

AFRICAN UNIVERSITY OF SCIENCE AND TECHNOLOGY

GRADUATE SCHOOL



**AN EXPERIMENTAL MODEL TO PREDICT AND CONTROL
OILFIELD EMULSION TIGHTNESS: A NOVEL APPROACH**

A THESIS

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfilment of the requirements

for the Degree of

MASTER OF SCIENCE

By

ADEKUNLE, OPAWALE

FCT, ABUJA.

December 2010

**AN EXPERIMENTAL MODEL TO PREDICT AND CONTROL OILFIELD
EMULSION TIGHTNESS: A NOVEL APPROACH**

RECOMMENDED BY:

Professor Samuel Osisanya

Advisory Committee chair

Professor Dulu Appah

Advisory Committee Co-chair

Professor David Ogbe

Committee Member

Dr. Alpheus Igbokoyi

Committee Member

APPROVED BY:

Professor Godwin Chukwu

Chair, Department of Petroleum Engineering, AUST, Abuja

Professor Charles Chidume

Provost Academic, AUST, Abuja

Date

© Copyright by ADEKUNLE OPAWALE, 2010

All Rights Reserved.

‘ to me, the greatest achievement in life is doing what has never been done ‘

‘Khunle -Opawale

To God, my creator, who in his infinite mercy and love has ordained my journey through time and has brought me to a wonderful place of fulfilment. No doubt he will keep me beyond here.

To my adorable family, my mum dad and siblings, whom i so much cherish with all my heart, for their prayers, support, and never wavering confidence in my God-given abilities.

To the love of my life; Yetunde, and my prospective kids whom i will forever love.

Specially to Olatunde Ojo; I could never have come this far without you. You have been of assistance to me Mentally, Morally and Academically. You know my personal struggles and you saw me through them all. I pray that i will be to you, what you have always been to me.

To Tunde Salaudeen; i can never but always appreciate you as a friend. You are a friend who has stood a test of time. You have been an instrument in the design and execution of my success. You gave me inspirations when i had none left. You will FOREVER be part of my success stories.

To Babatunde Meredith (‘de driller); I took you as my own elder brother, and you never let me down, the good social and academic times we shared together during the course of my study at AUST will forever last in my memory.

To all my intimate friends ; Adekunle Obisanya (fcuk), Bamgbade Ayobami, Aremu Samson, Alamu Adeleke, Odediran Tolulope, Adepoju Olaoluwa, Aborisade Opeyemi, Together, we started this struggle of searching for good life; we will not die in it. I believe very soon success and good fortunes will smile at us. We will all meet at the top and dine together in the prestigious places of the world.

ACKNOWLEDGEMENTS

I am deeply indebted to my supervisors Prof. Samuel Osisanya and Prof. Dulu Appah whose help, inspirations, suggestions and encouragement helped me at all the time during this research.

Special thanks and appreciation goes also to Mr Dimeji Akinsola, General Manager; NGC-Oil Services, portharcourt, where all my laboratory analysis was carried out. Thank you for the permission to freely use equipment provided in the laboratory. I also thank CMC chemicals for the provision of bentonite clay and some other materials needed for this research.

I would like to specially thank Solomon Otakoro, Clariant Oil Services, UK, for helpful discussions, ideas and assistance on this research.

My warm appreciation to Dwumfour Abdulaziz for all your assistance and contribution, especially while i was writing the java codes involved in this thesis.

My huge thanks to all my AUST colleagues, whom i had to consult at some point in time – Ogbene Alexis, Oyebimpe Yusuf, Bugasse Jonas, Tunde Ayeni, Mustapha Aguye, for their benevolence and prompt attention to my questions and needs concerning this study.

Finally, special thanks to the entire AUST community. You have made this a very wonderful experience for me, and i will forever cherish it. I believe in the dream of AUST and I'm proud to be part of it.

TABLE OF CONTENTS

DEDICATION	IV
ACKNOWLEDGMENTS	V
TABLE OF CONTENTS	VI
LIST OF TABLES	X
LIST OF FIGURES	XI
ABSTRACT	XV
CHAPTER 1: INTRODUCTION	1
1.1 Overview	1
1.2 Literature Review.....	3
1.3 Problem Description.....	8
1.4 Objectives and Significance of study.....	9
1.5 Organisation of thesis.....	10
CHAPTER 2: THEORY OF CRUDE OIL EMULSION FORMATION AND DEMULSIFICATION	11
2.1 Background of emulsion formation.....	11
2.1.1 Emulsions Formation criteria.....	14
2.2 Chemistry and stabilizing properties of emulsifiers	16
2.2.1 Asphaltenes.....	18
2.3 Morphology of Emulsion.....	21
2.3.1 External and Internal phase of an emulsion.....	23
2.3.2 Phase Inversion in Emulsion.....	25
2.4 Macroscopic physical behaviour of emulsion.....	25
2.4.1 Emulsion behaviour under stress.....	26

2.4.2	Temperature effect on emulsions.....	27
2.4.3	Gravitational effects on emulsion.....	28
2.4.4	Electromagnetic field effects on emulsion.....	29
2.5	Emulsion stability.....	31
2.5.1	Aggregation.....	32
2.5.2	Coalescence.....	34
2.5.3	Sedimentation and Creaming.....	35
2.6	Demulsification.....	36
2.6.1	Chemical methods.....	36
2.6.1.1	Actions of demulsifiers.....	37
2.6.1.2	Selection of demulsifiers.....	37
2.6.1.3	Chemistry of demulsifiers.....	38
2.6.1.4	Chemical demulsifier efficiency.....	39
2.6.2	Physical methods.....	40
2.6.2.1	Thermal methods.....	40
2.6.2.2	Mechanical methods.....	41
2.6.2.3	Electrical methods.....	42
CHAPTER 3: ANALYSING THE SHEARING ENERGY AT THE WELLHEAD: A NOVEL APPROACH.....		43
3.1	Model of shearing energy pipes	43
3.2	Application of Shearing energy analysis to wellhead choke.....	44
3.3	Discussion of Analysis.....	46
CHAPTER 4: EXPERIMENTAL STUDIES		48
4.1	Description of Materials	48
4.1.1	Oilfield Process description and crude oil sampling.....	48
4.1.2	Formation Water.....	49

4.1.3	Asphaltenes.....	50
4.1.4	Reservoir fines.....	51
4.1.5	Inorganic Scales.....	51
4.1.6	Demulsifier Chemicals and Reagents.....	51
4.2	Experimental Methods.....	51
4.2.1	Experimental Matrices.....	52
4.2.2	Description of equipments.....	53
4.2.3	Preparation of de-asphaltic oil samples.....	55
4.2.3.1	Bottle test analysis and Emulsion Tightness analysis.....	55
4.2.3.2	Description of Experiment 1.....	56
4.2.3.3	Description of Experiment 2.....	58
CHAPTER 5: EXPERIMENTAL RESULTS, DATA ANALYSIS AND MODELLING.....		60
5.1	Experiment 1: Investigation of factors affecting emulsion tightness.....	60
5.1.1	Effect of Dispersed water phase (Watercut).....	60
5.1.2	Effect of Asphaltene Concentration.....	63
5.1.3	Effect of Inorganic solid content- Sodium Benzoate and Calcite.....	65
5.2	Experiment 2: Combined effects of asphaltene, Shearing energy and watercut on Emulsion Tightness.....	71
5.3	Emulsion Classification Number (ECN) : A novel approach.....	77
5.4	Computer modelling of experimental 2 results.....	79
5.5	Application of developed program to solve Agip's OB-OB fields emulsion problem...81	
CHAPTER 6: SUMMARY, CONCLUSIONS, RECOMENDATIONS.....		90
6.1	Summary.....	90
6.2	Conclusions.....	91

6.3 Recommendations.....	92
NOMENCLATURE.....	93
REFERENCES.....	96
APPENDIX A- DATA SPREADSHEETS.....	103
APPENDIX B - TRENDLINE PLOTS FROM REGRESSION ANALYSIS.....	110
APPENDIX C - JAVA CODES FOR EMULSION TIGHTNESS PROGRAM.....	119
APPENDIX D – LABORATORY PICTURE GALLERY.....	126

LIST OF TABLES

Table 2.1: Description and application of mechanical equipments for breaking emulsion.....	41
Table 3.1: Spreadsheet showing shearing energy analysis for Obiafu well.....	46
Table 4.1: Average data of the properties of the crude oil samples.....	49
Table 4.2: Properties of formation water.....	50
Table 4.3: Matrix design for experiment 1.....	52
Table 4.4: Matrix design for experiment 2.....	53
Table 4.5: Standard conditions for experimental studies.....	58
Table 5.1: Effect of inorganic solids on emulsion tightness.....	68
Table 5.2: Threshold energy values of emulsion formation at 5%, 30% and 55% watercut...74	
Table 5.3: Production data for Obiafu wells.....	83
Table 5.4: Shearing energies estimated for the 21 wells at Obiafu field.....	84
Table A.1: Effect of Watercut on emulsion Tightness.....	104
Table A.2: Effect of Asphaltene on emulsion Tightness.....	104
Table A.3: Effect of Reservoir fines on emulsion Tightness.....	104
Table A.4: Effect of Inorganic solids on emulsion Tightness.....	105
Table A.5: Effect of Asphaltene and fines on emulsion Tightness.....	105
Table A.6: Effect of Asphaltene and inorganic solids on emulsion Tightness.....	105
Table A.7: Effect of Inorganic Solids and fines on emulsion Tightness.....	106
Table A.8: Effect of Asphaltenes, inorganic solids and fines on emulsion tightness.....	106
Table A.9: Combined effect of shearing energy and asphaltene on emulsion Tightness at 5% watercut.....	107
Table A.11: Combined effect of shearing energy and asphaltene on emulsion Tightness at 30% watercut.....	108
Table A.12: Combined effect of shearing energy and asphaltene on emulsion Tightness at 55% watercut.....	109

LIST OF FIGURES

Figure 2.1: Formation of emulsion in the petroleum production system.....	12
Figure 2.2: Simple deformation stages for liquid-liquid dispersion.....	12
Figure 2.3: Hydrocarbons and heteroatomic polycyclics present in crude oil.....	13
Figure 2.4: Bipolar nature of an emulsifier.....	15
Figure 2.5: Stabilization effect of Naphthoic acid on a water droplet dispersed in oil.....	17
Figure 2.6: Effect of emulsifiers on two water droplets in dispersion.....	17
Figure 2.7: Type of emulsifiers.....	18
Figure 2.8: Hypothetical diagram representing the molecular characteristics of the asphaltenes Precipitated from petroleum by n-alkane addition.....	19
Figure 2.9: Structures of asphaltene.....	20
Figure 2.11: Asphaltene Solubility in a crude oil as a function of pressure.....	21
Figure 2.12: Photomicrograph of emulsion types.....	23
Figure 2.13: Hydrophilic- Lypophylic Balance, HLB.....	24
Figure 2.14: Shear stress vs. shear rate for various fluids.....	26
Figure 2.15: Migration of ions in an electric field.....	30
Figure 2.16: Effect of high alternating current on the shape of the oil external phase.....	31
Figure 2.17: Destabilization mechanism showing flocculation and coalescence.....	31
Figure 2.18: Energy of interaction between two droplets.....	33
Figure 2.19: Typical Chemistry of demulsifiers.....	38
Figure 3.1: Shearing energy experienced by fluids flowing through a pipe.....	43
Figure 4.1: Process of asphaltene removal from crude oil.....	50

Figure 4.2: Schematic explanation of emulsion formation device.....	54
Figure 5.1: Effect of watercut on emulsion tightness.....	61
Figure 5.2: Three (3) behavioural segments shown on the effect of water on emulsion Tightness.....	63
Figure 5.3: Effect of Asphaltene concentration on emulsion tightness.....	64
Figure 5.4: Mechanism of emulsion stabilization by asphaltene.....	65
Figure 5.5: Wetting behaviour of solids at the oil/water interphase.....	68
Figure 5.6: Effect of asphaltene coated solids on emulsion tightness.....	69
Figure 5.7: Schematic diagram showing adsorption of asphaltene on inorganic solids.....	69
Figure 5.8: Schematic showing water droplets stabilized by asphaltene coated solids.....	70
Figure 5.9: Effect of asphaltene, asphaltene coated solids and uncoated solids on Emulsion tightness.....	70
Figure 5.11: Effect of asphaltene content and shearing energy on emulsion tightness at 5% water cut and showing threshold energies.....	71
Figure 5.12: Effect of asphaltene content and shearing energy on emulsion tightness at 30% water cut and showing threshold energies.....	72
Figure 5.13: Effect of asphaltene content and shearing energy on emulsion tightness at 55% water cut and showing threshold energies.....	72
Figure 5.14: Effect of asphaltene content and shearing energy on emulsion tightness at 5% watercut after threshold.....	75
Figure 5.15: Effect of asphaltene content and shearing energy on emulsion tightness at 30% watercut after threshold.....	75
Figure 5.16: Effect of asphaltene content and shearing energy on emulsion tightness at 55% watercut after threshold.....	76
Figure 5.17: Emulsion classification number scale.....	78
Figure 5.18: Desktop displaying icon of EMULS-K application.....	85
Figure 5.19: Inputting the name of the oilfield to be analysed.....	85
Figure 5.21: Inputting the location of field.....	85

Figure 5.22: Inputting the number of wells on the field.....	86
Figure 5.23: Inputting the watercut of the well.....	86
Figure 5.24: Inputting the asphaltene content of the well.....	86
Figure 5.25: Inputting wellhead shearing energy.....	87
Figure 5.26: Result of Emulsion Tightness from Emuls-K software.....	87
Figure 5.27: Excel refined Result from Emuls-K software.....	88
Figure B.1: Regression analysis of 5% Watercut and 0.5% asphaltene plot.....	111
Figure B.2: Regression analysis of 5% Watercut and 2.1% asphaltene plot.....	111
Figure B.3: Regression analysis of 5% Watercut and 5.4% asphaltene plot.....	112
Figure B.4: Regression analysis of 5% Watercut and 14.8% asphaltene plot.....	112
Figure B.5: Regression analysis of 5% Watercut and 21.1% asphaltene plot.....	113
Figure B.6: Regression analysis of 30% Watercut and 0.5% asphaltene plot.....	113
Figure B.7: Regression analysis of 30% Watercut and 2.1% asphaltene plot.....	114
Figure B.8: Regression analysis of 30% Watercut and 5.4% asphaltene plot.....	114
Figure B.9: Regression analysis of 30% Watercut and 14.8% asphaltene plot.....	115
Figure B.11: Regression analysis of 30% Watercut and 21.1% asphaltene plot.....	115
Figure B.12: Regression analysis of 55% Watercut and 0.5% asphaltene plot.....	116
Figure B.13: Regression analysis of 55% Watercut and 2.1% asphaltene plot.....	116
Figure B.14: Regression analysis of 55% Watercut and 5.4% asphaltene plot.....	117
Figure B.15: Regression analysis of 55% Watercut and 14.8% asphaltene plot.....	117
Figure B16: Regression analysis of 55% Watercut and 21.1% asphaltene plot.....	118

ABSTRACT

Formation of water-in-oil emulsions are among the major challenges encountered by production and surface facilities engineers during the recovery of crude oil, especially in a large multi-wells system in both onshore and offshore oilfields. The development of systematic approaches to handle emulsion problem has been very slow. Several important aspects of emulsion that have not being studied extensively to date include mechanism, kinetics and energy levels associated with emulsion formation. Such information is needed to understand the emulsification process, model it and hence solve lots of operational and economical emulsion issues. This study presents a novel experimental approach to model the process of water-in-oil emulsion formation and also study the shearing energy levels associated with its formation.

Oilfield emulsions were simulated using agitator rated between 0 to 1000 RPM. Mixture of crude oil, formation water, asphaltene, inorganic solid, scale precipitates and reservoir fines were agitated at various revolutions to form the emulsion. The emulsions that result were stabilized using re-solubilized asphaltene precipitated out of the crude oil. A demulsifier chemical sample was used to properly treat over 300 bottle samples, and the rate of separation of their emulsified water was used to determine their tightness.

Relationship between shearing energy at the wellhead chokes, pressure drop across it, and its size was first developed. This equation relates the production rate, type of the crude oil produced and the nature of the choke during production to shearing energy. The results from the experiments show that increase in the fraction of the dispersed water phase in an oil-water mixture, leads to formation of tight emulsions. This relationship existed until the point of inversion from water/oil emulsion to oil/water emulsion is reached at 60% watercut, and loose emulsions will start forming. Also asphaltene was seen to contribute tremendously to the formation of tight emulsions. At 2.9% concentration of asphaltene the emulsion becomes more difficult to treat, with a tightness of 18 %. Inorganic solids-sodium bentonite and calcite demonstrated little effects on emulsion stability. Further studies were carried out to study the wettability effect of asphaltene on the inorganic solids and consequently their stabilizing effect on emulsion. Result shows that these solids behaved as very strong emulsifiers when coated with asphaltene. Results from the second set of experiment shows that shearing energy, asphaltene concentration and water-oil-ratio are major factor that determines the formation of tight emulsion. A particular shearing energy threshold (SET) value is needed to form emulsion for a specific water oil ratio, regardless of the concentration of asphaltene present.

Lots of interesting trends relating watercut, asphaltene content and shearing energy are seen from the results in this study, and hence could be used to predict and rank emulsion samples according to their tightness. The emulsion diagnostic plots (EDP) produced were digitized and best line of fit for each of the data series plotted was gotten and their corresponding equations generated. These equations were then developed into a java executable application, EMULS-K. This application was used to analyse the emulsion problem in an oilfield of a major operator in Niger Delta. EMULS-K program generated

values of emulsion tightness (ET) for all the 21 wells in this field and hence spotted out the problematic ones. The result obtained from this analysis correlates perfectly well with those gotten by a service company using the old bottle test approach.

CHAPTER 1

INTRODUCTION

1.1 Overview

Crude oil is seldom produced alone from reservoirs. It is always produced as a complex mixture of hydrocarbons and formation water.¹ These mixtures undergo extreme agitation under high shear rate and turbulence as they flow from the reservoir pores through perforated casing into the wellbore, to the tubing and finally through the surface production facilities. This occurrence causes the water phase to be dispersed and stabilized as fine droplets in the bulk oil phase and hence forms emulsion. Emulsion is among the many problems encountered in the production, transport, and refining of crude oil and dealing with this complex structural arrangements account for much of the expenses incurred by oil companies in their daily operations.² Their control and resolution is among the major challenges encountered both onshore and offshore by production engineers, production chemists and facilities engineers during production, especially in a complex multi-wells system. Emulsion problems are usually more problematic in fields where heavy crude oils are produced.³

Emulsions are stabilised by rigid interfacial films that forms a ‘‘skin’’ on the water droplets and prevents them from coalescing.⁴ The stability of these interfacial films, and hence the tightness of the emulsions, depend on a number factors, including the heavy materials present in the crude oil (e.g. asphaltenes, resins, waxes), inorganic solids (e.g. clays, scales and corrosion products), temperature, droplet size and droplet size distribution, pH and brine composition.⁵ As the producing field depletes, the nature of petroleum emulsion changes continuously due to changes in some of these factors and production methods.⁵ Produced oilfield emulsions can be water-in-oil (W/O), oil-in-water (O/W) or multiple water and oil in water (W/O/W), but most produced oilfield emulsions are of the W/O type.¹ This depends on several conditions, which include but not limited to: fraction of each liquid phase, hydrophilic-Lypophylic balance (HLB) etc. From a purely thermodynamic point of view, a W/O emulsion is an unstable system. This is because there is a natural tendency for a liquid/liquid system to separate and reduce its interfacial area and hence, its interfacial energy. However, most oilfield emulsions are stable over a period of time (i.e. they possess kinetic stability).^{1,4} Produced oilfield emulsions have been classified on the basis of their

degree of kinetic stability.⁵ According to this, oilfield emulsions have been classified as loose, medium and tight emulsions. Loose emulsions separate in a few minutes, medium emulsions separate in ten minutes or more, while tight emulsions will separate in a matter of hours or even days.⁵

Emulsions from several production headers in the oilfield are usually commingled at the manifolds and then transported to the central processing facilities for treatment. They are usually very difficult to treat and cause a number of operational problems, such as overloading of surface separation equipments with water, increased cost of pumping wet crude, increased heating cost, tripping of separation equipments, high pressure drop in flowlines increase in cost of demulsifiers, production of off-specification crude oil, thick sludge in stock tank bottom, corrosion in export and subsea pipelines, catalyst poisoning at refineries and sometimes force the shutdown of processing equipments in the Wet Crude Handling Facility (WCHF).⁷ The overall effect of this is a significant loss in production and loss of revenue to the operators.

Different treating methods thus exist in the petroleum industry for demulsification of crude oil. They include thermal methods, mechanical methods, electrical methods and chemical treatment.⁸ In general, these methods are interrelated. Applying heat to the emulsion reduces the viscosity of the oil and increases the water settling rates. It also results in the destabilisation of the rigid films caused by interfacial viscosity. Application of heat for emulsion breaking should be based on an overall economic analysis of the treatment facility. Furthermore, some of the mechanical equipment available in the breaking of oilfield emulsions include free-water knockout drums, phase separators etc. High voltage electricity is also often used for breaking emulsion.⁶ It is generally theorized that water droplets move more rapidly when induced with an electric field, and hence collide with each other, and coalesce. The distance between the electrodes in some designs- is adjustable so that the voltage can be varied to meet the requirement of the emulsion being treated.¹ By far; the most common method of emulsion treatment is adding chemicals. Demulsifier chemicals account for approximately 40% (in value) of the world oilfield production chemical markets.⁹ They are deployed at virtually every crude oil processing station worldwide. Chemical additives, recognised as the second “aid”, are special surface active agents that migrates to the water – oil interface once added to the emulsion. They rupture the stabilising agent due to reduction in surface tension on the inside of the film.

Two or more methods are usually combined for optimal treatment efficiency.¹⁰ Electrostatic dehydration is rarely used alone as a method of breaking emulsions. It is generally used in conjunction with chemical and heat requirements. Some emulsions will readily break upon heating without chemicals added; others will respond to chemical treatment without heat. Furthermore, emulsion stability is strongly field and time dependent and will vary in character as the field matures and hence a regular update in the control methods are required. Extremely tight emulsions may be experienced in oilfields producing heavy oil containing metal porphyrins and/or with electric submersible pumps and gas lifts which constitutes a very high agitation source.¹¹

The design of emulsion-treating equipments and procedure for a given field or application requires experience and engineering judgement. The engineer must rely on laboratory data and data from nearby wells or fields and depend on experience. There is no standard solution available for striking a balance between, for example the amount of chemical and heat to resolve emulsions. Laboratory bottle tests can provide an estimate of treating temperatures and retention times that can be used for design and operations. However, the laboratory bottle testing procedure is based on arts and is done under static conditions though the field conditions are dynamic. Nevertheless it is the only reliable method for troubleshooting emulsion problem by screening different emulsion samples for relative tightness. Evaluating prospective demulsifiers and studying the effects of different variables on emulsion resolution is also done by bottle test.^{5,7}

1.2 Literature Review

Crude oil emulsion is a broad subject matter and several books^{2,4,34,35,36} have been published on it with the intent of understanding the mechanism of emulsion formation and developing models of crude oil emulsification process. These publications discuss the chemistry and mathematics involved in this subject. They also cover a variety of perspectives which include experimental, field trials, or theoretical (modelling) in nature. The most important factor in emulsion work is the understanding of the physics of emulsification and its stability.¹² Studies have shown that water is stabilized in oil by two forces – Viscous and inelastic forces – as a result of the interfacial action of resins and asphaltenes. This was noted as early as the 1970s¹³ when formation of emulsion correlated with the oil composition. What was particularly unclear was the mechanism and the relation of other components, such as

waxes, asphaltenes, fines etc. Further, the mechanism by which any of the components influenced emulsions was unclear. It also was noted that the more viscous oils would have a tendency to form emulsions more readily in some cases, but not in others, hence no well model of emulsification of crude oil have been developed as such. In recent years, studies have shown the composition effects and proposed clear reasons for the cause of water-in-oil

A 5-year study of several facets of emulsions have once been done by some group of researchers.^{14 - 18} The group has worked on the basic physics of emulsion formation, test of emulsion stability and characteristics of emulsions by measurement of their properties. This series of studies has shown that oil consists of hundreds of components and the emulsion consists of water interacting with certain of these components. The formation of emulsion is due to the surfactant-like action of the polar and asphaltene components of oil. These compounds behave like low HLB (hydrophilic to lipophilic Balance) surfactants and stabilize water droplets in the oil. The polars and asphaltenes are stabilized in many crude oils by the aromatic solvents, especially benzene, toluene, ethyl benzene and xylenes). If these compounds are low in quantity, or are lost through evaporation, the polars (or resins) and asphaltenes can precipitate and thus stabilize the water-in-oil droplets. A relatively large amount of energy is required to form these emulsions once the chemical conditions are correct. This mechanism of emulsion formation has been verified by several experiments including the creation of "artificial "crudes.

Sjoblom *et al.*,¹⁹ also conducted an extensive series of studies on emulsions from Norwegian continental shelf. It was found that the stability of emulsion was largely a result of the asphaltene content and that this stability increased when the resins and asphaltenes were aged. The amount of asphaltenes was the most important compositional factor related to stability of the water-in-oil emulsions. They extracted resins and asphaltenes from North Sea crudes and aged at elevated temperatures. The addition of these back into oils caused emulsion formation. It was found that the stability of the emulsion largely depends on the amount of asphaltenes and that the asphaltene resin ratio was important.

McClean *et al.*,²⁰ studied water-in-oil emulsions extensively and found that there were two stabilization factors, viscosity, and surface-active agents. Systems were studied using model emulsions with the addition of asphaltenes, resins, fine silts and fine clay particles. They found that asphaltene, resins and the other surface active materials accumulate at the oil-water interface and form a barrier to recoalescence. Asphaltene forms more stable

emulsion when it is used with other surface active materials, than when it was being solubilised alone. They also studied some model emulsions but used toluene and heptane dilutions from bitumen. It was found that asphaltenes and solid mineral particles were the main stabilizers of water-in-oil emulsions for such system.

Yan *et al.*,²¹ studied the stability of water-in-oil emulsion using fine solids such as kaolinite clay particles treated with asphaltenes, hydrophilic and hydrophobic colloid silica, and hydrophobic polystyrene latex microspheres as well as fumed silica dry powders treated with silanization. Their experimental results showed that hydrophilic colloidal silica could only stabilize oil-in-water emulsion for short time. If hydrophobic particles were suspended in the aqueous phase prior to emulsification, they could only produce oil-water emulsions. Only hydrophobic particles suspended in organic phase prior to emulsification could stabilize water-in-oil emulsion. The presence of solids also change emulsion viscosity. Volume of dispersed phase, the amount of solids present, and the wettability of solids affects emulsion viscosity.

As the study on crude oil emulsion continues, Cairns, *et al.*,²² carried out some experiments as well. They studied the effect of crude oil-water interfacial properties on water-in-oil emulsion stability. They found that the conditions favourable for the formation of a stable water-in-oil emulsion are a high oil-water viscosity ratio and a rapid initial adsorption of natural surfactants (rapid fall in interfacial tension). This should be followed by a rapid rise in interfacial viscosity. The high interfacial viscosity exhibited under some conditions is due to the part of the presence of basic surface-active species in the interface. The asphaltene content of a crude oil does indicate the existence of a high interfacial viscosity.

Singh and Pandey²³ studied the physical characteristics of natural crude oil-water interfacial films as a function of crude oil pH and the ionic composition of water. They also studied the effect of demulsifiers on film properties and correlated emulsion stability to film pressure. They concluded the following:

- As the concentration of salt in water is increased the separation of emulsified water decreased.
- As the pH value increases, emulsions become more stable and difficult to separate.
- As the effective surfactant concentration increases, the interfacial and particle sizes decrease and their interfacial viscosity increases.

Some studies on classification of crude oil emulsion according to their stability have also been done. According to Merv Fingas²⁴, a new empirical data and corresponding physical knowledge of emulsion formation is proposed. The density, viscosity, saturate asphaltene, resins and fine content were used to compute a classification index which yields either an unstable or entrained water-in-oil state or a meso stable or stable emulsion. Out of these four states, only stable and meso-stable states can be characterized as emulsions. It is suspected that the stability derives from the strong visco-elastic interface are caused by asphaltenes and resins. Mesostable emulsions are the emulsions between stable and unstable emulsions. It is thought that meso-stable emulsions lack sufficient quantities of asphaltenes to render them completely stable. The meso-stable emulsions may degrade to form layers of stable emulsions.

Studies have also been made to study and measure the effects of energy of agitation on emulsion formation. Kotlar *et al*,²⁵ studied the thermodynamics of emulsification process and reported that emulsion is the dispersion of liquids in liquids, and it's governed by surface forces. The free energy of formation of droplets is given by:

$$\Delta G_{\text{form}} = \Delta A \gamma_{12} - T \Delta S \quad (1.1)$$

Where ΔA is the increase in interfacial area and γ_{12} is the interfacial tension between the two liquids. ΔS is the change in entropy when a larger number of droplets are formed and usually $\Delta A \gamma_{12} \gg T \Delta S$. Thus generation of emulsion is a non spontaneous process and will require threshold energy to start. According to their publication, the energy requirement is larger than the thermodynamic energy. $\Delta A \gamma_{12}$ due to the fact that the new surfaces constantly need to be generated so that the spheres of the minor phase may have enough energy to be established in the major phase. The energy of turbulence is present mostly at the near wellbore region due to the inflow characteristics of the well, giving turbulent flow and good mixing conditions. Fines available at this region migrate to the interphase between the two fluids, and hence a change in ΔA . This change will be the sum of particle size, particle size distribution, shape and roughness and the concentration of the particles introduced. Furthermore, γ_{12} is also affected by these processes; this is usually caused by difference in electric charging of the particles, polar chemical components and changes in wettability of the particles. They

concluded that by combination of the effects explained above, $\Delta A\gamma_{12}$ may be changed to such an extent that stable emulsions can occur.

