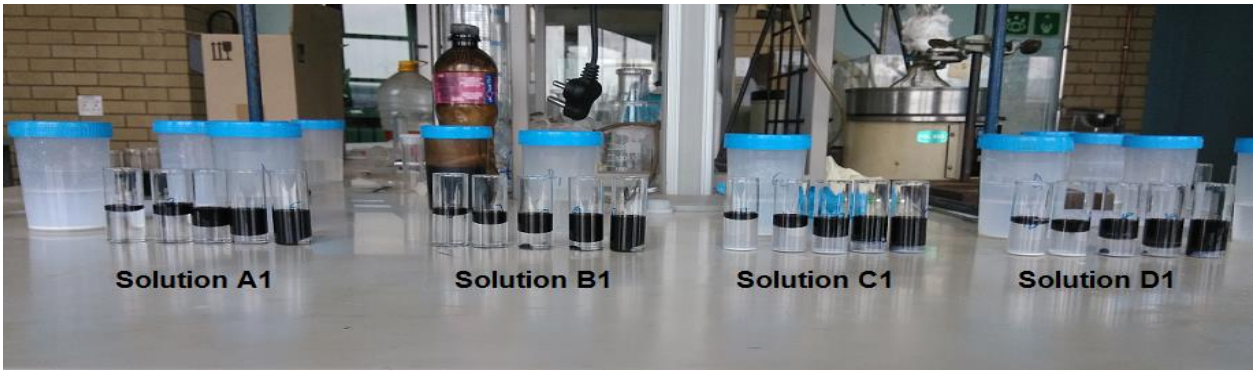


Figure 4.34: the effects on emulsion stability before mixing Experiment 1

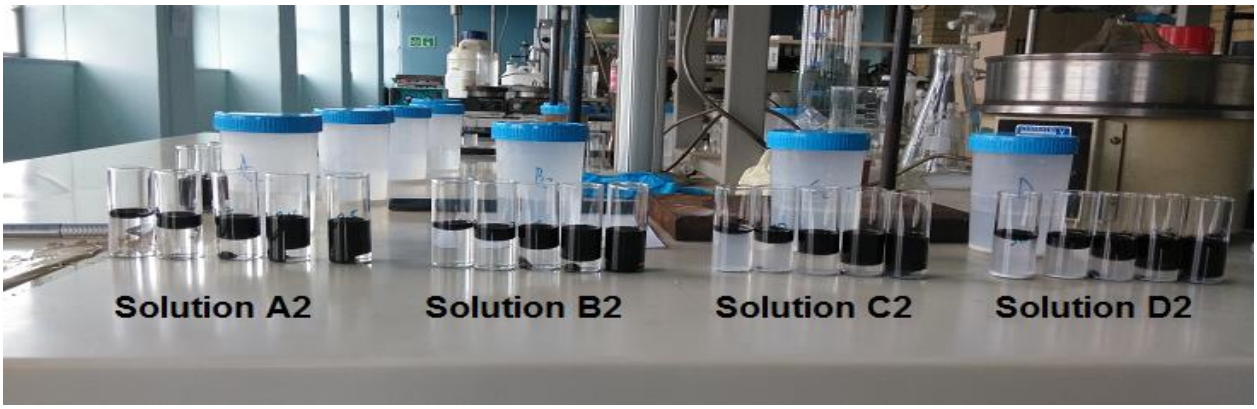


Figure 4.35: the effects on emulsion stability before mixing Experiment 2

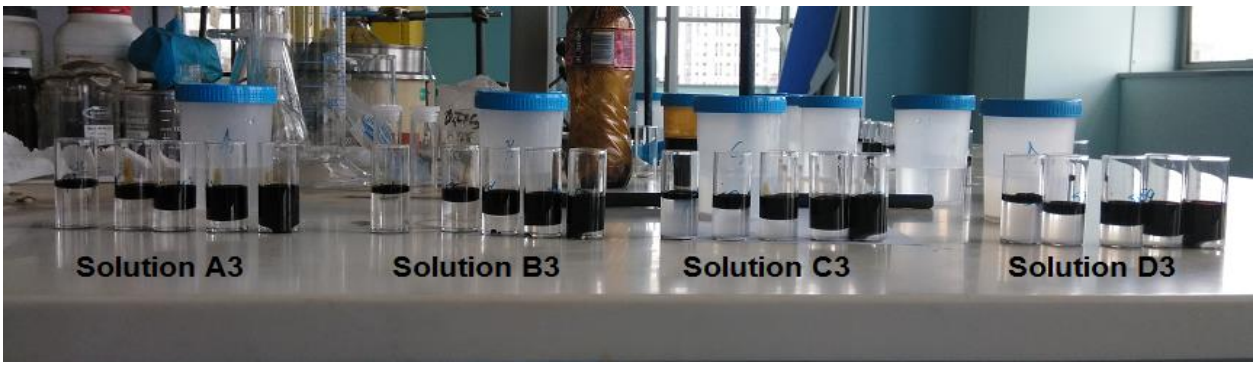


Figure 4.36: the effects on emulsion stability before mixing Experiment 3

4.5. Effects of phase ratios on Emulsion Stability after mixing

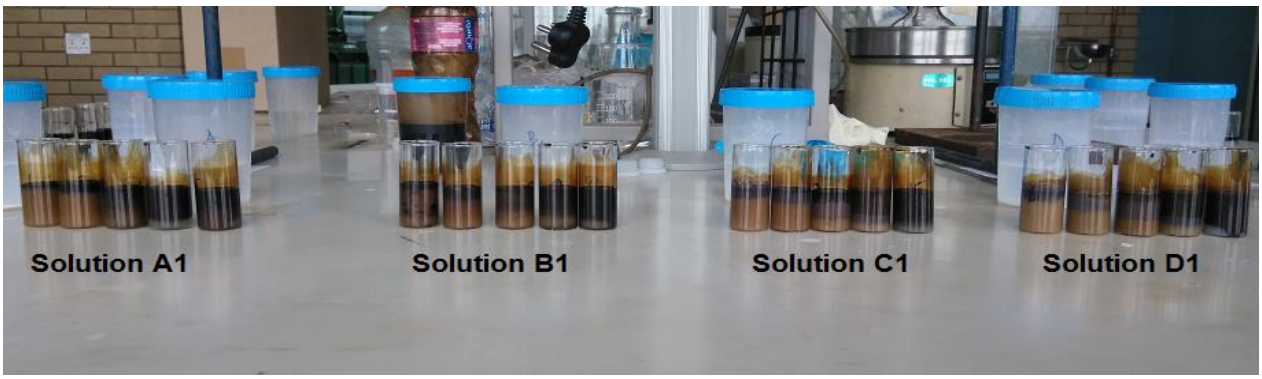


Figure 4.37: the effects on emulsion stability after mixing Experiment 1

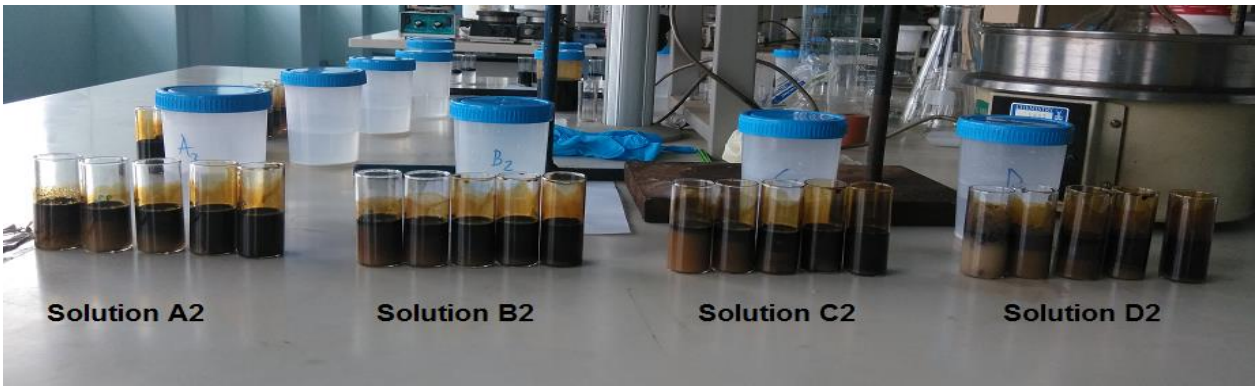


