

UNIVERSITY OF CALGARY

Effect of Change in Hydrophilic-Lipophilic Balance (HLB) on the State of Stable Invert
Emulsion Drilling Fluid

by

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ABSTRACT

The purpose of this project is to modify the wettability of emulsion from being oil-wet to water wet to improve drilling waste management. The adopted strategy is to use the Hydrophilic-Lipophilic Balance (HLB) to alter the affinity of emulsifiers towards the continuous phase of an emulsion system. Invert emulsions with 90:10 ratios of mineral oils (either Drisol or Distillate 822) to deionized water were prepared using HLB numbers ranging from 4.3 to 14.4. Desired HLB values were achieved by corresponding combinations of Span 80 (HLB 4.3)/Tween 80 (HLB 15.0). The emulsions were aged and centrifuged. Emulsion stability was measured by visual phase separation. Invert emulsion with HLB 4.9 showed the highest stability. Corrected Emulsifier Combinations (CEB) with HLB numbers ranging from 10.2 to 14.4 were added to the stable invert emulsions of HLB 4.9 and different properties of the emulsion (phase separation, optical density and viscosity) were studied. The results showed that increase in HLB lead to increase in droplet size which is a desirable effect towards destabilizing the invert emulsion.

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DEDICATION

I would like to dedicate this work to my parents and siblings for all the sacrifices, prayers and support they have given to me all through this period.

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List of Acronyms and Nomenclature

AU	Absorption Unit
CEB	Correcting Emulsifier Blend
CMC	Critical Micelle Concentration
C _p	Peak Concentration
DBF	Diesel Based Fluids
EPA	Environmental Protection Agency
GBDF	Gas Based Drilling Fluid
HLB	Hydrophilic Lipophilic Balance
KFR	Karl Fischer Reagent
MBC	Minimum Bacterial Concentration
MIC	Minimum Inhibitory Concentration
MSC	Minimum Suppressive Concentration
NADF	Non-Aqueous Drilling Fluid
OBM	Oil Based Muds
OD	Optical Density
PAH	Polyaromatic Hydrocarbon
ROC	Retention on Cuttings
SBF	Synthetic Based Fluids
WBM	Water Based Muds
Tween 80	Polyoxyethylene-20-sorbitan monooleate
Span 80	Sorbitan monooleate

List of Symbols

G	Gibbs free energy
T	Temperature
S	Entropy
A	Interfacial area
γ	Interfacial tension
H	Enthalpy
η	Apparent viscosity
ϕ	Volume fraction of the dispersed phase
v	Creaming (Sedimentation) rate
r	Droplets radius
ρ	Density of droplet
ρ_o	Density of the dispersion medium
g	Acceleration due to gravity
k_b	Boltzmann constant ($1.3806 * 10^{-23} \text{ m}^2\text{Kgs}^{-2}\text{K}^{-1}$)
τ	Shear stress
$\dot{\gamma}$	Shear rate
μ	Newtonian viscosity
μ_p	Plastic viscosity
τ_y	Yield stress

CHAPTER ONE: INTRODUCTION

1.1 Drilling Waste Problem Overview

In the oil and gas industry, over 75% of the sections drilled are made up of shales. Instability of borehole and other related drilling problems encountered in drilling shale formations present ubiquitous challenges to drilling operations; leading to a very high annual expenditure which is estimated to cost more than US \$ 1.3 billion per annum for the oil and gas industry in North America (Tare, et al. 2002). The physical and chemical properties of these shales are major contributors to the wellbore instability problems encountered in drilling operations (Oort, et al. 1999; Schlemmer, et al. 2003). The use of water-based mud due to the reactive nature of shale when it comes in contact with water leads to swelling of wellbore during drilling operations and is a major concern in drilling shale formation. Due to these technical difficulties (Shale swelling), Non-Aqueous Drilling Fluids (NADF) such as Diesel Based Fluids, Low Aromatic Based Fluids, Synthetic Based fluids and Reversible Invert Emulsion drilling fluids have been used to drill most of these shale formations.

NADF are generally toxic and poorly degradable such that their use has a very significant negative impact on the environment with regards to the drilling waste (which includes the oily drill cuttings and drilling mud itself) management (Muherei, et al. 2007). Due to the environmental impact of the NADF, the use is strictly regulated. These regulations have led to the continuous reductions of the discharge limits of allowable oil on cuttings content. Regulatory bodies in most of Europe specify that oily cuttings generated offshore have to be cleaned to below 1% residual oil on cuttings (10g oil per kg dry cuttings) following the pioneering ban imposed offshore North Sea countries by 1997 for Diesel Based Fluids (DBF) and 2001 for

Synthetic Based Fluids (SBF) (Smith, et al. 1999; Jones, et al. 2000; Martin, et al. 2002; OGP, 2003). For the liquid waste left after drill cuttings have been removed by the shale shakers, many techniques have been recommended for their disposal in Canada. These include onsite burial (pits, landfill), land applications (land farming, land spreading), bioremediation (composting, bioreactors, vermiculture) and slurry injection as stipulated on the Alberta Energy Regulator Directive 050. These aforementioned techniques require a lot of space and are expensive to operate.

For offshore drilling in the Gulf of Mexico, the EPA's Effluent Limitation Guidelines (2000) defines the amount of oil in drill cuttings as the Retention on Cuttings (ROC), defined by mass of oil/mass of cuttings and reported as percentage. For offshore drilling, the ROC of DBFs cuttings is set to 0%. For SBFs the discharge regulations require either containment of contaminated cuttings or drying below 6.9% ROC for base fluids that meet the environmental performance criteria for Internal Olefins 1618 and 9.4% ROC for base fluids that meet the environmental performance criteria for esters. For land-based drilling operations, the ROC values of DBF and SBF are similar (Muherei, et al. 2007).

Presently, the existing waste treatment technology such as the solid control separations processes are unable to clean oil below 1% retention and this inevitably leads to a discharge prohibition. This limitation can be attributed to the hypothetical mechanisms of oil retention on cuttings which include; adhesive forces, capillary forces and oil adsorption. These forces tend to be greater than the mechanical methods such as shale shakers and centrifuge to be ineffective. In this case, the drilling wastes are usually shipped onshore for treatment and disposal. As a result, this method of disposal is neither environmentally nor economically prudent (Junin, 1996).

Transporting drilling waste onshore for treatment is very expensive and it is also considered to be a risky operation. For onshore disposal, there are three very important components which include; transportation by water, onshore treatment plant and disposal method selected. This requires a large amount of equipment, effort and cost and also is dependent on the availability of facilities and local regulations. For instance, in ultra-deep-water drilling operations, there is difficulty in logistics: boat trips are long, mud volumes are usually high and deck loads are limited (Leoni, et al. 2002; Minton, 2004).

In the vast majority of less developed countries, onshore treatment facilities are often scarce or absent. In more developed countries, the cost of handling drilling waste can be prohibitive. There is thus a great need for most oil and gas companies to devise more cost effective and novel technologies and approaches to meet up with continuous strict environmental regulations on drilling waste disposal. Therefore, for offshore operations where cuttings re-injection is not available, there is a vital need for offshore waste treatment (Muherei, et al. 2007).

Drill cuttings discharge appears to be the most economical option in most environmental settings and work should be focused in developing and implementing new technologies for cutting treatments to reduce the fluid content on cuttings prior to discharge while the residual fluid can be recycled and reused. One way considered in this work to achieve this volume reduction and biodegradation enhancement is changing the wettability of these wastes from oil-wet to water-wet waste.

1.2 Changing emulsion wettability as a possible solution to drilling waste problem

A major problem with oil-based waste is that it is entirely covered in invert emulsion. Invert emulsion drilling fluids are macro emulsions consisting of a hydrocarbon continuous phase with an emulsified internal aqueous “brine” phase in addition to organophilic clays, weighting agents and other additives.

One of the many functions of a drilling fluid is to remove the excavated rock (i.e. drilled cuttings) from the borehole. The unearthed solids are continuously incorporated into the drilling fluids. Solids removal is one of the most important aspects of system control, since it has a direct impact on drilling efficiency and represents an opportunity to reduce overall drilling costs (Ball et al. 2011). The first step of separation involves circulation of the mixture of fluid and drill cuttings over a vibrating screen (Shale shakers) to separate out the solids. Drill cuttings are then collected and stored in a tank for further treatment to reduce the amount of oil retained on the cuttings to acceptable limit before disposal. Several methods have been in use for the disposal of drill cuttings such as; on-site or off-site burial, cutting re-injection, thermal treatment (incineration, gasification, desorption, stripping, volatilization and pyrolysis) and solidification/stabilization.

The resultant fluid that goes through the vibrating screens are processed further by additional mechanical process such as hydrocyclone, centrifugation and gravitational settling to further remove as many fine particles as possible as these particles tend to interfere with drilling performance. The recovered fine particles are stored alongside the drill cuttings for treatment. Not all the fine particles can be removed from the fluid waste using the mechanical process and due to this problem, the recycling and disposal of these fluid wastes becomes difficult because

the fine particles are embedded in the oil continuous phase and are difficult to separate them from the fluid system. Also, the resultant emulsions are further stabilized by the fine particles and becomes more difficult to destabilize these emulsions for separation. These fine solids affect the drilling fluid rheology making the drilling fluid useless and add to the waste.

Several methods have been designed for drilling waste management such as; landfill disposal, landfarming/land treatment, encapsulation/stabilization and thermal destruction but an alternative to these methods involves biodegradation of drilling waste by population of microorganisms present in soil. Bioremediation is an alternative approach because it is simple to maintain, applicable over large areas, cost-effective, leads to total destruction of contaminant and most especially, environmentally friendly but this aforementioned approach has an issue when dealing with invert emulsion drilling waste. This is because the fluids have higher toxicity especially when the hydrocarbon continuous phase is made up of polyaromatic hydrocarbons. This reduces the tolerance level and growth rate of microorganisms which are employed for bioremediation purposes thereby decreasing the rate of biodegradation.

We therefore propose that changing the wettability of these wastes (solids) will address the issue of separation and biodegradation of drilling waste. Wettability of solids by an invert emulsion drilling fluid can be defined as the ability of the fluid to incorporate foreign materials into the oil continuous phase. Therefore, changing the wettability implies transforming oil-wet waste to water-wet waste.

Changing the wettability of these wastes will address two main concerns. Firstly, by allowing the solids to water wet quickly, where simple gravity separation equipment can be used to recover the water-insoluble base fluids for re-use in the mud system, consequently, lowering the overall

organic loading to the environment. Also, the resultant solids can be compacted and reduce amount of space required for its storage. Secondly, the residual solids, which are no longer oil-wet will tend to stay suspended in the water column longer where they can biodegrade rapidly under aerobic conditions.

In this project, we hypothesis that increasing the HLB (increasing hydrophilicity of waste i.e. making the waste more water-wet) of an invert emulsion drilling fluid will enhance oil-water-solid separation and increases the rate of biodegradation of drilling waste.

1.3 Objectives of study

The main objective of this project is to study the effect of change in Hydrophilic-Lipophilic Balance (HLB) on the state of stable invert emulsion. Firstly, this study will start by considering the mixing parameters (emulsifier concentration and stirring rate) required for the formulation of an invert emulsion drilling fluid. Secondly, with the mixing parameters determined, invert emulsions with different HLB number will be prepared and the emulsion with the most stable invert emulsion will be ascertained. This will serve as the model for drilling fluid (emulator). Thirdly, the most stable invert emulsion will be treated with several emulsifier combinations to increase the initial HLB number of the emulsion. The effect of these treatments on the emulsion will be studied to see how they alter the stability of invert emulsion. The properties of the invert emulsion to be monitored as a result of these treatments are water content, phase separation, droplet size and viscosity. Finally, tolerance of microorganisms and biodegradation of the invert emulsion with different HLB numbers will be carried out. This part of the work will be carried out to see the viability of microorganisms in invert emulsions as the HLB number of the system is varied.

CHAPTER TWO: LITERATURE REVIEW

2.1. Drilling Fluids and its functions in drilling operations

Drilling fluids may be defined as a mixture of components designed to support rotary drilling operation and removal of cuttings from the borehole to the surface. The drilling fluid is one of the main contributors to safety of drilling operations, waste generation and the environmental footprint, and hence the cost of drilling process (Darley et al. 1988). The drilling fluid performs a variety of different functions to provide efficient rock penetration and avoid drilling problems in respect to operational conditions. The five main drilling fluid functions are listed below (Darley et al. 1988):

- Cool and lubricate the bit and drill string;
- Clean the bit and the bottom of the hole;
- Suspend solids and transport cuttings and sloughing to the surface;
- Stabilize the wellbore and control subsurface pressures;
- Assist in the gathering of subsurface geological data such as permeability, porosity, etc. and formation evaluation.

2.2. Types of Drilling Fluids

Petroleum drilling is associated with complex problems during drilling operations and this has resulted in the development of different formulations of drilling fluids (muds). Generally, drilling mud may be classified in three families:

- ***Gas Based Drilling Fluids*** (GBDF) (also known as reduced-pressure drilling fluid) can be further classified into: dry gas; mist (in which droplets of water or mud are carried in

the air stream); foam (in which air bubbles are dispersed in water containing a foam stabilizing agent); and gel foam (in which the foam contains film-strengthening agents such as organic polymer or bentonite). The most common gases used for drilling fluid formulation are air and natural gas (methane). GBDF provide high rates of penetration and good hole cleaning, and are widely used for underbalance drilling (also known as drilling while producing). Under other conditions, application of GBDF is inappropriate because the associated low pressure does not allow control of wellbore stability. Usually, water based and oil based fluids are used to control subsurface formation pressure.

- **Water Based Muds** (WBM) are cheap, in most cases environmentally friendly, alternatives widely used in drilling operations. This type of muds is mostly made up of fresh, salt and/or sea water in a continuous phase. WBMs are mainly composed of aqueous solutions of polymers and clays in water or brine with different types of additives incorporated to the aqueous solution. Usually, water based composition are very effective for drilling operations. However, most of the WBMs are sensitive to contamination and high temperature, and may have negative impact on stability and permeability of formations containing reactive clay (shale). Under these conditions, WBMs are usually replaced with oil based muds.
- **Oil Based Muds** (OBM) comprises base oil (diesel, mineral and synthetic) as the continuous phase. The most common OBMs are invert emulsions which comprise of droplets of brine dispersed in the oil continuous phase forming an emulsion stabilized by surfactants. Additives such as organophilic clay, organophilic polymers and wetting agents allowing dispersing barite and other water-wet chemicals in the oil continuous phase are often added to the invert emulsions to support drilling fluid functions. OBMs

are much more expensive because of the different constituents that make up the drilling fluid system and the complex treatment approach for the generated waste which include: transporting, processing and disposal.

The application of OBMs is necessary for many drilling operations. OBMs enhance drilling performance compared to WBM in the sense of higher rate of penetration, better lubricity, higher tolerance to high temperature and contaminants, better wellbore stability in shale formation due to the non-reactive nature of oil. However, they have adverse environmental impact because of the toxicity of the oil continuous phase.

Negative impacts of OBM have been addressed by replacement of diesel, containing high amounts of polyaromatic hydrocarbons (PAH), with mineral and synthetic oil which have very low PAH and high rate of biodegradability. Another challenge encountered with applications of OBMs is the waste management by oil-wetness of drilling waste (cuttings). The associated problems will be discussed later in greater detail.

2.3. Emulsions and Emulsion Stability

Emulsions are dispersions of one immiscible liquid (dispersed phase) in the other liquid, serving as the continuous phase (dispersion medium). Two liquids can form different types of emulsions. As an example, oil and water can form, an oil-in-water emulsion, wherein the oil is the dispersed phase and water is the dispersion medium; a water-in-oil emulsion, wherein water is the dispersed phase and oil is the dispersion medium; and multiple emulsions are also possible such as water-in-oil-in-water emulsions and oil-in-water-in-oil emulsion. Two immiscible liquids are separated by an interface.

Emulsions are thermodynamically unstable systems and can be stabilized by the use of surfactants or surface active solids to remain dispersed for any functionally relevant period of time. The stability of emulsions is determined by intermolecular interactions and surface forces. For an emulsion to be formed, large amounts of energy must be put into the system in the form of shear. This energy is required due to an increase in conformational entropy and surface area (Zanten et al, 2012). This requirement is best explained using a thermodynamic framework. The free energy change of a system is represented by Gibbs equation:

$$\Delta G = \Delta H - T * \Delta S \text{ or } \Delta G = \Delta A * \gamma_{ow} - T * \Delta S \quad (2.1)$$

where G is the Gibbs free energy, T is the temperature, S is the entropy, A is the interfacial area, γ is the interfacial tension at the oil-water interface and H is the enthalpy of the system.

If the free energy is less than zero, then the process is spontaneous. If it is greater than zero, then energy input is required into the system to cause the desired change. When creating an emulsion, the entropy is increased by the creation of several small droplets; however the creation of these droplets also causes a large increase in the oil/water interfacial area. The amount of surface area created can be very large; generating a large penalty from contacting oil/water. This energy penalty can be reduced by the addition of surfactants which lowers the interfacial tension, thus reducing the amount of energy required to form an interface (Zanten et al 2012).

In this project, emulsion stability is very important when formulating invert emulsion drilling fluids. Poor stability of the emulsion results in the two phases separating into two distinct layers. This results in wellbore instability especially when drilling shale formations. The free water layer hydrates shale in the formation which leads to a very costly problems such as hole erosion, bit balling, hole closure, hole collapse and poor mud condition. To achieve maximum stability of an

invert emulsion, suitable combinations of nonionic emulsifiers (Tween and Spans), emulsifier concentration and stirring speeds were considered.

2.3.1 Mechanisms for Emulsion Stability

The emulsion stability mechanism has been studied and the following are the most common interactions that play an important role in the stabilization of emulsion: Steric stabilization, Marangoni-Gibbs effect and Rigid film formation (Ekott, et al, 2010).

Steric stabilization:

Surfactants containing a hydrophilic, polar head group and hydrophobic tail group will typically position themselves at oil-water interfaces. The head group has a natural affinity for water while the tail group will preferentially remain in the oil phase. Dispersed water droplets (Water-in-Oil) will thus be coated by surfactant material with hydrophobic tails protruding into the oil phase. In the case of dispersed oil droplets (Oil-in-Water), the oil droplets will be coated by the surfactant material with the hydrophilic head protruding into the water phase. In both cases, when droplets approach each other, their adsorbed surfactant tails/heads prevent droplet contact and hence prevent coalescence of these droplets.

Marangoni-Gibbs effect:

The Marangoni-Gibbs effect can stabilize emulsions by preventing the drainage of the continuous phase from between two opposing droplets. As droplets approach, their surfaces eventually become plane parallel and the film layer attempts to drain. This outward convection draws surfactants towards the droplet edges leaving a region of low surfactant concentration in the middle. This process sets up an unfavorable interfacial tension gradient along the interface.

Surfactant diffusion thus proceeds in the direction opposing convection to eliminate the interfacial tension gradient. Stable emulsions can result from the balance of surface diffusion and film convection.

Rigid film formation

A third and the most probable mechanism of emulsion stabilization come from an adsorbed layer of material with high rigidity and elasticity. Surfactant aggregates in the oil phase will adsorb to the oil-water interface and form a consolidated film or skin that resists droplet coalescence. This process can be quite complex and depends on surfactants chemistry solvency and the kinetics of diffusion and adsorption. Other factors leading to stable emulsions are high viscosity of continuous phases, small dispersed phase volume and droplet size and low interfacial tensions.

The stability of an emulsion can be enhanced by a number of factors:

- The addition of surfactant/emulsifier decreases the surface tension, making the droplets more stable. The surfactant can also create a steric and/or electrostatic barrier to slow coalescence.
- Droplet-droplet, droplet-particle and particle-particle hydrodynamic interactions can lead to a more viscous fluid, which will slow the kinetics of coalescence. The viscosity roughly follows the model (Tadros, 2009):

$$\eta = \eta_{solvent} \left(1 + \frac{5}{2} \phi \right) \quad (2.2)$$

where η is the apparent viscosity, $\eta_{solvent}$ is the viscosity of the continuous phase and ϕ is the volume fraction of the dispersed phase. Thus, the higher the volume fraction of the internal phase, the more viscous the emulsion if it is dispersed properly. These

interactions can also be turned using various surfactant mixtures altering surface tension, contact angle/wettability of the droplets and particles. It is these interactions which enhance the yield point and gel strength of a fluid.