Another approach reported by authors²⁶ in an attempt to understand the mechanism of emulsification is to measure the stability of crude oil emulsions as function of the water separating from it after treatment. Simulated emulsion using crude oils from some specific oilfields, and varying their condition of formation have been used²⁶ by Sunil Kokal et al. They studied crude oils from some Saudi Arabian fields. Their study investigated the emulsion tendencies of crude oil from different reservoirs, the roots of the causes of the emulsion and then characterized them in terms of their stability after treatment. The effects of demulsifier chemical concentration, shear rate, water cut, mixing of different crudes, asphaltene contents, reservoir fines and inorganic solids were observed on the emulsion stability. A very clear link between asphaltenes, reservoir fines and emulsion tightness was demonstrated. The higher their concentration in the samples, the tighter the emulsion. They are said to have a stabilising effect on emulsions. Results show that reservoir fines play a very key role in emulsion stabilisation. Also, emulsion tightness increases with decreasing temperatures. Increase in shear (for example by choking a well) results in a tighter emulsion. High water cut wells were observed to show relatively looser emulsions. They reported that emulsion stability decreases (but not significantly) with increasing water cuts. This study only focused on physical analyses of emulsion stability and no mathematical model was developed.

Omole *et al.*,²⁷ also investigated the effect of different mixing conditions in a production system coupled with oil types and aqueous phase composition on some crude oil emulsions. Crude oil emulsions were prepared by dispersing a known volume of water in oil, using a blender whose speed was varied between the ranges of 1000 – 18000 rpm for two minutes. The type of emulsion were determined by measuring the conductivity of the emulsion using a digital conductivity meter, and by observing what happened when a drop of each emulsion was added to a volume of either pure oil or pure water. The stability of the emulsions was assessed by monitoring the increase with time of the position of the clear water emulsion interface. The percent water separated after a fixed period of time was also measure. It was concluded from this study that the production of fine droplets by mechanical emulsification requires sufficient energy density equivalent to about 5000 rpm. The efficiency of droplet disruption increases from high API gravity to low API gravity blends.

Emulsions were most stable at dispersed phase concentration of 0.7 and in acidic solution and paraffinic oils. In general, optimum pH for resolution of alkaline based emulsions was between 10 and 11 and between 6 and 7 for brine. However, unstable emulsions were produced at high pH while at low pH stable emulsions were formed.

However, most of the emulsion studies reviewed above was conducted with depressurised crude and water samples. Sunil Kokal *et al.*,²⁸ studied the effect of high pressure and high temperature on crude oil emulsion behaviour. A special visual pressure/volume/temperature (PVT) cell with the capability of observing emulsion phase behaviour at reservoir conditions was used for this study. Results show that emulsion can form at reservoir conditions, with mixing, especially if the crude has a tendency to precipitate asphaltenes. It also suggested that emulsion behaviour is linked very closely to the presence of fine reservoir solids through in-situ dynamic precipitation of organic solids and inorganic salts as well as through fines migration in the reservoir.

1.3 Problem Description

Individual wells often exhibit different emulsion problems even though they are being produced from the same reservoir.² This is because the magnitude of most of the factors causing emulsion changes as a function of the thermodynamic conditions in each well. Also, difference in the methods of production of each well contributes to this variation in emulsion property. Oilfield production practice involves comingling these crudes at the manifold. Main manifold production header combines flowlines from several wellheads into a larger trunk line proceeding to the central processing facilities (CPF). Troubleshooting and resolving emulsion problems at manifolds and processing facilities are always done with bottle testing. This is a test based more on art rather than science. Some fields operators had reported that certain wells appeared to cause plant upsets due to emulsion problem, while others do not.² Although, chemical injection points are occasionally stationed at individual wellheads, this is not always be practical and economical especially in a large multi-wells field. It results into a trade-off between cost and effectiveness.

Current daily field practises show that there are really no models or correlations relating the factors causing emulsion to the nature of the emulsion formed, i.e. its stability and tightness.² Although test separators are occasionally used to handle this problem, they are not well applicable in a large multi-well field because of loss of valuable production time

during this test, as isolated wells might be shut-in. Chemical service companies are hence usually invited to carry out bottle tests on each wellhead samples and the ease of resolution of the emulsions from each well is used as an approach to predict the source of the problem. However, this is a comparative test whose procedure and result interpretation is based on experience. It is based on art rather than science. Moreover, it is usually carried out on a NO CURE, NO PAY contract, and hence could lead to loss on revenue even for the chemical servicing company if the contract is eventually lost.

Selection of the particular troublesome well during production is a subject area to be studied. Variations in the kinetics of emulsion formation from each of the wells are still not well understood; hence mathematical models can not be built. Therefore, before one could proceed with physical and chemical characterization of the emulsions samples in an oilfield, correlations that would relate the tightness of an emulsion to the factors causing it are required. Also, an index capable of classifying crude oil emulsion according to their tightness is needed. All these remain the focus of this study.

Since crude oil emulsion can be said to be formed as a result of presence of oil and water, with a known ratio, quantifiable sources of energy used for agitation, presence of Asphaltenes, resins, reservoir fines and inorganic solids etc, all of known quantity, then an experimental study can be carried out to analyse the kinetics of emulsion formation in oilfields, and the energy levels associated with its formation at various parts of the production system. This would provide a good way to model the emulsification process and predict the nature of emulsion from each flowlines and hence a better way of controlling and classifying them.

1.4 Objectives and Significance of the Study

The objectives of this study are as follows:

1. To theoretically analyse and quantify the shearing energy encountered at the wellhead.
2. Study the effect of water cut, asphaltene, inorganic scale solids (calcite) and reservoir fines on the stability of water-in-oil emulsions, and also to rank their effects.
3. Develop an experimental approach to model the process of water-in-oil emulsion formation and study the shearing energy levels associated with it.
4. Develop an index to compare emulsion tightness from individual wells in a field.

5. Develop an emulsion tightness testing procedure. This will be built on a computer program to calculate the shearing energy and the tightness of emulsion expected at individual wellheads in a field and compares their emulsion tightness.
6. Use developed technology of this thesis to solve Agip's emulsion problem at OB-OB oilfield.

1.5 Organization of Thesis

This thesis is divided into six chapters including this chapter. Chapter 2 focuses on the fundamental and theoretical background of crude oil emulsion. The chemistry and physics behind emulsion formation and its resolution are extensively discussed here. Chapter 3 presents a novel approach for estimating agitation energy at several regions in the production system, especially at the regions where extreme turbulence is usually experienced. Chapter 4 discusses in detail, the experimental aspect of this study. The experimental materials, including crude oil samples and demulsifier chemical sample used for this experiment are also discussed in detail. Chapter 5 presents the experimental data, analysis and discussions. Chapter 6 presents the summary, conclusions and Recommendations of this study.

CHAPTER TWO

THEORY OF CRUDE OIL EMULSION FORMATION AND DEMULSIFICATION

Several studies^{2, 4, 5, 8, 23, 29, 34, 35} on crude oil emulsion handling have been published in different literature. However, a complete solution to the problem can only begin from comprehensive breakdown of the concepts surrounding the dispersion and stabilisation of water droplets in oil. This includes their physics, chemistry and mathematics.

2.1 Background of Emulsion Formation

Emulsions can be found in almost every part of the petroleum production system which includes near-wellbore region, wellhead, surface flowlines and facilities as shown in Figure 2.1. It can be defined as a colloidal dispersion of a liquid within another liquid.²⁹ The stability is conferred by the presence of agents at the interfaces that may delay the spontaneous tendency of the liquids to separate. Such agents are most commonly molecules with polar and non-polar chemical groups in their structure usually referred to as surfactants- or finely divided solids. The dispersed phase is commonly present in an emulsion in the form of spherical drops²⁹. The emulsion formation process is called emulsification and it can be made by the shearing action developed at regions of high turbulence within the petroleum system. Figure 2.2 shows the scenarios of deformation for liquid-liquid dispersion due to increased exertion of stress. Spontaneous emulsification occurs when the phases are contacted³⁰ and can also occur, for example, by chemical reactions³¹ or by the nucleation of one phase in another due to a reduction in temperature. During the process of crude oil retrieval from the production zone, the produced water undergoes a significant amount of shearing with it. It is the agitation effect combined with heat, pressure and surface-active compounds present in the crude oil that act to produce emulsions in the production system.

The type of compounds present in the crude oil are many and varied, and range from pure hydrocarbon (C_nH_{2n+2}) to complex hetero-atomic polycyclics as shown in Figure 2.3. When an oil well is brought into production, the quantity of water present in the oil is determined by the content of coincident water and oil present.

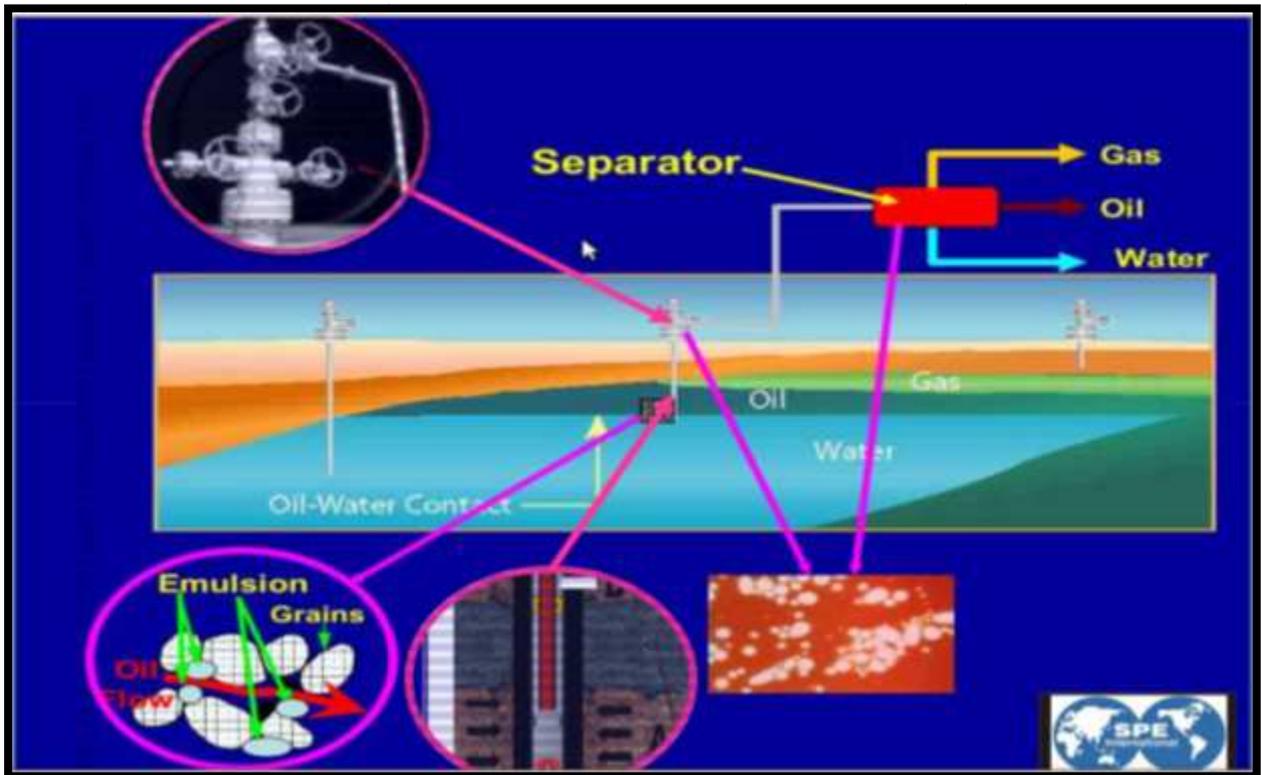


Figure 2.1: Formation of emulsion in the petroleum production system¹

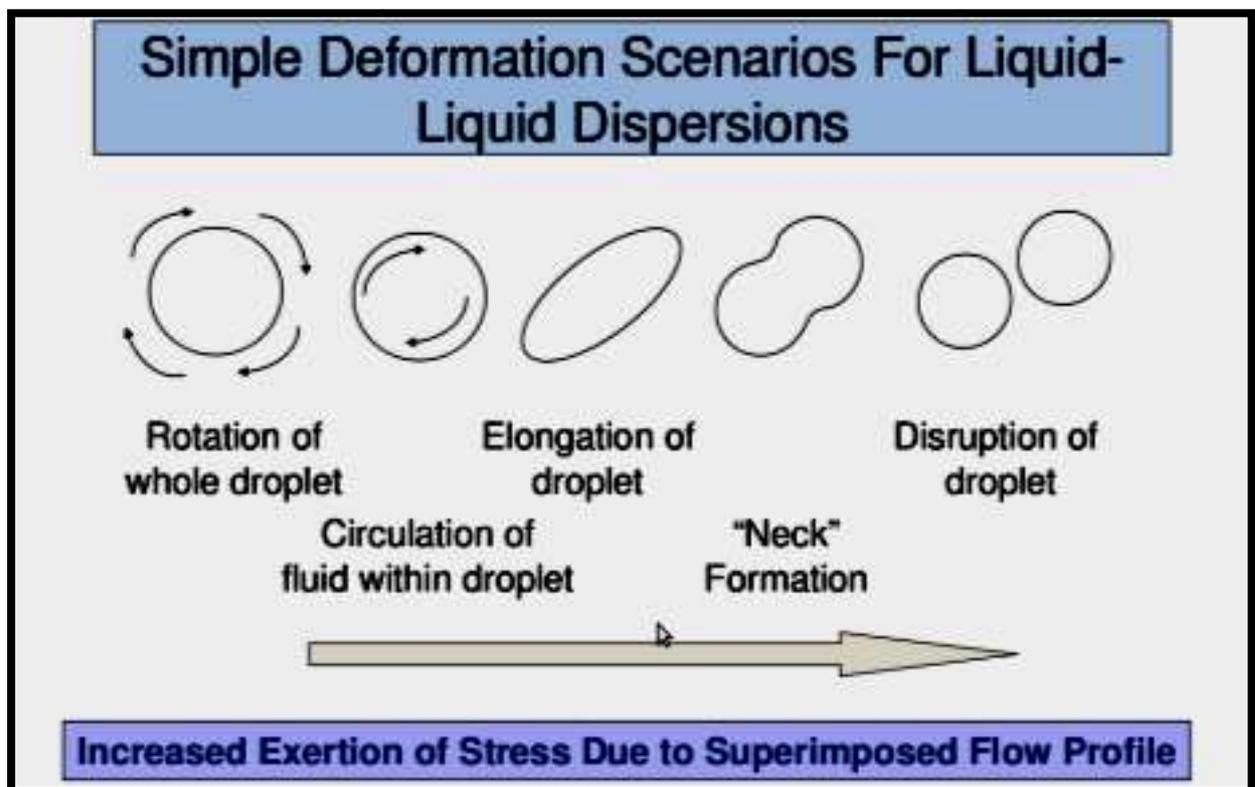
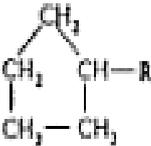
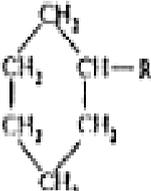
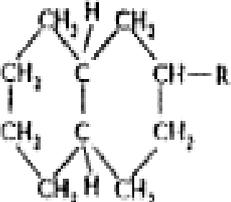


Figure 2.2: Simple deformation stages for liquid-liquid dispersion⁴

Type	Formula	Percent
Paraffin Hydrocarbons (Alkanes)		
Normal	$\text{CH}_3-\text{CH}_2-\text{R}$	14
Is	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{R} \end{array}$	18
Branched	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}_2-\text{CH}-\text{R} \end{array}$	
Cycloparaffins (Naphthenes)		
Alkyl Cyclopentanes		10
Alkyl Cyclohexanes		6
Bicycloparaffins		5
Aromatics		
Alkylbenzenes		18
Aromatic-Cycloparaffins		5
Fluorenes		3
Binuclear Aromatics		17
Polyuclear Aromatics	Like binuclear but more rings	4

R is usually CH_2-

Figure 2.3: Hydrocarbons and hetero-atomic polycyclics present in crude oil ⁴

Most of the crude oil produced is derived from sandstone formations.² These formations consist of combinations of silicon and oxygen that tend to form a partially-charged, anionic crystallites. The crystallites have a high affinity for water and are often found in close association. This close association is due to the phenomenon of hydrogen bonding, where the partially positive hydrogen of water interacts with the partially negative oxygen of the silicate (Si_nO_{2n}). This interaction results into a layer of water surrounding the crystallites, which is termed connate water. The connate water layer tends to remain closely associated with the silica surface, and maintains equilibrium with the free water contained in the crude oil. Over time, this association is established as a static condition, since no external force has acted as an agent to change this preferred state. When the reservoir is tapped, the equilibrium state is disturbed, and the pressure drives the fluid from the pore channels within the sandstone formation. The resulting increase in shearing forces combine with the equilibrium shift of free-water partial pressure in the oil phase and emulsion begins to form. Phase separation in emulsions is imposed by thermodynamics because as the oil and water form two continuous phases while they separate, the interfacial area and therefore the free energy of the dispersion are reduced. As a consequence, the characteristics of the emulsion (drop size distribution, mean drop size and other properties) cannot remain unchanged in time. Therefore, the stability of an emulsion refers to the ability of the dispersion to preserve its properties within a given timeframe²⁹. Most of the petroleum emulsions that will be encountered in practice contain oil, water and emulsifying agents and exist in a metastable state that has high potential barrier to prevent coalescence of the particles.

2.1.1 Emulsion Formation Criteria

According to Schubert and Armbruster³², the criteria for the formation of emulsion can be divided into three main categories:

- Difference in solubility between the continuous phase and the emulsified phase must exist.
- Intermediate agents having partial solubility in each of the phase must be present.
- Energy sources of the appropriate magnitude to shear the phases must be available.

The first criterion requires that the phases undergoing emulsification consist of molecules that exhibit wide separations in chemical composition, since their composition determines solubility. A corollary to this requirement is that the physical state of the two phases be the same and that each exists as liquids under prevailing conditions of temperature and pressure.

The hydrocarbon and formation water represents this condition in the petroleum reservoir.

The second criterion requires the presence of an agent called emulsifiers, possessing partial solubility in both phases. The class of compounds that represents these agents generally possess functional groups, and they confer bipolarity to these intermediary molecules. Figure 2.4 is a schematic diagram showing the nature of a bipolar molecule. The chemistry and stabilising properties of emulsifiers including asphaltene will be discussed later.

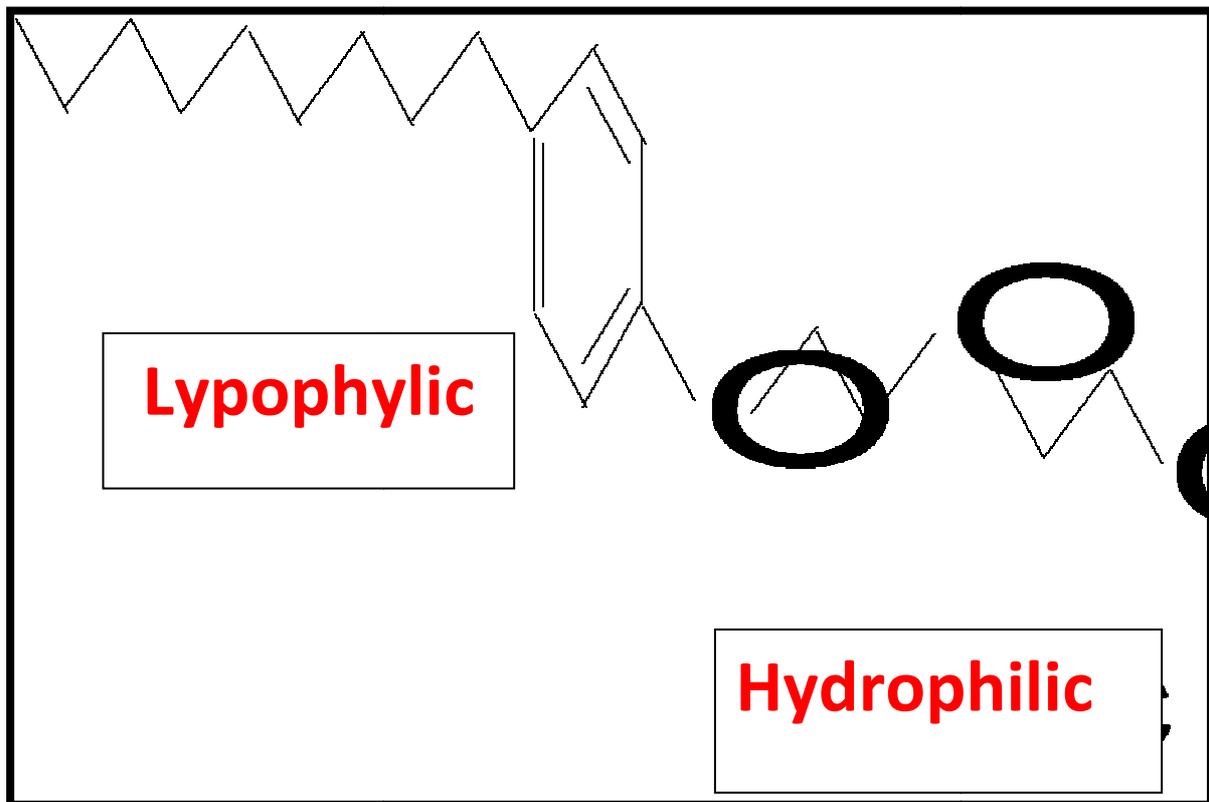


Figure 2.4: Bipolar Nature of an Emulsifier²

Finally, regions of high pressure drops and turbulence constitute the third criteria needed for emulsion formation.⁹ Figure 2.1 shows the various regions in a petroleum production system where high shear is experienced by flowing fluid mixture. As the crude passes through chokes, wellhead valves etc. extreme mixing conditions are experienced at the pressure gradient and this forms new water-oil (W/O) interfaces. The more shearing action (turbulent flow) applied to the oil-water mixture, the more the water will be divided into smaller droplets, and the more stable the emulsion. Hence the intensity of shear is therefore the main factor in determining how stable the emulsion will be and consequently how

difficult it will be to treat.⁹

2.2 Chemistry and Stabilizing properties of Emulsifiers.

Emulsifiers are surface active materials found in the crude oil or added to it as other production chemicals or in the case of surfactant flooding². The type as well as the amount of an emulsifier has an immediate effect on the type and stability of the resulting emulsion. An emulsifier tends to be soluble in one of the liquid phases. It thus concentrates at the interface. An example of such is Naphthoic acid. A picture of Naphthenic acid acting as an emulsifier on a water droplet dispersed in oil is described in Figure 2.5. At equilibrium, the bipolar molecules are aligned with their nonpolar alkyl (C_nH_{2n+2}) group extending into the non polar oil phase, and their polar groups in the polar water phase. This arrangement represents a state of stability that is favoured by group interactions and static conditions of temperature and pressure. As the continuous phase drains between two dispersed droplets, they stretch and surface tension decreases with increase in emulsifier concentration. Stability is maintained by transport of emulsifiers into the stretched film, lowering surface tension and reducing oil drainage. Figure 2.6 shows a schematic representation of two water droplets prevented from coalescing due to the action of emulsifiers.

The action of emulsifier can be visualized as one or more of the following^{22, 23}

1. It decreases the interfacial tension of the water droplet, thus causing smaller droplets to form and hence more stable emulsions result.
2. It forms a skin layer around the droplets that keeps them from coalescing into larger droplets when they collide thus promotes the formation of a stable emulsion.
3. The emulsifier molecules may be polar and align themselves in such a way as to produce similar electric charges on the surfaces of the droplets which results in strong repulsions between them, thereby reducing oil water separation.

Furthermore, four types of emulsifiers which have a stabilizing effect on the interfacial film between oil and water phases may be encountered³². These are:

1. Anionic emulsifiers, in which the water soluble group is positive.
2. Cationic emulsifiers, in which the water soluble group is positive
3. Nonionic emulsifiers, in which the water soluble remains uncharged
4. Amphoteric emulsifiers, in which the water soluble groups are both positively and negatively charged.

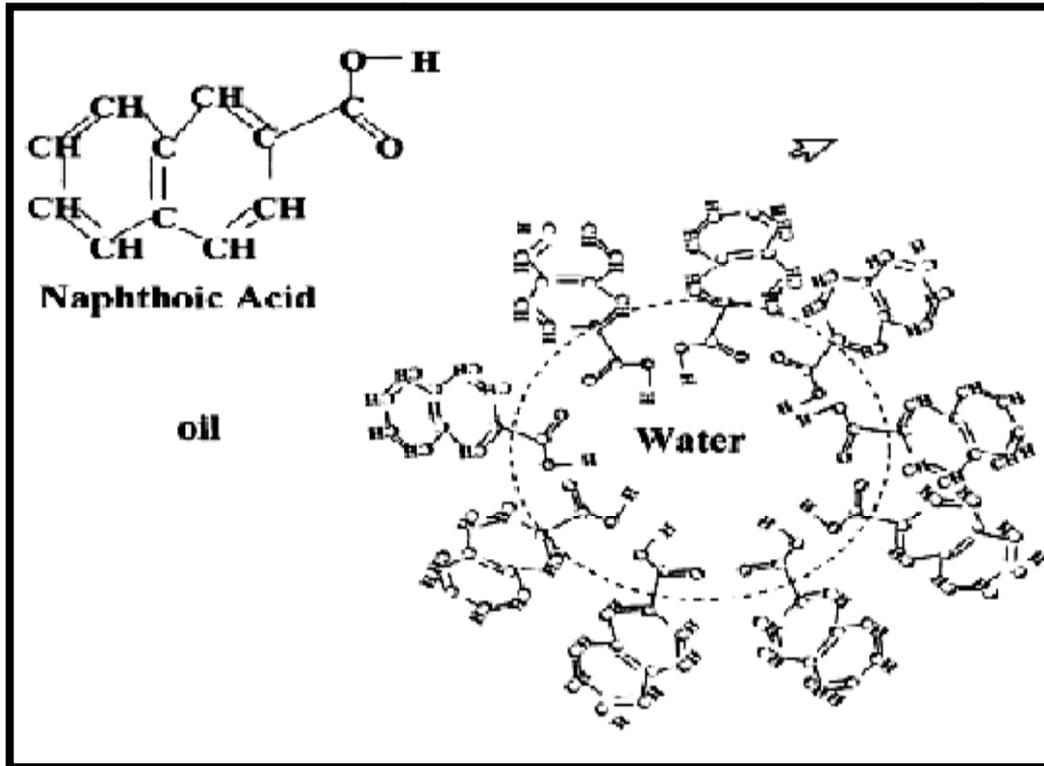


Figure 2.5: Stabilising effect of Naphthoic acid on a water droplet in oil ²

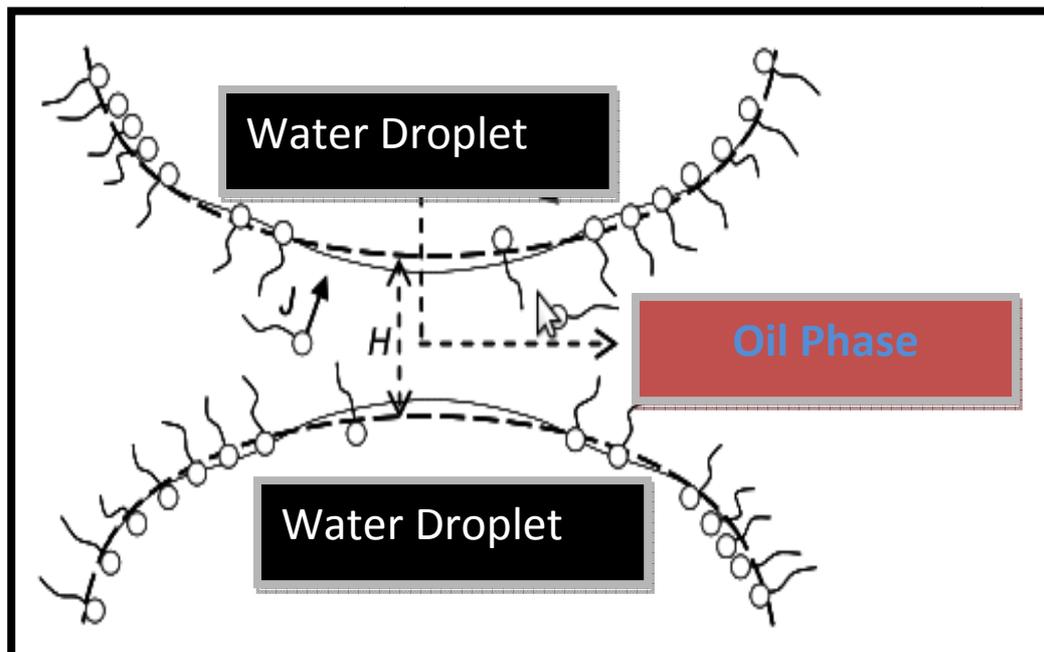


Figure 2.6: Effect of emulsifiers on two water droplets in dispersion ¹⁰

Schematic diagram showing these descriptions is seen in Figure 2.7. As already mentioned, typical examples of emulsifiers in the petroleum industry includes resins, asphaltene, metal porphyrin complexes and fatty carboxylic acids, which are all part of the higher boiling polar fraction of crude oil. Inorganic solids which also act as emulsifiers are silts, reservoir fines, scale deposits etc.