Figure 4.38: the effects on emulsion stability after mixing Experiment 2

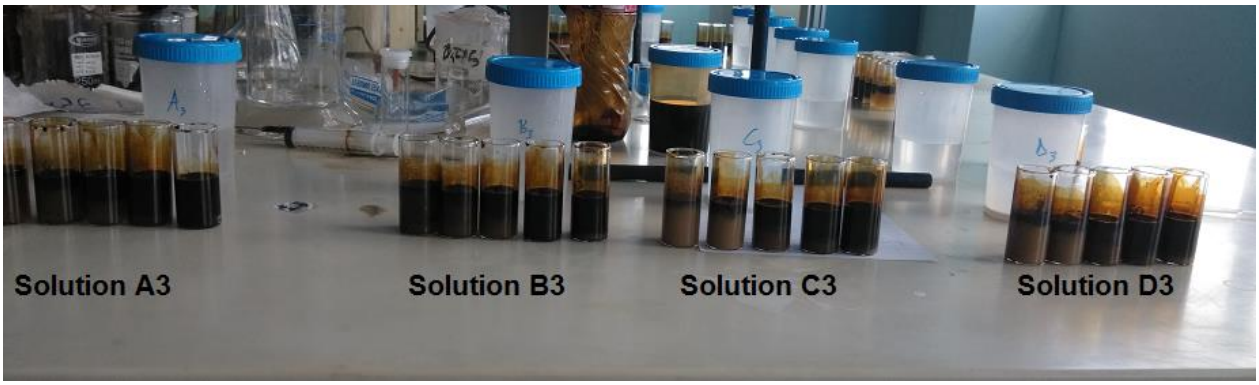


Figure 4.39: the effects on emulsion stability after mixing Experiment 3

4.6. Droplet size distribution of emulsions formed

The samples were analyzed using a microscope to determine which of the emulsions had tendency of being more stable with time .Thin samples of all solutions in experiment 1,experiment 2 and experiment 3 with w/o ratio 5:5 at 25^{o}C were placed under a microscope and pictures taken at 100µm .

