Resolution of Water-In-Crude Oil Emulsions Using Ionic Liquids

by

Luis Faustino Edu Angue

13973

Dissertation submitted in partial fulfilment of

the requirement for the

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CERTIFICATION OF APPROVAL

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January 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is mine except where specified in references and acknowledgements, and that the original work contained herein not been undertaken or done by unspecified sources or persons.

LUIS FAUSTINO EDU ANGUE

ACKNOWLEDGEMENTS

Foremost, I would like to thank the Almighty God for guiding and guarding me hitherto. The strength and will to carry on this far comes only from God.

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Not forgetting my university, Universiti Teknologi PETRONAS (UTP) for having created a citadel of learning to churn out well rounded students. I do appreciate the provided platform, facilities and funds to make this project a success.

ABSTRACT

The most common type of emulsion found in oil field is water-in-crude oil. Water-in-crude oil emulsions are unstable colloidal dispersions with water as the dispersed phase and oil as the continuous phase. It occurs in almost every phase of the oil field from the sand face to the surface. About 80% of crude oil produced in the world is recovered in emulsified form. Emulsions constitute numerous problems in the oil and gas industry ranging from flow problems due to high viscosity to increase in cost in the use of demulsifier. In resolving emulsions, heat, chemicals or a combination of both methods can be used. Demulsifiers destabilizes the emulsifier film in the emulsion and thus rupture the film to resolve the emulsion. While heat decreases the viscosity of the emulsion by increasing the entropy of the system, excites and ruptures the film.

Research has shown that the use of chemical and heat to resolve emulsion is effective. In this study, synthetic emulsions in water-oil ratios of 20/80, 40/60 and 50/50 were formed in the laboratory. Emulsions were separated into 10 mL measuring cylinders, and then 0.5 mL and 1.5 mL of ionic liquids (ILs) as demulsifier were added before exposing it to heat from a heating oven. Two cases were experimented; the use of heat only, and the combination of heat and ILs.

The results obtained showed the effectiveness in the combination of heat and ionic liquids in emulsion resolution. 75% water recovered for the case of 20/80 water-oil ratio at the heat exposure for 60 minutes. In the 40/60 water-oil ratio, 85% water was recovered. 100% water was recovered for the case of 50/50 water-oil ratio.

In resolving tight water-oil emulsions, the synergy effect of heat and ionic liquids is required for effectively resolve the emulsions. The findings showed an optimal exposure time to which the emulsion should be heated, after which it is a waste of energy to continue heating. It is recommended that this procedure be prepared for varying amount of demulsifier. Furthermore, various water-oil ratios such as 10/90, 30/70, and 45/65 should be experimented using this method to understand and analyze the effect on water-oil ratio in resolving emulsions using a combination of heat and ionic liquids as demulsifiers.

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ABBREVIATIONS AND NOMENCLATURE

ILs = Ionic Liquids

HO = Heat Oven

Vw = Settling velocity of water

ρw = Density of emulsified water

ρo = Density of oil

G = Gravitational constant

D^2 = Droplet diameter

μ_o = Viscosity of continuous phase (oil)

W/O = water/oil ratio

CHAPTER 1

INTRODUCTION

1.1. Background

The crude oil is normally emulsified with the water which decreases the quality and quantity of the crude oil in the process. Crude oil is composed of mostly hydrocarbons, both aliphatic and aromatic, as well as some naturally occurring surfactants (such as asphaltenes and resins) have been identified as largely responsible for stability of emulsions. An emulsion may be tight (difficult to break) or loose (easy to break), whether an emulsion is tight or loose depends on a number of factors such as the percentages of oil and water found in the emulsion, the amount of agitation, the types and amounts of emulsifying agents present, as well as the properties of oil and water (Ali and Algam, 2000) (Abdurahaman and Rosli, 2006).

Emulsions are thermodynamically unstable colloidal dispersions containing at least one immiscible fluid. In simplified terms, emulsion is the result of mixing two or more liquids with at least one of it being immiscible. In the process of this mixing or agitation, small droplets form due to the immiscibility of the liquids. Emulsions usually have two phases, the dispersed or internal phase and the continuous or external phase. The continuous phase suspends or carries the dispersed phase. The dispersed phase is contained in small droplets formed and this is carried or suspended by the continuous phase. Emulsions are found in various industries such as oil and gas, food and chemical industries. In the food industry for instance, emulsions are induced to form gelatinous foods. In the oil and gas industry which is the focus of this research, emulsions are formed naturally and not induced.

Generally, there are two common types of emulsions are found in the oil and gas industry, water-in-oil emulsions and oil-in-water emulsions. The first type has oil as the continuous phase and water as the dispersed phase while the second type has oil as the dispersed phase and water as the continuous phase. For the purpose of this research, water-in-oil emulsion is the focus because it is the most abundant type of emulsion found in the oil and gas industry.

Resolution of emulsions can be achieved by various means which includes but not limited to the use of heat, chemical and electricity. In the course of this research, the effective means of combining heat and chemical to resolve emulsions is being looked into.

1.2. Problem Statement

In the oil and gas industry emulsions constitute a major problem. Emulsion is almost inevitable in the industry. About two thirds of produced oil from new fields has water-in-oil emulsion problems. Emulsion can imperil production operations in two general ways: cause oil to be unsalable and slow the flow of production fluids. Emulsions are characteristically very viscous, making them thicker than base production fluids. This can cause the production flow to slow excessively because the fluid is so thick it cannot flow properly, and cause corrosion of production and pipelines infrastructure, subsequently the decaying of petroleum production. Also, emulsions causes increase in use of demulsifier; this in turns contributes to additional cost of production. Besides, emulsion reduces the quality of oil produced and sometimes makes it unsalable or sale it at a very low market price, thus the emulsion has to be resolved so as to enable the produced oil meet the international standard of contained basic sediment and water.

1.3. Project Objectives

At the completion of this research the following objectives are expected to be met:

1. Investigate and evaluate the kinetics behind the reaction involved in using ionic liquids and the mechanism of heat effects on emulsion resolution.
2. Evaluate the performance of ionic liquids in resolving water-in-crude emulsion.

1.4 Scope of Study

The scope of this study covers problem identification, intensive literature review of past works done that is related to the project, planning a comprehensive experimental design that will aid in solving the problem at hand and also meeting the research objectives. Experimenting and reporting the combined effect of the use of ionic liquids and heat on water-in-crude oil emulsion is included in the scope of study. That is, using a demulsifier, in this case ionic liquids (ILs) at varying amount or dosage together with heat from a heating oven which temperature is set at 70º C, then observing and reporting the corresponding effect of varying these parameters. The water-oil ratios were investigated are 20/80 (water/oil), 40/60 (water/oil) and 50/50 (water/oil); where 20/80 (water/oil) was for tight emulsions and 50/50 for weak emulsions. Ionic liquids (ILs) used for this experiment are HMIM NTF2, HMIM DOSS, and EMIM BF4 at different dosages (0.5 mL and 1.5 mL per emulsion ratios).

CHAPTER 2

LITERATURE REVIEW

2.1. Definition of emulsions

An emulsion is described as a type of colloidal dispersion of a liquid within another with which it exhibits limited miscibility and dispersed in the other in the form of small or tiny droplets. The relative stability referred to above is conferred by the presence of agents at the interfaces able to delay the spontaneous tendency of the liquids to separate. Such agents are most commonly molecules with polar and non-polar chemical groups in their structure – usually referred to as a surfactant or emulsify agents – or finely divided solids. These droplets are measured in micro meters (µm) and the size of the droplets range from 0.1 µm for tight emulsions to 100 µm for loose emulsions. Emulsions are thermodynamically unstable and also exhibit kinetic stability as it becomes stable overtime. Emulsions have two phases, the dispersed or internal phase and the continuous or external phase. The dispersed phase is the phase in droplets while the continuous phase is the phase that suspends the droplets. Emulsions are majorly of two types which includes water-in-oil and oil-in-water emulsions.

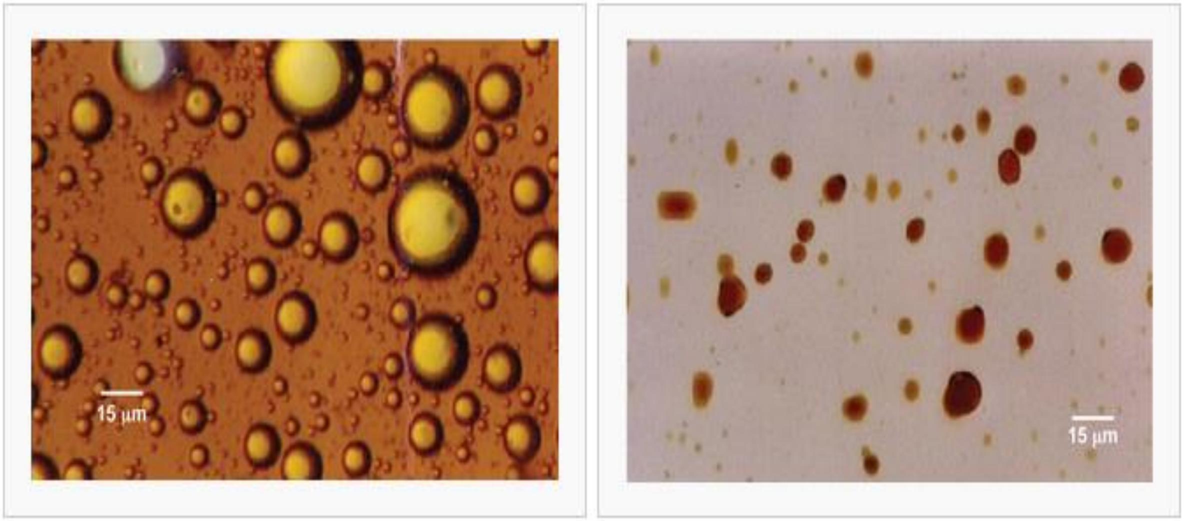

Figure 2.1: Schematics showing two types of emulsions (PetroWiki)

Describing these types in terms of phases, water-in-oil emulsions have water as its dispersed phase and oil as the continuous phase. On the other hand, oil-in-water emulsions have oil as its dispersed phase and water as the continuous phase (Emuchay et al, 2013; Merv & Ben, 2008; Hanapi et. al, 2006).

2.2. Formation process

The formation of emulsions in oil wells is due to presence of natural surfactants, such as asphaltenes and resins. These molecules strongly stabilize the water/oil interface and prevent coalescence of water droplets. The emulsifiers create a film or layer which encapsulates the dispersed phase. This film inhibits the coalescence of the dispersed phase thus keeps the emulsion stable. This film usually has viscoelastic properties which influences its stability. For instance, the more elastic the film, the more stable the emulsion as the elasticity is able to shield the dispersed phase from external interferences.