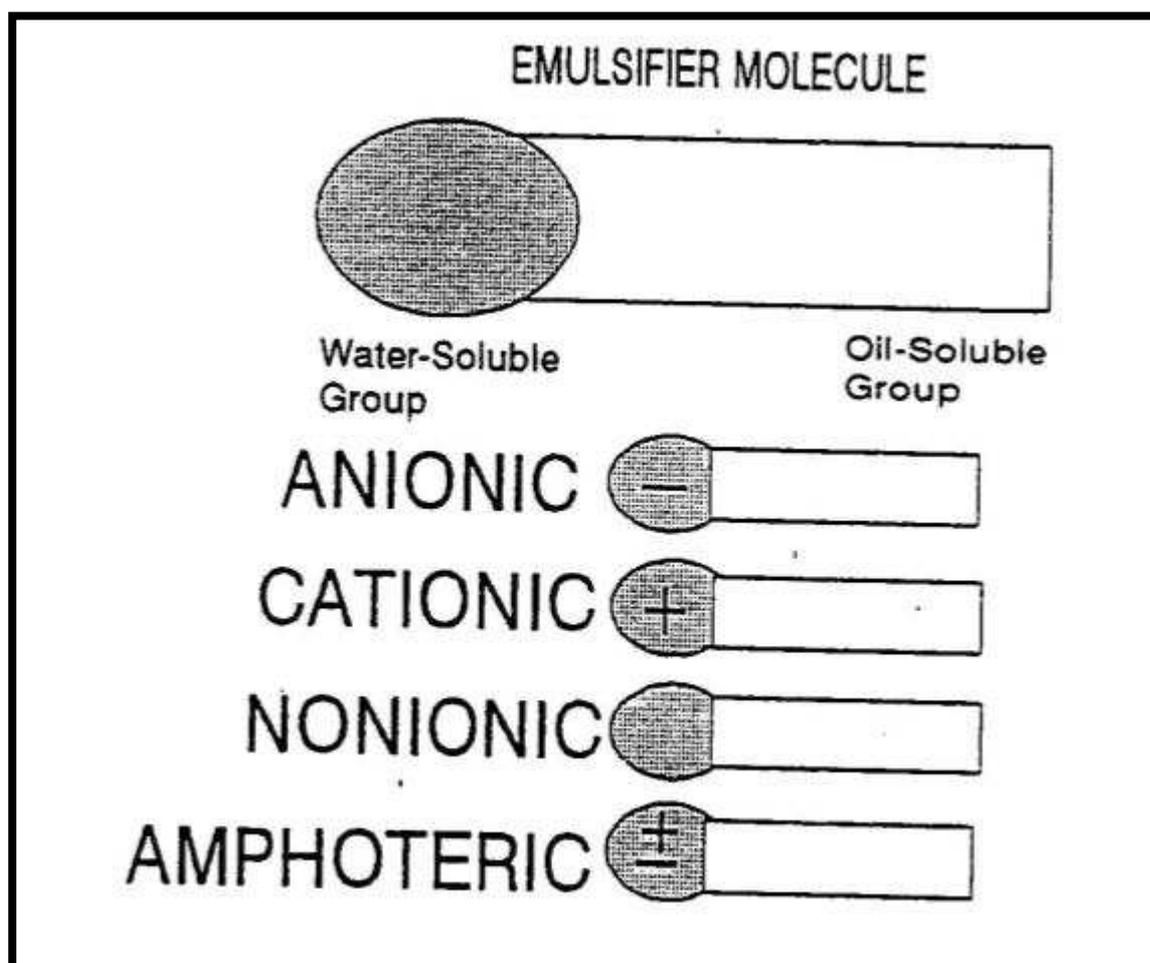


Figure 2.7: Types of Emulsifiers ³²

2.2.1 Asphaltenes

Asphaltenes are dark brown to black amorphous powder and have a specific gravity just above unity, and molar masses of 1000 to 10,000 g/mol.³² They have no definite melting point but decompose when the temperature exceeds 300-400°C. Many researches have shown that changing in pressure, temperature and oil composition can cause asphaltene precipitation. They are the non-volatile and polar fraction of petroleum that is insoluble in n-alkanes such as n-pentane or n-heptane. The polarity, molecular weight and aromaticity of

precipitated asphaltenes rise linearly with carbon number of n-alkane precipitant. Figure 2.2 represents the range of heavy compounds precipitated by mixing crude oil with n-pentane and n-heptane.

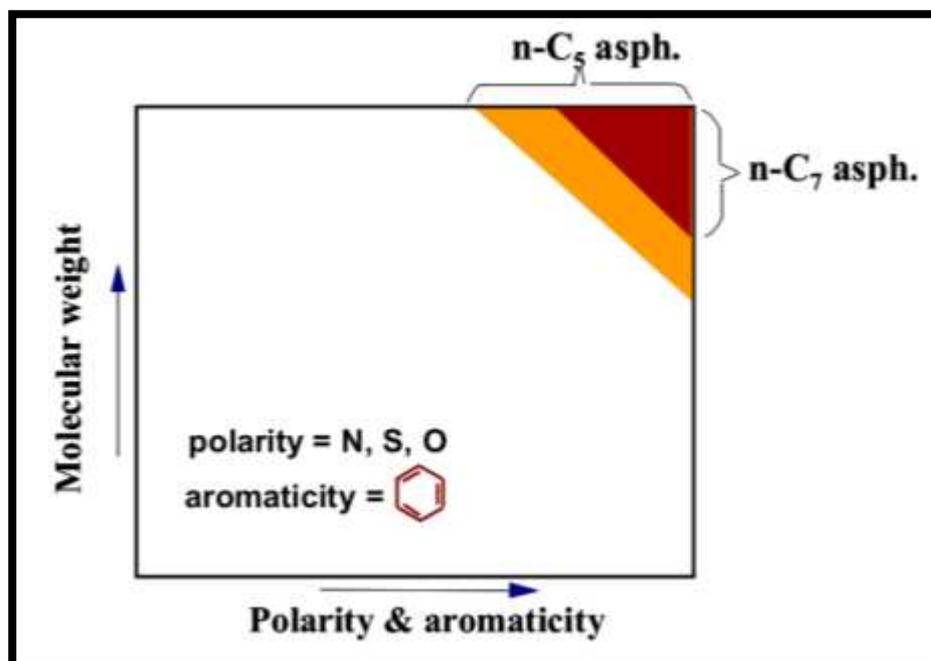


Figure 2.8: Hypothetical diagram representing the molecular characteristics of the asphaltenes precipitated from petroleum by n-alkane addition ³²

Asphaltenes are interfacially active substances that exist predominantly in the crude oil colloids. The interfacial active components of the asphaltenes are most active either directly before or during the start of flocculation. ²³ Asphaltenes also contain metals including nickel, vanadium and iron. The structure of asphaltenes is not well understood, but several possible structures have been proposed to explain the composition and properties of the asphaltene fraction. The structures for asphaltene are shown in Figure 2.9, which accounts for nitrogen, sulphur and oxygen in asphaltenes, excluding the organometallic. Asphaltenes are believed to be suspended as a microcolloid in the crude oil, consisting of particles of about 3 nm. Each particle consists of one or more aromatic sheets of asphaltene monomers, with adsorbed resins acting as surfactants to stabilize the colloidal suspension. The molecules are believed to be held together with π -bonds, hydrogen bonds, and electron donor-acceptor bonds. The solubility of asphaltene in the oil phase is one of the key determining factors on the emulsion-stabilizing role of asphaltenes.

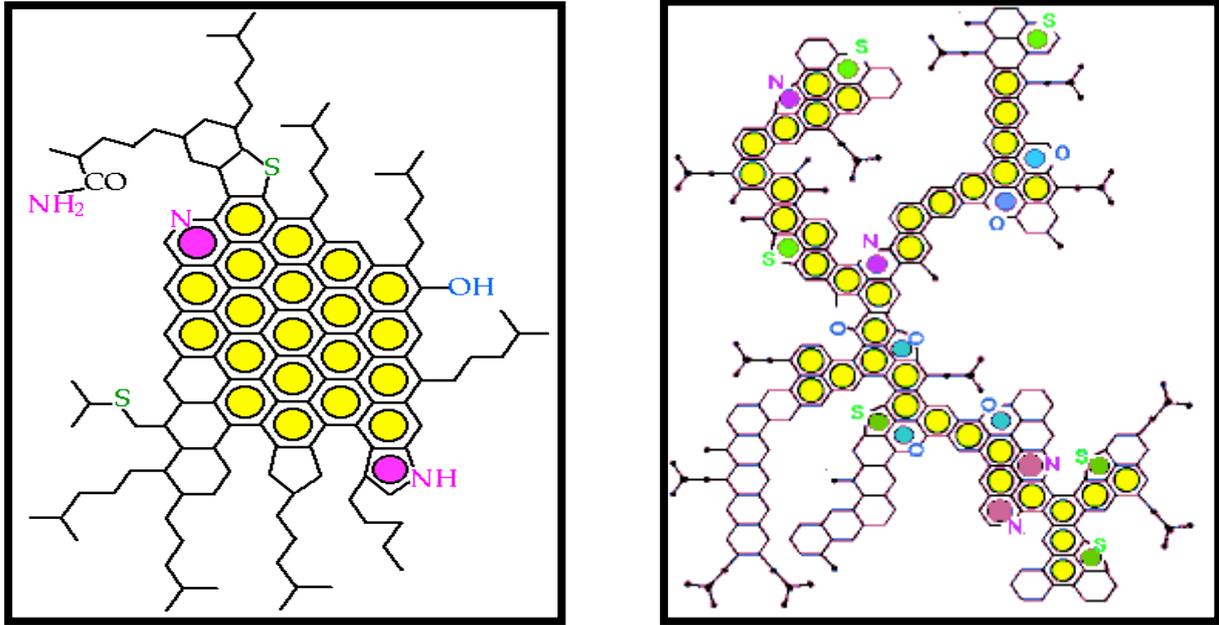


Figure 2.9: Structures of asphaltene²⁰

Since the state of Asphaltene has an effect on emulsion stability properties several studies have been done to measure the solubility of asphaltene in crude oil. One of these thermodynamic models is Florry-Haggins model.⁷²

$$S = \exp \left(-1 + V_a \left\{ \frac{1}{V_o} - \frac{(\delta_a - \delta_o)^2}{RT} \right\} \right) \quad (2.1)$$

Where S is the solubility of asphaltenes in the crude oil, V_a and δ_a is the molar volume and solubility parameter of the asphaltenes. V_o and δ_o are the molar volume and solubility parameter of the oil, and T is the temperature in °C. The amount of asphaltenes, S present in a particular crude oil sample at standard condition of 25°C and 1 atm can be determined using the ASTM method D2007. The values of S, T, and R are substituted into Equation 2.1 and assuming molar volume of asphaltene, V_a as 1 m³/kgmol. Also the values of oil molar volume and solubility parameter, V_o and δ_o can be obtained in correlations relating them to the reservoir pressure, temperature and composition in reference 79. The solubility of asphaltenes in the oil can then be estimated at any thermodynamic condition since its solubility parameter, δ_a is known. Figure 2.11 shows a pressure-solubility curve of asphaltene for a particular reservoir in Saudi Arabia.

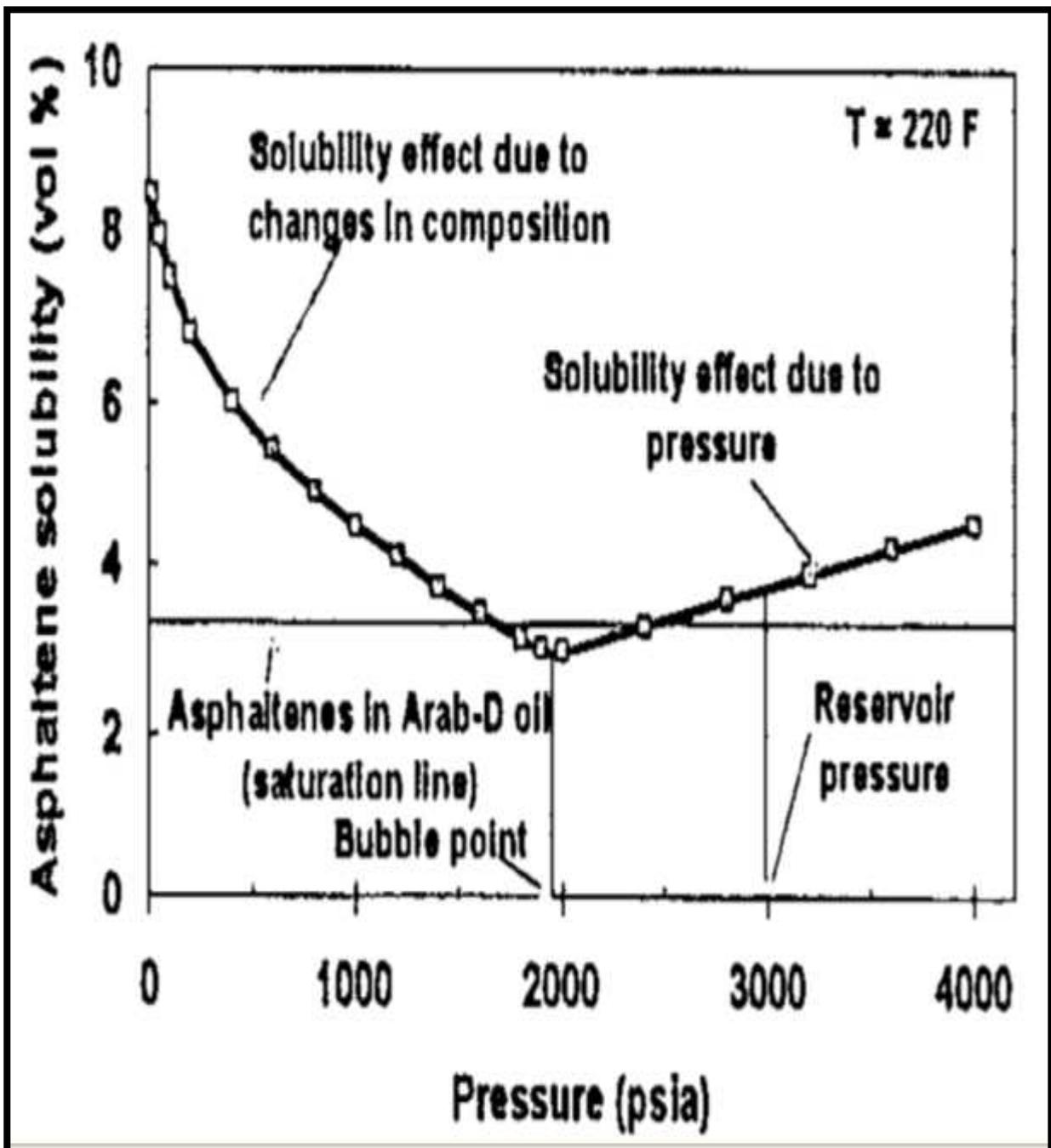


Figure: 2.11: Asphaltene Solubility in a crude oil as a function of pressure⁶.

2.3 Morphology of Emulsion.

An emulsion can be classified according to different criteria. In the classic type of emulsion, the two immiscible liquids involved are water and oil. As should be clear from the foregoing discussion, either of these two liquids can be defined as the dispersed phase. The dispersed phase is sometimes referred to as internal phase, and the continuous phase as the external phase. Depending on which one is the dispersed phase, emulsions of quite different

physical characteristics are usually obtained.⁴ The following types of emulsions are now readily distinguished in principle:

- Oil-in-water (O/W) for oil droplets dispersed in water
- Water-in-oil (W/O) for water droplets dispersed in oil
- Oil-in-water-in-oil (O/W/O) and
- Water-in-oil-water (W/O/W).

The last two types are called multiple emulsions and are also present in some cases in which the dispersed droplets themselves contain even more finely dispersed droplets of a separate phase. Thus, there may occur oil-dispersed-in- water-dispersed-in-oil (O/W/O) and water-dispersed-in-oil-dispersed-in-water (W/O/W) multiple emulsions. More complicated multiple emulsions are also possible. The morphology of emulsion means its presence as either W/O, O/W or multiple emulsions. It is the most basic characteristic of an emulsion, and there are usually some qualitative procedures that can be used to distinguish emulsion type. These are based on the observation of a physical phenomenon that depends on the prevailing polarity in the continuous phase.²⁹ The morphologies of some different type of emulsions are shown in Figure 2.11.

Contacting a drop of the emulsion with water or oil and observing whether the external phase is miscible or not with it is one of the simple methods that can be used to distinguish between simple and multiple emulsions. However, results from this type of test are sometimes unclear and do not allow to differentiate between them. The electrical conductivity measurements can also be used to determine the type of emulsion. The aqueous phase in an emulsion usually contains electrolytes and in most cases non-polar liquids exhibit very low electrical conductivity. Therefore, the conductivity of emulsion is very high when the aqueous phase is continuous and very low when the oil is the continuous phase.³⁴

Moreover, the optical microscopy method can also be used to discern between simple and multiple emulsions because of the difference between the water and oil phase under microscopy observation.⁴

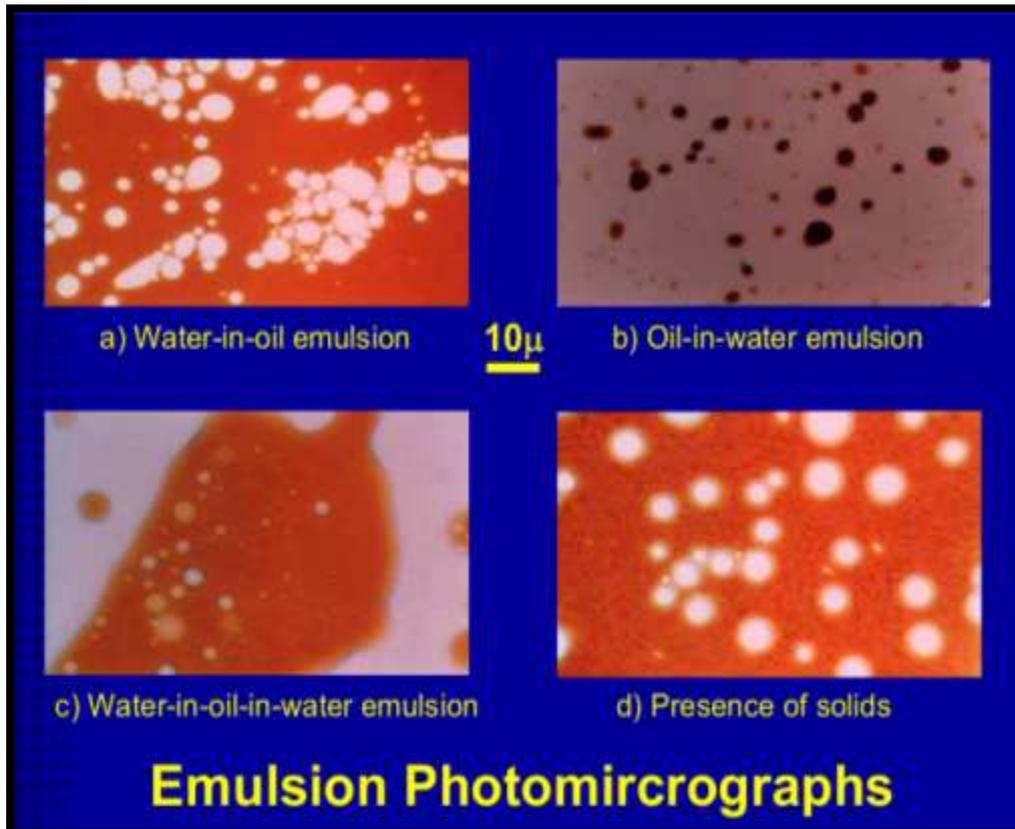


Figure 2.12: Photomicrograph of emulsion types ^{1,38}

2.3.1 External and Internal Phase of an Emulsion

The description of the two emulsion forms (water-in-oil, and oil-in-water) represents symmetrical images. What factors determine the internal and external phases? Given the oil and water phases, the type of emulsion that is formed depends on a number of factors.^{1, 35, 32} As a rule of thumb, when the volume fraction of one phase is very small compared with the other, then the phase that has the smaller fraction is the dispersed phase and the other will form the continuous phase. When the phase volume ratio is close to one, then other factors will determine the type of emulsion formed.¹ According to some other researchers, factors determining the type of emulsion formed are more than just phase volume ratios as said by Sunil Kokal.¹ The strength of the interactions of polar groups of one bipolar group and another, or the polar phase and interaction of non-polar groups with one another, or non-polar phase, helps determines the type of emulsion formed. This phenomenon constitutes the hydrophile-lipophile balance, (HLB) described in Figure 2.12

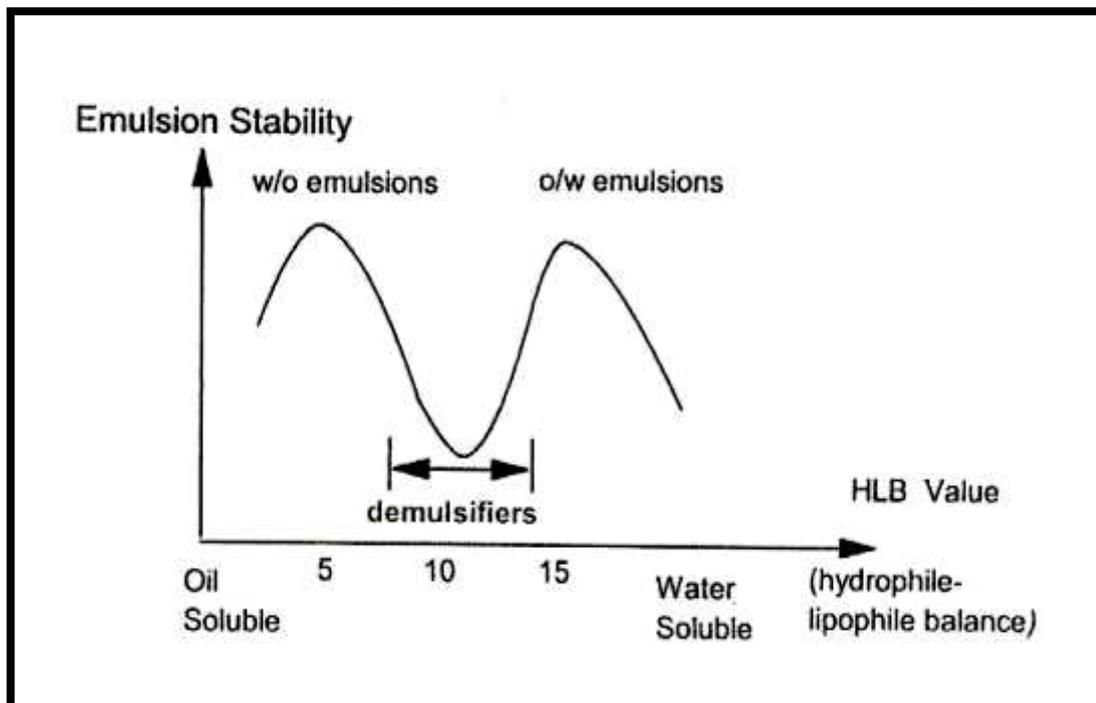


Figure 2.13: Hydrophilic-Lipophylic Balance, HLB ³⁴

The HLB of a surfactant is a measure of the degree to which it is water phase soluble (Hydrophilic) or oil phase soluble.³⁴ Surface active molecules with similar structures (homologous) show stability maxima corresponding to w/o emulsifiers and o/w emulsifiers. Between these two, there is a stability minimum whether neither hydrophilic nor hydrophobic groups dominate the interfacial region. HLB is determined by calculating values for the different regions of the molecules, as described by Griffin in 1949 and 1954. The HLB value can be used to predict the surfactant properties of a molecule:

- A value from 0 to 3 indicates an anti-foaming agent
- A value from 4 to 6 indicates a W/O (water in oil) emulsifier
- A value from 7 to 9 indicates a wetting agent
- A value from 8 to 18 indicates an O/W (oil in water) emulsifier
- A value from 13 to 15 is typical of detergents

According to Bancroft³², emulsion type depends more on the nature of the emulsifying agent than on the relative proportions of oil or water present or the methodology of preparing emulsion. The phase in which an emulsifier is more soluble constitutes the continuous phase. In O/W emulsions – emulsifying agents are more soluble in water than in oil (High HLB

surfactants). In W/O emulsions – emulsifying agents are more soluble in oil than in water (Low HLB surfactants).³⁶

2.3.2 Phase Inversion in Emulsion

The phenomenon of phase inversion refers to the process whereby the dispersed and continuous phases of an emulsion are inverted or suddenly change form, from O/W emulsion to W/O emulsion or vice versa. Phase inversion in emulsion can be one of two types: transitional inversion and catastrophic inversion. The former is induced by changing factors, such as temperature or salinity, which affect the affinity of surfactant towards the two phases. Changing the HLB of an emulsion, which depends on the nature and concentration of emulsifying agents, can lead to inversion. The catastrophic inversion is induced by increasing the volume fraction of the dispersed phase. This inversion usually occurs when the internal volume fraction exceeds some specific value, usually close to the limit of critical close-packing, 0.64 for random packing³⁷ and 0.74 for ordered packing⁴. Above this limit, droplets are compressed against each other and the interfaces are deformed causing the emulsion to adopt a foam-like structure. Arirachakaran et al³⁸ conducted an extensive study on oil-water flow in horizontal pipes for various viscosity values. They described the morphology of emulsion as function of water fraction as shown in Figure 2.11. It was shown that inversion can be achieved by increasing water cut where the system has no surfactant added to the emulsion and is maintained at constant temperature and shear.

There are other factors that have a bearing on phase inversion, and these include the nature and concentration of the emulsifiers, physical influences such as temperature or the application of mechanical shear. The emulsification protocol characteristics which indicate the way the emulsion is made or modified or how the formulation or composition are changed as a function of time or space, can also be considered to be among the factors that phase inversion depends on.^{39, 40}

2.4 Macroscopic Physical Behaviour of Emulsion

Among the important properties of emulsions are their flow properties, in other words their rheology. Rheology in general is defined as the study of the deformation and flow of materials under influence of an applied shear stress. The rheological behaviour of emulsions has been of great interest not only for fundamental scientific understanding but also for practical industrial applications.^{42, 43}

2.4.1 Emulsion Behaviour under Shear Stress

Viscosity effects exhibited by emulsions tend to be complicated due to their variable composition, average emulsion size, and the individual viscosities of their phases. The rheological behaviour of an emulsion can be either Newtonian or non-Newtonian depending upon its composition.² Factors affecting the shear viscosity of an emulsion are the viscosity of the continuous phase, the dispersed phase content (ϕ), the viscosity of the dispersed phase, shear rate, temperature and the mean size and size distribution of droplets. At low to moderate values of dispersed phase concentration, emulsions generally exhibit Newtonian behaviour. In the high concentration range, emulsions behave as either shear-thinning fluids or thixotropic.⁴ Two factors that determine whether or not these systems exhibit dilatant or thixotropic behaviour include the concentration of bipolar emulsifiers present at the interface and the equilibrium vapour pressure of the internal phase. In the case of bipolar emulsifier concentration, a possibility exists for a multilayer emulsion to redistribute the bipolar emulsifier when the system is subjected to shearing forces. Figure 2.13 shows a velocity profile diagram of emulsion and some other common fluids and materials.