4.6.1. The effects of different solutions on size and distribution of droplets Experiment 1

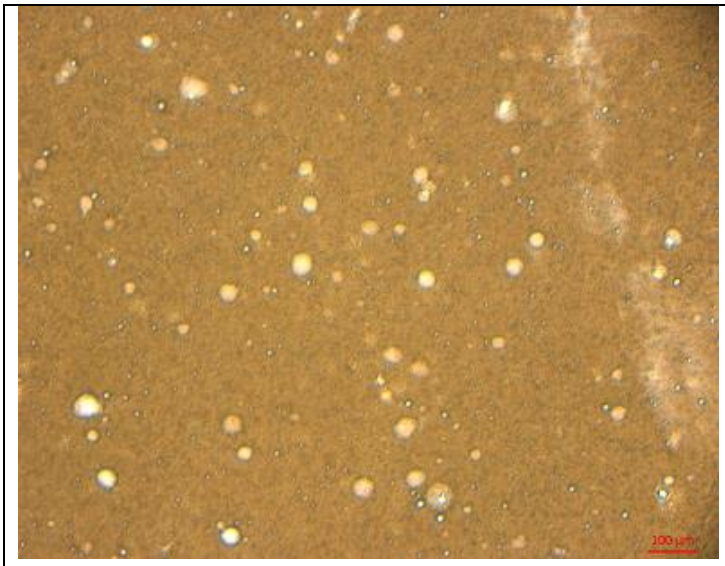
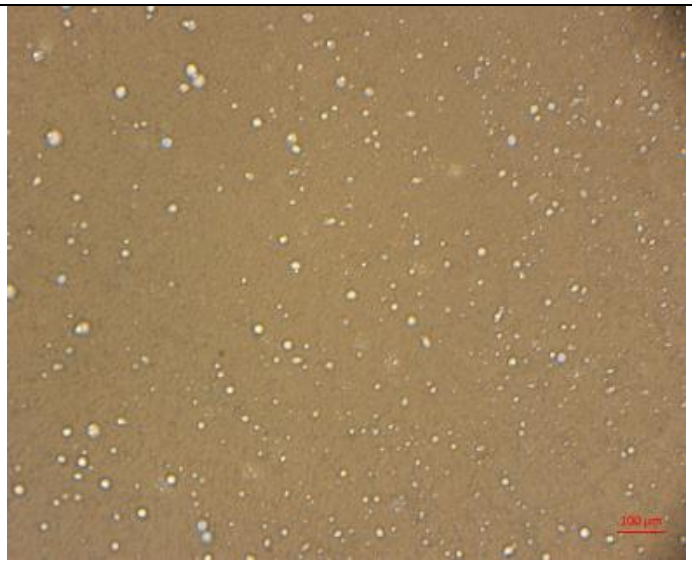
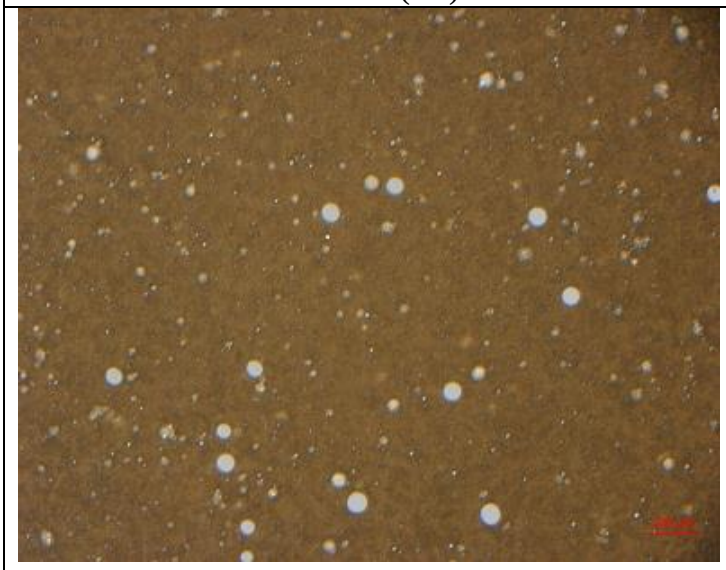
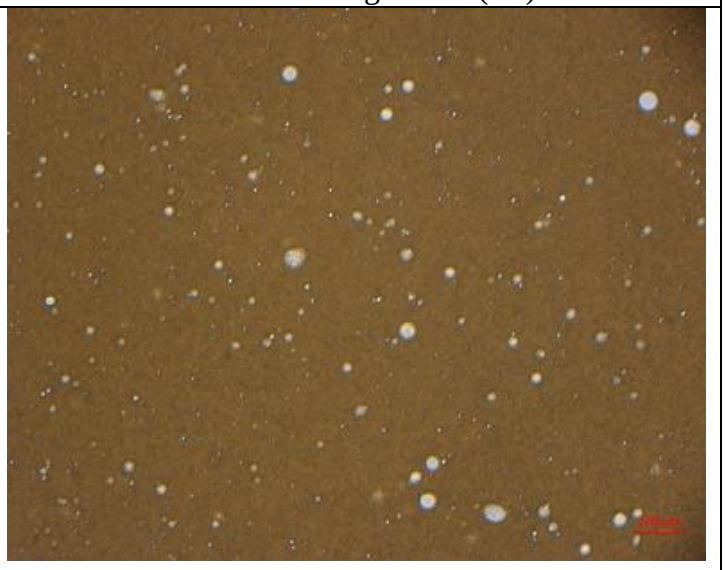
	
