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STUDY ON DEMULSIFIER FORMULATION FOR TREATING MALAYSIAN CRUDE OIL EMULSION

(KAJIAN TERHADAP FORMULASI BAHAN PENYAHEMULSI BAGI PERAWATAN EMULSI MINYAK MENTAH MALAYSIA)

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ABSTRACT

STUDY ON DEMULSIFIER FORMULATION FOR TREATING MALAYSIAN CRUDE OIL EMULSION

(Keywords: Malaysian crude oil emulsions, demulsifiers, Formulation, demulsification)

Water in oil emulsion occurs at many stages in the production and treatment of crude oil. About two third of petroleum production of every oil field exists in the form of water in oil emulsion. The emulsion stability results from the presence of interfacial barrier preventing coalescence of the dispersed water droplets. This is due to the present of polar components such as asphaltenes, resins, wax and naphtenic acids in the crude oil. Therefore before transporting or refining the oil, it is essential to separate the water for economic and operational reasons. Minimizing the water level in the oil reduces pipeline corrosion and maximizes pipeline usage. The most effective method to overcome the problem is to demulsify the crude by using demulsifiers. The demulsifiers will destabilize the interfacial film between the droplets. It has been reported that the combination of oil-soluble demulsifiers and water-soluble demulsifiers produced great result in water separation. From the screening process of single oil-soluble demulsifiers, the most effective chemicals as demulsifier are TOMAC, hexylamine and dioctylamine while methyl methacrylate, butyl acrylate and acrylic acid are the most effective chemicals in water-soluble group. The new formulation of demulsifier was formulated by using Statistical Analysis System software. From this analysis, the optimum concentration needed for TOMAC, hexylamine, dioctylamine, methyl methacrylate, butyl acrylate and acrylic acid are 48.7 ppm, 0 ppm, 8 ppm, 48.2 ppm, 26.5 ppm and 29.9 ppm, respectively. The combination of these chemicals resulted 53.7% to 60.4% water separation from the emulsion system. It was found that this formulation is better than other commercial demulsifier formulation. This new formulation was found to be effective for demulsification of water-in-oil emulsion of Tabu, Seligi, Guntong, Semangkok, Irong Barat and Tapis fields and single emulsion system. In order to obtain better understanding and results, optimizing on agitation and temperature conditions, the mechanism demulsification study are recommended for further study

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ABSTRAK

KAJIAN TERHADAP FORMULASI BAHAN PENYAHEMULSI BAGI PERAWATAN EMULSI MINYAK MENTAH MALAYSIA

(Kata kunci: Emulsi minyak mentah malaysia, bahan penyahemulsi, formulasi, penyahemulsion)

Emulsi air dalam minyak berlaku di banyak tahap pengeluaran dan perawatan minyak mentah. Sebanyak dua per tiga daripada pengeluaran petroleum di setiap lapangan wujud dalam bentuk emulsi air dalam minyak. Kestabilan system emulsi ini adalah disebabkan kehadiran halangan antaramuka yang menghalang pertautan titisan air. Ini adalah kerana dengan adanya komponen berkutub seperti asphaltin, resin, bahan berlilin dan asid naftenik di dalam minyak mentah. Oleh itu, air perlu dipisahkan sebelum minyak diangkut dan diproses atas alas an ekonomi dan operasi. Meminimumkan paras air dalam minyak mentah akan mengurangkan hakisan paip dan meningkatkan tempoh hayat paip. Cara yang paling berkesan untuk menyelesaikan masalah ini ialah dengan menyahemulsikan minyak mentah dengan menggunakan bahan penyahemulsi. Bahan penyahemulsi ini akan mengacau filem antaramuka di antara titisan-titisan. Didapati bahawa campuran bahan penyahmulsi larut-minyak dan bahan penyahemulsi larut-air menghasilkan keputusan yang lebih baik di dalam pemisahan air.Daripada proses pemilihan bahan penyahemulsi, yang menghasilkan pemisahan air yang terbaik ialah TOMAC, heksilamina dan dioktilamina untuk bahan penyahemulsi larut-minyak manakala metil metakrilat, butil akrilat dan asid akrilik untuk bahan penyahemulsi larut-air. Formulasi baru untuk pemisahan air ini dioptimumkan dengan menggunakan program Sistem Analisis Statistik. Daripada analisis yang dijalankan, didapati bahawa kepekatan optimum yang diperlukan untuk TOMAC, heksilamina, dioktilamina, metil metakrilat, butil akrilat dan asid akrilik ialah 48.2 ppm, 0 ppm, 8 ppm, 48.2 ppm, 26.5 ppm dan 29.9 ppm setiap satu. Campuran kesemua bahan penyahemulsi ini menghasilkan pemisahan air di antara 53.7% hingga 60.4% daripada system emulsi. Didapati bahawa formulasi ini adalah lebih bagus berbanding dengan formulasi komersial yang lain. Formulasi baru ini berkesan di dalam menyahemulsikan emulsi air dalam minyak dari lapangan Tabu, Seligi, Guntong, Semangkok, Irong Barat dan Tapis serta system emulsi tunggal. Untuk memperolehi pemahaman dan keputusan yang lebih baik, pengoptimuman ke atas pengacauan dan suhu serta mekanisma penyahemulsi adalah disarankan untuk kajian masa akan datang.

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LIST OF ABBREVIATIONS

EPMI - ESSO Production Malaysia Incorporated
BS&W - Basic sediment and water
SARA - Saturates (including waxes), aromatics, resin and asphaltene
O/W - Oil-in-water emulsion
W/O - Water-in-oil emulsion
O/W/O - Oil-in-water-in-oil emulsion
MSDS - Material Safety Data Sheets
TOMAC - Methyl trioctyl ammonium chloride
RSM - Response surface methodology
SAS - Statistical analysis system
ANOVA - Analysis of variance
SS - Sum of square
dF - Degree of freedom
MS - Mean Square
NaCl - Sodium Chloride

NOMENCLATURES

SYMBOL	DEFINITION	UNIT
Y	Salinity	%w/w
X	NaCl concentration	g/100 ml
x	NaCl amount	g
M_1	Initial concentration of demulsifier	ppm
M_2	Final concentration of demulsifier	ppm
V_1	Volume of demulsifier needed	ml
V_2	Volume of demulsifier and oil	ml
X_1	TOMAC concentration	ppm
X_2	Hexylamine concentration	ppm
X_3	Dioctylamine concentration	ppm
X_4	Methyl methacrylate concentration	ppm
X_5	Butyl acrylate concentration	ppm
X_6	Acrylic acid concentration	ppm

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CHAPTER I

RESEARCH BACKGROUND

1.1 Introduction

Malaysia is important to world energy markets because of its 75.0 trillion cubic feet of natural gas reserves and its net oil exports of over 260,000 barrels per day. Five oil fields (Guntong, Tabu, Palas, Semangkok and Irong Barat) of Esso Production Malaysian Incorporated (EPMI) contract areas in East Cost of Malaysia are having severe emulsion problem. The emulsion is either normal or inverted emulsion and stable. This crude oil has basic sediment and water (BS&W) between 2 to 11%, which is higher than specified BS&W (less than 0.5%). Petronas oil fields of East Malaysia have also face the same problems. As a result, they have to some extent to sell their crude oil in the form of emulsion at low price due to the high cost for treating the emulsions.

Water-in-oil emulsion are formed during the production of crude oil, which is often accompanied with water. The stability of the emulsion is ranging from a few minutes to years depending on the nature of the crude oil and to some extent the nature of water (Bhardwaj and Hartland, 1988). A recent report has suggested that an equivalent volume of water accompanied the daily production of some 60 million barrels of crude oil (Ivanov and Kralchevcky, 1996). Under the production conditions, a proportion of this water can become intimately dispersed throughout the crude oil as small droplets.

Crude oils consist of, in any case, a series of hydrocarbons such as alkanes, naphtenes, and aromatic compounds as well as phenols, carboxylic acids, and metals. A major fraction of sulfur and nitrogen compounds may be present as well. The carbon numbers of all these components range from 1 (methane) through 50 or more (asphaltenes). Some of these components can form films at oil surfaces, and others are surface active. So, the tendency to form stable or unstable emulsions of different kinds varies greatly among different oils (Schramm, 1992).

The natural petroleum emulsion resulting from the secondary production consists of crude oil as dispersion medium and brine as dispersed phase, normally stabilized by natural chemicals such as asphaltenes, resins, solid such as clays and waxes (Bhardwaj and Hartland, 1988). For asphaltenes in particular, the presence of heteroatoms in the essentially aromatic structure imparts amphiphilic characteristics (Selvarajan et al., 2001).

Emulsions are undesirable because the volume of dispersed water occupies space in the processing equipment and pipelines, increased operating and capital costs. Moreover, the characteristics and physical properties of oil change significantly upon emulsification. The density of emulsion can increase from 800 kg/m^3 for the original oil to 1030 kg/m^3 for the emulsion. The most significant change is observed in viscosity, which typically increases from a few mPa·s or less to about 1000 mPa·s (Fingas et al., 1993).

In crude oil processing or refining, the desalting techniques comprise the intentional mixing of the incoming crude with a fresh “wash water” to extract the water soluble salts and hydrophilic solid that were form. However, the presence of water in crude oil can interfere with refining operations, provoke corrosions, increase heat capacity and reduce the handling capacity of refining equipments and pipelines (Selvarajan et al., 2001). Emulsion resolution is therefore an important element in handling the petroleum, from the time it is produced until it enters the refining process.

In order to minimize the production problems related with crude oil emulsions and environmental concerns, petroleum operators need to prevent their formation or to break them (Gafonova, 2000). In some cases when the formation of emulsions is a result of poor operation practices, it is possible to prevent emulsion formation. Nevertheless, in many instances emulsion formation is predictable. The exclusion of water during recovery from the oil wells and prevention of agitation is difficult to realize, and emulsions must be treated.

The treatment of water-in-crude oil emulsions involves the application of, thermal, electrical, chemical process or their combinations. Thermal method or heat treatment in emulsion breaking is usually based on the overall economic picture of a treating facility. Excess heat is not supplementary when it is more commercial to add chemical or set up electrostatic heat. Temperatures are not high enough to significantly rise up water solubility in a particular crude oil, and high temperatures do not cause large amounts of asphaltenes to become insoluble in the crude oil and form an interface pad (Grace, 1992).

Electrical methods disturb the surface tension of each droplet, possibly by causing polar molecules to reorient themselves (Grace, 1992). This reorientation weakens the film around each droplet because the polar molecules are no longer intense at the droplets surface. This process does not typically resolve emulsions completely by itself, although it is an efficient and often required addition of chemicals or heat.

Chemical methods are the most common method of emulsion resolution in both oil field and refinery. The combination of heat and application of chemicals designed to neutralize the effects of emulsifying agents have great advantages of being able to break an interfacial film effectively; without the addition of new equipments or modifications of the existing equipment.

There are anionic, cationic, nonionic and amphoteric surfactants that have been used as demulsifiers. Emulsion breakers are typically specific for site or crude oil type. Conventional emulsion breakers are most commonly formulated from the following type of chemistries; polyglycols and polyglycol esters, ethoxylated alcohols and amines, ethoxylated resin, ethoxylated phenol formaldehyde resins, ethoxylated nonylphenols, polyhydric alcohols, ethylene oxide, propylene oxide block copolymer fatty acids, fatty alcohols, fatty amine and quaternaries and sulfonic acid salts. Basically, commercial emulsion breakers may contain one type of active ingredient.

Polymeric demulsifiers are also the most common demulsifiers used to break water in oil emulsion. The polymeric demulsifiers are capable of adsorbing at the oil or water interface by displacing the interfacial film. Interfacial active fraction presence in the oil posses a sufficient numbers of functional groups that can penetrate into the oil or water interface, and form an interfacial layer which can be broken by demulsifiers (Zaki et al., 1996).

The film that encapsulating the water droplets is formed by adsorbed solid particles or surface-active materials. The rigidity and structure of this film determines the stability of the emulsion. Unfortunately, since crude oil is an extremely complex mixture of many thousand of compounds, it is difficult to identify the role of any of these compounds in the crude oil emulsion stabilization. Despite extensive research, even the composition of the interfacial film is poorly understood. Therefore, it is almost impossible to predict the performance of demulsifiers or other treatment methods (Gafonova, 2000).

The applications of these chemicals as demulsifiers for treating crude oil are specially tailored to act at the oil/water interface. Their high efficiency makes their use a very economic way and attractive to separate oil and water (Staiss et al., 1991). Success of chemical demulsifying methods is dependent upon the adequate quantity of a properly selected chemical must be added into the emulsion, thorough mixing of the chemical with the emulsion, adequately heat may be required to facilitate or fully resolve an emulsion, and sufficient residence time must be allowed in treating vessels to permit settling of demulsified water droplets.

In order to devise optimum treatment for water-in-oil emulsions by using chemical treatment method, it is vital to understand how they are stabilized and destabilized the emulsion. Therefore, screenings of demulsifiers are very important in deciding the most effective demulsifiers in breaking the emulsion system. This result will be lead to demulsifiers formulation for treating Malaysian crude oil emulsion.

1.2 Objectives and Scopes

The objective of this study is to identify, screening the existing demulsifiers and create the new demulsifier formulation for demulsification of crude oil emulsion. Firstly, the study will be focused on single demulsifier in both water and oil-soluble groups. This test will be carried out by using bottle test method at the fixed concentration and temperature for real emulsion systems.

Secondly, by using the best demulsifiers from both groups, the test will be proceeding by varying the concentration to know the flow pattern of demulsification and concentration. Thirdly, the test will be carried out by using modifier instead of demulsifiers to make sure the importance of using modifier in these tests. The results of these studies will lead to the combination of demulsifiers and the optimum concentration will be optimized by using factorial design optimization.

Finally, the effectiveness of this formulation will be tested by using single emulsion system and will be compared with other commercial demulsifiers formulation. The excellent result will be measured from the water separation level.

1.3 Report Outline

Respective chapter of this thesis can be generally identified with one of the objective of research described in section 1.2. The thesis contains five chapters which each chapter respectively containing its own introduction, descriptions of the relative topics and scopes to achieve the objectives of research and summary. Chapter I basically discussed about the entire project study, which contains research background, objectives and scopes of this study and thesis outline.

The historical aspects of crude oil emulsion; characteristics of crude oil, theories of emulsions and demulsification, variability of applied chemicals, and limitation of present demulsifier techniques are presented will be described in Chapter II. This chapter reinforces the belief that a qualitative view of emulsion breaking is essential at this time for the petroleum industry.

All the materials and methods including the material that have been used in the experiments; either equipments or chemicals, experimental methods to break down the emulsion problems and a little bit of analytical methods to determine the physical and chemical properties of crude oil emulsion and demulsification are discussed in Chapter III. Besides, there are a lot of discussion about demulsifiers screening process and optimization by using two level factorial design.

The discussions and elaborations of experimental results, which are based on the combination of the theories from the literature studies and the results obtained from the research, are noticed in Chapter IV. The conclusions of this thesis are based on demulsification formulation on treating Malaysian crude oil emulsion and remarks are discussed in Chapter V. Beside that, the recommendations for future study are also included to give the ideas in doing this study.

1.4 Summary

Emulsion problems in crude oil production and processing have gained serious consideration either from fundamental and practical aspects by oil companies as well as researchers for the last few decades. One of the focuses is on developing effective demulsifiers, which involves screening, formulation, testing and demulsification study for crude oil demulsification process. This study will address some of the fundamental and practical aspects of these areas of interest.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Crude oil is a complex fluid containing asphaltenes, resins and napthenic acid. Asphaltenes is the heaviest and most polar fraction in the crude oil and responsible in rising up the variety of nuisances and stabilized the water in oil emulsion that occurred during crude oil production. It is widely known that deposition and flocculation of asphaltenes may be occurred when the thermodynamic equilibrium is disturbed (Auflem, 2002).

The potential of oil recovery will be reduced by the adsorption of asphaltenes on to the reservoirs mineral surfaces, whereby the wet ability of the reservoir is changed from water-wet to oil-wet. Furthermore, the asphaltenes may deposit on the steel walls and accumulate in the fluid processing units. Clean up of deposited asphaltenes caused reducing the oil production.

The water and oil phases are co-produced during oil production and transportation. The dispersion of water droplets in oil or oil droplets in water will be formed by sufficient mixing energy from the refinery. The interfacial active agents in the crude oil such as asphaltenes, resins and naphtenic acid may accumulate at the water-oil interface and hinder the droplets to separate. Among these components, asphaltenes are believed to be the major causes in stabilized the emulsion. This is because they tend to adsorb at water-in-crude oil interfaces to form a rigid film surrounding the water droplets and protect the interfacial film from rupturing during droplet-droplet collisions (Sjöblom et al., 1992). Consequently, the formation of particularly stable water-in-crude oil emulsion is facilitated.

Emulsion problems in crude oil productions resulted in a demand for expensive emulsion separation equipment such as water treaters, separators and coalescers. Hence, chemical demulsification is the suitable method from both operational and economic point of view to break the crude oil emulsion. A chemical agent typically acts on the interfacial film by either reacting chemically with the polar crude oil components or by modifying the environment of the demulsification. Among chemical agents, interfacial-active demulsifiers, which weaken the stabilizing films to enhance droplets coalescence, are preferred due to lower additions rates needed.

Crude oil specificity has long been recognized and many demulsifier products are formulated as a mixture of agents in a career solvent to improve performance. There are four types of surfactants that have been used as demulsifiers; ionic, anionic, cationic and zwitterionic. The early demulsification relied on the reversal of the emulsion type demulsifier as hydrophilic ionic surfactants followed by oil-compatible anionic surfactants.

The formulation of commercial demulsifiers is largely based on empirical approaches in an attempt to get the effective, which can work in shorter separation times and at smaller dosages (Selvarajan et al., 2001). Typically laboratory testing is followed by evaluation under more representative dynamic conditions in a pilot scale process unit and eventually in the field.

According to Grace (1992), emulsions of oil and water are one of many problems directly associated with the petroleum industry, in both oil-field production and refinery environments. Whether these emulsions are created inadvertently or are unavoidable, as in the oil field production area, or are deliberately induced, as in refinery desalting operations, the economic necessity to eliminate emulsions or maximize oil-water separation is present. Furthermore, the economics of oil-water separation dictate the labor, resources and monies dedicated to this issue. Before we describe the methods and economics of emulsion breaking at commercial facilities, we will restate several key concepts concerning emulsions and petroleum industry."

Therefore, considering many aspects that are related in petroleum processing, it is important to develop the demulsifier formulation to solve the emulsion problems. The aspects that are important to be studied are such as crude oil composition and characterization, emulsions and emulsion stability, stabilization of water-in-crude oil emulsions and destabilization of crude oil emulsions.

2.2 Crude Oil Emulsion Composition

2.2.1 Introduction

Crude oil contains complex mixture of organic composite. Its composition can vary due to its reservoir's place of origin, depth and age (Speight, 1991). Crude oils mainly consists the mixture of hydrogen and carbons, with little amount of sulphur, nitrogen and oxygen as well as structures with incorporated metallic molecules such as nickel, vanadium, copper and iron (Speight, 1991). There is a broad variation in physical properties from the lighter oils to the bitumens. For this reason, several classification systems of petroleum were proposed based on different criteria: viscosity, density (specific gravity or API gravity), pH, surface tension and interfacial tension.

Crude oils consist of light hydrocarbon such as gasoline, asphaltenes, resins, waxes and napthenic acid. The asphaltene content of petroleum is an important aspect of fluid process ability. The method of dividing crude oil into four major fractions: saturates (including waxes), aromatics, resins and asphaltenes is called SARA fractionation, based on their polarity and solubility in the solvent. The method of dividing crude oil into these four fractions is illustrated in Figure 2.1.

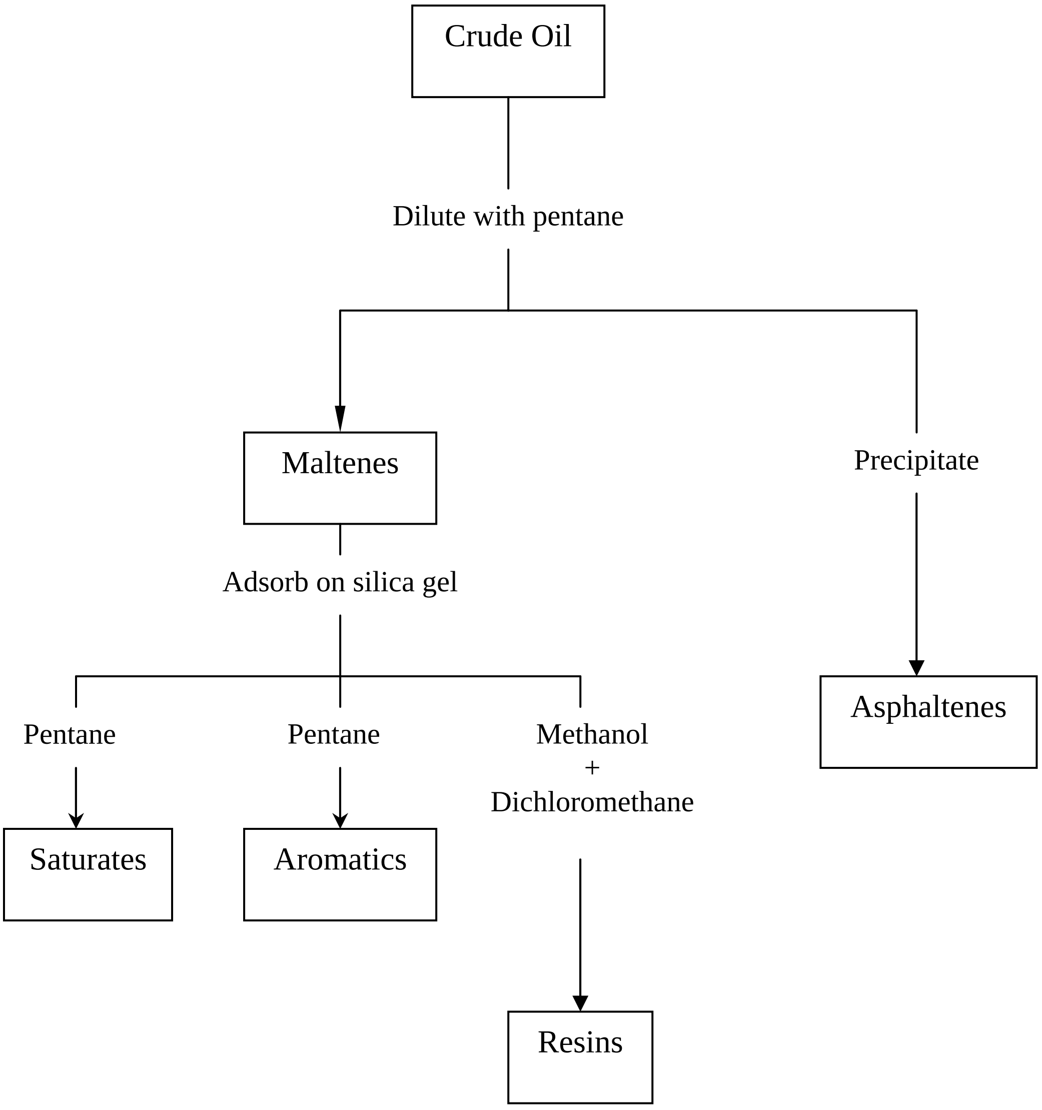

Figure 2.1: Schematic of SARA fractionation of crude oils (Auflem, 2002)

The fractions of crude oil that have been identified as contributing to the formation of water-in-oil emulsion includes asphaltenes, resins and waxes and can exist in both the dissolved and particulate form (Lee, 1999).

The basis method to remove asphaltenes is by precipitation in paraffinic solvent such as n-pentane. Chromatographic fractionation method is used to separate the deasphalted oil into saturates, aromatics and resins (Aske et al., 2001). From the four classes of compounds, only the saturated are easily discernible from the rest of the hydrocarbons in the mixture. This is because of the absence of π-bonds, which allows them to be readily differentiated from the aromatic components by asset of the difference in their polarity. The balance of the oil is contained aromatics and heteroatomic compounds of varying degree of functionalism, alkyl substitution and condensation.

Initially, the crude oil is deasphalted by mixing 1:5 volume ratio of crude oil to n-pentane. The precipitated fraction of the crude oil is the asphaltenes. Subsequently, the deasphalted oil is separated into saturates, aromatics and resins by using adsorbing process on silica gel and solvent method. The SARA analysis of Malaysian crude oil is shown in Table 2.1.

The saturates or aliphatics are non-polar hydrocarbons, having branched alkanes and straight-chain but without double bonds, as well as cycloalkanes or naphtenes. Cycloalkanes contain one or more rings, which may have several alkyl side chains. The proportion of saturates in a crude oil normally decreases with increasing molecular weight fractions, thus the saturates generally are the lightest fraction of the crude oil. Wax is a sub-class of the saturates, consisting primarily of straight-chain alkanes, mainly ranging from C_{20} to C_{30}. Wax precipitates as a particulate solid at low temperatures, and is known to effect emulsion stability properties of crude oil systems (Zaki et al., 2000).

Table 2.1: SARA fractionation of Malaysian crude oil (Ariany, 2001)

Types of Malaysian Crude Oil	**SARA Fractionation**			
	Asphaltenes (wt%)	**Resins (wt%)**	**Aromatics (wt%)**	**Saturates (wt%)**
Semangkok	1.31	35.32	17.43	70.62
Tabu	1.23	36.43	15.46	81.59
Irong Barat	0.37	32.01	45.95	45.63
Seligi	0.32	20.94	16.18	80.47
Tapis	0.11	29.81	18.14	77.51
Guntung	0.45	21.50	20.74	75.42

Each of the fraction consists of thousands of molecular species with various properties and chemical structures as SARA fractions are solubility classes and are separated by their physical properties rather than their chemical nature. The physical properties of Malaysia crude oil are shown in Table 2.2.

Table 2.2: Physical properties of Malaysian crude oils (Ariany, 2001)

Types of Malaysian crude oils	**Physical Properties**				
	Density (g/cm3), 25°C	**Viscosity (cP) 30°C/50°C**	**pH, (26°C)**	**Surface Tension (mN/m)**	**Interfacial Tension (mN/m)**
Semangkok	0.8131	4.56/3.0	7.04	27.2	27.7
Tabu	0.8120	6.48/3.6	6.10	25.6	35.7
Irong Barat	0.8648	8.76/6.5	7.03	29.6	32.8
Seligi	0.7816	3.48/2.9	7.09	25.3	29.6
Tapis	0.7947	3.60/2.9	6.94	25.7	33.8
Guntung	0.8222	5.40/4.3	6.54	26.4	36.7

The term aromatics refer to benzene and its structural derivates. Aromatics are common to all petroleum, and by far the majority of the aromatics contain alkyl chains and cycloalkane rings, along with additional aromatic rings. Aromatics are often classified as mono-, di-, and tri-aromatics depending on the number of aromatic rings present in the molecule. Polar, higher molecular weight aromatics may fall in the resin or asphaltenes fraction (Aske, 2002). The term of asphaltenes and resin will be discussed in Sections 2.2.2 and 2.2.3, respectively.

2.2.2 Asphaltenes

Asphaltenes are dark brown to black amorphous powder and have a specific gravity just above unity, and molar masses of 1000 to 10,000 g/mol (Speight, 1994). Asphaltenes has no definite melting point but decomposes when the temperature exceeds 300-400°C. Many research shown that changing in pressure, temperature and oil composition can cause asphaltene precipitation.

Asphaltenes are the non-volatile and polar fraction of petroleum that is insoluble in n-alkanes such as n-pentane or n-heptane. So, asphaltenes represent of crude oil components, rather than a chemical class. The polarity, molecular weight and aromaticity of precipitated asphaltenes are rise linearly with carbon number of n-alkane precipitant. Figure 2.2 represents the range of heavy compounds precipitated by mixing crude oil with n-pentane and n-heptane.

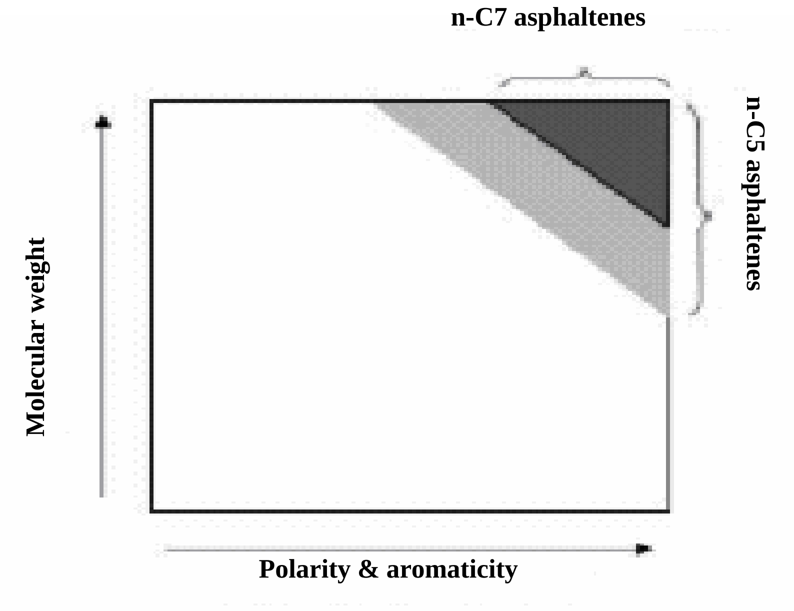

Figure 2.2: Hypothetical diagram representing the molecular characteristics of the asphaltenes precipitated from petroleum by n-alkane addition (Auflem, 2002)

The chemical composition of crude oils, gained from for instance a SARA-analysis, are not fully explain the crude oil behaviour with regard to emulsion stability and asphaltene deposition. The information of the structure of the crude oil, which is a result of interactions between the continuums of chemical constituents in the oil, is the most important. The interactions between the heavy end molecules, the asphaltenes and resins, play the most significant role in this sense.

The asphaltenes consist in part of polycyclic and cycloaliphatic naphtenic acids or of their oil-soluble calcium and magnesium salts, substituted phenols, and steroidcarbonic acids. Most of the inorganic bonds of the crude are in the asphaltenes. Asphaltenes are interfacial active substance exist predominantly in the crude oil colloids. The interfacial active components of the asphaltenes are most active either directly before or during the start of flocculation (Schorling et al., 1998). Asphaltenes also contain metals including nickel, vanadium and iron.

The structure of asphaltenes is not well understood, but several possible structures have been proposed to explain the composition and properties of the asphaltene fraction. The structure for asphaltene is shown in Figure 2.3, which accounts for nitrogen, sulphur and oxygen in asphaltenes, excluding the organometallic. An organometallic complex is also shown which is assumed to complex other asphaltene compounds in the micelle. Such asphaltene sheets appear to be regularly stacked in lamellar and such structures, which are found in other surfactant systems, are known to enhance the emulsion stability (Lee, 1999).

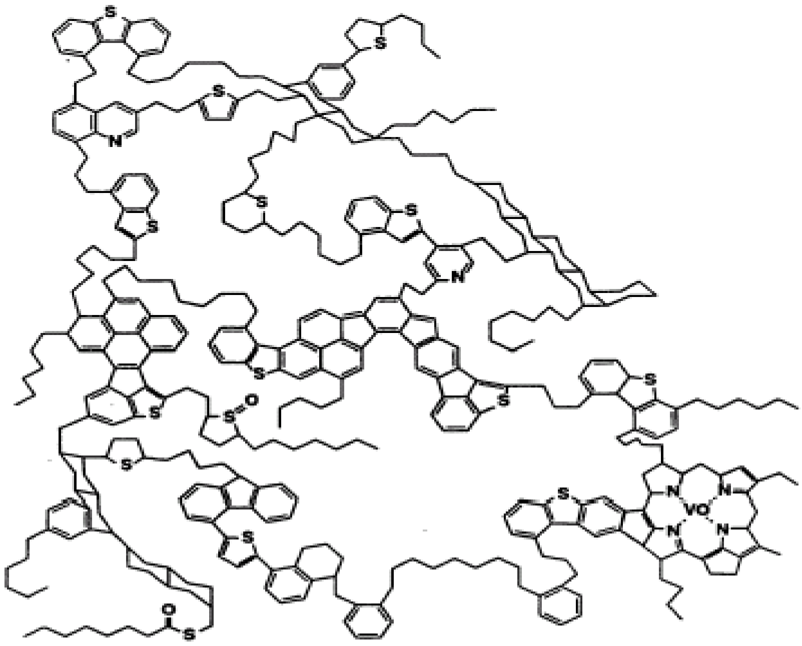

Figure 2.3: Hypothetical representation of an average asphaltene molecule (Gafonova, 2000)

Asphaltenes are believed to be suspending as a microcolloid in the crude oil, consisting of particles of about 3 nm. Each particle consists of one or more aromatic sheets of asphaltene monomers, with adsorbed resins acting as surfactants to stabilize the colloidal suspension. The molecules are believed to be holding together with π - bonds, hydrogen bonds, and electron donor-acceptor bonds (Aske, 2002).

2.2.3 Resins

Resins are black or dark brown semi solid, have a specific gravity near unity, molar mass ranging from 500 to 2000 g/mol and very adhesive materials (Gafonova, 2000). The content of resin in crude oils ranges from 2-40 wt%. From the Table 2.1, the content of resin in crude oil is higher compared to asphaltenes composition. Crude oil with a small amount or no asphaltenes has a lower concentration of resin than those with larger amount of asphaltenes. This is proved from data presented in the Table 2.2.