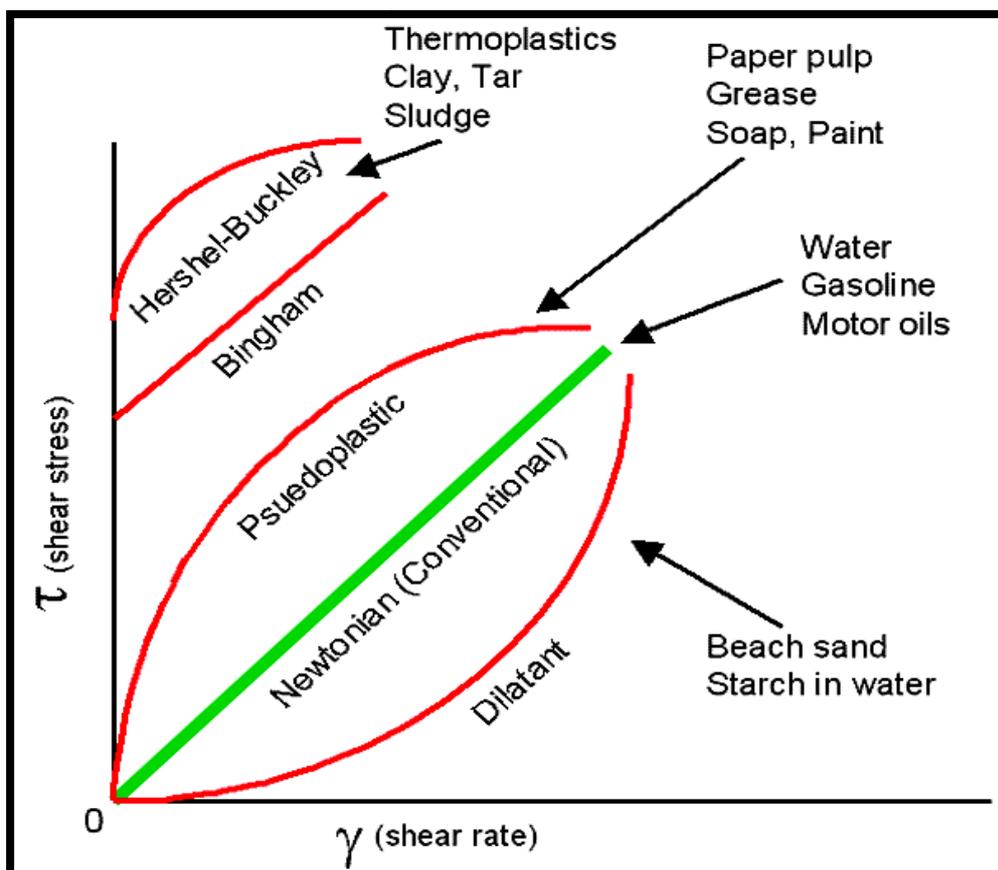


Figure 2.14: Shear stress vs. Shear rate for various fluids ⁴

2.4.1.1 Emulsion Viscosity models

Since emulsion viscosity is directly proportional to the continuous phase viscosity (η_c), most of the viscosity correlation equations proposed in literature are written in terms of relative viscosity (η_r) where:

$$\eta_r = \frac{\eta}{\eta_c} \quad (2.2)$$

One of the earliest studies developed by Taylor⁴⁴ from hydrodynamic considerations on suspensions of hard spheres considered the effect of both phases on the viscosity of emulsion with small concentration of dispersed spherical drops:

$$\eta_r = 1 + \left[0.25 \left(\frac{K+0.4}{K+1} \right) \right] \varphi \quad (2.3)$$

Where, K is the ratio of the viscosity of the dispersed phase to the continuous phase.

$$K = \frac{\eta_D}{\eta_c} \quad (2.4)$$

As stated earlier, emulsions usually exhibit non-Newtonian behaviour (shear-thinning fluids) at higher dispersed phase content. For this type of emulsion an empirical approach to correlate the viscosity data is needed. The corrected equation of Pal and Rhodes can be used⁴⁵:

$$\eta_r = \frac{\eta}{\eta_c} = \left[1 + \frac{(\varphi/\varphi^*)}{1.187 - (\varphi/\varphi^*)} \right]^{2.49} \quad (2.5)$$

here φ^* is the dispersed phase concentration at which the relative viscosity $\eta_r = 100$ and must be determined experimentally. The equation was based on an extensive amount of experimental data collected and can be used for both Newtonian and non-Newtonian emulsions.

2.4.2 Temperature Effects on Emulsions

Temperature effects on emulsion aggregate are quite dramatic since the partial pressures of the internal phase solvents increase or decrease in response to temperature shifts up or down respectively.³ Under conditions of constant temperature and pressure, emulsion

systems maintain a continuous equilibrium transfer of internal phase solvent between emulsion aggregates. When the temperature is increased, this equilibrium balance is shifted, and a more rapid interchange occurs. If the temperature becomes great enough, the solute molecules being transferred will obtain sufficient energy to escape the system, and the internal phase will be depleted of solvent. Meanwhile the external phase is also being depleted of some solvent, and the differential rate of solvent loss between the two phases determines the overall system stability.

There exist a potential non emulsified reservoir for the effective combination of solvent molecules at the interface between the emulsion aggregates and at the interface between the external and air.³ These reservoirs are extremely unstable since they are not surrounded by bipolar emulsifiers, and they can act as intermediary solvent sinks or as a coalescing locus. The larger these reservoirs becomes, the less stable they become. Therefore, when the temperature is increased, the solvent collision frequencies and energies increase, and the size of the reservoirs increase. Meanwhile, the external phase vapour pressure (molecular velocities) increases until the molecular momentum expressed over a distance per given time period is sufficient to overcome the surface tension of the system. The combined result is an increase in the relative size of the non-emulsified reservoirs, a decrease in the size of the emulsion aggregates, and reduction in the volume of the external phase. This process suggests that the effects of temperature increase results in a less tight emulsion (smaller) and higher exchange rates of solvent.

2.4.3 Gravitational Effects on Emulsions

The temperature effects discussed above seem to lead to either solvent depleted systems or tighter (smaller) emulsions, when considered alone, but gravitational factors are overlooked in this discussion. Stoke's law² is used to study the effects of gravity on emulsion aggregate systems. This law is vital to the understanding of emulsion behaviour.² The Stoke's law equation is as follows:

$$V = \frac{2gr^2(\rho_1 - \rho_2)}{9\eta_c} \quad (2.6)$$

where:

r = is the radius of the sphere.

- ρ_1 = density of sphere
- ρ_2 = density of medium
- η_c = viscosity of the continuous phase

The combination of this law and the discussion of the effects of temperature clarify the behaviour of an aggregate emulsion system. When the temperature is raised the sizes of the solvent reservoirs increase, and the emulsion sizes decrease. The reservoirs are pure solvent, while the emulsions are combinations of solute and solvent.² The reservoir's density is therefore less than that of the emulsion, and consequently the ratio of phase density is also less. Thus, in accordance with Stokes' law, it is expected that the differential densities ($\rho_1 - \rho_2$) will oppose a settling velocity (V) increase. However, the r^2 term in the equation will have a more dramatic effect on the settling velocity V than the differential densities. Thus, it can be seen that the dynamics of diffusion and the effects of gravity and temperature combine to have a huge effect on the mechanism of emulsion formation.

Finally, the viscosity term in Stokes' equation can be examined in terms of the effect of temperature. A molecular kinetic theory expression for the behaviour of viscosity with temperature is given by the following expression:

$$\eta_c = A e^{\frac{\Delta E}{RT}} \quad (2.7)$$

where:

- A = constant
- ΔE = change in activation energy.
- R = Ideal gas constant
- T = Temperature of fluid.

Thus it can be said that as the temperature increases, the viscosity is exponentially lowered, which leads to an increase in the settling velocity V in accordance with Stokes' law

2.4.4 Electromagnetic Field Effects on Emulsions

Emulsions are susceptible to forces exerted by electric fields, but the strength of the electric field effects is dependent upon the external phase's ability to conduct electricity.² Thus, a polar external phase emulsion is more susceptible to an externally applied current

than an externally nonpolar emulsion. From the description of oil/internal-water/external emulsions like the stearic acids system, an overall negative emulsion surface is suspected.

When an electric current is supplied to a stearic acid emulsion of oil in water, a migration of the counterbalance cation to the anode (negative pole) and the anionic emulsion aggregate to the cathode (positive pole) is expected. This migration is possible because the water phase is conductive to electricity. However, in the case of water-in-oil emulsion, the non polar oil external phase is nearly an insulator since its resistivity is extremely high. Therefore, the migration of ions as a result of current flowing through the external phase is minimized.

Although current is not conducted to any significant degree through an oil external emulsion, the electric field is still present between the capacitor plates depicted in Figure 2.14. When a changing field force vector is imposed across the capacitor plates as it is with an alternating current source, the relatively small cations in the water-in-oil emulsion are caused to vibrate more rapidly than the larger anions. This displacement from an equilibrium position causes a deformation of the emulsion, and a destabilization of the interface surface. Figure 2.15 shows the effects of a high alternating current on the shape of an oil external emulsion. It is noted that a frequently changing electric vector distorts the spherical geometry and by doing so destabilizes the emulsion surface.

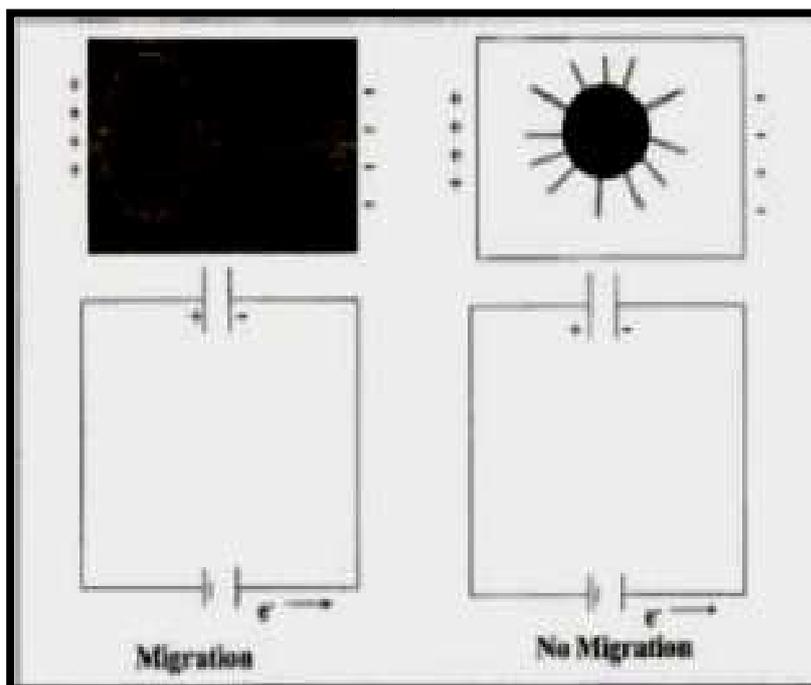


Figure 2.15 Migration of ions in an electric field ²

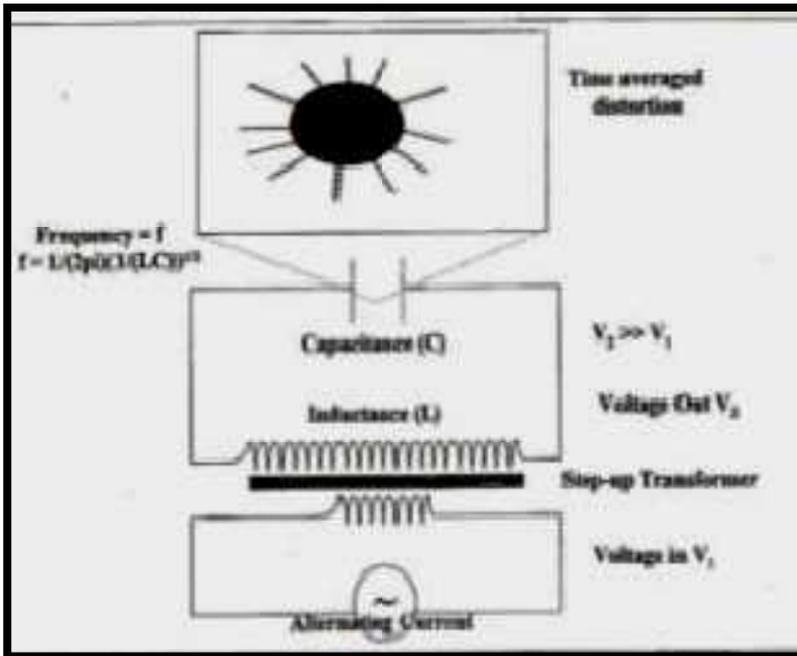


Figure 2.16 Effect of high alternating current on the shape of oil-external emulsion ²

2.5. Emulsion Stability

Most emulsions are, by nature, thermodynamically unstable; that is; they tend to separate into two distinct phases or layers over time due to the high interfacial area and hence total surface energy of the system.³⁵ Therefore, the emulsion characteristics (drop size distribution, mean drop size and other properties) will also change with the time. The stability of emulsion is characterized by the time-dependent behaviour of its basic parameters. Figure 2.16 demonstrates how flocculation and coalescence happens. Various emulsion breakdown

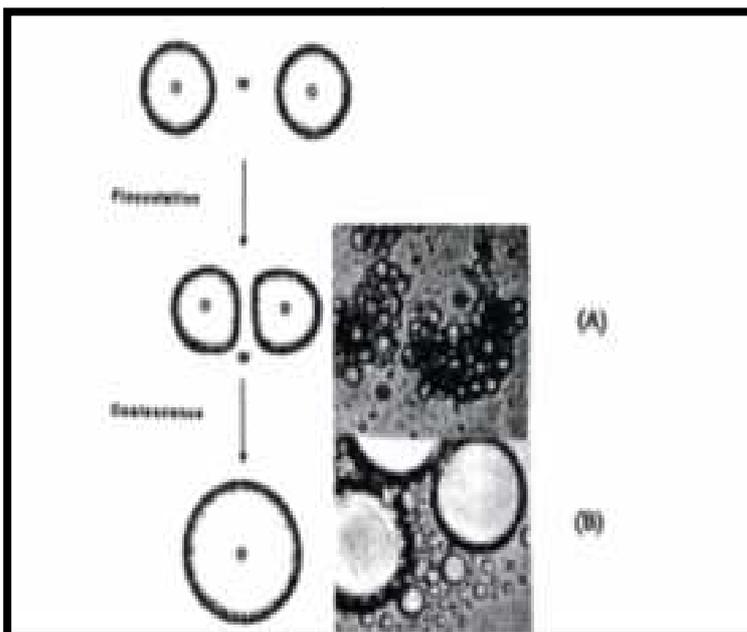


Figure 2.17: Destabilisation mechanism showing flocculation and coalescence³⁵

processes can be identified. Some of these instability mechanisms that lead to phase separation in emulsions are represented schematically in Figure 2.13. These physical instability mechanisms are Sedimentation and Creaming, Aggregation and Coalescence. The theory of these physical breakdown processes will be briefly summarized below. In addition to these physical instability mechanisms, mass-transfer processes, such as Ostwald or Compositional ripening, can also take place in emulsions and their basic theory can be found elsewhere.^{46, 47}

2.5.1 Aggregation

Aggregation occurs when droplets stay very close to one another and form flocs. In other words, it is the process of forming a group of droplets that are held together. This process is sometimes referred to as coagulation or flocculation. The approach that is most often referred to in emulsion literature to explain emulsion interaction is the so-called DLVO theory, developed by Derjaguin, Landau⁴⁸, and independently, Verwey and Overbeek⁴⁹, based on the long range London- van der Waals attractive forces and repulsive electrostatic forces between two close spheres.

For the case of two spherical particles, Hamaker⁵⁰ derived an expression for the London-van der Waals attraction by integrating the interaction energy dU_A over the total volumes of the two particles to obtain:

$$U_A = -\frac{A}{6} \left[\frac{2a^2}{h^2 + 4ah} + \frac{2a^2}{h^2 + 4ah + 4a^2} + \ln \left(\frac{2a^2}{h^2 + 4ah + 4a^2} \right) \right] \quad (2.8)$$

Where $h = H - 2a$

Here a is particle radius, H is the center-center separation distance and h is the minimum distance between the two approaching surfaces. If $h \ll a$ Eq. 2.8 can be simplified to:

$$U_A = \frac{Aa}{12h} \quad (2.9)$$

In these expressions, A is the so-called Hamaker constant and depends on the dielectric properties of the two interacting particles and the intervening medium. When such properties are known, one can calculate Hamaker constant. For two identical particles (subscript 1) interacting across a medium (subscript 2), Hamaker's constant is calculated as below:

$$A = \frac{A_1}{h^6} + \frac{A_2}{h^9} + \frac{A_3}{h^{12}} \quad (2.11)$$

The hydrocarbon-water Hamaker constant usually has values in the range between 3 and $7 \times 10^{-21} \text{ J}$. On the other hand, the electrostatic interaction energy U_E for two approaching spheres exhibiting electrical double layers cannot be resolved analytically, and only approximate expressions have been provided.

$$U_E = \frac{C_0 N_A z^2 e_0^2 \psi_0^2}{2 \kappa} \exp(-\kappa h) \quad (2.12)$$

Here C_0 is the bulk concentration of the ionic specie, N_A is the Avogadro's number ($6.02 \times 10^{23} \text{ mol}^{-1}$), $X = \text{Tanh}(ze_0\psi_0/4kt)$ with z being the magnitude of the ion valence, e_0 the electronic charge ($1.60 \times 10^{-19} \text{ C}$), κ^{-1} the so-called Debye length, which is a measure of the electrical double layer thickness, and ψ_0 the electrical potential at the interfaces. Eq. 2.15 is valid when the radius is much larger than the Debye length, i.e., $\kappa R \gg 1$. Now, the overall interaction energy U is given by:

$$U = U_A + U_E \quad (2.13)$$

Here U_A and U_E are the attraction and repulsion energy respectively. Figure 2.17 shows a typical profile for U that can be calculated accordingly²⁹. When two droplets are very close ($h \rightarrow 0$), attractive forces dominate and droplets are expected to aggregate irreversibly,

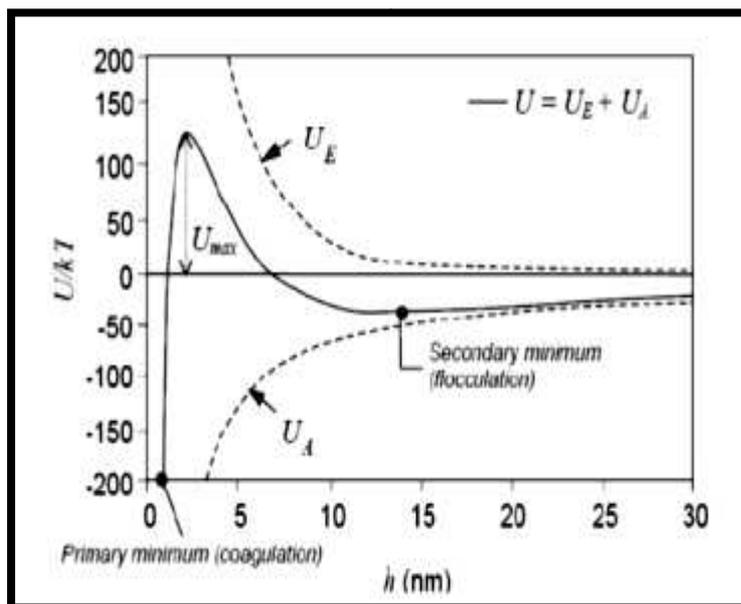


Figure 2.18: Energy of interaction between two droplets²⁹

which is referred to as coagulation. When h reaches secondary energy minimum, droplets may form aggregates reversibly that can be re-dispersed which is usually termed flocculation. Generally aggregation is used to describe either coagulation or flocculation.

If $U_{\max} \leq 0$, there is no energy barrier to prevent the two surfaces from approaching each other. In this case, so-called fast aggregation takes place. In contrast, if $U_{\max} > 0$, an energy barrier must be overcome to achieve aggregation. This process is usually referred to as slow aggregation. The DLVO theory discussed above provides the basis to understand the role of inter-particle interactions on aggregation and emulsion stability. However, it is strictly valid in a reduced number of practical cases, particularly when emulsions are of the O/W type and are stabilized by small-molecule ionic surfactants⁵³. In the case of W/O emulsion, the theory can be extended to account for the steric repulsion mechanism, in which the molecules adsorbed at the interfaces are large and provide a physical barrier against flocculation and coalescence. In this case, an additional contribution to U due to steric repulsion, U_S , must be considered, i.e.

$$U = U_A + U_E + U_S \quad (2.14)$$

U_A and U_E are affected by the presence of the adsorbed molecules at the interfaces. U_S can be defined by two contributions, (a) a repulsive energy due to volume restrictions UVR, and (b) an energy of mixing U_M , associated with the osmotic pressure that arises when the overlapping region of two approaching interfaces stabilized by macromolecules is depleted of solvent molecules⁵⁴. Solvency is another important factor that has a significant effect on the overall interaction energy because it strongly affects the energy of mixing U_M . Another contribution to the overall energy of interaction arises in the presence of non-adsorbing macromolecules in the bulk phase, due to a phenomenon referred to as depletion interaction.²⁹

2.5.2 Coalescence

Coalescence is defined as the combination of two or several droplets to form a large drop. It takes place when the thin film of continuous phase between two drops breaks and they fuse rapidly to form a single droplet. The stability of an emulsion system, therefore, depends on the rate of coalescence and it is obvious that the properties of this film will determine the stability of the emulsion. Many authors have provided notable theoretical and

experimental efforts to provide better understanding of the formation and thinning of a flat film between drops. Weber number is imported here, which refers the internal Laplace pressure P_L and external stress τ_{ext} exerted upon the doublet of drops:

$$W_e = \frac{\tau_{ext}}{P_L} \quad (2.15)$$

If $W_e \ll 1$, the stability criterion is suggested as⁵³:

$$\frac{d^2 U(h)}{dh^2} - \frac{dU(h)}{hdh} > -C \frac{\sigma}{R^2} \quad (2.16)$$

Here $U(h)$ is the interaction and repulsion energy in DLVO theory, $C > 0$ is a constant, σ is interfacial tension. From Eq. 2.19, coalescence would only take place if the drops get close enough as to reach the primary minimum (in Figure 2.5). When $W_e \gg 1$, large flat films will form. Deformation is favoured by large drop sizes and low interfacial tensions. In this case, coalescence is preceded by the drainage of the liquid present in the film. For the symmetrical drainage of a film of Newtonian liquid with viscosity η between two flat disks of radii r and separated by a distance h ($h/r \ll 1$) with the pressure difference ΔP , the rate of thinning of the film $-dh/dt$ is⁵⁴

$$-\frac{dh}{dt} = \frac{2r\Delta P}{3\eta} \left(\frac{h}{r}\right)^3 \quad (2.17)$$

If the electrostatic repulsion is strong enough as to balance vander Waals attraction and the capillary pressure, the film is referred to as common black film ($h \sim 20-30$ nm). If the electrostatic repulsion is weak and short range repulsive forces dominate instead, the film is very thin ($h \sim 5-10$ nm) and is referred to as Newton black film.²⁹

2.5.3 Sedimentation and Creaming

Creaming is the opposite of sedimentation that results from density difference between the two liquid phases. The term sedimentation is used if the particles are displaced in the direction in which gravity acts ($\Delta\rho > 0$). Otherwise ($\Delta\rho < 0$), the process is referred to as creaming. The former applies to most W/O emulsions and solid dispersions, whereas the latter applies to most O/W emulsions and bubbles dispersed in liquids²⁹. In both cases, the emulsion can be easily re-dispersed by shaking. If the density differences exist between the dispersed and continuous phases, dispersed droplets experience a vertical force in a

gravitational field. This force is opposed by the fractional drag force. The resulting creaming (or sedimentation) rate of a single droplet can be given by Stokes law as earlier described.

However, this equation has several limitations and is strictly applicable only for non-interacting spherical droplets at low concentration with mono-disperse droplet size distribution (only satisfied for very dilute dispersions) and assumes that there is no internal flow within drops.⁵³ Thus an empirical relation is required taking the effect of the volume fraction of the dispersed phase into account. If the volume fraction of the dispersed phase ϕ is significant (say $\phi > 0.01$), so-called hindered sedimentation takes place. In general, the effect of increasing ϕ is to reduce the sedimentation rate due to hydrodynamic interactions among droplets. This is seen in expressions such that of Richardson and Zaki:⁵⁵

$$\frac{V_{eff}}{V_s} = (1-\phi)^n \quad (2.18)$$

Here ϕ is the volume fraction of the dispersed phase V_{eff} is the effective terminal sedimentation velocity; n is an empirical constant, which ranges from 6.5 to 8.6.

2.6 Demulsification

Crude oils are, in the vast majority of cases, produced together with formation water in the form of water-in-oil emulsions. Crude oil emulsions must be properly treated because of numerous reasons already discussed in chapter one. Two principal approaches of demulsification are chemical and physical methods. The chemical method is the addition of a proper demulsifier to the emulsion, and typical physical treatment techniques include heating, electrical, or a mechanical method such as centrifugation. Heating along with the addition of the demulsifier, which is called thermal chemical method, and electrical techniques, are the most popular methods in the industry.⁵⁷

2.6.1 Chemical Methods

Demulsifier chemicals are designed to neutralize the effect of emulsifying agents, already discussed that stabilize emulsions. They migrate to the oil/water interface, rupture or weaken the rigid film, and hence coalescence of water droplets. Optimum emulsion breaking with a demulsifier requires a properly selected chemical for the given emulsion, adequate

quantity of the chemical, adequate mixing of the chemical in the emulsion, sufficient retention time in emulsion treaters to settle water droplets and addition of physical method to facilitate or completely resolve the emulsions.

2.6.1.1 Action of Demulsifiers

A given demulsifier may operate by one or more of several mechanisms that are proposed to explain their efficiency.⁹

Adsorption: Effective demulsifiers overcome the stabilizing effect by adsorbing at positions vacant as the interfacial film is stretched. Mobility and strong partitioning behavior of the demulsifier to the interface are important factors. Coalescence is the result of rupture of the treated film causing formation of larger droplets.

Displacement: By preferentially adsorbing, they also displace the pre existing stabilizing emulsifiers from the interface and this removes the steric barrier. Interfacial tension and rheology studies confirm that this mechanism thus operates.

Solubility: Modern demulsifiers have very limited solubility in crude oil and initially coats the interface of only a small portion of the water droplet.

Wettability: Solids such as asphalts, fine silts, iron oxides or sulphides collect at the interface. The wetting of these solids by demulsifiers will cause them to be moved into either the oil or the water phases. It is generally more desirable to move inorganic contaminants to the water phase, and this can be achieved with a suitable wetting agent. If wax or asphalt is the main contaminant, it will be more desirable if they are entrained in the oil phase such that water quality is not compromised.

2.6.1.2 Selection of Demulsifier

Selection of the right demulsifier is crucial in the emulsion breaking process, and still viewed as an art rather than a science. Demulsifier are chemicals that contain solvents (e.g., benzene, toluene, xylene, short-chain alcohols, and heavy aromatic naphtha), surfactants, flocculants, and wetting agents. The demulsifiers act by total or partial displacement of the indigenous stabilizing components (polar materials) of the interfacial film surrounding the emulsion droplets. This displacement also brings about a change in properties such as

interfacial viscosity or elasticity of the protecting film, thus enhancing destabilization. In some cases, the chemicals act as a wetting agent and alter the wettability of the stabilizing particles, which lead to a breakup of the emulsion film. Testing procedures are available to select appropriate demulsifiers.^{5, 7} These tests include bottle tests, dynamic simulators, and actual plant tests. These tests also determine the amount of chemical to be added. Too little emulsion will leave the emulsion unresolved. On the other hand, a high dosage of demulsifier (an over treating condition) may be detrimental to the treatment process. Because demulsifiers are surface-active agents too like emulsifiers, an excess quantity of demulsifier may also produce very stable emulsions. In this case, the demulsifier simply replaces the natural emulsifiers at the interphase.

2.6.1.3 Chemistry of Demulsifier

Demulsifiers are generally specific for a given emulsion and may be completely ineffective for another emulsion. Demulsifiers are typically formulated with polymeric chains of ethylene oxide and polypropylene oxides of alcohol, ethoxylated phenols, ethoxylated alcohols and amines, ethoxylated resins, ethoxylated non-phenols, polyhydric alcohols and sulphuric acid salts.¹ Typical demulsifier chemistries are shown in Figure 2.51. Commercial demulsifiers may contain one type of active ingredient or a mixture of several of these intermediates. There is a wide variation within the intermediates as well.

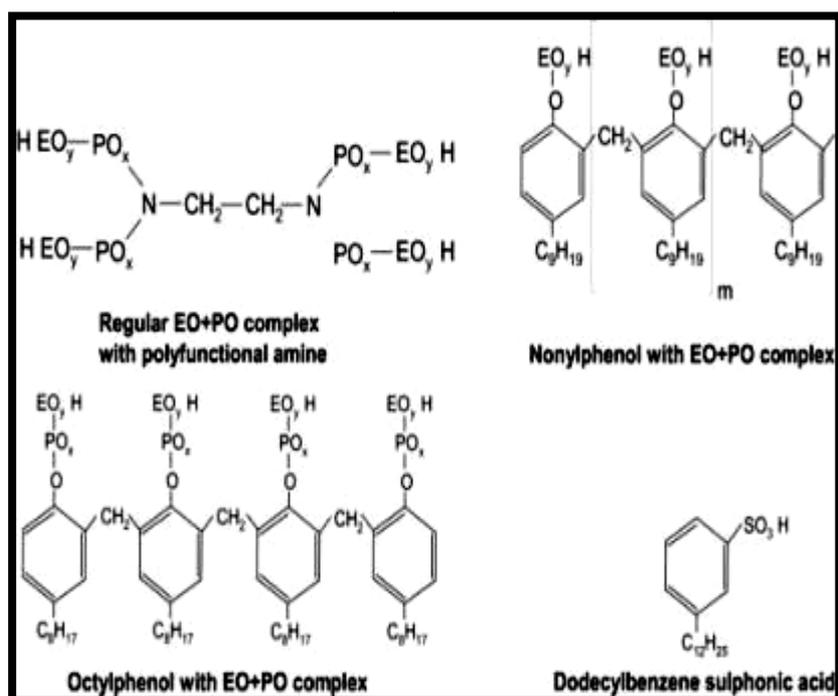


Figure 2.19: Typical chemistry of demulsifiers¹

2.6.1.4 Chemical Demulsifier Efficiency

The demulsification ability of a demulsifier is mainly controlled by two factors: one is its hydrophilic-hydrophobic properties; the other is the ability to displace indigenous materials that are present at the water/oil interfaces, and to modify the mechanical and rheological properties of the films that prevent droplet coalescence.^{58, 59} The structure of the demulsifier can influence both of above two factors. The demulsification mechanism of the demulsifiers is quite complicated, and no demulsifier can be applied to break all kinds of crude oil emulsions.^{60, 61} In formulation of demulsifiers, many components can play specific roles in their performance. A typical classification of demulsifiers can be according to their molecular weight as high molecular weight (HMW), low molecular weight (LMW) and pure solvents.⁶² Amphiphilic molecules with moderate-to-high molecular weight (typically 3,000-10,000 Da), such as polyalkoxylated alkylphenolformaldehyde resins and complex block copolymers, are usually responsible for the separation of a large fraction of the dispersed aqueous phase. These molecules penetrate the stabilizing film at the water/oil interfaces and modify its compressibility and rheological properties by disrupting the tight conformation of adsorbed asphaltenes, which in turn favors coalescence.⁶³

Molecules with very high molecular weight (HMW) (>10,000 Da) such as ethoxylated/propoxylated amine polyols act as flocculants by adsorbing at the water/oil interfaces and interacting with like molecules also adsorbed at the interfaces of nearby drops. Different parts of a polyols molecule may adsorb on different drops, producing flocculation by a bridging mechanism. Such flocculation can enhance sedimentation rates. These molecules act more slowly due to their lower diffusivities, and are effective in removing remaining small water drops and tight, fine emulsions once most of the dispersed phase has been removed by the water droppers.⁶⁴

Low molecular weight (LMW) compounds (<3,000 Da), such as common surfactants, aid phase separation through several mechanisms.⁶² Initially, they exhibit high interfacial activity and diffuse faster than other components with higher molecular weight. Therefore, they can suppress more effectively the interfacial tension gradients.