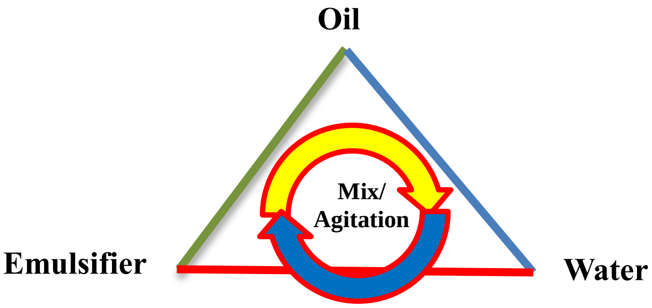

Figure 2.2: Emulsion Formation Triangle

In the oil and gas industry, these conditions exist in almost every phase, from the reservoir to surface facilities. Oil is produced alongside with water as they both coexist in the reservoir, also in the course of production, there is a mixture of these fluids and oil and water being immiscible, with natural emulsifiers such as asphaltenes, waxes and resins present in oil, the formation of emulsion is almost inevitable. Asphaltene as the primary emulsifier, with the help of resins which keep the asphaltene in solution where it functions best, form rigid and elastic films which encloses the dispersed phase (Dosunmu et al, 2012; Darrell et al, 2010; Merv & Ben, 2008, 2011).

2.3. Resolution methods

Methods introduced for separation of water-in-crude oil emulsions are mechanical or physical, electrical and chemical or a combination of both methods is used. Physical method includes the use of agitation (use of centrifugal machine or enhanced gravity), settling time, electricity and heat. Heat or the use of temperature influence destabilizes the emulsion by increasing the entropy of the system. Due to the increase in temperature, the system becomes more disordered and this affects the interfacial film that was formed by the emulsifier, this effect causes the emulsion to be resolved. Although temperature helps break emulsions, it should be noted that a severe increase in temperature leads to loss of light components in the crude oil and also some emulsions get more stable as temperature significantly increases, this gives rise to the use of chemical methods.

2.3.1 Chemical resolution of emulsions

Chemical method includes the use of chemicals called demulsifiers which attacks the film or layer that encloses the dispersed phase, by so doing it breaks the film and allows for coalescence. The use of demulsifiers is effective in breaking emulsion (Jones et. Al, 1978; Paul, 1965; Darrell et al, 2010; Roslan & Niven, 1993, Hanapi et.al, 2006).

The Figure 2.3 shown below illustrates the process of emulsion breakdown. Sedimentation is when the heavier liquid settles down due to the density differences. Creaming occurs as a direct opposite of sedimentation, forming a concentration gradient of droplets. Coalescence is when the droplets join together to from a bigger droplet or unit, thus reducing the total surface area.

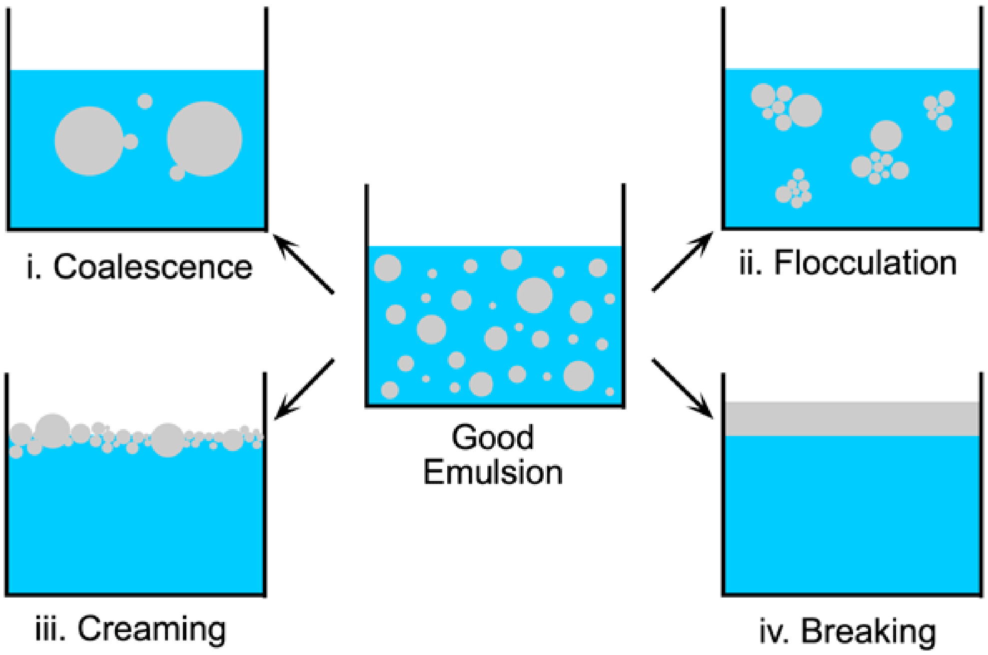

Figure 2.3: Process of emulsion breakdown (PetroWiki)

Heat from heating oven resolves water-in- crude oil emulsions by acting in two ways. Firstly, it increases temperature which in turn decreases viscosity of the continuous phase being oil. By so doing, the causes the film encapsulating the dispersed phase being oil to be disturbed and eventually ruptures. After the rupturing, coalescence begins. Secondly, it rearranges the electrical charge distribution of water molecules as it rotates, therefore moving the ions around the droplet. Water being dipolar, allows selective heating by these heats. Due to this, the problem of lighter components in oil evaporating because of excessive heating is reduced significantly as the heat affects only the dipolar water molecules (Vega et al, 2002; Binner et al, 2013; Martínez-Palou et al, 2013).

For the past two decades ionic liquids have been widely studied because of their unique properties, as solvents, ecological alternatives, co-solvents, and catalyst in organic synthesis and chemical industry. Ionic liquids have very low vapor pressure, thermal stability and non-flammable (Diego, Guzman, Lucero et al., 2014).

2.3.2 Heat resolution of emulsions

The use of heat destabilizes emulsion by increasing the entropy of the system. Due to the increase in heat, the system becomes more disordered and this affects the interfacial film that was formed by the emulsifier, this effect causes the emulsion to be resolved. Although heat help break emulsions significant increase in heat leads to loss of light components in the crude oil. Also, some emulsions get more stable as temperature significantly increases (Paul, 1965; Martinez et. al., 2013).

Heat from heat can also be applied in resolving emulsions. Heat heating uses radiation to perform bulk heating of emulsions. Heat heating resolves water-in-crude oil emulsions by acting in two ways. Firstly, it increases temperature which in turn decreases viscosity of emulsions. By so doing, it causes the film encapsulating the dispersed phase to be distributed and eventually ruptures. After the rupturing, coalescence begins. From Stoke's law, for water-in-oil emulsions where oil is the continuous phase, the settling velocity of water droplets through oil is given by the equation below:

$$\boldsymbol{Vw = \frac{(\rho w - \rho o) * g * D^2}{18 * \mu o}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.1)$$

where:

Vw = Settling velocity of water

ρw = Density of emulsified water

ρo = Density of oil

g = Gravitational constant

D^2 = Droplet diameter

μ_o = Viscosity of continuous phase (oil)

Equation 2.1 shows that the settling velocity is directly proportional to the density difference, gravity and square of droplet diameter, and inversely proportional to the viscosity of the continuous phase, in this case being oil.

By heating, viscosity decreases rapidly in comparison to the density difference, this leads to the separation of the dispersed phase (Abdurahaman & Rosli, 2006).

Secondly, it causes the coagulation of the dispersed droplets. Due to increase in temperature and decrease in viscosity, this enhances coagulation of the water (dispersed) phase. This coagulation results in larger diameter particles, this increase in diameter lead to rapid separation. This is proven by Stoke’s law (Equation 2.1) where the settling velocity is directly proportional to the square of the droplet diameter (Abdurahaman & Rosli, 2006; Anisa et al., 2011).

Heat energy causes the bulk and direct heating of the dispersed (water) phase through interaction with the molecules caused by the electromagnetic field that the heat creates. Also, heat rearranges the electrical charge distribution of water molecules as it rotates, therefore moving the ions around the droplet. Water being dipolar, allows selective heating by these heats. Due to this, the problem of lighter components in oil evaporating because of excessive heating is reduced significantly as the heat affects only the dipolar water molecules (Vega et al., 2002; Binner et al., 2013; Martinez-Palou et al., 2013).

CHAPTER 3

METHODOLOGY

3.1. Introduction

Persistent with the highlighted objectives in this study, this research adopts an experimental research design. To meet these objectives, a number of materials were used. Also, experimental and analytic procedures were adopted from the reviewed literature.

These materials and procedures are discussed in details in the subsequence sections of this chapter.

3.2. Material and Equipment

All materials (except for the ionic liquids which was obtained from Chemical Engineering department) used in the course of this research were obtained from the core analysis laboratory and geochemical laboratory of Petroleum Engineering department of Universiti Teknologi PETRONAS. The list of materials and equipment used is given below:

Equipment:

- Stop Watch
- 10 mL graduated measuring cylinder
- 100 mL graduated measuring cylinder
- 1000 mL graduated measuring cylinder

Figure 3.1: Beaker containing crude

Figure 3.2: Constant Speed

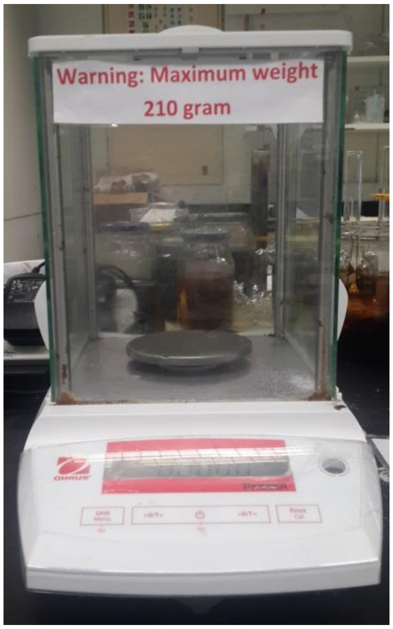

Figure 3.3: Digital Scale

Figure 3.4: Heating Oven

Figure 3.5: Magnetic Stirrer

Materials:

- Crude oil sample
- Distilled water
- Sodium chloride (N_aCl)
- Demulsifier (Ionic Liquids - ILs)
  - HMIM NTF2
  - HMIM DOSS
  - BMIM BF4

3.3. Experimental Procedure

This section discusses the procedures adopted to carry out the experiment. The method of preparing emulsions as well as the demulsification process is discussed.