The resins are defined as the non volatile and polar fraction of crude oil that is soluble in n-pentane, n-heptane and aromatic solvents such as toluene but insoluble in methanol and propanol. The molecular species within the resin are same as to those in the aromatics. But, resins species have higher molar mass, greater polarity, higher heteroatom content and lower H/C ratio compared to aromatics.

The resin fraction consists of carbon, hydrogen, oxygen, nitrogen and napthenic acids. The content of these elements in resin of various crude varies over a narrow range. The widest range is observed in sulfur content (Speight, 1991).
Resins have a much higher H/C ratio compared to asphaltenes, indicating that they are less aromatic than asphaltenes. Asphaltenes are presumed to be maturation products of resin; in the maturation process the cyclic portion of resin molecules undergoes aromatization (Speight, 1991).

It is generally believed that resin molecules are composed of a highly polar end group, which may incorporated sulfur, oxygen or nitrogen, and a long non-polar end group. Nitrogen is present in resins in the form of pyrolle and indole groups. Infrared spectroscopic data indicated the presence of ester, ketone and acid functional groups. Sulfur is present in the form of cyclic sulfides (Gafonova, 2000).

However, structural studies of resin molecules have not been as intensive as they have been for asphaltenes. Resin were presented either as long parrafinic chain molecules with naphtenic rings in the center, or as condensed aromatic and naphtenic ring systems with heteroatoms scattered in different location. The molecular structure of resin is shown in Figure 2.4 (Gafonova, 2000).

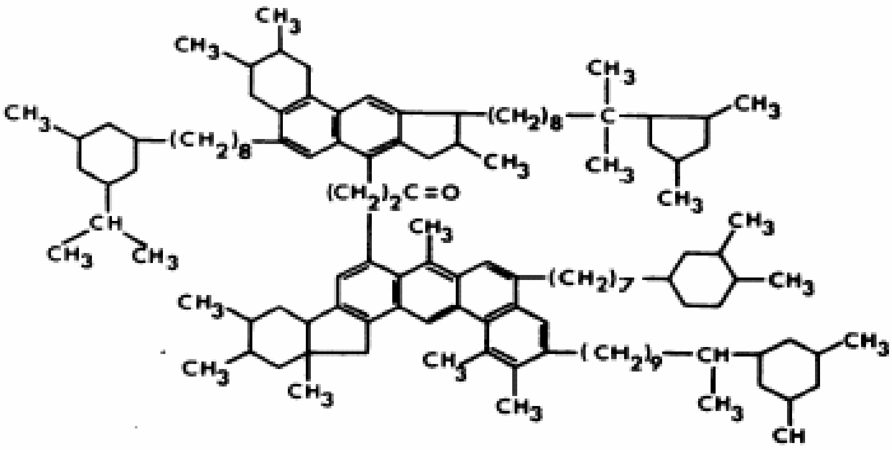

Figure 2.4: Hypothetical representation of an average resin molecule (Gafonova, 2000).

2.2.4 Waxes

Waxes are high molecular weight alkanes. A sensible description of wax is anything with a waxy feel and a melting point above body temperature and below the boiling point of water. According to Becker (1997), waxes have been defined as esters of long-chain (C_{16} and above), monohydric (one hydroxyl group), or alcohols with long-chain (C_{16} and above) fatty acids. Actually, the natural waxes are mixtures of esters and frequently contain hydrocarbon as well.

Waxes form higher-order structures through solubility and inductive force, and the degree of structural complexity is a measure of their concentration and individual molecular weights. It is possible for multiple physical state (gas, liquid, and solid) to coexist under particular condition of pressure and temperature.

Majority of the waxes present in crude oil are in the form of monoxidized alkanes. This is because of the anaerobic (lack of oxygen) conditions under which biodegradation of organic matter takes place to form crude oils. These alkanes

(C_nH_{2n+2}) may also exist as submatic, hetero-cyclic, and polymeric poly-sulfide parents (Becker, 1997).

Figure 2.5 shows the average structure of paraffin wax molecule system (Mussen, 1998). From the diagram, the wax molecules can combine with the fatty tails of the carboxylic acids stabilizing the interface. The crystal structure of waxes is the reason for the combination of wax in solids, asphaltenes and resins.

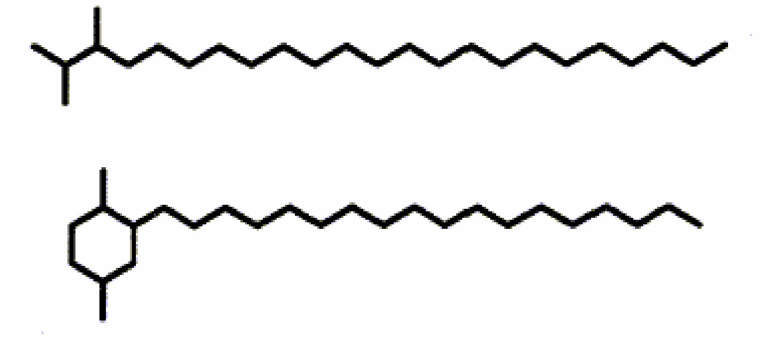

Figure 2.5: Average structure of paraffin wax molecule (Mussen, 1998)

2.2.5 Solids

Asphaltenes that precipitated from bitumen contain some other insoluble material referred as "solids". This finely divided solids such as sand, wax crystals and clay particles can stabilize emulsions (Isaacs and Chow, 1992). The recent studies of Isaac and Chow (1992) demonstrated that solids prevent thinning of the thin film and the caused of the crude-oil film are so persistent.

According to Pal et al. (1992), the role, which solids played in stabilizing emulsions is affected by the size of the solids. Smaller solids tend to give a higher yield stress, whereas larger solids tend to induce more pronounced shear thickening behaviour. When the emulsion-solids mixtures are of shear-thinning nature, smaller solids yield a higher viscosity compared to larger solids. However, when shear thickening occurs, the effect of solids size on the viscosity of the mixtures seems negligible.

When the oil droplets in an emulsion are sufficiently smaller than solids, the emulsion is the continuous phase for the solids. The solids cannot be treated as oil droplets even if the size and size distribution of the solids are similar to the oil droplets. The addition of solids to an emulsion generally give a higher viscosity than the pure emulsion at the same total concentration.

2.2.6 Hydrocarbons

Hydrocarbons exist in the liquid, solid or gaseous state, generally depending on the number and arrangement o f the carbon atoms in their molecules. At normal temperature and pressure, those hydrocarbon molecules with up to four carbons are gaseous, those with twenty or more carbons are solid and those in between are liquid such as crude oils. Crude oils are mixture of hydrocarbon usually with a small portion of nonhydrocarbon such as oxygen, sulphur and nitrogen.

The simplest hydrocarbon is methane, it is comprises o f one carbon atom surrounded by four hydrogen atoms. Two or more carbon atoms joined to one another as well as to hydrogen atoms. The carbon atoms may link together in a straight chain, a branched chain or a ring. The simpler hydrocarbons found in crude oils are paraffins (saturated hydrocarbon) in which each carbon atom is linked with the maximum possible number o f hydrogen atoms with the generic formula of $C_n H_{2n+2}$. Hydrocarbons with straight or branched carbon atom chains and contains less than the maximum of hydroqen atoms per carbon atom are called "unsaturated" or "olefinic" and have the generic formula of $C_n H_{2n}$. Petroleum crude oils contain hundreds of different hydrocarbons, some of which are as complex as$C_{85}H_{60}$ (Rhee et al., 1989).

2.2.7 Oilfield brine

Binks (1993) studied that o/w droplets increase in size solubilizing more oil with increasing salt concentration while w/o droplets decrese in size. At low and high salt concentrations, the monolayer constrained to lie at the flat interface has a preferred tendency to curve and increase the tension. At intermediate concentrations, the tension is least because the flat monolayer has no tendency to curve.

Tambe and Sharma (1993) studied the effect of inorganic salts such as sodium chloride and calcium chloride on emulsion stability for some pH values. Seems that the presence of salt has an adverse effect on emulsion stability and decrease as pH increase. They concluded that the stability of oil-in-water emulsion decrease in favour of relatively more stable water-in-oil emulsion as pH increased.

2.3 Crude Oil Emulsion Formations and Stability

2.3.1 Classification of emulsions

Emulsion have long been of great practical interest due to their widespread occurrence in everyday life. They may be found in important areas such as food, cosmetics, pulp and paper, pharmaceutical and agricultural industry. Petroleum emulsions may not be as familiar but have a similar long-standing, widespread, and important occurrence in industry, where they are typically undesirable and can result in high pumping costs, pipeline corrosions, reduced throughput and special handling equipment. Emulsions may be encountered at all stages in the petroleum recovery and processing industry (drilling fluid, production, process plant, and transportation emulsions.

An emulsion is usually defined as a system in which one liquid is relatively distributed or dispersed, in the form of droplets, in another substantially immiscible liquid. The emulsion formation is a result of the co-production of water from the oil reservoir. During processing, pressure gradients over chokes and valves introduce sufficiently high mechanical energy input (shear forces) to disperse water as droplets in the oil phase (Aske, 2002).

Emulsions are a special kind of colloidal dispersions, which have at least one dimension between about 1 and 1000 nm. The dispersed phase is sometimes referred to as the internal phase, and the continuous as the external phase. Emulsions also form a rather special kind of colloidal system in that the droplets often exceed the 1000 nm limited size (Schramm, 1992).

In the petroleum industry the usual emulsions encountered are water droplets dispersed in the oil phase and termed as water-in-oil emulsion (W/O), conversely, if the oil is the dispersed phase, it is termed oil-in-water (O/W) emulsion. Figure 2.6 shows the two simplest kinds of this emulsion.

Oil-in-Water (O/W)

Water-in-Oil (W/O)

Figure 2.6: The schematic representation of two types of emulsion (Modified from Schramm, 1992)

In addition to the usual emulsion types, multiple emulsions for instance, oil droplets dispersed in water droplets that are in turn dispersed in a continuous oil phase (O/W/O) can occur.

The type of emulsion that is formed depends upon a number of factors. If the ratio of phase volumes is very large or very small, then the phase having the smaller volume is frequently the dispersed phase. If the ratio is closer to 1, the other factors determine the type of emulsion formed. Table 2.3 shows some simple examples of petroleum emulsion type.

Table 2.3: Examples of emulsion in the petroleum industry (Schramm, 1992)

Occurrence	**Usual Type**[a]
Undesirable Emulsions	
Well-head emulsions	W/O
Fuel oil emulsions (marine)	W/O
Oil sand flotation process, froth	W/O or O/W
Oil sand flotation process, diluted froth	O/W/O
Oil spill mousse emulsions	W/O
Tanker bilge emulsions	O/W
Desirable Emulsions	
Heavy oil pipeline emulsion	O/W
Oil sand flotation process slurry	O/W
Emulsion drilling fluid, oil-emulsion mud	O/W
Emulsion drilling fluid, oil-base mud	W/O
Asphalt emulsion	O/W
Enhance oil recovery in situ emulsions	O/W

[a] W/O means water-in-oil; O/W means oil-in-water.

2.3.2 Emulsion formation

According to Schubert and Armbruster (1992), there are three main criteria that are necessary for formation of crude oil emulsion:

1. Two immiscible liquids must be brought in contact;
2. Surface active component must present as the emulsifying agent;
3. Sufficient mixing or agitating effect must be provided in order to disperse one liquid into another as droplets.

During emulsion formation, the deformation of droplet is opposed by the pressure gradient between the external (convex) and the internal (concave) side of an interface. The pressure gradient or velocity gradient required for emulsion formation is mostly supplied by agitation. The large excess of energy required to produce emulsion of small droplets can only be supplied by very intense agitation, which needs much energy.

A suitable surface active component or surfactant can be added to the system in order to reduce the agitation energy needed to produce a certain droplet size. The formation of surfactant film around the droplet facilitates the process of emulsification and a reduction in agitation energy by factor of 10 or more can be achieved (Becher, 1955).

A method requiring much less mechanical energy uses phase inversion. For example, if ultimately a W/O emulsion is desired, then a coarse O/W emulsion is first prepared by the addition of mechanical energy, and the oil content is progressively increased. At some volume fraction above 60-70%, the emulsion will suddenly invert and produce a W/O emulsion of much smaller water droplet sizes than were the oil droplets in the original O/W emulsions (Schramm, 1992).

2.3.3 Emulsion stability

Stability is widely used to refer to the persistence of an emulsion in the environment, and has been identified as an important characteristic of water-in-oil emulsions. Some emulsions quickly decompose into separate oil and water phases once removed from the sea surface, while more stable emulsions can persist for days to years. Recent work indicates that the viscosity of an emulsion is correlated with its stability (NRT Science & Technology Committee, 1997).

Stability is a consequence of the small droplet size and the presence of an interfacial film on the droplets in emulsions, which make stable dispersions. That is the suspended droplets do not settle out or float rapidly, and the droplets do not coalesce quickly.

According to Schramm (1992), "colloidal species can come together in very different ways. In the definition of emulsion stability, it is considered against three different processes; creaming (sedimentation), aggregation and coalescence" as shown in Figure 2.7.

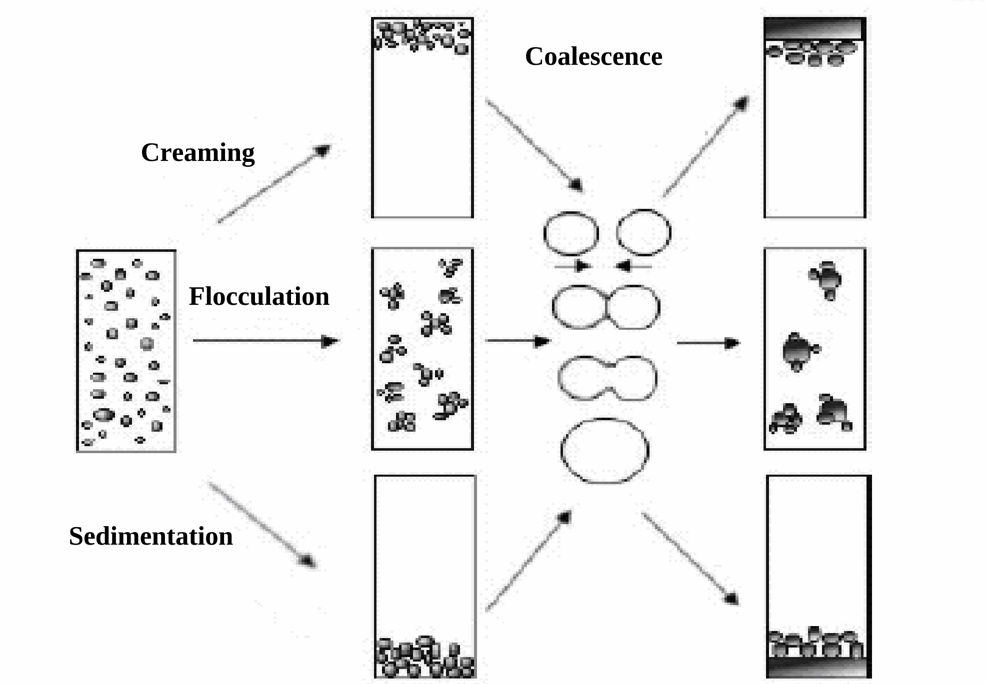

Figure 2.7: Processes taking place in an emulsion leading to emulsion breakdown and separation (Auflem, 2002)

Creaming is the opposite of sedimentation and results from a density different between the two liquid phases and creates a droplet concentration gradient, which result in a close packing of droplets. In aggregation, two or more droplets clump together, touching only at certain points, and with virtually no change in total surface area. So, aggregation of droplets may be said to occur when they stay very close to each other for a far longer time than if there were no attractive forces acting between them. The species retain their identity but lose their kinetic independence because the aggregation moves in single unit. Aggregation of droplets may lead to coalescence and the formation of larger droplets until the phase becomes separated.

In coalescence, two or more droplets fuse together to form a single larger unit with a reduced total surface area. The mechanism of coalescence occurs in two stages; film drainage and film rupture. In order to have film drainage there must be a flow of fluid in the film, and a pressure gradient present (Auflem, 2002). However, when the interfacial film between the droplets has thinned to below some critical thickness, it ruptures, and the capillary pressure difference causes the droplets to rapidly fuse into one droplet. Hence, the properties of the thin film are of extremely important for the separation. If the droplets deform, the area of the interface increases with the drainage path in the film also increase, and resulting in lower drainage rates. On the other hand, the original species lose their identity and become part of a new species.

All emulsions, perhaps with the exception of microemulsions, are thermodynamically unstable but may be relatively stable in kinetic sense (Schramm, 1992). An emulsion can be kinetically stable with respect to coalescence but unstable with respect to aggregation.

According to NRT Science & Technology Committee (1997), emulsion can be categorized into stable, unstable and meso-stable emulsions according to stability and operational definitions:

- Stable emulsions will persist for days, weeks and longer. They showed the viscoelastic properties and viscosities are at least three orders of magnitude greater than that of the starting oil. In addition, stable emulsion will increase with viscosity over time. It has been postulated that the stability is derived from the strong viscoelastic that were caused by asphaltenes and perhaps along with resins. Increasing alignment of asphaltenes at the oil-water interface may cause the increasing of viscosity.

- Unstable emulsions usually persist for only a few hours after mixing stops. These emulsions are ready to separate into oil and water due to insufficient water particle interactions. However, the oil may retain small amounts of water, especially if the oil is viscous.

- Meso-stable emulsions are probably the most common emulsion that was formed in the fields. These emulsions can be red or black in appearance. This emulsion has the properties between stable and unstable emulsions. It is suspected that these emulsions contained either insufficient asphaltenes to render them completely stable or contained too many destabilizing materials such as smaller aromatics. The viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Meso-stable emulsions may also degrade to form layers of oil and stable emulsions.

Other factors that usually support emulsion stability are relatively small volumes of dispersed phase, high viscosity of the bulk phase and low interfacial tension. A narrow droplet distribution of droplets with small sizes is also advantageous, since polydisperse dispersion will result in a growth of large droplets will form at the expense of small one, an effect termed as Ostwald Ripening (Urdahl and Sjoblom, 1995).

In the petroleum production industry, the flocculation and coalescence is overcome by the present of the natural occurring surface-active component such as asphaltenes, resins, waxes and clay that stabilize the emulsion. These surfactants facilitate the emulsion formation and stability by lowering the interfacial tension and there, by favored the droplet break-up beside prevents recoalescence and flocculation of dispersed droplets.

Otherwise, the droplets may prevented to come into contact with each other because of the electrical double layer repulsion, or stearic stabilization by surfactants and polymer with protruding molecular chains. A strong mechanical and elastic interfacial film will be formed in the presence of the polymer, surfactant and adsorbed particles. The most stable emulsion occur when the contact angle is close to 90°C and a film of closed packed particles has considerable mechanical strength, so that the particles will collect at the interface. Particles, which are water-wet tend to stabilize O/W emulsions while those oil-wet tend to stabilize W/O emulsions (Auflem, 2002).

Water-in-oil emulsion will be formed when certain crude oils mixed with seawater (which have their natural brine, NaCl) and produced droplets of water, dispersed in the oil (Figure 2.8). Mixing energy, required to form emulsions, is provided in the ocean by wind or wave turbulence (Lee, 1999).

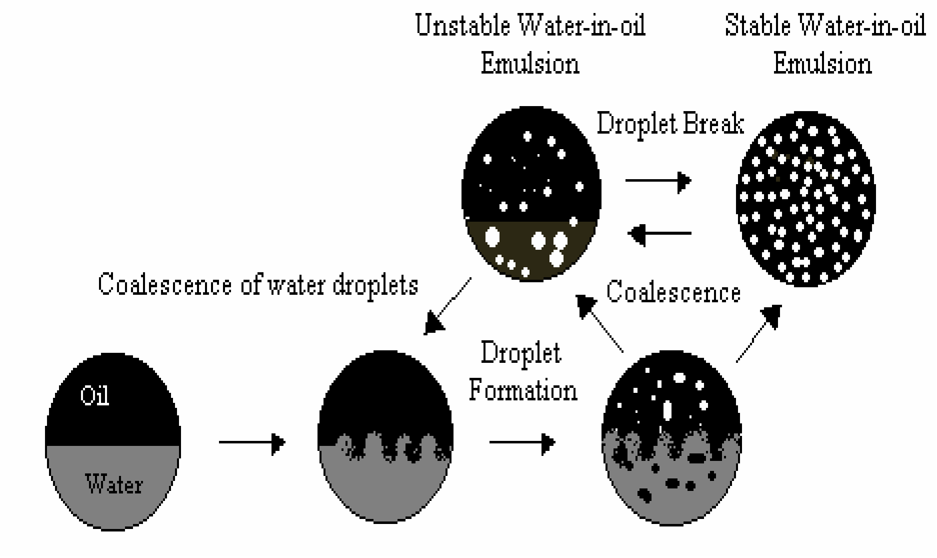

Figure 2.8: Formation of water-in-oil emulsion (Modified from Lee, 1999)

Water-in-crude oil emulsion can form in the processing of fluids from hydrocarbon reservoirs to the refinery or in production facilities during extraction and cleaning. The emulsified water adds significant volume to the crude oil, causes corrosion in the pipelines and increases the cost of transportation and refining. Beside that, water-in-crude oil emulsions can form in oceanic spills. This emulsion is very stable and the oil phase is difficult to recover, leading to great environmental damage. They are often named as chocolate mousse due to their colour and semisolid. Because of that reasons, many oil industry interested in crude oil emulsions.

Knowledge of the factors, which help the stabilization of these emulsions and the manner in which these emulsion are stabilized as discussed in section 2.3.3, will be used in demulsification of these emulsions (Bhardwaj and Hartland, 1998). The predominant mechanism whereby petroleum emulsion is stabilized, through the formation of a film where consists of a physical, cross-linked network of asphaltenic molecules, which aggregate through lateral intermolecular forces to form primary aggregates or micelles at the oil-water interface (Auflem, 2002). The film is elastic or viscous properties.

This interfacial film plays an important role in stabilizing the water droplets against coalescence and these films offer extremely high resistance to drainage. The parameters that control film drainage include film viscosity and elasticity. Film drainage depends on a number of factors including interfacial tension and tension gradient, as well as the rheological properties of bulk and surface phases (Aveyard et al., 1992)

The interfacial activity of crude oils was thought to result from the presence of polar components including asphaltenes, resins and organic acids. Asphaltenes were thought to be peptized in the oil phase by the resinous components, and are hence prevented from precipitation. However, when water is introduced to the crude oil, the asphaltenic aggregates in the oil phase adsorb to the new oil-water interface. For asphaltenes in particular, the presence of heteroatoms in the essentially aromatic structure impart amphiphilic characteristics.

Kilpatrick et al. (2001) have shown that the resins are unnecessary in the stabilization of the asphaltenic film. The exact conformation in which asphaltenes organize at oil-water interfaces and the corresponding intermolecular interactions have yet to be agreed upon. The often suggested explanations are either H-bonding between acidic functional groups (such as carboxyl, pyrollic and sulfoxide), electron donor-acceptor bonding between transition metal atoms and electron-rich polar functional groups, or some other type of force such as π-bonding between delocalized π electrons in fused aromatic rings. The relative strength and importance of each in forming the viscoelastic film and their consequent roles in stabilizing water-in-oil emulsions have still not been fully explained.

As stated above, certain fractions of crude oil that have been identified include waxes, asphaltenes and resins which can exist in both the dissolved and particulate form as contributing to the formation of water-in-oil emulsions. A number of studies have demonstrated the importance of asphaltenes, resins and waxes in promoting and stabilizing water-in-oil emulsions. Removal of asphaltenes from crude oils by silica column produced oil that did not form water-in-oil emulsion (Lee, 1999).

Many researchers suggested that stable water-in-oil emulsions can be produced by a variety of compounds and mixtures. While asphaltenes and resins clearly play an important role in the formation of stable emulsions, there are oils with significant amounts of asphaltenes, which do not produce stable emulsions. Certain type of compounds in the asphaltenes and resins with surfactant properties likely play a major role in producing stable emulsions. Compounds with higher solubility in the oil phase than in the aqueous phase are the most likely emulsifying agents to produce stable water-in-oil emulsions.

Waxes and sea water particles, such as clays can contribute to the stability of water-in-oil emulsions, but cannot by themselves produce stable emulsions as discussed in Sections 2.2.4 and 2.2.5. Similarly, surfactants produced during the photo-oxidation of oil are assumed to still require the presence of asphaltenes and resins to produce stable water-in-oil emulsions. Photo-oxidation of oil means that emulsions formed with fresh crude were unstable, while after exposure to light, these crudes formed stable emulsions (Lee, 1999). Thus, essential to the formation of stable water-in-oil emulsion are sufficient amounts of certain polar compounds, such as nickel porphyrins, found in the asphaltenes and resins of crude oil. If insufficient amounts of these polar compounds are present in the oil, then the presence of waxes and other particles will not lead to the formation of stable emulsions.

Besides asphaltenes, resins and waxes, emulsion stability is strongly influenced by solvents, temperature, the pH of the water phase, and the presence of solid particles such as clays and sand.

2.4 Chemical Demulsification of Crude Oil Emulsion.

2.4.1 Introduction

Crude oil is found in the reservoir in association with gas and saline formation water. As the reservoir becomes depleted a time will be reached when water is coproduced with oil. The number of wells now coproducing water with crude oil is steadily increasing; these immiscible fluids are readily emulsified by the simultaneous action of shear and pressure drop at the well head, chokes and valves (Bhattacharyya, 1992).

Demulsification or emulsion breaking is necessary in many practical applications such as the petroleum industry, coating, painting, and waste water treatment in environmental technology (Kim, 1995). Demulsification has gained in importance because the use of steam and caustic injection or combustion process, for in-situ recovery of heavy crude oils, is complicated by the production of viscous emulsions of oil, water and clay. The demulsification of crude oil emulsions forms an integral part of crude oil production.

Destabilization of water-in-crude oil emulsion is carried out by using either four methods such as mechanical, chemical, thermal, or electrical. Other methods such as pH adjustment, filtration, membrane separation and heat treatment techniques, may also be used (Gafonova, 2000). The knowledge about the properties and characteristics of the emulsion and the mechanisms that are taking place during coalescence of water droplets are required in a fast separation (Ese et al., 1999).

There are many kinds of mechanical separation tools that are typical equipment used in destabilization the crude oil emulsion such as cyclones, gravity settling tanks, centrifugal separators and so on. However, this hardware is considerable volume as well as expensive to install on offshore platforms typical for North Sea conditions. Therefore, it is a great economical benefit whenever the installation can be kept at a minimum in number and size (Auflem, 2002)

Thermal method is by the addition of heat to enhance emulsion breaking in both refinery and oil field. In the oil-field environment, resolution may occur with light oils in which paraffin forms the prime emulsifying agents. An increase in temperature above the paraffin melting point ranging between 50-65°C may completely destabilize an emulsion (Grace, 1992). So, the optimum operating temperature at refinery is 70°C. The application of heat alone is rarely providing sufficient emulsion resolution.

Electrical method is the principle of electrostatic dehydration in demulsification for both oil-field production and refinery desalting. The electric field produced disturbs the surface tension of each droplet, possibly by causing polar molecules to reorient themselves. This reorientation weakens the film around each droplet because the polar molecules are no longer concentrated at the droplets surface. Besides, a mutual attraction of adjacent emulsion particles receives induced and oriented charges from the applied electric field (Grace, 1992). This mutual attraction places oppositely charged particles in close proximity to each other. So, the film is weakened and the droplets are electrically attracted to each other and lead to coalescence to occur.

The most common method of demulsification in both oil-field and refinery application is the combination of heat and application of chemical design to neutralize and eliminate the effects of emulsifying agents (Grace, 1992; Auflem, 2002). The capital cost of changing and implementing a chemical emulsion-breaking program is relatively small and can be done without shutdown. The separation rate of W/O emulsion is due to the demulsifier with the emulsion stability, the temperature, the process vessel, the concentration, the process residence time and the mixing energy.

The most common method of determining relative emulsion stability for lab-scale is the simple bottle test. The bottle test is an empirical test in which varying amounts of potential demulsifiers are added into a series of tubes or bottles containing subsample of an emulsion to be broken. After some specific time, the extent of phase separation and appearance of the interface separating the phases are noted. In addition of demulsifiers, a solvent may be added to reduce viscosity. There are probably as many different bottle test procedures as there ere people who routinely use them. In general, they involve shaking agitating to homogenize the emulsion or to mix in the demulsifier to be evaluated, and a waiting and watching period during which the extent of phase separation is monitored along with the clarify of the interface and the turbidity of the water phase.

The optimization of the amount and type of chemical employed, contributes to reduce the oil content in the produced water offshore. The development and use of environmentally friendlier chemicals is facilitated through building up more fundamental knowledge concerning the process involved in stabilizing and breaking the emulsions. Success of chemical demulsifying methods dependent upon the following:

1. An adequate quantity of a properly selected chemical must enter the emulsion.
2. Thorough mixing of the chemical in the emulsion must occur
3. Sufficient heat may be required to facilitate or fully resolve an emulsion.
4. Sufficient residence time must exist in treating vessels to permit settling of demulsified water droplets.

Chemical demulsification is the most widely applied method of treating water-in-oil and oil-in-water emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. The stability of emulsions is largely affected by the nature of the interface/film and surfactant adsorption mechanisms (Kim, 1995).

The process of chemical demulsification of a water-in-crude oil emulsion involves the acceleration of the coalescence as well as the film rupture process. Dispersed water droplets approach each other and flatten to form a thin film of continuous oil phase between them, the outward drainage flow of the film can create gradients in interfacial tension which then oppose and slow down such drainage. The rate of coalescence will depend upon the factors that bring the droplets together, e.g. concentration, and then on the balance of forces that stabilizes and disrupt the interface. The tendency for the drops to coalesce will be the van der Waals forces when the lamellae are thin enough, and the restoring forces will be the Gibbs-Marangoni effect (Figure 2.9). This effect will operate due to the distortion and increase in surface area of the drops as they get close together. So, it can be concluded that the stability of emulsions is largely affected by the nature of the interfacial film and surfactant adsorption mechanisms.

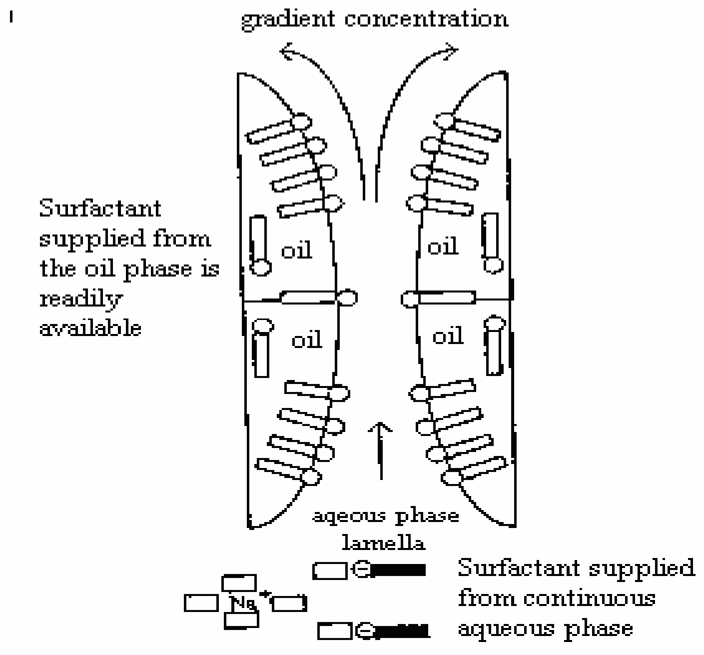

Figure 2.9: The Gibbs-Marangoni effect (Porter, 1994)

2.4.2 Demulsifiers characteristics

Demulsifiers are molecules that aid the separation of oil from water usually at low concentrations. They prevent formation of a water and oil mixture. Demulsifiers typically have limited solubility in the oil phase and migrate to the oil-water interface when the oil is mixed with water. The structures of demulsifiers are not easily categorized as emulsifiers. Some demulsifiers are polymers. Others have structures similar to non-ionic emulsifiers. Demulsifiers are surfactants that are important in breaking the emulsion system.

2.4.2.1 Physical and chemical properties of demulsifiers

Since demulsifiers are surfactants, understanding the role of demulsifiers as a surface active agents are very important. Basically, there are two groups in the demulsifier molecule; hydrophobic (water disliking) group and a hydrophilic group (water liking group). A demulsifier molecule can be shown as in Figure 2.10.