- Solids can also act as secondary emulsifiers at the oil-water interface, stabilizing emulsions. The energy required to displace a solid particle from the interface is roughly 10-100 times that required to displace a surfactant/emulsifier from the same interface. Thus, solid/surfactant stabilized emulsions can have enhanced stability over just surfactants alone or solids alone.

2.3.2 Destabilizing mechanisms in emulsions

Most emulsions are naturally thermodynamically unstable, that is, they tend to separate into two distinct phases or layers over time due to high interfacial area and hence total surface energy of the system. Therefore, the emulsion characteristics such as droplet size distribution, mean droplet size and other properties will change with time. The stability of emulsion is characterized by the time-dependent behavior of its basic parameters.

Various emulsion breakdown processes can be identified. Some of these instability mechanisms that lead to phase separation in emulsions are represented schematically in **Figure 2.1**. These physical instability mechanisms are creaming/sedimentation, flocculation, Oswald ripening, coalescence and phase inversion.

Creaming and Sedimentation: This process results from external forces, usually gravitational or centrifugal. When the forces exceed the thermal motion of the droplets (Brownian motion), a concentration gradient builds up in the system such that the larger droplets move more rapidly

either to the top i.e. creaming (if their density is less than that of the medium) or to the bottom i.e. sedimentation (if their density is greater than that of the medium) of the container.

The creaming or sedimentation rate can be estimated from the Stokes' equation (Technical Brief 2011 Volume 2):

$$v = \frac{2r^2(\rho - \rho_o)g}{9\eta} \quad (2.3)$$

Where v is the creaming (sedimentation) rate, r is the droplets radius, ρ is the density of droplet, ρ_o is the density of the dispersion medium, η is the viscosity of the dispersion medium (continuous phase) and g is the local acceleration due to gravity. The density difference, $(\rho - \rho_o)$, is negative for creaming but positive for sedimentation. The Stokes' equation shows that creaming/sedimentation is delayed by a small droplet radius, a highly viscous continuous phase and a low density difference between oil and water phases.

Flocculation: This process refers to aggregation of the droplets (without any change in primary droplet size) into larger units. It is the result of the van der Waals attractions which are universal with all disperse systems. Flocculation occurs when there is not sufficient repulsion to keep the droplets apart at distance where the van der Waals attraction is weak. Flocculation may either be strong or weak depending on the magnitude of the attractive energy involved. Flocculation maybe subdivided into two general categories: that resulting from sedimentation aggregation and that from Brownian motion aggregation of the droplets. In polydisperse emulsions, droplets of different size cream at different rates and this leads to a tendency for the faster-moving (larger) droplets to collide with and potentially trap slower moving smaller droplets. In sedimentation aggregation, it is assumed that all the paths in sedimentation are vertically linear; Brownian

aggregation is the result of random Brownian movement of the droplets. An estimate of the relative rates of each type of flocculation can be determined using the equation:

$$\Gamma_{\max} = \frac{2\Pi(\rho - \rho_o)gr^4}{3k_bT} \quad (2.4)$$

Where k_b is the Boltzmann constant ($1.3806 * 10^{-23} \text{ m}^2\text{Kgs}^{-2}\text{K}^{-1}$), T is the absolute temperature (Kelvin), r is the radius of droplet (meter) and Π is the *Pi* constant (3.142). When $\Gamma_{\max} > 10$, the Brownian aggregation is negligible; when $\Gamma_{\max} < 0.1$, sedimentation is negligible.

Ostwald Ripening: This effect results from the finite solubility of the liquid phases. Liquids described as being immiscible often have mutual solubilities which are not negligible. With emulsions which are usually polydisperse, the smaller droplets will have a greater solubility when compared to larger droplets (due to curvature effects). With time, the smaller droplets disappear and their molecules diffuse to the bulk and become deposited on the larger droplets. With time, the droplets size distribution shifts to larger values.

Coalescence: This refers to the process of thinning and disruption of the liquid film between the droplets, with the result that fusion of two or more droplets occurs to form larger droplets. The limiting case for coalescence is the complete separation of the emulsion into two distinct liquid phases. The driving force for coalescence is the surface or film fluctuations; this results in a close approach of the droplets whereby the van der Waals forces are strong and prevent their separation.

Phase Inversion: Phase inversion is the phenomenon where there is a swap in continuous phase and internal phase of an emulsion. For instance, when water-in-oil emulsions changes to an oil-

in-water emulsions or vice versa. There are two main types of phase inversion, namely; catastrophic inversion and transitional inversion. Catastrophic inversion occurs when there is a large change in the relative volume fraction of the two components of an emulsion while transitional inversion occurs when there is a shift in surfactant affinity.

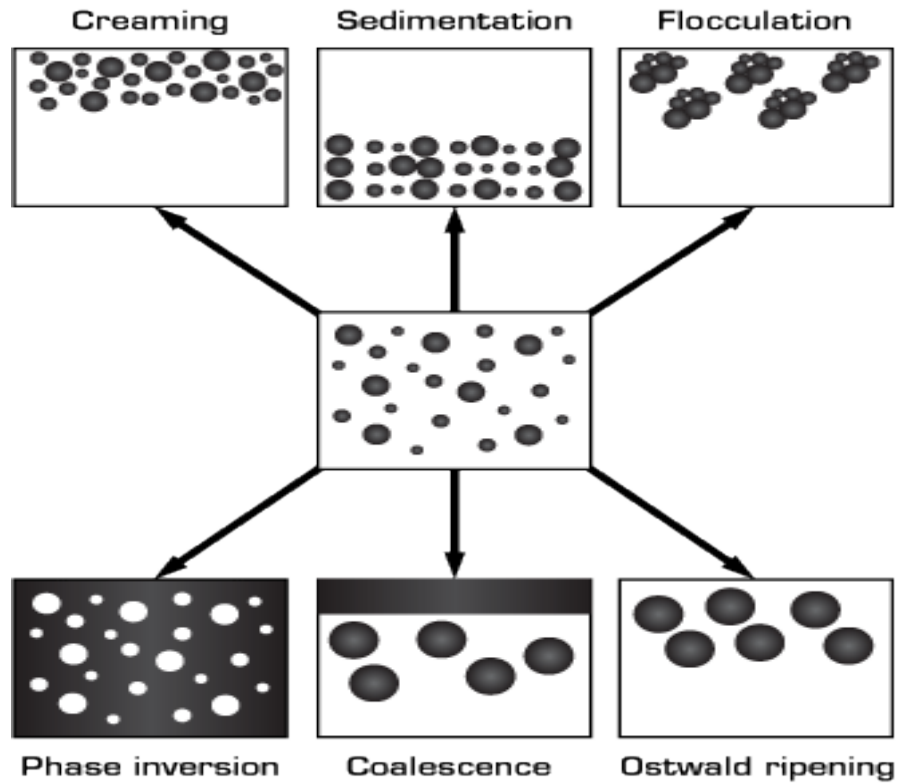


Figure 2.1 Schematic representation of the various breakdown processes in emulsion (Tadros, 2009)

2.3.3 Hydrophilic-Lipophilic Balance (HLB) of emulsions

Nowadays, the selection of different surfactants in the preparation of either O/W or W/O emulsions is often made on an empirical basis. One such semi-empirical scale for selecting surfactants is the Hydrophilic-Lipophilic Balance (HLB) number developed by William Griffin (Griffin, 1954). This scale is based on the relative percentage of hydrophilic to lipophilic

(hydrophobic) groups in the surfactant molecule(s). For O/W emulsion droplet, the hydrophobic chains reside in the oil phase droplet, while the hydrophilic head group resides in the aqueous phase. On the other hand, for a W/O emulsion droplet the hydrophilic group(s) reside in the water droplet, while the lipophilic groups reside in the hydrocarbon phase. HLB number of the system determines its behavior. **Table 1.1** represents a guide to the selection of surfactants for particular applications according to the HLB value. More specifically, HLB responsible for stability of the emulsion depends not only on surfactant used, but also oil chemistry. Table 1.2 illustrates the HLB numbers required to emulsify various oils.

$$HLB = 20 * \frac{\mu_L}{\mu} \quad (2.5)$$

Where μ_L = molecular mass of hydrophilic portion of the molecule and μ = molecular mass of the whole molecule

Table 1.1. A summary of surfactant HLB ranges and their applications (ICI Americas, 1980)

HLB range	Application	
2 - 3	Antifoaming agents	Lipophilic (oil soluble)
4 - 6	W/O emulsifier	
7 - 9	Wetting agent	
8 - 18	O/W emulsifier	Hydrophilic (water soluble)
13 - 15	Detergent	
10 - 18	Solubilizers	

Table 1.2. HLB numbers required for the emulsification of various oils (Tadros, 2009)

Oil	W/O emulsion	O/W emulsion
Paraffin oil	4	10
Beeswax	5	9
Linolin, anhydrous	8	12
Cyclohexane	-	15
Toluene	-	15

The relative importance of the hydrophilic and lipophilic groups was first recognized when using mixtures of surfactants containing varying proportions of low and high HLB numbers. The efficiency of any combination (as judged by phase separation) was found to pass a maximum when the blend contained a particular proportion of surfactant with the higher HLB number. This is illustrated in Figure 2.2, which shows the variation of emulsion stability, droplet size and interfacial tension in relation to the percentage of surfactant with a high HLB number.

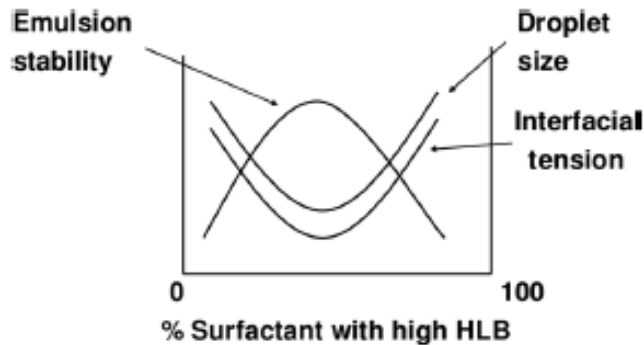


Figure 2.2. Variation of emulsion stability, droplet size and interfacial tension in relation to the percentage of surfactant with high HLB number (Tadros, 2009).

Recently, research has been done on ionic and nonionic demulsifiers. Studies have shown that the presence of more hydrophilic parts in demulsifiers can cause more separation of water from oil and this can be attributed to the great effect on the HLB number of the surfactants. Tweens have appropriate hydrophilic parts because of their high oxy-ethylene groups. This group allows the surfactant that can make more hydrogen bonds and has stronger hydrophilic parts (Roodhari et al, 2011).

Bancroft stated that “a hydrophilic liquid has a tenacity to make water as a dispersing phase but hydrophobic one has a tenacity to make oil as a dispersing phase” (Bancroft, 1913). Griffin stated the hydrophilic-lipophilic balance (HLB) concept to show the amphiphilicity for nonionic surfactants, surfactants with low HLB surfactant gives water-in-oil emulsions (invert emulsions) while high HLB surfactant gives oil-in-water emulsions (Griffin, 1949). Since Tweens have high HLB number, they probably can help the water-in-oil emulsion crude oil to break. Research has shown that increasing the HLB number of surfactants is more effective in demulsification processes (Roodhari et al, 2011).

This concept of increasing the HLB number of surfactants can be applied in drilling waste management. Increasing the HLB number of emulsion increases the water wetness of materials associated with drilling waste i.e. cuttings, fine solids. Making these materials water-wet will enhance the efficiency of separation, thereby reducing the amount of waste generated and also increase the rate of biodegradation.

2.3.4 Rheology of Emulsions

Flow properties of emulsion, in other words their **rheology**, are amongst the most important properties when characterizing emulsions. In general, rheology can be defined as the study of the deformation and flow of materials under the influence of applied shear stress. The rheological behavior of emulsions has been of great interest not only for fundamental scientific understanding, but also for practical industrial applications (Barnes, 1994, Tadros, 1994). A fluid does not have one determined viscosity; it can vary depending on the shear rate. The rheological behavior of an emulsion falls into two main groups depending on its composition: Newtonian and non-Newtonian fluids. Only Newtonian fluids have a determined viscosity (i.e. a linear relationship between shear stress and shear rate) and the most common Newtonian liquid is water.

Drilling fluids are generally non-Newtonian. A rheology profile is used to determine if a given drilling fluid is Newtonian or non-Newtonian. This is achieved by measuring the shear stress versus shear rate. Shear stress, τ is defined as an applied force, F , acting parallel on a unit surface area, A . Shear rate $\dot{\gamma}$ is defined as the rate of change in velocity normal to the direction of motion (i.e. the relative motion of two parallel layer of fluid) (Azar, et al, 2007).

Mathematically, they can be described as:

$$\text{Shear Stress: } \tau = \frac{F}{A} \quad (2.6)$$

$$\text{Shear Rate: } \dot{\gamma} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \quad (2.7)$$

Where u and v are x and y components of velocity respectively. A plot of shear stress versus shear rate is known as a consistency curve.

Four main rheological models are commonly used to describe drilling fluids namely: Newtonian, Bingham, Power Law and Herschel-Bulkley Models.

Newtonian Model: The viscous force present in a simple Newtonian fluid is characterized by the fluid viscosity. Water, gases and mineral oil are common examples of a Newtonian fluid. The Newtonian model satisfies the following relationship:

$$\tau = \mu \cdot \dot{\gamma} \quad (2.8)$$

where τ = shear stress, μ = Newtonian viscosity, is assumed to be dependent on temperature (T) and pressure (P) and $\dot{\gamma}$ = shear rate.

The consistency curve is a straight line from origin with shear rate on the x -axis and shear stress on the y -axis in a Cartesian plot, at a constant temperature and pressure, the shear rate and shear stress are directly proportional and the constant of proportionality is the Newtonian viscosity (μ). The slope of the line is the Newtonian viscosity. Since μ does not change with shear rate, it is the only parameter needed to characterize the flow properties of a Newtonian fluid.

Bingham Model: These types of fluids behave approximately in accordance with the Bingham theory of plastic flow, which postulates that a finite stress (yield stress, τ_y) must be applied to initiate flow, and that at greater stresses, the flow will be Newtonian (Xiuhua et al, 2010). The consistency curve for a Bingham model is a straight line but does not go through the origin

(Figure 2.3). The yield stress determines how much stress is required before the fluid starts to move (Azar, et al, 2007). The shear stress against shear rate slope is the plastic viscosity. The Bingham model describes the fluid with the equation:

$$\tau = \tau_y + \mu_p \dot{\gamma} \quad (2.9)$$

Where μ_p is the plastic viscosity and τ_y is the S.

Power Law Model: The Power law model is one of the most widely used models for non-Newtonian constitutive fluids. These fluids are known as pseudoplastic or shear thinning/thickening fluids. The equation that describes the shear stress for these fluids is:

$$\tau = K \dot{\gamma}^m \quad (2.10)$$

Where K is the consistency index and the m is the exponent or power law index. The effective viscosity from this relationship is defined as:

$$\mu_a = K \dot{\gamma}^{m-1} \quad (2.11)$$

where μ_a is non-Newtonian apparent viscosity. If $m < 1$, a shear-thinning fluid is obtained, this is characterized by a progressively decreasing apparent viscosity with increasing shear rate. If $m > 1$, we have a shear-thickening fluid in which the apparent viscosity increases progressively with increasing shear rate. When $m = 1$, the fluid is Newtonian. The power law model does not have the capability to handle the yield stress.

Herschel-Bulkley Model: The Herschel-Bulkley model is an extension of simple power law model by including a yield stress. It is sometimes called yield-pseudoplastic because it

encompasses both yield behavior of non-Newtonian fluid and also allow for shear-thinning. It can be described mathematically:

$$\tau = K \cdot \dot{\gamma}^m + \tau_y \quad (2.12)$$

Where K is the consistency index, m is the exponent or power law index and τ_y is the yield stress.

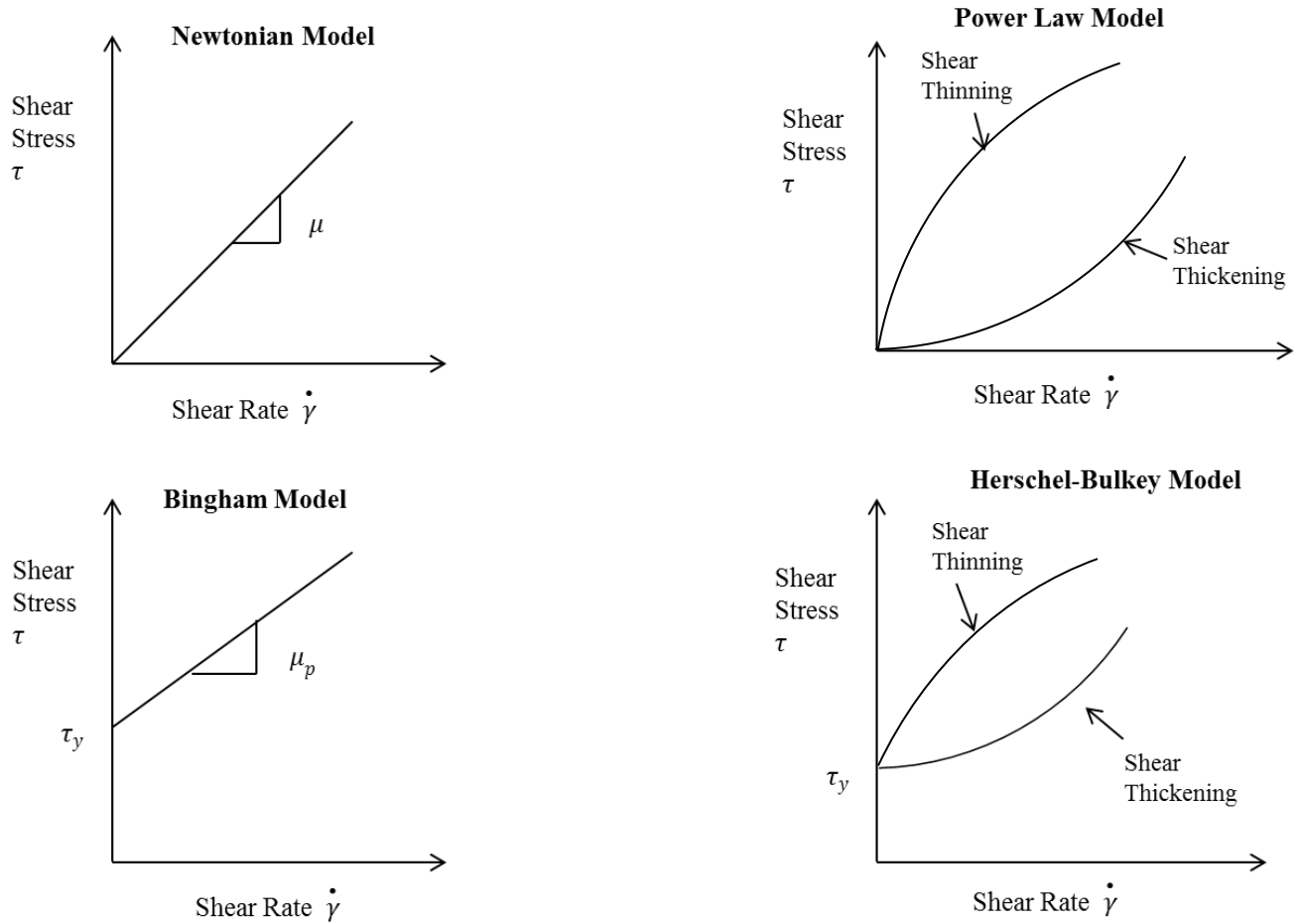


Figure 2.3.The consistency curve of rheological models of drilling fluids (Skalle, 2011)

2.4 Biodegradation of Hydrocarbons (drilling fluid base oil)

Biodegradation is a process that occurs naturally in which hydrocarbons are converted to less harmful products through the metabolic or enzymatic activity of microorganisms. Hydrocarbons may be mineralized to carbon dioxide, water and microbial biomass or it can be destabilized to smaller compounds which in turn go through successive degradation until the compound is completely mineralized (Mango, 1997). These microorganisms use hydrocarbons as both energy and carbon source. This implies that microorganisms derive energy during degradation of hydrocarbons which are needed for cellular functions and also hydrocarbons serve as a carbon source in which degraded smaller compounds are incorporated into cell materials. This degradation process is a combination of anabolic (building up) and catabolic (breaking down) processes (Brock et al, 1994).