Solvents are used to carry the active components. Since demulsifiers need to be surface active for their performance, solvents should be chosen which minimize aggregation. Aromatic hydrocarbons such as toluene and xylene and water-miscible hydroxyl compounds are often used as solvents for demulsifiers.⁶⁵ The removal of water from emulsion is usually

found to be affected by demulsifier composition, such as by an increase in the degree of ethoxylation (i.e., an increase in the hydrophilic-liphophilic balance (HLB)); or by an increase in the number of polar groups or in aromaticity as found by Abdel-Azim et al.⁶⁶ The authors showed in the same study that in all cases there is an optimum dosage for demulsification where addition of demulsifiers beyond this optimum resulted in an increase of the stability of the emulsion, probably due to the formation of a new stabilizing film in which the excess of demulsifier plays a significant role. Also, oil phase aromaticity can play an important role in influencing demulsifier efficiency. Breen⁶⁴ shows that the efficiency of a given chemistry depends heavily on the H/C ratio of the oil phase. In this study, he found that demulsifiers are more effective when the oil phase exhibits high aromaticity.

2.6.2 Physical Methods

Physical treatment techniques include heating, electrical, or a mechanical method such as centrifugation.⁸

2.6.2.1 Thermal Methods

Heating alone does not cause an emulsion to breakdown, except in rare instances. Usually the application of heat is an auxiliary process to enhance the breaking or separation of emulsion. It reduces the viscosity of the oil and increases the water settling rate according to Stokes law. Increase in temperature also results in the destabilization of rigid films caused by reduced interfacial viscosity. Furthermore, the coalescence frequency between water droplets is increased because of the higher thermal energy of the droplets. Increasing the temperature has some negative effects. Firstly, it costs money to heat the emulsion stream. Second, it can result in the loss of light ends from the crude oil, reducing its American petroleum institute (API) gravity and the treated oil volume. Finally, increasing temperature leads to an increased tendency toward scale deposition and an increased potential for corrosion in treating vessels.

Application of heat for emulsion breaking should be based on an overall economic analysis of the treatment facility. The cost effectiveness of adding heat should be balanced against longer treatment time (larger separator), loss of light ends and a resultant reduced oil-price, chemical costs, and the costs of installation of electrostatic grids, or retrofitting. Some common types of heaters in the oil industry include Tubular heaters, fluid-jacket heaters, internal firebox heaters, volume, or jug-type heaters.⁸

2.6.2.2 Mechanical Methods

There is a wide variety of mechanical equipment available in the breaking of oilfield produced emulsions. These include free-water knock out drums, wash tanks, two-three phase separators, desalters, settling tanks. This method provides an environment of low turbulence. They are usually designed for different residence time based on the layout of the oilfield.

Table: 2.1 Description and application of mechanical equipment for breaking emulsion⁵

	EQUIPMENTS	APPLICATION	COMMENTS
1	Free water knock out type separators	For high water cut crude oils where the bulk of the water separates out quickly.	Final crude polishing to export can be carried out using other methods.
2	Dehydration type	For low water cut crudes where dehydration is about 1-5 % water is required	Usually located downstream of FWKO separators in offshore environment.
3	Separators	Considered for dehydration of difficult emulsions or very viscous crudes	Choice is based on economic arguments, and can be operated at high temperatures than 100 ⁰ C.
4	Heater treaters	General purpose, particularly used for high water cut crudes.	Careful design of internal requirements to avoid channelling and flooding.
5	Wash tanks Concentric wash tanks Settling tanks	Particularly used for heavy water cuts General purpose	More expensive and difficult to operate. Not a good choice for high water cut crudes.
6	Electrostatic coalescers	Considered when deep dehydration is required (to about 0.5 % water.	More sophisticate and more potential problems are experienced.

2.6.2.3 Electrical Methods

High voltage electricity (electric Grids) is often an effective means of breaking emulsion. It is generally theorized that water droplets have an associated charge and, when an electric field is applied, the droplets move rapidly, collide with each other, and coalesce.⁶ The electric field also disturbs the rigid interfacial film by rearranging the polar molecules thereby weakening the tight film and enhancing coalescence. The electrical system consists of a transformer and electrodes that provide high voltage alternating current alternating current. The electrodes are placed in such a way as to provide an electric field that is perpendicular to the direction of flow. The distance between the electrodes – in some designs – adjustable so that the voltage can be varied to meet the requirement of the emulsion being treated. Electrostatic dehydration is rarely used as a method of breaking emulsions. It is generally used in conjunction with chemical and heat requirements. Invariably, the use of electrostatic dehydration will result in a reduction of heat addition. Lower temperatures result in fuel economy, reduced problems with scale and corrosion formation, and reduced light ends loss. Electrostatic grids also can lead to a reduction in the use of emulsion-breaking-chemicals. Table 2.51 shows a summary of the emulsion treating facilities and their applications.

CHAPTER 3

ANALYSING THE SHEARING ENERGY AT THE WELLHEAD: A NOVEL APPROACH

This chapter demonstrates a novel approach of estimating shearing energy in relation to the pressure drop, the choke area (bean size) and a characteristic length of flow along the wellhead. The intensity of shearing (agitation) as the oil/water mixture flows through the wellhead is seen as the main factor in determining how stable and tight the emulsion will be and consequently how difficult it will be to treat.⁹ As discussed in Chapter 2, the regions where serious shearing action on the oil/water mixture takes place in the petroleum production system are through the formation pores itself,²⁸ perforations, wellhead chokes, manifolds and surface facilities. However, this study will be limited to analysing only the shearing energy through wellhead choke. Other analysis will be recommended for future studies.

3.1 Model of shearing energy

Let us consider two immiscible fluids of known properties flowing through a circular pipe of length D_o and known internal surface area, as shown in Figure 3.1.

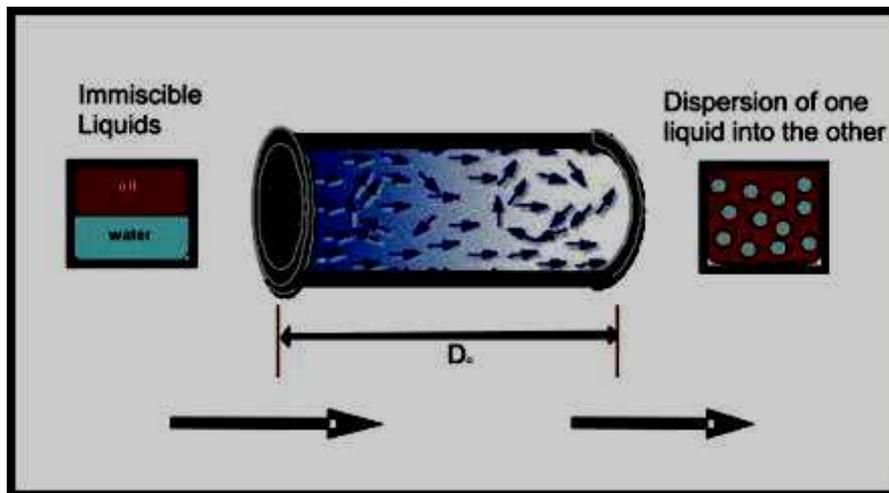


Figure: 3.1 Shearing energy experienced by fluids flowing through a pipe

According to Abdel-Aal et al⁶⁷ the shearing energy responsible for dispersion of one phase of the liquid into the other as the fluid flows through the pipe is dependent on the

turbulence available in the pipe This is a function of the pressure drop along the characteristic length D_o of the pipe, and its total internal surface area available for shear as flow occurs.

The shearing energy is given as follows:

$$\text{Shearing Energy, } SE = \Delta P \cdot A_s \cdot D_o \quad (3.1)$$

Where:

ΔP = Pressure drop along the length of pipe,

A_s = Total surface area of pipe available for shearing,

D_o = Characteristic length of flow along the pipe.

Pressure drop in a pipe could be associated to lots of factors as described in literatures.⁷⁷ These factors include roughness of the pipe, change in property of flowing fluid, sudden reduction in flow area etc. This shearing energy overcomes the viscous force between the liquid layers, leading to their separation into thin sheets or parts, and, formation of ‘‘surface energy’’, which occurs as a result of the separation of the molecules at the plane of cleavage.

3.2 Application of Shearing Energy Analysis to Wellhead Choke

The wellhead incorporates a means of hanging the production tubing, installing Christmas tree and surface flow-control facilities in preparation for the production phase of a well. Chokes are usually located on or near the Christmas tree that is used to control the production of fluid from a well. They also protect surface equipment from slugging, avoid sand problems due to high drawdown and prevent water and gas coning.⁷⁸ They are available in several configurations for both fixed and adjustable mode of operation. Adjustable chokes enable the fluid flow and pressure parameters to be changed to suit production requirements. Fixed chokes do not provide this flexibility, although they are more resistant to erosion under prolonged operation.

In a typical petroleum system, production choke is one of the regions where high pressure gradient are experienced and causes a vigorous shearing which can cause emulsion to form. The choke constitutes flow constriction and hence high pressure drop leading to turbulence. Extreme mixing conditions are hence experienced as the fluid mixtures flow through the wellhead. New water/oil interfaces are thus formed which contributes to the

formation of tight emulsions. The shearing energy experienced by the oil/water mixture as it leaves the tubing hanger and flow through the wellhead to the flowline is analysed as below using Abdel-Aal's principle.

$$S.E = \Delta P_{choke} \cdot \left(\frac{\pi d_m}{4x}\right)^2 \cdot D_o \quad (3.2)$$

Assuming the choke area is circular.

Where:

ΔP_{choke} is the pressure loss between the tubing hanger and the outlet of the choke.

X is the percentage of choke open to flow. It is defined as the ratio of the choke size, d_b to the maximum choke size attainable, d_m . i.e. $x = \frac{d_b}{d_m}$

d_m is the maximum choke size area that can be attained in $\frac{1}{64}$ inches.

d_b is the choke size (bean size) used for production. It is assumed that the choke restriction is responsible for the shear. The bean is also assumed circular in this study. It is measured in the unit of $\frac{1}{64}$ inches.

D_o is the characteristic length of flow within the wellhead. (ft)

Choke performance correlation is used to analyse the pressure drop, ΔP across the wellhead, and multiphase nature of the produced fluid is put into consideration. Correlations developed for this relationship include Ashford-Pierce, Achong, Baxendell, Gilbert, Omana et al, and Ros.⁷⁸ The Achong's correlation will be used for this study.

$$P_u = \frac{3.829 q_1 R_p^{0.65}}{d_b^{1.88}} \quad (3.4)$$

Where:

P_u = Upstream Pressure, psia.

q_1 = Liquid Flowrate, bbl/day.

R_p = Producing gas-Liquid ratio, scf/bbl.

Let P_d be the choke downstream pressure. Hence pressure drop, $\Delta P_{choke} = (P_u - P_d)$.

$$\text{Hence, } S.E = \left(\left(\frac{3.829 q_1 R_p^{0.65}}{d_b^{1.88}} \right) - P_d \right) \cdot \left(\left(\frac{\pi d_m}{4x} \right)^2 \right) \cdot D_0 \quad (3.5)$$

It is also assumed that only the choke area and the pressure drop are assumed to change significantly, and hence contribute to the turbulence.

A spreadsheet showing shearing energy analysis for a particular wellhead is shown in Figure 3.3

Table: 3.1: Spreadsheet showing shearing energy analysis

SHEARING ENERGY ANALYSIS @ THE WELLHEAD			
q	Liquid flow rate	1274	bb/d
Rp	Gas to liquid ratio	2100	scf/bbl
db	Choke size during production	28	64th of an inch
dm	Maximum allowable choke size for wellhead	64	64th of an inch
x	percentage of choke open to flow	0.44	
pd	Flowline Pressure	412	psia
Do	Characteristic Length of flow within the choke	0.58	ft
pu	Tubing head Pressure	1340	psia
ΔP	Pressure drop accross choke	928	psia
	Shearing Energy, SE	7145669.69	(lbf. Ft)
	Shearing Energy, SE	9687730.062	(Joules)
	Laboratory Scale	9.69	(Joules)

3.3 Discussion of Analysis

One of the main objectives of this study is to develop correlations that will relate the several conditions (shearing energy, watercut, organic and inorganic solids present) responsible for emulsion formation to the tightness of the formed emulsion. Although shearing energy has been ranked a major factor amongst all these condition, there has never

been any technical approach to estimate its magnitude at regions of turbulence in the petroleum production system. Equation 3.5 shows the relationship developed for calculating shearing energy at the wellhead. This equation relates the production rate, type of the crude oil produced and the nature of the choke during production to shearing energy. Figure 3.2 shows the excel spreadsheet developed for this equation. Values are inputted into the cells with white colour, and values in the cells with a light green colour are automatically calculated. The total liquid produced is entered in barrels per day, and the gas to liquid ratio is inputted in scf per barrel. The size of the choke also contributes greatly to the turbulence experienced at the well head. This is inputted into this spreadsheet in 64th of an inch, and hence the percentage of area of choke open to flow is calculated. It is taken in this study that the maximum allowable choke size is 64/64 inches, and that the choke size restriction area is the surface area responsible for shear in this region. Comparison of the tubing head and the flowline pressure gives the pressure drop across the choke. From equation 3.5, the higher the pressure drop the more is the shearing energy experienced.

However, the shearing energy experienced on the field is also very enormous especially when fluids with a high Gas-Liquid Ratio (GLR) is made to flow through a small choke size, and hence high pressure drop. It's very difficult to simulate such energy in the laboratory and hence a reducing scale of 10^6 is used to reduce the values calculated from equation 3.5. Figure 3.2 shows the analysis of shearing energy at choke with a fluid flow rate of 1274 bbls, GLR of 2100 scf/bbl, choke size of 28/64th inch and flowline pressure of 412 psia. The energy calculated is approximately 9.69×10^6 J. This is reduced to a laboratory scale of 9.69 J as already discussed.

CHAPTER 4

EXPERIMENTAL STUDIES

This chapter discusses the several sets of emulsion experiments done in order to achieve the objectives and scope of this research. The first experimental set investigates the effect of various factors, known to contribute to emulsion stability. Also a comprehensive second series of experiments was performed to study the combined effect of asphaltene precipitation and shearing energy on emulsion tightness at various watercuts.

4.1 Description of Materials used.

The materials used for this experimental study include crude oil sample and separated effluent water collected from an Agip field in the Niger Delta region of Nigeria. The reagents and chemicals used are n-pentane, toluene and demulsifier chemical samples which were all provided by Clariant oil servicing company. The bentonite clay used to simulate reservoir fines and calcite used as inorganic scales were provided by CBC chemicals (a Drilling servicing company) in Portharcourt. Asphaltene samples precipitated from the crude oil samples were used for this experiment.

4.1.1 Oilfield Process Description and Crude oil sampling

Crude oil from LAR field (comprising of wells from Kwale, Akri, OB-OB, Ebocha, Oshie, and Idu) co-mingled, and flown to Brass terminal. There is demulsifier injection in all the flow stations, except Akri. Treated crude from Kwale gas plant co-mingled, and flown through Akri to Ebocha (then to Brass). This co-mingling of crude oil is the same for SAR field (Obama, Tebidaba, Ogboinbiri, and Clough Creek). At Brass, arrivals from SAR and LAR production headers co-mingle at a common manifold (demulsifier injection here), then flows into the gun-barrel. Residence time here is estimated as 30 minutes. Separated produced water flows to the oil skimming processing plant. Separated crude oil from gun-barrel passes to storage tanks, where it resides before export. Further water settlement and drainage occurs in the storage tanks.

Crude oil emulsion samples used for this study were collected from the major trunk line outlet of the SAR and LAR manifold header leading to the gun-barrel at the terminal in

Brass. The crudes as explained is made up of several wells from the land and swamp region, and span a wide range of API gravities, of 24⁰ to 39⁰. Table 4.1 shows the average values of physical properties of the emulsion samples. The trunk line was chosen as the sampling point because it is a good representation of all the wells feeding the terminal.

Table 4.1: Average values of the Properties of the crude oil emulsion samples

Properties	Ranges for all the wells	Stock tank Properties
° API	21 - 39	28
Water cut (%)	5 - 52	NIL
Viscosity @ 40 deg C (cp)	2.6 – 13.6	5.6
Specific Gravity	0.856 – 0.916	0.845
Asphaltene Content (wt %)	0.54 – 9.53	9.43
Solid Content (wt %)	5.9 – 34.6	12.3
Sulphur content (wt %)	0.01 – 0.18	0.13
Pour Point °F	21 – 40	36
Nickel (ppm)	0 – 5	0.5
Vanadium (ppm)	0 - 3	0.5

4.1.2 Formation water

Effluent water separated from the crude oil at the central processing terminal of these fields after treatment was used to simulate the formation water. It was collected at the outlet of the gun barrel at the terminal. Table 4.2 shows the results of water sample analysis. The water had been de-oiled to a total petroleum hydrocarbon, TPH of about 5 ppm before use.

Table 4.2: Properties of the formation water

Composition		$K^+ + Na^+$	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}
Concentration (mg/l)		1452.2	5.6	16.8	425.5	20.2	2927.7	121.1

4.1.3 Asphaltenes

All the crude oil samples used in this study were first de-asphalted, and the asphaltene samples were re-solubilised again at known amounts prior to the experiment. Black friable samples of Asphaltene were extracted from the crude oil sample by n-pentane precipitation

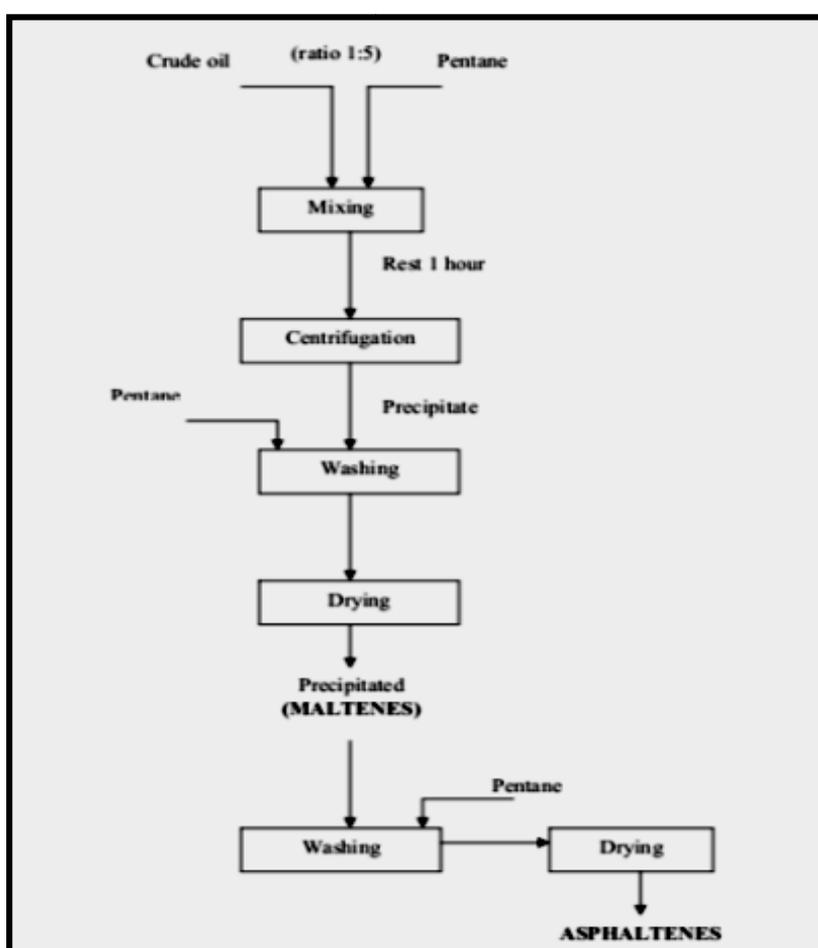


Figure 4.1: Process of Asphaltene Removal from Crude oil

using ASTM D2007 and Institute of Petroleum IP 143 method. This procedure is described with the flow chart shown in Figure 4.1. However, the lower molecular weight alkanes used in these procedures was n-pentane. Sufficient quantities of dry asphaltenes were obtained

from the crude oil and used throughout the experiment. A detailed description including the chemistry and stabilization act of Asphaltenes and other major emulsifiers are already discussed in Chapter two.

4.1.4 Reservoir Fines

Types of reservoir fines include montmorillonite, bentonite, calcite, siltstone, shale, sandstone etc.²⁷ However, sodium bentonite was used as the reservoir fines in this research. It is a material composed of clay minerals, predominantly montmorillonite with minor amounts of other smectite group. This is one of the major types of fines migrated in the reservoir. Whitish-pink bentonite powders are accurately measured in weight percent and mixed with the dry crude oil and formation water according to the experiment design. It was provided by CBC chemicals (a Drilling servicing company) in Portharcourt.

4.1.5 Inorganic Scales (Calcite) CaCO_3

Salts of calcium, magnesium and barium are the most common constituent of scale found in the petroleum production system. Calcium carbonates, which always have the highest composition amongst all these salts, are simulated in this study using dry and fine powder of calcium carbonate, also provided by CBC chemicals (Drilling servicing company) in Portharcourt.

4.1.6 Demulsifier Chemicals and Reagents:

As indicated in the literature⁸, demulsifiers counteract the emulsifiers present in an emulsion. They create unstable emulsion that separates readily with good settling action. All chemical intermediates (demulsifiers) and reagents were obtained from Clariant oil services. A particular demulsifier product used for this study is Phasetreat 4633. It has been tested over time in major Niger Delta fields to be a very good emulsion treating chemical with a reasonable residence time of action. Phasetreat 4633 is a polyoxyethylene (EO)/polyoxypropylene (PO) alkylphenolformaldehyde resins. It has molecular weight of around 3500 Da, and varying amount of EO/PO groups in their structure with a constant EO/PO ratio of 3:1.

4.2 Experimental Methods

Several sets of emulsion experiments were carried out in the production chemistry lab at NGC oil services in Portharcourt. Preliminary studies were first performed to examine the

effects of various factors on emulsion formation and stabilization, and how much they contribute to it. A second set of experiment was performed to study the effect of agitation energy, coupled with other production conditions on the tightness of emulsion. The threshold values of shearing energy to form each of these emulsions as classified in the experiment were also estimated.

4.2.1 Experimental Matrices

The first experimental sets investigated the effects of water cut, asphaltenes precipitation, reservoir fines and inorganic scales on emulsion tightness. The effect of several combinations of these factors was also investigated. While the parameter to be studied is varied, all other factors were kept constant. Hence, the number of tests performed is based on the number of times each parameter is being varied as illustrated in the Table 4.3. A total of 65 bottle tests were performed for experiment 1 as shown in the experimental matrix design in Table 4.3.

Table 4.3: Matrix Design for Experiment 1

S/N	Parameter	No. Of Variations in parameter	Matrix	Number of Test
1	Water cut	9	9 × 1	9
2	Asphaltene	8	8 × 1	8
3	Reservoir Fines	8	8 × 1	8
4	Inorganic solids, CaCO₃	8	8 × 1	8
5	Asphaltene + Res. Fine	8	8 × 1	8
6	Asphaltene + CaCO₃	8	8 × 1	8
7	CaCO₃ + Fines	8	8 × 1	8
8	Asphaltene + Fine + CaCO₃	8	8 × 1	8
Total Number of Tests performed				65

The second set of experiment studied the combined effect of asphaltene contents and shearing energy on emulsion tightness at various water cuts, as all other conditions were kept constant. Five different concentrations of asphaltene were tested over 20 shearing energy

levels. This was done for water cuts of 5%, 30% and 65%. The matrix design of the experiment is shown in Table 4.4 and indicates a total of 300 tests.

Table 4.4: Matrix Design for Experiment 2

Parameter Variation	No. Of Variations in parameter			
	Water Cut= 5%	Water Cut = 30%	Water Cut = 55%	
Asphaltene content	5	5	5	
Agitation	20	20	20	
	(5 × 20)	(5 × 20)	(5 × 20)	(3 × 5×20)
Total Number of Tests performed				300

Each test involves the creation of an emulsion and properly demulsifying it with Phasetreat 4633 to measure its tightness.

4.2.2 Description of Equipments

The equipments used in this study include, but not limited to the following: Thermostat installed Water bath, Thermometer (Checktemp1 digital thermometer), digital top loading balance (Mettler Toledo XP8002S), Rotary arm agitator for bottle tests (Fenske HT 5001-201), Crude oil Test bottles (Six ounce Pyrex bottles, 200ml), Micropipette: Socorex Syringe (Model: Dossy TM 174 premium), Centrifuge Machine: (Robinson Centrifuge, Model T.0.2, serial No: T724), 10ml measuring cylinder: (Pyrex), and other glass wares.

The Rotary arm agitator was used to homogenize the mixture of the oil, water and emulsifiers. The rotational rate of the equipment over time dictates the amount of energy it dissipates. This is assumed to be the only energy available for emulsion formation. The simplest way to calculate the total energy exerted on the oil and water in the device is to calculate the total kinetic energy of the system. Figure 4.2 shows a schematic of the equipments set-up operation.

$$K.E = \frac{1}{2} M_s V^2 \quad (4.1)$$

Introducing angular terms; $V = \omega R$

$$K.E = \frac{1}{2} M_s (\omega R)^2 \quad (4.2)$$

$$\text{Where, } \omega = \frac{2\pi N}{60} \quad (4.3)$$

Where:

K.E = Kinetic energy developed in the system, J

M_s = Mass of the system, kg

ω = Angular velocity, m/s²

N = Rotation of the equipment, RPM.

R = Radius of arm holding the bottles, m

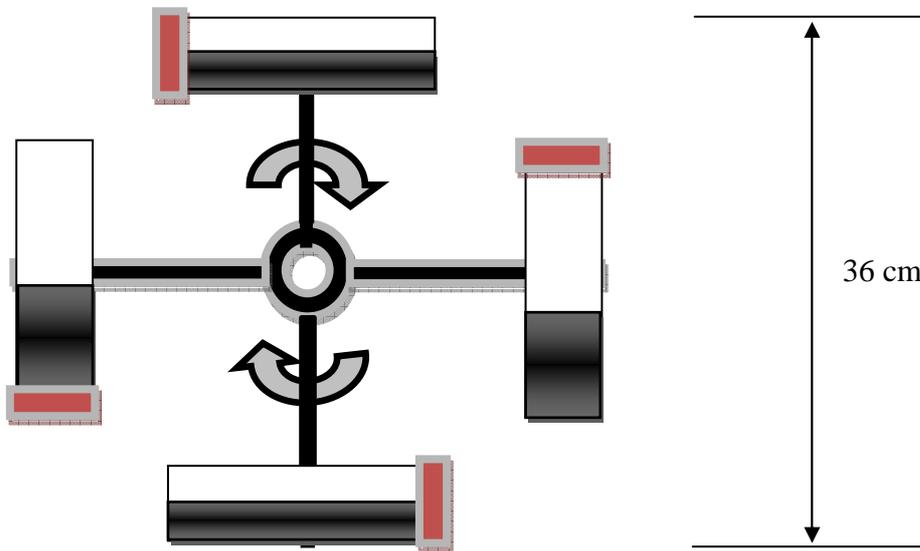


Figure 4.2: Schematic Explanation of Emulsion formation device

$$K.E = \frac{1}{2} M_s \left(\frac{2\pi N}{60} \right)^2 R_a^2 \quad (4.4)$$

Mass of entire top bottle arm system, M_a = 198 g

Mass of each test bottle (100ml, filled 1:1), M_b = 94 g, (\times 4 bottle set) = 376 g

Mass of system, M_s = (198 + 376) g = 574 g

Radius of arm, R_a = 18 cm

$$\begin{aligned} \text{K.E} &= \frac{1}{2} (0.574) \left(\frac{2\pi N}{60} \right)^2 (0.0324) & (4.5) \\ &= (1.01999\text{E-}4) N^2 \text{ Joules.} \end{aligned}$$

Where N is the number of Revolutions revolved per minute, RPM of the machine

During this study, the machine speed was varied from 0 to 1000 RPM, and an equivalent energy of approximately 0 to 100 joules was obtained. However, the shearing energy experienced on the field is very greater than what the mixing equipment could produce in the lab; hence a form of scale to reduce them to lab scale will be used.