The hydrophobic group such as long chain alkyl group is not repelled by water, since the attraction of the hydrocarbon chain for water is approximately the same as itself. In fact, at very low concentration of demulsifier in the water the hydrocarbon chains will lie flat on the surface

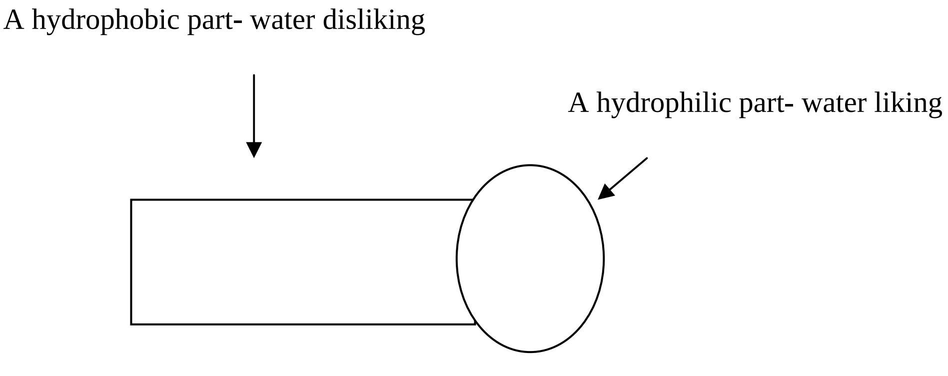

Figure 2.10: Basic structure of demulsifier (Porter, 1994)

The hydrophilic effect is referred to the water-preferring nature of species (atom, molecule, droplet and particle). Hydrophilic usually means that a species prefers the aqueous phase rather than the oil phase. In this sense, hydrophilic has the same meaning of oleophobic.

Hydrophilic molecules are believed to decrease the degree of order in water molecules around them. So, ions in solution are hydrophilic such as carboxylate, sulphate, phosphate, sulphonate and quaternary ammonium. Primary amines, amine oxides, phosphine oxide and sulphoxides are polar groups with a highly electronegative character which shown strong electrophilic properties (Porter, 1994).

If the molecules contain electronegative atoms capable of associating with the hydrogen-bonding network in water, these molecules are considered as hydrophilic. The examples of molecules that include in this group are ethers, aldehydes, amides, esters, oxygen atom in alcohol, nitrogen atom in amides, amines, ketones and nitroalkanes.

This effect sometimes can be diminished when the molecules, which contain the hydrophilic effect are attached to the hydrophobic group. But this phenomena will not be happened if a number of such nonpolar groups are attached to the hydrophobic groups, so that limited or entire water solubility can be achieved, depending upon the relative size of the hydrophobic effect and the number of hydrophilic groups.

Beside that, there are a lot of water soluble polymeric demulsifiers such as the emulsion tetrapolymer of methylmethacrylate, butyl acrylate, acrylic acid and methacrylic acid and dispersions of water soluble cationic polymers (Bhattacharyya, 1992).

The hydrophobic effect is referred to the water-avoiding nature of a species (atom, molecule, droplet, and particle). Hydrophobic usually means that a species prefers the oil phase to the aqueous phase. In this sense, hydrophobic has the same meaning as oleophilic. Oil soluble demulsifiers are also known as hydrophobic groups.

There are a lot of reasons that causes the insolubility of the hydrogen chain in water. These reasons include the mechanism that involve both entropic and enthalpic contributions and the unique multiple hydrogen bonding capability of water (Porter, 1994). There is a reorientation and restructuring of water around nonpolar solutes, which disrupts the existing water structure and imposes a new and more ordered structure on the surrounding water molecules. This will result the decreasing in entropy value. Hydrophobic groups tend to increase the degree of order in water molecules around them.

The aqueous solubility of alone demulsifier molecule will depend upon the relative strengths of the hydrophobic and hydrophilic effects. They are not independent, since both rely on the structure of the hydrogen bonds around the hydrophilic and hydrophobic groups.

2.4.2.2 Demulsifiers classification

There are four types of demulsifiers that are used to break the crude oil emulsion. They are anionic, cationic, nonionic and amphoteric. Early demulsification relied on the reversal of the emulsion type demulsifier such as hydrophilic ionic demulsifiers. These types were followed by oil-compatible non-ionic surfactants based on ethylene and propylene oxide resins (Selvarajan et al., 2001). The most effective demulsifier formulations are by the combination of all types of demulsifiers. The classification given is based on the chemical structure of the hydrophilic group (Porter, 1994).

Anionics are used in practically every type of detergents, which are the main application of demulsifiers. This is because they are easy to produce and have low manufacturing cost. Anionics are manufactured and used in greater volume compared to the all other types of demulsifiers (Porter, 1994). The surface-active part of the anionics molecule carries a negative charge and has a long chain hydrophobe carrying the negative charge.

The anionics have the advantage of being high and stable foaming agents; however, they do have the disadvantage of being sensitive to minerals and the presence of minerals in water (water hardness) or pH changes.

Nonionic demulsifiers are demulsifiers that do not have a charged group. Nonionic surface-active agents have a hydrophobic/hydrophilic balance wherein there is neither a negative nor a positive charge in either part of the molecule, thus giving it the nonionic terminology.

These surface-active agents have the advantage that they are not affected by water hardness or pH changes as the anionic and cationic demulsifiers are, and in many cases it is an advantage that they are considered medium to low foaming agents. It is especially advantageous when a very low foaming surface-active agent is required. A water-soluble group that does not ionize to any great degree provides the hydrophilic group. Those groups used in practice are shown in Table 2.4.

Table 2.4: Water-soluble group (Porter, 1994)

Hydroxyl	C-OH	Poor hydrophilic properties
Ether	C-O-C	Poor hydrophilic properties
Amine oxide	N→O	Excellent hydrophilic properties
Phosphine oxide	P→O	Excellent hydrophilic properties
Sulphoxide	S→O	Excellent hydrophilic properties
Triple unsaturation	C≡C	Very poor hydrophilic properties
Ester group	COO-	Very poor hydrophilic properties
Amide group	CONH-	Very poor hydrophilic properties

The word amphoteric is from the Greek word *amphi*, means both (Porter, 1994). So, this term is used to describe demulsifiers that have both a positive (cationic) and a negative (anionic) group. They form cations in acidic solutions and form anions in alkaline solutions. In the middle pH range, they form zwitterions that are molecules with two ionic groups of opposite charge. The term ampholyte are used sometimes. So, these groups of demulsifiers are depending on the pH value

By adjusting the pH of aqueous solution the anionic or cationic character of the amphoteric can be changed. At some intermediate pH value, not necessary 7, both ionic groups show equal ionization and this pH is called the isoelectric point or area. This type of molecule is called zwitterions.

The ionic nature of amphoteric is seldom wholly anionic or cationic above and below the isoelectric range. The difference between betaines, glycinates and propionate is being unaffected in alkali as shown in Table 2.5.

The cationics are named after the parent nitrogenous phosporus or sulphur starting material (Porter, 1994). Cationics are formed in reactions where alkyl halides react with primary, secondary, or tertiary fatty amines. Here the water-insoluble part of the molecule has a positive charge and the water-soluble part of the molecule is negatively charged, thus giving it the name of a cationic surface-active agent.

Table 2.5: Effect of pH on betaines compared to glycinate or propionates (Porter, 1994)

pH	**Glycinates or propionates**	**Betaines**
Acid	N^+-$(CH_2)_nCOOH$	N^+-CH_2COOH
Zwitterion	$NH(CH_2)_nCOOH$ and N^+-$(CH_2)_nCOO^-$	N^+-CH_2COO^-
Alkali	$NH(CH_2)_nCOO^-$	N^+-CH_2COO^-

2.4.3 Demulsification process

A number of general rules help to form the basic philosophy of how emulsion behave within commercial emulsion breaking (Grace, 1992). Firstly, petroleum emulsions are composed primarily of immiscible liquids. Separation should be the natural tendency of these liquids, by providing the density different between the liquid that are exists. Secondly, the gravitational settling rate is dependent on the surface tension of the droplets that form the internal phase of the emulsion. Large droplets have less surface tension as a function of mass than small droplets. Therefore, anything that can be done to increase the droplets size or coalescence will increase the rate of separation. Thirdly, an emulsion is stable within a given environment. Varying the environment may affect the stability of an emulsion and allow the phases separation. Finally, a stable emulsion exists only when emulsifying agents are present. Neutralization, alteration or elimination of the emulsifying agents will allow immiscible liquids to separate.

From the above four generalizations it becomes noticeable that a number of options exist in emulsion breaking. Any single change in these areas may result in the resolution of an emulsion. There are six factors that affect the emulsion stability such as:

i) Viscosity

Higher viscosity caused the ability of oil to hold up more and large water droplets compared to oil which has low viscosity. The application of heat, the addition of a diluents and the addition of chemicals can be reduced the viscosity. As the results, the rate of water droplets settle and the mobility of water are increased and thereby lead to collisions, coalescence, and further increase in the rate of separation.

ii) Density difference

Heat application to the emulsion will decrease the density of the oil at a greater rate than that of water and thus allows more rapid settling of the water. This is because the difference in densities of the two liquid phases may be increased. Dehydration of heavier oil is typically more difficult compared than light oil., as its density is closer to that of water. The density of water is important because fresh water will tend to separate from oil at a slower rate than salt water.

iii) Water percentage

The relative proportion of an oil and water affects the stability of an emulsion. The maximum stability of an emulsion will occur at a set ratio of water to oil. Typically this maximum is found at low water percentages at low water percentages as these droplets have a much smaller chance of colliding with other water droplets and coalescing. The stability of an emulsion may destroy with increasing the water percentage.

iv) Age of emulsion

Age of emulsion is generally increasing the emulsion stability. The ratio of emulsifying agents within oil may increase because of oxidation, photolysis, evaporation of light ends, or bacterial action. This is because light ends are low-molecular weight and low-density hydrocarbons such as pentane, hexane and butane that will vaporize xylene significantly over time. Breaking the emulsion as soon as possible after the emulsion formation will reduce the affects of ageing.

v) Control of emulsifying agents

Emulsifying agents or surfactants are important in the emulsion formation process. The surfactants are either natural or synthetic. The elimination, alteration or neutralization of these materials allows the prevention or resolution of emulsions.

Elimination of emulsifying agents may include corrosion inhibition programs to reduce the amount of iron sulfide, to avoid emulsification tendencies, or elimination of incompatible crude oils from crude oil blends. Alteration of emulsifying agents are includes the addition of an asphaltene dispersant to “tie up” asphaltene polar sites, addition of paraffin crystal modifiers to prevent large paraffin crystals from stabilizing emulsions, or by raising the treating temperatures above the paraffin cloud point of a crude oil. Neutralization of emulsifying agents such as by neutralization of polar charges associated with the film of emulsifying agents formed around the emulsified droplets. Neutralization is the function carried out by commercial demulsifiers or coagulants that promote coalescence and thereby accelerate by gravity settling.

vi) Agitation control

Emulsion stability will be reduced by reducing or eliminating the agitation of oil-and-water mixture. The effectiveness of any demulsifier added to treatment system is directly dependent upon its making optimum contact with the emulsion. Therefore, the emulsion must be sufficiently agitated after the chemical demulsifier has been added. Increase of the mild agitation, is beneficial in promoting coalescence. Re-emulsification may occur if an emulsion is agitated severely once it has broken into oil and water (Leopold, 1992).

The factors that influence emulsion formation and breaking show wide variation from site to site. Smart action would provide the most effective method in emulsion breaking of the producers and transporters.

2.4.4 Mechanisms of demulsification process

Chemical demulsification is a dynamic process since it is a phenomenon that occurs under non-equilibrium conditions. Coalescence of the dispersed phase often happens before the interface is at equilibrium. Therefore, it is paramount to consider dynamic and dilatational properties in the analysis of the demulsification mechanism (Krawczyk, 1990).

An important feature of dispersants is the ability to break water-in-oil emulsions that form naturally as the oil slick weathers and tosses about on the sea surface. Recent laboratory and field experience have demonstrated the ability of some dispersants to break emulsions formed at sea, particularly before the extremely viscous and stable ‘mousse’ stage of emulsion forms. This demulsification activity promotes coalescence of the water droplets in the emulsion, which in turn causes separation of water and lowering of viscosity. This step will slow down the dispersion process and can make effectiveness monitoring more difficult since oil releases more slowly into the water column. In addition, since a portion of the dispersant can be used up in the demulsification step, application of additional dispersant may be needed to increase the dispersion rate (Fiocco and Lewis, 1999).

Since the stability of emulsions can be traced to the presence of surfactant films at the water/oil interface, the rupture of the thin film separating droplets in a water-in-oil emulsion is affected primarily by the adsorption kinetics and interfacial rheological properties of the demulsifier. The role of the demulsifier, therefore, is the suppression of the interfacial tension gradient in addition to the lowering of interfacial shear viscosity, thus causing accelerated film drainage and coalescence.

Demulsifiers are very similar to emulsifiers because both are surfactant in nature. Consequently, the action of the demulsifier in emulsion breaking is to “unlock” the effect of the emulsifying agents present. This unlocking is accomplished in three fundamental steps, which are flocculation, coalescence and solids wetting (Leopold, 1992).

Flocculation is the first action of the demulsifier on an emulsion involves a joining together of flocculation of the small water droplets. When magnified, the flocks take on the appearance of bunches of fish eggs. If the emulsifier film surrounding the water droplets is very weak, it will break under this flocculation force and coalescence will take place without further chemical action. Bright oil is an indicator of good flocculation. The term bright oil refers to the shiny color that is characteristic of treated oil. In most cases, however, the film remains intact, and therefore, additional treatment is required.

Coalescence is the rupturing of the emulsifier film and the uniting of water droplets. Once coalescence begins, the water droplets grow large enough to settle out. Good coalescence is characterized by a distinct water phase.

In most crude oil, solids such as iron sulfide, silt, clay, drilling mud solids, and paraffin complicate the demulsification process. Often such solids are the primary stabilizing material, and their removal is all that is necessary to achieve satisfactory treatment. To remove solids from the interface, they can either be dispersed in the oil or water-wetted and removed with water. Figure 2.11 shows the level of demulsification of water in oil emulsion (Kim et al., 1996).

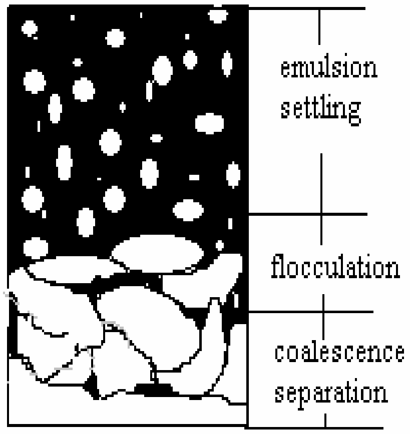

Figure 2.11: The level of demulsification process of water in oil emulsion (Separation of water from water in oil emulsion by gravity force)

Ese et al. (1999) state that the kinetics of chemical demulsification process is caused by the three main effects:

i) The displacement of the asphaltenic film from the water/oil interface by the demulsifier
ii) Flocculation
iii) Coalescence of water droplets

The demulsifiers will increase the water separation when present at low or moderate concentration, but at high concentration, the water droplets is dissolution and formed condense liquid phase. Beside that, water separation is reduced as a result of stearic stabilization of larger water drops.

Bhardwaj and Hartland (1998) summarized in their work that a lowering of interfacial tension and adsorption of demulsifier at the crude oil/water interface is necessary condition, but not a sufficient condition for an effective demulsifier. More important characteristics of a good demulsifier are sufficient surface pressure and good partition between the two phases.

Ese et al. (1999) conclude that an effective oil soluble demulsifier will decrease the interfacial tension gradient and interfacial viscosity and caused the increasing rate of film thinning and decrease the time to reach a certain thickness. The correlation between the rate of interfacial tension lowering and the demulsification efficiency of demulsifiers has been found. So, the kinetics of adsorption and the resulting dynamic elasticity of the interface are the main factors to consider the demulsification mechanism and performance.

Thus, most emulsion treating agents are composed of surfactants which modify the properties of the oil/water interface, by displacing, mixing with, or chemically neutralizing the naturally occurring emulsifying surfactant in the oil, thus inhibiting or destabilizing the emulsion.

2.5 Demulsifiers Development, Formulation and Performance

2.5.1 Historical development

Rigorous attempts have been in trying to correlate between demulsifier performance and physical properties such as molecular structure, interfacial tension, Hydrophilic-Lipophilic balance (HLB), interfacial viscosity, partition viscosity, dynamic interfacial tension and relative solubility number. A quick look on the chemical demulsifiers history reveals that prior to the knowledge of polyether condensates synthesis, chemicals such as Turkey red oil, sulphuric acid, sulphated caster oil, mahagony soaps, polyamines and polyhidric alcohols were used directly as demulsifiers (Monson, 1969).

In early 1940's, the technology of alkylene oxide condensation started to evolve world wide, and since then almost all demulsifier components were made up of condensation products of ethylene, propylene and butylenes oxide. Most of these are alkoxylated polymers that are mainly etoxylated and propoxylated and sometimes both. They are macromolecules held in chains, industrially synthesized from petroleum chemicals.

After World War II, the whole branch of chemistry was opened to companies involved in surfactant (surface-active agents) technology. With the beginning of condensed polyether made possible by large-scale production of ethylene and propylene oxides (Becker, 1997), a new class of nonionic detergents began to appear. The condensation products of the ethylene oxide were found to be water soluble and the high reactivity of the oxirane ring made it useful in a host of chemical reactions. It was found that the propylene oxide gave poly condensation products that tended to be oil soluble

The polymer most employed in the demulsification industry is surfactant that exhibits both hydrophilic and hydrophobic groups. The polymeric surfactant when added to the petroleum emulsion located itself in the interface between the water and oil molecules. The hydrophilic groups orient themselves towards water whist the hydrophobic ones orient themselves towards the oil.

The best polymeric surfactants used nowadays throughout the world are alkoxylated material derivatives. Because they are alkoxylated, they are considered as nonionic polymers. Sometimes mixtures of nonionic, cationic or anionic materials are used together, depending on the oil characteristics. Etoxylated nonionic surfactants are effective multi-purpose and versatile substances. Commercial products are obtained by reaction of ethylene oxide with a hydroprobe having an active hydrogen group (e.g. fatty acids, akylphenols or fatty alcohols) in the presence of suitable catalysts. Table 2.6 shows the development and evolution of chemical demulsifiers.

Sjoblöm et al. (1990) stated that a similar destabilization sequence for model and authentic crude oil emulsions can be obtained when medium-chain alcohols and fatty amines are used as destabilizers. The commercial demulsifiers that used to break up water-in-oil emulsion are oil soluble and water soluble demulsifiers. Table 2.7 shows the comparison between those demulsifiers.

Table 2.6: The development and evaluation of chemical demulsifiers (Selvarajan et al., 2001)

Year	**Demulsifiers**
1920-1930	Soap, naphtenic acid salts and alkylaryl sulphonate, sulphated caster oil
1930-1940	Petroleum sulphonates, derivatives of sulpho-acid oxidized caster oil and sulphosucinic acid ester
1940-1950	Fatty acids, fatty alcohols, alkylphenols
1950-1960	Ethylene oxide/propylene oxide copolymer, Alkoxylated cyclic p-alkylphenol formaldehyde resins
1960-1970	Amine alkoxylate
1970-1980	Alkoxylated cyclic p-alkylphenol formaldehyde resins
1980-1990	Polyesteramine and blends

Table 2.7: Comparison between oil soluble demulsifier and water soluble demulsifiers (Bhattacharyya, 1992)

Types No.	**Oil soluble demulsifiers**	**Water soluble demulsifiers**
1.	Moderately 2000-50,000 molecular weight (mw). High mw are the preference.	10,000-15,000 molecular weight. Lower mw are the preference.
2.	Polydispersed interfacially active polymers.	Tetrapolymer or pentapolymer
3.	Mostly non-ionic block polymer with hydrophilic and hydrophobic segments.	The polymer present hydrophilic (-COOH) and hydrophobic (alkyl) groups.
4.	Dangerous and expensive chemicals like ethylene and propylene oxide.	Easy handling chemicals like methyl metachrylate, butyl acrylate, acrylic acid and methacrylic acid.

In water-in-oil emulsion cases, the most effective demulsifiers are oil-soluble or hydrophobic. This is because oil is the continuous phase while water is the dispersed phase. Thus, the surfactants will absorb straightly into the continuous phase without any resistance in optimum temperature.

Typically, these oil soluble demulsifiers are formulated in organic solvent alone such as toluene, xylene, tetrahydrofuran, dioxane, lower alcohols and light gasoline fractions having boiling limits of from 50 to 200°C, or in co-solvents comprising organic solvents and water where in the organic solvent are usually C_3 to C_{10} alkanols, ethylene diamine, diethylene triamine or ethanolamines including diethanolamine (Mercant et al., 1988).

Among the disadvantages of having organic solvents in a demulsifier formulation are increased cost, flammability, and toxicity. Therefore a demulsifier formulation, which does not include organic solvents, would represent an advance in the art of demulsification.

2.5.2 Demulsifier formulation

Demulsifiers can be used singularly or in combinations of two or more. Finding a demulsifier system that works well is often done by trial and error. Grace (1992) stated that the selection process has historically been viewed as a “black art”, which produces as many failures as successes. But the failures can be eliminated with the increasing understanding of emulsions and emulsion-breaking chemicals, the development of new test procedures and devices, and well-organized method of chemical selection.

To date, most demulsifier products are hydrophilic surfactant that is surfactants with a strong tendency to make oil-in-water emulsions from water-in-oil emulsions. These surfactants are more soluble in water than oil, and therefore have the ability to revert the water-in-oil emulsion into two separate phases. Therefore, such demulsifier products are most effective when used in a confined environment; they are likely ineffective on open water. Meso-stable emulsions, the most frequent emulsion produced at sea, are relatively easy to break and may be broken with as little as 1/100 of the same demulsifier products. Some demulsifier products are not capable of breaking these emulsions.

The best demulsifiers are one that can reduce the interfacial shear viscosity, increases the interfacial mobility and destabilizing the water-in-oil emulsion. To ensure the high quality performance, a demulsifier should posses the following characteristics (Krawzcyk et al., 1991):

- The demulsifier should be able to partition into the water phase;
- Dissolved in the oil phase;
- The concentration of the demulsifier in the droplet must be sufficient to ensure a high enough diffusion flux to the interface;
- The interfacial activity of the demulsifier must be high enough to suppress the interfacial tension gradient, thus accelerating the rate of film drainage hence promoting coalescence.

According to Sharma et al. (1982), there are three possibilities to cause the process of inversion where; if the demulsifier applied is not sufficient to convert the crude oil emulsion, the natural emulsion remains unbroken, if the demulsifier is ever sufficient, then natural emulsion will be broken, but a certain amount of crude oil will contaminate the water effluent and may caused re-emulsification of the oil in water and if the demulsifier is just sufficient, then the best separation of oil and water phase will be occurred.

There are a lot of commercial formulation published by various authors such as VX7079 Demulsifiers from ESSO, D1 and D2 (Bhattacharyya, 1992). These formulation are shown in Appendix A. According to (Bhattacharyya, 1992), both D1 and D2 completely demulsified an East Texas crude oil after 10 minutes by using 10 to 15 ppm of each demulsifiers formulation.

2.5.3 Demulsifiers performance

Different types of demulsifiers will give the different way in demulsification process. Knowledge of formation and stability of crude oil emulsions, types of demulsifiers, demulsification mechanisms and so on are very important since it can be useful in the demulsification process of crude oil emulsions. Thus, it is frequently observed in studies of parameters that can affect the formation of stability of the crude oil emulsion. All parameters that are being identified to affect demulsifiers performance are: -

i. Temperature

The suitable temperatures considered for demulsification process for lab scale are between 50 to 70°C, which are similar to the actual refinery process (Grace, 1992). The interfacial viscosity of the internal phase will decrease to the increasing of the temperature. This is because the rate of film drainage is increased proportional to the temperature. The momentum between two water droplets will increase before coalescence is occurred. The two phases of immiscible liquids will be separated due to the different density among them.

ii. pH

Tambe and Sharman (1993) studied that oil-in-water emulsions are preferential at low pH value ranging between 4 to 6, while water-in-oil emulsions are favored at high pH values that are between pH 8 to 10. Based on their experiments, the stability of oil-in-water emulsion formed increased as pH was increased from 4 to 6, but further increasing in pH, from 6 to 8 and finally 10 resulted in formation of relatively less stable oil-in-water emulsions and more stable water-in-oil emulsions. (Johansen et al., 1989) concluded that at very high and low pH values, the emulsions seem to be stable, while intermediate pH seems to cause instability. The optimum pH values in treating crude oil emulsions are between 5 to 12. Furthermore, the demulsifiers that are used in treating the emulsion problem are depending on the pH value.

iii. Solvents/Diluents

Solid or high viscous demulsifiers need to be dissolved in suitable solvents to increase the pour point and the solubility of demulsifiers in oil. This is because the surfactants are classified according to the polar (hydrophilic) part of the molecule (Schramm, 1992). As the result, the demulsification process will be completed successfully. The stability of emulsions is depends on the solubility of aromatic solvents. When the solubility parameter of the solvent decreases, for example; the oil is more aromatic, the oil forms more stable.

Gafonova (2000) stated that the influence of solvents of various aromatic and structure including benzene, toluene, xylene, ethylbenzene, tert-butyl benzene and cymene on emulsion stability. The results indicate that the more aromatic solvents (i.e. with the highest content of the aromatic carbon) are more effective in destabilizing emulsions.

iv. Salinity of oilfield brine

The presence of divalent cations in the brine decreases the optimal salinity of the surfactant formulations. Binks (1993) studied that oil-in-water droplets are increase in size solubilizing more oil with increasing of salt concentrations, while water-in-oil droplets decrease in size. At low and high salt concentrations, the monolayer constrained to lie at the flat interface has a preferred tendency to curve and the tension becomes high.

Tambe and Sharman (1993) used some inorganic salts such as sodium chloride and calcium chloride to study the effect of emulsion stability for some pH values. They suggested that the presence of inorganic cations in the systems has an adverse effect on emulsion stability. Calderon et al. (1993) studied that adding salts to the asphalt emulsions cause the depletion force is reduced at low salt concentrations, leading to a melting aggregates, whereas at high concentrations, rapid aggregation occurs as a consequence of van der Waals attractive force.

Aqueous-phase substrate salt differences will result the pronounced change in interfacial film behaviour. The salts ions lead to an increased relaxation of the film formed and a decrease in the resistance to press ion compared to distilled water (Jones et al., 1978).

v. Natural surfactants (asphaltene and resin)

Many researchers have been trying to relate the emulsion stability to the asphaltene/resin ratio. When both asphaltenes and resins are present, the range is larger than for either resins or asphaltenes alone. But the opposite results are pointed out by many researches that too much resins destabilizes emulsions (Gafonova, 2000). The investigation of the film formed by the adsorption of asphaltene/resin mixture indicated that resins start to predominate the film properties when their content exceeds 40% (Ese et al., 1998).

Sjoblom et al. (1992) suggested that the amount of resin and asphaltene were quite decisive for the stability of the emulsion system from the interfacial tension point of view. They also suggested that the asphaltene fractions would give a higher stability than resin. The emulsion stability would decrease if the high components were mixed.

vi. Solid particles/waxes/crystals

Solid particles are often part of an emulsion formulation and they may be used to stabilize the emulsion. The key factor for the use of particles as a stabilizing agent is their wetting by the two liquids. They serve as a mechanical barrier to prevent the coalescence of the droplets.

Sjoblom et al. (1990) concluded that there is a correlation between a high content of wax particles and a high viscosity. In two specific cases, the interfacial tension exceeds the surface tension. The melting and crystallization (and re-crystallization) sequence of the waxes is important for stabilizing the properties of waxes. If the melting point is exceeded, the waxes will mainly act as a component in the crude oil bulk and their activities at the oil-water interface is normally substantially reduced.

vii. Pressure

Reservoir pressure has a less significant effect on emulsion stability than temperature. Interfacial tension decreases as the pressure of the system increases. Pressure effects probably have an indirect effect on emulsion stability because of the dependence of physical properties on pressure (Kokal et al., 1992).

Chemical programs applied in commercial emulsion breaking are selected from a wide variety of emulsion-breaking chemistries and auxiliary chemicals that control very specific agents within the emulsion. These chemicals and parameters that involved in demusification process provided a measure of performance of the performance of treating chemicals with a specific crude oil and treating system.

2.6 Factorial Design Optimization

Factorial designs are widely used in experiments involving several factors where it is necessary to study the joint effect of these factors on a response (Montgomery, 1984). This method is very important in creating new formulation by knowing the optimize value for each demulsifiers.

There are two types of factorial design, which are 2^k and 3^k factorial designs. k is the number of factors investigated in the study. A 2^k design is particularly useful in the early stages of experimental works, when there are likely to be many factors investigated. A 2^k design is useful at the start of a response surface study where screening experiments should be performed to identify the important process or system variables. This design is often used to fit a first-order response surface model and to generate the factor effect estimates required to perform the method of steepest ascent. The 2^k design which use “low” and “high” level of factors is a basic building block to create other response surface design such as two level central composite design which is one of the most important design for fitting second-order response surface models.

The 3^k factorial design is a factorial arrangement with k factors each at three levels. Factors and interactions will be denoted by capital letters. This design involves three levels of factors as low (0), intermediate (1) and high (2). The type of design that is used in this study is discussed in Chapter III.

2.6.1 Response Surface Methodology (RSM)

Response Surface Methodology is a collection of mathematical and statistical techniques that are very useful in analyzing problems influence a dependent variables and independent variables or response. The main objective is to optimize the response according to the type of response surface formed from the result of factorial design tests. (Myers and Montgomery, 2002).

Since the relationship between the response and independent variables is unknown, finding the suitable approximation for the true functional relationship between y and the set of independent variables is important by using low-order polynomial in some region of the independent variables is employed. The function is first-order model if the response is well modeled by a linear function of the independent variables (Montgomery, 1984).

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \ldots\ldots + \beta_k x_k + \varepsilon \qquad (2.1)$$

If there is curvature in the system, then a polynomial of higher degree such as the second order model must be used.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{\substack{i \\ i<j}} \sum_{j} \beta_{ij} x_i x_j + \varepsilon \qquad (2.2)$$

RSM is a sequential procedure. The eventual objective of RSM is to determine the optimum operating conditions for the system or to determine a region of factor space in which operating specifications are satisfied. Optimum in RSM term is used in special sense. The hill climbing procedures of RSM guarantee coverage to a local optimum only. Chapter III and IV present the used of RSM in this study to gain the best concentration of demulsifiers in order to create the demulsifiers formulation.

2.7 Summary

In the petroleum industry, mixtures of oil and water will occur as emulsions in both production and refining segments. The types of emulsions will vary widely, although all emulsions will be result of normally immiscible oil and water subjected to agitation and stability by a wide variety of emulsifying agents. There are four types of emulsions that are readily distinguished in principle, which are Oil-in-Water (O/W) and Water-in-Oil (W/O), Oil-in-Water-in-Oil (O/W/O) and Water-in-Oil-in-Water (W/O/W) emulsions. But the majority of crude oil emulsion is from Water-in-Oil (W/O) emulsion type.

Crude oil is a mixture consisting of at least a range of hydrocarbons (alkanes, naphtenes and aromatic compounds) as well as phenol, carboxylic acid, resin and asphaltene. Interfacial active components from the polar fraction such as carboxylic acid, phenol, wax, resin and asphaltene are responsible to stabilize the water in crude oil emulsion.

In order to destabilize the emulsions, a combination of thermal, chemical and time factors is applied. The economics of emulsion breaking determines the method to emulsion resolution. Chemical programs applied commercial emulsion breaking are selected from a wide variety of emulsion-breaking chemistries and auxiliary chemicals that control very specific agents which called demulsifiers.

Demulsifiers are surfactants. There are four types of surfactants; anionic, nonionic, cationic and amphoteric from two major groups which are water-soluble demulsifiers and oil-soluble demulsifiers. These chemicals are selected from screening test by using bottle test method. The formulation of chemicals is based on factorial design optimization by using Response Surface Methodology (RSM).

The factors that influence emulsion formation and resolution are different from site to site. So, there are no universal rules exist for applying emulsion-breaking technology. Each emulsion-breaking facility must be viewed as an individual case by applying the theories of demulsification to a specific situation in a carefully organized, directed and documented effort to provide the most effective methods of achieving the goals in emulsion breaking of the producer and refinery.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

In order to achieve the outlines of the objectives and the scope of the research, several materials, experimental and analytical procedures used in this study are presented and discussed with more details in the following sections. The chemicals and methods used in this study are depending exactly on the research needed by considering all factors except cost saving. This is because the effectiveness of demulsifiers is the main target in achieving the objectives of this study. The materials and methodology used in this study are referred from the literature studies.

3.2 Materials

3.2.1 General chemicals

The chemicals required for experimental study were obtained from various suppliers such as n-Pentane (>95%, from J.T Baker) that required in asphaltenes recovery; acetone (>99.5%, from Mallinckrodt) as sterilize solvent; dikloromethane (100%, from Mallinckrodt) as solvent in resin recovery; silica gel (130-270 mesh, 60Å from Aldrich) and petroleum ether (40-60°C, from SureChem Products LTD) are required for wax recovery; methyl alcohol anhydrous (99.9%, from Mallinckrodt), Toluene (99.9%, from J.T Baker), benzene (from Fisher Chemical) and ethanol (from Fluka Chemika) were used as solvents to dissolve oil-soluble demulsifiers. Natrium chloride (above 99.5, from Merck KGaA) was used in preparation of synthetic formation water. n-Decane and ethanol were used in preparing synthetic oil which was used in single emulsion preparation which is 70 %v/v n-Decane is mixed with 30 %v/v ethanol.

3.2.2 Chemical demulsifiers

There are wide ranges of demulsifiers that can be used in demulsification of crude oil emulsions. From the literature study and surveys, the demulsifiers used in this study are shown in Table 3.1. The Material Safety Data Sheets (MSDS) for all the demulsifiers are given in Appendix B. The 21st and 22nd chemicals that listed in Table 3.1 were used as the comparison with the new formulation obtained in this study. Majority of the chemicals used in this study is supplied from Fluka Chemika.