The metabolic ability required for the utilization of hydrocarbons as a carbon and energy source is commonly found among bacteria and fungi (Peng et al, 2008) consequently, using the genetic potential of microbial community is a positive approach to remediation of drilling fluid waste. The ability of microorganisms to degrade hydrocarbons is thought to result from the utilization of naturally occurring hydrocarbons produced by plants, algae and other organisms as well as those released from natural oil seeps (MacDonald, 1993 and Orcutt, 2010). Generally, the biodegradability of hydrocarbons can be ranked as: linear alkanes > branched alkanes > low-molecular-weight alkyl aromatics > monoaromatics > cyclic alkanes > polyaromatics > > asphaltenes (Van Hamme et al, 2003).

Biodegradation of complex hydrocarbons usually needs the cooperation of more than a single microbial strain (species). In a case of a pollutant that consists of several different compounds (e.g. crude oil) where complete mineralization to carbon dioxide and water are desired, a consortium of microorganism will be required. Individual microorganisms can metabolize only a limited range of hydrocarbon substrate, so incorporation of mixed populations with overall broad enzymatic capacities are required to bring the rate and extent of hydrocarbon biodegradation further (Ghazali et al, 2004).

The rate and extent of biodegradation of hydrocarbons are determined by the following factors: chemical structure of hydrocarbons, the presence and capabilities of organisms, the presence of nutrients, the presence of electron acceptor and finally the availability of the substrate hydrocarbon to appropriate organisms (Brock et al, 1994). The availability is defined by the presence of the substrate in a state which can be processed by the organism. For the purpose of this project, the last factor which is the availability of the substrate hydrocarbons to the microorganisms (bioavailability) and toxicity of the hydrocarbons on the microorganisms are the areas of major concern.

2.4.1 Bioavailability of hydrocarbons

Bioavailability of hydrocarbons has a great influence on the degradation of hydrocarbons by microorganisms. The chemical properties of hydrocarbons determine its bioavailability. For a compound to be bioavailable to the microbes they have to be absorbed by these microorganisms and this process is called **Transmembrane Transportation**. These compounds are usually dissolved in water or attached to the organisms. Therefore, an increase in bioavailability implies an increase in biodegradation rate. In the case of hydrocarbons which are hydrophobic

compounds, they seldom dissolve in water which reduces the amount of hydrocarbon that are bioavailable to the microbes and ultimately reduces the rate of biodegradation.

Microbial degradation of recalcitrant compounds may be improved through emulsification and solubilisation in the aqueous phase which can be achieved through the use of surfactants to increase bioavailability. Since hydrocarbon oxidation is performed by intracellular enzymes, the solubilisation of hydrocarbons enhances the mass transfer rate of hydrocarbons to aqueous phase and into microbial cells, hence increases the degradation rate. Furthermore, emulsification increases the bioavailability of hydrocarbons, hence biodegradation rate as a result of increased oil-water interface available to microbial growth (Kostenko et al, 2013). The effect of surfactant on the bioavailability of hydrophobic compounds can be explained by three main mechanisms which are as follows (Volkeing, et al. 1995):

- I. Dispersion of non-aqueous phase liquid hydrocarbons, leading to an increase in contact area, which is caused by a reduction in the interfacial tension between the aqueous phase and the non-aqueous phase,
- II. Increased solubility of the pollutant, caused by the presence of micelles which may contain high concentrations of hydrophobic organic compounds and
- III. Facilitated transport of the pollutant from solid phase to the aqueous phase, which can be caused by a number of phenomena such as lowering of the surface tension of the pore water in soil particles, interaction of surfactant with solid interfaces and interaction of the pollutant with single surfactant molecules.

2.4.2 Toxicity of drilling fluids against biodegrading microorganisms

Toxicity is a critical aspect which may adversely affect the biodegradation of drilling fluids. Toxicity is the degree to which a substance can harm or damage an organism. Biodegradable, but toxic materials, such as hydrocarbons and surfactants in drilling fluid emulsions, have a dual effect: serve as nutrient at relatively low concentrations, but inhibit and even kill microorganisms when the concentration increases.

Considering drilling fluid emulsion toxicity, the critical level of toxicity is determined by microbial tolerance, *i.e.* microorganism's ability to grow and degrade in the presence of toxic materials. The drilling fluid with low toxicity and/or microorganisms with incredibly high tolerance allow microbial growth proportional to drilling fluid load without any limitation. However, the reality is that drilling fluid can enhance microbial growth when its concentration increases to a certain level known as the Peak Concentration (C_p). The first sign of toxic effect can be associated with the suppression of the microbial growth. The minimum concentration causing growth rate reduction compared to drilling fluid free media defines the Minimum Suppressive Concentration (MSC). Increasing drilling fluids concentration further reduce microbial metabolic activity until microbial growth completely stopped at the Minimum Inhibitory Concentration (MIC) of drilling fluid. The drilling fluids at concentrations above MIC level kill microbial cells. The killing of 99.9% of the microbial population by the drilling fluid is defined as the Minimum Bacterial Concentration (MBC).

Surfactants applied at high concentration are often found to badly affect the growth of microorganisms on rich media or in the presence of easily degradable substrate. Surfactants added to resting cells at a high concentration have been reported to cause a decrease in oxygen

uptake rate (Mohanty et. al, 2013). The structure of surfactants used and the nature of the microorganisms play an important role on how the adverse effects of the surfactant concentration are manifested. In contrast, growth inhibition, reduced substrate and oxygen uptake rate in the presence of oil and petroleum hydrocarbons are not necessarily a manifestation of toxicity since they may result from reduced bioavailability of substrate. The toxicity of any surfactant is related to its capacity to be adsorbed and penetrate through the bacterial cell membrane (Rosen, et al, 2001). There are two main mechanisms of surfactant toxicity which are disruption of the cell membrane by interaction with membrane lipids and by interaction of surfactants with protein molecules essential for cell functioning (Volkering, et al, 1998). In addition to the surfactant type and concentration, environmental conditions such as pH conditions are also factors that determine the toxic effect. Cationic surfactants are more toxic at higher pH conditions (>7), whereas anionic surfactants are more toxic at lower pH conditions (Kim, et al, 2003).

2.4.3. Impact of surfactant HLB on biodegradation

Surfactants with similar chemical structure but varying in terms of their HLB value are reported to differ in terms of their toxicity to bacteria (Mohanty et. al, 2013). It may be noted that HLB may increase due to the increase in hydrophilic chain length or due to the decrease in the hydrophobic chain length. The increase in HLB is thus expected to reduce nonspecific toxicity due to the reduction in hydrophobicity which inhibits its entrance into the lipid bilayer of the cell membrane (Li, et al, 2009 and Jurado, et al, 2009). During the biodegradation of acetate and glucose, Triton X-165 (HLB 15.8) was found to be less toxic to mixed microbial cultures than Triton X-100 (HLB 13.5) (Gu, et al, 1997). Studies with luminescent bacteria and various groups of non-ionic surfactants, such as fatty alcohols, ethoxylates, nonylphenol polyethoxylates and alkylpolyglucoside, have also confirmed the relationship between toxicity, structural

characteristics and physiochemical properties (CMC, HLB and interfacial properties) of surfactants (Jurado, et al, 2009). For the alkylpolyglucoside EC_{50} was found to be dependent on the hydrophobic alkyl chain length, HLB and CMC of surfactant such that toxicity increased as the alkyl chain length increased and HLB decreased. The toxicity of alkylpolyglucoside increased as the CMC decreased. For fatty-alcohol ethoxylates, increasing the alkyl chain length lowered EC_{50} and increased toxicity, whereas increasing ethoxylation increased the HLB and lowered the toxicity.

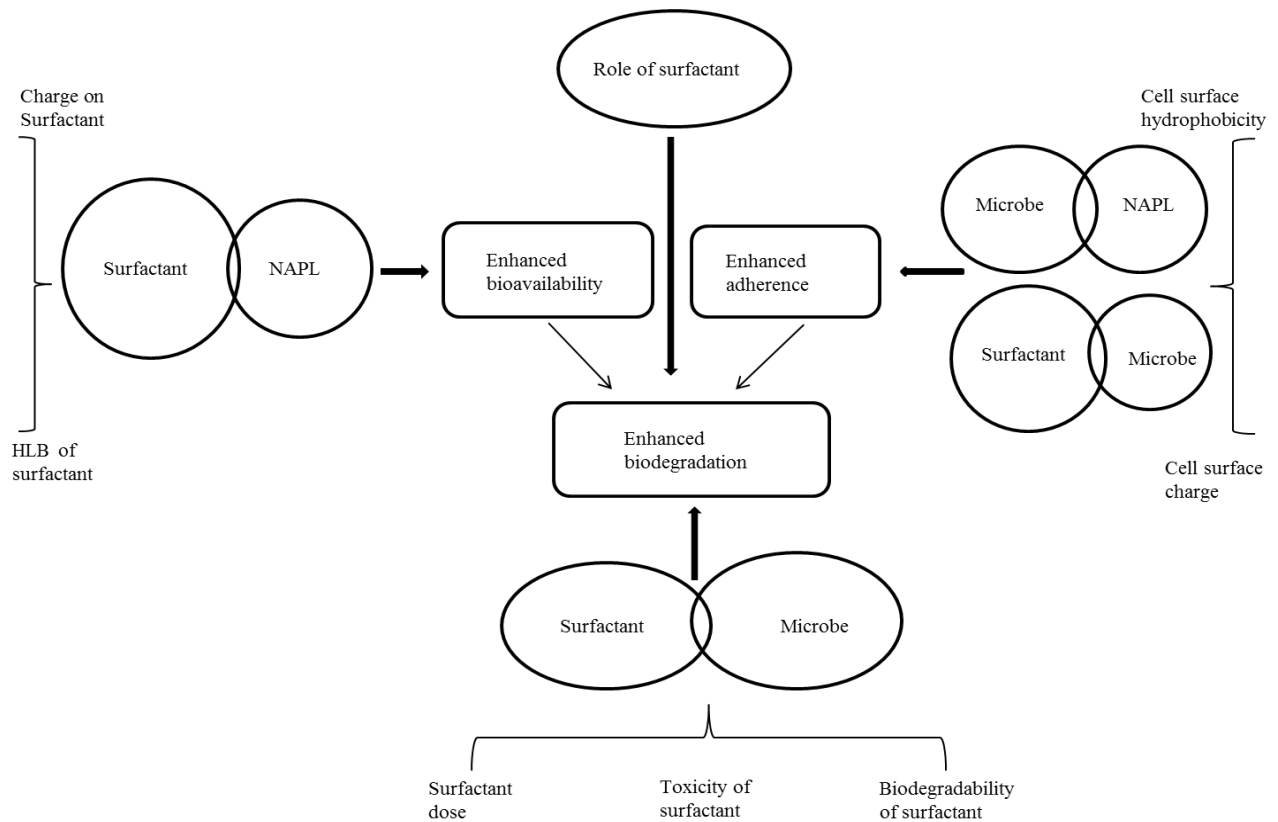


Figure 2.4 Schematic diagram illustrating the complexity interplay of interactions between surfactant, microorganism, and substrate during surfactant enhanced biodegradation (Mohanty et. al, 2013)

The following shows the summary of the literature review done on this chapter:

- A review was conducted on the drilling fluid types, its functions and stability. Oil Based Muds (OBM) is the most stable fluid in drilling operation especially in shale formations. It gives better rate of penetration, lower tolerance to contaminant and better lubricity. Irrespective of these advantages, it has some negative impact in drilling waste management.
- Emulsions stability was reviewed and was gathered that unstable emulsions present very costly problems such as hole erosion, bit balling, hole closure, hole collapse and poor mud conditions. Several emulsion breakdown processes were mentioned and they include: creaming/sedimentation, flocculation, Ostwald ripening, coalescence and phase inversion.
- Hydrophilic Lipophilic Balance (HLB) of an emulsion system was reviewed. It was gathered that HLB concept is a method to determine the type of surfactants used and their concentration in formulating a stable emulsions. Emulsion rheology was studied and the four rheological models commonly used to describe drilling fluids were reviewed which include: Newtonian, Bingham, Power Law and Herschel & Bulkley models.
- Biodegradation of hydrocarbons was reviewed. In this section, bioavailability of hydrocarbons (substrate) and toxicity of hydrocarbons/surfactant were observed to be the major factors that affect the viability of microorganisms in drilling fluid waste and these two factors are major contributors to the rate of biodegradation of the waste.

In view of the findings from the literature review, the information gathered will be used in the formulation of a stable invert emulsion drilling fluid. Two mixing parameters (emulsifier concentration and stirring rate) will be considered in the formulation of the stable invert

emulsion. Also, HLB concept will be adopted in order to obtain the optimum HLB number for emulsifier combinations for the invert emulsion.

Lastly, tolerance and viability studies will be conducted on the invert emulsion to ascertain the level of toxicity of these emulsions to microorganisms. This will enable us to know the biodegradation rate of the invert emulsion.

CHAPTER THREE: EXPERIMENTAL PROCEDURE

This chapter presents the experimental set up and procedure. Firstly, the materials used for the formulation of invert emulsion are identified. The microbial strains and the media used for their preparation for biodegradation test are presented. The next section shows the preliminary procedure of optimizing the emulsifier concentration and stirring rate to achieve a stable invert emulsion. The optimized emulsifier concentration and stirring rate was used in preparing invert emulsion at HLB values ranging from 4.3 to 14.4. The most stable of these emulsions was selected for destabilization treatment and the basis for stability was done based on the level of phase separation. Emulsifier combinations of HLB values ranging from 10.2 to 14.4 were used in the treatment of the stable invert emulsion. The state of the resulting emulsion as a result of change in HLB values are characterized using the parameters: phase separation, water content, droplet size and viscosity measurement. Finally, a biodegradation test was done to ascertain how changes in HLB values affect the viability of microorganisms in invert emulsion.

3.1 Materials

The two different type of mineral oil used for invert emulsion preparation were Drisol and Distillate 822 (kindly provided by Marquis Alliance Energy Group Inc., Canada). Surfactants used as emulsifiers were Polyoxyethylene-20-sorbitan monooleate (Tween 80) and Sorbitan monooleate (Span 80) (purchased from Sigma-Aldrich Chemical, Canada). Material Safety Data Sheet attached at the appendix.

3.2 Microorganisms and Incubation media

Eleven microbial strains were screened to establish their level of tolerance on the mineral oil and surfactant and they are as follows:

- *Alcaligenes piechaudii* KN1 (PTA-5580);
- *Pseudomonas putida* KN3 (PTA-5579);
- *Flexibacter sancti* BPB (PTA-5570);
- *Pseudomonas fredriksbergensis* BPC (PTA-5571);
- *Staphylococcus warneri* (BPE);
- *Sphingomonas sp.* BPF (PTA-5573);
- *Sphingomonas sp.* BPH (PTA-5574);
- *Phylobacterium sp.* BPI (PTA-5575);
- *Serratia ficaria* BPJ (PTA-5576);
- *Agrobacterium tumefaciens* BPK (PTA-5577) and
- *Rhizobium sp.* BPL (PTA-5578).

The strains were isolated from hydrocarbon-contaminated Czechowice-Dziedzice Oil Refinery Waste Lagoon (RWL) and kindly provided by Savannah River National Laboratory (USA). At the end of the screening, six strains showed the highest tolerance and constituted the microbial consortia for the study and they are as follows: BPB, BPF, BPI, BPK, BPL and KN1. Microorganisms were incubated in the mineral R2A media containing casein hydrolysate (0.5 g/l), peptone (0.5 g/l), yeast extract (0.5 g/l), K₂HPO₄ (0.3 g/l), MgSO₄ (0.05 g/l), NH₄Cl (0.5 g/l) and CaCl₂ (0.05 g/l). Two types of basic media were used for the preparation of challenge media loaded with drilling fluids and surfactants namely: rich R2A media with glucose (0.5 g/l)

and sodium pyruvate (0.3 g/l) and lean R2A media with glucose (0.05 g/l) and sodium pyruvate (0.03 g/l).

3.3 Determination of emulsifier concentration and stirring rate for stable invert emulsion

According to the ICI Americas Inc. guidelines, a combination of 80% of Span 80 and 20% of Tween 80 was used to obtain an emulsifier mixture with HLB number of 4.6. The surfactant mixture was added to Distillate 822 mineral oil at concentration of either 1%, 5%, 7% or 10%. Deionized water with pH adjusted to 10 was added in a drop-like manner to the oil-surfactant mixture to an oil-water ratio of 90:10. The emulsions were stirred with a Cole-Parmer LabGEN 700 homogenizer at either 10,800 rpm or 15,000 rpm for a period of 5 minutes. The stability of the emulsion was determined by visual observation of phase separation (oil, water and transition phase separation) immediately after stirring and after 1, 4 and 6 days of aging.

3.4 Emulsion formulation under different HLB values

The emulsions consisted of two non-ionic emulsifiers which include Span 80 and Tween 80. Span 80 (HLB 4.3) and Tween 80 (HLB 15.0) were mixed in proportion outlined by the ICI Americas Inc. guidelines (ICI Americas, 1980) to prepare surfactant solution of desired HLB value. HLB values and corresponding Span-Tween proportions are listed in Table 3.1. Desired volume of oil-soluble Span 80 was dissolved in the mineral oil Distillate 822. Desired volume of water-soluble Tween 80 was dissolved in deionized water. The Distillate 822/Span mixture was stirred at 15,000 rpm for 30s before water/Tween mixture was added to the oil phase in a drop-like manner and stirred for additional 5 min at 15,000 rpm. The oil/water ratios for the emulsions were 90:10; the total concentration of surfactant mixture was 5%.

Table 3.1 HLB values and corresponding proportions of Span 80 and Tween 80

HLB	Percentage of Span 80	Percentage of Tween 80
4.3	100	0
4.9	95	5
5.3	90	10
5.9	85	15
6.4	80	20
7.0	75	25
10.2	45	55
11.2	35	65
12.3	25	75
13.4	15	85
14.4	5	95

Emulsions were left standing at a temperature of 25⁰C for a period of 14 days, and then centrifuged (Thermo Electron Corporation, Model: Centra CL3R) at 3000g for 50 min (these centrifugation parameters were determined to be optimum for emulsion breaking in preliminary experiments, data not shown). Phase separation was monitored immediately after mixing, after 24 hour static conditions, and after centrifugation.

3.5 Determination of emulsion state in response to HLB changes

Stable invert emulsions were prepared according to the protocol described in section 3.4. Mineral oil bases (either Drisol or Distillate 822) were mixed with deionized water at ratio 90:10 in the presence of Span 80- Tween 80 mixture with HLB of 4.9. After aging over 7 days, emulsions were treated with additional surfactant blends to adjust HLB to 10.2 – 14.4 values. The treatment surfactant blends are based on initial mixture of Span 80 and Tween 80 with HLB 4.9 and Tween 80 with HLB 15. The amount of each of the emulsifier mixture added is calculated according to the following equation (ICI Americas, 1980):

$$\text{HLB} = xA + (1 - x) B \quad (3.1)$$

where, x is the volume fractional component (i.e. between 0 and 1) of a surfactant having a HLB value of A and the other surfactant has a HLB of B. The calculated percentage compositions of Tween 80 and emulsifier mixture of HLB number 4.9 and corresponding HLB values are shown in the **Table 3.2**

Table 3.2 HLB values and corresponding proportions of Tween 80 and emulsifier mixture at HLB 4.9

HLB	Tween (%) Vol.	Emulsifier mixture @4.9 (%) Vol.
10.2	52.5	47.5
11.2	62.4	37.6
12.3	73.3	26.7
13.4	84.4	15.6
14.4	94.1	5.9

Each of the emulsifier mixtures were prepared and left for a period of 24 hours to allow proper mixing. 1 ml of each emulsifier mixture were added to the invert emulsion, mixed for 5 minutes using the VWR minivortex 945300 at 3200 rpm and were allowed to age for a period of 24 hours at a temperature of 25⁰C. Subsequently, an additional 1 ml of the emulsifier mixture was added to these emulsions daily with the same procedure until a total volume of 5 ml have been added. Untreated emulsions were used as a control. At the end of the treatment period, the samples where centrifuged (Thermo Electron Corporation, Model: Centra CL3R) for 20 minutes at 3000g. Phase separation, optical density, water content and viscosity were monitored, as described below.