3.3.1 Emulsion Preparation

In preparing the synthetic emulsion, synthetic brine was used together with crude oil sample. The synthetic brine was made by dissolving sodium chloride (N_aCl) in distilled water. This percentage salinity was adopted from the Tabu oilfield in Malaysia (Hampi et al., 2006). The salinity equation used was:

$$Y = 8.3566x - 0.3582 \qquad (3.1)$$

where Y = Salinity (%w/w); % per thousand

X = N_aCl concentration (g/100 mL)

Adopting salinity of 9.4% as used by, the equation becomes:

$9.4 = 8.3566X - 0.3582$, this yields $X = 1.1672$ g.

Therefore, 5.0g of Sodium chloride was dissolved in 20 mL of distilled water to form a synthetic brine of 9.4% salinity. This percentage salinity was adopted from the Tabu oilfield in Malaysia (Hampi et al., 2006).

Figure 3.6 shows after the synthetic brine was made, the synthetic emulsion was made by mixing the brine with crude oil in its appropriate proportions using a constant speed mixer at 1800 rpm for 5 minutes.

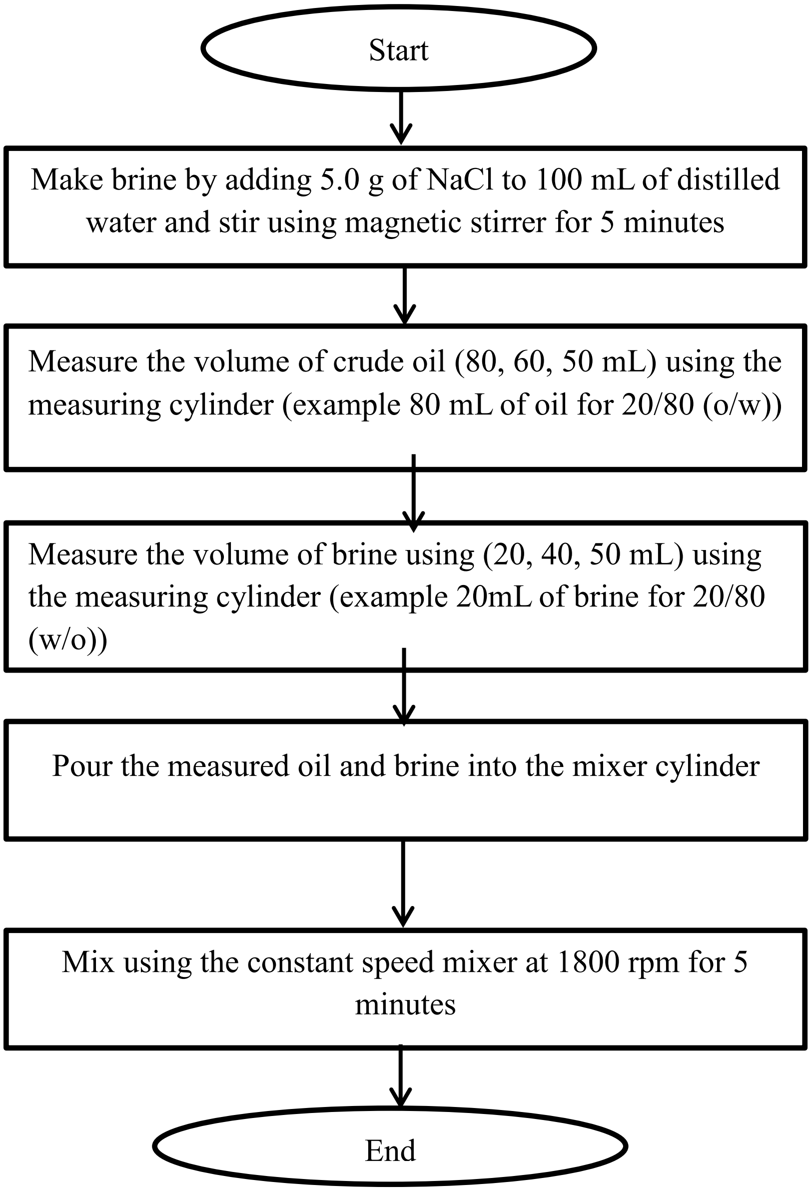

Figure 3.6: Process flowchart for preparing emulsions

3.3.2 Selection of water-oil ratios

To select the appropriate proportion of water and oil to be used, a stability test was done using these different water-oil ratios. Water-oil ratios of 20/80 (water/oil), 40/60 (water/oil), 50/50 (water/oil) were used. Emulsions corresponding to these ratios were prepared and left at room temperature for a week, after which no water was separated from the 80/20 (water/oil), and 60/40 (water/oil) emulsions. For the 50/50 (water/oil) emulsion, 40% water was separated. Thus, two water-oil ratios were selected to conduct further experiments in this research. The 20/80/ (water/oil) was selected to serve as a strong or tight emulsions while the 50/50 (water/oil) was chose to act as a weak or loose emulsion.

3.3.3 Demulsification Procedure

In carrying out the actual demulsification process, three conditions were experimented. The first method involved the use of heat heating only, while the second technique involved the combination of heat and ionic liquids. In each of the cases, after corresponding treatment, the sample was observed over separations time of 60 minutes for method one and two. Figure 3.7 shows the demulsification process. The volume of water separated was recorded at 60 minutes interval for method one and two. For the first condition, heat only was used. The emulsion sample was put in 10mL graduated cylinder, covered the top of the cylinder with aluminum foil, the temperature level of the heat was set to 70º C, then the emulsion sample was put in the heat for an exposure time of 60, 120, 180, 240, and 300 minutes. Figure 3.7 shows the demulsification process for all the emulsion prepared for the purpose of this experiment.

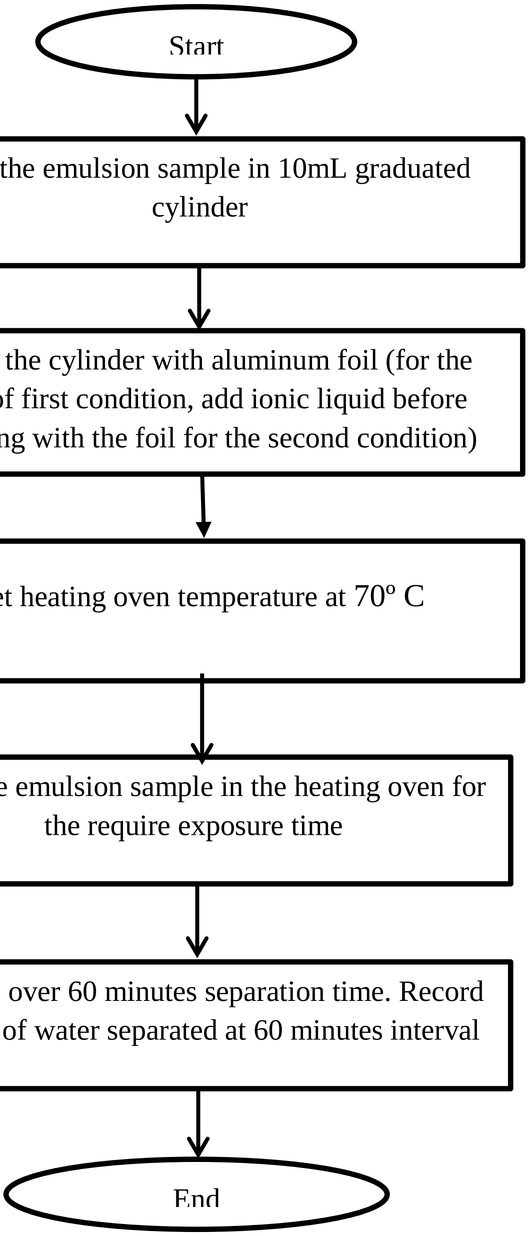

Figure 3.7: Process flowchart for demulsification procedure

For the second method, the combined effect of heat and ionic liquids was experimented. In this case, after emulsion sample was poured into the 10 mL graduated cylinder, 0.5 mL and 1.5 mL of ionic liquids was added then aluminum foil was used to cover it before putting it in the heat for the desire temperature and exposure time.

3.4. Project activities

The major project activities are as shown in figure 3.8:

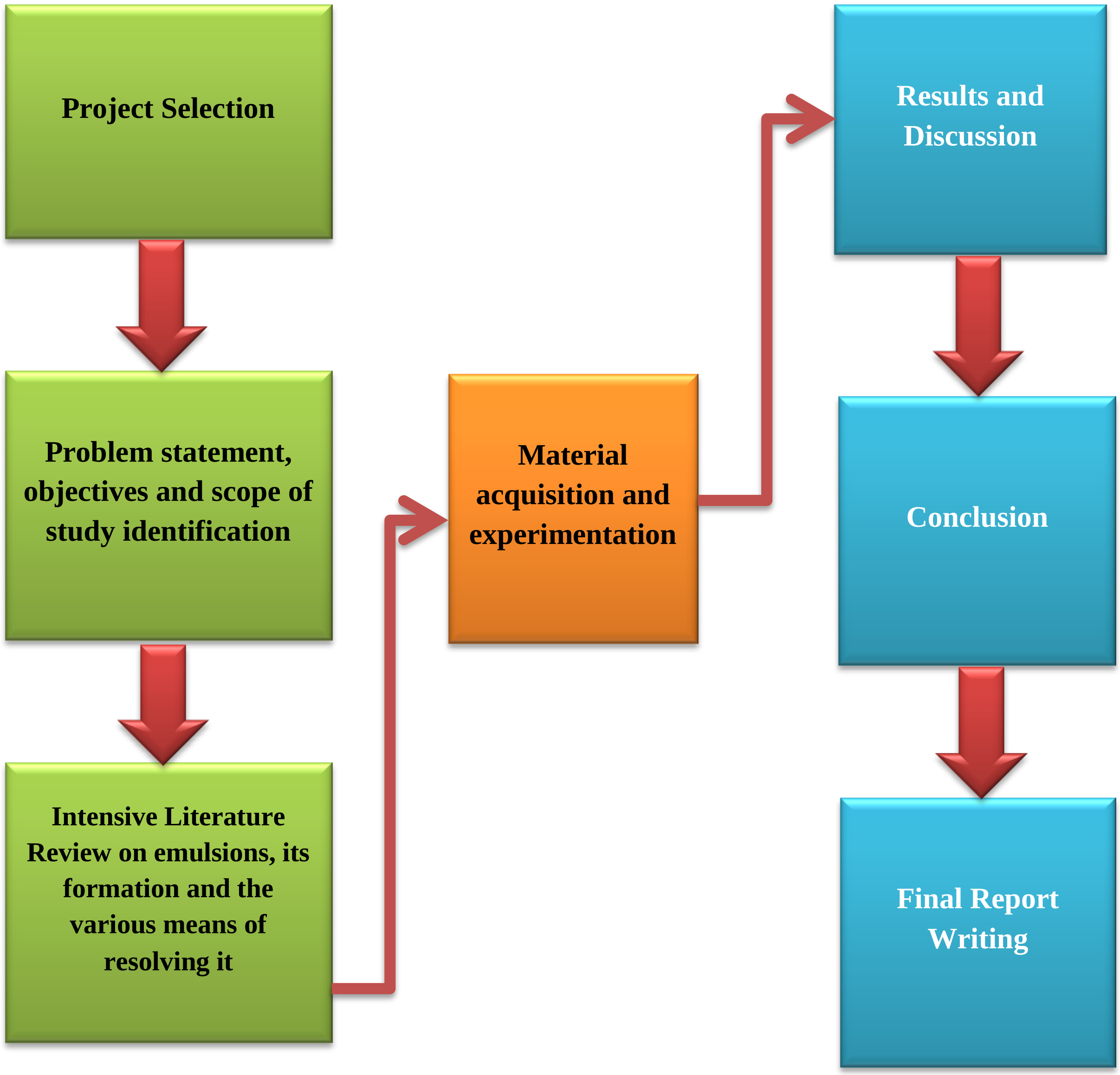

Figure 3.8: Project activities involved

3.2. Project Gantt chart

Weeks Activities	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32
Problem Identification	🟩	🟩														
Intensive Literature review			🟩	🟩	🟩											
Developing method to solve the problem					🟩	🟩	🟩									
Material acquisition and Experimentation								🟩	🟩	🟩	🟩					
Results, findings and discussion											🟩	🟩	🟩			
Conclusions														🟩	🟩	
Report writing															🟩	🟩