2%Brine (A1)	2%Brine + 0.2gPMMA(B1)
	
2%Brine + 0.2gZnO nanoparticles(C1)	2%Brine +0.2gZnO + 0.2gPMMA (D1)

Figure 4.40: Effects of Polymer and nanoparticles on size and distribution of droplets (W/O 5:5)

Emulsions that have smaller size droplets (≤10 micron) will generally be more stable. The droplet size distribution affects emulsion viscosity because it is higher when droplets are smaller Since emulsion stability depends on droplet size, droplet size distribution and formation of interfacial films (known to decrease ITF and as a result increases emulsion stability), figure 4.18 compares droplet sizes formed and its effect on emulsion stability for the polymer (PMMA), the nanoparticle (ZnO) and both polymer and nanoparticles.

When looking at the samples with water to ratio of 5:5, the droplets formed for B1 is much smaller in size compared to A1, C1 and D1. For all samples interfacial film did form, for this phase ratio, A1 is less stable than B1 because of the larger droplet sizes that formed. B1 is also more stable than C1 and D1 due to the large droplets present in them. But C1 and D1 are more stable than A1 because the droplets are more evenly distributed.

Emulsion droplets size is a key indicator of the emulsion quality and often determines the emulsion effectiveness in reducing permeability in high permeable zone to increase sweep efficiency. The size of droplet particles are less likely to be ensured as the oil concentration in the emulsion increases. Schramm [51], recommends size between 0.001 μm to 0.01 μm. However it is the size distribution which leads to a clear indication of stability. More stable emulsions may have a size distribution shifted to smaller sizes for a longer period of time. Droplets sizes may also be linked to emulsion viscosity. It's higher when droplet sizes are relatively homogeneous, implying when droplet size distribution is narrow rather than wide.