3.6 Phase separation measurement

Phase separation of the emulsions prepared was monitored using the electronic caliper by measuring the height of the separated phases and the total height of the emulsion column. The separation efficiency (S) was determined as the percentage of the separated phase (h) to the initial total height of drilling fluid column (H): $S = h/H \times 100\%$. The separation behavior was described with types of separated layers as shown in Figure 3.1.

Group A: Separation of phases with a clear oil phase at the top and emulsion at the bottom.

Group B: Separation of phases with a transition phase at the top and emulsion at the bottom.

Group C: Separation of phases with transition phase at the top and water phase at the bottom.

Group D: No separation of phases.

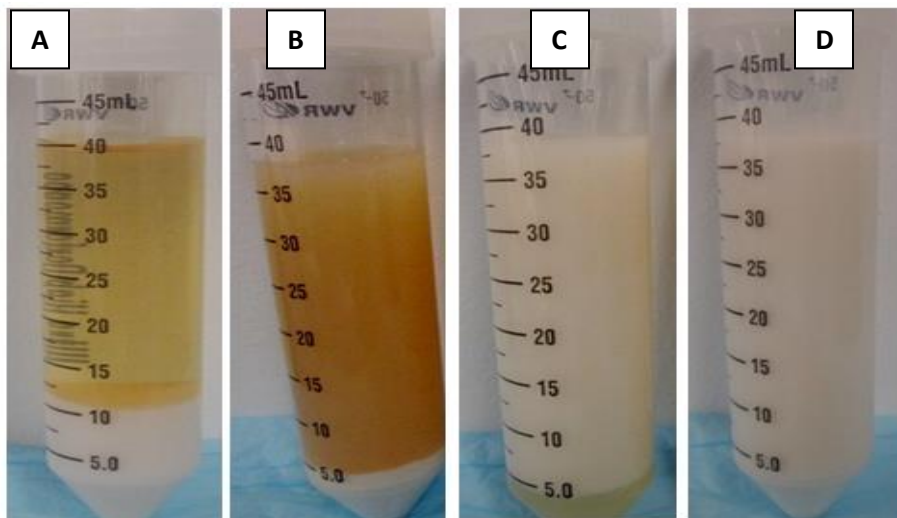
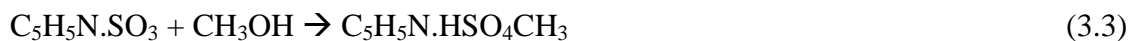
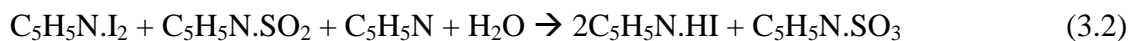


Figure 3.1. Separation behavior of the emulsions. **A:** oil release. **B:** transition separation. **C:** water release. **D:** no separation

To compare intensity of separation in transition phases, optical density at 570nm was measured using the Molecular Device SpectraMax Plus384 machine.

3.7 Water content measurement

The water content in emulsion was determined by titration with Karl Fischer reagent as follows:



The sample is mixed with a pyridine-methanol solvent containing iodine and sulphur dioxide. As per Equation (3.2), the oxidation of sulphur dioxide by iodine to sulphur trioxide and hydrogen iodide consumes water. In the presence of excess methanol, Equation (3.3) occurs. This prevents the pyridine-sulphur trioxide from consuming water:

Water and Iodine are consumed in a 1:1 ratio in the above reaction. Once all the water present is consumed, the presence of excess Iodine is detected voltametrically by the titrator's indicator electrode (Karl Fischer titrator-870 KF Titrimo plus). That signals the end-point of the titration. The amount of water present in the sample is calculated based on the concentration of Iodine in the Karl Fischer titrating reagent and the amount of Karl Fischer reagent consumed in the titration.

The sample is added by weight difference. That is, the weight injected is the difference between a syringe with oil and the syringe with the oil displaced. The oil sample amount is up to 5 grams. The volume used is determined by trial and error to yield a Karl Fischer Reagent (KFR) volume approximately similar to the standardization. The following are the steps followed for the titration:

- A needle is fitted onto a glass syringe,
- Syringe is used to pick up emulsion sample,
- The syringe with emulsion sample were weighed and the weight recorded,
- Three drops of the sample is injected into the Karl Fischer titrator,
- The syringe with the emulsion sample displaced was weighed after injection and recorded,
- When the titration is complete, the volume of KFR used for titration of sample will be obtained from the apparatus.

The volume of water in the sample is calculated using the formula:

$$\mu\text{L H}_2\text{O Total} = \frac{\text{Volume KFR}_{\text{sample}} \times (30 \mu\text{L H}_2\text{O}/\text{mL KF Reagent})_{\text{stdzn}} \times \text{Wt Sample}}{\text{Wt of Titration Sample}} \quad (3.4)$$

3.8 Droplet size observation using microscopes

The emulsions were analyzed in respect to droplet size and orientation with microscope using the Axiovert S100, Invert microscope with Axiocamera and Axio Vision software. A drop of emulsion is placed on a slide and placed on the microscope. The microscope is tuned to obtain the best focus of the emulsion under the microscope. Several shots (photographs) were taken and were used to ascertain the droplet size and orientation of the invert emulsion. This experiment was only done once due to time constraint and repeatability of this experiment was not ascertained.

3.9 Viscosity measurement

Viscosity measurement was carried out on the emulsions treated with surfactants. Brookfield DV-II + Pro viscometer with spindle # 40 (viscosity range = 1.6 – 32,000 cP) was used and the measurement done at 25⁰C and different speeds: 3, 10, 20, 50 and 100 rpm. The shear stress (dynes/cm²) and Shear rate (s⁻¹) were obtained from the viscometer while the Plastic Viscosity (cP) and Yield Point (dynes/cm²) were calculated from the rheological consistency curves.

A batch of invert emulsion sample was prepared for each HLB number and shared into three equal replicates. Viscosity for these samples (replicates) were measured and recorded. For HLB 10.2, the viscosity, shear stress and shear rate was obtained at speeds; 3, 10, 50 and 100 rpm. For HLBs 11.2, 12.3 and 13.4, measurements were obtained at speeds; 3, 10 and 50 rpm. For HLB 14.4, measurements were obtained at 3, 10 and 20 rpm. The regression for the shear stress against shear rate was plotted for each HLB number at various speeds used for the measurement. The error bars represent range of results for the measurement of the replicate sample.

3.10 Tolerance of microorganisms to drilling fluids and surfactants

The rich R2A media with 0.5% glucose and 0.3% sodium pyruvate was supplemented with either 10 % mineral oil (Drisol or Distillate 822) or 10% surfactant mixtures with HLB values ranging from 10.2 to 14.4 (challenge media). The rich R2A media without mineral oil and surfactant were used as control.

The challenge and control media were 10-fold serially diluted in rich R2A in 96-well microplates until 0.0001% of challenged component and seeded with microorganisms to a final concentration of 10^7 cell/ml. The plates were incubated at 27⁰C with agitation of 150 rpm for 24 hours using NEW BRUNSWICK SCIENTIFIC, incubator shaker series, model: INNOVA 40. Then, optical density at 570 nm was monitored to determine the minimum inhibitory concentration of mineral oil and surfactants at different HLB values, which is the minimum concentration of the contaminant which prevent microbial growth. The OD values of 0.1 AU and higher indicated microbial growth.

3.11 Microbial growth capacity and viability in drilling fluids

Microbial strains with high tolerance to mineral oil and surfactants were mixed in consortia and tested for their growth capacity in invert emulsion drilling fluids with different HLB values. A batch of invert emulsion sample was prepared for each HLB number and shared into three equal replicates. Each replicates represented the sample of invert emulsion used in preparing the challenge media. The rich (0.5% glucose and 0.3% pyruvate) and poor (0.05% glucose and 0.03% pyruvate) R2A media were supplemented with 10% invert emulsions with HLB values ranging from 10.2 – 14.4. Media without invert emulsions were used as control. The control and challenge media were seeded with microbial consortia to final concentration of microorganisms

of 10^7 cell/ml and incubated at 25°C with agitation at 100rpm for 3 weeks. After incubation, microorganisms were separated from residual emulsion and/or hydrocarbons by centrifugation at 3000g for 20 min. The microbial biomass pellets were resuspended in rich R2A to the volume equivalent to the volume of cultures before centrifugation. The resuspended microbial cultures were 10-fold serially diluted in rich R2A test plates and allowed growing for 24 hours. Optical density at 570 nm was monitored to determine growth capacity in test plates. The growth capacity was determined based on the absorption unit (AU) values and the maximum dilution allowing microbial growth.

CHAPTER FOUR: RESULTS AND DISCUSSIONS

In this chapter, the results are presented, synthesized and discussed. Section 4.1 addresses the best emulsifier concentration and stirring rate for producing stable invert emulsion. Section 4.2 shows the impact of HLB numbers on invert emulsion stability. Rheological properties of the invert emulsions in response to HLB changes are presented in section 4.3. Finally, section 4.4 shows microbial growth due to consumption of hydrocarbons from emulsions with different HLB values.

4.1 Optimum emulsifier concentration and stirring rate for stable invert emulsion

Experiments were performed to determine the formulation of the most stable invert emulsion. Two mixing parameters were considered: emulsifier concentrations (v/v %) and stirring rate (rpm). The emulsifier (surfactant) blend of Span 80 and Tween 80 was tested at 1%, 5%, 7% and 10% (v/v) while stirring rates were 10,800 rpm and 15,000 rpm. The HLB value used for this experiment was 4.6 as reported to be the optimum for mineral oil based emulsions (ICI Americas, 1980). Distillate 822 was used as the mineral oil for the preparation of the invert emulsion. The emulsions were considered stable if phase separation was not observed after 6 days aging at static conditions and at a temperature of 25⁰C. Temperature can significantly affect emulsion stability. This is because, temperature affects the physical properties of oil, water, interfacial films and surfactant solubilities in the oil and water phases which in turn affects the stability of the emulsion (http://petrowiki.org/Stability_of_oil_emulsions).

The addition of the 1% emulsifier blend did not allow the emulsification of water in Distillate 822 regardless of the stirring speed used (data not shown). Increased concentrations of emulsifier blend (5% to 10%) provided good emulsification after stirring at both speeds: 10,800 rpm and

15,000 rpm for 5 min (Fig. 4.1). However, phase separation was observed after 24 hours under static conditions in emulsions containing 7% and 10% (Fig. 4.3 and 4.4) emulsifier regardless of the stirring rate used to formulate these emulsions. The emulsion containing 5% emulsifier remained stable (Fig. 4.2) after 24 hour aging. After 6 day static aging, phase separation was observed in emulsions with 5% emulsifier and prior stirred at 10,800 rpm. However, emulsion with 5% emulsifier stirred at 15,000 rpm remained stable after 6 days (Fig. 4.5).

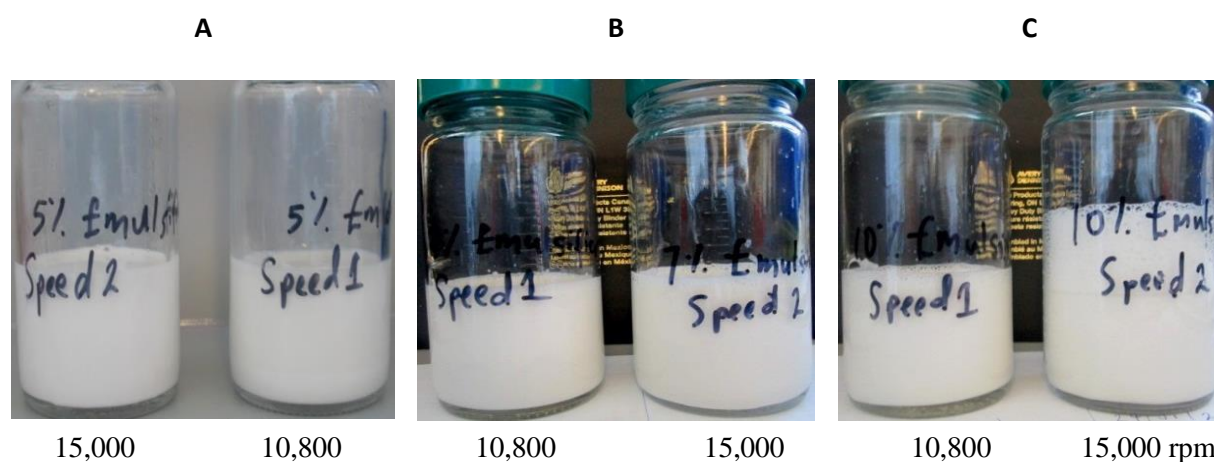


Figure 4.1 Pictures of emulsion obtained immediately after mixing of Distillate 822 with water in the presence of 5 % (A), 7 % (B) and 10 % (C) emulsifier (Span-Tween) blend at either 10,800 rpm or 15,000 rpm show no phase separation.

A



Figure 4.2 Pictures of emulsion obtained after 24 hour static aging of emulsions with 5 % emulsifier (A) blend showing no phase separation

B



Figure 4.3 Pictures of emulsion obtained after 24 hour static aging of emulsions with 7 % emulsifier (B) blend showing phase separation

C

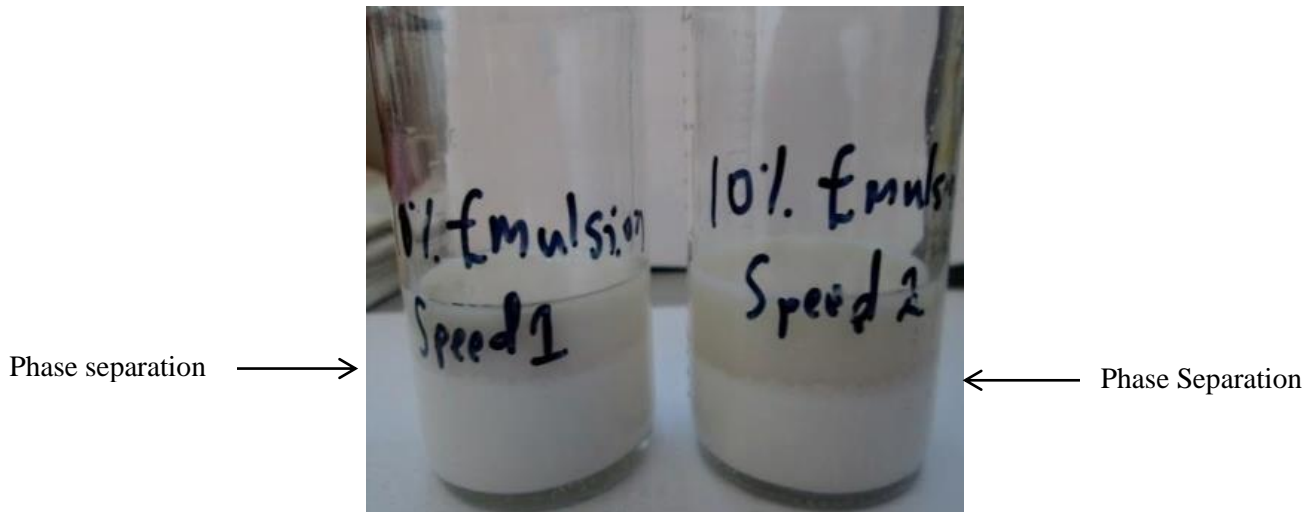


Figure 4.4 Pictures of emulsion obtained after 24 hour static aging of emulsions with 10 % emulsifier (C) blend showing phase separation

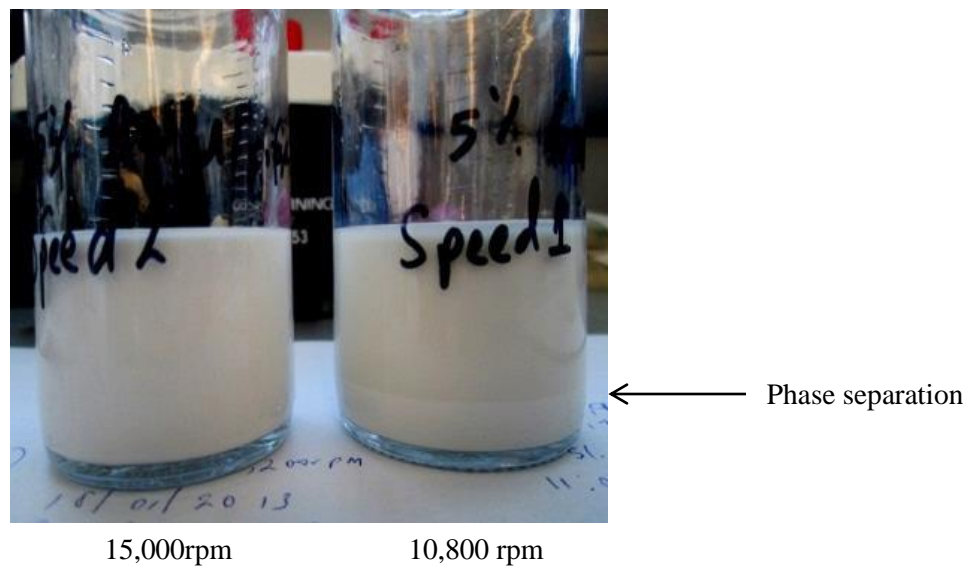


Figure 4.5 Pictures of emulsion obtained after 6 days static aging of emulsions mixed with 5 % emulsifier blend at either 10,800 rpm showing phase separation or 15,000 rpm showing no phase separation

The emulsifier (surfactant) is the main component responsible for the stability of emulsions. Amphiphilic molecules of emulsifier build up in the interface of two immiscible liquid such as oil and water. They reduce the interfacial tension of the liquids and also forms a thin film around the droplets of the dispersed phase thereby preventing coalescence of these droplets when they come in contact with each other, therefore, enhancing the stability of an emulsion. Thus, emulsifier concentration is one of the most important factors influencing the stability of emulsions (Ostberg et al., 1995). Chen et al., (2004) did an experimental study of stability of oil-water emulsions where emulsifier concentration was one of the factors considered for a stable emulsion. Sorbitan monooleate and commercial diesel in China were used as the emulsifier and continuous phase respectively for this experiment. According to the results, they observed that there existed a concentration window, out of which the stability quickly deteriorated. The emulsifier dosage was thus determined to be 0.5% by weight for the most stable emulsion (Chen et al., 2004).

Al-Sabagh (2001) carried out an investigation on the relevance of HLB of surfactants on stability of asphalt emulsion (AE). Asphalt was used as the continuous phase and thirteen non-ionic surfactants (Glycomul 50C, Span 60, Brij 92, Arlacel 40, Tween 61, Tween 81, Tween 85, Brij 96 and Tween 21, Tween 80, Tween 20 and Brij 58) were used as emulsifiers. The emulsifier mixtures used for preparation of oil-in-water emulsions have HLB range from 9.6 to 17.6, while emulsifiers for water-in-oil have a HLB values from 4.7 to 6.7. The effect of emulsifier concentration on the stability of the AE was investigated and it was observed that the maximum stability of emulsion was recorded between 0.7 and 0.9% by weight.