4.2.3 Preparation of De-Asphaltic Oil Samples

Crude oil emulsion sample collected from the field were first properly demulsified, and made free of emulsified water, free-water and chemicals. This confirmed the effectiveness of Phase treat 4633 as a good demulsifier for this study. The crude samples were also made free of asphaltene and inorganic solid. They were de-asphalted by mixing with excess pentane to precipitate out all asphaltene present. About 2.5 litres of crude oil was agitated with 10 litres of pentane at room temperature for 20 minutes and allowed to stand for 24 hrs. The precipitated asphaltene fraction was filtered and washed with smaller portions of pentane, dried and re-grinded to micron-sized fine particles. This process was repeated until substantial amount of asphaltenes was extracted. A similar process was also carried out to remove all inorganic solids present, although not re-used for the experiment. About 300% excess of toluene was also mixed with the de-asphalted crude, and majorly white precipitate of calcite was extracted from the oil. The crude oil was also distilled and made free of n-pentane and toluene. The dry and de-asphalted crude, free of inorganic solids was used for this study. The pentane and toluene used for extraction were properly distilled from the crude oil before use for this experiment.

4.2.3.1 Bottle Test Analysis and Emulsion Tightness (ET) Analysis

The entire laboratory works carried out in this study involves the formation of water-in-oil emulsions samples using the de-asphalted oil and effluent water from the terminal, under varying formation conditions. Demulsification of these samples was carried out and the amount of emulsified water separated as a function of time for 20 minutes was then observed

and recorded. This forms the basis of developing the correlation for emulsion tightness in this study. The procedure used for creating and demulsifying the emulsions in this experiment are outlined as below:

- Prepare a mixture of oil, formation water and the emulsifying ingredients in a 100ml test bottle. All is assumed to have been measured in the right amount.
- Place these mixtures in the water bath and heat to a temperature of about 80 °C, to allow all emulsifiers dissolve properly and enhance homogenous mixing.
- Agitate the mixture in the formation device. The agitation action (i.e. Agitation energy × time, J.S) is varied by varying the speed (in RPM) of the machine, as designed in the experimental matrix.
- After emulsion is formed, cool samples back to room temperature in the water bath.
- After 30 minutes of cooling, heat the samples again, but now to a temperature of 60 °C, and inject the demulsifier chemical sample at a know injection rate. 60 °C represents the process temperature used on this field.
- Agitate the mixture again for a minute and place the samples in the bottle rack.
- Observe the amount of water that separates out in all the samples within 20 minutes.

The stability of the emulsion is measured with a new approach called emulsion tightness index, ETI developed in this thesis.

$$E_T = \frac{[Amount\ of\ water\ blended - Amount\ of\ water\ separated\ after\ time,\ t]}{Amount\ of\ water\ blended} \% \quad (4.6)$$

E_T would give values ranging from 0 to 100 percent. Zero means emulsion is very loose i.e. almost all emulsified water separated while 100 mean a tight emulsion, which would not drop any water after a particular time. Note values of E_T should be coated with the time of separation and demulsifier used for the test. E.g. E_T [10 minutes, PT 4633/3ppm] = 23.3%.

4.2.3.2 Description of Experiment 1:

Water-in-oil emulsion was made in the rotary arm agitator as earlier described. The experiments were done in sets to study the effect some factors known to contribute to

emulsion tightness. These factors include water-oil-ratio, asphaltenes content, fines content and inorganic solids (calcite). Additionally, several forms of combination of these factors were also observed. e.g. asphaltene + fines, asphaltene + calcite, calcite + fine, and (asphaltene + calcite + fine). The tightness of the formed emulsion in each sample was recorded in percentage of emulsion tightness, E_T as earlier described.

For each parameter (except water oil ratio) studied, 8 sets of bottle sample were prepared with different concentration of the parameter under investigation. These concentrations are 0.05wt%, 0.5wt%, 1.3wt%, 2.9wt%, 4.8wt%, 9.4wt%, 14.80wt%, and 21.1wt%. In these bottle samples, all other parameters known to affect emulsion tightness were made constant. Table 4.5 shows the set of standard constant conditions used for this experiment. These samples were then placed in water bath and heated to a temperature of 80°C before being transferred to the shearing machine and sheared for 2 minutes, with a speed of 900 rpm. Stable emulsions were formed in each bottle and thereafter were cooled back to room temperature before treating. 15 ppm of Phasetreat 4633 was injected into each bottle samples at 60 °C (process temperature at terminal) and the rate of resolution was strictly observed within 20 minutes. Emulsion tightness, E_T was then calculated following the earlier described procedure.

However, for the variation in water cut, 9 bottle samples of oil and water mixture, labelled 10, 20, 30, 40, 50, 60, 70, 80 and 90 percent according to the experimental matrix design were made. 80 and 90 percent of water were included to see the effect of emulsion inversion on emulsion tightness. Equal amounts of emulsifying ingredients were added (measured in weight percent) to each bottle of the oil-water mixtures. These samples formed stable emulsions just as the other variables tested earlier. They were also cooled back to room temperature and the same procedure of treatment and resolution were followed. Emulsion tightness was then measured upon demulsifier injection

The results from these set of experiment was used to rank how much each of these variables experimented contributes to emulsion tightness.

Table 4.5: Standard Conditions for experimental studies

WATER CUT	30%
API GRAVITY	28°
TEMPERATURE	80 °C
ASPAHALTENE	1.3 wt %
FINE CONTENT	12.7 wt %
INORGANIC SOLIDS (CACO3)	4.1 wt%
RPM	900
MIXING TIME	2 Min
AGITATION ENERGY	82.6 J
SHEARING ACTION	9912 J-S
DEM. TEMP.	60 C
DEM. CONC.	15 PPM
DEM. AGITATION TIME	1 Minute

4.2.3.3 Description of Experiment 2

These set of experiments were designed to measure the combined effect asphaltene content and shearing energy on the properties of emulsion at several water cuts. The same set of standard conditions used in experiment 1 for all the unvaried parameters were also used here, as seen in Table 4.5

Unlike experiment 1, only 5 variations in the concentration of asphaltene were studied over 20 different shearing energies. The asphaltene concentrations were varied as 0.5wt%, 2.1wt%, 5.4wt%, 14.80wt%, and 21.1wt%. They were all prepared with 5% water. The prepared samples were placed in the water bath and heated to a temperature of 80 °C before being transferred to the shearing device and sheared for 2 minutes. They were subjected to shearing energy of 0.01 Joules as the equipment rotated at a rate of just 10 rpm. The resulting emulsions produced were cooled back to room temperature before treating with 15 ppm of Phasetreat 4633 at 60 °C and the rate of resolution was strictly observed within 20 minutes. Emulsion tightness, E_T was then calculated following the earlier described procedure for experiment 1.

After this is completed, another new set of 5 bottle samples with the same composition were prepared again, following the same procedure of formation and resolution. However, they are now mixed with an increased shearing energy. After forming the

emulsions, the standard procedure of emulsion resolution were then followed, and the E_T 's for these new set were also measured accordingly. However, this study is aimed at studying the effect of agitation energy on emulsion tightness; hence the procedure was repeated with 20 different 5-sets of bottle samples and subjected to different Shearing energy levels ranging from 0 to approximately 100 Joules.

Furthermore, the entire experiments were repeated for 30% and 55% water phase. According to the experimental matrix design, experiment 2 amounts to 300 bottle sample test. All the results gotten from this study were carefully observed to see if any trend could exist between emulsion tightness, E_T , at various water cuts (5%.30% 65%), shearing energy and the Asphaltene content.

CHAPTER 5

EXPERIMENTAL RESULTS, DATA ANALYSIS AND MODELLING

This chapter mainly discusses the results obtained from the experiments in this study. It starts with the section which investigates the effect of several factors (including water cut and asphaltene) on emulsion tightness, and how much they contribute to it. Section 5.2 discusses the series of experiments which described the effect of asphaltene concentration and shearing energy on emulsion tightness at different water cuts. Section 5.3 explains the trend observed in these results, and how they have been used to develop models, leading to the design of an emulsion testing device which can be used to troubleshoot emulsion problem on the field studied. Appendix 5A shows the raw data for all experiments.

5.1 Experimental Set 1: Investigation of Factors Affecting Emulsion Tightness

5.1.1 Dispersed Water Phase (Watercut)

The water cut is a parameter that increases progressively as an oilfield field matures, especially when some forms of water injection has commenced. It becomes a problem when a high quantity, which is more than expected, is breaking through at an early stage of production of a well. The results of emulsion resolution after 20 minutes and at various water cuts are presented and discussed.

As the amount of water used in forming the emulsion (as discussed in Chapter 4, experimental set 1) increases from 10% to about 60%, the tightness of the emulsion formed, measured in E_T , increases significantly from about 4% to 40%. At a water cut of about 60 %, the increase in emulsion tightness reached a maximum value, and further increase in water led to the formation of unstable and loose emulsion as shown in Figure 5.1. As the water cut increases towards 90%, this inverse relationship becomes more pronounced. The emulsion tightness dropped from approximately 40% to less than 12%, and tending to lower values. The peak value as seen in Figure 5.1 represents the point of inversion from water-in-oil emulsion to oil-in-water emulsion.

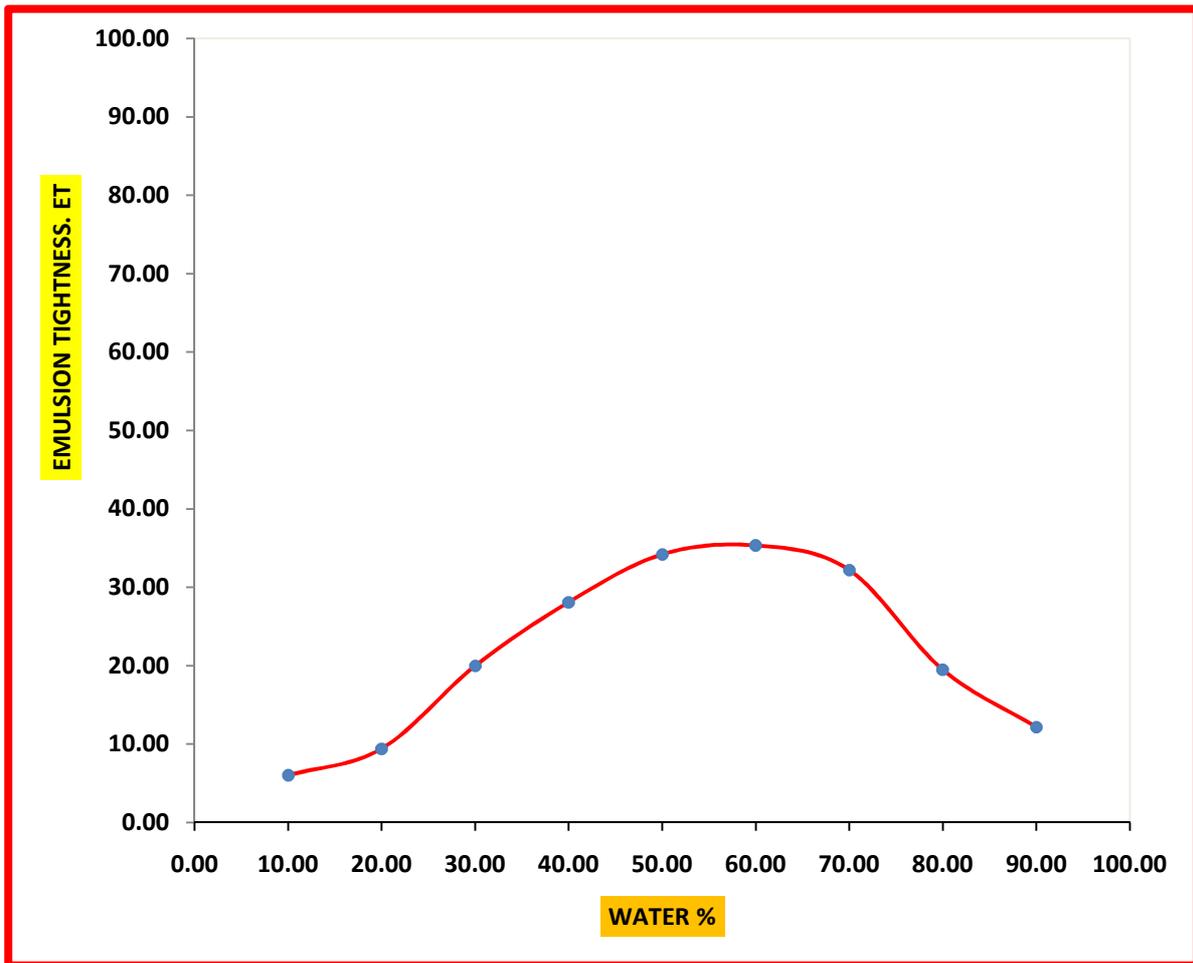


Figure 5.1: Effect of percentage of water phase on Emulsion Tightness

However, the effect of increase in water cut on emulsion tightness can be discussed according to the three major segments observed in Figure 5.2. The first two segments, discusses the formation of water/oil emulsions and the third segment discusses the inversion to loose oil/water emulsion. Segment 1, shows that small fractions of the dispersed water phase between 10% and 20% have a very mild effect on the tightness of the emulsion produced. The slope of the graph in this segment is almost linear and its highest degree of tightness is only about 9%. At higher amounts of dispersed water phase between 21% to about 58%, a more significant effect is felt on emulsion tightness as observed in segment 2. About 60% dispersed water marks the beginning of the third segment. Subsequent increase in dispersed water leads to the formation of loose emulsions of oil dispersed in water.

According to Oldroyd equation⁶⁸, which describes the effect of dispersed phase fraction on emulsion viscosity, the factor that is most likely to affect emulsion viscosity is the

volume fraction of the dispersed phase. Small amount of dispersed water demonstrates very little effect on the viscosity of emulsion according to this equation. At higher water cuts, significant effect on emulsion viscosity is experienced. El Gamel et al ⁶⁹ also studied the viscosity behaviour of water in oil emulsions with watercut of 10 to 50%. Their result showed that kinematic viscosity of emulsion steadily increased as a function of increasing watercut. They also demonstrated that the higher the viscosity of an emulsion, the more stable it will be.

The result presented by El-Gamel et al also shows some correlation with the range of 28 to 50% reported by Benayoune et al., ⁷⁰. According to their report, increasing the water cut above the inversion point makes the emulsion less stable. This phenomenon has also been observed in several emulsion studies done on some Saudi Arabian field as reported by Sunil Kokal²⁶. He conducted experiments with emulsion samples in which watercut was varied from 5% to 80%. The study reported that the emulsions become less tight as the water cut is increased beyond 65%. According to Elsharkarwy et al., ⁷¹ crude oil with higher amounts of water requires more energy to form emulsion, which are always very viscous and would not breakup easily.

Generally, it can be concluded that increase in the fraction of the dispersed water phase in an oil-water mixture, leads to formation of tight emulsions. This relationship would exist until the point of inversion from water/oil emulsion to oil/water emulsion is reached, thereafter loose emulsions will start forming.

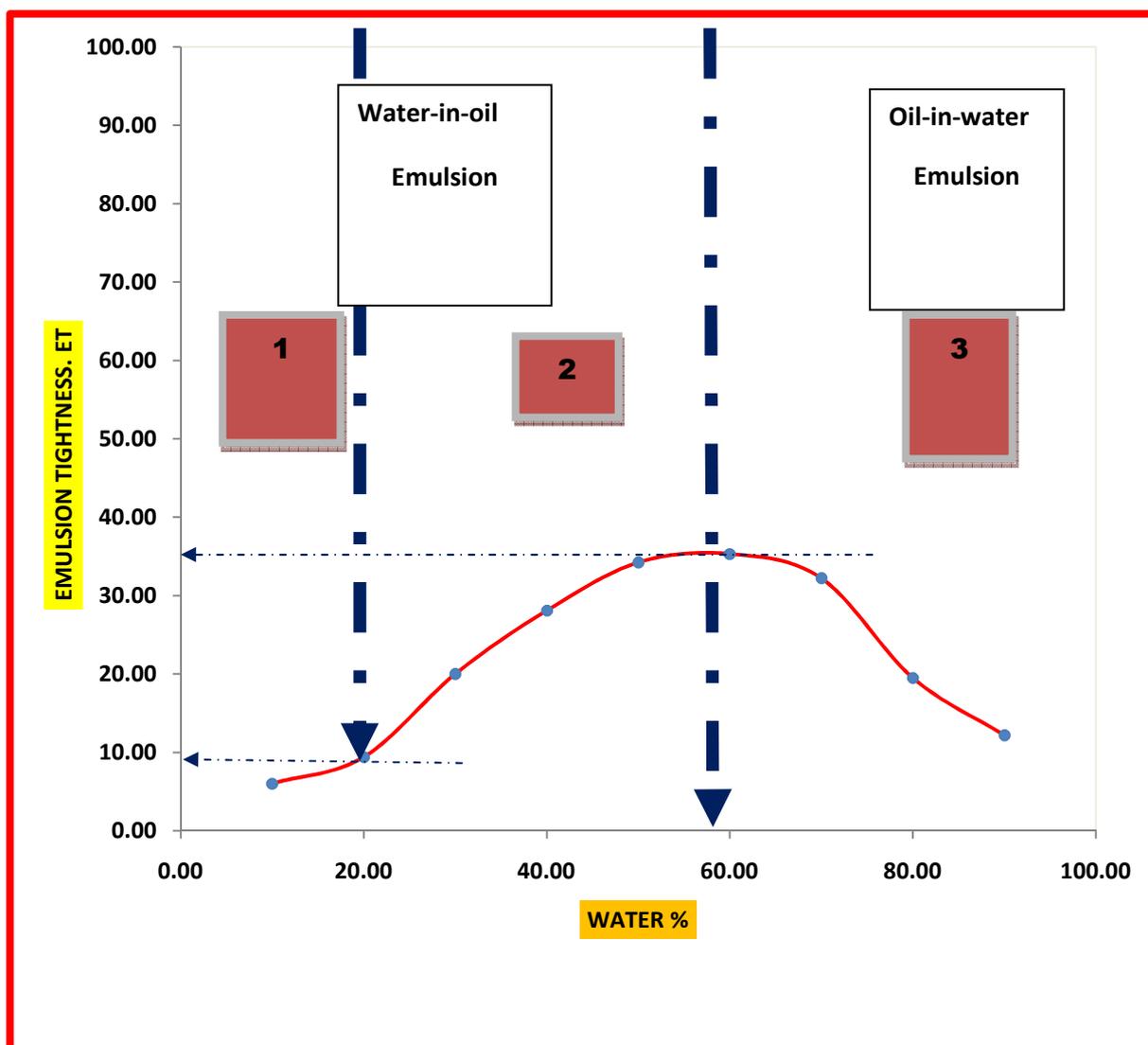


Figure 5.2: Three behavioural segments shown on the Effect of water on Emulsion Tightness

5.1.2 Asphaltene Content

Asphaltenes are believed to exist in the oil as a colloidal suspension and are stabilized by resins absorbed on their surface. They precipitate out of crude oil due to changes in thermodynamic conditions such as pressure, temperature and composition of the crude oil.⁷² The effect of adding various amounts of asphaltene extracted from the Agip crude oils on the tightness of water-in-oil emulsion is studied. The water separated from each sample with 20 minutes after treatment was recorded and used in calculating emulsion tightness, E_T of the samples. Figure 5.3 shows the effect of asphaltenes at various concentrations on emulsion tightness. At very small content of asphaltene, 0.05%, amount of emulsified water separated was substantially high. About 29.3 ml out of the entire 30ml blended were separated. The emulsion tightness was calculated to be 2.3 %. At 0.5% concentration of asphaltene the

emulsion becomes more difficult to treat, with a tightness of 8.2 %. There is a critical asphaltene concentration beyond which further increase in asphaltene forms extremely tight emulsions. As seen in Figure 5.3, this phenomenon is experienced at asphaltene concentration of 2.9%. Subsequent asphaltene content increase to 4.8 %, 9.4%, 14.8 to 21.1 % produced very tight emulsions of E_T 43.2%, 76.3%, 80% and even 90.3% respectively.

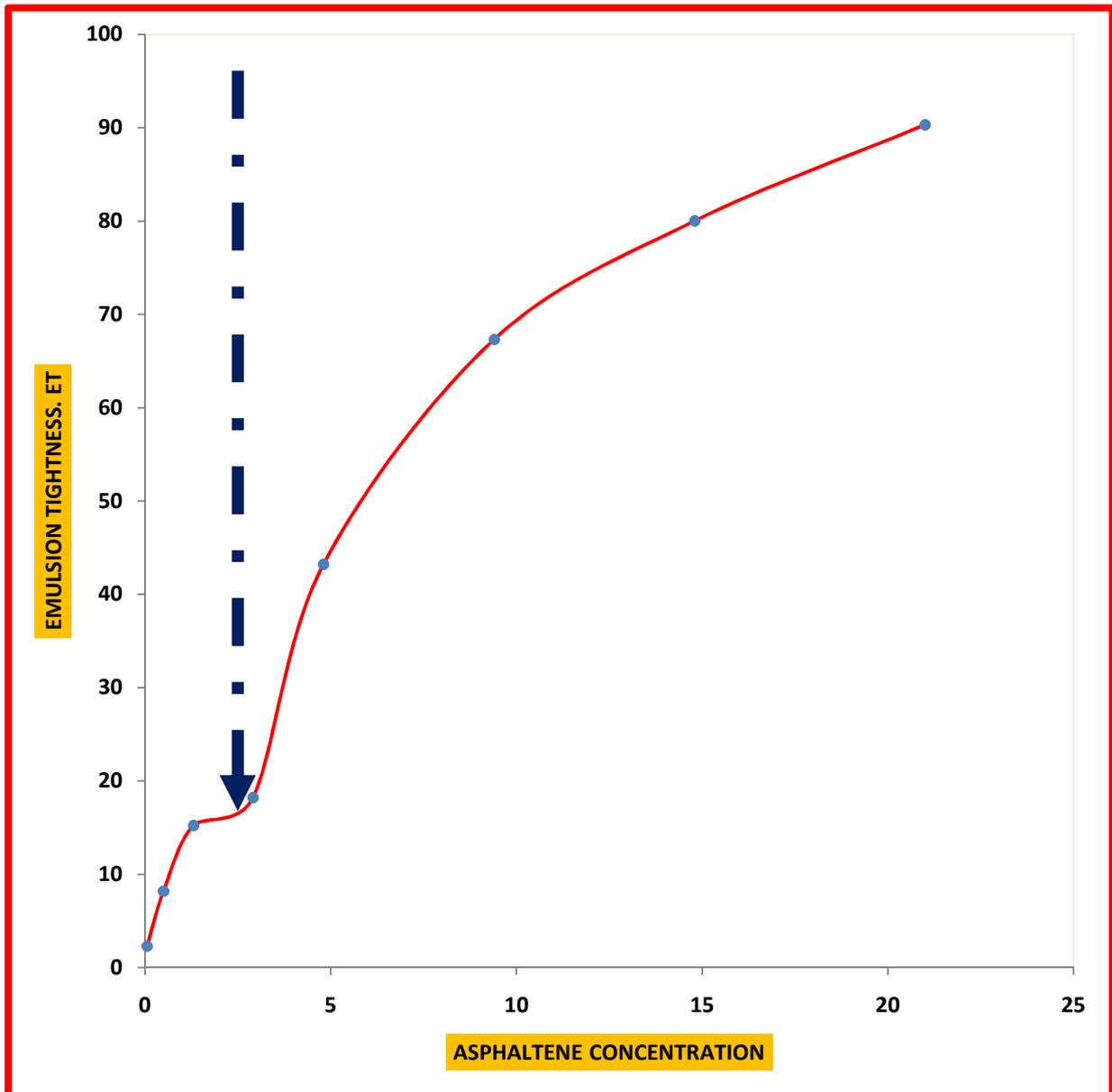


Figure 5.3: Effect of Asphaltene concentration on Emulsion Tightness

These tight emulsions due to asphaltene relates to the formation of solid films^{1,4} as shown in Figure 5.4. Below asphaltene concentration of 2.9 %, the films formed are mobile and weak but beyond this value solid films formed are very difficult to break.

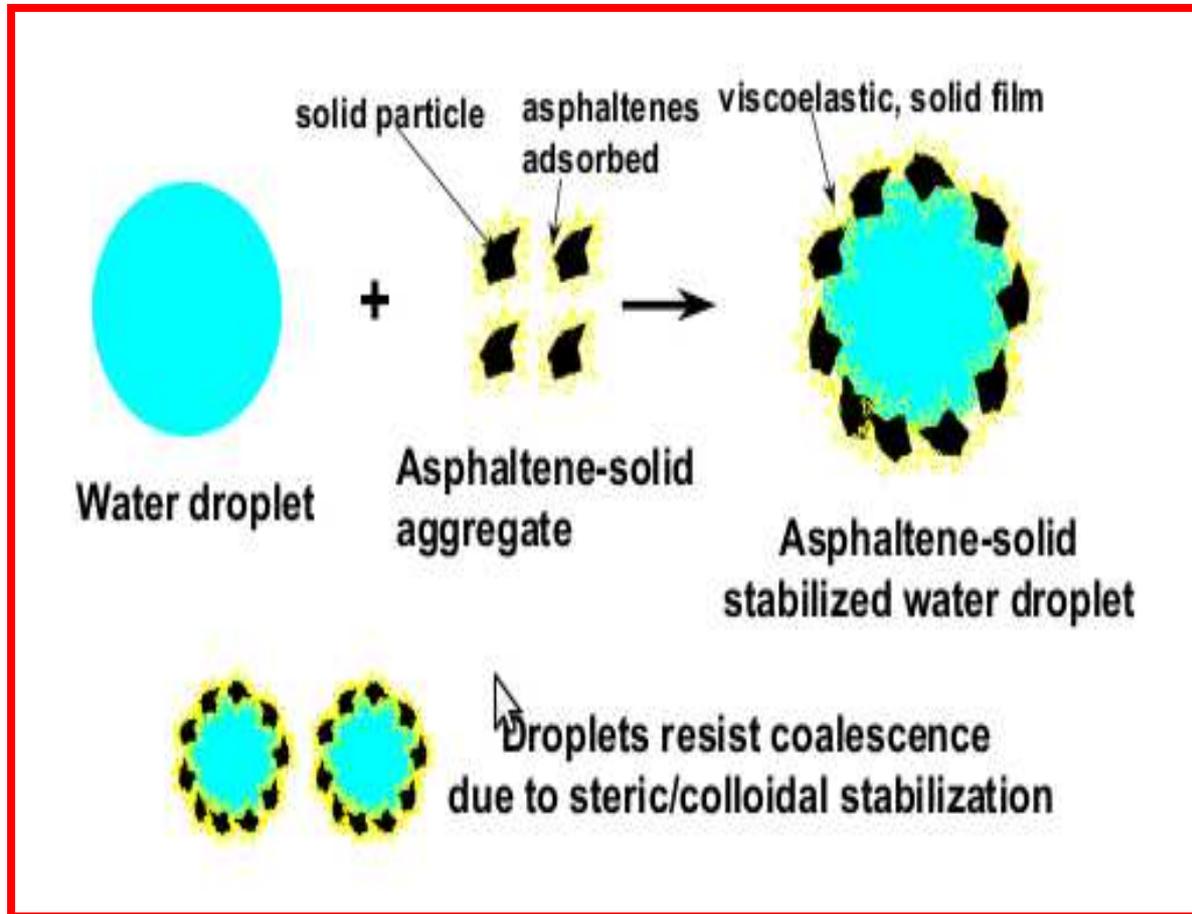


Figure 5.4: Mechanism of emulsion stabilization by asphaltenes.

Polar molecules of asphaltene which are oil wet can precipitate during oil production especially when the reservoir pressure falls below bubble point pressure⁷² and crude oil composition changing. They have a strong affinity and adsorb on other organic and inorganic solids, producing emulsion stabilized films at oil/water interface and contributing tremendously to the formation of tight emulsions.^{73 - 75}

5.1.3 Inorganic Solid Contents – Sodium Bentonite and Calcite

Inorganic solids are introduced into the petroleum system through either through precipitation and migration of reservoir fines, scales or as products of corrosion and fouling in tubing and flowlines.⁷⁶

De-asphalted oil was used in preparing emulsion samples with varying concentration of inorganic solids, simulated with sodium bentonite and calcium carbonate (calcite) powders. After 20 minutes, the amount of water separated from each prepared emulsion sample was used in calculating tightness of the emulsions, and the results are presented in Table 5.1. It was found that the amount of bentonite clay solids had little effects on emulsion stability and very loose emulsions were produced. At a concentration of 0.05 wt%, almost all the dispersed water drained off as free water in less than 5 minutes, and only 0.3ml of water remained unseparated after 20 minutes, which is equivalent to a tightness of 1.01%. The same effect was observed for concentrations of 1.3%, 2.9%, 4.8% and 9.8%. There was no significant change in the emulsion tightness as shown in table 5.1. When the solid content was increased to such a high concentration of 21 wt%, an emulsion tightness of only 7.18% was recorded. Pink-White coloured particles of the clay solids were found to deposit at the bottom of the test bottle at all these concentrations tested.