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Introduction

This chapter reports the result obtained from the experiments. The results are presented in two parts. The first part is the results obtained for the tight emulsion, that is, the 80/20 (water/oil) emulsion. The second part is the results obtained for the weak emulsion that is the 50/50 (water/oil) emulsion. However, 40/60 (water/oil) emulsion was investigated. The bottle test was used to evaluate the synthesized compounds as demulsification agents of stable W/O emulsions, and also to determine and select suitable ionic liquids for the application on medium crude oils. The first step carried out was crude oil characterization; one kind of crude oil was employed for this study. The physio-chemical properties of crude oil sample are presented.

SARA ANALYSIS

- Saturates (wt%) = 48.7
- Aromatics (wt%) = 34.6
- Resins (wt%) = 4.5
- Asphaltenes (wt%) = 12.2

PHYSICAL PROPERTIES OF OIL

- Gravity of oil = 19.13° API
- Density (gcc) = 0.947
- Viscosity (mPas) = 290.3

Ionic liquids synthesis, ionic liquids were designed with amphiphilic characteristics containing a charge head (cationic surfactant-like structure and its thermal stability and physicochemical properties have the potential to be used for breaking water-in-oil emulsions.

Ionic liquids were synthesized under heat irradiation is considerably shorted time and higher yields than using conventional heating according to the procedures described in the experimental section.

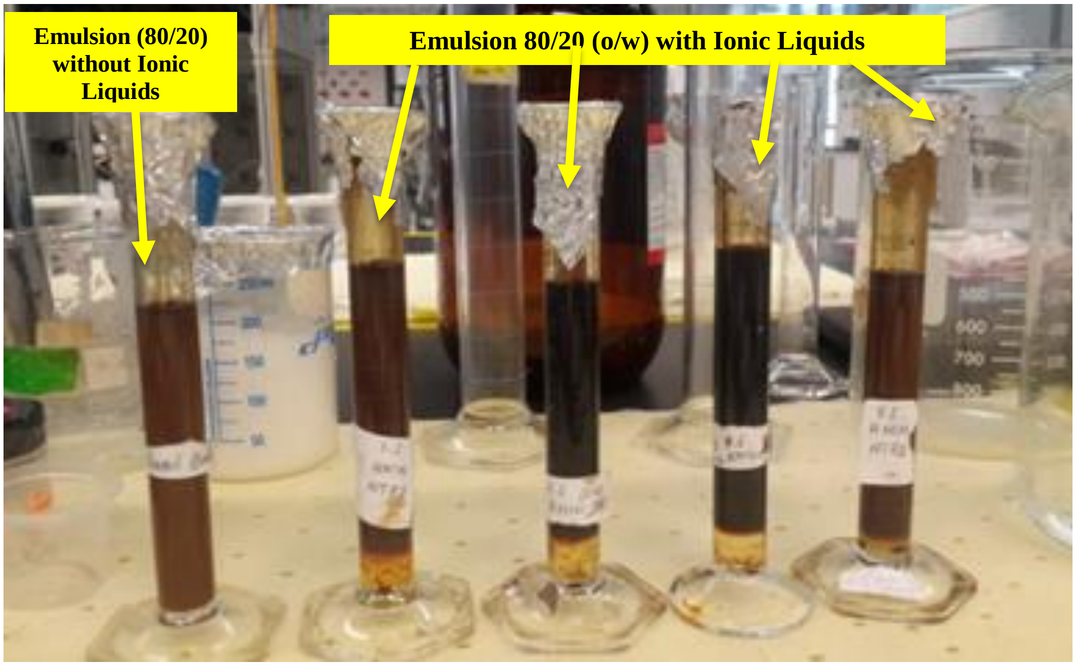

Figure 4.1a: Photographs of the graduated cylinders showing results of demulsification

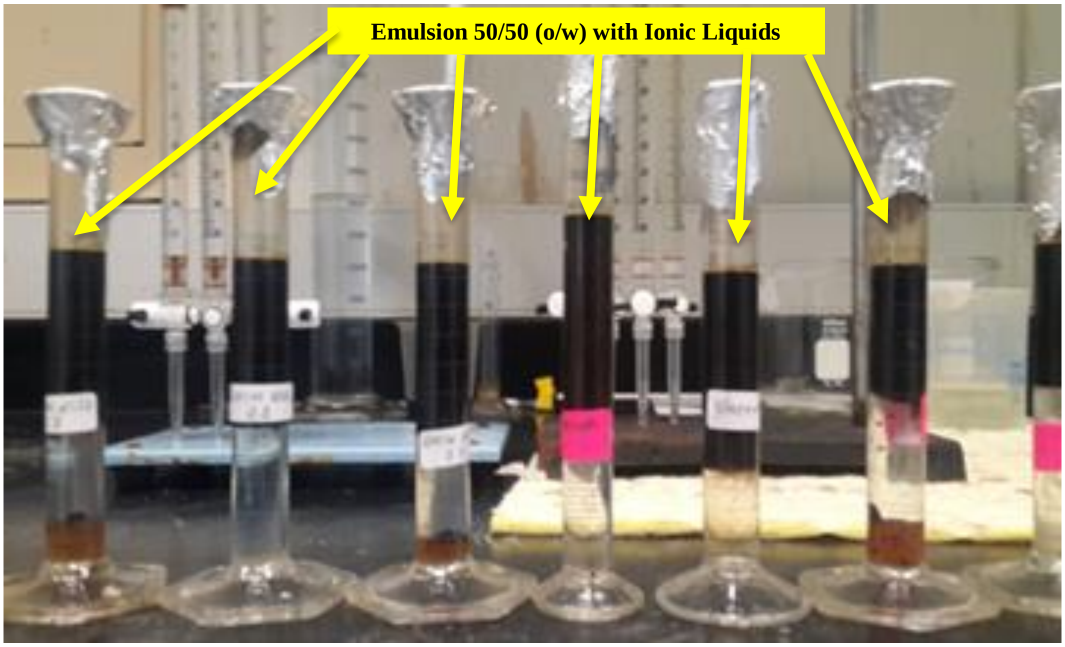

Figure 4.1b: Photographs of the graduated cylinders showing results of demulsification

Technique used: Evaluation of amphiphilic ionic liquids as demulsification agents by means of the bottle test.

The bottle test was used to evaluate the synthesized compounds as demulsification agents of stable W/O emulsions. Compounds were evaluated using three kinds of W/O emulsions obtained from the crude oils described in Table 4.2 with a water content of 20%. The results of the screening of the ionic liquids synthesized to observe their performance as demulsifiers with emulsions are shown in Table 4.1. In addition, photographs of the bottles showing the qualitative results of three experiments and their correspondence with our classification are presented as examples in Figure 4.1 and Figure 4.2 showing the result of ionic liquids as demulsifier for emulsions (20/80, W/O).

Despite the API density lower than 20 (in this case, 19^{o}API) corresponding to a crude oil with specific density slightly higher than the pure water density, the image in Figure 4.2 shows a clear aqueous phase separated from the medium crude oil and positioned at the bottom of the tube.

4.2 Results of heat effect for different water-oil ratios

This section discusses a demulsification condition as described in the methodology. In this section heat is used as demulsification agent. The volume of separated water is calculated in percentage using the equation 4.1(Abdurahman et al., 2006). Both Table 4.1 and Figure 4.2 show the results of emulsion separation using heat only.

$$\textbf{Separated water } (\mathbf{W}\%) = \frac{\textbf{Vol. of separated water volume (mL)}}{\textbf{Original amount of water (mL)}} * \mathbf{100} \text{…………..(4.1)}$$

Table 4.1: Separated water (mL) in separation time (hrs.) using heat only for three types of emulsions.

Exposure/separation time (hrs.)	**Separated water (mL) in separation time (hrs.) for 20/80 (w/o)**	**Separated water (mL) in separation time (hrs.) for 40/60 (w/o)**	**Separated water (mL) in separation time (hrs.) for 50/50 (w/o)**
1	0.0	0.0	1.8
2	0.0	0.0	1.8
3	0.0	0.0	1.8
4	0.0	0.0	1.8
5	0.0	0.8	1.8

Table 4.1: Elaborates that for tight emulsion, no water was recovered for the different exposure times. This result seems to be abnormal as water is expected to be separated because the exposure time and heat medium had 0 mL separated. Excessive heat can sometimes stabilize the emulsion instead of breaking it. However, for 50/50 (w/o) there is an increase of the amount of 1.8 mL of water separated.