The optimum emulsifier concentration (5%) determined in the present study was high when compared to the concentration used in the above mentioned works of Al-Saagh (2001) and Chen

et al (2004). It can be deduced that optimum concentration of emulsifiers for emulsion formulation depend on the type of emulsifier used and the type of oil used as the continuous phase. These emulsifiers enter into some form of molecular association at the oil-water interface. It will require a certain concentration of emulsifier to stabilize an emulsion and anything below or above this concentration will decrease the stability of the emulsion. This is because at low emulsifier concentrations, the emulsions is not stable due to aggregation (flocculation) of the droplets while at high emulsifier concentrations, the emulsion loses its stability as a result of rapid coalescence.

The emulsifiers used for this project were emulsifiers (Span 80 and Tween 80) used mainly in cosmetic industry with known HLB numbers. This type of emulsifier are not the type of emulsifiers that are regularly used for the formulation of invert emulsion drilling fluids but we used them to investigate the optimal HLB value for invert emulsions which will serve as the emulator (since their HLB numbers are already known) that will give the most stable emulsions for the type of mineral oil (Distillate 822) used for the invert emulsions. When the optimum HLB number of the invert emulsion system is established, regular emulsifiers used for drilling fluid purposes adjusted to the optimum HLB will be used for the formulation of the invert emulsion system.

The shearing action whose shearing strength would directly influences the water droplet size in the emulsion. Hence, a sufficient level of shearing is a necessary condition to disperse water phase into oil phase. The invert emulsion was stirred at high-shear speeds of 10,800 and 15,000 rpm respectively. A simple reasoning could first lead to think that an increase in stirring speed would mainly magnify the rupture mechanism of droplets, with a resulting decrease in droplet size which ultimately enhances the stability of the emulsion. The two speeds (10,800 and 15,000

rpm) used, proved to give a stable emulsion after 24 hours static incubation but the later speed shows greater stability after a longer period of static aging.

4.2 Impact of HLB numbers on emulsion stability

The influence of the HLB number on invert emulsions build-up, stability and behavior is investigated in this section.

4.2.1 Emulsion formulation under different HLB values

Invert emulsions were formulated with Distillate 822 mineral oil, water and emulsifier (Span 80-Tween 80) blends with HLB values ranging from 4.3 to 14.4. The HLB numbers were achieved with emulsifier combinations shown in Table 3.1 and the steps followed in formulating emulsions as described in Section 3.4. Phase separation and optical density of the invert emulsions were studied to characterize emulsion stability and the results obtained are discussed.

Phase separation was monitored in the emulsions over the range of HLB values immediately after mixing, after 24-hour aging, and after centrifugation. The emulsions with oil-water ratio of 90:10 developed with surfactant mixtures with HLB in the range 4.3 – 12.3 had no visual phase separation immediately after mixing (Fig. 4.6). At HLB 13.4 and 14.4, stable emulsions were not formed, suggesting that higher HLB numbers do not support invert emulsions, but favor the formation of direct emulsions (ICI Americas, 1980). However, the very low water cut (10%) used in this study prevented direct emulsion formation.



Figure 4.6 Pictures of emulsions with HLBs of 4.3, 12.3, 13.4 and 14.4 immediately after mixing showing no phase separation for HLB 4.3 and 12.3 while showing phase separation for HLB 13.4 and 14.4

After 24 hour static aging at 25⁰C temperature, the phase separation was observed for emulsion with HLB 4.3 (Fig. 4.7). The observed separation was classified as Group B: separation with a transition phase at the top and emulsion at the bottom. High turbidity of the transition phase indicates high presence of water droplets (high droplet concentration and small droplet sizes) in this phase. The increase of HLB values led to emulsion stabilization until HLB number reached 10.2 and no phase separation was observed at this range (Group D, Fig. 3.1 in section 3.6). At HLB 11.2, separation of water layer on the bottom of the column was observed with emulsion layer on the top (Group C, Fig. 3.1 in section 3.6). Further increase of the HLB values supported oil separation from the emulsion. However, at HLB 12.3, the separation was transitional (Group B, Fig. 3.1 in section 3.6), but HLBs of 13.4 and 14.4 allowed separation of a clear oil fraction (Group A, Fig. 3.1 in section 3.6).



Figure 4.7 Pictures of emulsions with a range of HLB values after 24 hour aging showing phase separation for HLB 4.3, 11.2, 12.3, 13.4 and 14.4 (X) while no phase separation for HLB 4.9 and 10.2

Centrifugation caused phase separation in the emulsions with all, but 4.9, HLB values (Table 4.1). However, separation type and intensity varied according to the HLB value. The transition separation was observed in the emulsion with HLB 4.3. The transition layer under this condition was 75 % of the total emulsion column. While emulsion with HLB 4.9 was stable even after centrifugation, transitional separation was again observed at HLB 5.3 with 79.8% separation efficiency and further increased up to 85.5% for HLB 7.0. While separation efficiency of the emulsion with HLB 4.3 was lowest in this group, the turbidity of the transition layer was also lowest (0.80 AU compared to 1.71 – 2.44 AU at other HLB values). In contrast, turbidity of transitional layers reduced from 2.44 AU at HLB 5.3 to 1.71 AU at HLB 7.0, which correlates well with the increase in separation efficiency. The reduction of turbidity may be attributed to two phenomena: increase of size of the droplets via flocculation or coagulation, and reduction of the number of the droplets via Ostwald ripening.

Table 4.1. Separation efficiency (%), turbidity of transition layer (AU) and classification of the separation behavior associated with HLB values

HLB #	Composition of (% v/v) Span80/Tween 80	Transition/oil phase (%)	OD _{570nm} (AU)	Group
4.3	100/0	75.0 ± 1.5	0.80 ± 0.20	B
4.9	95/5	-	2.60 ± 0.10	D
5.3	90/10	79.8 ± 1.1	2.44 ± 0.07	B
5.9	85/15	79.9 ± 1.1	2.07 ± 0.09	B
6.4	80/20	82.5 ± 1.0	2.05 ± 0.05	B
7.0	75/25	85.5 ± 1.3	1.71 ± 0.48	B
10.2	45/55	78.6 ± 1.0	2.07 ± 0.06	C
11.2	35/65	72.1 ± 0.3	1.56 ± 0.07	C
12.3	25/75	64.6 ± 1.5	0.79 ± 0.07	B
13.4	15/85	60.2 ± 0.7 *	0.06 ± 0.00	A
14.4	5/95	64.3 ± 1.4*	0.06 ± 0.00	A

* oil phase

Further increase of the HLB values resulted in the reduction of the separation efficiency: to 78.6 % at HLB 10.2 and 72.1 % at HLB 11.2 (Table 4.1). However, turbidity of transition layers correlated well with those of HLB 6.4 and 7.0 respectively. That indicates the transitional separation with reduced number of very small droplets. This assumption is supported by microscopic observation of the very tiny droplets (Fig. 4.8); while the concentration of water

droplets reduction is attributed to the precipitation of water at the bottom of the emulsion column.

Further increase of HLB values led to further reduction of the transition layer (60 – 64 %), but also a reduction of transition layer turbidity (Table 4.1). At HLB 12.3, separation behavior was similar to that observed for HLB 4.3. However, HLBs 13.4 and 14.4 allowed release of nearly pure oil phase (OD of 0.06 AU) with some emulsion left on the bottom of the column. Microscopic images revealed only few droplets in these samples (Fig. 4.8).

It can be concluded that surfactant with low HLB number supports the stability of water-in-oil emulsion while higher HLB supports oil-in-water emulsions as observed in the present work. According to work carried out by Boyd et al, (1971), HLB of surfactants affect the rate of coalescence of direct or invert emulsions. For invert emulsion (W/O), the coalescence rate was lowest at $HLB < 5$. This is consistent with the present experimental results because the most stable emulsion was at HLB 4.9. At other HLB values, there was some type of phase separation which qualifies the emulsion unstable which implies that at range of HLB numbers other than the optimum HLB number, the emulsion tends to be unstable.

It can be speculated that optimum HLB numbers for stable invert emulsion is different for emulsions made of different mineral oil and is dependent on the type of oil used as the continuous phase and the emulsifiers used for the formulation of the emulsion.

In our experiment it can be observed that, preparation of emulsion with HLB 4.3 where a single emulsifier was used (Span 80) produced an unstable emulsion but a combination of emulsifiers (Tween 80 and Span 80) showed a more stable emulsion just like in emulsion with HLB 4.9. While a proper surfactant HLB value is a key factor for the formulation of stable emulsions,

mixtures of different surfactants types usually exhibit synergism in their effects on the properties of a system due to interaction of surfactant molecule. Span and Tween enter into some form of molecular association at the oil-water interface and this can be said since the stability of the W/O emulsions to coalescence is greater for Span-Tween blends than when using single emulsifiers. Boyd et al, (1971), demonstrated molecular association of surfactants, where they showed how Span 80 and Tween 40 association can increase the stability of emulsion. From their work, Tween 40 molecule provide a gel like structure at the oil- water interface which provides good stability for droplets coalescence and Span 80 provides a closely packed hydrocarbon chains which also provides an additional stability mechanism.

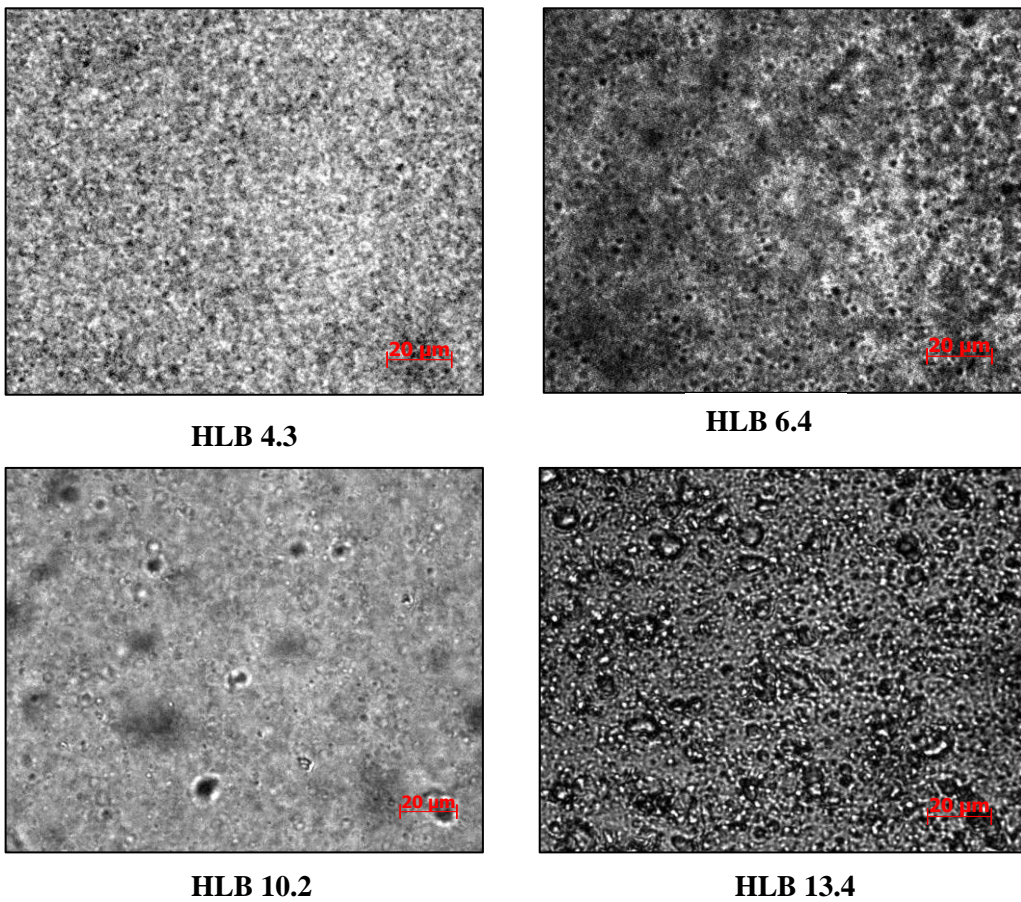


Figure 4.8 Microscopic observation of transition layer after centrifugation which indicates the reduction in number of droplets as the HLB number increases from 4.3 to 13.4

4.2.2 State of emulsion due to change in HLB numbers and emulsifier concentration

Stable invert emulsions (control emulsions) were prepared using Span 80 – Tween 80 blend with HLB of 4.9 as this value were determine to be optimum for invert emulsion stability (Section 4.2.1) . To investigate the impact of HLB values on emulsion stability, the control emulsions were treated with additional Correcting Emulsifier Blend (CEB) to reach HLB numbers ranging from 10.2 – 14.4 (compositions of CEBs are shown in Section 3.5). To investigate the impact of the emulsifier concentration on the emulsion stability, CEBs were added to the control emulsion in the amount increasing from 1 ml to 5 ml. After addition of the first portion (1 ml) of CEBs, emulsions lost their milky appearance (Fig. 4.9). Emulsions became semitransparent, but without clear phase separation. With increasing CEB concentration, transparency of the emulsions increased. However, it was difficult to quantify by visual inspection changes in emulsions associated with the impacts of HLB values and emulsifier concentrations. For the purpose of the clarification of the emulsion state in response to HLB value and CEB concentration, optical density, viscosity and water content were investigated in control and treated emulsions. The results obtained are presented and discussed in the sections below.

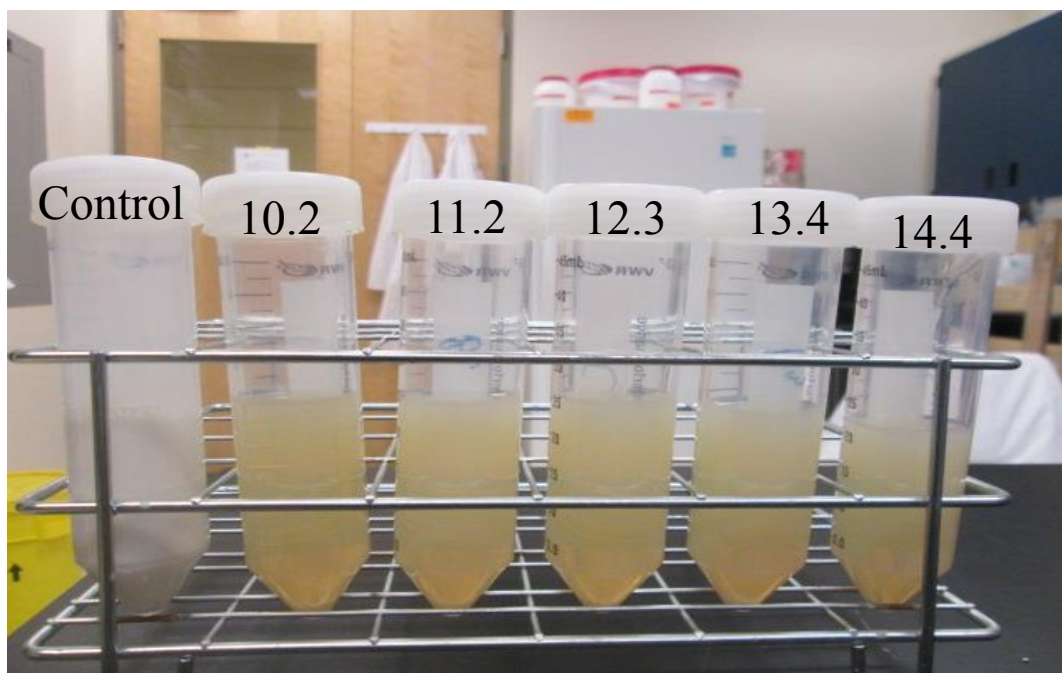


Figure 4.9 Image of Distillate 822 invert emulsion untreated (control) and after treatment with CEBs with HLB values ranging from 10.2 to 14.4 showing transparency as a result of increase in HLB number

4.2.2.1 Optical Density of invert emulsions treated with CEB with different HLB values

Transparency of Distillate 822 and Drisol invert emulsions before and after treatment with CEBs with HLB values of 10.2 – 14.4 was monitored with light absorption (optical density) at 570nm and presented in absorption units in Figures 4.10 and 4.11, respectively, as a function of CEB concentration. Addition of 1 ml of CEBs to Distillate 822 emulsion reduced optical density of the invert emulsions from 2.7 AU to 2.0 – 2.3 AU (Figure 4.10). At this concentration of CEBs, HLB values did not play significant role. As CEBs volumes increased to 2 ml, optical density of the emulsion with HLB 10.2 further decreased (1.2 AU) while optical density of the emulsions with higher HLBs remained constant. When CEBs volumes reached 3ml, optical density of emulsion with HLB 10.2 was further reduced and reached 0.2 AU. Further increase of CEB volume had no impact on optical density of this emulsions. Significant reduction of optical

density was also observed when 3 ml of CEBs with HLBs 11.2 – 13.4 was added to emulsion; and then slowly reduced up to 5 ml of CEBs reaching 0.2 AU. Optical density of the emulsion with HLB 14.4 reduced less compared to emulsions with lower HLBs when 3 ml of CEB was added; but, continued reducing at the same rate with 4 ml and then 5 ml of CEB.

In the emulsions formulated with Drisol, addition of 1 ml of CEBs resulted in optical density reduction from 2.5 AU to 2.0 – 2.1 AU regardless the HLB value (Fig. 4.11), similar to Distillate 822. However, in the case of Drisol, significant reduction of optical density was observed for emulsions with HLB ranging from 10.2 to 12.3, which continued reducing until 5 ml of CEBs were added (up to 0.2 AU). With 2 ml of CEBs, optical density in emulsions with HLBs 13.4 and 14.4 reduced slightly, if any, but nearly linearly reduced when next portions (3 ml, 4 ml and 5 ml) of CEBs were added.