4.6.2. The effects of different solutions on size and distribution of droplets Experiment 2

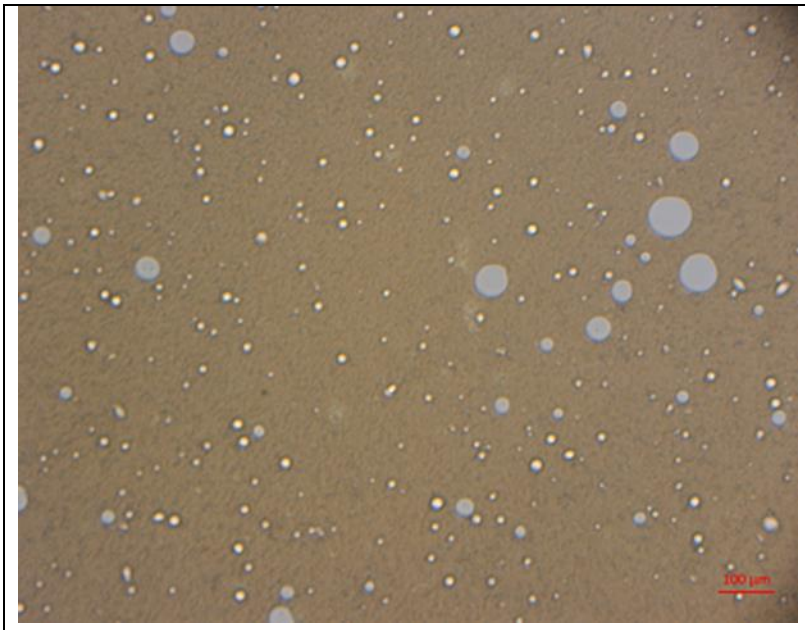
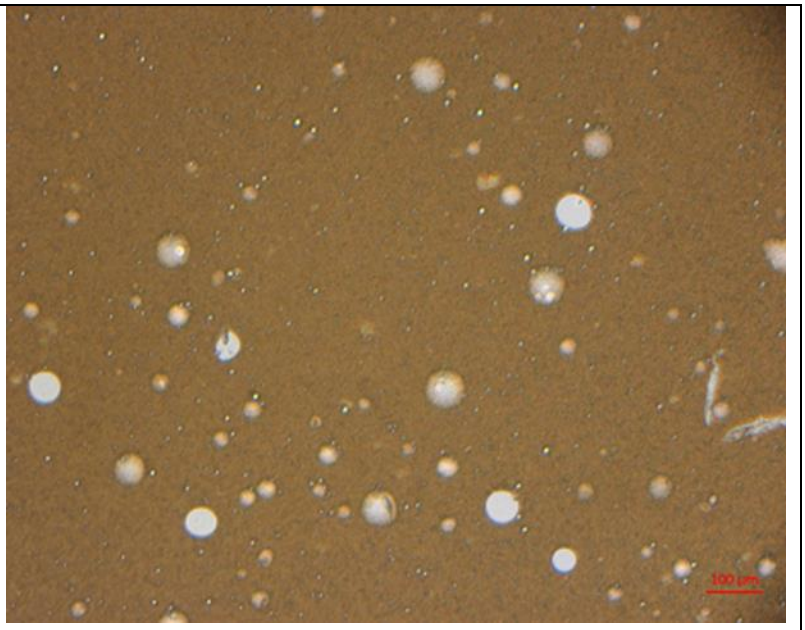
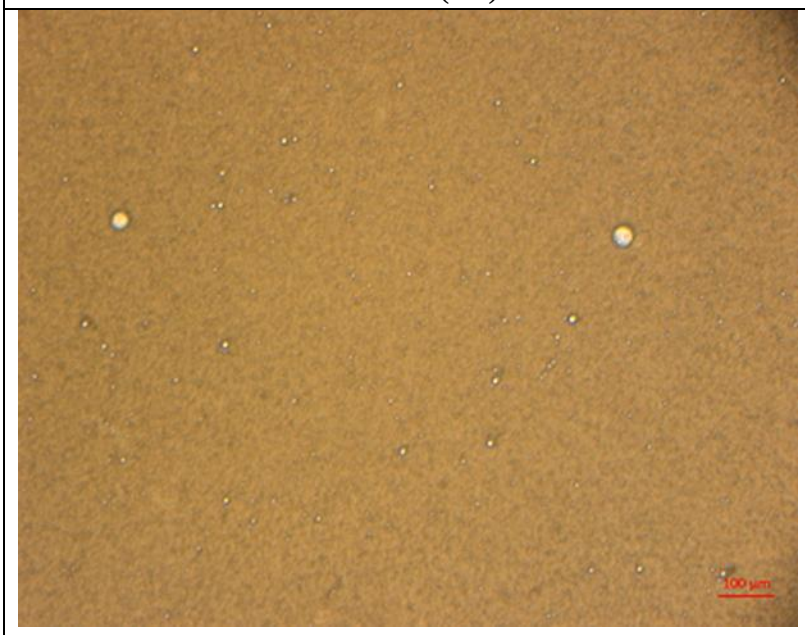
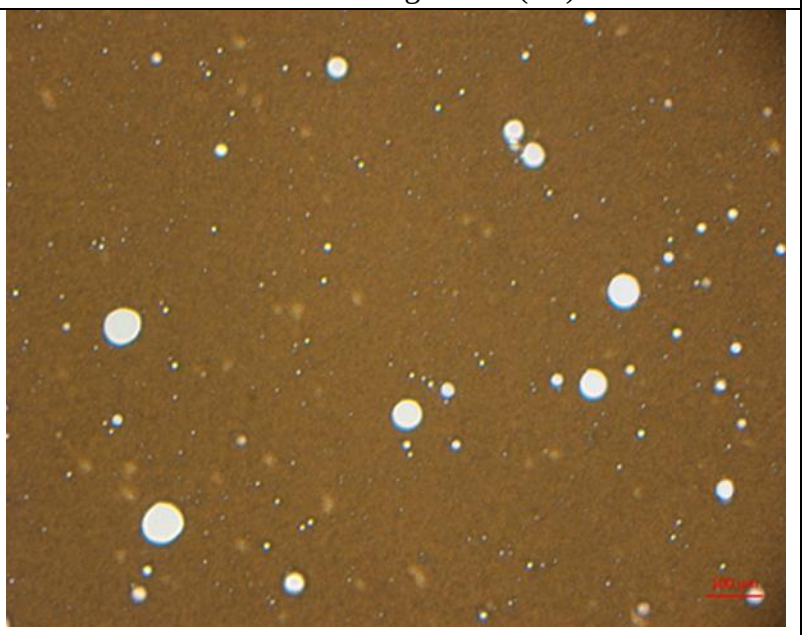
	
2%Brine (A2)	2%Brine + 0.5gPMMA(B2)
	
2%Brine + 0.g5ZnO nanoparticles(C2)	2%Brine +0.5gZnO + 0.5gPMMA (D2)

Figure 4.41: Effects of increasing Polymer and nanoparticles concentrations on size and distribution of droplets (W/O 5:5)

Emulsions that have smaller size droplets (≤10 micron) will generally be more stable. The droplet size distribution affects emulsion viscosity because it is higher when droplets are smaller Since emulsion stability depends on droplet size, droplet size distribution and formation of interfacial films (known to decrease ITF and as a result increases emulsion stability), figure 4.18 compares droplet sizes formed and its effect on emulsion stability for the polymer (PMMA) ,the nanoparticle(ZnO) and both polymer and nanoparticles.

When looking at the samples with water to ratio of 5:5, the droplets formed for C2 is much smaller in size compared to A2, B2 and D2. For all samples interfacial film did form, for this phase ratio, A2 is less stable than C2 because of the larger droplet sizes that formed. C2 is also more stable than B2 and D2 due to the large droplets present in them. But B2 and D2 are more stable than A2 because the droplets are more evenly distributed.