3.2.3 Crude oil samples

Samples from Semangkok, Tabu, Guntong, Irong Barat and Seligi fields were used for this experiment. For the demulsifiers screening, emulsion from Tabu's field were used. This is because it contains a lot of interfacial active fraction and one of the most stable emulsions. The other fields are used to test the efficiency of the demulsifier formulation obtained through this study. All crude oil and oilfield brine samples were provided by ESSO (M) Incorporated.

Table 3.1: Types of chemical demulsifiers

No.	**Name**	**Supplier**
1	Acrylic acid anhydrous	Fluka Chemika
2	Polyvinylpyrrolidone	Aldrich Chemical Co.
3	epsilon – Caprolactam 99 +%	Aldrich Chemical Co.
4	Sodium dodecyl sulfate	Fluka Chemika
5	Hexylamine	Fluka Chemika
6	Methyl trioctyl ammonium chloride (TOMAC)	SIGMA Chemical Co.
7	Poly(ethylene-co-propylene-co-5-methylene-2-norbornene; 70 wt% ethylene, 4 wt% 5 methylene-2-norbornene	Aldrich Chemical Co.
8	Polyethylene glycol 1000	Fluka Chemika
9	N,N,N’,N’-Tetramethyl-2-butene-1,4-diamine, 95%	Aldrich Chemical Co.
10	N-Ethyl-N-Sulfopropyl-m-Toluidine	SIGMA Chemical Co.
11	N,N-Dimethylacetamide	Fluka Chemika
12	Maleic anhydride	Fluka Chemika
13	2-Aminophenol-4-Sulfonic Acid	Fluka Chemika
14	Methacrylic acid	Fluka Chemika
15	Methyl methacrylate	Fluka Chemika
16	Butyl acrylate	Fluka Chemika
17	2-Ethyl hexyl acrylate	Fluka Chemika
18	Pseudocumene	Fluka Chemika
19	Naphtalene	Fluka Chemika
20	Dioctylamine	Fluka Chemika
21*	VX7079 Demulsifier	ESSO
22*	D1 and D2	Bhattacharyya, 1992

*Note: Commercial formulation

3.2.4 Oilfield brines

The oil field brine was obtained from the same oilfield of the crude oil samples, from ESSO (M) Incorporated. In this study, the synthetic oilfield brine was used in preparing the emulsion systems. The synthetic oilfield brine were prepared by dissolving NaCl in deionized water in order to obtain the required salinity similar to Tabu’s field, which is 9.4% by using the Equation 3.1 (Lee Cho Hing, 1998).

Salinity Equation: $Y = 8.3566X - 0.3582$ (3.1)

where Y = Salinity (%w/w); % in per thousand
X = NaCl concentration (g/100 ml)

$$9.4 = 8.3566x - 0.3582$$
$$x = \underline{11.6722\ g}$$

So, 11.6722 g of NaCl is dissolved in 100 ml of deionized water in order to obtain 9.4% salinity of synthetic oilfield brine.

3.3 Experimental Methods

Figure 3.1 shows the flowchart of experimental work in order to create the new formulation in treating crude oil emulsion. This study was carried out by using two types of water-in-oil emulsions, which from real and synthetic oil. Bottle test method was used in both single and composite demulsifiers screening in different concentration in order to find out the most effective demulsifiers as discussed in Section 2.4.1. The optimum condition of selected demulsifiers was found by using Factorial Design Optimization. The formulation that was obtained is tested by using Malaysian crude oil emulsions, synthetic emulsion and compared with the commercial demulsifiers formulation.

3.3.1 Emulsion preparation

Water in oil emulsion was prepared by mixing crude oil with the synthetic oilfield brine (1:1 v/v). The emulsification was carried out by using a homogenizer at a speed of 8000 rpm for 2.5 minutes to get a stable emulsion with the diameter of the droplets are about 10μm (Ariany, 2003). About 10 ml of emulsion sample was prepared in this study. The synthetic crude oil emulsion (asphalt emulsion) was prepared in accordance to the same procedure as real sample by mixing n-decane/toluene mixture with interfacial active fractions (asphaltene) and the synthetic oilfield brine. The asphaltene present in the crude oil was separated by using the method shown in Figure 3.2.

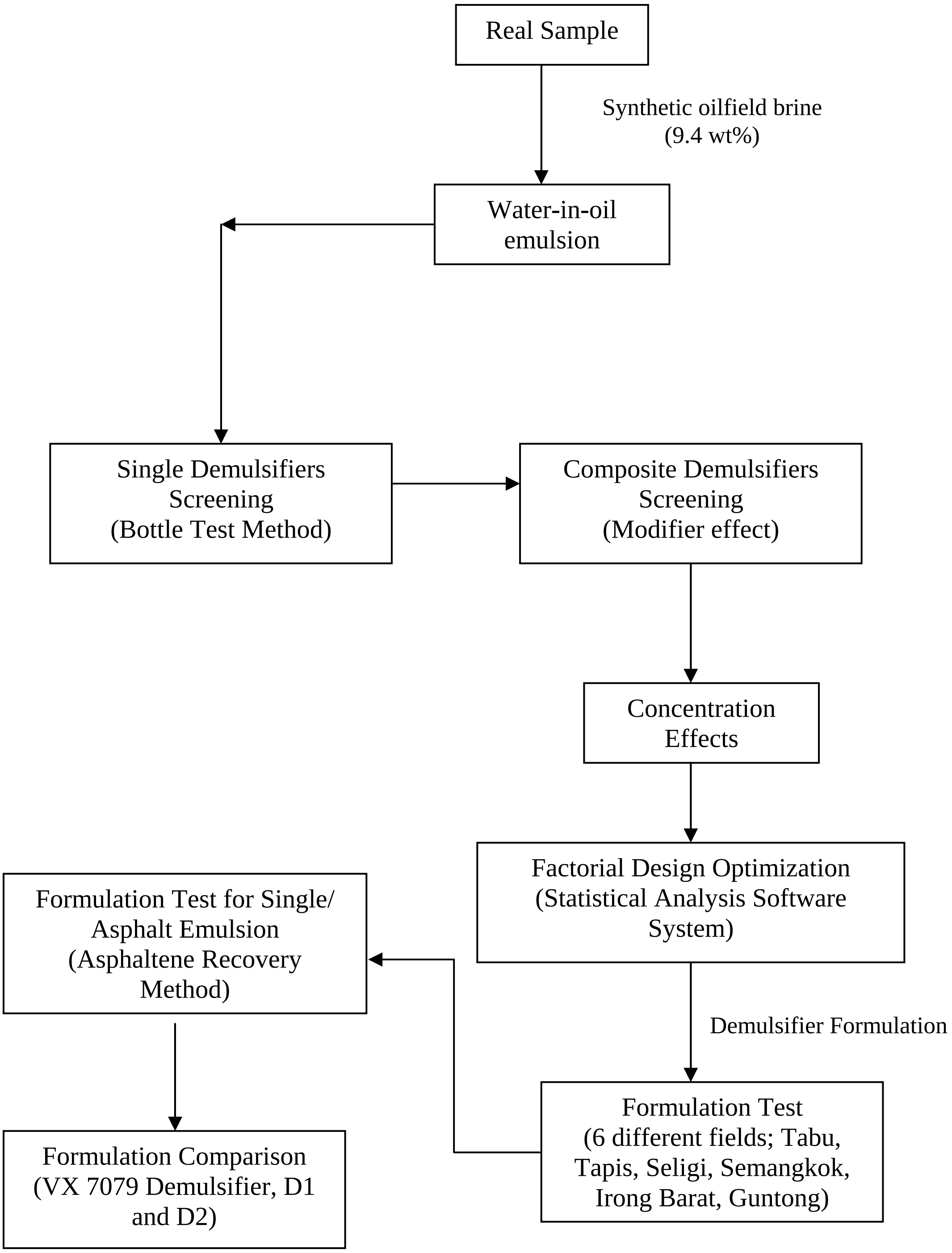

Figure 3.1: Experimental work flowchart

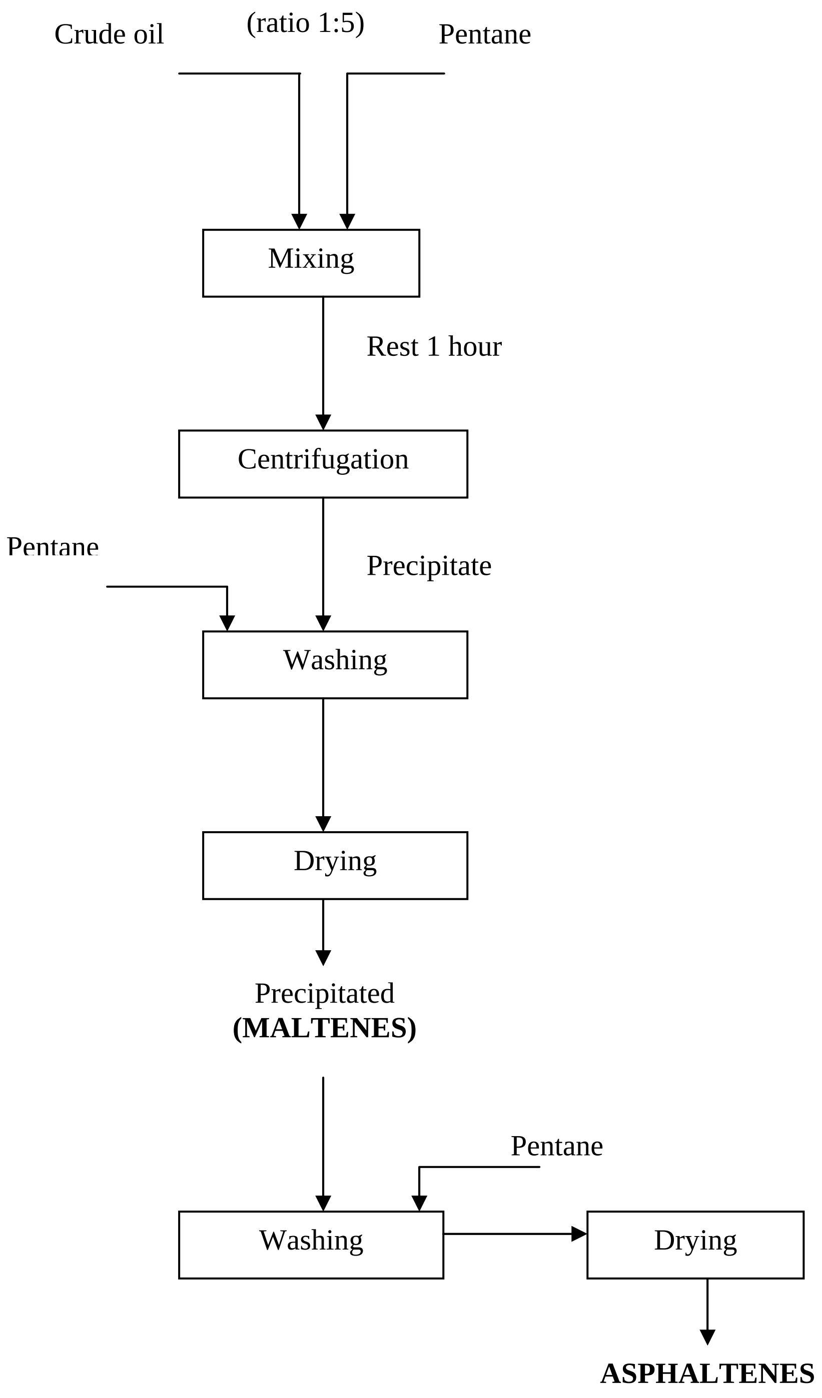

Figure 3.2: Asphaltenes recovery procedure to form single or asphaltene emulsion (Ese et al., 1997)

3.3.2 Single demulsifiers screening

The purpose of this screening process is to test the effectiveness of single demulsifiers in breaking crude oil emulsion. This demulsifiers was divided into two groups, which are oil-soluble demulsifiers and water-soluble demulsifiers. Twenty types of demulsifiers were used in this study. The list of demulsifiers is shown in Table 3.1, are the latest demulsifiers that were used in demulsification process according to the literature study and surveys.

The demulsifiers were screened by using bottle test method. A series of centrifuge bottles were used for this purpose because of their precise data obtained. The screening process was running by fixing the temperature and demulsifier concentration. So, the most effective single demulsifier was obtained based on the water separation from emulsion system. The bottles are immersed in water bath at controlled temperature, which is 70°C. The result of water separation is read from the measured range at the bottles. 10 ppm of demulsifiers concentration is injected in each bottle. The experiments took 7 days observation.

The demulsifiers used in this screening process was diluted with the suitable solvents to 1000 ppm (M_1). The volume of 10 ppm (M_2) demulsifier was calculated using Equation 3.2.

$$M_1V_1 = M_2V_2 \tag{3.2}$$

where, M_1 = Initial concentration –prepared demulsifier concentration, (ppm);
V_1 = Volume of demulsifier needed, (ml);
M_2 = Final concentration – needed concentration, (ppm);
V_2 = Final volume – demulsifier + oil, (ml).

10 ppm of each demulsifier was injected in 10 ml emulsion system. The preparation of emulsion sytems was discussed in Section 3.3.1. The system was stirred rigorously for 1 minute to mix the demulsifier and emulsion system. The

volume of water and oil separation from the emulsion system was observed and the graph of % water separation versus time and % oil separation versus time were plotted.

3.3.3 Composite demulsifiers screening

The results obtained from single demulsifier screening study was combined to check the ability of the composite demulsifiers in breaking water-in-oil emulsion system. The temperature, demulsifier concentration and experimental procedure are same as discussed in Section 3.3.2. The composite demulsifier system is the combination of oil-soluble demulsifier and water-soluble demulsifier. The effect of methanol as modifier present in the system was also examined. The volume of water and oil separation from the emulsion system was observed and the results of % water and oil separation versus time were plotted.

3.3.4 Effect of concentration on demulsification performance

Four different concentrations were used to examine the effects toward the emulsion system. The concentration varied from 10 ppm, 20 ppm, 50 ppm and 100 ppm. The temperature is fixed at 70°C and the experimental procedure was same as discussed in Section 3.3.2. The volume of water and oil separation from the emulsion system was observed and the results of % water s time and oil separation versus time were plotted, which will be discussed in Chapter IV.

3.3.5 Optimization of demulsifier formulations

The results from the previous section were used as the factor in optimizing the formulation in order to produce the best results in breaking water-in-oil emulsion system by using the experimental design. The experimental design has been used to minimize the number of experimental conditions, which must be investigated. An experimental design consists a set of experimental run, and each run was defined by a combination of factor levels (Murphy, 1977). The factors that effect the crude oil demulsifiers formulation are concentration of oil-soluble (TOMAC, hexylamine and dioctylamine) and concentration of water-soluble (metyhl methacrylate, butyl acrylate and acrylic acid). Two run of experimental design were used to optimize the concentration for both oil-soluble and water-soluble. The optimum concentration for both factors were combined as a new formulation in treating crude oil emulsion systems.

3.3.5.1 The factorial design

As discussed in Section 2.6, the design that frequently used for screening experiments is two level factorial designs where each factor was evaluated a low setting and high setting. In this experimental study, two levels factorial design were used, because of the easy of interpretation and effectiveness (Strange, 1990).

There are two types of two level factorial designs. The first one is two levels full factorial design. The other one is two level fractional factorial design, which is efficient in reducing the sample size (Box et al., 1987). In this study, two levels full factorial design were used because the size of sample is small.

3.3.5.2 The 2^3 design

Supposing that three factors for both screening groups that are concentration of TOMAC, hexylamine and dioctylamine for oil-soluble demulsifiers and concentration of methyl methacrylate, butyl acrylate and acrylic acid for water-soluble demulsifiers, each at two level are under study. Since “low” and “high” level of each concentration was used in the experiment, the design is then called a 2^3 factorial (Montgomery, 1984) as discussed in Section 2.6. The eight treatment combinations can be displayed graphically as in Figure 3.3. The design matrix in 2^3 factorial design is shown in Table 3.2.

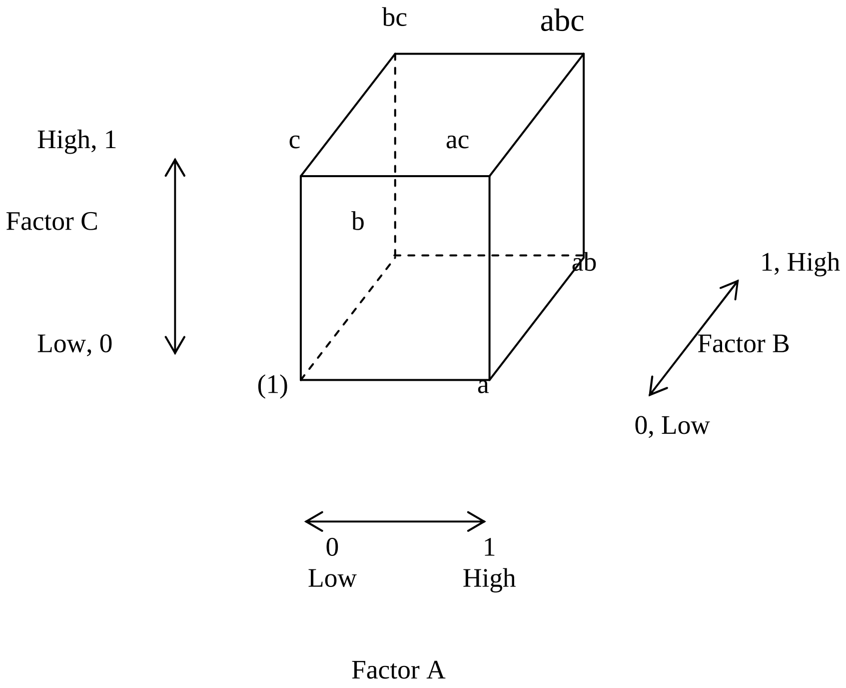

Figure 3.3: Eight treatment combinations for 2^3 full factorial design (Montgomery, 1984)

Table 3.2: Algebraic signs for calculating effects in the 2^3 design (Myres and Montgomery, 2002)

Run	Factor		
	A	**B**	**C**
1	-	-	-
2	+	-	-
3	-	+	-
4	+	+	-
5	-	-	+
6	+	-	+
7	-	+	+
8	+	+	+

From Table 3.2, signs for the main effects are determined by associating a plus with the high level and a minus with the low level. The '+ and –' notation is often called as the geometric notation. There are other notational schemes could be used, this geometric notation is preferred because it facilitates the translation of the analysis of variances results into a regression model. This notation is widely used in response surface methodology.

The range and the levels of variables of oil-soluble demulsifiers investigated in this study was given in Tables 3.3 and 3.4 which show the experimental range and levels of independent variables for water-soluble demulsifiers. 2^3 full factorial design for oil-soluble demulsifiers and water –soluble demulsifiers were shown in Tables 3.5 and 3.6, respectively. The concentration values for both water-soluble demulsifiers and oil-soluble demulsifiers are gained from trial and error test run by using bottle test method.

Table 3.3: Experimental range and levels of independent variables for oil-soluble demulsifiers system

X, Variables (ppm)	Variable Levels	
	-1	**+1**
X_1, TOMAC	30.0	50.0
X_2, Hexylamine	20.0	40.0
X_3, Dioctylamine	10.0	20.0

where, X_1 = TOMAC concentration (ppm);
X_2 = Hexylamine concentration (ppm);
X_3 = Dioctylamine concentration (ppm).

Table 3.4: Experimental range and levels of independent variables for water-soluble demulsifiers system

X, Variables (ppm)	**Variable Levels**	
	-1	**+1**
X_4, Methyl Methacrylate	25.0	30.0
X_5, Butyl Acrylate	10.0	15.0
X_6, Acrylic Acid	50.0	60.0

where, X_4 = Methyl Methacrylate concentration (ppm);
X_5 = Butyl Acrylate concentration (ppm);
X_6 = Acrylic Acid concentration (ppm).

Table 3.5: 2^3 full factorial design for oil-soluble demulsifiers

Number of Experiments	**Coded Variables**		
	X_1	**X_2**	**X_3**
1	30.0	20.0	10.0
2	50.0	20.0	10.0
3	30.0	40.0	10.0
4	50.0	40.0	10.0
5	30.0	20.0	20.0
6	50.0	20.0	20.0
7	30.0	40.0	20.0
8	50.0	40.0	20.0

Table 3.6: 2^3 full factorial design for water-soluble demulsifiers.

Number of Experiments	**Coded Variables**		
	X_4	**X_5**	**X_6**
1	25.0	10.0	50.0
2	30.0	10.0	50.0
3	25.0	15.0	50.0
4	30.0	15.0	50.0
5	25.0	10.0	60.0
6	30.0	10.0	60.0
7	25.0	15.0	60.0
8	30.0	15.0	60.0

3.3.5.3 Optimization by using Response Surface Methodology (RSM)

As discussed in Section 2.6.1, Response Surface Methodology (RSM) are very useful in analyzing problems influence a dependent variables and independent variables or response. The main objective is to optimize the response (Montgomery, 1984).

In most RSM problems, the form of the relationship between response and independent variables is unknown. So, the first step is to decide a model that can express the response as a function of independent variable in the process. The different types of model have been used to predict the optimal response such as first and second degree polynomial as discussed in Section 2.6.1.

3.3.5.4 Evaluating the model

The parameters of the mathematical model were estimated based on the data obtained by using Statistical Analysis System (SAS) software in first order regression analysis.

The statistical analysis begun with the estimation of the effects of each experimental factor and their two factors interaction, estimation the regression coefficient and standard error for each coefficient. The significance of each coefficient was determined by using the student t-test and p-value. The R-squared value was estimated by Analysis of Variance (ANOVA) to measure the variability in the observed response values could be explained by the experimental factors and their interactions. The value of R-squared is always between zero to one. A practical rule of thumb for evaluating the R-squared is that it should be at least 0.75 or greater. The values above 0.90 are considered very good (Myers and Montgomery, 2002).

3.3.6 Formulation effects on different fields of crude oil system

By using the results obtained from Section 3.3.5, the formulation was tested in 6 different fields of crude oil. From Equation (3.2), 1 ml or 15 ppm of the demulsifier formulation was injected into 10 ml emulsion systems. The emulsion preparation was the same as discussion in section 3.3.1. The fields that were used for this purpose are Tabu, Tapis, Seligi, Semangkok, Irong Barat and Guntong. The experimental procedure is the same as in Section 3.3.2. The volume of water and oil separation from the emulsion system was observed and the graph of % water separation versus time and % oil separation versus time are plotted.

3.3.7 Formulation effects on single emulsion system

Single emulsion system that was used in this study is asphaltene emulsion system. This is because resin, wax and solids cannot form emulsion by itself. As discussed in Chapter II, the characteristics and molecular structure of asphaltene are the reason of the emulsion formation and its stability. The emulsion was prepared by using the procedure as discussed in Section 3.3.1 and the experimental procedures are the same as discussed in Section 3.3.2. The volume of water and oil separation from the emulsion system was observed and the graph of % water separation versus time and % oil separation versus time are plotted.

3.3.8 Commercial demulsifier formulations comparison

By using the same experimental procedure as discussed in Section 3.3.2, the effectiveness of three commercial demulsifier formulations were examined in order to get the comparison with the new formulation created. The commercial formulations are VX7079 Demulsifiers (from ESSO) and D1 and D2 formulation (Bhattacharyya, 1992). 15 ppm of each formulation was injected to 10 ml emulsion system and the volume of water and oil separation was observed in 7 days duration. The results of % water and oil separation versus time were plotted.

3.4 Summary

Screening of the best demulsifiers is the most important test in this study. This test is run by using the well-known method, which is called jar test method or bottle test method. Since, there are no specific techniques or method in finding the effective demulsifiers, the method is considered as trial and error. The link existed in each tests discussed in this chapter caused the test must be done step by step until the new formulation found by using Response Surface Methodology (RSM) resulted from two level full factorial design (2^3 full factorial design).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

The types and characteristics of demulsifiers and mechanisms of demulsification process as reported in the literature was reviewed and discussed in Chapter 2. This chapter presents all the results obtained in formulating a new type of demulsifier for breaking the crude oil emulsion by using the methods described in Chapter 3. In achieving the objectives of this study, the screening process is done without considering the price of demulsifiers used in the formulation and the stability of demulsifiers formulation itself. The main aim is to find the most effective demulsifiers in emulsion resolution or specifically in separating water phase from the emulsion system. The formulation was based on the screening process of demulsifiers using Tabu crude oil emulsion. The data for all tests are shown in Appendix C.

4.2 Demulsifiers Screening Process

In this study, two types of demulsifiers were used which are water-soluble demulsifiers and oil-soluble demulsifiers. Water-soluble demulsifiers are commonly used to destabilize the water-in-oil emulsion (Bhattacharyya, 1992). This is because the oil droplets are dispersed in continuous aqueous phase. So, the absorption of the demulsifiers injected in the system becomes easier. Oil-soluble demulsifiers are effective in breaking water-in-oil emulsion because of the same reason. The emulsion system in the Malaysian crude oil emulsion is water-in-oil emulsion. So, the uses of oil-soluble demulsifiers is expected to give better result from this study but the combination of water-soluble demulsifiers and oil-soluble demulsifiers in the formulation created in this study is expected to give excellent result.

Based on the literature study (Bhattacharya, 1992), there are a lot of advantages and drawback for both types of demulsifiers. This study is aimed to find the effect of water and oil separation in emulsion systems by using the combination of both types of demulsifiers. The screening process in determining the most effective demulsifiers was carried out by using single demulsifier.

4.2.1 Water-soluble demulsifiers

The results for water and oil separation by using water-soluble demulsifiers are shown in Figures 4.1 and 4.2 respectively. There are seven chemicals categorized in this type which are acrylic acid, sodium dodecyl sulfate, poltethylene glycol 1000, methacrylic acid, butyl acrylate, 2-ethyl hexyl acrylate and methyl methacrylate.

It was found that, the most three effective demulsifiers in water separation are methyl methacrylate (40.0%), butyl acrylate (30.0%) and acrylic acid (17.4%). It was observed that oil phase is easy to separate compared to water. So, in a few minutes, the oil will break up from the emulsion and rise up in the top layer. The same reason could be used in determining the oil separation without using the chemical addition.

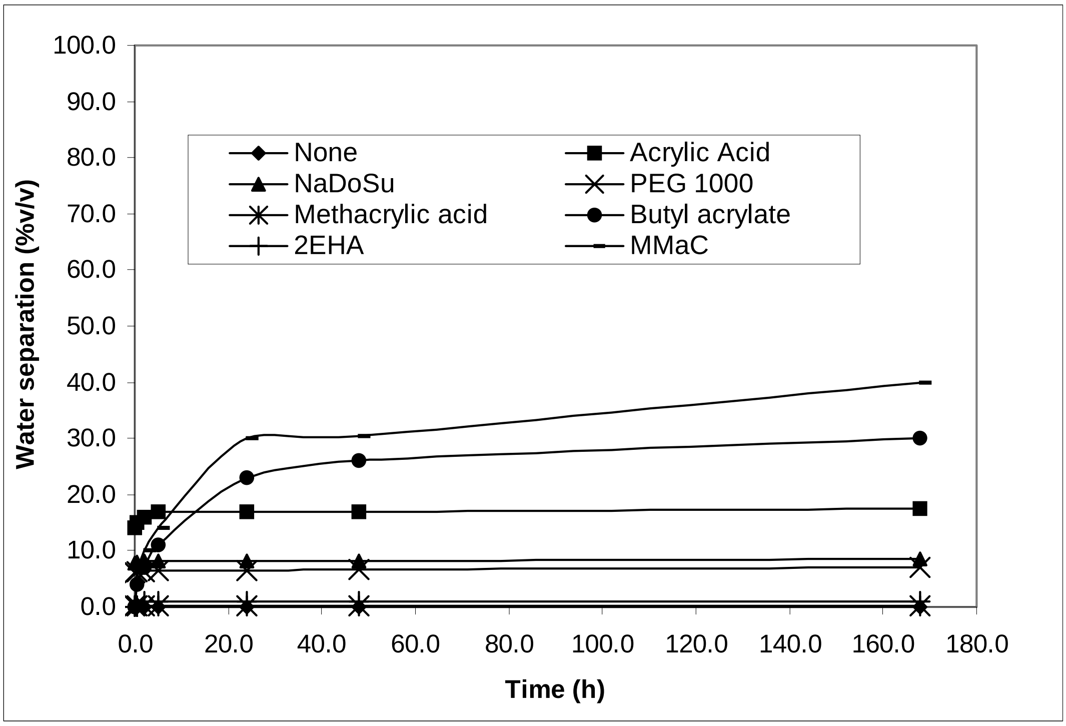

Figure 4.1: Water separation by using water-soluble demulsifiers. Experimental conditions: T, 70°C; Demulsifier concentration, 10 ppm

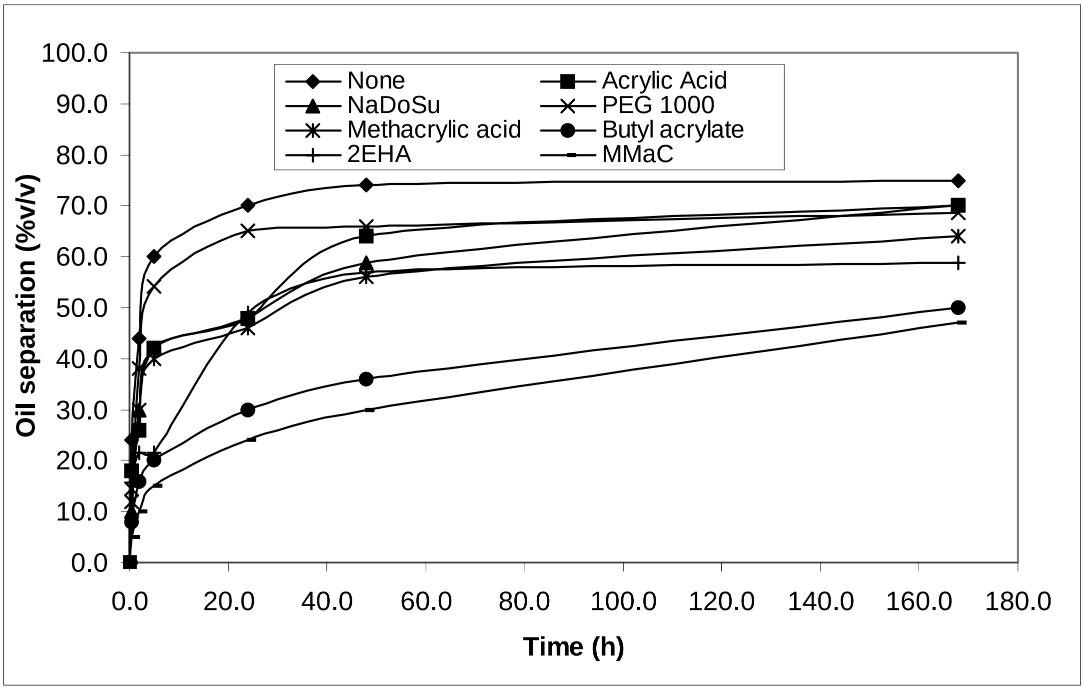

Figure 4.2: Oil separation by using water-soluble demulsifiers. Experimental conditions: T, 70°C; Demulsifier concentration,10 ppm

It was also found that, the demulsifiers that are efficient in water separation are inefficient in oil separation. This can be seen by the potential of methyl methacrylate and butyl acrylate in both water and oil separation. According to the result obtained, the only demulsifier that are efficient in both oil and water separations is acrylic acid. The water-soluble demulsifier will adsorb the water phase via oil phase. It will cause the film drainage and help in aggregation and coalescence formation of the water phase.

Based on the above results, one can concluded that the water-soluble demulsifier such as methyl methacrylate, butyl acrylate and acrylic acid is more efficient in breaking water-in-oil emulsion.

4.2.2 Oil-soluble demulsifiers

There are 13 types of demulsifiers from this categorizes used in this study such as methyl trioctyl ammonium chloride (TOMAC), maleic anhydride, polyvinylpyrrolidone, poly(ethylene-co-propylene-co-5-methylene-2-norbornene), 2-aminophenol-4-sulfonic acid, epsilon-caprolactam 99+%, N,N,N’,N’-tetramethyl-2-butene-1,4-diamine,95%, pseudocumene, dioctylamine, N-ethyl-N-sulfopropyl-m-toluidine, naphthalene, hexylamine and N,N-dimethylacetamide. Based on the literature study, this type of demulsifier is very effective in W/O emulsion resolution (Bhattacharyya, 1992). By using the same method and experimental condition used in water-soluble demulsifier screening, the results for both water and oil separation by using oil-soluble demulsifiers are shown in Figures 4.3 and 4.4.