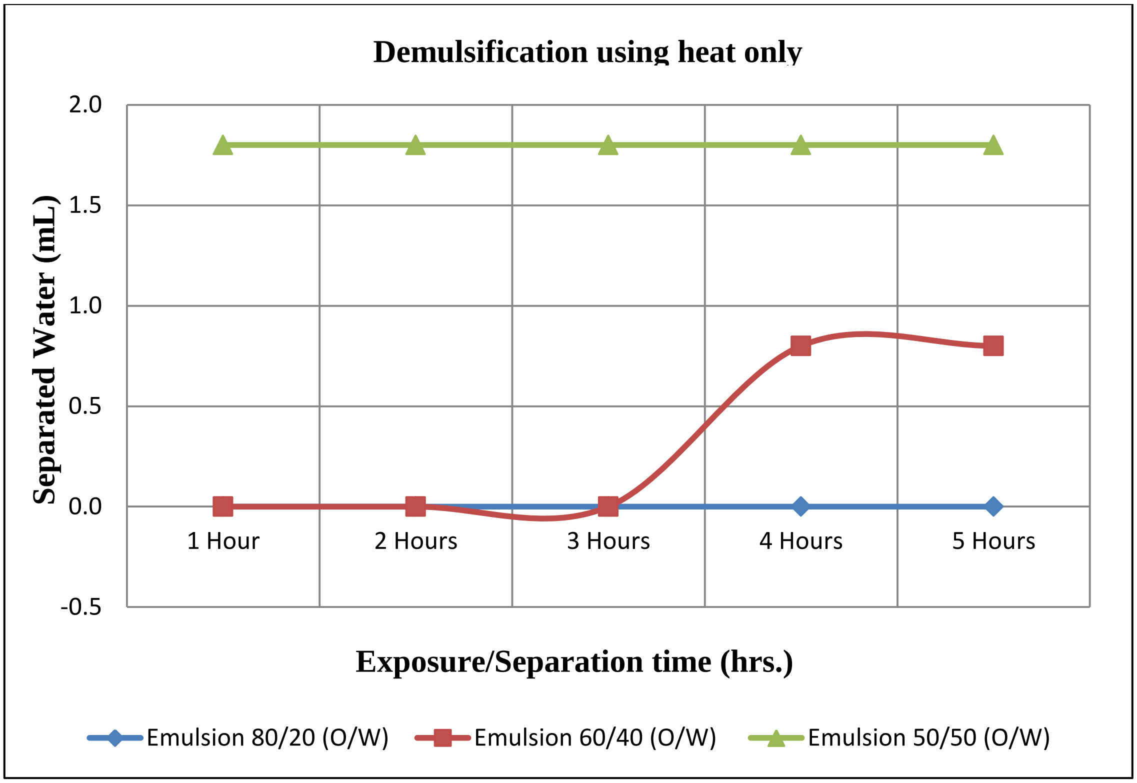

Figure 4.2: Graph of separated water (mL) vs. separation time (hrs.) using heat only for three types of emulsion.

Figure 4.2: Shows that at different water-oil ratios the amount of water separated varied. For tight emulsions, no water was recovered. For 40/60 after 3 hours of exposure there is a sudden change in separation from 0.0 mL to 0.8 mL due to heat effect and 50/50 at different exposure time the amount of water separated was the same 1.8 mL. This percentage recovery is very low as higher percentage recovery is required in the industry.

4.3. Results for tight emulsion 20/80 (w/o)

This section is divided into two subsections. Each subsection discusses a demulsification condition as described in the methodology. The conditions are: heat only, heat and ionic liquids (ILs) as demulsifier. The volume of separated water is calculated in percentage using the equation (3) (Abdurahman et al., 2006). Refer to equation 4.1.

4.3.1 Effect of using heat on separation only

In this section, the effect of using heat only in resolving three (3) types of emulsions is observed. Table 4.2 shows the results of water separation with respect to the exposure time in hours using heat only.

Table 4.2: Separated water (mL) in separation time (hrs.) using heat only for three types of emulsions.

Exposure/separation time (hrs.)	**Separated water (mL) in separation time (hrs.)**
1	0.0
2	0.0
3	0.0
4	0.0
5	0.0

Table 4.2: Elaborates that for tight emulsion, no water was recovered for the different exposure times. This result seems to be abnormal as water is expected to be separated because the exposure time and heat medium had 0.0 mL separated.

The effect of heat in water-in-oil emulsion is shown in figure 4.3.

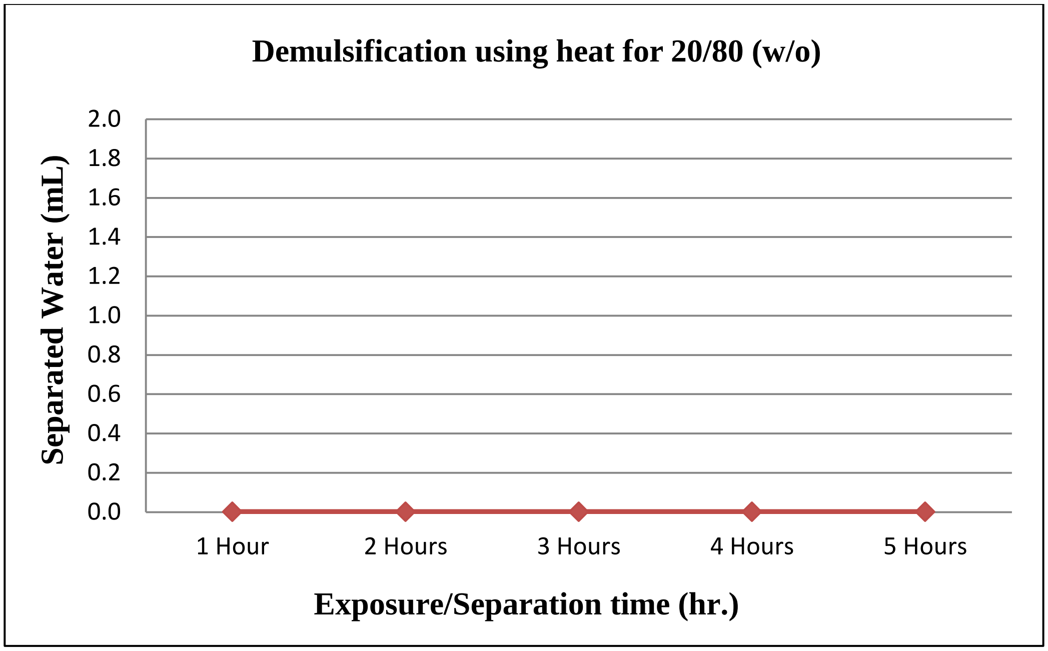

Figure 4.3: Graph of separated water (mL) vs. separation time (hrs.) using heat only for 20/80 (w/o).

Figure 4.3: Shows the effect of heat separates water. The highest separated water for this case goes to EMIM BF4 and 5 hours exposure time which yields 3.4 mL of separated water at separation time of 2 hours and 5 hours respectively.. It can also be observed that in relation to heat and ionic liquids, a jump from 2.0mL to 3.4 mL of separated water is seen.

4.2.2 Effect of ionic liquids (ILs) and heat on separation

In this section, the effect of both using ionic liquids and heat in resolving tight emulsions is observed. The effect of ILs and heat is shown in the table 4.3 and figure 4.4.

Table 4.3**:** Separated water (mL) in separation time (hrs.) using ILs and heat for 20/80 (w/o)

Exposure/separation time (hrs.)	**HO+0.5 HMIM DOSS**	**HO+ 1.5 HMIM DOSS**	**HO + 0.5 HMIM NTF**	**H. O+ 1.5 HMIM NTF2**	**HO+ 0.5 EMIM BF4**	**HO+ 1.5 EMIM BF4**
1	1.5	1.6	1.0	1.8	1.4	2.2
2	1.8	1.6	1.0	2.2	1.6	2.5
3	1.8	1.6	1.0	2.2	2.0	2.8
4	1.8	1.6	1.0	2.3	2.4	3.0
5	1.8	1.6	1.0	2.3	2.8	3.4

Table 4.3: Elaborates that at different ILs dosage for 20/80 water-oil ratio the amount of water separated varied. At this point EMIM BF4 yields more water separation compared to other ILs used. This percentage recovery is very low as higher percentage recovery is required in the industry.

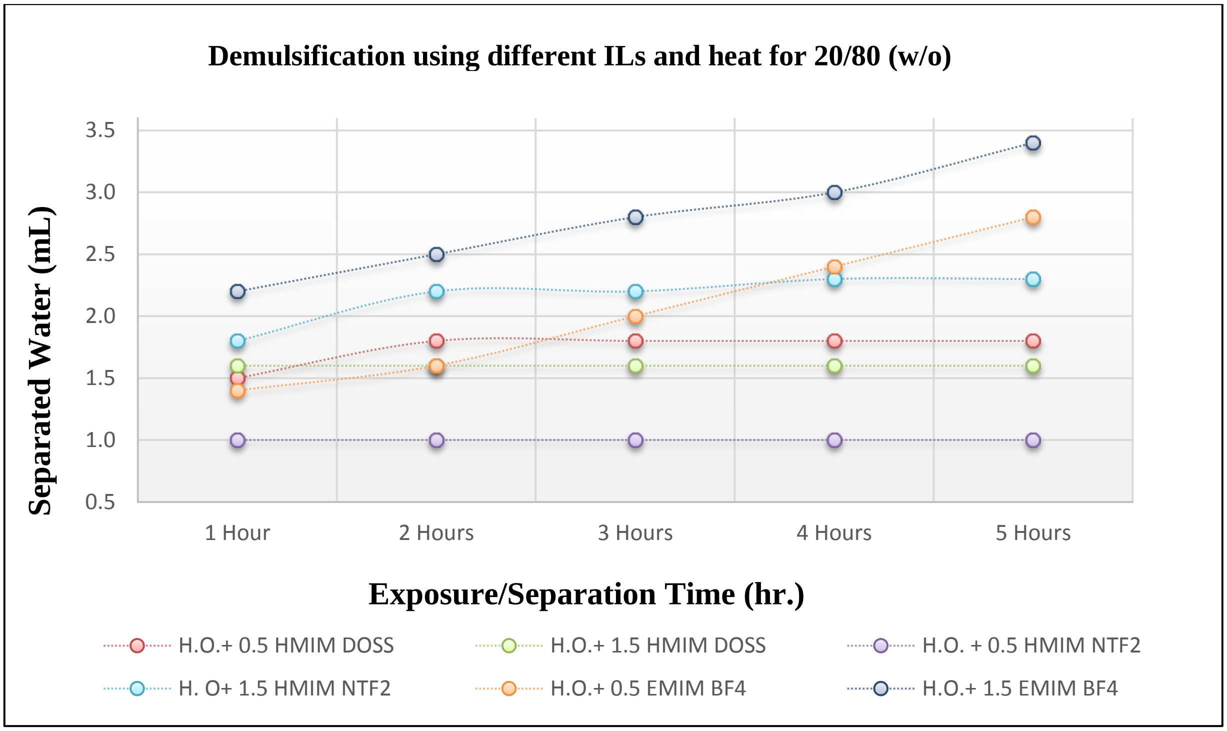

Figure 4.4: Graph of separated water (mL) vs. separation time (hrs.) using ILs and heat for 20/80 (w/o).

Figure 4.4: Shows the effect of a combination of heat and ionic liquids 0.5 mL and 1.5 mL as demulsifier separates water. The highest separated water for this case goes to EMIM BF4 and 5 hours exposure time which yields 3.4 mL of separated water. It can also be observed that in relation to heat and ionic liquids, a jump from 2.0mL to 3.4 mL of separated water is seen.