4.6.3. The effects of different solutions on size and distribution of droplets Experiment 3

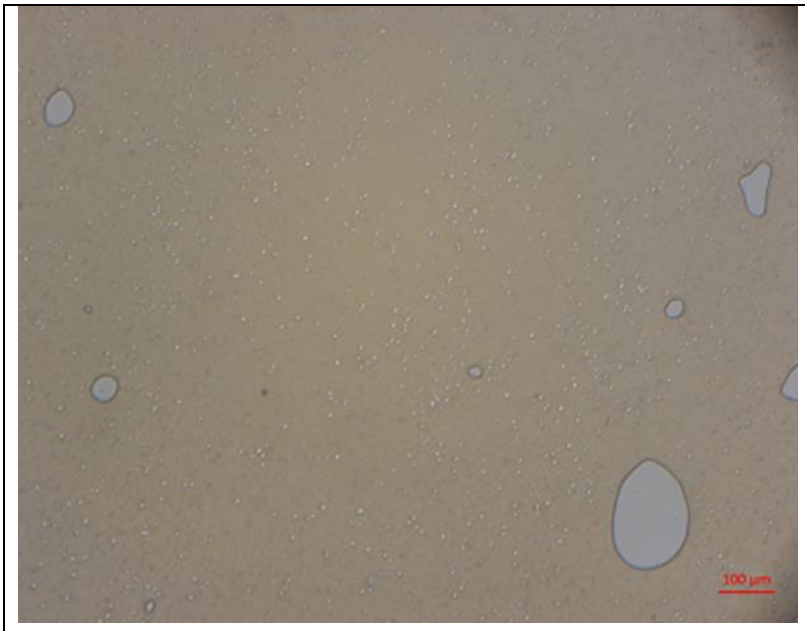
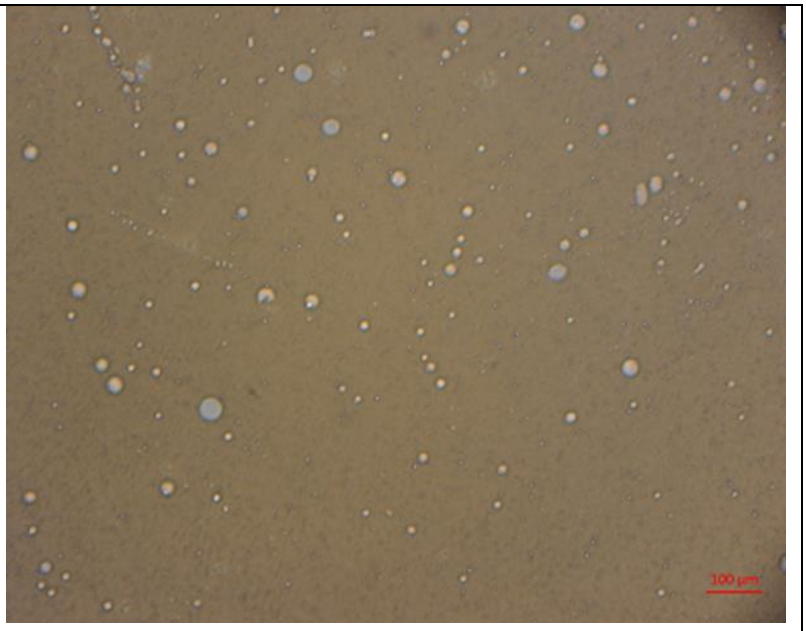
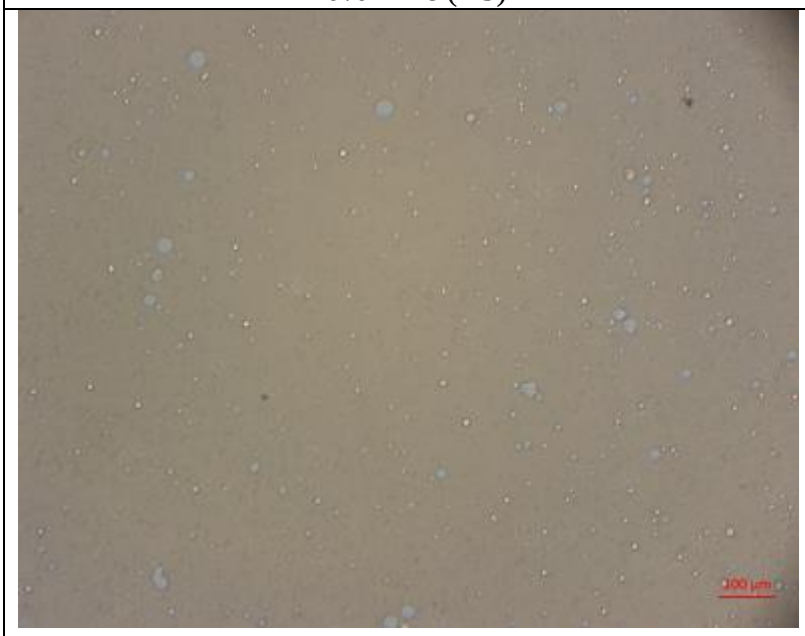
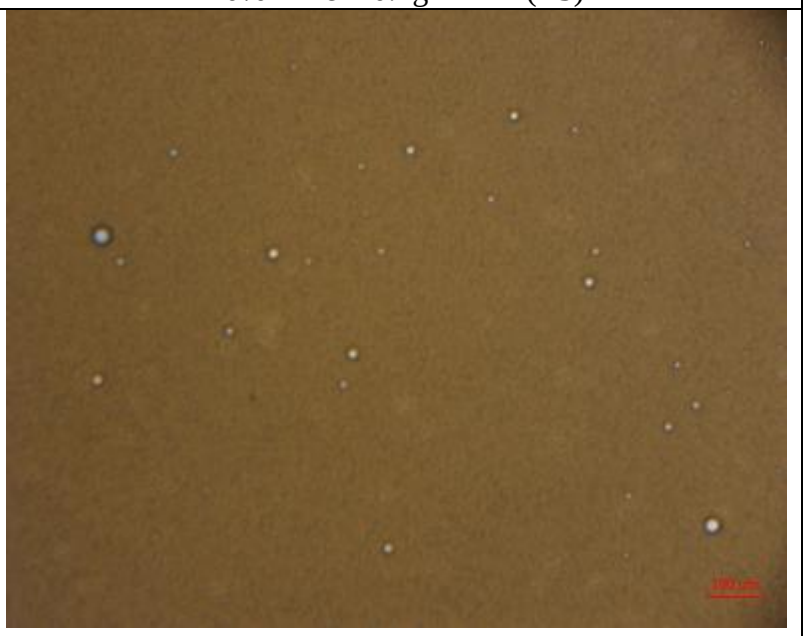
	