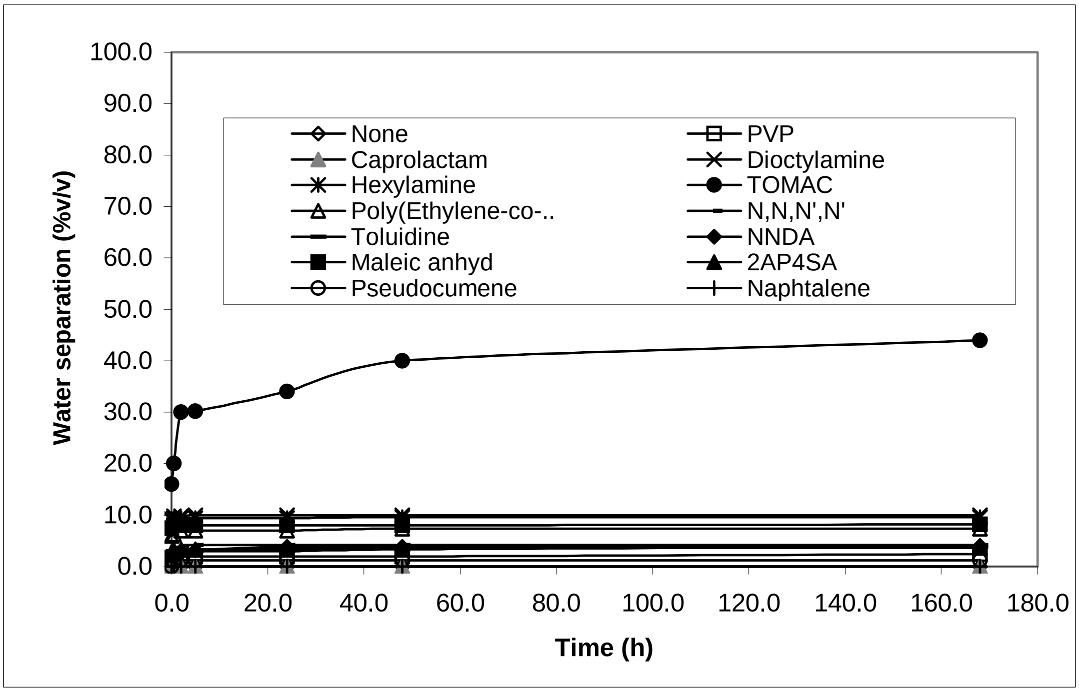

Figure 4.3: Water separation in 168 hours observation by using oil-soluble demulsifiers. Experimental conditions: T, 70°C; Demulsifier concentration, 10 ppm

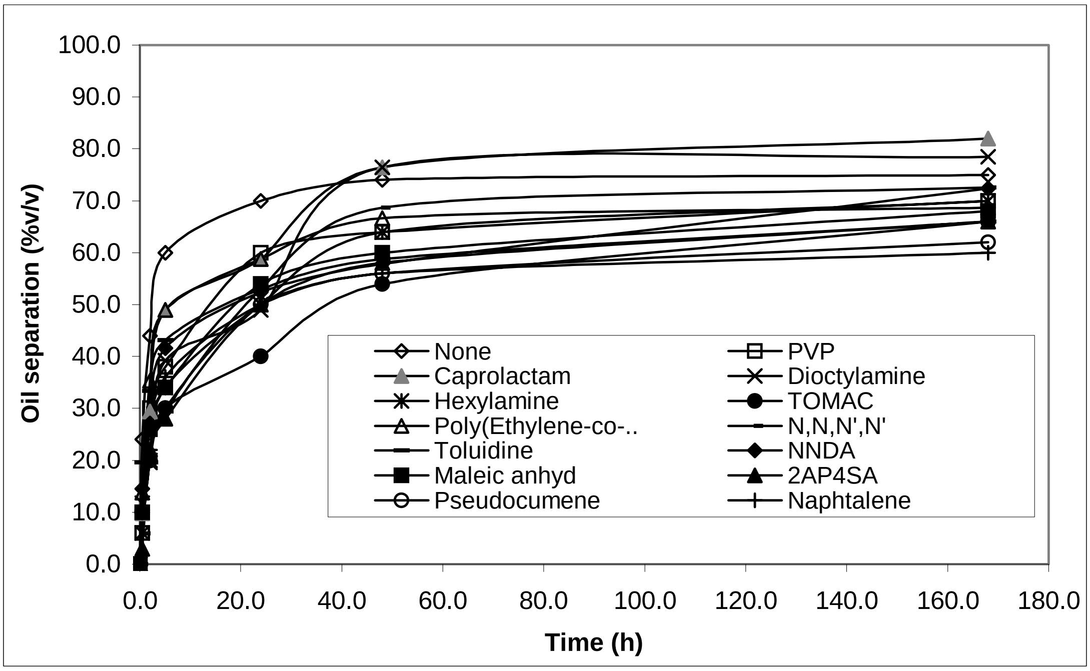

Figure 4.4: Oil separation during 168 hours by using oil-soluble demulsifiers. Experimental conditions: T, 70°C; Demulsifier concentration, 10 ppm.

Figure 4.3 shows the percentage of water separation by using oil-soluble demulsifiers. TOMAC (Methyl trioctyl ammonium chloride) gives the best result compared to the others. Although this is an expensive chemical, but it’s role in resolving emulsion problem is very excellent, which is higher than 40.0%. It seems that the other chemicals did not performed well in breaking W/O emulsion. This is because water separation obtained is ranging from 0.0% to 10.0%. Dioctylamine and hexylamine gave 10.0% and 9.6% respectively.

From results presented in Figure 4.4, the conclusion that can be made is all of the demulsifiers are very effective for oil separation. The separation occurred is ranging from 60.0% to 82.0%. The most effective demulsifier in oil separation are caprolactam (82.0%) followed by dioctylamine (78.4%) and the blank (75.0%). It seems that TOMAC gives only 66.0% of oil separation in this test.

From results presented in both figures, it can be concluded that the demulsifier that performed well in water separation are not very effective in oil separation. The oil separation can be easily happened although without the addition of demulsifier. It can be occurred almost by just applying heat. This observation is proven from the Figures 4.2 and 4.4. The better results obtained in oil-soluble demulsifiers because this types of demulsifiers can be easily adsorbed through the continuous phase (oil phase).

In the field of demulsification, the most important observation is the ability of water to separate from the emulsion system. This is because the trapped water in oil phase is very difficult to handle despite of using demulsifiers. This phenomenon created a lot of problems as discussed in Chapter 2. For this reason, a lot of researches are done in creating the good formulation to help in releasing water from the emulsion system.

Based on this screening process, TOMAC, dioctylamine and hexylamine are choosen for further study. From the literature surveys, there are a lot of formulations involved water-soluble and oil-soluble demulsifiers itself. The result of the emulsion resolution is depending on the characteristics and geological factors of the crude oils. Because of this reason, the combination of these two types of demulsifiers will help in providing a better result of emulsion resolution.

4.3 Effects of Various Concentrations

The representative for both types of demulsifiers was used in this test. The selection was based on the ability of the demulsifier in separating of both water and oil from the emulsion system resulted in Figures 4.1,4.2,4.3 and 4.4. As the result, acrylic acid and TOMAC were chosen for this test. Acrylic acid represents from water-soluble group while TOMAC from oil-soluble group.

The concentrations used in this test are 10 ppm, 20 ppm and 100 ppm. This is because 10 ppm is considered the lowest concentration and 100 ppm is the highest concentration that are used in this test. The concentration, which is above 100 ppm is worse in this area because the higher the concentration, a lot of money will be used in buying demulsifiers. The smaller dosage of formulation, which is 10 ppm and lower that are able in resolving emulsion problem is considered a best result in this area. So, three different concentrations are enough in this test. This test was aimed to obtain the relationship between concentration and emulsion resolution efficiency.

The effects of concentration of water and oil separation by using acrylic acid are shown in Figures 4.5 and 4.6 while Figures 4.7 and 4.8 show of water and oil separation by using TOMAC.

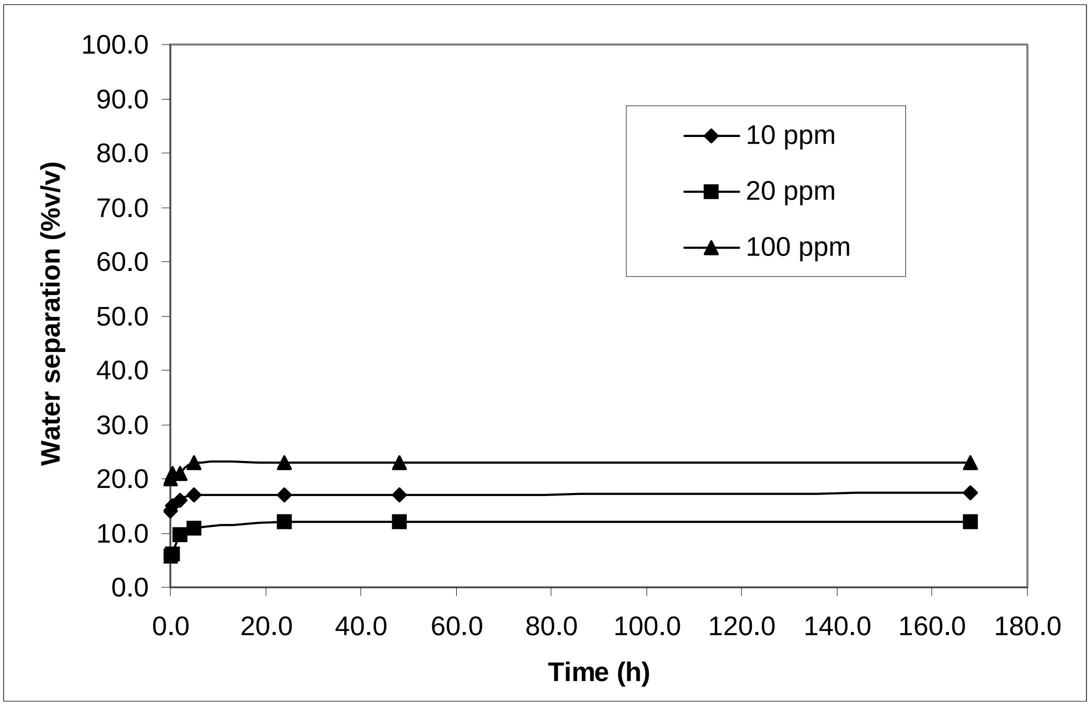

Figure 4.5: Effects of water separation by using various concentrations of acrylic acid at 70°C

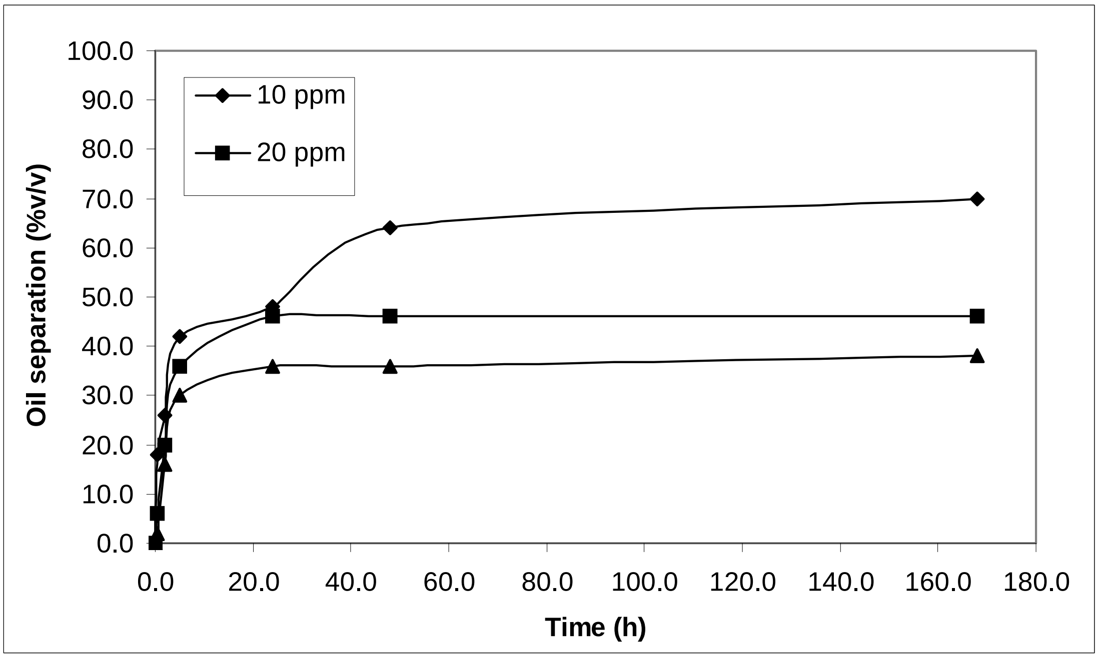

Figure 4.6: Effects of oil separation by using various concentration of acrylic acid at 70°C.

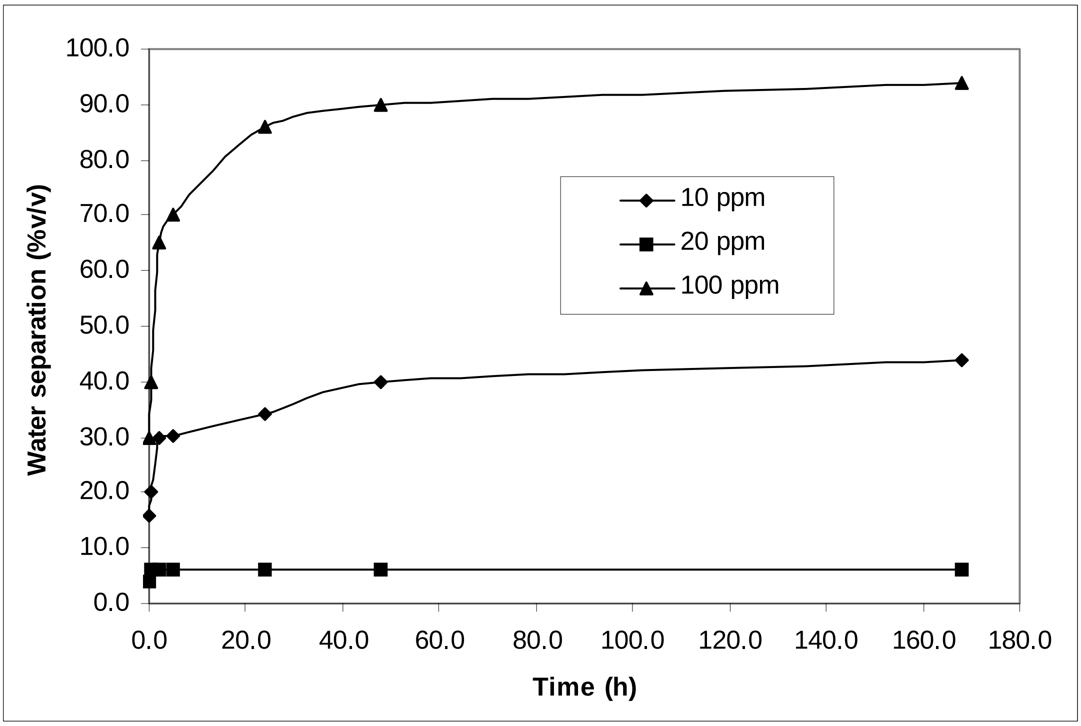

Figure 4.7: Effects of water separation by using various concentrations of TOMAC at 70°C

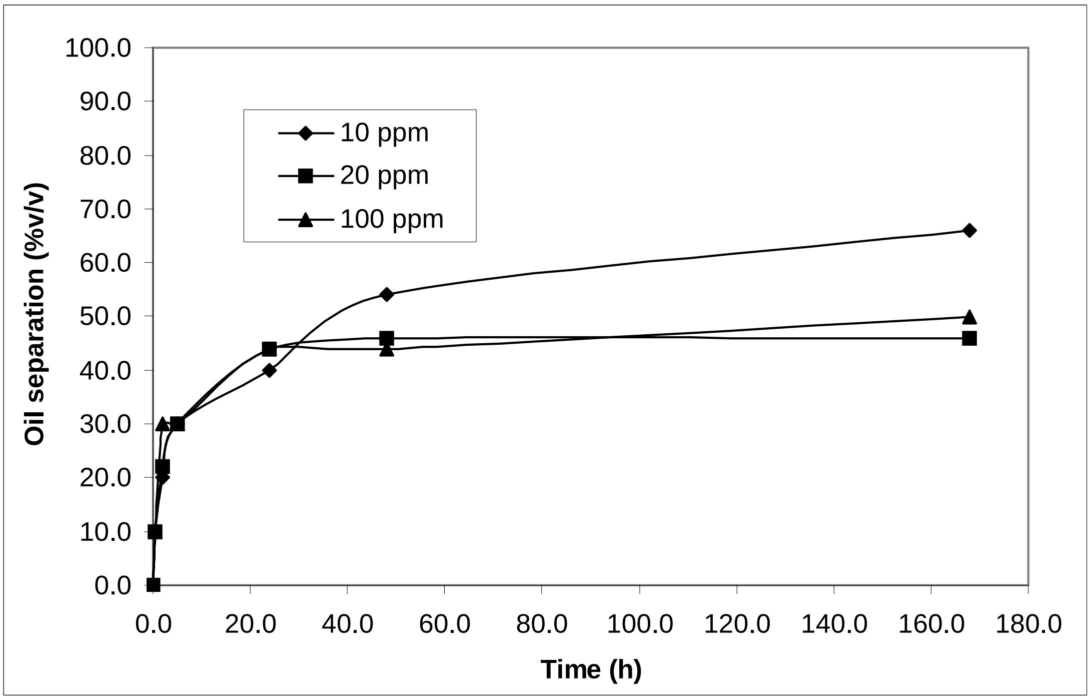

Figure 4.8: Effects of oil separation by using various concentration of TOMAC at 70°C.

From Figure 4.5, it can be seen that in all concentration, water separations are lower than 25.0%. 10-ppm concentration gave about 17.4% separation, 20-ppm gave about 12.0% separation and 23.0% separation occurred by using 100-ppm of acrylic acid. The lowest separation was by injecting 20-ppm of acrylic acid. So, concentration plays an important role in demulsification process. The successful of demulsification process depends on the suitable concentration of demulsifier.

Figure 4.6 proved the same pattern of flow as discussed in section 4.2. It can be seen that the best concentration in water separation became the worst in oil separation and vice versa. The 10-ppm concentration gave the best oil separation (70.0%) while 100-ppm concentration gave the worst result (38.0%). 20-ppm of acrylic acid gave 46.0% oil separation.

Figure 4.7 shows the effects of water separation by using different concentration of TOMAC. 100-ppm of TOMAC gave 94.0% of water separation, followed by 44.0% and 6.2% by using 10-ppm and 20-ppm respectively. From this figure, it can be seen that 20-ppm of TOMAC could not perform well in separating the water phase from emulsion system.

From Figure 4.8, the oil separation obtained in a small range, from 46.0% to 66.0%. 10-ppm of TOMAC gave 66.0% of oil separation followed by 50.0% and 46.0% by using 100-ppm and 20-ppm respectively. The rate of separation increasing with increasing of concentration except at very low concentration (<20 ppm). This phenomena needs further investigation. This is because TOMAC is from the oil-soluble groups of demulsifier. The result of water separation for both acrylic acid and TOMAC is representing in Figure 4.9.

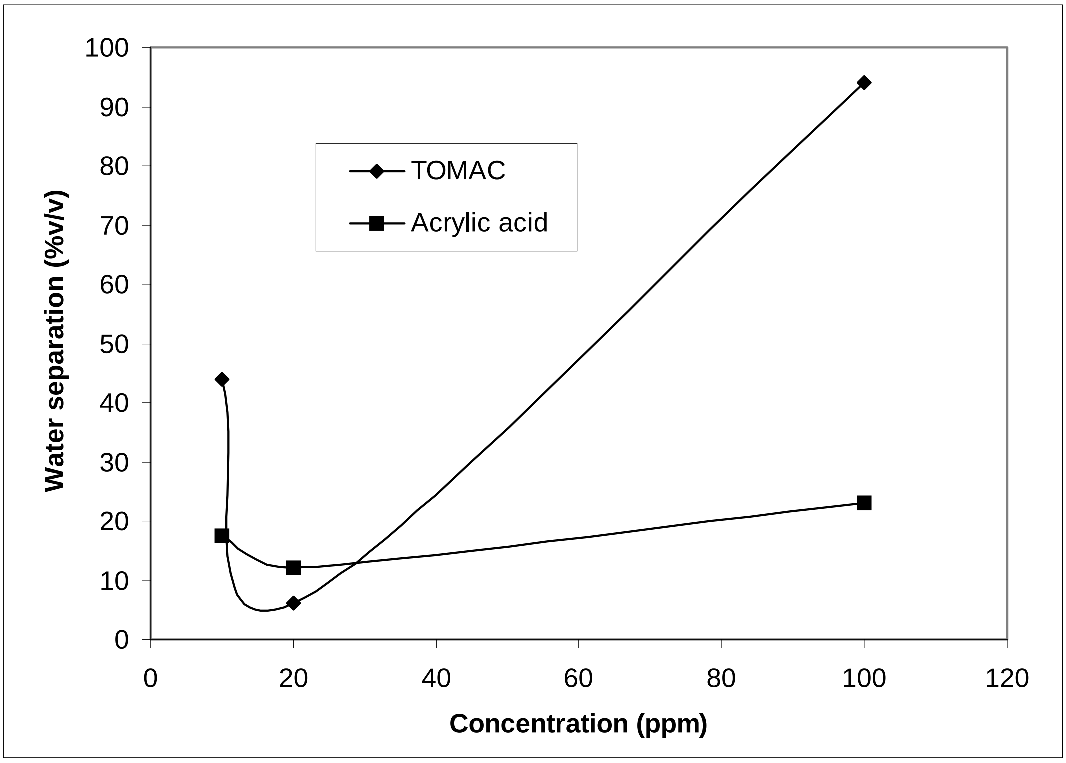

Figure 4.9: The relationship between concentrations and percentage of water separation by using TOMAC and acrylic acid

4.4 Effects of Modifier Addition.

From the literature study, it was found that almost all the researchers found that the best individual emulsion destabilizers are fatty amines. The addition of modifier normally from alcohol groups mostly help the demulsification process. Fatty amines seem to interact directly and strongly through the surface groups of the interfacial film while alcohol groups seem to destabilize through the diffusion or portioning mechanism (Sjoblom et al., 1990).

Normally, short and medium chain alcohols are used as modifier. This is because these groups of alcohols are soluble in aqueous phase. In order to determine the addition of modifier needed in this formulation, three alcohols were used, which are methanol, butanol and octanol. Figures 4.10 and 4.11 show the percentage of water and oil separation by using these alcohols.

Figure 4.10 shows that methanol has a good ability in promoting water separation from the emulsion system compared to butanol and octanol. This is because short chain alcohols are very soluble in the water and long chain alcohols are very soluble in oil. Methanol itself gaves 2.6% water separation followed by butanol (2.4%) and octanol (1.4%). But as discussed earlier, methanol and butanol did not help in oil separation compared with octanol. Both methanol and octanol give 50.0% oil separation while octanol gives 60.0%. 75.0% of oil was easily separated without the addition of any demulsifiers (Figure 4.11).

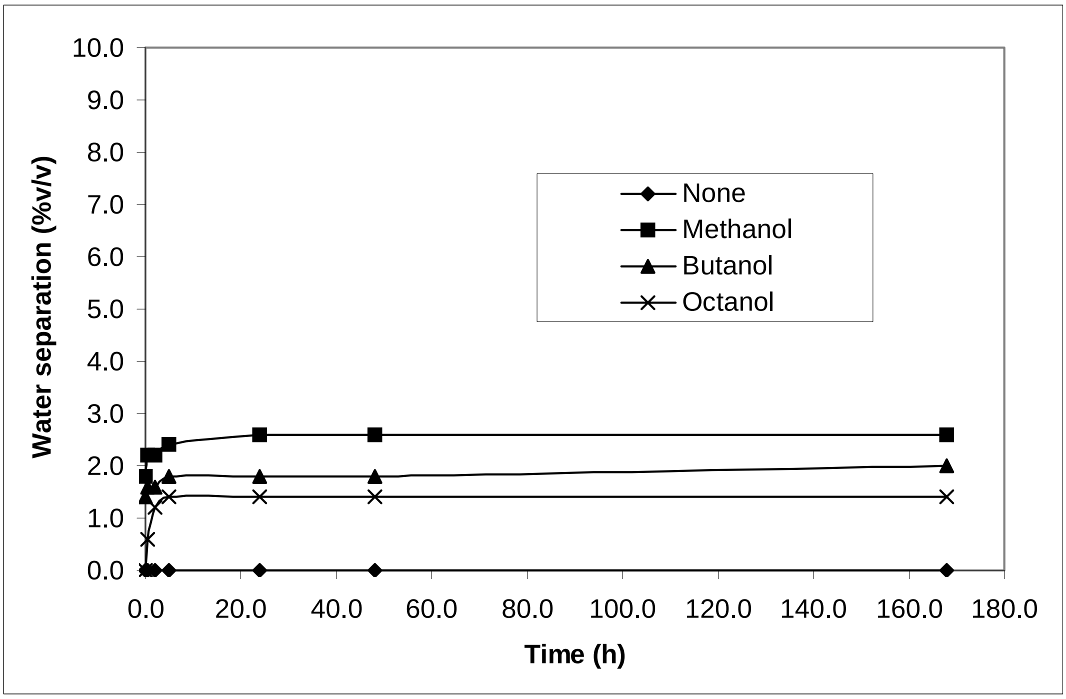

Figure 4.10: Percentage of water separation by using alcohols. Experimental conditions: T, 70°C, Demulsifier concentration, 10 ppm.

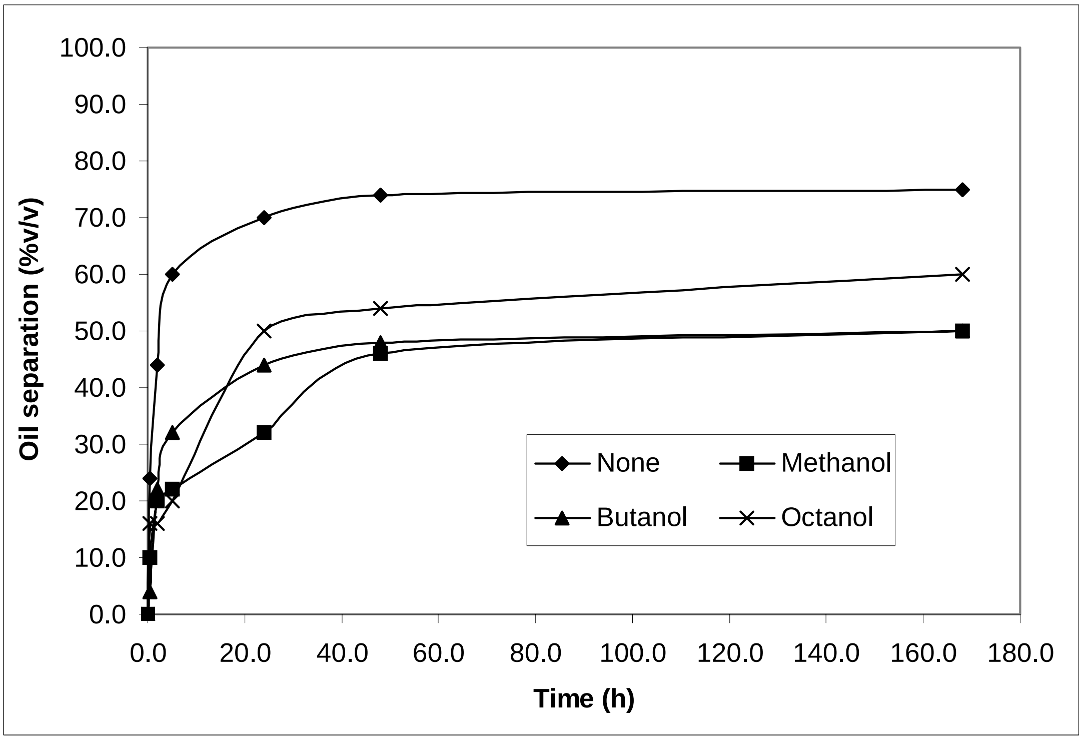

Figure 4.11: Results in oil separation by using of alcohols. Experimental conditions: T, 70°C, Demulsifier concentration, 10 ppm

Methanol was selected to be a modifier in this test based on the result of the previous test. While, TOMAC and acrylic acid were chosen as oil-soluble and water-soluble demulsifier respectively based on their performance and ability in separating water and oil from the emulsion system.

For comparison, the blank was prepared, that is where the emulsion system is injected firstly without modifier. The second system of emulsion was injected with the addition of modifier. Figures 4.12 and 4.13 show the results of water and oil separation from these two tests.

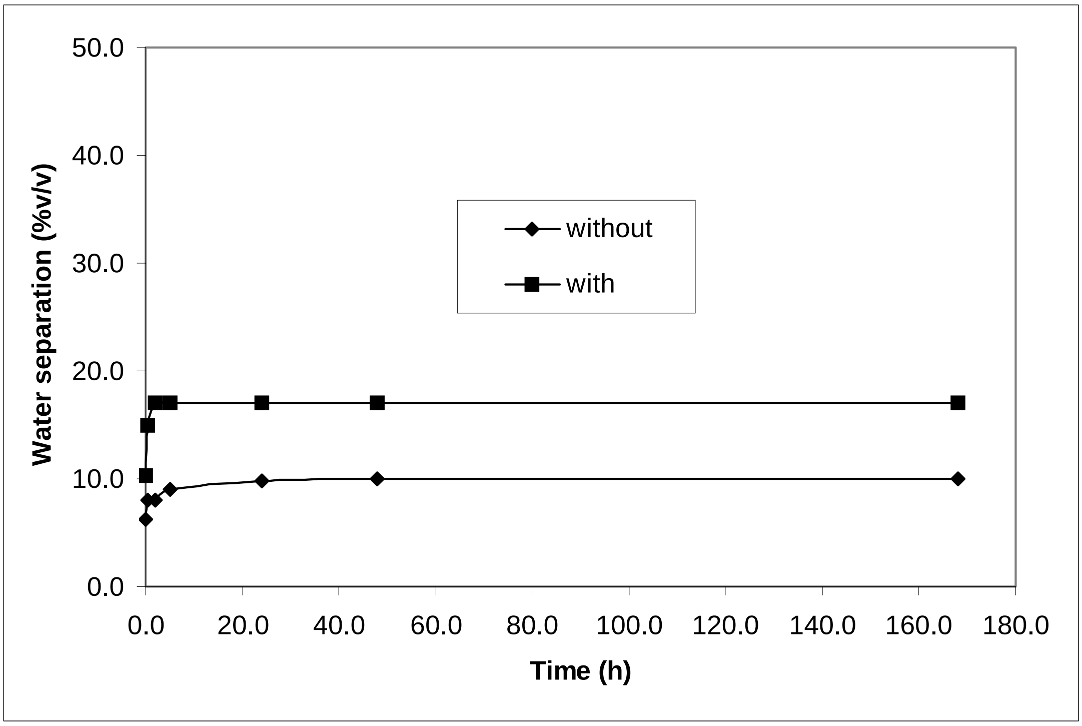

Figure 4.12: Comparison of water separation with and without modifier. Experimental conditions: T, 70°C; modifier concentration, 10 ppm

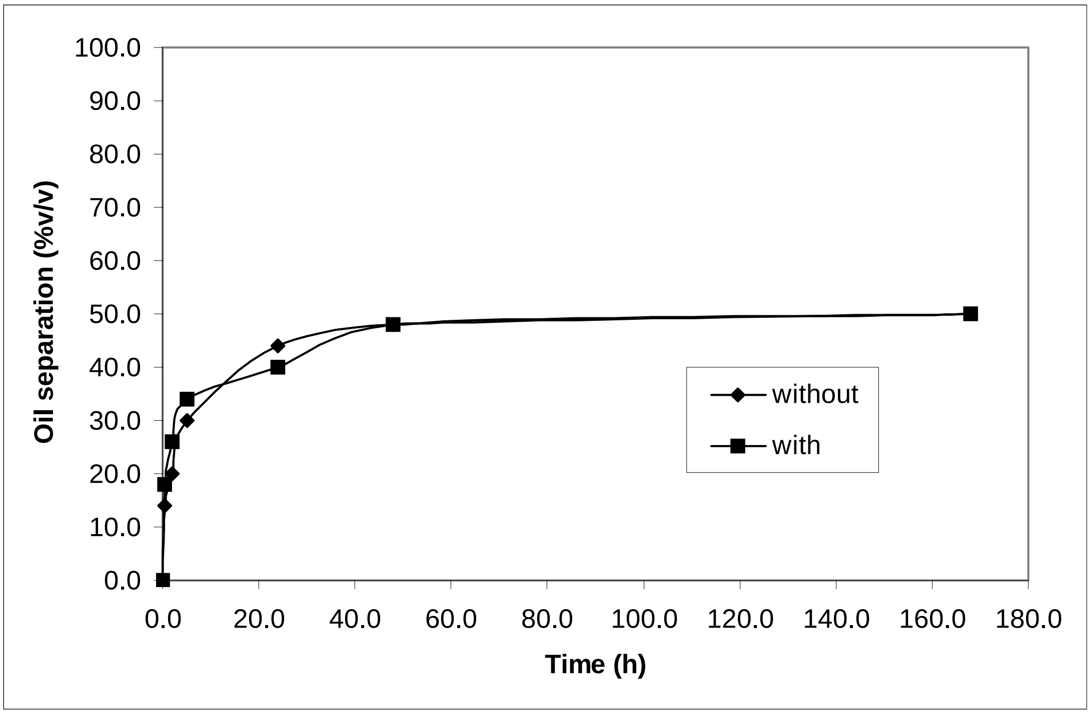

Figure 4.13: Comparison of oil separation with and without modifier. Experimental conditions: T,70°C; modifier concentration, 10ppm.