4.3. Results for 40/60 Emulsions

Similar to section 4.2, this section is divided into three subsections. Each subsection discusses a demulsification condition as described in the methodology. The conditions are: heat only, and heat and ionic liquids (ILs) as demulsifier. The volume of separated water is calculated in percentage using the equation (3) (Abdurahman et al., 2006). Refer to equation 4.1.

4.3.1. Effect of heat on separation

In this section, the effect of using heat only in resolving weak emulsions is observed. Table 4.4 and figure 4.5 shows the effect of using heat only to resolve water-in-oil emulsions.

Table 4.4: Separated water (mL) in separation time (hrs.) using heat only for 40/60 (w/o)

Exposure/separation time (hrs.)	**Separated water (mL) in separation time (hrs.)**
1	0.0
2	0.0
3	0.0
4	0.8
5	0.8

Table 4.4: Elaborates that for this water-oil emulsion, small amount of water was recovered for the different exposure times. This result seems to be abnormal as water is expected to be separated because the exposure time and heat medium had 0.8 mL separated.

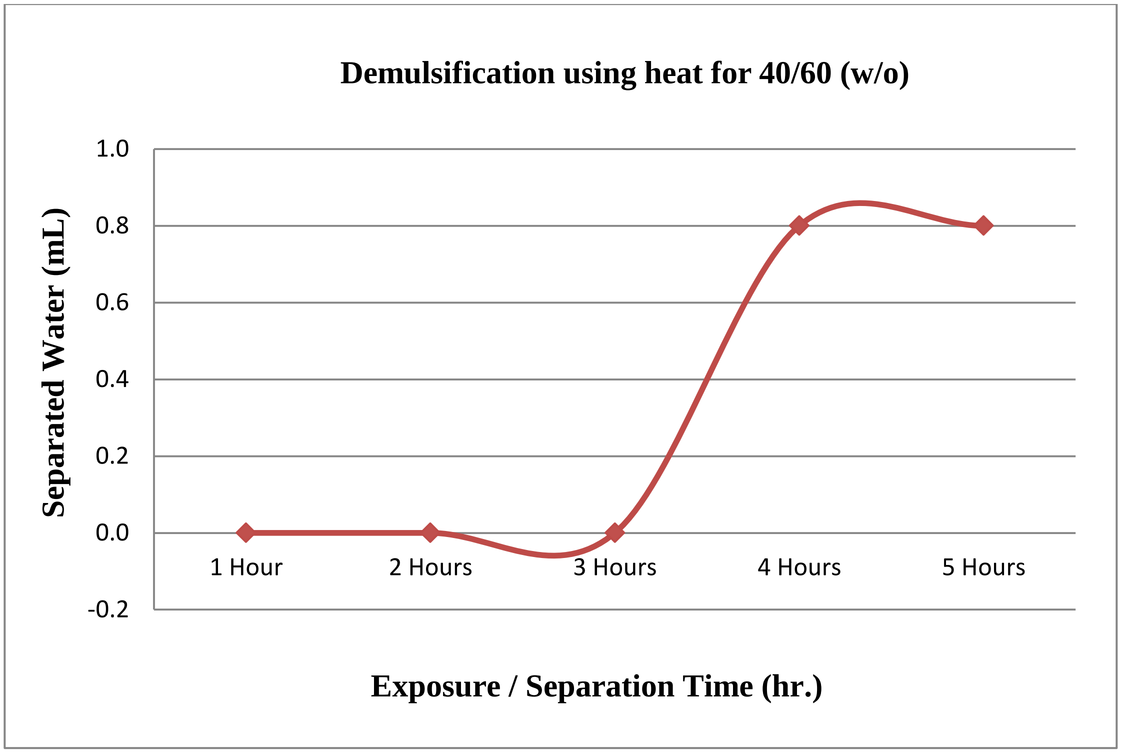

Figure 4.5: Graph of separated water (mL) vs. separation time (hrs.) using heat only for 40/60 (w/o)

Figure 4.5: Shows the effect of heat to separate water. It can also be observed that there is sudden change after the exposure of 3 hours to 5 hours. The amount of water separated goes from 0.0 mL to 0.8 mL in relation to heat effect.

4.3.2 Effect of ionic liquids (ILs) and heat on separation

In this section, the effect of both using ionic liquids and heat in resolving emulsions is observed. Table 4.5 and figure 4.6 shows the effect of using ILs and heat for emulsion separation.

Table 4.5: Separated water (mL) in separation time (hrs.) using ILs and heat for 40/60 (w/o).

Exposure/separation time (hrs.)	**HO + 0.5 HMIM NTF2**	**H. O+ 1.5 HMIM NTF2**	**HO+ 0.5 EMIM BF4**	**HO+ 1.5 EMIM BF4**
1	3.4	4.2	2.8	4.0
2	3.5	4.4	3.0	4.2
3	3.6	4.4	3.0	4.4
4	3.6	4.7	3.2	4.7
5	3.6	4.7	3.7	4.8

Table 4.5: Elaborates that for this water-oil emulsion, there is a small amount of water was recovered for the different exposure times. This result seems to be abnormal as water is expected to be separated because the exposure time and heat medium had 0.8 mL separated.

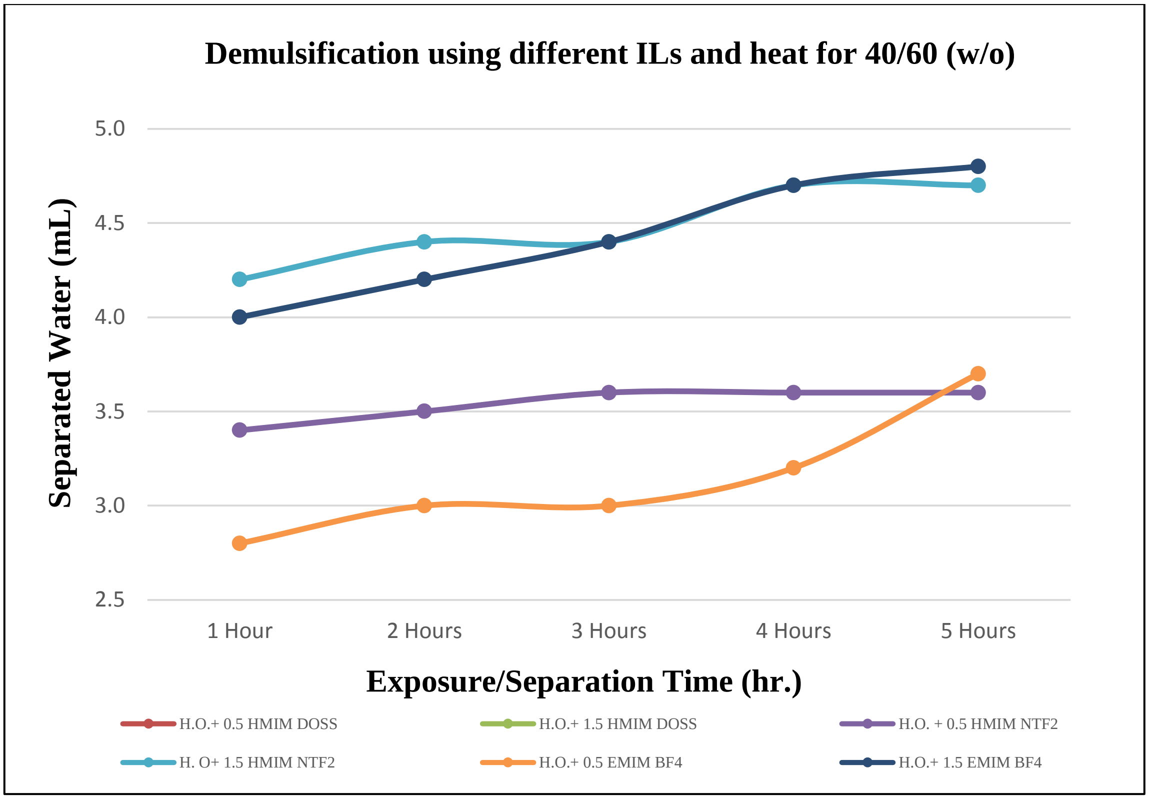

Figure 4.6: Graph of separated water (mL) vs. separation time (hrs.) using ILs and heat for 40/60 (w/o).

Figure 4.6: Shows the effect of a combination of heat to separate water. It can also be observed that there is sudden change after the exposure of 3 hours to 5 hours for all the ILs being used. The amount of water separated goes from 2.8 mL to 4.8 mL due to the combined effect of ILs and heat.

4.4. Results for Weak Emulsion 50/50 (w/o)

Similar to section 4.3, this section is divided into three subsections. Each subsection discusses a demulsification condition as described in the methodology. The conditions are: heat only, heat and ionic liquids (ILs) as demulsifier. The volume of separated water is calculated in percentage using the equation (3) (Abdurahman et al., 2006). Refer to equation 4.1.

4.4.1. Effect of heat on separation

In this section, the effect of using heat only in resolving weak emulsions is observed. Table 4.6 and figure 4.7 shows the effect of using heat only for emulsions separation.

Table 4.6: Separated water (mL) in separation time (hrs.) using heat only for 50/50 (w/o)

Exposure/separation time (hrs.)	**Separated water (mL) in separation time (hrs.)**
1	1.8
2	1.8
3	1.8
4	1.8
5	1.8

Table 4.6: Elaborates that for this water-oil emulsion, constant amount of water was recovered for the different exposure times. This result seems to be abnormal as water is expected to be separated because the exposure time and heat medium had 1.8 mL separated.