10%Brine (A3)	10%Brine + 0.2gPMMA(B3)
	
10%Brine + 0.2gZnO nanoparticles(C3)	10%Brine +0.2gZnO + 0.2gPMMA (D3)

Figure 4.42: Effects of Polymer and nanoparticles on size and distribution of droplets (W/O 5:5) when brine concentration is increased

Emulsions that have smaller size droplets (≤10 micron) will generally be more stable. The droplet size distribution affects emulsion viscosity because it is higher when droplets are smaller Since emulsion stability depends on droplet size, droplet size distribution and formation of interfacial films (known to decrease ITF and as a result increases emulsion stability), figure 4.18 compares droplet sizes formed and its effect on emulsion stability for the polymer (PMMA) ,the nanoparticle(ZnO) and both polymer and nanoparticles.

When looking at the samples with water to ratio of 5:5, the droplets formed for D3 is much smaller in size compared to A3, B3 and C3. For all samples interfacial film did form, for this phase ratio, A3 is less stable than D3 because of the larger droplet sizes that formed. D3 is also more stable than B3 and C3 due to the large droplets present in them. But B3 and C3 are more stable than A3 because the droplets are more evenly distributed.

4.7. Summary of Results

Table 4.1: Stability results of Experiment 1

W/O ratio	A1 (2%Brine)	B1 (0.2g PMMA)	C1 (0.2gZnO)	D1(0.2g PMMA + 0.2g ZnO)
9:1	Unstable at all temperatures 25°C,50°C,70°C	Unstable at All temperatures 25°C,50°C,70°C	Unstable at All temperatures 25°C,50°C,70°C	Unstable at All temperatures 25°C,50°C,70°C
7.5:2.5	Unstable at all temperatures 25°C,50°C,70°C	Unstable at All temperatures 25°C,50°C,70°C	Unstable at All temperatures 25°C,50°C,70°C	Unstable at All temperatures 25°C,50°C,70°C
5:5	Unstable at all temperatures 25°C,50°C,70°C	Unstable at All temperatures 25°C,50°C,70°C	Unstable at All temperatures 25°C,50°C,70°C	Unstable at All temperatures 25°C,50°C,70°C
2.5:7.5	Unstable at all temperatures 25°C,50°C,70°C	Stable at all temperatures 25°C,50°C,70°C	Stable at all temperatures 25°C,50°C,70°C	Stable at 25°C,but unstable at temperatures,50°C,70°C
1:9	Stable at temperatures 25°C,50°C and slightly unstable at 70°C	Stable at all temperatures 25°C,50°C,70°C	Stable at all temperatures 25°C,50°C,70°C	Stable at all temperatures 25°C,50°C,70°C

We can see that samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions as phase separation occurred while samples 1:9, 2.5:7.5 showed more stable emulsions within 28hours for all temperatures.

Samples 9:1, 7.5:2.5 and 5:5 had unstable emulsions within 4hours for solution A1,while unstable emulsions for B1,C1 and D1 were only observed after 16hours.

Sample 2.5:7.5 had stable emulsions for solutions B1, C1 and D1 at all temperatures, but had unstable emulsions for solution A1 at 25°C, 50°C, and 70°C.

Sample 1:9 had stable emulsions for solutions A1, B1, C1 and D1 at all temperatures, but showed slight unstable emulsions for solution A1 at 70°C.Thus at 70°C crude oil emulsions will be unstable in the absence of polymer or nanoparticles or both.

Table 4.2: Stability results of Experiment 2

W/O ratio	A2 (2%Brine)	B2 (0.5g PMMA)	C2 (0.5gZnO)	D2(0.5g PMMA + 0.5g ZnO)
9:1	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C
7.5:2.5	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C
5:5	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C
2.5:7.5	Unstable at all temperatures 25°C,50°C,70°C	Stable at 25°C but unstable at temperatures,50°C,70°C	Stable at all temperatures 25°C,50°C,70°C	Stable at temperatures 25°C and 50°C but unstable at 70°C
1:9	Stable at temperatures 25°C,50°C and slightly unstable at 70°C	Stable at temperatures 25°C,50°C and slightly unstable at 70°C	Stable at all temperatures 25°C,50°C,70°C	Stable at temperatures 25°C and 50°C but unstable at 70°C

We can see that samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions as phase separation occurred while samples 1:9, 2.5:7.5 showed more stable emulsions within 28hours for all temperatures.