By referring to both Figures 4.12 and 4.13, it was found that the difference in water separation is only 7.0%, where 17.0% with modifier (methanol) addition and 10.0% without methanol addition. Hence, the presence of methanol in this demulsifiers composition influences very little effect on demulsification process. In addition, the oil separations in both conditions are almost the same, which is 50.0%. From the test results, it seems that modifier addition is unneeded in this formulation.

4.5 Optimization of Demulsifiers Formulation.

4.5.1 Introduction.

After knowing that there is no other chemical (modifier) was needed in this formulation, optimization was done to make sure the optimum concentration and yield gained from the formulation. As discussed in Chapter 3, the whole results were presented and discussed in this section.

4.5.2 Optimization for oil-soluble demulsifiers formulation.

The water separation yield obtained from the experiments that based on the experimental design was given in Table 4.1. The model was considered as a second-order model for the transistor gain data.

To measure the variability of the observed response values, Statistical Analysis System (SAS) software was used. The value of R-squared from regression coefficient table is 0.9838. That is, the second- order model explains about 98.38% of the variability observed in the gain. The adjusted R^2 for this model is 0.88628. This value is considered a good fit for the observed response values and second-order model because when linear terms are added to this model, R^2_{adj} = 0.8551; that is the adjusted R^2 actually decreases when linear terms are included in the model. This is a strong indication that the linear terms are unnecessary.

Table 4.1: 2^3 full factorial design with the response

Run	**[TOMAC] (ppm)**	**[Hexylamine] (ppm)**	**[Dioctylamine] (ppm)**	**Water separation yield (%v/v)**
1	30.0	20.0	10.0	19.6
2	50.0	20.0	10.0	50.0
3	30.0	40.0	10.0	18.0
4	50.0	40.0	10.0	34.0
5	30.0	20.0	20.0	19.6
6	50.0	20.0	20.0	48.0
7	30.0	40.0	20.0	22.0
8	50.0	40.0	20.0	50.0

The application of the response surface methodology yielded the following regression equation, which is an empirical relationship between water separation yield and the test variables in coded unit given in equation (4.1). All the variables in the equation (4.1) are given in regression coefficient table as shown in Table 4.2.

$$Y = 1.465X_1 – 0.258X_2 - 2.2X_3 - 0.0185X_1X_2 + 0.025X_1X_3 + 0.055X_2X_3 – 3 \qquad (4.1)$$

Table 4.2: Regression coefficient values

Factor	**Regression Coefficients**
Mean/Constant	-3.0000
(1) X_1	1.4650
(2) X_2	-0.2500
(3)X_3	-2.2000
X_1X_2	-0.0185
X_1X_3	0.0250
X_2X_3	0.0550

Subsequently, significances of factors and interactions are shown in an analysis of variance (ANOVA) (Table 4.3).

Table 4.3: Analysis of variance

Factor	**SS**	**df**	**MS**	**F**
(1) X_1	1320.980	1	1320.980	53.91755
(2) X_2	21.780	1	21.780	0.88898
(3) X_3	40.500	1	40.500	1.65306
X_1X_2	27.380	1	27.380	1.11755
X_1X_3	12.500	1	12.500	0.51020
X_2X_3	60.500	1	60.500	2.46939
Error	24.500	1	24.500	
Total SS	1508.140	7		

Each of the observed values Yo is compared with the predicted values Yp obtained from the model is shown in Table 4.4 and Figure 4.14. The values of residual are ranging from –1.75 to 1.75. The comparison of the residual with the residual variance (MS = 24.5) indicates that none of the individual residual exceeds twice the square root of the residual variance. All of these considerations indicate a good adequacy of the regression model.

Table 4.4: Observed responses and predicted values

Run	Yo	Yp	Residual (Yo-Yp)
1	19.60	21.35	-1.75
2	50.00	48.25	1.75
3	18.00	16.25	1.75
4	34.00	35.75	-1.75
5	19.60	17.85	1.75
6	48.00	49.75	-1.75
7	22.00	23.75	-1.75
8	50.00	48.25	1.75

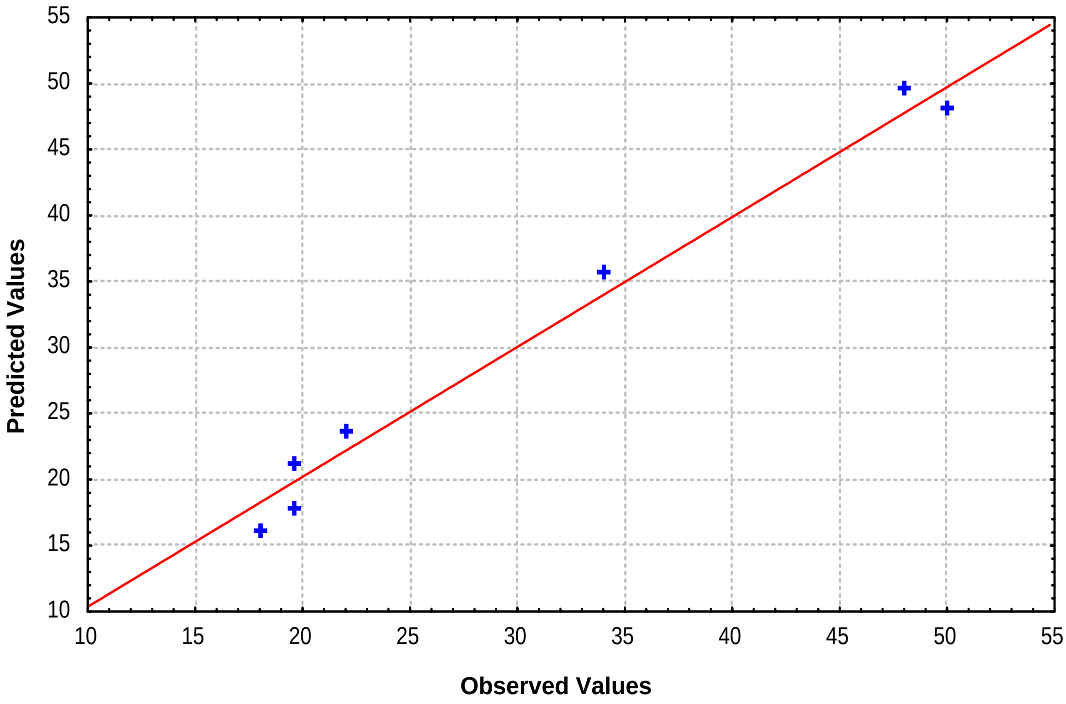

Figure 4.14: Predicted values versus observed values for the model

The significance of each coefficient was determined by using the student t-test and p-value as given in Table 4.5. The larger the magnitude of *t*-value and smaller the *p*-value indicates the high significance of the corresponding coefficient.

Table 4.5: Significance of regression coefficients

Variables	**Computed *t* value**	**Significance level, *p* value**
Mean/Constant	-0.08529	0.9458
X_1	1.92054	0.3056
X_2	-0.28017	0.8261
X_3	-1.23273	0.4339
X_1*X_2	-1.05714	0.4823
X_1*X_3	0.71429	0.6051
X_2*X_3	1.57143	0.3608

Based on Table 4.5, the highest value for computed *t* value is X_1, which is concentration of TOMAC. This statement is supported by Pareto Chart, which is shown in Figure 4.15.

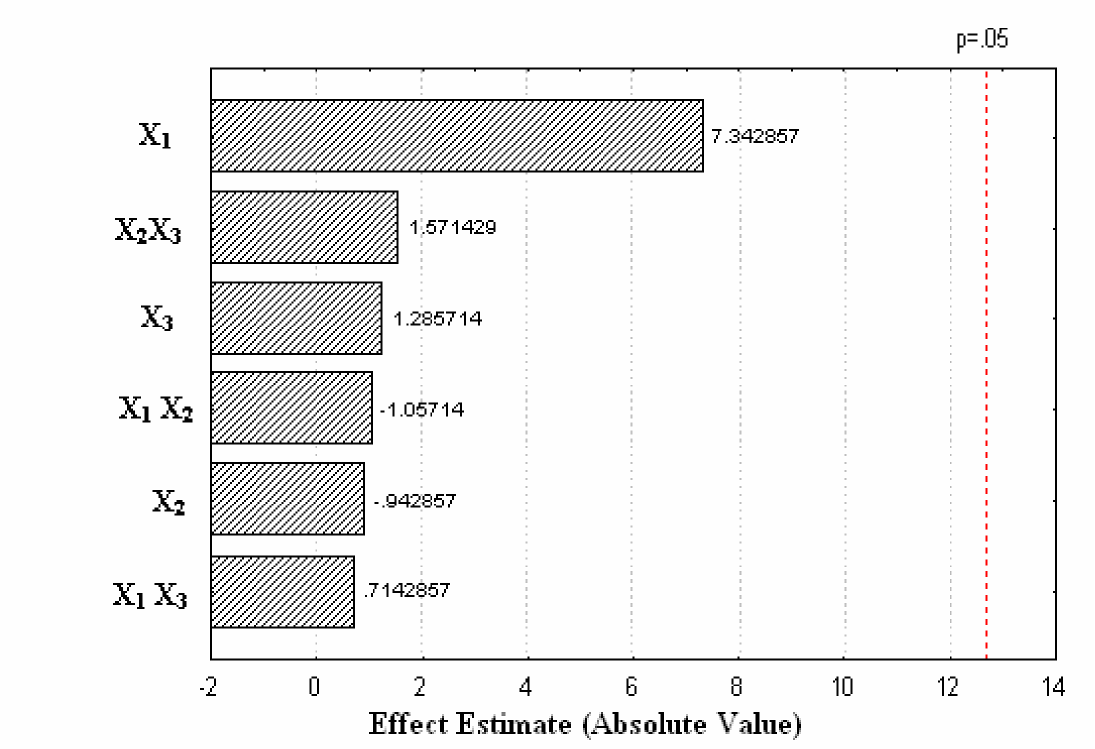

Figure 4.15: Pareto Chart of standardized effects for oil-soluble demulsifiers formulation; X_1 = [TOMAC], X_2 = [Hexylamine], X_3 = [Dioctylamine]

From Figure 4.15, it can be concluded that the main effects for the optimum yield or response is concentration of TOMAC followed by concentration of dioctylamine and hexylamine. So, the influence of hexylamine in this formulation is small compared to the others.

The maximum yield of water separation predicted from the response surface is when the TOMAC concentration of 48.7 ppm, hexylamine concentration of 0 ppm and dioctylamine concentration of 8 ppm. The response surface plots in Figure 4.16(a) and 4.16(b) gives a graphical display of these quantities. The type of surface obtained for this model is stationary ridge. This combination gives 60.423% of water separation from the crude oil emulsion.

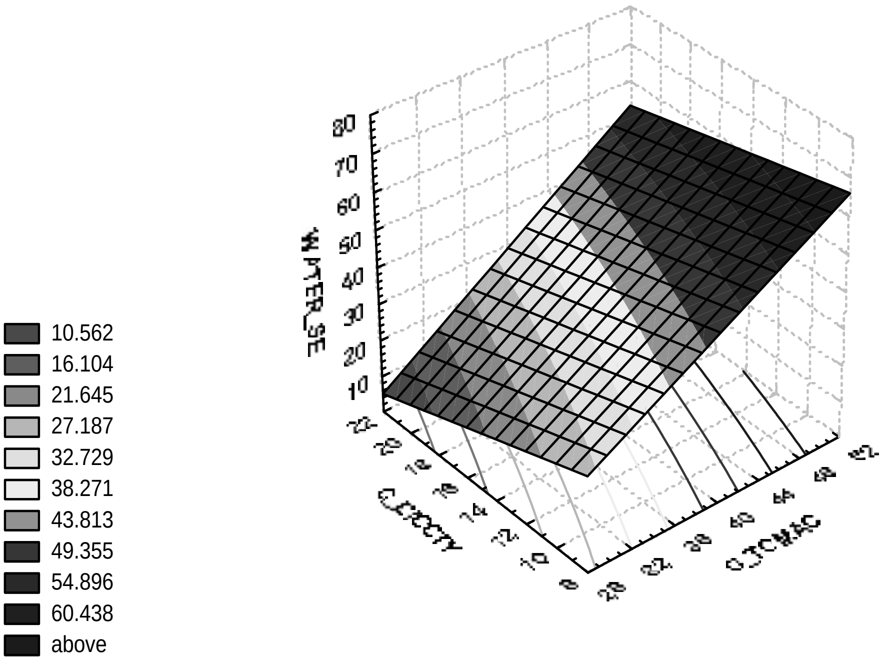

Figure 4.16(a): Response surface of predicted water separation; WATER_SE = Water separation, C_TOMAC = [TOMAC], C_DIOCTY = [Dioctylamine]

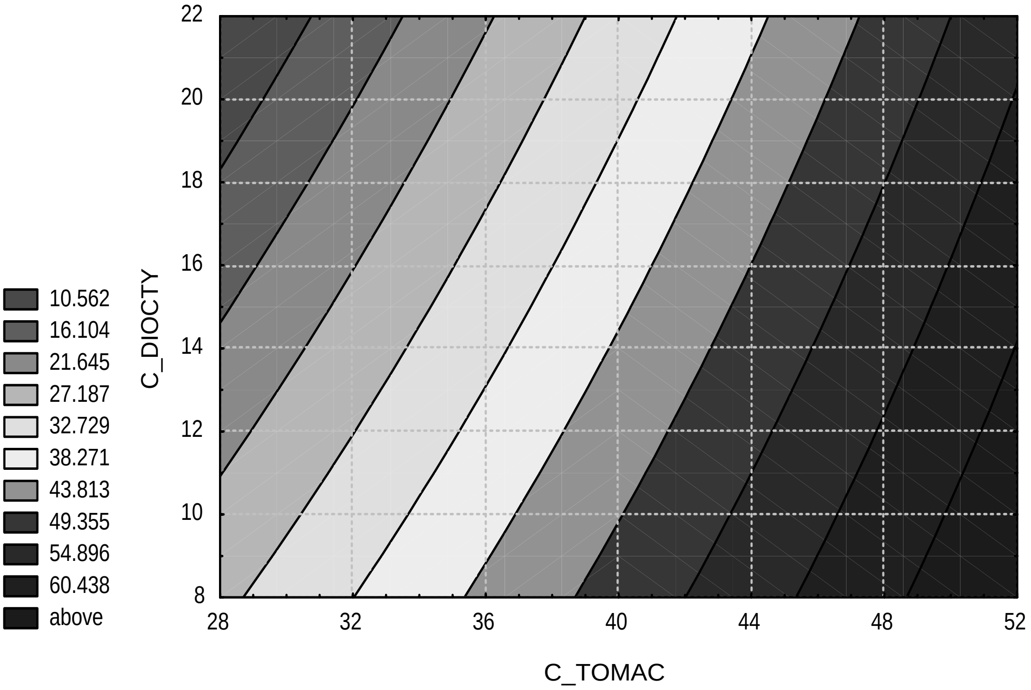

Figure 4.16(b): Contour plot of predicted water separation; C_TOMAC = [TOMAC], C_DIOCTY = [Dioctylamine].

4.5.3 Optimization of water-soluble demulsifiers formulation

The steps in optimization of water-soluble demulsifiers formulation were exactly same as in the previous steps. The water separation yield obtained from the experiments that based on the experimental design is given in Table 4.6. The model was considered as a second-order model for the transistor gain data.

Table 4.6: 2^3 full factorial design with the response

Run	[Methyl Metachrylate] (ppm)	[Butyl acrylate] (ppm)	[Acrylic Acid] (ppm)	Water separation yield (%v/v)
1	25.0	10.0	50.0	4.4
2	30.0	10.0	50.0	18.0
3	25.0	15.0	50.0	18.0
4	30.0	15.0	50.0	22.0
5	25.0	10.0	60.0	16.0
6	30.0	10.0	60.0	24.0
7	25.0	15.0	60.0	16.0
8	30.0	15.0	60.0	22.0

From the Statistical Analysis System (SAS), the R-squared value is 0.9722. This means that the second order model explains about 97.22% of the variability observed. The value of adjusted R^2 for this model is 0.80512. The other regression coefficients are shown in Table 4.7.

Table 4.7: Regression coefficient values

Factor	Regression Coefficients
Mean/Constant	-326.050
X_4	6.460
X_5	17.940
X_6	3.830
X_4X_5	-0.232
X_4X_6	-0.036
X_5X_6	-0.196

Based on Table 4.7, the regression equation obtained for this model is shown in equation (4.2).

$$Y = 6.460\ X_4 + 17.940\ X_5 + 3.830\ X_6 – 0.232\ X_4X_5 - 0.036\ X_4X_6 - 0.196\ X_5X_6 – 326.050 \qquad (4.2)$$

The analysis of variance may be used to confirm the magnitude of these effects. This test procedure is called analysis of variance because it is based on a decomposition of the total variability in the response variable, Y. The analysis of variance (ANOVA) is summarized in Table 4.8. Each of the observed values Yo is compared with the predicted values Yp obtained from the model is shown in Table 4.9 and Figure 4.17.

Table 4.8: Analysis of variance

Factor	**SS**	**df**	**MS**	**F**
X_4	124.8200	1	124.8200	17.28809
X_5	30.4200	1	30.4200	4.21330
X_6	30.4200	1	30.4200	4.21330
X_4X_5	16.8200	1	16.8200	2.32964
X_4X_6	1.6200	1	1.6200	0.22438
X_5X_6	48.0200	1	48.0200	6.65097
Error	7.2200	1	7.2200	
Total SS	259.3400	7		

Table 4.9: Observed responses and predicted values

Run	**Yo**	**Yp**	**Residual (Yo-Yp)**
1	4.400	5.350	-0.95
2	18.000	17.050	0.95
3	18.000	17.050	0.95
4	22.000	22.950	-0.95
5	16.000	15.050	0.95
6	24.000	24.950	-0.95
7	16.000	16.950	-0.95
8	22.000	21.050	0.95

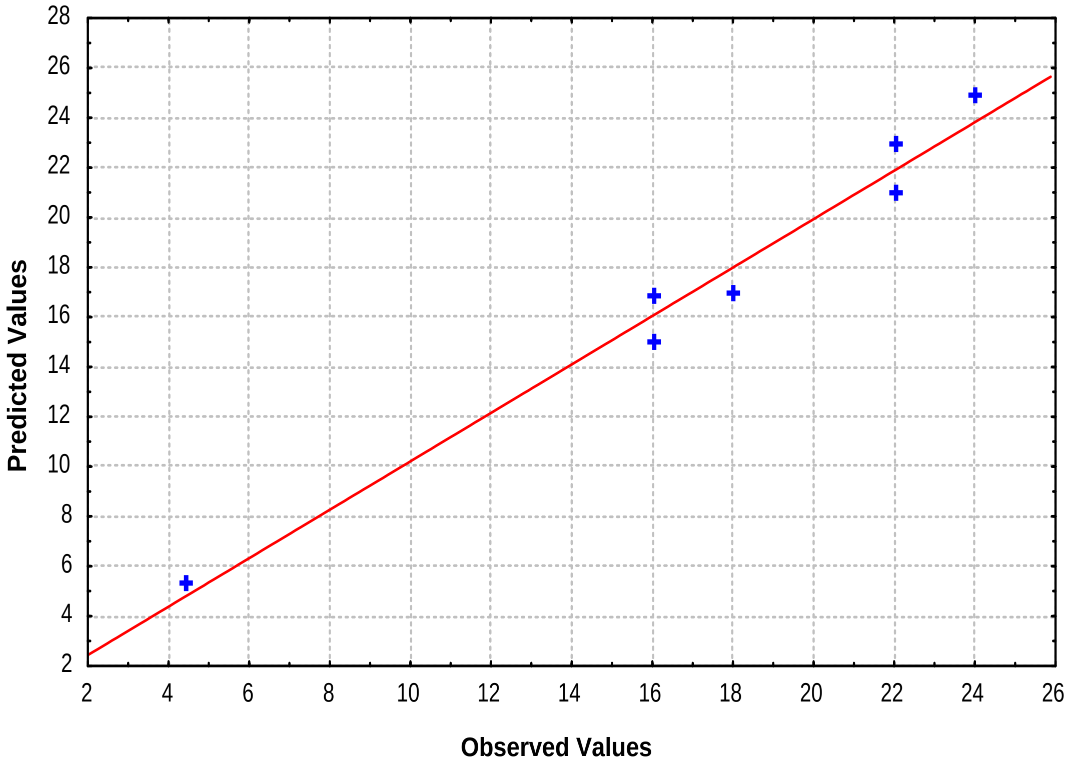

Figure 4.17: Predicted values versus observed values

Based on Table 4.9, the differential values between observed and predicted is ranging between –0.95 and 0.95. Table 4.8 shows that MS Residual error for this model is 7.22. The comparison of the residual with the residual variance indicates that none of the individual residual exceeds twice the square root of the residual variance. All of these considerations indicate a good adequacy of the regression model.

The significance of each coefficient was determined by using the student t-test and p-value as given in Table 4.10. The larger the magnitude of *t*-value and smaller the *p*-value indicates the high significance of the corresponding coefficient.

Table 4.10: Significance of regression coefficients

Variables	**Computed *t* value**	**Significance level, *p* value**
Mean/Constant	-2.37069	0.254121
X_4	1.40214	0.394404
X_5	3.02856	0.203030
X_6	1.66260	0.344729
X_4*X_5	-1.52632	0.369241
X_4*X_6	-0.47368	0.708376
X_5*X_6	-2.57895	0.235490

Based on Table 4.10, it seems that the highest computed *t* value is X_5, which is concentration of butyl acrylate followed by acrylic acid and methyl methacrylate. The most critical factor in this model can be obtained from Pareto Chart as shown in Figure 4.18.

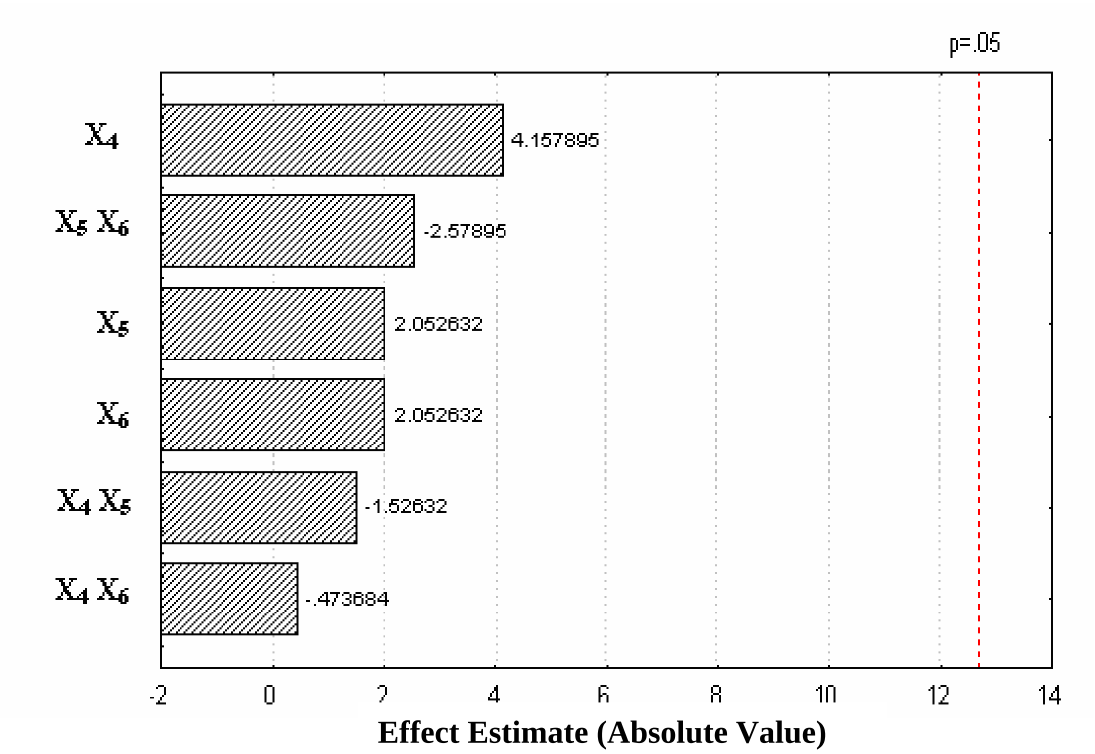

Figure 4.18: Pareto Chart of standardized effects for water-soluble demulsifiers formulation; X_4 = [Methyl methacrylate], X_5 = [Butyl acrylate], X_6 = [Acrylic acid]

From Figure 4.18, the factors that responsible to obtained maximum yield of water separation is concentration of methyl methacrylate followed by butyl acrylate and acrylic acid. The concentrations of butyl acrylate and acrylic acid have the same effects. So, all factors are considered very important in producing a good formulation for breaking the emulsion problem.

Response Surface Methodology (RSM) is used in finding the optimum concentration of all three factors in producing a maximum yield. Figures 4.19(a) and 4.19(b) present the response surface and contour plot for this case.

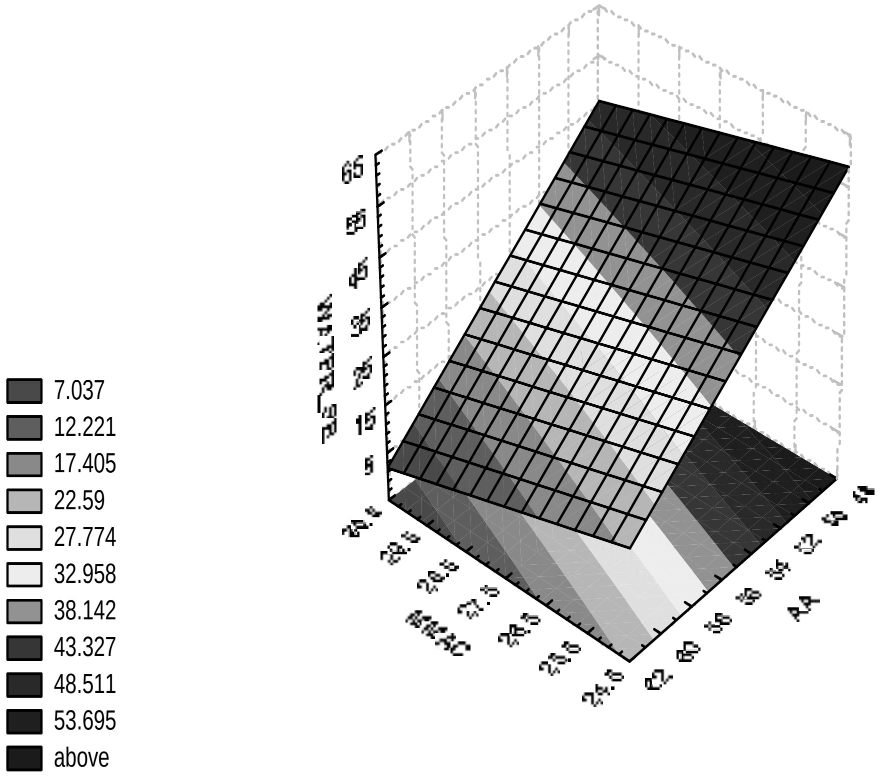

Figure 4.19(a): Response surface for the predicted water separation; WATER_SE = Water separation, MMAC = [Methyl methacrylate], AA = [Acrylic acid]

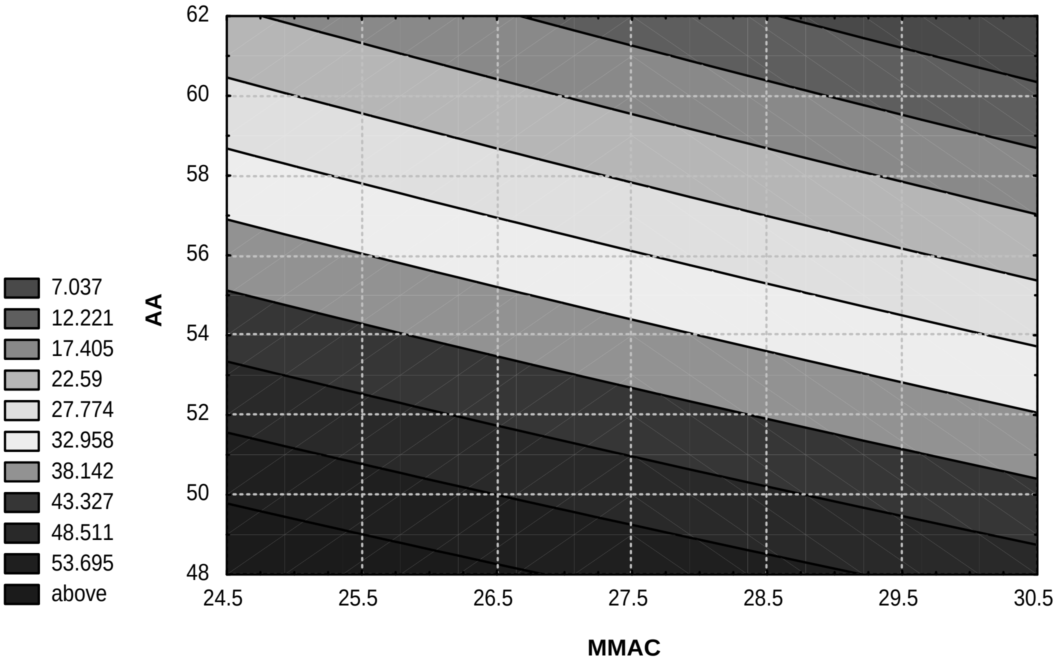

Figure 4.19(b): Contour plot for the predicted water separation; MMAC = [Methyl methacrylate], AA = [Acrylic acid]

Based on Figures 4.19(a) and 4.19(b), it is found that the best concentration for acrylic acid, methyl methacrylate and butyl acrylate is 48.2 ppm, 26.5 ppm and 29.9 ppm respectively. This formulation will produce maximum yield (53.695% and above) for water separation. The response surface for both oil-soluble and water-soluble demulsifiers is in the same type, which is called as stationary ridge.

4.5.4 Optimum demulsifiers formulation

Optimum demulsifiers formulation gained by Statistical Analysis System software will be used to do the next testing steps in order to know the intensity of this new formulation. But in this test, the response surface and contour plot for both oil-soluble demulsifiers and water-soluble demulsifiers resulted no optimum concentration gained. These results may be caused by the small range of concentration used in this optimization. Table 4.11 shows the composition of all demulsifiers and the best concentration used in this formulation.

Table 4.11: Formulation composition

No.	Demulsifier	Concentration (ppm)
1	TOMAC	48.7
2	Acrylic acid	48.2
3	Butyl acrylate	29.9
4	Methyl methacrylate	26.5
5	Dioctylamine	8.0

Based on Table 4.11, the most important demulsifier in this formulation is TOMAC while dioctylamine plays the smallest role in completing this formulation. There are three demulsifiers from water-soluble group and two from oil-soluble group. This formulation is able to treat Malaysian crude oil emulsion especially for W/O emulsion.

4.6 Formulation Effects on Single Emulsion System

The formulation was firstly tested by using single emulsion system. Single emulsion system meant that the emulsion system created contained only one interfacial active agents in crude oil whether asphaltenes, resins or waxes. According to Gafonova (2000), resins and waxes cannot form emulsion alone. However, only asphaltenes alone can form emulsion. The asphaltenes recovery from crude oil and method of emulsion formation were discussed in Chapter 3. Figure 4.20 presents the water and oil separation for asphaltenes emulsion system by using this formulation.

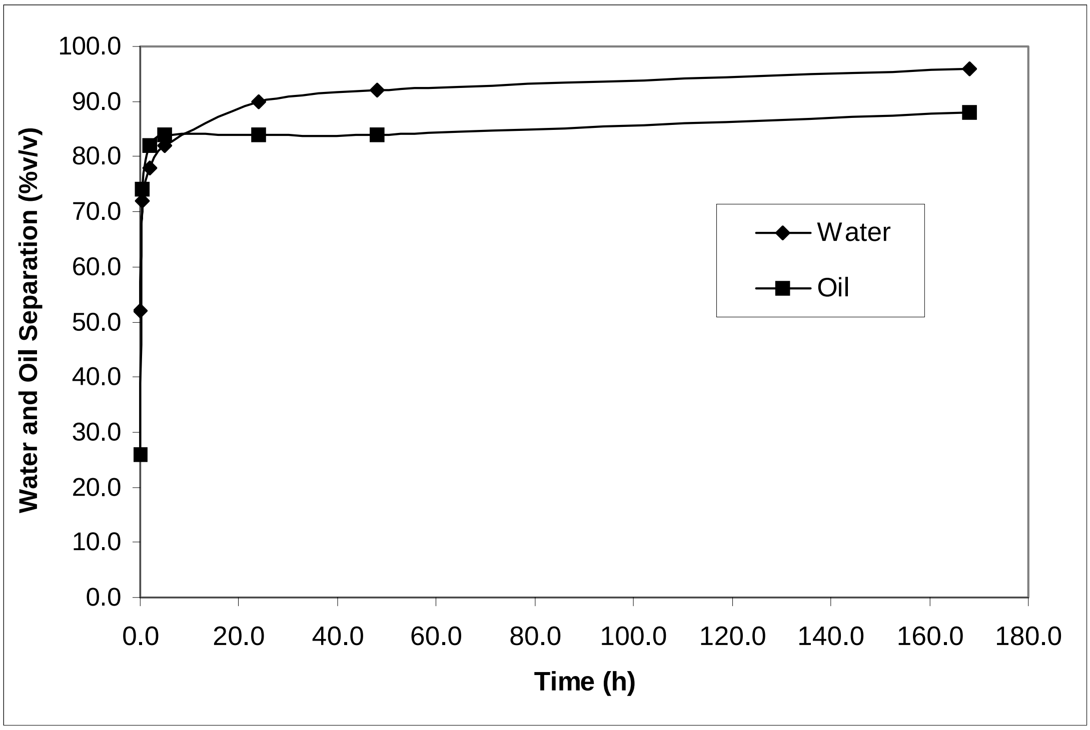

Figure 4.20: Water and oil separation in asphaltenes emulsion for 168 hours. Experimental conditions: T, 70°C; formulation concentration, 15ppm

Based on Figure 4.20, it was found that water and oil separation for asphaltenes emulsion are in same pattern. The difference of both results is only 8.0% in 168 hours. In this case, water separation is higher than oil separation, which is 96.0% and 88.0% respectively. After 2 hours, it was found that the separation level of oil is better than water separation till 5 hours before water separation is raised slowly

To visibly observe demulsification process in crude oil (water-in-oil), a crude oil was replicate by a 7:3 (volumetric) combination of n-decane and toluene. This combination of n-decane and toluene is termed herein the “crude oil replicate” base, a solution. To verify that asphaltenes are the natural emulsifier (surfactant) in an indigenous crude oil containing dispersed water, asphaltenes were separated from a natural Tabu’s field crude oil and two grams were added to a liter of the crude oil replicate base; the resultant solution was then mixed with water in a 5:5 (volumetric) ratio resulting in a very stable W/O emulsion as was expected.