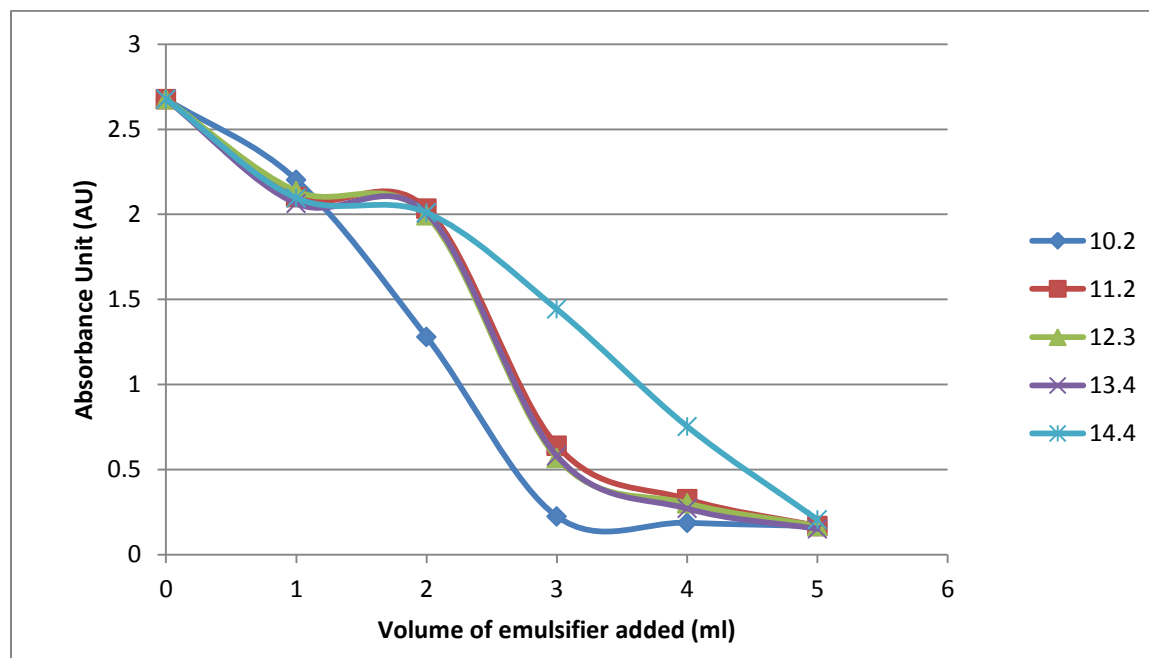


Figure 4.10 Optical density of Distillate 822 invert emulsions treated with 1 ml to 5 ml of CEBs with HLBs ranging from 10.2 to 14.4

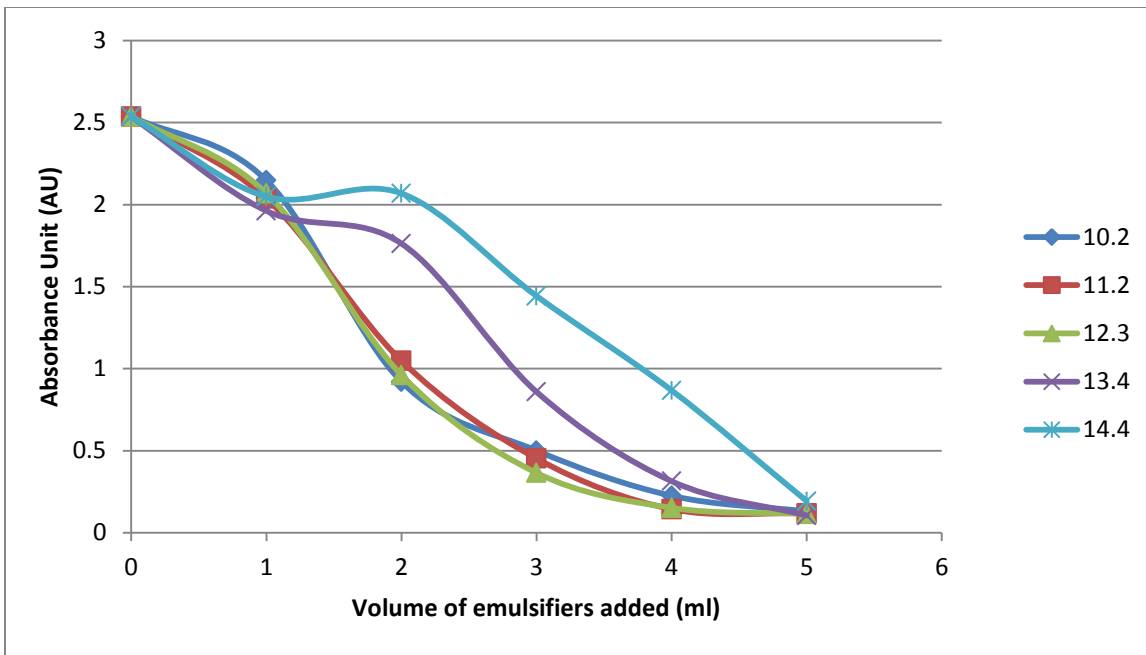


Figure 4.11 Optical density of Drisol invert emulsions treated with 1 ml to 5 ml of CEBs with HLBs ranging from 10.2 to 14.4

The turbidity of an emulsion is a function of particle size (water droplets) and concentration. Therefore, the change in turbidity indicates the change in particle size and concentration. It can be concluded from the experiment that increasing HLB of emulsions increases the flocculation of water droplets which decreases the turbidity of the emulsion. The turbidity of resulting emulsion was observed to decrease as the HLB number increase. This can be attributed to high flocculation of the droplets and increase in droplet sizes which is an effect of the increase in HLB. Flocculation of these droplets reduces the concentration of the droplets in the system thereby decreasing the turbidity of the emulsion. This same observation was observed from the results obtained in section 4.2.1. It can be observed that increasing the HLB number of the invert emulsion started the process of destabilization of the emulsion system but could not carry on to full destabilization.

4.2.2.2 Water Content of treated invert emulsions

The water content in emulsions was determined (see section 3.7) to confirm the absence of phase separation after treatment with CEBs with different HLB values. The water content in the treated invert emulsion was around 0.01mg per g of sample aliquot for all the HLB numbers in both the Distillate 822 and Drisol (Table 4.2) and equivalent to water content in control emulsion with 90:10 oil/water ratio. Thus, we can conclude that changes of HLB in invert emulsion did not cause phase separation

Table 4.2 Content of water (mg/g sample) in Distillate 822 and Drisol invert emulsions treated with CSBs with HLB ranging from 10.2 to 14.4

HLB	Distillate 822	Drisol
10.2	0.09 ± 0.007	0.09 ± 0.007
11.2	0.10 ± 0.003	0.11 ± 0.001
12.3	0.10 ± 0.004	0.11 ± 0.001
13.4	0.10 ± 0.001	0.11 ± 0.001
14.4	0.10 ± 0.003	0.10 ± 0.002

4.3 Emulsion viscosity in response to HLB changes

In this study, experiments were performed to determine the viscosity of invert emulsions as a result of HLB number. The viscosity of these emulsion were measured at different speeds of the rotating spindle which are as follows: 3, 10, 20, 50 and 100 rpm at room temperature (25⁰C) and

constant atmospheric pressure. The shear stress, τ and shear rates, $\dot{\gamma}$ were also recorded to observe their variation due to the change in HLB number of the invert emulsion.

Figure 4.12 shows the relationship between shear stress and shear rate for Distillate 822 invert emulsion at different HLB numbers. This illustrates different fluid behavior for the invert emulsions with respect to the HLB numbers. Invert emulsions of HLB 10.2 exhibited a Newtonian behavior which can be observed in the plots where the coefficient of regression is zero (Table 4.3). As the HLB number increases (11.2 – 14.4), the emulsions were observed to behave as a non-Newtonian fluid which fits into the Bingham model. Plastic viscosity of emulsions increased (0.20 – 0.91 Poise) as the HLB numbers increased (10.2 – 14.4). The yield stress of the emulsions also showed an increase (0 – 14.7 Dynes/cm²) as the HLB numbers increased (10.2 – 13.4) but showed a slight decrease at HLB 14.4 (13.6 Dynes/cm²).

Figure 4.13 shows the relationship between shear stress and shear rate for Drisol invert emulsion at different HLB numbers. The emulsion exhibited similar behavior to the Distillate 822 emulsions. Emulsion with HLB number 10.2 exhibited a Newtonian behavior where the coefficient of regression was zero (Table 4.4). As the HLB number increases, the emulsions behave like a non-Newtonian fluid with the characteristic of a Bingham fluid. Plastic viscosity increased (0.1 – 0.89 Poise) as the HLB numbers increased (10.2 – 14.4). Also, the yield stress, τ_o , increased (0 – 43.6 dynes/cm²) as the HLB numbers increased (10.2 – 14.4).

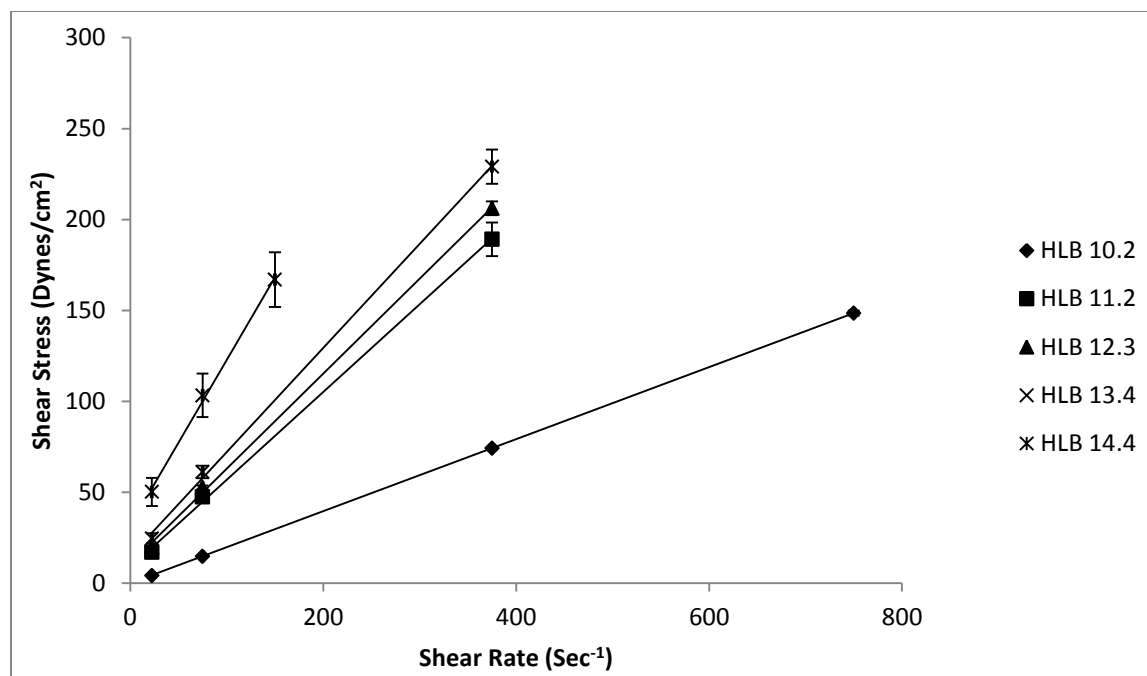


Figure 4.12 Shear stress against Shear rate for Distillate 822 invert emulsion. Error bars show the range of all measurements.

Table 4.3 Summary of plastic viscosity, yield stress, coefficient of regression and fluid behavior for Distillate 822 invert emulsion at different HLB numbers.

HLB number	Plastic Viscosity, μ (Poise)	Yield Stress, τ_0 (dynes/cm ²)	R ²	Fluid Behavior
10.2	0.20	0	0.99	Newtonian
11.2	0.48	8.4	0.99	Bingham
12.3	0.52	10.5	0.99	Bingham
13.4	0.57	14.7	0.99	Bingham
14.4	0.91	13.6	0.96	Bingham
Control	0.08	0	1.00	Newtonian

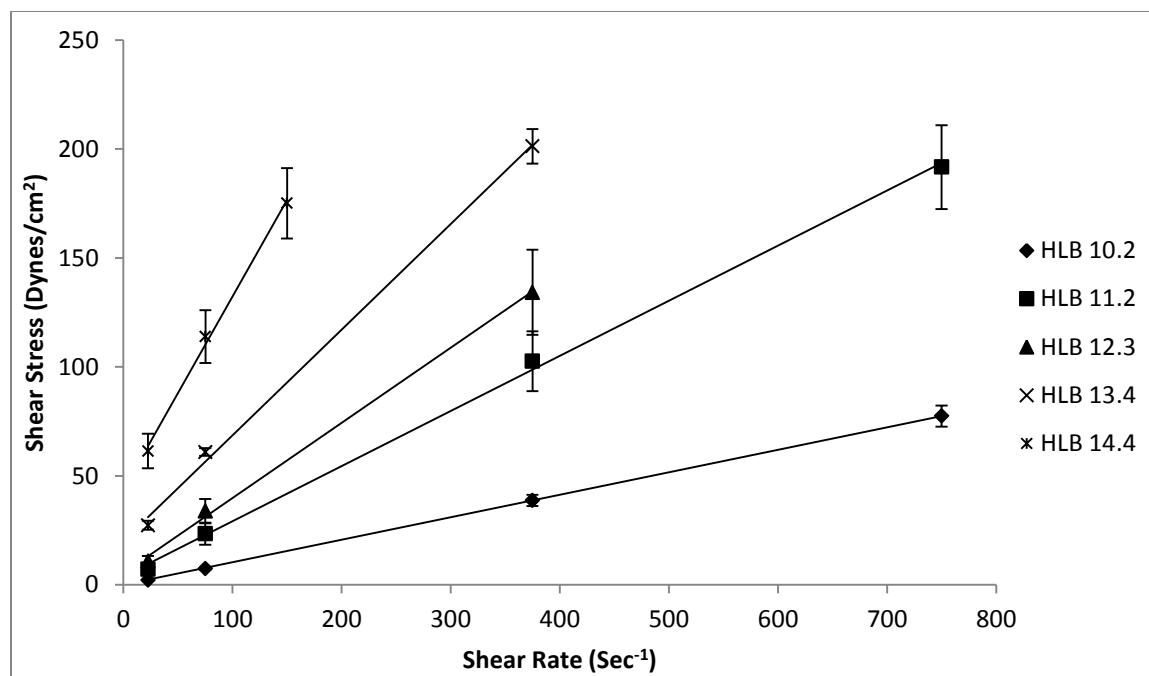


Figure 4.13 Shear stress against Shear rate for Drisol invert emulsion. Error bars show the range of all measurements.

Table 4.4 Summary of plastic viscosity, yield stress, coefficient of regression and fluid behavior for Drisol invert emulsion at different HLB numbers.

HLB number	Plastic Viscosity, μ (Poise)	Yield Stress, τ_0 (dynes/cm ²)	R ²	Fluid Behavior
10.2	0.10	0	0.99	Newtonian
11.2	0.25	3.9	0.99	Bingham
12.3	0.34	5.3	0.97	Bingham
13.4	0.48	20.2	0.99	Bingham
14.4	0.89	43.6	0.95	Bingham
Control	0.05	0	0.99	Newtonian

Both sets of experiments illustrate a change in viscosity. It can be observed from the experiments, that there was an increase in viscosity as the HLB number increases for both set of emulsions (Distillate 822 and Drisol). Finally, it can be concluded that HLB number of an emulsion system has a significant effect on the viscosity of emulsion.

Increase in viscosity can also be attributed to increase cross linkage of chains of emulsifiers and continuous phase which is as a result of increase in HLB number of the emulsion system. Increase in viscosity will inhibit the movement of droplets towards each other thereby decreasing the chances of these droplets coming together and coalescing (destabilize). For instance, the emulsions that exhibited Bingham behavior which requires certain amount of shear stress for it to flow will offer the most resistance to the movement of these droplets since the emulsion remains in static position therefore, slowing down the destabilization process.

4.4 Microbial growth due to consumption of hydrocarbons from emulsions with different HLB values

Microbial consortia consisted of strains with high tolerance to hydrocarbons and surfactants selected in tolerance study as above was grown in the media containing either Distillate or Drisol and glucose at either 0.5 and 0.05 % (rich and lean media, respectively). The lean medium was used to support initial microbial growth and facilitate hydrocarbon degradation. The rich medium provides normal growth rate of the consortium unless there is a toxic impact of the hydrocarbon, and hence was used to determine toxic effect of hydrocarbons on microbial cells in response to HLB values. The number of viable microbial colony forming units (CFU) after exposure to drilling fluids was determined by re-growth of microbial biomass pellet after 100-fold dilution. The optical density of the re-grown microbial suspension was used as indicator of microbial growth capacity.

The growth rate of the microbial consortia at HLB 4.9 (Control) was higher in the presence of Distillate than those in the presence of Drisol (OD 1.0 vs. OD 0.4 in lean media and OD 0.7 vs. 0.5 in rich media, respectively; Fig. 4.15 – 4.18). When HLB values switched to hydrophilic region (10 and more), growth rates in the media containing Drisol increased reached maximum values at 13.4 HLB in lean media and 10.2 in rich media. Further increase of the HLBs above these values reduced microbial growth rate, which, however, still was higher than that in the media with HLB 4.9. In Distillate-containing media, growth rates under hydrophilic HLB decreased compared to hydrophobic HLB. In lean media, growth rates were similar when HLB increased from 10.2 to 13.4, and were reduced when HLB increased to 14.3. In rich media, no difference in growth rates was observed between HLB values from 10.2 to 14.3.

Analysis of the chemical composition of the oils revealed that Distillate contains higher concentrations of *n*-paraffins with C10 to C17, while Drisol contains higher concentration of *n*-paraffins with C18 to C26 (Fig. 4.14). Thus, we observed better consumption of C17 and below paraffins at hydrophobic HLB (4.9 in our case); while C18 and more paraffins was better degraded under hydrophilic HLB values. Consumption of the C18+ paraffins increased with increasing HLB. However, HLB above 13.4 reduced microbial growth. Tolerance to C18+ paraffins was also affected by HLB: with increasing HLB values, tolerance increased, but reaching maximum at 10.2 and then reduced. Tolerance to C17 was higher at hydrophobic HLBs; hydrophilic HLBs did not play a role in microbial tolerance to C17 and below.

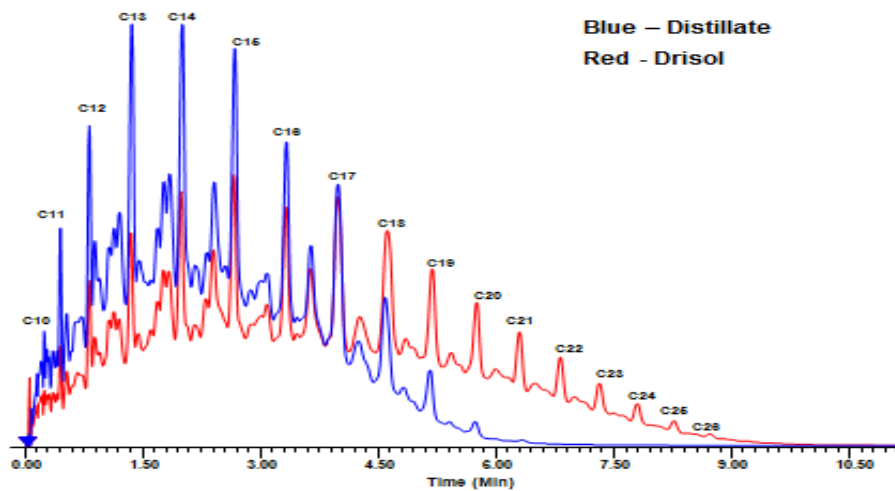


Figure 4.14 Simulated Distillation of Distillate 822 and Drisol mineral oil using Gas Chromatography

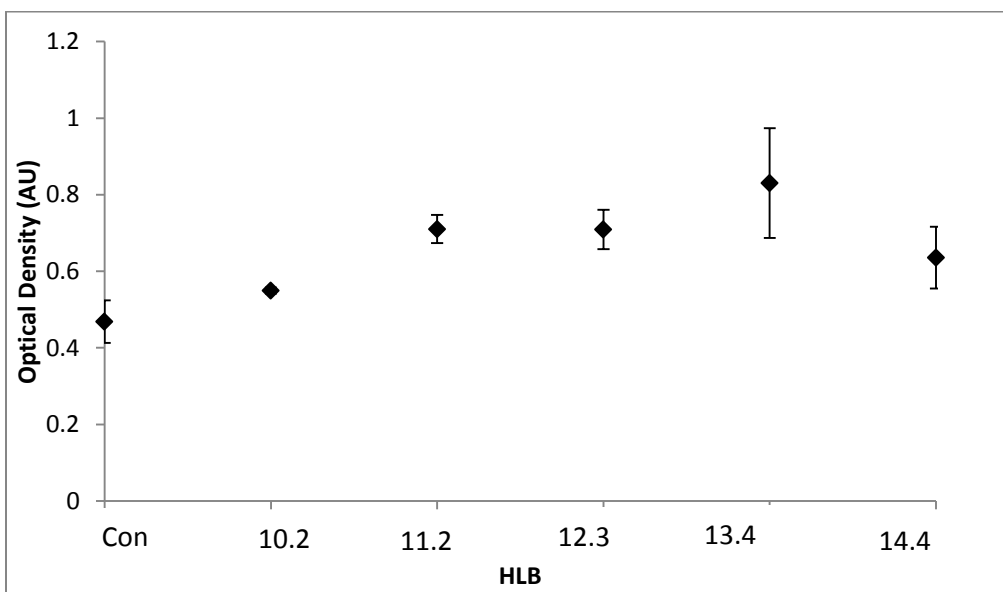


Figure 4.15 Measurement of viable growth cells for Drisol emulsion in lean media. Error bars show the range of all measurements.