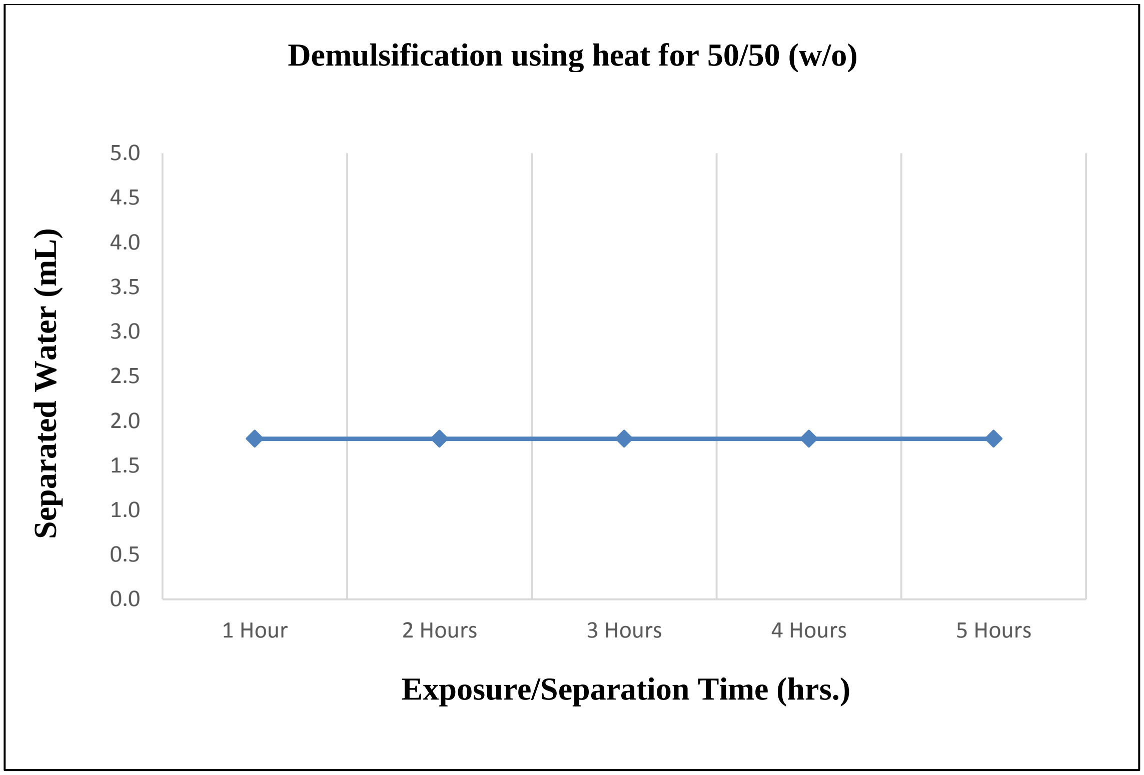

Figure 4.7: Graph of separated water (mL) vs. separation time (hrs.) using heat for 40/60 (w/o).

Figure 4.7: Shows the effect of a combination of heat to separate water.. It can also be observed that there is sudden change after the exposure of 3 hours to 5 hours for all the ILs being used. The amount of water separated goes from 2.8 mL to 4.8 mL due to the combined effect of ILs and heat.

4.4.2 Effect of ionic liquids (ILs) and heat on separation

In this section, the effect of both using ionic liquids and heat in resolving emulsions is observed. Table 4.7 and figure 4.8 shows the effect of using ILs and heat for water separation.

Table 4.7: Separated water (mL) in separation time (hrs.) using ILs and heat for 50/50 (w/o)

Exposure/separation time (hrs.)	**HO + 0.5 HMIM NTF2**	**H. O+ 1.5 HMIM NTF2**	**HO+ 0.5 EMIM BF4**	**HO+ 1.5 EMIM BF4**
1	4.6	5.0	3.8	4.8
2	4.7	5.2	4.0	5.0
3	4.8	5.4	4.2	5.0
4	4.8	6.0	4.5	5.2
5	4.8	6.0	4.5	5.2

Table 4.7: Elaborates that the combined effect of ILs and heat in resolving weak emulsion, high amount of water was recovered for the different exposure times and for the different ILs. EMIM NTF2 water recovered was more than 5 mL. This result seems to be normal as water is expected to be separated because the exposure time and heat medium.

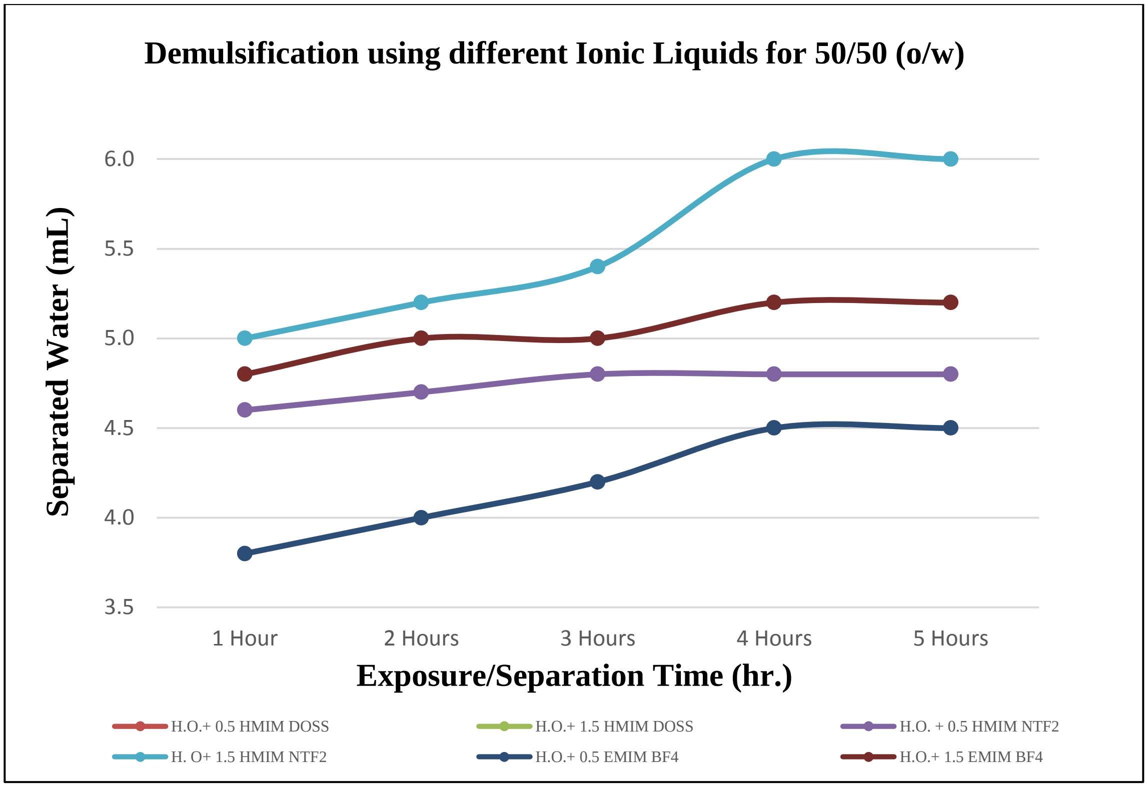

Figure 4.8: Graph of separated water (mL) vs. separation time (hrs.) using ILs and heat for 50/50 (w/o).

Figure 4.8: Shows the effect of a combination of heat to separate water. It can also be observed that EMIM NTF2 the amount recovered is high compared to other ILs. The amount of water separated goes from 2.8 mL to 4.8 mL due to the combined effect of ILs and heat.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1. Conclusion

The combined effect in the use of heat (in this case from heating oven radiation) and use of ILs was observed. The kinetics of the mechanism was observed to be that, as the demulsifier attacks the emulsifier film, and tries to rupture it, the bulk heating provided by the heating oven increases the entropy of the encapsulated water molecules. The combination of these effects, leads to the rupturing of this emulsified film which leads to coalescence of the water. It is worthy to conclude that the synergy effect of heat from heating oven and ionic liquids increases the effectiveness of emulsion resolution.

The use of ILs as demulsifiers of heavy crude oil emulsions is a new area of study. Results obtained on the current work shows that ILs, based on imidazolium cations and the NTF2 anion can be successfully used during the demulsification of water-in-heavy crude oil emulsions. Their effects are greatly accelerated by action of heat, which can be explained by a strong interaction of radiation with these ionic species. For some tests, high demulsification efficiencies (beyond 90%) were obtained in a short time. Concerning the structure of ILs, the results indicated that the demulsification is favored when hydrophobic ILs containing cations with long alkyl chains are involved, such as [HMIM+][NTF2−] when the demulsification performance of these ILs concentration still necessary.

However, the selection of a proper solvent can improve the mixing of the ILs into the heavy crude oil, yielding better demulsification results at lower concentrations.

5.2 Recommendations

To test and further justify these results, the following points are recommended:

- This same procedure should be carried out where the amount of demulsifier (ILs) used is varied as well as the heat temperature. This is to obtain a more accurate optimal point for amount of demulsifier (ILs) use.
- Repeating the same procedure for oil-in-water emulsions. This to observe the combined effect of heat and chemical on oil-in-water emulsion.
- This same procedure should be repeated for various water-oil ratios. Such as 10/90, 30/70, 45/55. This is to further understand the effect of water ratio in resolving emulsion using a combination of heat and demulsifier (ILs).
- The use of water bath and centrifugal machine in order to observe the effect of both in emulsion resolution using ionic liquids (ILs) as demulsifiers.
- Student, whose experiment requires the use of the centrifugal machine, needs to undergo some short of training that will enable him/her to use the centrifugal machine in the absence of the UTP Laboratory Technician.

REFERENCES

Al-Ghamdi, A., Noik, C., Dalmazzone, C., & Kokal , S. (2007). Experimental Investiagtion of Emulsion Stability GOSPs-Part I: Analyses of Seperated Phases. Presented at the SPE International Symposium on Oilfield Chemistry 28 February - 2 March. (pp. 1-9). Houston, Texas: SPE International.

Alan Junji Yamaguchi (2013). A Numerical Study on the Oil-Water Separation Process.

Presented at the SPE International Student Paper Contest at the SPE Annual Technical Conference and Exhibition held September 30 – 2 October 2013 in New Orleans, Louisiana: SPE International.

Al-Ghamdi, A., Noik, C., Dalmazzone, C., & Kokal, S. (2009). Experimental Investigation of Emulsion Stability Gas/Oil Seperation Plants. SPE Journal, 595-605.

Bansbach, P. (1965). Treating Emulsions produced by thermal recovery Operations. Presented at the 36th Annual Califronia Regional Fall Meeting of the Society of Petroleum Engineers November 4-5. (pp. 1-4). California: SPE International.

Binner, E., Robinson, J. P., Silvester, S. A., Kingman, S. W., & Lester, E. H. (2014). Investigation into the mechanisms by which heat heating enhances separation of water-in-oil emulsions. Fuel, 116, 516-521.

Diego Guzman-Lucero, Patricia Flores, Tania Rojo, and Rafael Martınez-Palou (2010). Ionic Liquids as Demulsifiers of Water-in-Crude Oil Emulsions: Study ofthe Heat Effect.

Dosunmu, A., Otikiri, A. E., & Fekete, P. O. (2012). Evaluation of Emulsion Treatment Using Different De-emulsifiers. Presented at the Nigerian Annual International Conference and Exhibition 6-8 August. (pp. 1-6). Abuja: SPE International.

Emuchay, D., Onyekwonu, M. O., Ogolo, N. A., & Ubani, C. (2013). Breaking of Emulsions Using Locally Formulated Demulsifiers. Presented at the Nigerian Annual International Conference and Exhibition 30 July - August 14. (pp. 1-10). Lagos: SPE International.