The different result detected in this test, which is the level of water separation is higher than oil separation. This is because the absent of waxes and resin will decrease the influence of asphaltenes in stabilized W/O emulsion. The emulsion is low in viscosity and caused the demulsifiers absorbed easily through the continuous phase. This phenomenon gave more film drainage by lowering the interfacial and surface tension to the aqueous phase and hence coagulated and aggregated to the bottom of the centrifuge bottle, which was used in this experiments.

4.7 Formulation Effects on Crude Oil Emulsions

In this experiments, six fields of Malaysian crude oil (Tabu, Semangkok, Tapis, Guntong, Irong Barat and Seligi) were used to examine the ability of this formulation in demulsify real emulsion system. Real emulsion is very stable compared to synthetic emulsion (asphaltene emulsion alone). This is because four main interfacial active agents contained in crude oil, which were asphaltenes, resins, waxes and solid parts. The combination of these agents produced a very stable emulsion. The stability of emulsion for each fields are different depending on their geological and age of the emulsion field.

4.7.1 Stability of crude oil emulsion.

As discussed in previous section, the emulsion stability from one field to another is different according to geological and ageing factors. This statement could be proved by referring to the results presented in Figure 4.21.

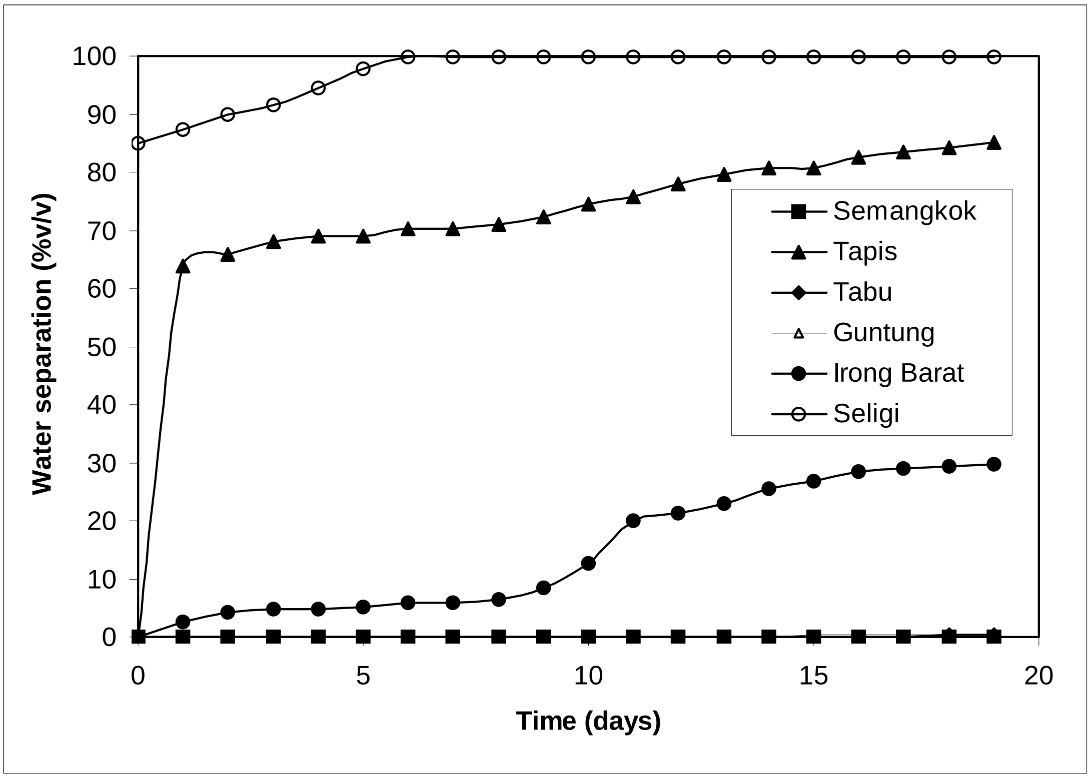

Figure 4.21: Stability of crude oil emulsions (Ariany, 2003)

From Figure 4.21, the most stable emulsion fields were Tabu, Semangkok and Guntong, which produced no water separation at all during the experimental period. Irong Barat can be categorized in stable emulsion field even 30% of water was separated during the final day of experiment. Seligi and Tapis were categorized as unstable emulsion field because of the high observation in water separation level.

The stability of emulsion in all fields could explain by referring to chemical and physical properties of each crude oil. Chemical properties play important roles in the stability of crude oil emulsion. Table 4.12 presents chemical properties for all crude oil.

Table 4.12: Chemical properties for all crude oils (Ariany, 2003)

Crude oils **Chemical analysis (%w/w)**	**Semangkok**	**Tabu**	**Irong Barat**	**Seligi**	**Tapis**	**Guntong**
Asphaltene	1.31	1.23	0.37	0.32	0.11	0.45
Resin	35.32	36.43	32.01	20.94	29.81	21.50
*R/A	26.96	29.62	85.51	65.44	27.10	47.78
Free oil: Non-volatile Volatile	33.24 14.94	43.38 0.28	44.96 4.12	55.51 13.56	51.78 9.13	24.97 21.49
Wax	11.81	13.41	15.37	9.13	24.97	21.49
Solid part	0.45	0.73	0.26	0.15	0.08	0.46
Water content	2.93	4.54	2.91	0.39	0.41	17.71
Saturated Hydrocarbon	70.62	81.59	45.63	80.47	77.51	75.42
Aromatic Hydrocarbon	17.43	15.46	45.95	16.18	18.14	20.74
Polar	11.95	2.95	8.42	3.35	4.35	3.84

*Note: R/A is ratio of resin and asphaltene.

Based on Table 4.12, by concentrating on three most stable emulsion fields, it seems that Semangkok contained highest asphaltene followed by Tabu and Guntong. Resin contains most in Tabu followed by Semangkok and Guntong. Guntong contains the highest percentage of wax followed by Tabu and Semangkok; while a lot of solid parts observed in Tabu followed by Guntong and Semangkok. Semangkok had the lowest ratio of resin and asphaltene compared to Tabu and Guntong. From these data, one can conclude that the combination of four interfacial active agents in crude oil produced stable water-in-oil emulsion.

4.7.2 Demulsification of crude oils emulsion.

Six crude oils emulsion was prepared by using the method presented in Chapter 3. 1 ml (15 ppm) of demulsifier formulation was injected in each emulsion. The results obtained in this experiment are shown in Figures 4.22 and 4.23.

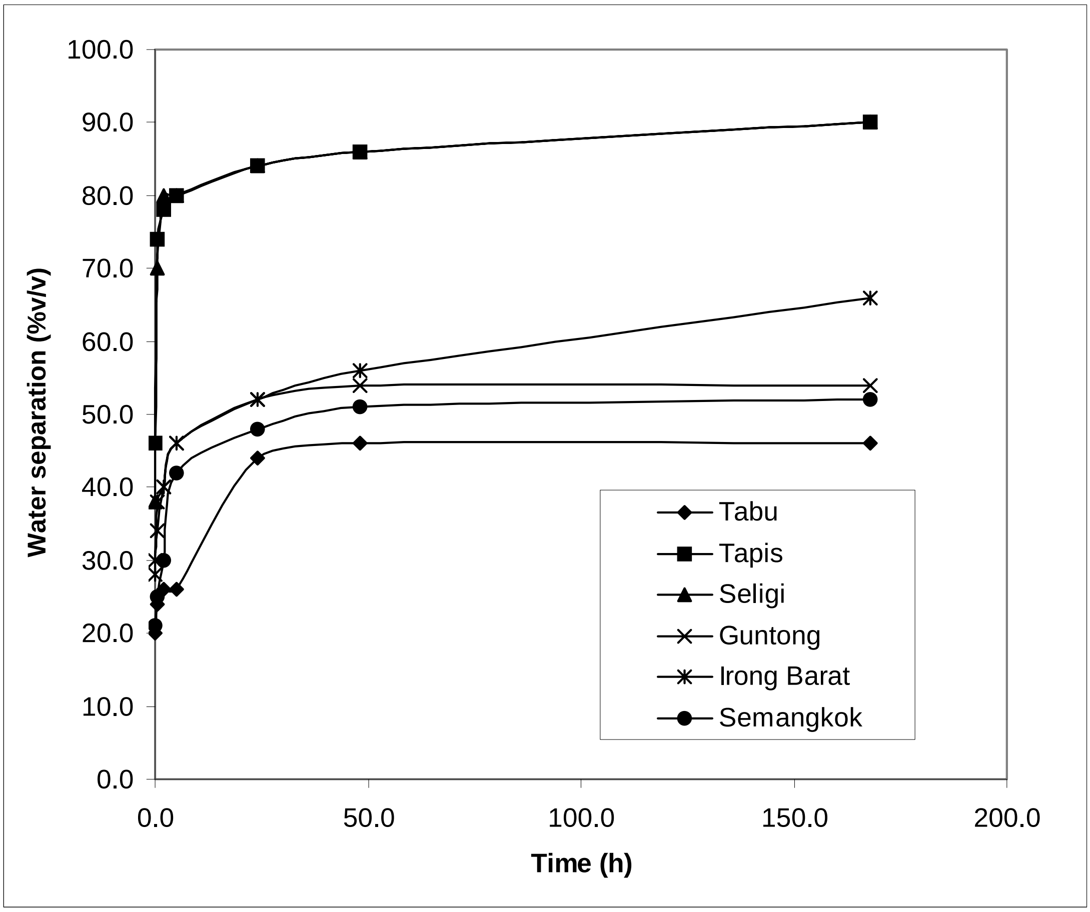

Figure 4.22: Water separation in six different fields by using new formulation. Experimental condition: T, 70°C

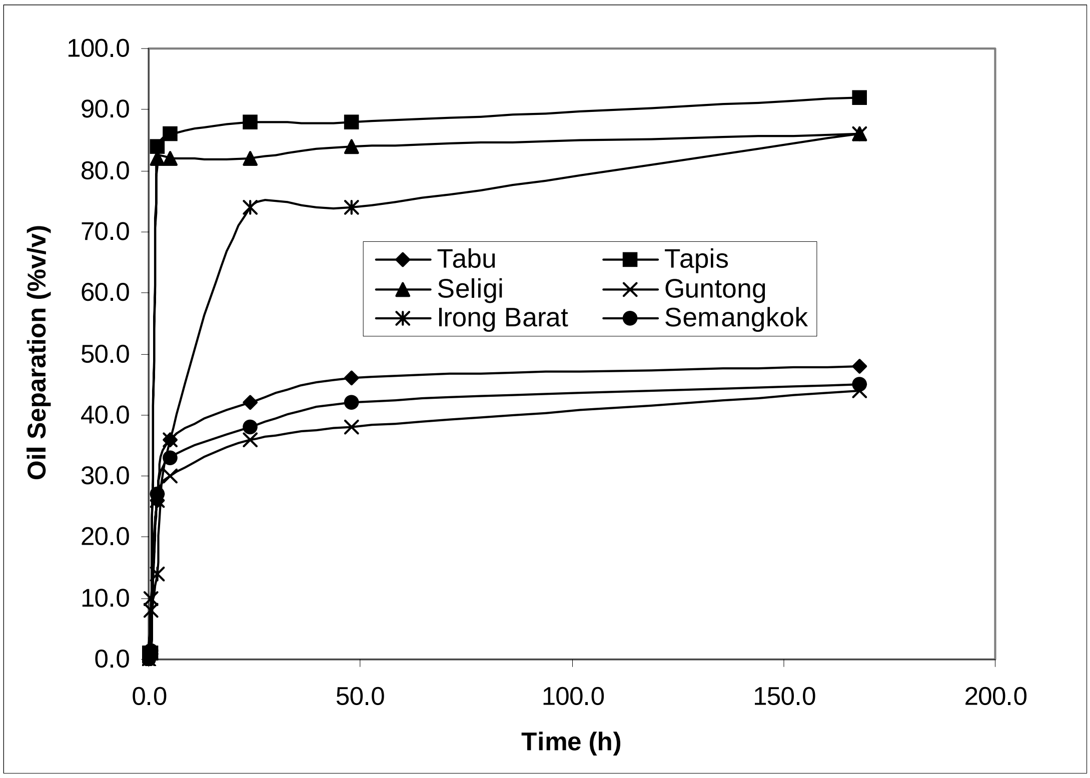

Figure 4.23: Oil separation in six different fields by using new formulation. Experimental condition: T, 70°C

A water phase separate after demulsifier was added to the emulsions. It seems that Tapis and Seligi were excellently break down their emulsion. While other three stable fields ranging from 46.0% to 54.0%. Percentage of water separation from Tabu's field was 46.0%; Semangkok's field was 52.0% while Guntong's field was 54.0%. Irong Barat's field produced 66.0% water separation (Figure 4.22).

By referring to Figure 4.23, excellent oil separation occurred in three fields, which are Tapis (92.0%), Seligi and Irong Barat (86.0%). Three stable fields noticed less oil separation where Tabu (48.0%), Guntong (44.0%) and Semangkok (45.0%). Even oil separation was not quite important in determining the efficiency of this formulation, the comparison and observation on formulation's characteristics could be made. Oil was easily separate from the emulsion system, either by injecting nothing or single demulsifiers.

Based on the results obtained, this formulation is better in water separation compared to oil separation. Water separation is important in describing the potential and ability of formulation in demulsification process compared to oil separation.

The lowest water separation occurred in Tabu's field. Based on Table 4.12, Tabu has the highest resin and solid parts compared to Semangkok and Guntong. From literature studies, major part of stability roles came from asphaltenes and lowest water separation should occurred in Semangkok and Guntong fields. Based on this phenomenon, the natural emulsifiers and solids were displaced by demulsifiers and weaken the film so the water droplets can coalesce when they contact each other.

In fact, the resin/asphaltene ratio clearly influences emulsion stability. As the resin/asphlatene ratio increase, i.e. as the influence of the resins increases, the emulsion stability decreases. This can be attributed to a lower interfacial activity of the crude oil resins as compared to that of the asphaltenes (Schorling et al., 1992). In this case, the lowest water separation was Tabu's field. This means that the present of wax and solid parts in this field helped in stabilized the water-in-oil emulsion.

By referring to the results obtained, the action of demulsifiers is based on counteracting or displacing emulsion stabilizers. This blends of demulsifiers was first reached the oil/water interface, migrate to protective film surrounded the emulsified droplets, and displaced or minimize the effect of the emulsifying agent at the interface. This leads to the coalescence.

The overall coalescence in this demulsifying process can be conveniently divided into the movement of two single (non-interacting droplets), deformation of joint approaching droplets and formation of a plane-parallel film and thinning of the film to a critical thickness at which the film become unstable, ruptures and the two water droplets merge to form a single larger droplet. Figure 4.24 shows the mutual approaching droplets and formation of a plane-parallel film.

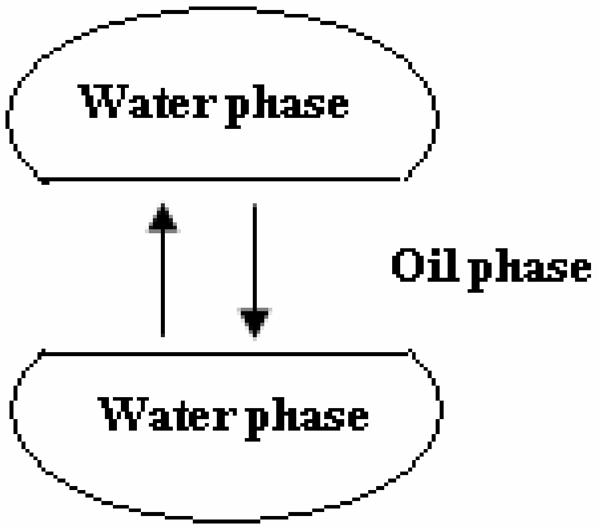

Figure 4.24: Mutual approach of two droplets and subsequent formation of plane-parallel film (Wasan, 1992)

By using the combination of thermal and mechanical method, the efficiency of this demulsifiers formulation in treating Malaysian crude oil emulsions become very effective. Although small dosage of demulsifiers added in the emulsion systems (15 ppm), high operational temperature (70°C) and 1 minutes mixing time was used in destroying the oil/water interfacial film to promote film drainage and permits water droplets to coalescence at the bottom of the test bottle. The specific gravity difference between components permits a distinct phase separation.

Table 4.13 shows the comparison of water separation for all crude oil fields with and without demulsifiers addition for 168 hours.

Table 4.13: The comparison of water separation for all crude oil fields with and without the demulsifiers addition at 168 hours

Crude oil fields / % of water separation	Tabu	Tapis	Seligi	Guntong	Irong Barat	Semangkok
With	46.0	90.0	90.0	54.0	66.0	52.0
Without	0.0	68.5	100.0	0.0	5.0	0.0

4.8 Comparison With Commercial Demulsifier Formulations.

There are three commercial demulsifier formulations used in this test to compare the yield of emulsion resolution. They are VX7079 Demulsifier from ESSO, D1 and D2 from US Patent No. 5,100,582 (Bhattacharyya, 1992). Emulsion from Tabu's field was prepared because Tabu resulted the lowest water separation by using the new formulation. Figures 4.25 and 4.26 present the results of water and oil separation respectively.

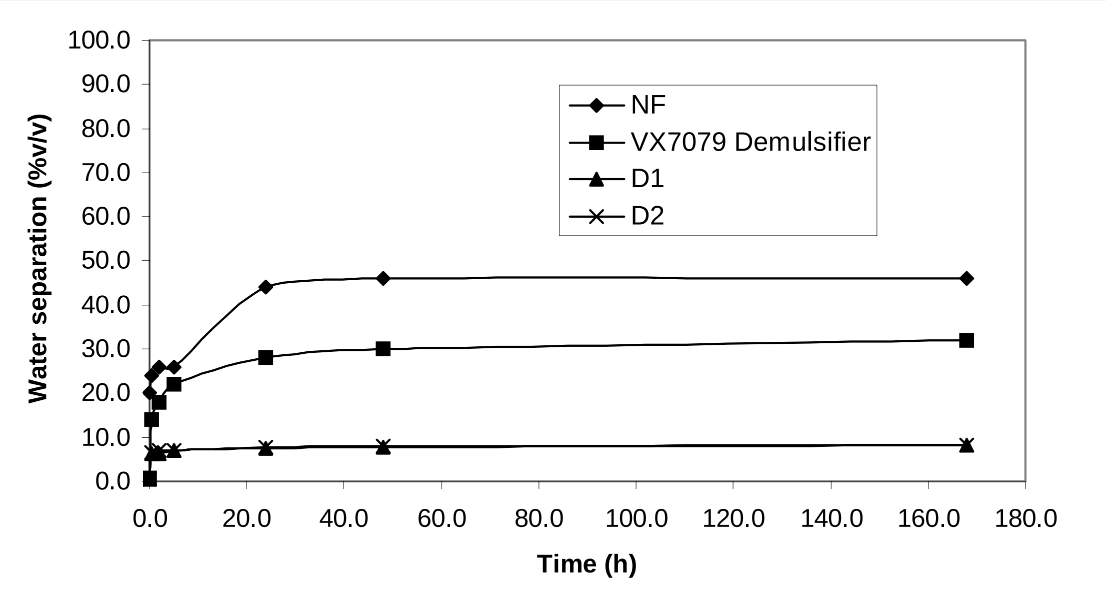

Figure 4.25: Comparison of water separation from Tabu's emulsion by using new and commercial demulsifier formulations

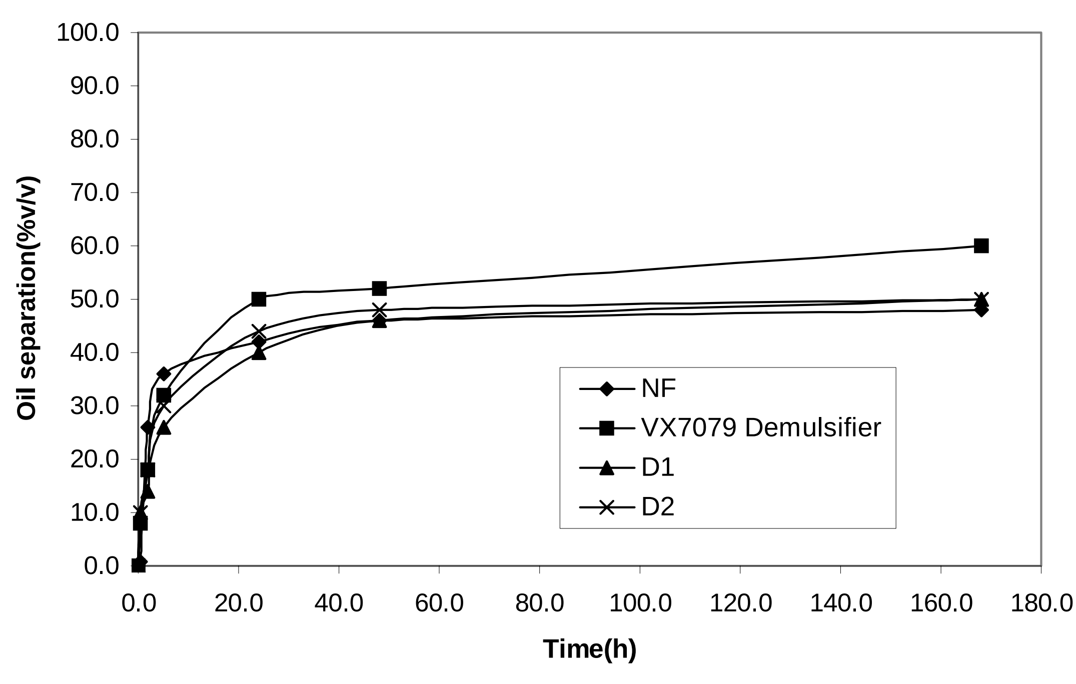

Figure 4.26: Oil separation from Tabu's emulsion system by using new and commercial demulsifier formulations

Figure 4.25 show that the best result obtained when the emulsion was injected with new formulation (46.0%). 32.0% of water was separated by using VX7079 Demulsifier and 8.2% by using D1 and D2. This result proved that this new formulation created is more efficient compared to the new commercial demulsifiers formulation used in this test.

Figure 4.26 shows that the VX 7079 Demulsifier was effective in oil separation. Almost 60.0% of oil was separated by using this formulation while 48.0% of oil was separated by using new formulation. 50.0% of oil was separated by using D1 and D2 formulation. This means that the commercial formulations are efficient in oil separation compared to the new formulation. Since the critical observation in determining the best emulsion resolution is by using water separation, so, the obtained formulation is more proficient.

The potential of this formulation was tested by using asphaltene emulsion (single emulsion) system. The experiment was carried out as in the real emulsion system. The results obtained are presented in Figures 4.27 and 4.28.

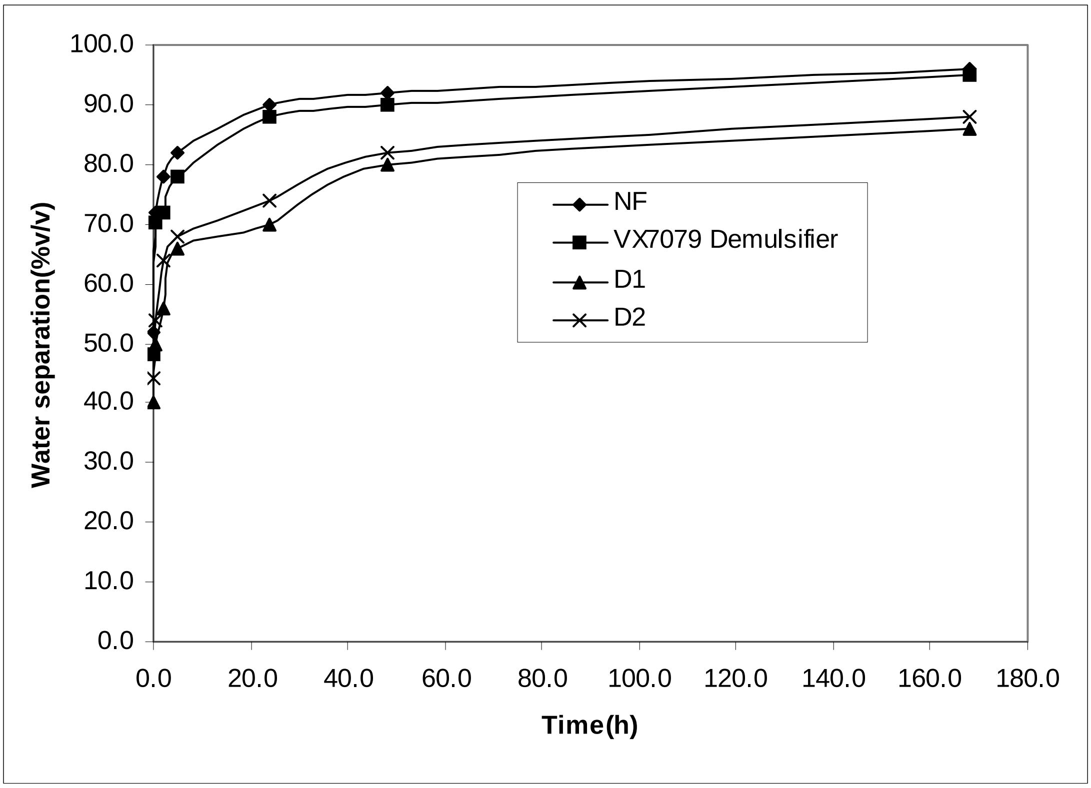

Figure 4.27: Water separation of asphaltenes emulsion by using new and commercial demulsifier formulations

Figure 4.27 shows the difference in water separation is just a small value (1.0%) by using new formulation and VX 7079 Demulsifier. 96.0% water was separated when new formulation was injected into the emulsion system while 95.0% water was separated by using VX 7079 Demulsifier. D1 resulted 86.0% of water separation level while 88.0% of water separation was resulted by using D2. This means that the potential of new commercial formulation is higher in resolved single emulsion system compared to real emulsion system.

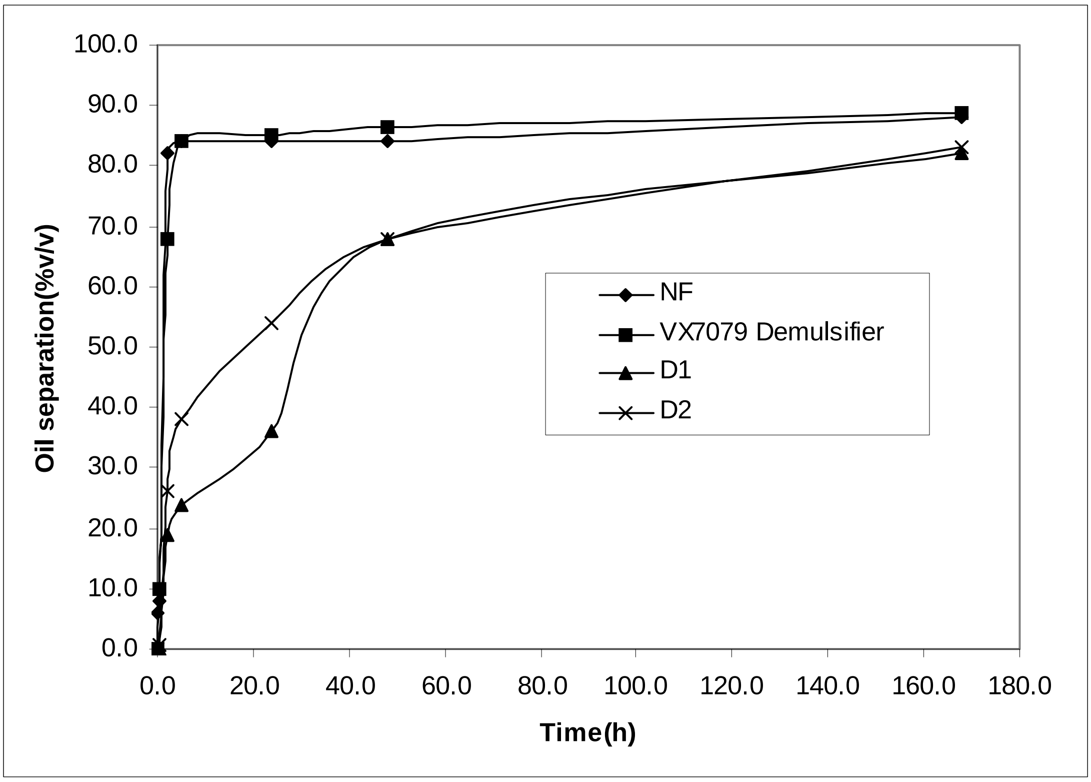

Figure 4.28: Oil separation of asphaltenes emulsion by using new and commercial demulsifier formulations

This result proved that VX 7079 Demulsifier is better in oil separation in both real and model emulsion systems. In this test, VX 7079 Demulsifier gave 88.6% oil separation, which is 0.6% higher than new formulation (88.0%). Both D1 and D2 were not so good in breaking Malaysian emulsion problem in both cases. Almost 82.0% oil was separated by using D1 while 83.0% by using D2.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Crude oils are mainly consists of asphaltenes, resins and waxes. The presence of these agents results the formation of stable emulsion. Stability is the persistence of an emulsion and presence of an interfacial film on the droplets to coalesce due to the present of interfacial active agents. As a result, the suspended droplets do not settle out, float and coalesce quickly.

Crude oil in the reservoir is found together with formation water. The stable emulsion resulted from the stress caused from the flow of crude oil and formation water . Emulsions create a lot of problems such as corrosion. For these reasons, crude oils must be treated by using demulsification process. There are four types of emulsion; W/O, O/W, W/O/W and O/W/O but in the petroleum industry, the most critical emulsion formed is W/O.

The most widely used method in this treatment process is by using chemical demulsification. This process involves the use of chemical additives (demulsifiers) in order to accelerate the emulsion breaking process. The demulsifier adsorbs at the interfacial film, weaker the interfacial barrier and separate the water droplets.

Bottle test method or jar test method is commonly used in developing a new formulation of demulsifiers composition and the results is read from the water separation level. To choose the most effective demulsifiers, screening process is used without considering the price of the demulsifiers. Basically, oil-soluble demulsifiers are more expensive compared to water-soluble demulsifiers.

The demulsifiers used in screening process include acrylic acid, sodium dodecyl sulfate, polyehtylene glycol 1000, methacrylic acid, butyl acrylate, 2-ethyl hexyl acrylate and methyl methacrylate in water-soluble demulsifiers group while polyvinyl pyrollidone, caprolactam, dioctylamine, hexylamine, methyl trioctyl ammonium chloride (TOMAC), poly (ethylene-co-propylene-co-5-methylene-2-norbornene, N,N,N',N'-tetramethyl-2-butene-1,4-diamine, N-ethyl-N-sulfopropyl-m-toluidine, N,N-dimethylacetamide, maleic anhydride, 2-aminophenol-4-sulfonic acid, pseudocumene, and naphtalene in oil-soluble demulsifiers group. All oil-soluble demulsifiers are diluted with the suitable solvent such as toluene, benzene and xylene before used in the screening test.

Based on literature study, oil-soluble demulsifiers are very efficient in treating W/O emulsion. Due to this reason, a lot of oil-soluble demulsifiers were used in this screening process. In single demulsifier category, methyl methacrylate, butyl acrylate and acrylic acid from water-soluble demulsifier group were very effective in treating Tabu's emulsion system while TOMAC, hexylamine and dioctylamine from oil-soluble demulsifier were chosen. These tests were run by using 10 ppm of demulsifiers at 70°C.

In both groups, the most efficient demulsifiers in water and oil separations are acrylic acid and TOMAC. By using three different concentrations for both demulsifiers which are 10 ppm, 20 ppm and 100 ppm, it was found that 100 ppm give the best result followed by 10 ppm and 20 ppm.