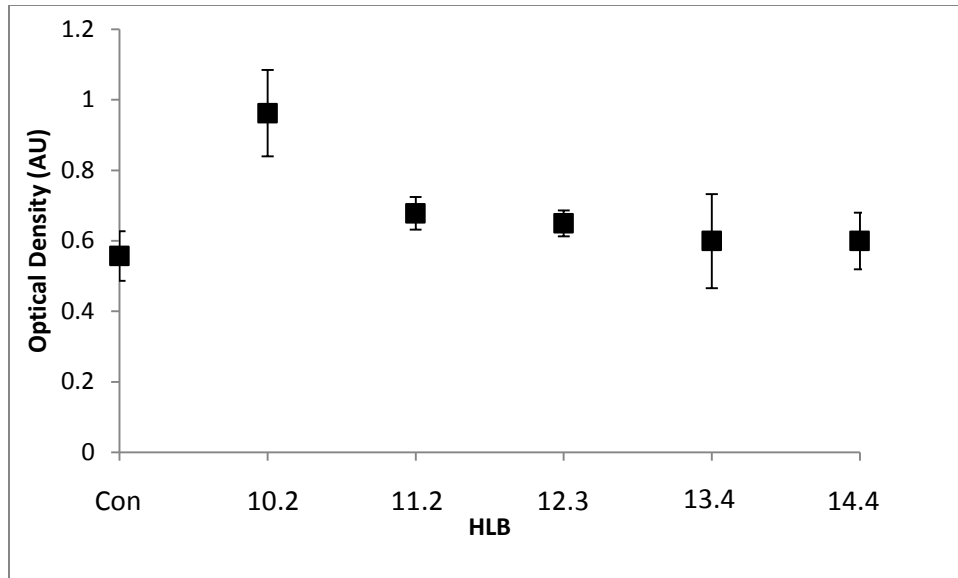


Figure 4.16 Measurement of viable growth cells for Drisol emulsion in rich media. Error bars show the range of all measurements.

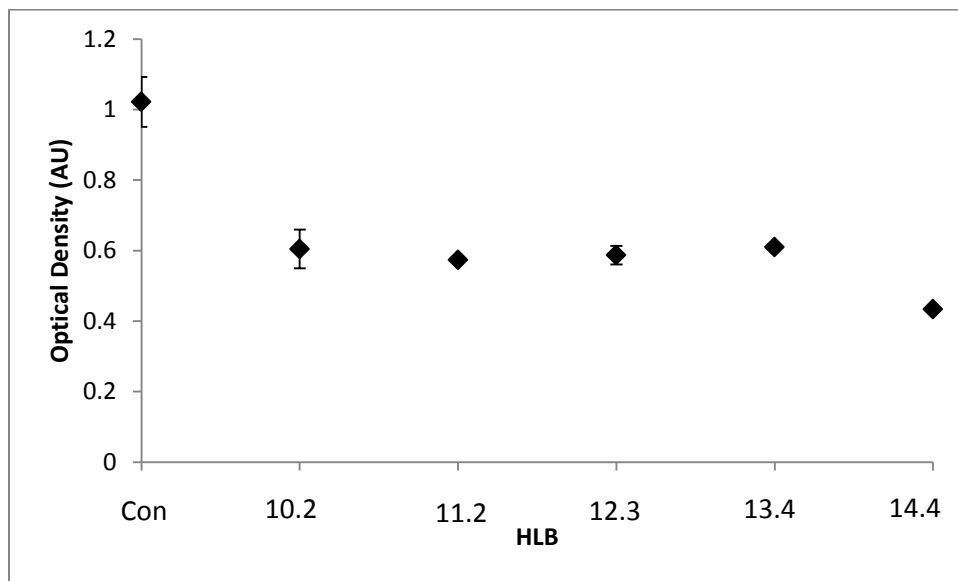


Figure 4.17 Measurement of viable growth cells for Distillate 822 emulsion in lean media. Error bars show the range of all measurements.

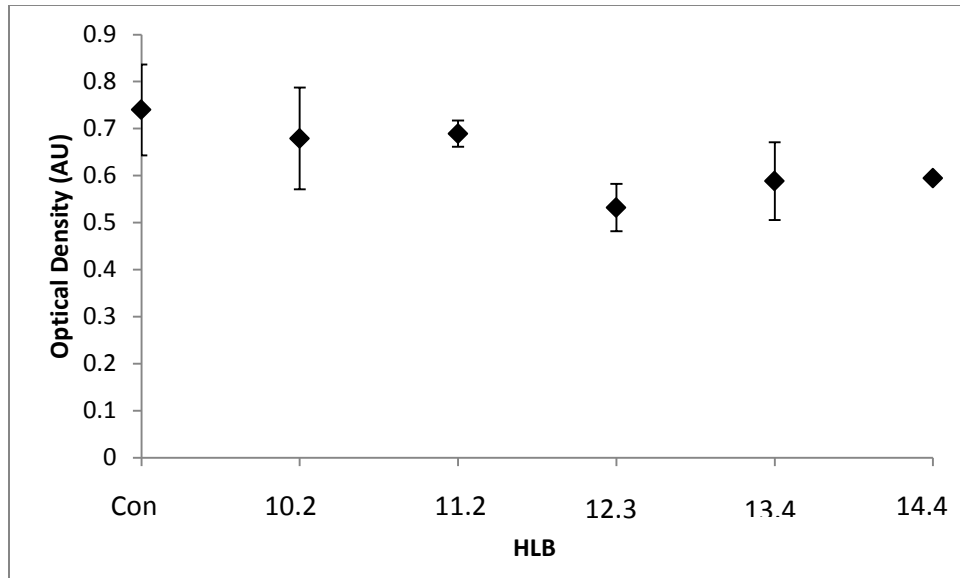


Figure 4.18 Measurement of viable growth cells for Distillate 822 emulsion. Error bars show the range of all measurements.

CHAPTER FIVE: SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 Summary

Drilling fluid waste management remains one of the most difficult issues facing the oil and gas industry. Consequently, significant efforts have been and continue to be invested in formulating drilling fluids that are more environmentally friendly in order to reduce the cost and resource associated with storing or remediating drilling waste. Invert emulsions have proved to be effective fluids for drilling shale formations due to their ability to provide better wellbore stability during drilling. This is due to the non-reactive nature of the hydrocarbon (towards shale) used as the continuous phase of the emulsion. But the use of these invert emulsion drilling fluids generates oil-wet drilling waste (cuttings) which are difficult and expensive to treat. In this context, the main objective of this project was to study the effect of change in Hydrophilic-Lipophilic Balance (HLB) on the state of stable invert emulsion. Conceptually, modifying the HLB can change the wettability of these drilling wastes (to water-wet waste) which allows better solid-liquid separation and enhanced biodegradation of these wastes before disposal.

This study was done by the formulation of a stable invert emulsion using several emulsifier combinations at different HLB numbers and treatment of this stable invert emulsion by increasing the initial HLB numbers and observing the effect on the emulsion stability due to this treatment. This study started by determining the mixing parameters (emulsifier concentration and stirring rate) required for the formulation of a model invert emulsion drilling fluid. Emulsifier concentration of 1%, 5%, 7% and 10% (v/v) and stirring rate of 10,800rpm and 15,000rpm were tested and the result showed that emulsifier concentration of 5% (v/v) and stirring rate of

15,000rpm showed the most stable emulsion after 6 days static aging at 25⁰C. Span 80 and Tween 80 were the emulsifiers used in the formulation of the invert emulsion

After determining the mixing parameters, invert emulsions were formulated with HLB values ranging from 4.3 to 14.4. The result showed that stable emulsions were obtained at HLB value of 4.9 which was used as an emulator for a stable invert emulsion drilling fluid. The invert emulsions below and above HLB 4.9 showed different degrees of instability after static aging and centrifugation.

The stable invert emulsion obtained at HLB value 4.9 (emulator) was treated with Correcting Emulsifier Blend (CEB) with HLB ranging from 10.2 to 14.4. This was done to increase the hydrophilicity of the stable emulsion in order to enable destabilization (phase separation) of the emulsion, which will lead to changing the wettability of the waste from being oil-wet to water-wet. However, this approach did not achieve total destabilization. Moreover, the optical density and the viscosity were observed to change. The optical density decreased, which implies increase in droplet size as the HLB value increased while the plastic viscosity increased as the HLB number increases. Increase in droplet size is a desirable effect towards the destabilization of the invert emulsion but the increase in viscosity reduced the motion of these droplets thereby maintaining the stability of the emulsion, hence reducing the propensity for phase separation.

Finally, the tolerance of microorganisms to the invert emulsion with different HLB numbers was tested. The tolerance and growth rate of the microbial consortia was observed to depend on the HLB value. This was dependent on the composition of the hydrocarbons (number of carbon atoms) of the continuous phase (Distillate 822 and Drisol) and the media. This part of the work was done to see the viability of microorganisms in invert emulsions as the HLB number of the

system is modified. Assessing the viability of microorganisms in these environments is a first step towards developing a bioremediation strategy.

5.2 Conclusions

The main objective of this project is to study the effect of change in Hydrophilic-Lipophilic Balance (HLB) on the state of stable invert emulsion. The following conclusions were reached after analyzing the experimental results from this work.

1. In the drilling fluid industry, the Hydrophilic-Lipophilic Balance (HLB) has never been applied in emulsifier selection. Most of the formulations of drilling fluid have always been based on trial and error method which requires extensive testing and is thus time consuming. This work has shown that adopting the HLB number method is also a better strategy for the formulation of stable invert emulsion in the shortest possible time in this type of application
2. The optimum emulsifier concentration of 5% (v/v) was established for the formulation of a stable invert emulsion for the materials studied in this project. It can be concluded that an invert emulsion will require an optimal concentration of emulsifier to be stable and anything below or above this concentration will decrease the stability of the emulsion. This is because, at low emulsifier concentration, the emulsion will be unstable as a result of aggregation (flocculation) of droplets while at higher emulsifier concentration, the emulsion loses its stability due to rapid coalescence of droplets. This was observed from the results obtained where at 1% (v/v) emulsifier concentration which is below the optimum concentration, emulsion was unstable while at 7% and 10% (v/v) emulsifier

concentration which is above the optimum concentration the emulsion was destabilized after 24 hours static aging.

3. The optimum HLB value for the formulation of a stable invert emulsion for the materials studied in this project was established. Invert emulsion with HLB 4.9 can be concluded to be the most stable invert emulsion. This is because there was no phase separation observed visually after static aging and centrifugation of this emulsion unlike other ranges of HLB values that showed some degree of phase separation after aging and centrifugation. This further buttresses the fact that low HLB values support the stability of water-in-oil (invert) emulsion while higher HLB values support the stability of oil-in-water (direct) emulsion.
4. Emulsifier mixtures give better stability when compared to emulsions with single emulsifier package. This is because mixtures of different emulsifier types usually exhibit synergism in their effects on the properties of a system due to interaction of emulsifier molecules. This was observed when Span 80 (HLB 4.3) was used in formulating an invert emulsions that lost its stability after 24 hours ageing at 25⁰C. But when compared with the emulsion of HLB 4.9 with emulsifier mixture of both Span 80 and Tween 80, the emulsion remained stable after static aging and centrifugation.
5. It was established that increasing the HLB number of emulsions increases the flocculation and Ostwald ripening of water droplets which decreases the turbidity of the emulsions as a result of formation of larger droplets. Flocculation and Ostwald ripening of droplets will significantly increase the chances of these droplets colliding together which results from the increase in hydrophilicity of the system, thereby increasing the rate of droplet coalescence which leads to phase separation. Also, the decrease in

turbidity can be attributed to increase in the droplet size due to fusion of the flocculated droplets or Ostwald ripening which involves diffusion of materials from small droplets through continuous phase to large droplets thereby forming larger droplets. This was observed when the optical density of the treated emulsion decreased as the HLB number increases.

6. Plastic viscosity of emulsions increased as the HLB number of the emulsion system increased. The invert emulsion (HLB 4.9) which served as the control exhibited a Newtonian behavior but as the HLB number increased (10.2 – 14.4), the viscosity increased and also exhibited a Bingham fluid behavior. The Newtonian and Bingham behavior was based on the consistency curves (shear stress vs shear strain) of the emulsions which fits a linear regression. Increase in viscosity can also be attributed to droplet-droplet hydrodynamic interactions and this is as a result of increase in HLB number of the emulsion system. Increase in viscosity will inhibit the movement of droplets towards each other thereby decreasing the chances of these droplets coming together and coalescing (destabilize). For instance, the emulsions that exhibited Bingham behavior which requires certain amount of shear stress for it to flow will offer the most resistance to the movement of these droplets since the emulsion remains in static position therefore, slowing down the destabilization process.
7. Tested microbial consortia easily consume Distillate 822 with hydrocarbon fractions below C18 than Drisol with hydrocarbon fractions up to C26. Increasing HLB value of emulsions reduced microbial growth and hence biodegradation of hydrocarbons below C18; while consumption of hydrocarbons with Carbons more than 18 was enhanced by increasing HLB to a critical value 10 - 13 depending on the medium

composition and then reduced with further increase in HLB values. Biodegradability of the invert emulsion will depend on the hydrocarbon fractions and HLB value of the system. Furthermore, the choice of emulsifier constituents significantly affects the biodegradability of the invert emulsions. This is because, increasing the hydrophilicity (via HLB) will increase the droplet size which in turn increases the bioavailability of the waste for the microorganisms.

In the drilling fluid industry, the Hydrophilic-Lipophilic Balance (HLB) has never been applied in emulsifier selection. Most of the formulations of drilling fluid have always been based on trial and error method which requires extensive testing and is thus time consuming. This work has shown that adopting the HLB number method is also a better strategy for the formulation of stable invert emulsion in the shortest possible time in this type of application. For instance, optimum HLB number for non-ionic emulsifiers when using Distillate 822 and Drisol as base oil has been established based on this work and this will immensely reduce the amount of time and cost required in formulating a stable invert emulsion using these two base oil. It was established that increasing the HLB numbers of stable invert emulsion is not a sufficient condition to fully destabilize the emulsion. This is because, increase in droplet size (decrease in optical density) which was observed from the experiment was a desirable effect towards destabilization of emulsion but due to increase in viscosity of the emulsion, the movement of these droplets was reduced which decreases the coalescence (phase separation) rate of the emulsion. But further research can be done on this to see if the process can be completed especially by using different type of surfactants at different compositions. These surfactants will further increase the forces of attractions between droplets thereby increasing the chances for coalescence of these droplets and

facilitating the destabilization process. Also, it was established that increase in HLB number could enhance biodegradation of the drilling fluid to a certain degree as was observed in the tolerance and viability test.

5.3 Recommendations

Based on the experimental work carried out and conclusions reached at the end of this work, the following recommendations for future work are proposed.

1. Future work would require gas chromatography analysis to analyze the biodegradation capacity of hydrocarbons which will show the rate at which the microorganisms degrade the hydrocarbons as the HLB value of the emulsion varies, a higher resolution microscopy to analyze the water droplet size and distribution and finally, repeating the experiments several times to ensure that the results obtained are reproducible.
2. Recommended industrial emulsifiers used in the formulation of invert emulsion drilling fluid at optimum HLB value obtained from the experiment will be used to replace the emulsifiers (Tween 80 and Span 80) used in this work. This is because Span 80 and Tween 80 are not regular emulsifiers used in formulation of drilling fluids. The optimum HLB number could change, but the observed trends are expected to remain consistent.
3. Other additives such as barite, wetting agents, secondary emulsifiers, etc. which are regularly used in drilling fluid formulation should be incorporated in the invert emulsion and the emulsion tested to ascertain their effect to the stability of the invert emulsion.
4. Other surfactants should be considered for this work in the future to see if the process of destabilization can be achieved. For instances other classes of non-ionic emulsifiers (surfactants) such as Brij, Arlacel, Atmos and Atmul should be used in future work.

5. Further research should be conducted in order to have a better understanding of the interaction of microorganisms (tolerance mechanism) with invert emulsions. This will be necessary in order to provide favorable conditions to the microorganisms which will enhance biodegradability.
6. Field test should be carried out using the stable invert emulsion fluid formulated by this work to investigate the effectiveness of the drilling fluid in actual drilling conditions.

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APPENDIX

Optical Density Measurement of treated invert emulsion

The tables and figures below shows the results obtained for the optical density of the treated invert emulsions:

Optical Density measurements of treated invert emulsion (Distillate 882) using emulsifier mixtures of different HLB numbers at respective volumes.

	Average Absorbance Units (AU)				
HLB #	1ml	2ml	3ml	4ml	5ml
10.2	2.2038	1.28	0.2247	0.1869	0.1671
11.2	2.1017	2.0335	0.6404	0.3261	0.1678
12.3	2.1366	1.9941	0.5683	0.3016	0.1682
13.4	2.064	2.0068	0.58	0.2704	0.1506
14.4	2.0965	2.01	1.4426	0.7532	0.2055
Control	2.6733	2.6953	2.7001	2.7566	2.5625

Optical Density measurements of treated invert emulsion (Drillsol) using emulsifier mixtures of different HLB numbers at respective volumes.

	Average Absorbance Units (AU)				
HLB #	1ml	2ml	3ml	4ml	5ml
10.2	2.1477	0.9202	0.5003	0.225	0.1297
11.2	2.0375	1.0477	0.4523	0.1436	0.1174
12.3	2.0687	0.961	0.3648	0.1515	0.1145
13.4	1.9617	1.7624	0.8585	0.3139	0.105
14.4	2.0483	2.0684	1.4426	0.8674	0.1925
Control	2.4714	2.5383	2.551	2.6042	2.5175

Water content measurement using Karl Fischer

The tables below shows the results obtained for the water content measurement:

Water content measurements for invert emulsion (Distillate 822)

HLB #	Vol H2O/wt Sample (mL H20/g sample)			Average (mL H20/g sample)
10.2	0.0979	0.0927	0.0844	0.0917
11.2	0.1060	0.0994	0.1046	0.1033
12.3	0.0927	0.1050	0.1029	0.1002
13.4	0.1010	0.1004	0.1027	0.1014
14.4	0.0921	0.1029	0.1017	0.0989

Water content measurements for invert emulsion (Drillsol)

HLB #	Vol H2O/wt Sample (mL H20/g sample)			Average (mL H20/g sample)
10.2	0.0907	0.0843	0.1082	0.0944
11.2	0.1061	0.1061	0.1032	0.1051
12.3	0.1067	0.1059	0.1084	0.1070
13.4	0.1054	0.1050	0.1049	0.1051
14.4	0.1055	0.1021	0.0990	0.1022

Viscosity Measurement using Brookfield Viscometer

The following tables are the viscosity results obtained from the viscometer at different spindle speeds:

Viscosity measurements of treated invert emulsion (Distillate 822) using emulsifier mixtures of different HLB numbers at respective volumes at 3 rpm spindle speed.

HLB	Speed(rpm)	3		
		Viscosity (cp)	Shear Stress (Dynes/cm ²)	Shear Rate (Sec ⁻¹)
10.2	A1	18.5	4.17	22.5
	A2	18.5	4.17	22.5
	A3	18.5	4.17	22.5
	Average	18.5	4.17	22.5
11.2	B1	82.8	18.6	22.5
	B2	74.1	16.7	22.5
	B3	69.8	15.7	22.5
	Average	75.6	17.0	22.5
12.3	C1	86.1	19.4	22.5
	C2	88.3	19.9	22.5
	C3	88.3	19.9	22.5
	Average	87.6	19.7	22.5
13.4	D1	109	24.5	22.5
	D2	95.9	21.8	22.5
	D3	121.1	27.5	22.5
	Average	108.7	24.6	22.5
14.4	E1	248.5	55.9	22.5
	E2	183.1	41.4	22.5
	E3	238.7	53.2	22.5
	Average	223.4	50.2	22.5

Viscosity measurements of treated invert emulsion (Distillate 822) using emulsifier mixtures of different HLB numbers at respective volumes at 10 rpm spindle speed.

HLB	Speed(rpm)	10		
		Viscosity (cp)	Shear Stress (Dynes/cm ²)	Shear Rate (Sec ⁻¹)
10.2	A1	19.6	14.7	75
	A2	19.6	14.7	75
	A3	19.6	14.7	75
	Average	19.6	14.7	75
11.2	B1	67	50.3	75
	B2	64.1	47.6	75
	B3	59.5	44.1	75
	Average	63.5	47.3	75.0
12.3	C1	70.3	53	75
	C2	69.3	51.7	75
	C3	71	53.5	75
	Average	70.2	52.73	75
13.4	D1	82.7	61.3	75
	D2	77.2	57.6	75
	D3	86.7	64.5	75
	Average	82.2	61.13	75
14.4	E1	150.1	112.6	75
	E2	119.4	89.8	75
	E3	143.2	107.4	75
	Average	137.6	103.3	75.0

Viscosity measurements of treated invert emulsion (Distillate 822) using emulsifier mixtures of different HLB numbers at respective volumes at 50 and 20 rpm spindle speed.