Elisangela B. Silva, Denisson Santos, Douglas R.M. Alves, Milson S. Barbosa, Regina C.L. Guimaraes, Bianca M.S. Ferreira, Ricardo A. Guarnieri, Elton Franceschi, Claudio Dariva, Alexandre F. Santos, and Montserrat Fortuny. Demulsification of Heavy Crude Oil Emulsions Using Ionic Liquids (2013).

Keith E. Johnson (Spring 2007). What's an Ionic Liquid? The Electrochemical Society Interface

Fingas, M., & Fieldhouse, B. (2003). Studies of the formation process of water-in-oil emulsions. Marine Pollution Bulletin, 47 , 369-396.

Fingas, M., & Fieldhouse, B. (2009). Studies on crude oil and petroleum products emulsions: Water resolution and rheology. Collodial and Surfaces A: Physiochemical and Engineering Aspects, 333, 67-81.

Gallup, D. L., Denny, V., & Khandekar, C. Y. (2010). Inhibition of Sodium Soap Emulsions, West Seno, Indonesia Field. Presented at the SPE International Conference on Oilfield Scale 26-27 May. (pp. 1-11). Aberdeen: SPE International.

Gianna Pietrangeli, Lirio Quintero, Thomas Jones, & Q. Darugar (2014). Treatment of Water in Heavy Crude Oil Emulsions with Innovative Microemulsion Fluids. Presented at the SPE Heavy and Extra Heavy Oil Conference 24-26 September. Latin America, Medellin, Colombia: SPE International.

Jones, T. J., Neustadter, E. L., & Whittingham, K. P. (1978). Water-in-crude oil emulsion stability and emulsion destablization by chemical demulsifiers. The Journal of Canadian Petroleum Technology , 100-108.

Martínez-Palou, R., Cerón-Camacho, R., Chávez, B., Vallejo, A., Villanueva-Negrete, D., Castellanos, J., . . . Aburto, J. (2013). Demulsification of heavy crude oil-in-water emulsions: A comparative study between heat and thermal heating. Fuel,113, 407-414.

Murillo-Hernandez Jose-Alberto and Aburto Jorge. Current Knowledge and Potential Applications of Ionic Liquids in the Petroleum Industry

Nguyen, D. T., & Sadeghi, N. (2011). Selection of the Right Demulsifier for Chemical Enhanced Oil Recovery. Presented at the SPE International Symposium on Oilfield Chemistry 11-13 April. (pp. 1-12). Texas: SPE International.

Rasha Mohammed Abd, Abdurhman Hamid Nour, and Ahmad Ziad Sulaiman. Kinetic Stability and Rehology of Water-In-Crude Oil Emulsions Stabilized by Cocamide at Different Water Volume Fractions. International Journal of Chemical Engineering and Applications, Vol.5.No.2, April 2014.

Soffian, M. R., & Niven, T. L. (1993). Emulsion Treatment Program. Presented at SPE International Meeting on Petroleum Engineering 8-10 February. (pp. 1-8). Singapore: SPE International.

Vega, C., Delgado, M., Bolívar, U. S., & Vega, B. (2002). Treatment of waste-water/oil emulsions using heat radiation. Presented at the SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production 20-22 March. (pp. 1-12). Kuala Lumpur: SPE International.

APPENDICES

Figure: 1 Graduated cylinders filled with crude oil for analysis.

Figure 2: Beaker containing heavy crude oil for the experiment

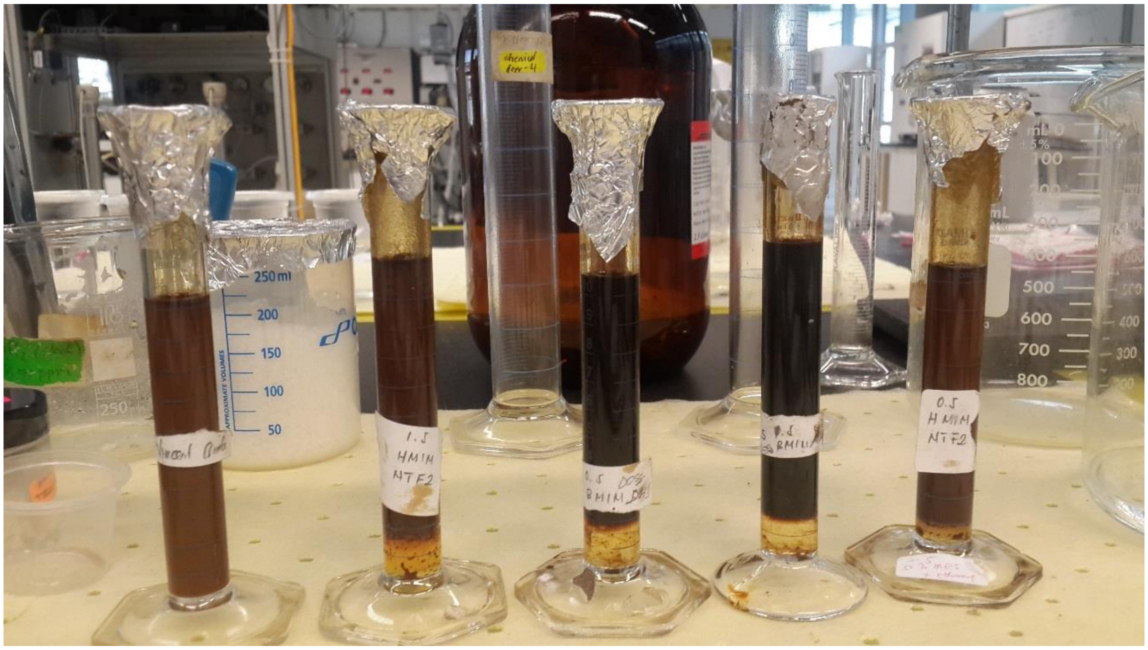

Figure 3: Graduated cylinders after exposure time to heating oven.

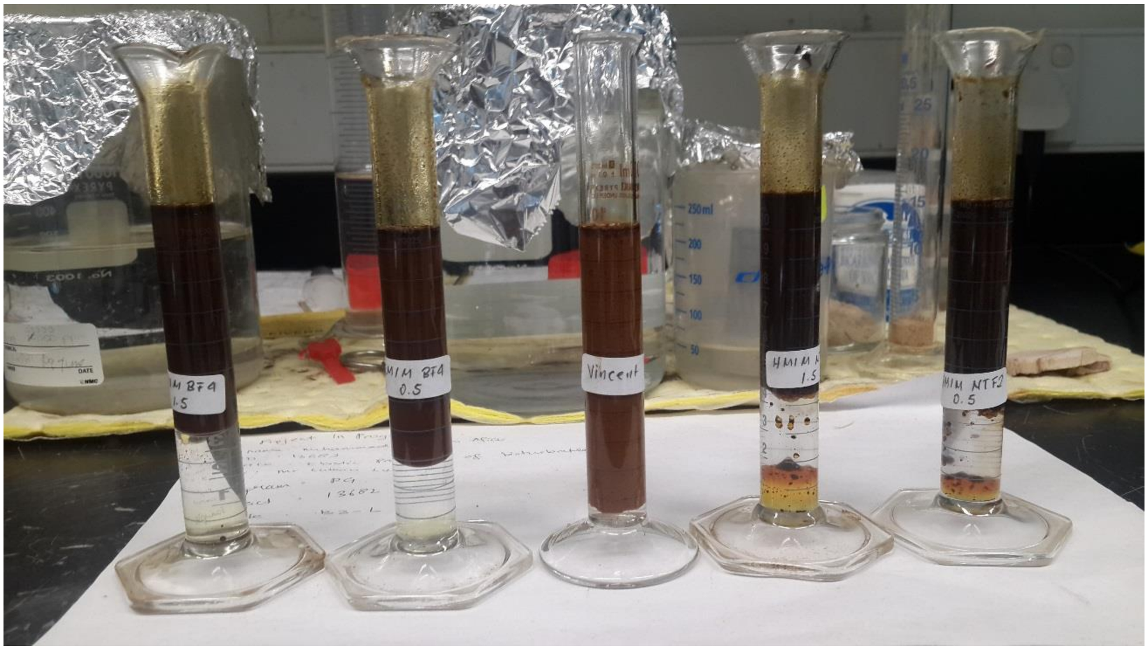

Figure 4: Showing weak emulsion water separation using ILs and heat

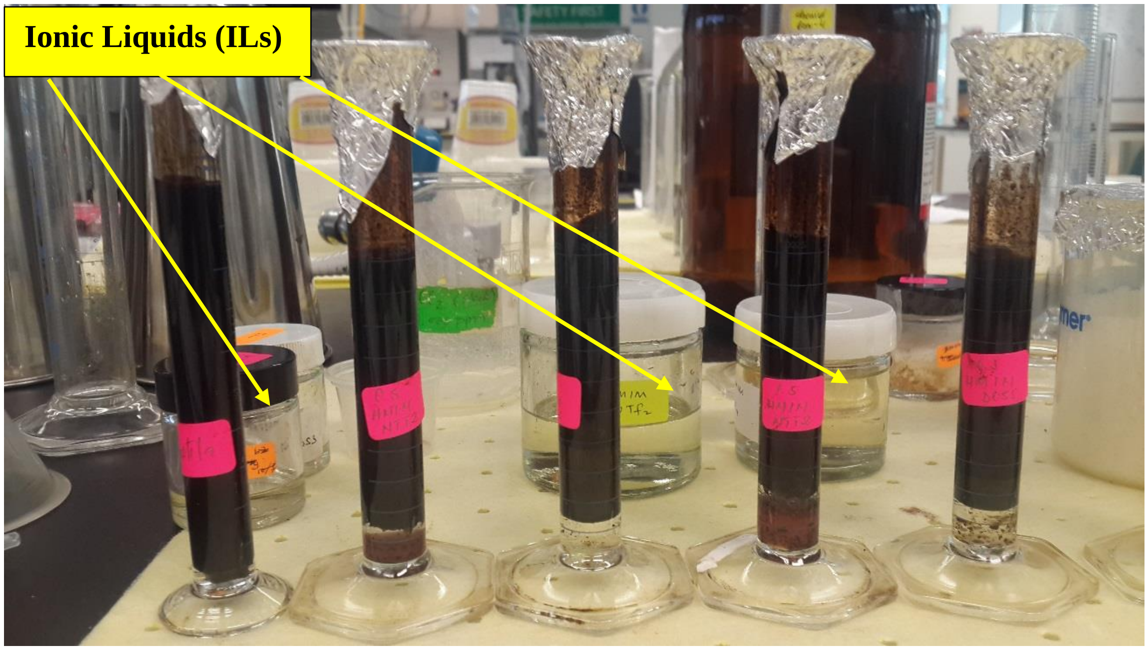

Figure 5: Shows the ionic liquids (ILs) used for the experiment.