Although Calcite solids also demonstrated a similar effect on the stability and tightness of the emulsion formed, they showed some significant effects at higher concentrations. At concentrations of 2.9%, 4.8%, 9.4%, 14.8% and 21.0% the emulsion tightness observed were 13.05%, 15.32%, 16.00%, 17.48% and 23.00% respectively. The effects are relatively higher compared to the effect of bentonite solids of the same concentration. Although white solid deposits were also found at the bottom of the test bottles used here, but in a lower quantity. In addition, a combination of both bentonite and calcite solids were also tested. This was performed to observe any cumulative effect of these solids on emulsion tightness. The results obtained remained similar to that of their individual effects. Hence it can be said that inorganic solids do not really have a strong effect on emulsion tightness as seen in this study.

According to Bancroft's rule⁵³ emulsifying agents that are soluble in or wettable by water will stabilize only water-in-oil emulsions and vice versa. By nature, inorganic solids are water wet, and would only remain in dispersion as colloids in the water phase. In the experiments with bentonite and calcite clays, these solids remained only in the water phase, and hence settled out of the emulsion mixture after sometime. They could not form strong rigid films that can sterically prevent water droplets coalescence as observed for asphaltene solids. The wetting behaviour of these solid particles at the water surface is described in Figure 5.5.

However, several researchers who had worked on this subject matter reported that very small inorganic particles contribute to water-in-oil emulsion stability.^{1, 74} They would only do so if their particles are small enough to become interfacially active, with the adsorption of resins and asphaltenes from crude oil. Hence, further experiments were carried out on these inorganic solids after they were coated with asphaltene. These tests were done to study the wettability effect of asphaltene on the inorganic solids and consequently their stabilizing effect on emulsion. Sufficient amount of Bentonite and calcite solids were suspended in toluene solutions of asphaltenes separately for 24hrs. The solids were then filtered and added to the oil/water mixture prepared, and the experiment repeated. Figure 5.6 presents a comparison of the effect of asphaltene coated and uncoated inorganic solids on emulsion tightness. Tight emulsions were produced from each of these samples. Tightness as high as 21.0 % and 19.0 % were observed when only 2.9% of coated Bentonite and Clay were studied respectively. These emulsions became even tighter as the concentrations of these solids were increased for both bentonite and calcite. In fact at higher solid concentrations of 21wt% the emulsions produced with bentonite and calcite coated solids was 92% and 98% respectively, and could not be properly resolved with 15 ppm of Phasetreat 4633 within 20 minutes. Deposits were also obtained at the bottom of these samples in the test bottles after the treatment, but at a very low quantity compared to experiments with uncoated solids. Also the colour of the deposited solids was black.

Asphaltene aggregates adsorb on the hydrophilic inorganic solids. This makes them intermediately wet and hence becomes very active emulsifying agents in these experiment. Figure 5.7 schematically describes the mechanism of adsorption of asphaltene aggregates on the inorganic solids. They formed strong interfacial films, and hence produced very tight emulsions as their concentration increased. Figure 5.8 also shows a schematic illustration of a stabilized water droplet by Asphaltene coated solids.

Figure 5.9 shows a general comparison of tightness in the emulsion samples produced as they were stabilized by all the conditions tested. This includes asphaltene, inorganic solids coated with asphaltene, and finally when they were uncoated. Uncoated inorganic solids contribute least to emulsion tightness. Ordinary asphaltenes and asphaltene coated solids have similar effects on emulsion tightness.

Table 5.1: Effect of Inorganic solids on emulsion tightness

Solid Conc. (wt %)	Emulsion Tightness, ET (%)		
	Clay Fines	Calcite powder	Fines + caco3
0.05	1.01	1.3	1.92
0.50	2.28	4.11	3.86
1.30	3.91	9.34	8.98
2.90	4.00	13.05	11.32
4.80	4.31	15.32	14.3
9.40	4.94	16.00	13
14.80	5.32	17.48	14.12
21.00	7.18	23.00	21.7

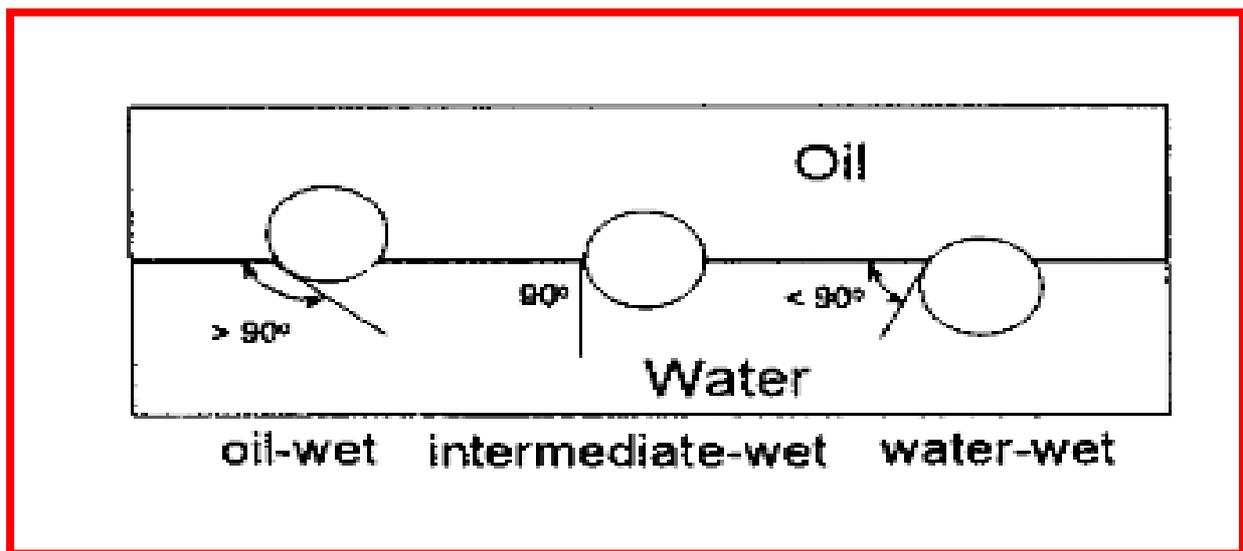


Figure 5.5: Wetting behaviour of solids at the oil-water interface.

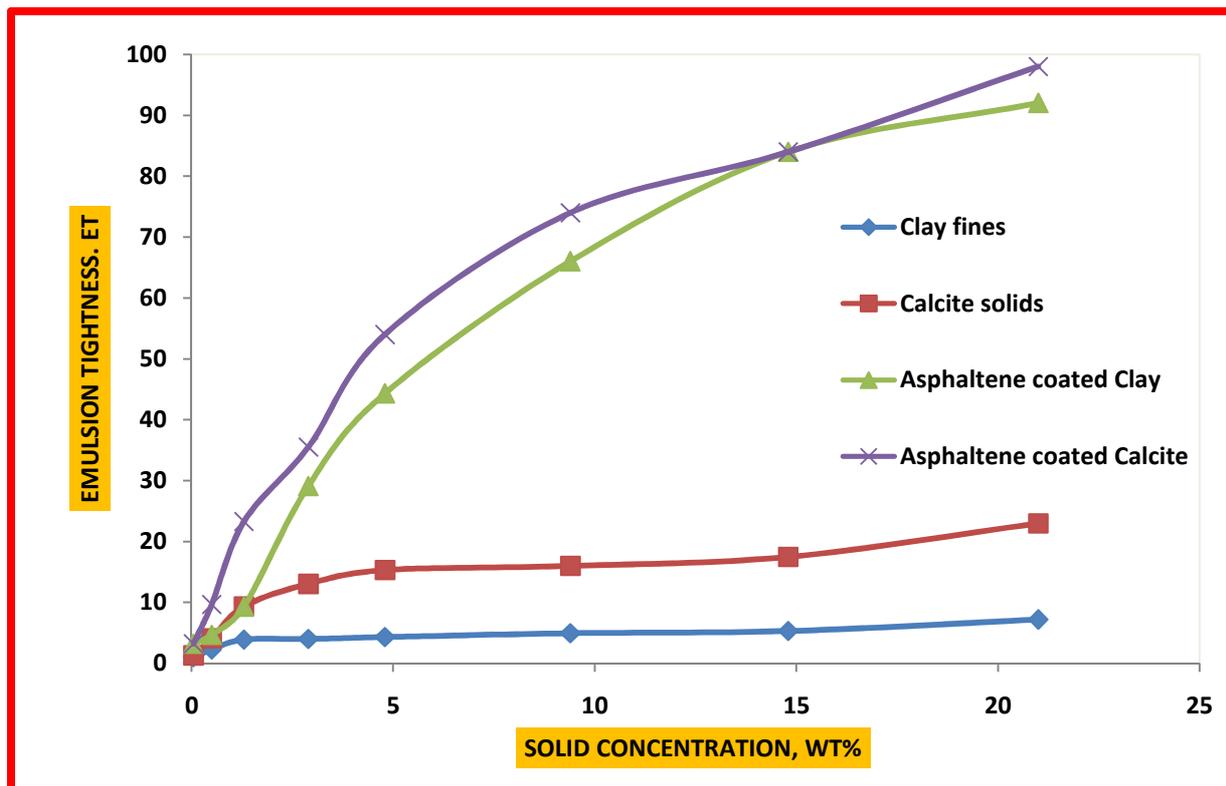


Figure 5.6: Effect of Asphaltene coated solids on emulsion tightness

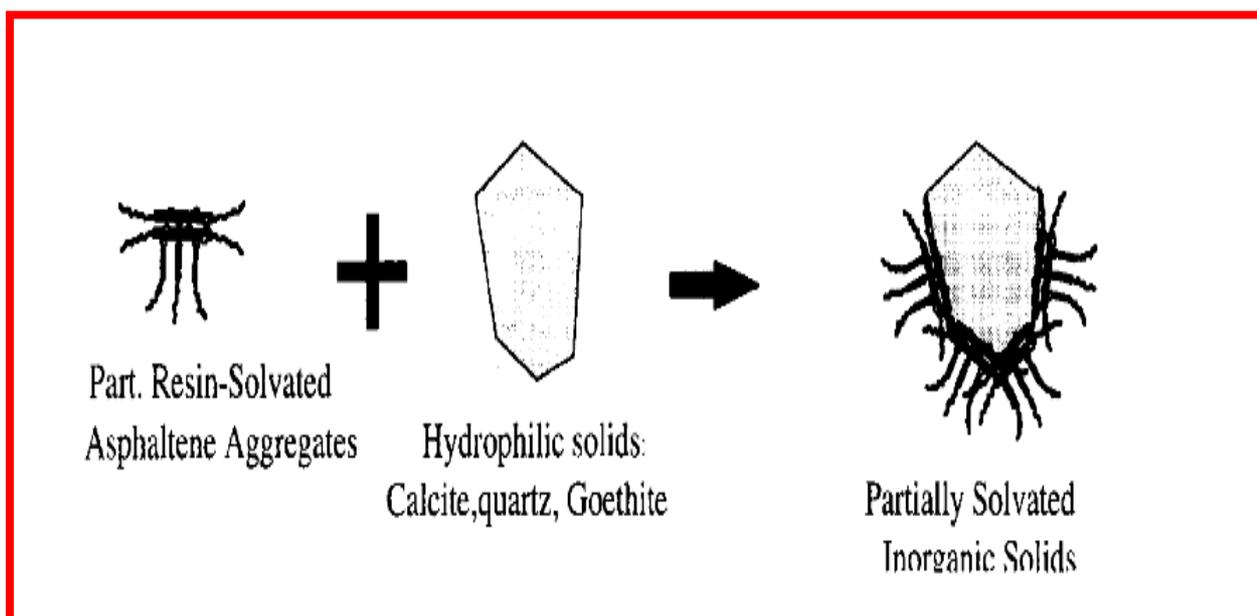


Figure 5.7: Schematic diagram showing the Adsorption of asphaltene on inorganic solids

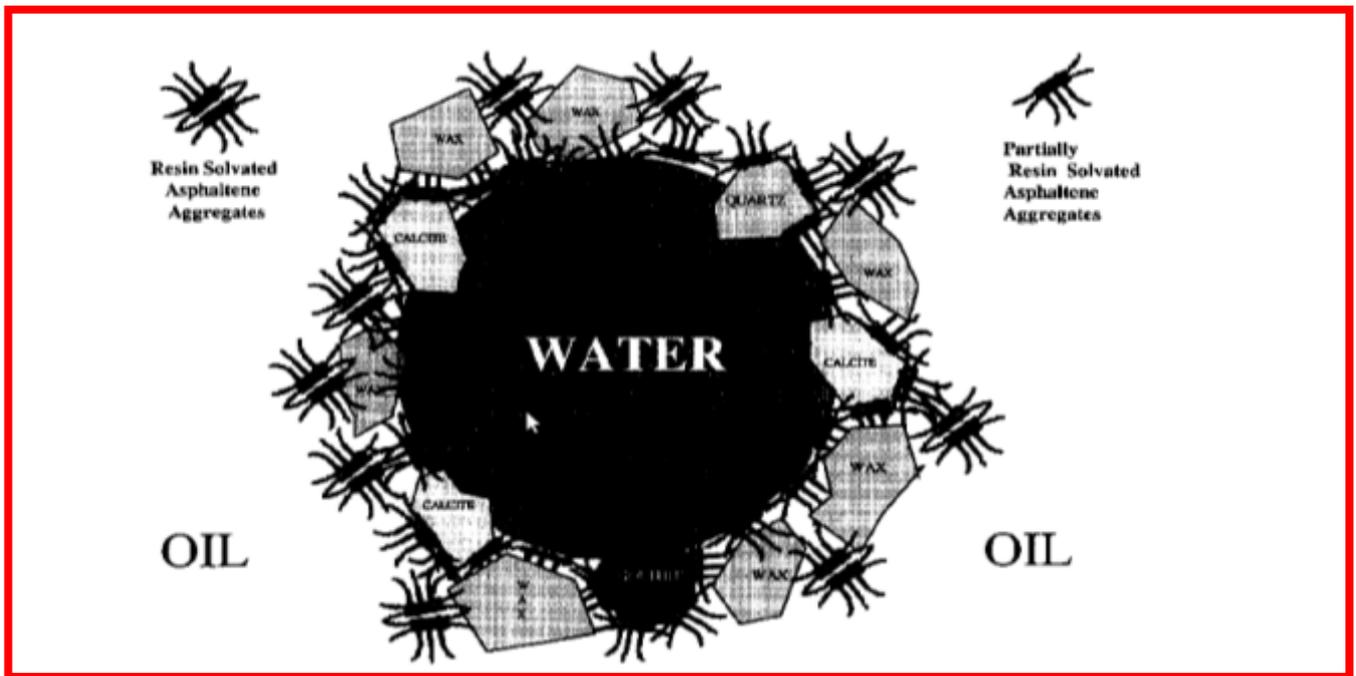


Figure 5.8: Schematic showing water droplets stabilized by asphaltene coated solids

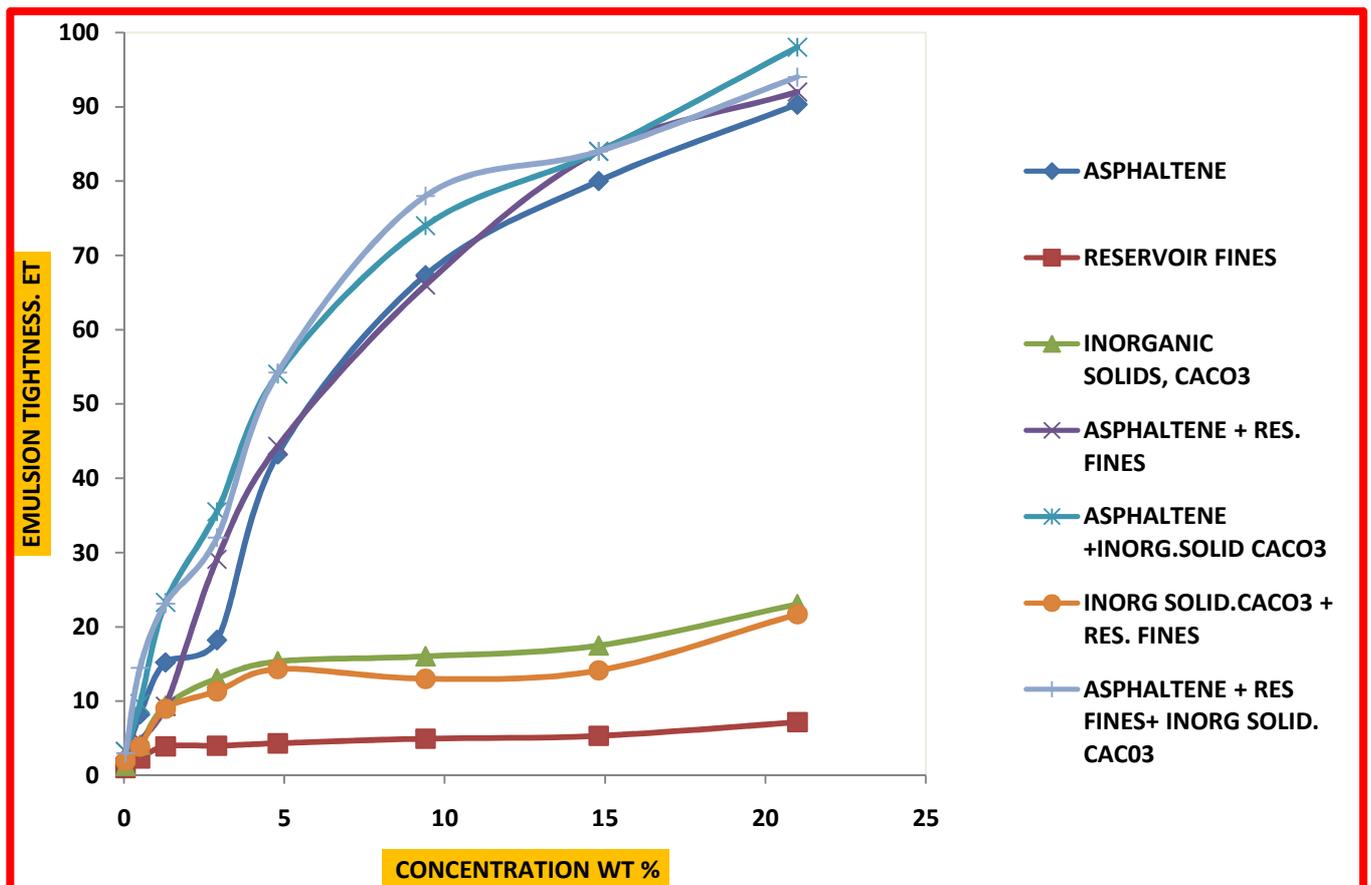


Figure 5.9: Effect of asphaltene, asphaltene coated and uncoated solids on emulsion tightness

5.2 Experimental Set 2: Combined Effects of Asphaltene Concentration, Shearing Energy and Water Cut on Emulsion Tightness

Studies in Experiment 2 were designed to measure the combined effect of asphaltene concentration and shearing energy on the tightness of emulsion. This was done for several percentages of watercut. The same sets of standard conditions in experiment 1 were used for all the constant parameters here as well. Also the shearing energy thresholds for emulsion formation were observed. Results obtained demonstrate some interesting trends relating shearing energy and asphaltene concentration to emulsion tightness.

At the onset of shearing, no stable emulsion was formed even in samples with the highest concentration of asphaltene for all the cases of watercut studied. Stable emulsions started forming when a particular threshold value of shearing energy was reached. This energy varied for all the watercut studied. Figures 5.11 to 5.13 presents the shearing energy threshold (SET) values for the 3 watercut studied. I.e. 5 %, 30 % and 55%.

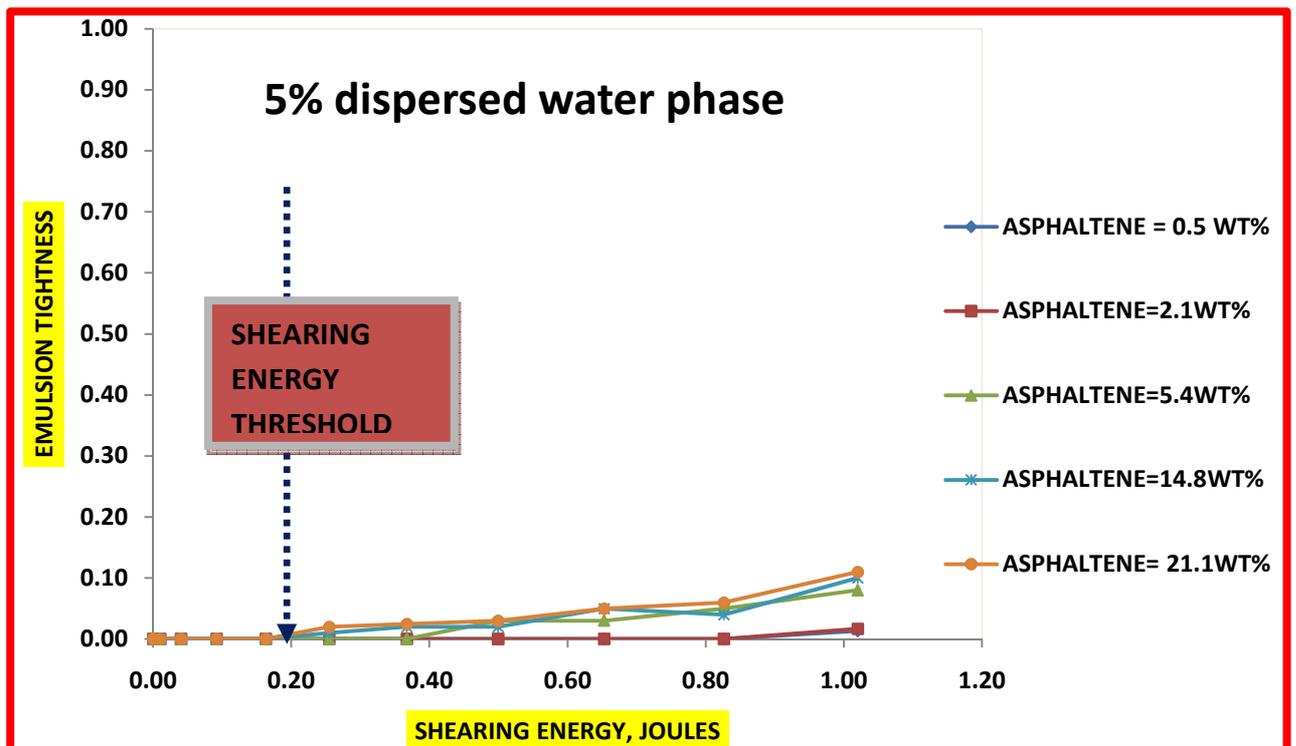


Figure 5.11: Effect of asphaltene content and shearing energy on emulsion tightness at 5% watercut and showing threshold energy of emulsion formation

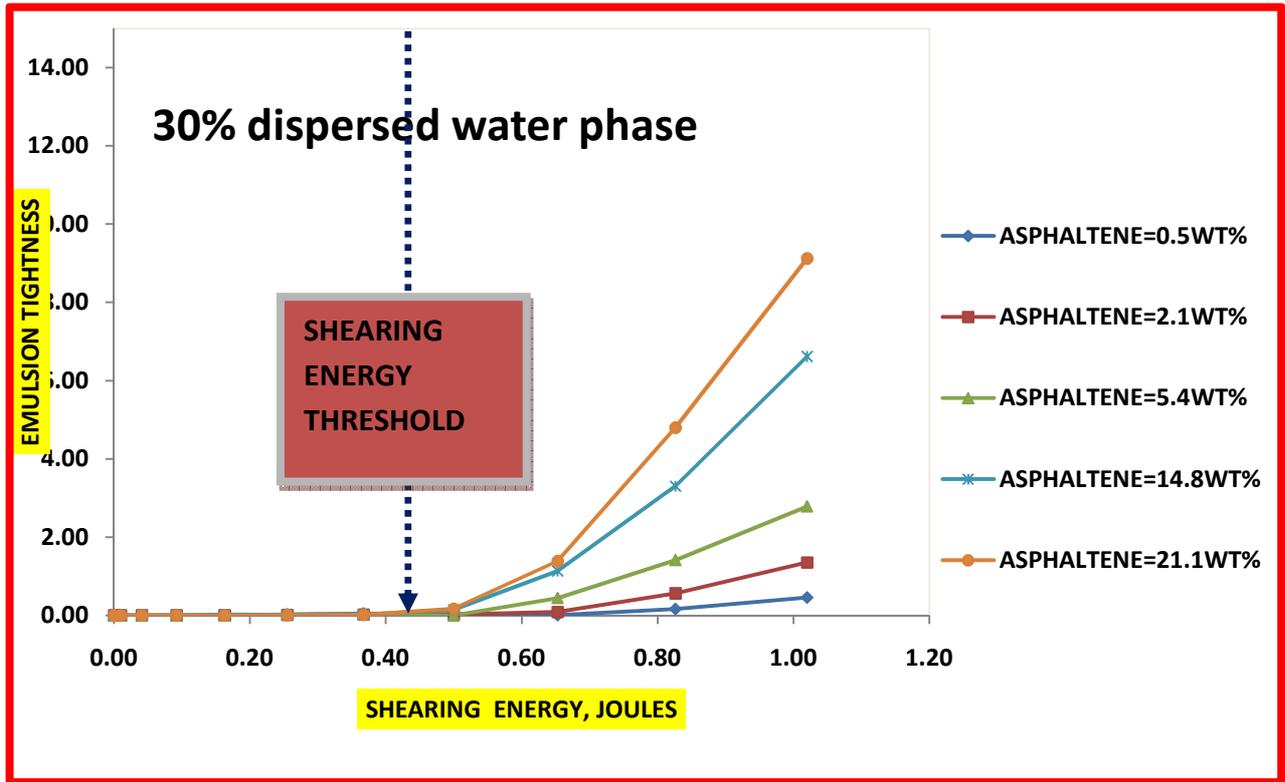


Figure 5.12: Effect of asphaltene content and agitation energy on emulsion tightness at 30% watercut and showing threshold energy of emulsion formation.

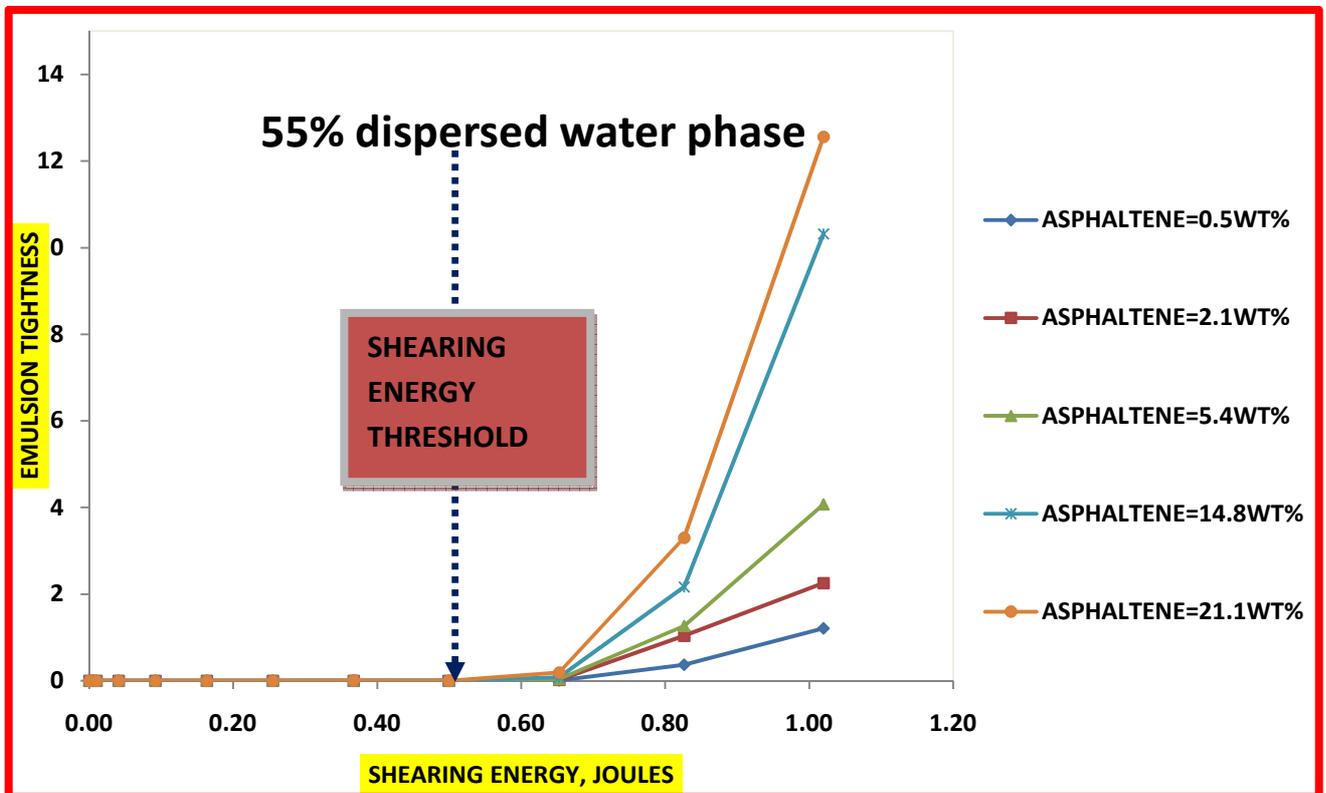


Figure 5.13: Effect of asphaltene content and agitation energy on emulsion tightness at 55% watercut and showing threshold energy of emulsion formation.