HLB	Speed(rpm)	50		
		Viscosity (cp)	Shear Stress (Dynes/cm ²)	Shear Rate (Sec ⁻¹)
10.2	A1	19.7	73.8	375
	A2	19.9	74.6	375
	A3	19.8	74.3	375
	Average	19.8	74.23	375
11.2	B1	52.8	197.9	375
	B2	50.8	190.1	375
	B3	47.9	179.5	375
	Average	50.5	189.17	375
12.3	C1	54.9	205.5	375
	C2	54.3	202.8	375
	C3	56.4	210.2	375
	Average	55.2	206.17	375
13.4	D1	61.3	228.8	375
	D2	58.7	219.7	375
	D3	63.2	238.6	375
	Average	61.1	229.0	375.0
Speed @ 20 rpm				
14.4	E1	118.9	177.6	150
	E2	100.2	149.8	150
	E3	116.9	173.4	150
	Average	112	166.93	150

HLB	Speed(rpm)	100		
		Viscosity (cp)	Shear Stress (Dynes/cm ²)	Shear Rate (Sec ⁻¹)
10.2	A1	19.6	146.9	750
	A2	19.9	149.6	750
	A3	19.8	148.9	750
	Average	19.8	148.5	750.0

Viscosity measurements of control sample and pure Distillate 822 oil at different spindle speed.

		Control Sample		
Speed(rpm)	Viscosity (cp)	Shear Stress (Dynes/cm²)	Shear Rate (Sec⁻¹)	
3	7.63	1.72	22.5	
10	7.85	5.89	75	
20	8.01	12	150	
50	8.11	30.2	375	
100	8.11	60.8	750	
Distillate 822 Oil				
Speed(rpm)	Viscosity (cp)	Shear Stress (Dynes/cm²)	Shear Rate (Sec⁻¹)	
3	4.36	0.98	22.5	
10	4.91	3.68	75	
20	5.07	7.6	150	
50	5.17	19.4	375	
100	5.17	38.7	750	

Viscosity measurements of treated invert emulsion (Drisol) using emulsifier mixtures of different HLB numbers at respective volumes at 3 rpm spindle speed.

HLB	Speed(rpm)	3		
		Viscosity (cp)	Shear Stress (Dynes/cm²)	Shear Rate (Sec⁻¹)
10.2	A1	9.81	2.21	22.5
	A2	9.81	2.21	22.5
	A3	8.72	1.96	22.5
	Average	9.45	2.13	22.5
11.2	B1	37.1	8.34	22.5
	B2	26.2	5.89	22.5
	B3	-	-	-
	Average	31.65	7.12	22.5
12.3	C1	40.3	9.07	22.5
	C2	55.6	12.5	22.5
	C3	-	-	-
	Average	47.95	10.79	22.5
13.4	D1	127.5	28.9	22.5
	D2	110.1	25	22.5
	D3	123.2	28	22.5
	Average	120.27	27.30	22.50
14.4	E1	235.4	52.5	22.5
	E2	301.9	67.7	22.5
	E3	283.4	64	22.5
	Average	273.57	61.40	22.50

Viscosity measurements of treated invert emulsion (Drisol) using emulsifier mixtures of different HLB numbers at respective volumes at 10 rpm spindle speed.

HLB	Speed(rpm)	10		
		Viscosity (cp)	Shear Stress (Dynes/cm ²)	Shear Rate (Sec ⁻¹)
10.2	A1	10.8	8.09	75
	A2	10.1	7.6	75
	A3	9.16	6.87	75
	Average	10.02	7.52	75
11.2	B1	36	27	75
	B2	26.8	19.9	75
	B3	-	-	-
	Average	31.4	23.45	75
12.3	C1	39.6	29.9	75
	C2	50.4	37.8	75
	C3	-	-	-
	Average	45	33.85	75
13.4	D1	80.1	59.1	75
	D2	81.8	61.3	75
	D3	83.7	62.5	75
	Average	81.87	60.97	75
14.4	E1	134.4	100.6	75
	E2	166.1	124.3	75
	E3	156.6	117	75.5
	Average	152.37	113.97	75.17

Viscosity measurements of treated invert emulsion (Drisol) using emulsifier mixtures of different HLB numbers at respective volumes at 50 and 20 rpm spindle speed.

HLB	Speed(rpm)	50		
		Viscosity (cp)	Shear Stress (Dynes/cm ²)	Shear Rate (Sec ⁻¹)
10.2	A1	10.9	41.2	375
	A2	10.4	39	375
	A3	9.61	36.1	375
	Average	10.30	38.77	375
11.2	B1	30.3	112.3	375
	B2	24.9	92.9	375
	B3			
	Average	27.6	102.6	375
12.3	C1	32.8	120.4	375
	C2	39.6	148.1	375
	C3			

	Average	36.2	134.25	375
13.4	D1	52.6	196	375
	D2	52.9	197.4	375
	D3	56.6	210.4	375
	Average	54.03	201.27	375
	Speed @ 20 rpm			
14.4	E1	105.1	157.5	150
	E2	126.2	189.3	150
	E3	119	178.5	150
	Average	116.77	175.1	150

Viscosity measurements of treated invert emulsion (Drisol) using emulsifier mixtures of different HLB numbers at respective volumes at 100 rpm spindle speed.

HLB	Speed(rpm)	100		
		Viscosity (cp)	Shear Stress (Dynes/cm ²)	Shear Rate (Sec ⁻¹)
10.2	A1	10.9	81.9	750
	A2	10.4	78.2	750
	A3	9.65	72.3	750
	Average	10.32	77.47	750
11.2	B1	27.4	205.3	750
	B2	23.8	178.1	750
	B3			
	Average	25.6	191.7	750

Viscosity measurements of control sample and pure Drisol oil at different spindle speed.

Control Sample			
Speed(rpm)	Viscosity (cp)	Shear Stress (Dynes/cm ²)	Shear Rate (Sec ⁻¹)
3	4.36	0.98	22.5
10	4.58	3.43	75
50	4.84	18.1	375
100	4.84	36.3	750
Drisol Oil			
Speed(rpm)	Viscosity (cp)	Shear Stress (Dynes/cm ²)	Shear Rate (Sec ⁻¹)
3	3.27	0.79	22.5
10	2.94	2.21	75
50	3.14	11.5	375
100	3.17	23.8	750

SAFETY DATA SHEET

Version 4.5
 Revision Date 07/03/2014
 Print Date 08/13/2014

1. PRODUCT AND COMPANY IDENTIFICATION

Product name	: TWEEN® 80		
Product Number	: P1754		
Brand	: Sigma-Aldrich		
Product Use	: For laboratory research purposes.		
Supplier	: Sigma-Aldrich Canada Co. 2149 Winston Park Drive OAKVILLE ON L6H 6J8 CANADA	Manufacturer	: Sigma-Aldrich Corporation 3050 Spruce St. St. Louis, Missouri 63103 USA
Telephone	: +1 9058299500		
Fax	: +1 9058299292		
Emergency Phone # (For both supplier and manufacturer)	: 1-800-424-9300		
Preparation Information	: Sigma-Aldrich Corporation Product Safety - Americas Region 1-800-521-8956		

2. HAZARDS IDENTIFICATION

Emergency Overview

WHMIS Classification

Not WHMIS controlled.

GHS Classification

Skin irritation (Category 3)
 Eye irritation (Category 2B)

GHS Label elements, including precautionary statements

Pictogram	none
Signal word	Warning
Hazard statement(s)	
H316	Causes mild skin irritation.
H320	Causes eye irritation.
Precautionary statement(s)	
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

HMIS Classification

Health hazard:	0
Flammability:	0
Physical hazards:	0

Potential Health Effects

Inhalation	May be harmful if inhaled. May cause respiratory tract irritation.
Skin	May be harmful if absorbed through skin. May cause skin irritation.
Eyes	May cause eye irritation.
Ingestion	May be harmful if swallowed.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Sigma-Aldrich - P1754

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Synonyms : Polyethylene glycol sorbitan monooleate
Polyoxyethylenesorbitan monooleate
Polysorbate 80

CAS-No.	EC-No.	Index-No.	Concentration
Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivative			
9005-65-6	500-019-9	-	<=100%

4. FIRST AID MEASURES

General advice

Consult a physician. Show this safety data sheet to the doctor in attendance.

If inhaled

If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact

Wash off with soap and plenty of water. Consult a physician.

In case of eye contact

Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed

Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

5. FIREFIGHTING MEASURES

Conditions of flammability

Not flammable or combustible.

Suitable extinguishing media

Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Special protective equipment for firefighters

Wear self contained breathing apparatus for fire fighting if necessary.

Hazardous combustion products

Hazardous decomposition products formed under fire conditions. - Nature of decomposition products not known.

Explosion data - sensitivity to mechanical impact

no data available

Explosion data - sensitivity to static discharge

no data available

6. ACCIDENTAL RELEASE MEASURES

Personal precautions

Use personal protective equipment. Avoid breathing vapours, mist or gas. Ensure adequate ventilation.

Environmental precautions

Do not let product enter drains.

Methods and materials for containment and cleaning up

Soak up with inert absorbent material and dispose of as hazardous waste. Keep in suitable, closed containers for disposal.

7. HANDLING AND STORAGE

Precautions for safe handling

Avoid contact with skin and eyes. Avoid inhalation of vapour or mist.

Conditions for safe storage

Keep container tightly closed in a dry and well-ventilated place.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Personal protective equipment

Respiratory protection

Where risk assessment shows air-purifying respirators are appropriate use a full-face respirator with multi-purpose combination (US) or type ABEK (EN 14387) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Hand protection

Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

Full contact

Material: Nitrile rubber
Minimum layer thickness: 0.11 mm
Break through time: 480 min
Material tested: Dermatril® (KCL 740 / Aldrich Z677272, Size M)

Splash contact

Material: Nitrile rubber
Minimum layer thickness: 0.11 mm
Break through time: 480 min
Material tested: Dermatril® (KCL 740 / Aldrich Z677272, Size M)

data source: KCL GmbH, D-36124 Eichenzell, phone +49 (0)6659 87300, e-mail sales@kcl.de, test method: EN374
If used in solution, or mixed with other substances, and under conditions which differ from EN 374, contact the supplier of the CE approved gloves. This recommendation is advisory only and must be evaluated by an industrial hygienist and safety officer familiar with the specific situation of anticipated use by our customers. It should not be construed as offering an approval for any specific use scenario.

Eye protection

Safety glasses with side-shields conforming to EN166 Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin and body protection

impervious clothing, The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Hygiene measures

Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

Specific engineering controls

Use mechanical exhaust or laboratory fumehood to avoid exposure.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form	viscous
Colour	yellow

Safety data

pH	no data available
Melting point/freezing point	no data available
Boiling point	100 °C (212 °F)
Flash point	> 113 °C (> 235 °F) - closed cup
Ignition temperature	no data available
Auto-ignition temperature	no data available

Lower explosion limit	no data available
Upper explosion limit	no data available
Vapour pressure	< 1 hPa (< 1 mmHg) at 20 °C (68 °F)
Density	1.064 g/cm ³
Water solubility	soluble
Partition coefficient: n-octanol/water	no data available
Relative vapour density	no data available
Odour	no data available
Odour Threshold	no data available
Evaporation rate	no data available

10. STABILITY AND REACTIVITY

Chemical stability

Stable under recommended storage conditions.

Possibility of hazardous reactions

no data available

Conditions to avoid

no data available

Materials to avoid

Bases, Heavy metal salts, Strong oxidizing agents

Hazardous decomposition products

Hazardous decomposition products formed under fire conditions. - Nature of decomposition products not known.
Other decomposition products - no data available

11. TOXICOLOGICAL INFORMATION

Acute toxicity

Oral LD50

LD50 Oral - mouse - 25,000 mg/kg

Inhalation LC50

no data available

Dermal LD50

no data available

Other information on acute toxicity

no data available

Skin corrosion/irritation

Skin - rabbit - Mild skin irritation - 24 h

Serious eye damage/eye irritation

Eyes - rabbit - Mild eye irritation

Respiratory or skin sensitisation

no data available

Germ cell mutagenicity

no data available

Carcinogenicity

This product is or contains a component that is not classifiable as to its carcinogenicity based on its IARC, ACGIH, NTP, or EPA classification.

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

ACGIH: No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH.

Reproductive toxicity

no data available

Teratogenicity

no data available

Specific target organ toxicity - single exposure (Globally Harmonized System)

no data available

Specific target organ toxicity - repeated exposure (Globally Harmonized System)

no data available

Aspiration hazard

no data available

Potential health effects

Inhalation	May be harmful if inhaled. May cause respiratory tract irritation.
Ingestion	May be harmful if swallowed.
Skin	May be harmful if absorbed through skin. May cause skin irritation.
Eyes	May cause eye irritation.

Signs and Symptoms of Exposure

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Synergistic effects

no data available

Additional Information

RTECS: WG2932500

12. ECOLOGICAL INFORMATION

Toxicity

no data available

Persistence and degradability

no data available

Bioaccumulative potential

no data available

Mobility in soil

no data available

PBT and vPvB assessment

no data available

Other adverse effects

no data available

13. DISPOSAL CONSIDERATIONS**Product**

Offer surplus and non-recyclable solutions to a licensed disposal company.

Contaminated packaging

Dispose of as unused product.

14. TRANSPORT INFORMATION**DOT (US)**

Not dangerous goods

IMDG

Not dangerous goods

IATA

Not dangerous goods

15. REGULATORY INFORMATION**WHMIS Classification**

Not WHMIS controlled.

This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations and the MSDS contains all the information required by the Controlled Products Regulations.

16. OTHER INFORMATION**Text of H-code(s) and R-phrase(s) mentioned in Section 3****Further information**

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SAFETY DATA SHEET

Version 4.6
Revision Date 07/03/2014
Print Date 08/13/2014

1. PRODUCT AND COMPANY IDENTIFICATION

Product name : Span® 80

Product Number : S6760
Brand : Sigma
Product Use : For laboratory research purposes.

Supplier : Sigma-Aldrich Canada Co.
2149 Winston Park Drive
OAKVILLE ON L6H 6J8
CANADA

Telephone : +1 9058299500
Fax : +1 9058299292
Emergency Phone # (For both supplier and manufacturer) : 1-800-424-9300

Preparation Information : Sigma-Aldrich Corporation
Product Safety - Americas Region
1-800-521-8956

Manufacturer : Sigma-Aldrich Corporation
3050 Spruce St.
St. Louis, Missouri 63103
USA

2. HAZARDS IDENTIFICATION

Emergency Overview

WHMIS Classification

Not WHMIS controlled.

GHS Classification

Skin irritation (Category 3)

GHS Label elements, including precautionary statements

Pictogram : none

Signal word : Warning

Hazard statement(s)
H316 : Causes mild skin irritation.

Precautionary statement(s) : none

HMIS Classification

Health hazard: 0
Flammability: 0
Physical hazards: 0

Potential Health Effects

Inhalation : May be harmful if inhaled. May cause respiratory tract irritation.
Skin : May be harmful if absorbed through skin. May cause skin irritation.
Eyes : May cause eye irritation.
Ingestion : May be harmful if swallowed.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Synonyms : Sorbitane monooleate

Formula : C24H44O6

Molecular Weight : 428.62 g/mol

CAS-No.	EC-No.	Index-No.	Concentration
Sorbitan oleate			
1338-43-8	215-665-4	-	<=100%

4. FIRST AID MEASURES

General advice

Consult a physician. Show this safety data sheet to the doctor in attendance.

If inhaled

If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact

Wash off with soap and plenty of water. Consult a physician.

In case of eye contact

Flush eyes with water as a precaution.

If swallowed

Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

5. FIREFIGHTING MEASURES

Conditions of flammability

Not flammable or combustible.

Suitable extinguishing media

Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Special protective equipment for firefighters

Wear self contained breathing apparatus for fire fighting if necessary.

Hazardous combustion products

Hazardous decomposition products formed under fire conditions. - Carbon oxides

Explosion data - sensitivity to mechanical impact

no data available

Explosion data - sensitivity to static discharge

no data available

6. ACCIDENTAL RELEASE MEASURES

Personal precautions

Use personal protective equipment. Avoid breathing vapours, mist or gas. Ensure adequate ventilation.

Environmental precautions

Do not let product enter drains.

Methods and materials for containment and cleaning up

Soak up with inert absorbent material and dispose of as hazardous waste. Keep in suitable, closed containers for disposal.

7. HANDLING AND STORAGE

Precautions for safe handling

Normal measures for preventive fire protection.

Conditions for safe storage

Keep container tightly closed in a dry and well-ventilated place.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Personal protective equipment

Respiratory protection

Where risk assessment shows air-purifying respirators are appropriate use a full-face respirator with multi-purpose combination (US) or type ABEK (EN 14387) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Hand protection

Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

Eye protection

Safety glasses with side-shields conforming to EN166 Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin and body protection

impervious clothing. The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Hygiene measures

Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

Specific engineering controls

Use mechanical exhaust or laboratory fumehood to avoid exposure.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form	liquid, clear, viscous
Colour	dark brown

Safety data

pH	no data available
Melting point/freezing point	no data available
Boiling point	no data available
Flash point	> 113.00 °C (> 235.40 °F) - closed cup
Ignition temperature	no data available
Auto-ignition temperature	no data available
Lower explosion limit	no data available
Upper explosion limit	no data available
Vapour pressure	no data available
Density	no data available
Water solubility	no data available
Partition coefficient: n-octanol/water	no data available
Relative vapour density	no data available
Odour	no data available
Odour Threshold	no data available
Evaporation rate	no data available

10. STABILITY AND REACTIVITY

Chemical stability

Stable under recommended storage conditions.

Possibility of hazardous reactions

no data available

Conditions to avoid

no data available

Materials to avoid

Strong oxidizing agents

Hazardous decomposition products

Hazardous decomposition products formed under fire conditions. - Carbon oxides

Other decomposition products - no data available

11. TOXICOLOGICAL INFORMATION

Acute toxicity

Oral LD50

no data available

Inhalation LC50

no data available

Dermal LD50

no data available

Other information on acute toxicity

no data available

Skin corrosion/irritation

Skin - rabbit - Mild skin irritation

Serious eye damage/eye irritation

no data available

Respiratory or skin sensitisation

no data available

Germ cell mutagenicity

Genotoxicity in vitro - Human - lymphocyte

DNA inhibition

Carcinogenicity

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

ACGIH: No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH.

Reproductive toxicity

no data available

Teratogenicity

no data available

Specific target organ toxicity - single exposure (Globally Harmonized System)

no data available

Specific target organ toxicity - repeated exposure (Globally Harmonized System)

no data available

Aspiration hazard

no data available

Potential health effects

Inhalation

May be harmful if inhaled. May cause respiratory tract irritation.

Ingestion

May be harmful if swallowed.

Skin

May be harmful if absorbed through skin. May cause skin irritation.

Eyes

May cause eye irritation.

Synergistic effects

no data available

Additional Information

RTECS: WG2932400

12. ECOLOGICAL INFORMATION

Toxicity

no data available

Persistence and degradability

no data available

Bioaccumulative potential

no data available

Mobility in soil

no data available

PBT and vPvB assessment

no data available

Other adverse effects

no data available

13. DISPOSAL CONSIDERATIONS

Product

Offer surplus and non-recyclable solutions to a licensed disposal company.

Contaminated packaging

Dispose of as unused product.

14. TRANSPORT INFORMATION

DOT (US)

Not dangerous goods

IMDG

Not dangerous goods

IATA

Not dangerous goods

15. REGULATORY INFORMATION

WHMIS Classification

Not WHMIS controlled.

This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations and the MSDS contains all the information required by the Controlled Products Regulations.

16. OTHER INFORMATION

Sigma - S6760

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Text of H-code(s) and R-phrase(s) mentioned in Section 3

Further information

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