Samples 9:1, 7.5:2.5 and 5:5 had unstable emulsions within 4hours for solution A2, while unstable emulsions for B2, C2 and D2 were only observed after 16hours.

Sample 2.5:7.5 had stable emulsions for solutions B2, C2 and D2 at all temperatures, but had unstable emulsions for solution A2 at 25°C, 50°C, and 70°C.

Sample 1:9 had stable emulsions for solutions A2,B2,C2 and D2 at all temperatures, but showed slight unstable emulsions for solutions A2 and B2 at 70°C. Thus at 70°C crude oil emulsions will be unstable in the presence of high concentration of polymer (due to PMMA polymer degradation) and the absence of nanoparticles or nanoparticles and low concentration of polymer.

Table 4.3: Stability results of Experiment 3

W/O ratio	A3 (10%Brine)	B3 (0.2g PMMA)	C3 (0.2gZnO)	D3(0.2g PMMA + 0.2g ZnO)
9:1	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C
7.5:2.5	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C
5:5	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C	Unstable at all temperatures 25°C,50°C,70°C
2.5:7.5	Unstable at all temperatures 25°C,50°C,70°C	Slightly unstable at all temperatures 25°C,50°C,70°C	Slightly unstable at all temperatures 25°C,50°C,70°C	Slightly unstable at all temperatures 25°C,50°C,70°C
1:9	Stable at temperatures 25°C,50°C and slightly unstable at 70°C	Stable at all temperatures 25°C,50°C,70°C	Stable at all temperatures 25°C,50°C,70°C	Stable at 25°C and slightly unstable at temperatures 50°C,70°C

We can see that samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions as phase separation occurred while samples 1:9, 2.5:7.5 showed more stable emulsions within 28hours for all temperatures.

Samples 9:1, 7.5:2.5 and 5:5 had unstable emulsions within 4hours for solution A3, while unstable emulsions for B3, C3 and D3 were only observed after 16hours.

Sample 2.5:7.5 had slightly unstable emulsions for solutions B3, C3 and D3 at all temperatures and had unstable emulsions for solution A1 at 25°C, 50°C, and 70°C.

Sample 1:9 had stable emulsions for solutions all solutions A3, B3, C3 and D3 at all temperatures. But slight unstable emulsions were observed for A3 at 70°C and D3 at temperatures 50°C, 70°C.

5. CONCLUSION AND RECOMMENDATION

Based on the results from the experimental work conducted it is evident that PMMA,ZnO nanoparticles and a combination of PMMA + ZnO nanoparticles can help improve emulsion stability. ZnO nanoparticles alone showed tendency of forming more stable emulsions compared to PMMA and combination of PMMA + ZnO nanoparticles.

When different water to oil ratios were used we observed that Samples 9:1, 7.5:2.5 and 5:5 formed unstable emulsions as phase separation occurred while samples 1:9, 2.5:7.5 showed more stable emulsions within 28hours for all temperatures. In general, samples containing only brine showed faster demulsification within 4hours at 25°C, while samples with PMMA or ZnO nanoparticles or PMMA + ZnO nanoparticles showed slower demulsification within 16hours.

Increasing the concentration of PMMA had a negative impact on the emulsion stability at higher temperature 50°C and 70°C compared to increasing the concentration of ZnO nanoparticles, which instead had a positive effect on emulsion stability. This may be attributed to the degradation of PMMA at high temperatures.

Increasing the concentration of brine had a negative impact on the emulsion stability at higher temperature 50°C and 70°C for the composite PMMA + ZnO nanoparticles compared to ZnO nanoparticles and PMMA alone in which the stability was slightly impacted.

Visual observation showed faster demulsification within an hour for 70°C and 2hours for 50°C.The greater the continuous phase the stable the emulsion. Sample 7.5:2.5 is water (aqueous) continuous with a thin oil rim at surface. This is expected since the concentration of

crude oil is far less than the aqueous. Once the samples became accustomed to the new temperature, the emulsion stability becomes stable and constant. A much more stable emulsion is seen with samples that have oil as the continuous phase compared to aqueous solution as the continuous phase. This is due to the viscosity of the crude oil itself.

We can thus conclude that the composite PMMA + ZnO nanoparticles will aid in improving emulsion stability with low concentration of brine and temperatures lower than 50°C.

Recommendations

We recommend that in future nuclear magnetic resonance (NMR) spectroscopy be used to conduct the droplet size distribution analysis. Droplet size distribution information is required to back-up the observation made from microscopic analysis for the droplets formed. Also, a pH analysis of samples is required to investigate the effects of pH at different temperatures, oil/water ratios and material concentrations on emulsion stability. Additional experiments should also be conducted with different nanoparticle sizes and much higher concentrations of polymer, nanoparticles and brine in other to investigate their effects on the emulsion stability. Furthermore investigation is required to look into the demulsification processes that are economical to separate the brine solution from the crude oil.

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