Based on literature study, a lot of formulation used modifier to increase the efficiency of the water separation from the emulsion system. Normally, short and medium chain of alcohols was used as modifier. Methanol, butanol and octanol were used in modifier's screening test. In the test, methanol gave the best result in water separation. This is because short chain alcohols are very soluble in water phase and long chain alcohols are very soluble in oil phase. The additionl of methanol in the combination of TOMAC and acrylic acid gaves a small different of result compared to the one without the methanol addition. So, the modifier addition is unneeded in this formulation.

Based on the result obtained in single demulsifiers screening process, the demulsifiers from both groups were combined together as composite demulsifiers. Optimization method was used in determining the optimum concentration of demulsifiers by using Statistical Analysis Software system. The results obtained from response surface and contour plot for both oil-soluble and water-soluble demulsifiers are not in optimum condition. This is because of the small range used in this study. As the result, the best concentration for all demulsifiers chosen is TOMAC (48.7 ppm), dioctylamine (8.0 ppm), acrylic acid (48.2 ppm), methyl methacrylate (26.5 ppm), butyl acrylate (29.9 ppm) and null value required for hexylamine.

This formulation is very efficient in treating asphaltenes emulsion. By using 15 ppm of the formulation, almost 96.0% of water is separated. In real emulsion system, 46.0% water is separated from Tabu's field, 52.0% from Semangkok's field, 54.0% from Guntong's field, 66.0% from Irong Barat's field and both 90.0% from Tapis and Seligi's field. Hence, by using small dosage of this formulation, an excellent water separation results are obtained from all fields.

In comparison with commercial demulsifier formulations (VX 7079 Demulsifier, D1 and D2), the ability of this new formulation is very good. By using Tabu's emulsion system, 46.0% of water is separated by using this formulation compared to 32.0% by using VX7079 Demulsifiers and both 8.2% by using D1 and D2. This result proved that the combination of oil-soluble demulsifiers and water-soluble demulsifiers formulation is very efficient in treating Malaysian crude oil emulsions.

5.2 Recommendations for Future Study.

In order to get more effective water separation, this formulation should be tested combining together with continuous stirring process as well as the suitable temperature (70°C). Continuous stirring will help the demulsifiers to absorb into the interface of water and oil phases quickly. Since this formulation is developed based on laboratory test result, therefore, it is practically important that this new demulsifier is tested at pilot scale or even at real field test. This will provide a real and practical ability of this new formulation in treating real emulsion system.

The mechanism of the demulsification process should be examined conscientiously in order to understand the molecular interaction between the demulsifiers and interfacial active agents existed in crude oil. As discussed previously, the interfacial active agents (asphaltenes, resins and waxes) in crude oil helped most in stabilized crude oil emulsion. So, special attention is needed in knowing the group of demulsifiers that effective in demulsifying emulsion stabilized by each interfacial agent. This fundamental knowledge is very crucial in designing new chemicals which can act as demulsifier quickly and cheaper, as well as helping in demulsifier formulation for specific crude oil emulsion system.

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APPENDIX A

DEMULSIFIERS FORMULATION

1) Demulsifiers formulation (Selvarajan et al., 2001):

   - Combination of a dicarbamate (product of toluene diisocyanate and oxyalkylated polyol) or ethoxylated/ propoxylated nonylphenol formaldehyde condensate
   - Combination of sulfated nonylphenol ethoxylate & octylphenol ethoxylate (0.2:1 to 1.2:1)
   - Water

2) Demulsifiers formulation (Taylor, 1997):

   - Unsaturated diacid, diester/diacid anhydride (preferably maleic anhydride)
   - Polyalkylene glycol (PAG)
   - Ethylene Oxide (EO)
   - Polyoxyalkylene alcohol (Preferably oxyalkylated phenol formaldehyde resin & oxyalkylated p-nonylphenol formaldehyde resin)
   - Vinyl monomer (preferably acrylic acid)
   - Xylene

3) Demulsifiers formulation (Merchant et al., 1985):

- Ethylene glycol, propylene glycol/ a poly(alkylene glycol)
- Alkylene oxide alkyl phenol-formaldehyde condensate
- Water
- Isopropanol (co solvent)

4) Demulsifiers formulation (Salathiel, 1985):

- Alkyl benzene sulphonic acid esters & alkylbenzene phosphoric acid esters
- 2-hydroxy propyl dodecyl benzene sulfonate & hydroxy ethyl dodecyl benzene sulfonate
- Water

5) Demulsifiers formulation for D1 (Bhattacharyya, 1992):

- Methyl methacrylate –55.0 wt %
- Butyl acrylate –30.0 wt %
- Acrylic acid –5.0 wt %
- Methacrylic acid – 10.0 wt %
- n-butyl mercaptopropionate –1.43 wt %

6) Demulsifiers formulation for D2 (Bhattacharyya, 1992):

- Methyl methacrylate –63.0 wt %
- 2-ethyl hexyl acrylate – 22.0 wt %
- Acrylic acid – 5.0 wt %
- Methacrylic acid – 10.0 wt %
- n-butyl mercaptopropionate –1.43 wt %

7) Demulsifiers formulation for VX7079 Demulsifiers (ESSO):

- Acetic acid – 10-30 wt %
- Aromatic hydrocarbon – 1-5 wt %
- Heavy aromatic solvent naphtha – 30-60 wt %
- Naphthalene – 1-5 wt %
- Organic sulfonic acid – 30-60 wt %
- Trimethylbenzene – 1-5 wt %

APPENDIX B

MATERIAL SAFETY DATA SHEETS (MSDS) FOR DEMULSIFIERS

1) MSDS for acrylic acid

General:

Synonyms: propenoic acid, ethylenecarboxylic acid, 2-propenoic acid, vinylformic acid
Molecular formula: CH_2:CHCOOH

Physical data:

Appearance: colourless liquid with an acrid odour
Melting point: 12 C
Boiling point: 141 C
Vapour density: 2.5 (air = 1)
Vapour pressure: 3.1 mm Hg at 20 C
Density (g cm^{-3}): 1.06
Flash point: 49 C (closed cup)
Explosion limits: 2 - 8%
Water solubility: complete

Stability: Unstable - may contain p-methoxyphenol as an inhibitor. **Prone to hazardous polymerization.** Combustible. Incompatible with strong oxidizing agents, strong bases, amines. Contact with oxidizers may cause fire. Light and air sensitive.

Toxicology: Corrosive - causes burns. Harmful if swallowed or inhaled, and in contact with skin. Severe respiratory irritant. May cause serious burns to the eyes.

Personal protection: Safety glasses, good ventilation.

2) MSDS for polyvinylpyrollidone

General:

Synonyms: povidone, PVP, agent AT 717, agrimer, albigen A, aldacol Q, AT 717, bolinan, 1-ethenyl-2-pyrrolidone polymer, Ganex P 804, hemodesis, demodez, K15, K25, K30, K60, luviskol k90, kollidon, kollidon 17, kollidon 30, numerous other trade names
CAS No: 9003-39-9 (CAS No. for cross-linked polyvinylpyrrolidone 25249-54-1)
EINECS: 294-352-4

Physical data:

Appearance: solid
Melting point: depends on MW, typically ca. 300 for a molecular weight of around 29,000
Boiling point: depends on MW (may decompose on heating)

Stability: Stable. Incompatible with strong oxidizing agents. Light sensitive. Hygroscopic.

Toxicology: May be harmful or act as an irritant - toxicology not fully investigated

Personal protection: Handle with due caution.

3) MSDS for epsilon-caprolactam 99+%

General:

Synonyms: 2-Oxohexamethyleneimine; 6-Aminocaproic acid lactam; 6-Aminohexanoic
acid cyclic lactam; 1-aza-2-cycloheptanone;
Hexahydro-2H-azepin-2-one

Physical and chemical data:

Physical State: Crystals
Appearance: white
Odor: Unpleasant odor.
pH: Not available.
Vapor Pressure: 6.0 mm Hg @ 120C
Vapor Density: Not available.
Evaporation Rate: Not available.
Viscosity: Not available.
Boiling Point: 180 deg C @ 50 mm Hg
Freezing/Melting Point: 70-72 deg C
Decomposition Temperature: Not available.

Solubility: Soluble.
Specific Gravity/Density: Not available.
Molecular Formula: C6H11NO
Molecular Weight: 113.16

Stability and reactivity:

Chemical Stability:
Stable under normal temperatures and pressures.
Conditions to Avoid:
Incompatible materials, dust generation, exposure to moist air or `water.`
Incompatibilities with Other Materials: Strong oxidizing agents, strong bases.
Hazardous Decomposition Products: Nitrogen oxides, carbon monoxide, carbon dioxide.
Hazardous Polymerization: Has not been reported

Personal protection: Do not inhale dust, avoid contact with skin and eyes, wear suitable protective clothing, gloves and eye/face protection, if swallowed, seek medical advice immediately and show this container or label.

4) MSDS for sodium dodecyl sulfate

General:

Synonyms: AI3-00356, akyposal SDS, aquarex ME, aquarex methyl, Avirol 101, berol 452, carsonol SLS, carsonol sls paste B, conco sulfate WA, conco sulfate WA-1200, conco sulfate WA-1245, conco sulfate wag, conco sulfate wa, duponol QX, orvus WA paste, sodium dodecyl sulphate, sodium lauryl sulphate, lauryl sodium sulfate, sipon WD, sodium lauryl sulfate, SDS, numerous further trade and non-systematic names
Molecular formula: $CH_3(CH_2)_{11}OSO_3Na$
CAS No: 151-21-3
EC No: 205-788-1

Physical data:

Appearance: white crystalline powder
Melting point: 204 - 207 C
Specific gravity: 0.4
Water solubility: 250g/l at 20 C

Stability: Stable. Incompatible with strong acids, strong oxidising agents. Hygroscopic.

Toxicology: Respiratory, skin and eye irritant. Harmful if swallowed. Nuisance dust. Typical TLV 10 mg m^{-3}.

Personal protection: Safety glasses.

5) MSDS for hexylamine

General:

Synonym: 1-Aminohexane

Physical and chemical data:

Physical State: Liquid
Appearance: colourless
Odor: None reported.
pH: Not available.
Vapor Pressure: 24 hPa @ 20 C
Vapor Density: 3.5
Evaporation Rate: Not available.
Viscosity: Not available.
Boiling Point: 131.0 - 132.0 deg C @ 760.00m
Freezing/Melting Point: -23 deg C
Decomposition Temperature: Not available.
Solubility: 12 g/l (20 c)
Specific Gravity/Density: .7660g/cm3

Stability and reactivity:

Chemical Stability: Stable under normal temperatures and pressures.
Conditions to Avoid: Incompatible materials, ignition sources, excess heat, strong oxidants.
Incompatibilities with Other Materials: Strong oxidizing agents, acids, acid chlorides, acid anhydrides.
Hazardous Decomposition Products: Nitrogen oxides, carbon monoxide, irritating and toxic fumes and gases, carbon dioxide, nitrogen.
Hazardous Polymerization: Has not been reported.

Personal protection: Keep away from sources of ignition (No Smoking), in case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Take precautionary measures against static discharges. Wear suitable protective clothing. Keep container in a well-ventilated place.

6) MSDS for methyl trioctyl ammonium chloride (TOMAC)

General:

Synonyms: Polyethylene Plastics, Ethylene/Olefin Copolymer Plastics

Physical data:

Appearance and Odor: Black or Colored Pellets
Boiling Point: Not Applicable

Solubility: Insoluble in Water
Evaporation: Not Applicable
Specific Gravity: 0.935-0.970 (G/CM@ 23ºC)
Vapor Pressure: Not Applicable
Melting Point: 230-275ºF
Vapor Density: Not Applicable
Percent Volatile: Negligible

Stability and reactivity:

Stability: This material is stable.
Hazardous Polymerization: Hazardous Polymerization will not occur.
Conditions to Avoid: Avoid Temperatures over 650ºF. Avoid storage or contact with strong oxidizing agents.
Combustion Products: The following combustion products may be generated: Carbon Dioxide, Carbon Monoxide, water vapor, and trace volatile organic compounds.

Personal protection: Wear safety glasses, face shield or chemical goggles to avoid getting material in the eyes during bulk handling. Wear protective sleeves when processing material at elevated temperatures to minimize possibility of thermal burns. Adequate ventilation is recommended to minimize accumulation of fines or vapors during processing and handling. An approved respirator may be needed in areas with a high accumulation of fines.

7) MSDS for polyethylene glycol

General:

Synonyms: PEG; Carbowax®; Polyglycol; Polyethylene glycol 200, 300, 400, 600,1000,1450, 3350, 4000, 6000, 8000 and 20000.
CAS No.: 25322-68-3
Molecular Weight: Not applicable to mixtures.
Chemical Formula: (C2H4O) n.H2O

Physical and chemical properties:

Appearance: Clear liquid or white solid.
Odor: Mild odor.
Solubility: Soluble in water.
Density: range: 1.1 to 1.2 (increases as molecular weight increases)
Melting Point: Melting point increases as molecular weight increases: PEG 400 = 4-8C (39-46F) PEG 600 = 20-25C (68-77F) PEG1500 = 44-48C (111-118F) PEG 4000 = 54-58C (129-136F) PEG 6000 = 56-63C (133-145F)
Vapor Pressure (mm Hg): Vapor pressure is very low; as molecular weight increases, vapor pressure decreases.

Stability and reactivity:

Stability: Stable under ordinary conditions of use and storage.

Hazardous Decomposition Products: Carbon dioxide and carbon monoxide may form when heated to decomposition.
Hazardous Polymerization: Will not occur.
Incompatibilities: Incompatible with polymerization catalysts (peroxides, persulfates) and accelerators, strong oxidizers, strong bases and strong acids.
Conditions to Avoid: Incompatibles.

Personal protection: Wear protective gloves and clean body-covering clothing. Use chemical safety goggles. Maintain eye wash fountain and quick-drench facilities in work area.

8) MSDS for maleic anhydride

General:

Synonym: cis-butenedioic anhydride

Physical and chemical properties:

Appearance: Colourless crystalline needles or white lumps or pellets
Odor: Sharp acrid, irritating odor
Boiling point, 760 mmHg: 395 F (202C)
Melting point: 127F (53C)
Vapor pressure: 0.98 mmHg (@40C), 60 mmHg (@122C), 750 mmHg (@202C)
Vapor density (Air =1): 3.38
Solubility in water: Hydrolizes readily, soluble in acetone, ethyl acetate, chloroform and benzene.
Specific gravity: 1.3 (Molten) @70/70C
: 1.48 (Solid)
Chemical formula: $C_4H_2O_3$

Stability and reactivity:

Stability: React with water and moist air to form heat and maleic acid. If keep dry, stable under normal conditions of storage and use. Molten product should be store under 158F.
Materials to avoid: Alkali metal ions and amines.
Hazardous decomposition products: Smoke, soot, carbon monoxide and hydrocarbon.
Hazardous polymerization: Will not self polymerize.

Personal protection: Wear chemical goggles, protective clothes and chemical resistance gloves.

9) MSDS for 2-aminophenol-4-sulfonic acid

General:

Synonyms: 2-amino-1-phenol-4-sulphonic acid, 2-aminophenol-4-sulphonic acid, 3-amino-4-hydroxy benzenesulphonic acid, o-aminophenol-p-sulphonic acid
Molecular formula: $C_6H_7NO_4S$

Physical data:

Appearance: brown crystals
Melting point: > 300 C (decomposes)

Stability: Stable. Incompatible with strong oxidizing agents, strong acids and strong bases.

Toxicology: Skin, eye and respiratory irritant. May be harmful by ingestion, inhalation or through skin contact. Toxicology not fully investigated.

Personal protection: Safety glasses, adequate ventilation.

10) MSDS for methacrylic acid

General:

Synonyms: 2-methylacrylic acid, 2-methylpropenoic acid, 2-methacrylic acid, alpha-methacrylic acid, 2-methylene propionic acid
Use: synthetic reagent
Molecular formula: $C_4H_6O_2$

Physical data:

Appearance: colourless liquid or crystals with an unpleasant odour.
Melting point: 16 C
Boiling point: 163 C
Vapour density: 2.97
Vapour pressure: 1 mm Hg at 25 C
Specific gravity: 1.015
Flash point: 76 C
Explosion limits: 1.6 - 8.1 % vol.

Stability: May be stabilized by the addition of MEHQ (Hydroquinone methyl ether, ca. 250 ppm) or hydroquinone. In the absence of a stabilizer this material will readily polymerize. Combustible. Incompatible with strong oxidizing agents, hydrochloric acid.

Toxicology: Corrosive. Contact with eyes, respiratory tract or skin will cause burns. Harmful by skin contact. Typical OEL 20 ppm. May act as a mutagen.

Personal protection: Safety glasses, adequate ventilation.

11) MSDS for methyl methacrylate

General:

Synonyms: 2-methyl acrylic acid methyl ester, diakon, methyl methacrylate monomer, methyl alpha-methacrylate, methyl 2-methyl-2-propenoate, MME, NCI-C50680, methacrylic acid methyl ester, diakon, 2-methyl-2-propenoic acid methyl ester
Use: acrylic bone cements, acrylic polymers, fillers, adhesives and many other uses
Molecular formula: $CH_2=C(CH_3)COOCH_3$

Physical data:

Appearance: colourless liquid
Melting point: -48 C
Boiling point: 100 C
Vapour density: 3.45 (air = 1)
Vapour pressure: 29 mm Hg at 20 C
Density (g cm^{-3}): 0.936
Flash point: 10 C
Explosion limits: 2.1 - 12.5%
Water solubility: moderate

Stability: Prone to autopolymerisation; typically inhibited with ca. 10 ppm hydroquinone momomethyl ether or 25 ppm hydroquinone. Incompatible with strong oxidizing agents, peroxides, bases, acids, reducing agents, amines, halogens, nitric acid, nitrates, polymerisation catalysts. Light sensitive. Flammable. May react violently with polymerization initiators.

Toxicology: Harmful if swallowed, inhaled or absorbed through the skin. Lachrymator. Corrosive. May act as a sensitizer. Typical TLV/TWA 100 ppm.

Personal protection: Safety glasses, good ventilation. Keep off skin.

12) MSDS for butyl acrylate

General:

Molecular Formula: $C_7H_{12}O_2$
Molecular Weight: 128.2

Physical data:

Appearance: Clear, colorless liquid with a fruity odor. It is freely miscible with most organic solvents.
Boiling Point: 148°C

Freezing Point: –64°C
Density @ 20°C (g/cm): 30.898
Refractive Index nD @ 20°C: 1.415
Heat of polymerization, (kJ/kg): 504
Vapor Pressure:
@ 0°C, (mbar): 1.0
@ 20°C, (mbar): 4.3
@ 50°C, (mbar): 25.5
@ 100°C, (mbar): 28
@ 200°C, (mbar): 3620
Flash Point (Tag closed cup), (°C): 40.0
Autoignition Temperature, (°C): 267
Explosion Limits (vapor in air), (% volume): 1.5–9.9
Latent Heat of Evaporation @ boiling point, (kJ/kg): 278.9
Viscosity:
@ 20°C, (mPa·s): 0.75
@ 40°C, (mPa·s): 0.50
@ 60°C, (mPa·s): 0.45
@ 80°C, (mPa·s): 0.37
Solubility of butyl acrylate in water @ 25°C, (g/100g): 0.2
Solubility of water in butyl acrylate @ 25°C, (g/100g): 0.7

13) MSDS for 2-ethyl hexyl acrylate

General:

Synonyms: octyl acrylate, 2-ethylhexyl propenoate, 2-propenoic acid 2-ethylhexyl ester
Molecular formula: $C_{11}H_{20}O_2$

Physical data:

Appearance: light yellow liquid
Melting point: -90 C
Boiling point: 214 - 218 C
Flash point: 82 C
Water solubility: negligible

Stability: Stable, but polymerizes readily unless inhibited with hydroquinone or its monomethyl ether. Susceptible to hydrolysis. Combustible. Incompatible with oxidising agents.

Toxicology: May be harmful if inhaled or swallowed. Skin, eye and respiratory irritant.
Personal protection: Safety glasses, adequate ventilation.

14) MSDS for naphtalene

General:

Synonyms: albocarbon, mighty 150, mighty rd1, moth flakes, NCI-C52904, white tar, naphthalin, naphthene, camphor tar, tar camphor, moth balls
Molecular formula: $C_{10}H_8$

Physical data:

Appearance: white crystals
Melting point: 77 C
Boiling point: 218 C
Specific gravity: 1.14
Vapour pressure: 1 mm Hg at 20 C
Vapour density: 4.4 g/l
Flash point: 88 C
Explosion limits: 0.9 - 5.9%

Stability: Stable. Flammable - avoid sources of ignition. Incompatible with oxidising agents. Heat-sensitive. Sublimes slowly at room temperature.

Toxicology: May cause irritation. Toxic by inhalation or ingestion. TLV 10 ppm. Sensitizer. Possible carcinogen.

Personal protection: Safety glasses. Use efficient ventilation.

15) MSDS for dioctylamine

General:

Synonyms: di(2-ethylhexyl)amine, 2,2'-diethylhexylamine, 2-ethyl-N-(2-ethylhexyl)-1-hexanamine
Use: synthetic agent
Molecular formula: $C_{16}H_{35}N$

Physical data:

Appearance: colourless liquid
Boiling point: 281 C
Vapour density: 8.35 (air = 1)
Density (g cm^{-3}): 0.81
Flash point: 132 C
Water solubility: negligible

Stability: Stable. Combustible. Incompatible with oxidizing agents.

Toxicology: Harmful if swallowed, inhaled or absorbed through the skin. Skin, eye and respiratory irritant. Lachrymator.

Personal protection: Safety glasses, adequate ventilation.

APPENDIX C

DATA OF TESTS DONE TO OBTAIN DEMULSIFIERS FORMULATION

Table C (1): Water separation (%) for single demulsifier screening by using water-soluble demulsifiers. Experimental conditions: T, 70°C; Demulsifier concentration, 10 ppm.

Time (h) Demulsifiers	0.0	0.5	2.0	5.0	24.0	48.0	168.0
None	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Acrylic Acid	14.0	15.0	16.0	17.0	17.0	17.0	17.4
NaDoSu	7.0	8.0	8.2	8.2	8.2	8.2	8.6
PEG 1000	6.0	6.2	6.2	6.4	6.7	6.7	7.0
Methacrylic acid	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Butyl acrylate	0.0	4.0	7.0	11.0	23.0	26.0	30.0
2EHA	0.0	0.0	1.0	1.0	1.0	1.0	1.0
MMaC	0.0	6.0	10.0	14.0	30.0	30.4	40.0

Table C (2): Oil separation (%) for single demulsifier screening by using water-soluble demulsifiers. Experimental conditions: T, 70°C; Demulsifier concentration, 10 ppm.

Time (h) Demulsifiers	0.0	0.5	2.0	5.0	24.0	48.0	168.0
None	0.0	24.0	44.0	60.0	70.0	74.0	75.0
Acrylic Acid	0.0	18.0	26.0	42.0	48.0	64.0	70.0
NaDoSu	0.0	10.0	30.0	42.0	48.0	58.8	70.0
PEG 1000	0.0	14.5	38.0	54.2	65.1	66.0	68.7
Methacrylic acid	0.0	12.0	30.0	40.0	46.0	56.0	64.0
Butyl acrylate	0.0	8.0	16.0	20.0	30.0	36.0	50.0
2EHA	0.0	15.7	21.6	21.6	49.0	56.9	58.8
MMaC	0.0	5.0	10.0	15.0	24.0	30.0	47.0

Table C (3): Water separation (%) for single demulsifier screening by using oil-soluble demulsifiers. Experimental conditions: T, 70°C; Demulsifier concentration, 10 ppm.

Time (h) Demulsifiers	0.0	0.5	2.0	5.0	24.0	48.0	168.0
None	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PVP	1.8	1.9	2.0	2.0	2.0	2.0	2.4
Caprolactam	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Dioctylamine	9.0	9.8	9.8	10.0	10.0	10.0	10.0
Hexylamine	9.2	9.4	9.4	9.4	9.4	9.6	9.6
TOMAC	16.0	20.0	30.0	30.2	34.0	40.0	44.0
Poly(Ethylene-co-..	6.0	6.2	7.0	7.0	7.0	7.4	7.4
N,N,N,N	3.0	3.6	4.0	4.2	4.2	4.2	4.2
Toluidine	2.0	2.4	2.4	3.0	3.0	3.4	3.8
NNDA	2.0	2.2	2.6	3.2	3.8	3.8	4.0
Maleic anhyd	7.5	8.0	8.0	8.0	8.0	8.0	8.2
2AP4SA	2.8	3.2	3.4	3.4	3.4	3.6	3.6
Pseudocumene	0.0	1.0	1.2	1.2	1.2	1.2	1.2
Naphtalene	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table C (4): Oil separation (%) for single demulsifier screening by using oil-soluble demulsifiers. Experimental conditions: T, 70°C; Demulsifier concentration, 10 ppm.

Time (h) Demulsifiers	0.0	0.5	2.0	5.0	24.0	48.0	168.0
None	0.0	24.0	44.0	60.0	70.0	74.0	75.0
PVP	0.0	6.0	30.0	38.0	60.0	64.0	70.0
Caprolactam	0.0	9.8	29.4	49.0	58.8	76.5	82.0
Dioctylamine	0.0	11.8	19.6	39.2	49.0	76.5	78.4
Hexylamine	0.0	6.0	20.0	34.0	50.0	64.0	70.0
TOMAC	0.0	10.0	20.0	30.0	40.0	54.0	66.0
Poly(Ethylene-co-..	0.0	13.7	35.3	49.0	58.8	66.7	68.6
N,N,N,N	0.0	5.9	19.6	29.4	52.9	68.6	72.5
Toluidine	0.0	19.6	33.3	43.1	52.9	68.6	72.5
NNDA	0.0	14.5	27.1	41.6	52.4	57.9	72.3
Maleic anhyd	0.0	10.0	26.0	34.0	54.0	60.0	68.0
2AP4SA	0.0	3.0	22.0	28.0	50.0	58.0	66.0
Pseudocumene	0.0	10.0	20.0	30.0	50.0	56.0	62.0
Naphtalene	0.0	10.0	22.0	36.0	50.0	56.0	60.0

Table C (5): Effects of water separation by using various concentrations of acrylic acid at 70°C.

Time (h)	10 ppm	20 ppm	100 ppm
0.0	14.0	5.8	20.0
0.5	15.0	6.2	21.0
2.0	16.0	9.8	21.0
5.0	17.0	10.8	23.0
24.0	17.0	12.0	23.0
48.0	17.0	12.0	23.0
168.0	17.4	12.0	23.0

Table C (6): Effects of oil separation by using various concentration of acrylic acid at 70°C.

Time (h)	10 ppm	20 ppm	100 ppm
0.0	0.0	0.0	0.0
0.5	18.0	6.0	2.0
2.0	26.0	20.0	16.0
5.0	42.0	36.0	30.0
24.0	48.0	46.0	36.0
48.0	64.0	46.0	36.0
168.0	70.0	46.0	38.0

Table C (7): Effects of water separation by using various concentrations of TOMAC at 70°C.

Time (h)	10 ppm	20 ppm	100 ppm
0.0	16.0	4.0	30.0
0.5	20.0	6.0	40.0
2.0	30.0	6.0	65.0
5.0	30.2	6.2	70.0
24.0	34.0	6.2	86.0
48.0	40.0	6.2	90.0
168.0	44.0	6.2	94.0

Table C (8): Effects of oil separation by using various concentration of TOMAC at 70°C.

Time (h)	10 ppm	20 ppm	100 ppm
0.0	0.0	0.0	0.0
0.5	10.0	10.0	10.0
2.0	20.0	22.0	30.0
5.0	30.0	30.0	30.0
24.0	40.0	44.0	44.0
48.0	54.0	46.0	44.0
168.0	66.0	46.0	50.0

Table C (9): Percentage of water separation by using alcohols. Experimental conditions: T, 70°C, Concentration, 10 ppm.

Time (h)	None	Methanol	Butanol	Octanol
0.0	0.0	1.8	1.4	0.0
0.5	0.0	2.2	1.6	0.6
2.0	0.0	2.2	1.6	1.2
5.0	0.0	2.4	1.8	1.4
24.0	0.0	2.6	1.8	1.4
48.0	0.0	2.6	1.8	1.4
168.0	0.0	2.6	2.0	1.4

Table C (10): Results in oil separation by using of alcohols. Experimental conditions: T, 70°C, Concentration, 10 ppm.

Time (h)	None	Methanol	Butanol	Octanol
0.0	0.0	0.0	0.0	0.0
0.5	24.0	10.0	4.0	16.0
2.0	44.0	20.0	22.0	16.0
5.0	60.0	22.0	32.0	20.0
24.0	70.0	32.0	44.0	50.0
48.0	74.0	46.0	48.0	54.0
168.0	75.0	50.0	50.0	60.0

Table C (11): Comparison of water separation with and without modifier. Experimental conditions: T, 70°C; Concentration, 10 ppm.

Time (h)	without	with
0.0	6.2	10.3
0.5	8.0	15.0
2.0	8.0	17.0
5.0	9.0	17.0
24.0	9.8	17.0
48.0	10.0	17.0
168.0	10.0	17.0

Table C (12): Comparison of oil separation with and without modifier. Experimental conditions: T, 70°C; Concentration, 10ppm.

Time (h)	without	with
0.0	0.0	0.0
0.5	14.0	18.0
2.0	20.0	26.0
5.0	30.0	34.0
24.0	44.0	40.0
48.0	48.0	48.0
168.0	50.0	50.0

Table C (13): Water and oil separation in asphaltenes emulsion for 168 hours. Experimental conditions: T, 70°C; Demulsifier concentration, 15ppm.

Time (h)	Water	Oil
0.0	52.0	26.0
0.5	72.0	74.0
2.0	78.0	82.0
5.0	82.0	84.0
24.0	90.0	84.0
48.0	92.0	84.0
168.0	96.0	88.0

Table C (14): Water separation in six different fields by using new formulation. Experimental condition: T, 70°C; Concentration, 15 ppm.

Time (h)	Tabu	Tapis	Seligi	Guntong	Irong Barat	Semangkok
0.0	20.0	46.0	38.0	30.0	28.0	21.0
0.5	24.0	74.0	70.0	34.0	38.0	25.0
2.0	26.0	78.0	80.0	40.0	40.0	30.0
5.0	26.0	80.0	80.0	46.0	46.0	42.0
24.0	44.0	84.0	84.0	52.0	52.0	48.0
48.0	46.0	86.0	86.0	54.0	56.0	51.0
168.0	46.0	90.0	90.0	54.0	66.0	52.0

Table C (15): Oil separation in six different fields by using new formulation. Experimental condition: T, 70°C; Concentration, 15 ppm.

Time (h)	Tabu	Tapis	Seligi	Guntong	Irong Barat	Semangkok
0.0	0.0	1.0	1.0	0.0	0.0	0.0
0.5	0.8	1.0	1.0	10.0	8.0	1.4
2.0	26.0	84.0	82.0	26.0	14.0	27.0
5.0	36.0	86.0	82.0	30.0	36.0	33.0
24.0	42.0	88.0	82.0	36.0	74.0	38.0
48.0	46.0	88.0	84.0	38.0	74.0	42.0
168.0	48.0	92.0	86.0	44.0	86.0	45.0

Table C (16): Comparison of water separation from Tabu's emulsion by using new and commercial demulsifier formulations.

Time (h)	NF	VX7079 Demulsifier	D1	D2
0.0	20.0	0.8	0.5	0.5
0.5	24.0	14.0	6.2	6.6
2.0	26.0	18.0	6.4	7.0
5.0	26.0	22.0	7.0	7.0
24.0	44.0	28.0	7.6	7.8
48.0	46.0	30.0	7.8	8.0
168.0	46.0	32.0	8.2	8.2

Table C (17): Oil separation from Tabu's emulsion system by using new and commercial demulsifier formulations.

Time (h)	NF	VX7079 Demulsifier	D1	D2
0.0	0.0	0.0	0.0	0.0
0.5	0.8	8.0	10.0	10.0
2.0	26.0	18.0	14.0	18.0
5.0	36.0	32.0	26.0	30.0
24.0	42.0	50.0	40.0	44.0
48.0	46.0	52.0	46.0	48.0
168.0	48.0	60.0	50.0	50.0

Table C (18): Water separation of asphaltenes emulsion by using new and commercial demulsifier formulations.

Time (h)	NF	VX7079 Demulsifier	D1	D2
0.0	52.0	48.0	40.0	44.0
0.5	72.0	70.2	50.0	54.0
2.0	78.0	72.0	56.0	64.0
5.0	82.0	78.0	66.0	68.0
24.0	90.0	88.0	70.0	74.0
48.0	92.0	90.0	80.0	82.0
168.0	96.0	95.0	86.0	88.0

Table C (19): Oil separation of asphaltenes emulsion by using new and commercial demulsifier formulations.

Time (h)	NF	VX7079 Demulsifier	D1	D2
0.0	6.0	0.0	0.0	0.0
0.5	8.0	10.0	0.0	0.8
2.0	82.0	68.0	19.0	26.0
5.0	84.0	84.0	24.0	38.0
24.0	84.0	85.0	36.0	54.0
48.0	84.0	86.4	68.0	68.0
168.0	88.0	88.6	82.0	83.0