Samples with 5% water cut had a shearing Energy Threshold (SET) of about 0.25J. SET value for 30% water is about 0.37 J and finally 0.5 J for 55% watercut. According to Oldroyd equation⁶⁸ which describes the viscosity of emulsion, the factor that is most likely to affect emulsion viscosity is the volume fraction of the dispersed phase. As more water is sheared with the oil, the viscosity of the resulting emulsion increases significantly especially for high percentages of water. For emulsions having a high viscosity or high resistance to flow, more energy is required to create the emulsion. Hence as the quantity of dispersed water increases, the shearing energy threshold needed for emulsion formation increases. Asphaltene content does not have any significant effect on SET values. At all asphaltene concentrations, the SET was reached before any stable emulsion started forming. Table 5.2 shows a summary of the shearing energy threshold values for emulsion formation at 5%, 30% and 55% watercut at all corresponding asphaltene concentrations.

However the behaviour of the produced emulsions became very different after SET value. Figure 5.14-5.16 present these experimental results. For emulsion samples prepared with 5% water, further increase in shearing energy produced very loose and unstable emulsions. When the shearing device was made to rotate at 400RPM which is an equivalent energy of 16.32 J, loose emulsions with tightness 1.19%, 1.82%, 2.53%, 3.89% and 4.21% were produced from oil/ water mixture with asphaltene concentrations of 0.5wt%, 2.1wt%, 5.4wt%, 14.8wt% and 21.1wt% respectively. Also for a higher shearing energy of 100J, emulsions with tightness 6.30%, 8.18%, 14.30%, 20.87% and 21.32% were produced from oil/ water mixture with asphaltene concentrations of 0.5wt%, 2.1wt%, 5.4wt%, 14.8wt% and 21.1wt% respectively. Although loose emulsions were formed in this study, their relative tightness increased with increase in both asphaltene content and shearing energy as shown in Figure 5.14.

Samples with 30% water cut demonstrated some different behaviour compared to the 5% samples. Stable and tight emulsions were produced as the shearing energy increases beyond the threshold value. Although increase in asphaltene concentration for definite energy values also led to increase in the emulsion tightness as observed in studies with 5% watercut, the rate of increments are more pronounced here. Figure 5.15 illustrates that at energy value of 1Joules, E_T values of the emulsions formed are 0.46%, 1.36%, 2.79%, 6.62% and 9.12% at respective asphaltene concentrations of 0.5wt%, 2.1wt%, 5.4wt%, 14.8wt% and 21.1wt%. As the shearing energy was increased to 36 Joules, tighter emulsions with E_T 1.94 %, 7.42%, 10.29%, 22.87% and 28.50% were formed at respective asphaltene concentrations of 0.5wt%,

2.1wt%, 5.4wt%, 14.8wt% and 21.1wt%. Furthermore, very tight emulsions were observed at high shearing energy values and asphaltene concentration. They could not be resolved even after 20 minutes. At energy of 82.6 joules emulsions as tight as 89.2% and 97% E_T were formed with asphaltene concentrations of 14.8wt% and 21wt% respectively. A very stubborn emulsion that was 100% tight was also produced with shearing energy of 102 Joules and asphaltene concentration of 21wt%.

Results from experiments with 55% watercut showed a similar trend as that of 30% as presented in Figure 5.16. However, emulsions formed with this ratio of dispersed water required the highest amount of energy to be created as seen in Table 5.2. Their shearing energy threshold for forming emulsion increased to about 0.8J. They form the tightest emulsion even though with a larger amount of separated free water after about 5 minutes. The effect of asphaltene increase on emulsion tightness at definite energy levels showed the same trend as seen for 30% watercut samples. At high asphaltene concentration and shearing energy, very stable and tight emulsions were also formed as compared to 30% water cut samples.

Generally, it can be said that shearing energy and the concentration of asphaltene determines the degree of emulsion tightness. A particular threshold value of shearing energy is needed to form emulsion for a specific water oil ratio, regardless of the asphaltene concentration present. This energy increases as the water increases until the emulsion reaches its inversion point, where loose emulsions start forming. This has already been proved in experimental set 1. Moreover, the tightness of an emulsion increases with asphaltene content.

Table 5.2: Threshold Energy values of emulsion formation at 5%, 30% and 55% Watercut

Asphaltene Concentration (wt %)	Shearing energy Threshold values		
	5%	30%	55%
0.1	0.19	0.29	0.65
2.4	0.19	0.37	0.65
5.4	0.18	0.37	0.65
14.8	0.19	0.34	0.67
21.1	0.19	0.37	0.65

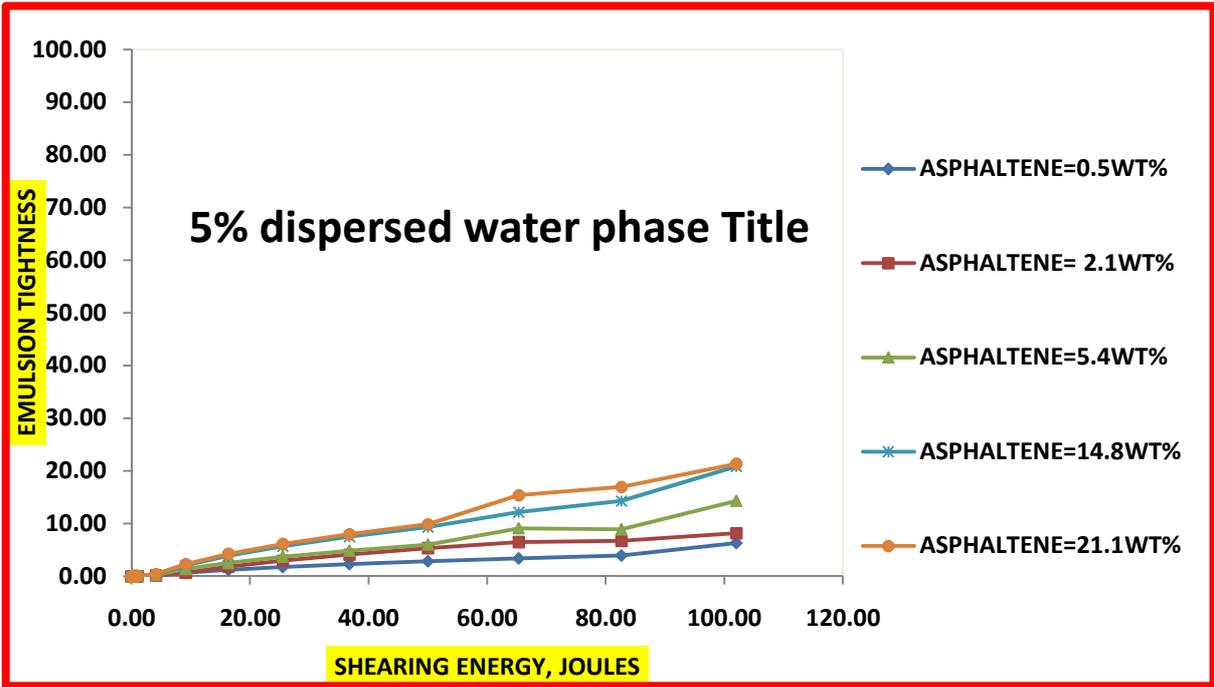


Figure 5.14: Effect of asphaltene content and shearing energy on emulsion tightness at 5% water cut and after threshold

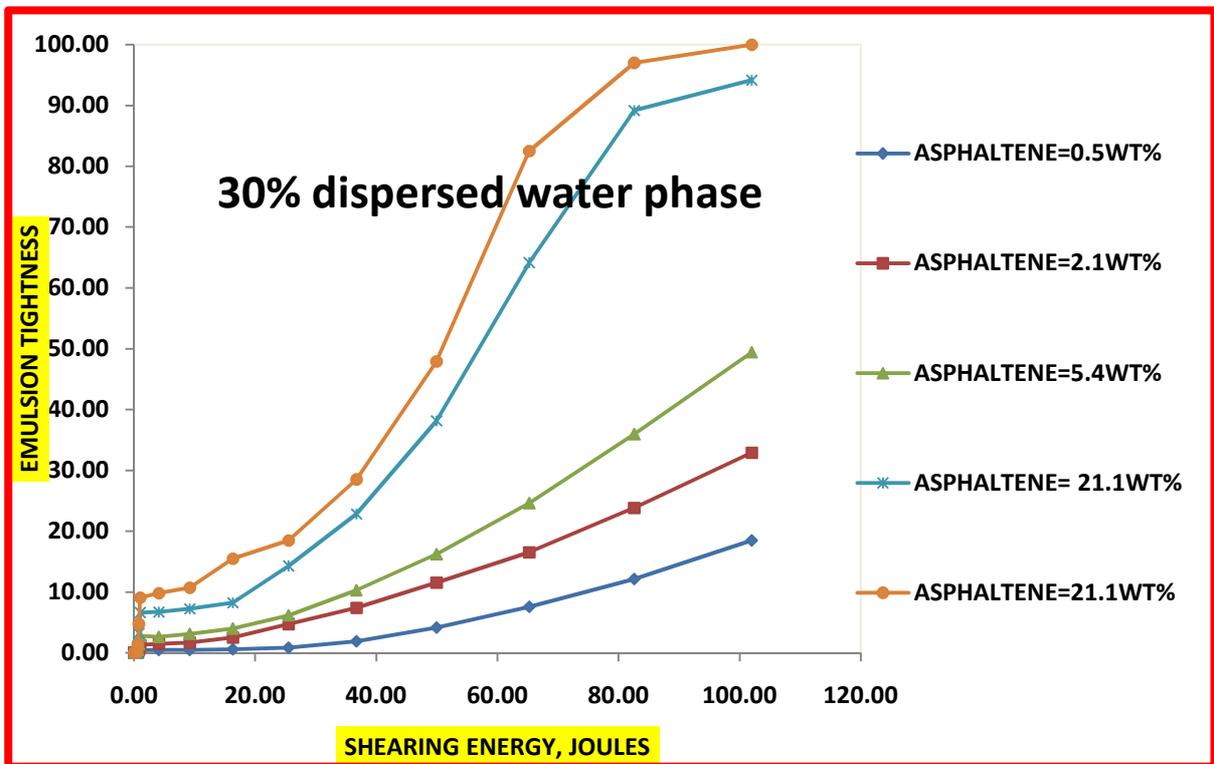


Figure 5.15: Effect of asphaltene content and shearing energy on emulsion tightness at 30% water cut and after threshold

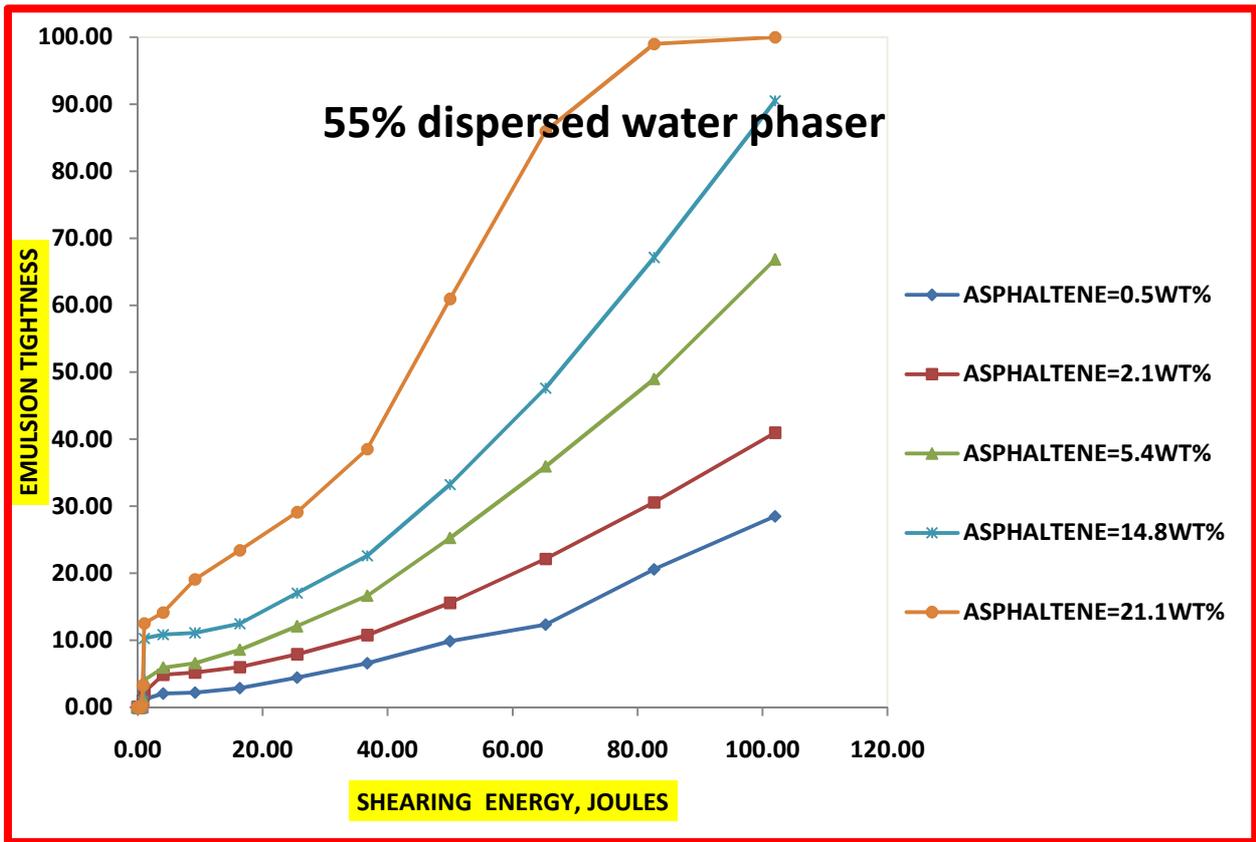


Figure 5.16: Effect of asphaltene content and shearing energy on emulsion tightness at 55% water cut and after threshold

5.3 Emulsion Classification Number (ECN): A Novel Approach

The tightness of the produced emulsion samples used in this study is measured with a new approach called emulsion tightness, E_T developed in this thesis.

$$E_T = \frac{[\text{Amount of water blended} - \text{Amount of water separated after time, } t]}{\text{Amount of water blended}} \% \quad (5.3)$$

It should be noted that values of E_T should be coated with the time of separation and demulsifier used for the test. E.g. E_T [10 minutes, PT 4633/3ppm] = 23.3%.

E_T would give values ranging from 0 to 100 percent. This range of emulsion tightness numbers is called EMULSION CLASSIFICATION NUMBER, (ECN). Zero means no stable emulsion is formed and all the water phase came out as free water. Values from 1 to about 5 means emulsion is very loose i.e. almost all emulsified water separated. While 100 mean a tight emulsion, which would not drop any water after a particular time. The ECN scale is developed as shown in Figure 5.17. Movement along the scale from 0 to 100 means produced emulsion varies from very loose to extremely tight.

Just like E_T values should be reported with the time of separation and the type demulsifier used for the test, ECN classification should also be done in this manner.

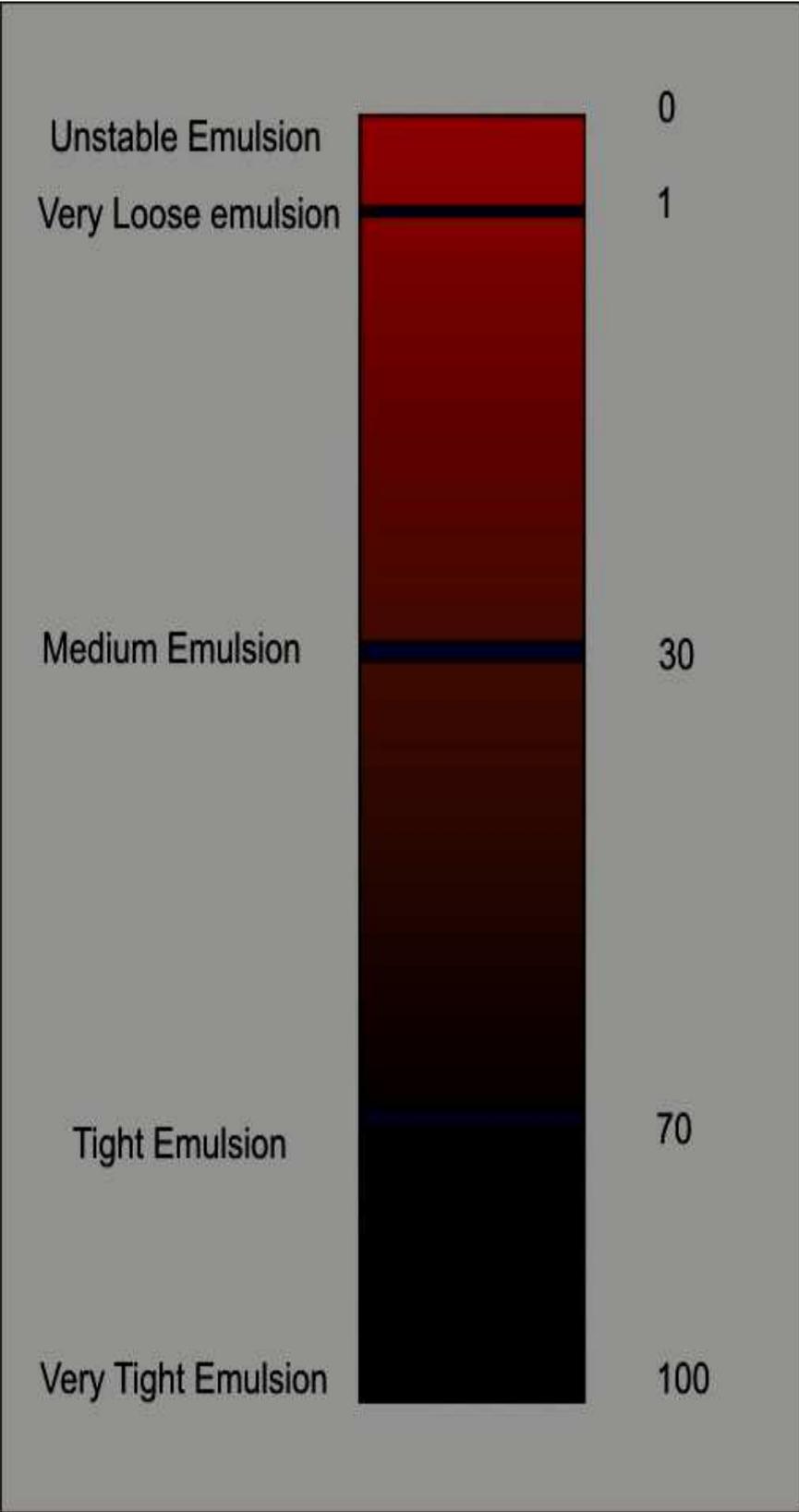


Figure 5.17: Emulsion Classification Number scale.

5.4 Computer Modelling of Results from Experiment 2

Studies in Experiment 2, shows the effect of asphaltene concentration, watercut and shearing energy on the tightness of emulsion. Results obtained demonstrate lots of interesting trends relating these parameters, and hence could be used to predict and rank emulsion samples according to their tightness. Samples produced from different wells, will have different values of tightness according to the approach developed in this thesis.

Figures 5.11 to 5.16 show the plots of Emulsion tightness versus shearing energy, and at different asphaltene contents and watercuts. These plots are referred to as EMULSION DIAGNOSTIC PLOTS, (EDP) as developed in this thesis. They have been digitized using Regression analysis in Microsoft excel spreadsheet. Best line of fit for each of the data series plotted were analysed and their corresponding equations generated. 5 concentrations of asphaltenes were studied over 3 water cuts, and hence yielding 15 different equations. Shearing energy was made the independent variable in this experiment. The trendline graphs gotten from the regression analysis are shown in Appendix C.

However, the equations generated are polynomials of 4th, 5th and 6th orders. Their ranges of applicability have been provided alongside according to the threshold value of energy responsible for emulsion formation for each watercut. Equations 5.1-5.16 show the generated equations.

WATERCUT = 5 %

$$\text{ASP-0.5\%}; E_T = (1 \times 10^{-10} A^6) - (3.71 \times 10^{-8} A^5) + (4.37 \times 10^{-6} A^4) - (2.334 \times 10^{-4} A^3) + (0.0051 A^2) + (0.034 A) - (0.01548) \quad (5.1)$$

$$\text{ASP-2.1\%}; E_T = (-2.8 \times 10^{-9} A^5) + (8.96 \times 10^{-7} A^4) - (1.03 \times 10^{-4} A^3) + (0.0043 A^2) + (0.05791 A) - (0.031539) \quad (5.2)$$

$$\text{ASP-5.4\%}; E_T = (-2.7 \times 10^{-8} A^4) + (5.1291 \times 10^{-6} A^3) - (0.0011137 A^2) + (0.169674 A) - (0.08123) \quad (5.3)$$

$$\text{ASP-14.8\%}; E_T = (-5.1 \times 10^{-9} A^5) + (1.376 \times 10^{-6} A^4) - (0.00012851 A^3) + (0.003303 A^2) + (0.2044 A) - (0.09431) \quad (5.4)$$

$$\text{ASP-21.1\%}; E_T = (-1 \times 10^{-9}A^5) + (3.06 \times 10^{-7} A^4) - (3.279 \times 10^{-5}A^3) - (0.0001546A^2) + (0.260769A) - (0.1146055) \quad (5.5)$$

WATERCUT = 30 %

$$\text{ASP-0.5\%}; E_T = (1.14 \times 10^{-8}A^5) - (3.013 \times 10^{-6}A^4) + (2.778481 \times 10^{-4} A^3) - (0.0084198A^2) + (0.113776A) + (0.032647656) \quad (5.6)$$

$$\text{ASP-2.1\%}; E_T = (-8 \times 10^{-10}A^6) + (2.409 \times 10^{-7}A^5) - (2.675 \times 10^{-5} A^4) + (0.001367A^3) - (0.029562A^2) + (0.38553A) + (0.056904) \quad (5.7)$$

$$\text{ASP-5.4\%}; E_T = (2.6 \times 10^{-8}A^5) - (7.0597 \times 10^{-6}A^4) + (6.6774 \times 10^{-4} A^3) - (0.022278A^2) + (0.479625A) + (0.27724) \quad (5.8)$$

$$\text{ASP-14.8\%}; E_T = (5.5 \times 10^{-8}A^5) - (1.85 \times 10^{-5}A^4) + (0.00194 A^3) - (0.06787A^2) + (1.26232A) + (0.6247884) \quad (5.9)$$

$$\text{ASP-21.1\%}; E_T = (2.19 \times 10^{-7}A^5) - (5.896 \times 10^{-5}A^4) + (0.0053456A^3) - (0.181068915A^2) + (2.6954A) + (0.410177166) \quad (5.11)$$

WATERCUT = 55 %

$$\text{ASP-0.5\%}; E_T = (-5.6 \times 10^{-9}A^5) + (8.79 \times 10^{-7}A^4) - (1.3381 \times 10^{-6} A^3) - (0.00274A^2) + (0.24350234A) + (0.11077062) \quad (5.12)$$

$$\text{ASP-2.1\%}; E_T = (4.84 \times 10^{-8}A^5) - (1.31 \times 10^{-5} A^4) + (0.0012645A^3) - (0.04929732A^2) + (0.9442998A) + (0.05632010) \quad (5.13)$$

$$\text{ASP-5.4\%}; E_T = (-1.9 \times 10^{-9}A^6) + (6.12 \times 10^{-7}A^5) - (7.51 \times 10^{-5} A^4) + (0.004374A^3) - (0.117A^2) + (1.593A) - (0.0355) \quad (5.14)$$

$$\text{ASP-14.8\%}; E_T = (1.051 \times 10^{-7}A^5) - (2.86 \times 10^{-5}A^4) + (0.00278 A^3) - (0.108 A^2) + (2.024 A) + (0.5651) \quad (5.15)$$

$$\text{ASP-21.1\%}; E_T = (-2.7 \times 10^{-9}A^6) + (1.028 \times 10^{-6}A^5) - (1.482 \times 10^{-4} A^4) + (9.9368 \times 10^{-3} A^3) - (0.2991A^2) + (4.2989A) - (0.0544) \quad (5.16)$$

In equations 5.1 – 5.16, ET represents the Emulsion Tightness while A represents the shearing energy in Joules.

Generated equations have been written with JAVA programming Language. This program has been integrated into an executable application file. The source codes for this program are detailed in Appendix C. This program first estimates the shearing energy associated with individual well heads according to the analysis made in chapter three. The programmed equations of the Emulsion Diagnostic Plots, EDP are then automatically solved once the asphaltene content and water cut of the well is inputted. However, this study was made only for precipitated asphaltene concentrations (wt %) of 0.5, 2.1, 5.4, 14.8 and 21.1 over watercuts of 5%, 30% and 55%. All other values of asphaltene and watercut inputted to this programme are approximated to the nearest value of these parameters as written in the programme.

These equations developed are valid between certain ranges of shearing energy. This ranges account for the threshold energy required for emulsion formation and the maximum energy that could be generated in the laboratory. 5% water cut equations are only valid between shearing energy of 0.5 J and 75 J. The equations generated for 30% are valid 0.55 J and 100 J, and lastly 55% water cut equations are valid between 0.6 J and 100 J.

5.5 Application of Developed Program to Agip OB-OB Field Emulsion Problem

As described in chapter three, crudes from Kwale, Akri, OB-OB, Ebocha, Oshie, and Idu fields all comingle into a trunk line, LAR leading to brass terminal. This co-mingling of crude is the same for SAR line (Obama, Tebidaba, Ogboinbiri, and Clough Creek fields). At Brass, arrivals from SAR and LAR production headers co-mingle at a common manifold then flow into the gun barrel. The technology developed in this thesis is used to classify the crudes produced from OB-OB field. This field has 21 producing wells. Since the crude oil emulsion samples used for this study were collected from the major trunk line outlet of the SAR and LAR manifold header leading to the gunbarrel at the terminal in Brass, and then it's assumed to be representative enough for the OB-OB field. Problematic wells in this field are easily spotted out without any further bottle test using the Emulsion Tightness concept developed in this thesis.

An emulsion problem was encountered in this field in 2008. Some of the Obiafu wells became problematic due to changes in the produced fluid property and production condition. Clariant oil services, was invited to carry out bottle tests on all the 21 wells samples and some other samples from Ebocha. The production data for this field as of 27th Of June 2008 is provided in Table 5.3. The developed technology in this thesis is used to handle this problem, and the results obtained is compared to what clariant oil services obtained after the bottle testing exercise which lasted for about 2weeks. They reported that Obiafu-9T, Obiafu 32LS, Obiafu-25LS and Obiafu 31SS were the problematic wells and Phasetreat 4633 was recommended for their control.

Applying the technology developed in this thesis, the shearing energy of the 21 wells was firstly determined using the approach described in chapter three. It was observed that wells with relatively high production rate and small choke size have a relatively high pressure drop and hence higher values of shearing energy. Table 5.4 shows the shearing energy of all the 21 wells as calculated by the spreadsheet developed. As earlier explained, simulating exactly the intensity of turbulence experience on the field to that in the laboratory might be quite challenging. Hence a multiplication factor of 10^{-6} is used to reduce all the shearing energy values calculated to suite the range of values obtained in the lab. The developed EMULS -K software is then run to compute and compare the tightness of emulsion for all the 21 wells. This program runs by first requesting for the details of the field and the total number of wells it contain. Asphaltene content, watercut and the shearing energy of each of these fields are then entered individually. Figure 5.18-5.25 display snapshots of this process.

Table 5.3: Production data of Obiafu wells.

Data was collected on 27th, June 2008

S/N	Well	Reservoir	API	Asphaltene (wt%)	FTHP psia	FLP psia	Choke size 1/64 in	Gross bbls/day	Oil+cond bbls/day	Water bbls/day	BS&W %	Gas mmscf/day	GLR scf/bbl
1	Obiafu - 2LS	A9.200X	37	1.6	122	66	48	783	660	123	15.7	0.42	531
2	Obiafu - 2SS	A9.200X	24	0.2	387	110	32	720	683	37	5.2	0.79	1100
3	Obiafu - 4SS	A9.210X	40	0.1	247	101	35	820	722	98	12.0	0.48	584
4	Obiafu - 3LS	A9.200X	38	0.21	453	88	33	1065	852	213	20.0	0.89	840
5	Obiafu - 3SS	A9.200X	24	2.44	286	193	28	544	467	77	14.2	0.39	722
6	Obiafu - 6LS	E2.000X	20	5.9	176	66	28	364	175	189	52.0	0.23	635
7	Obiafu - 6SS	E2.000X	20	6.7	180	143	32	590	354	236	40.0	0.27	459
8	Obiafu - 9T	E2.000X	21	5.3	2640	305	24	2423	1333	1090	45.0	3.44	1420
9	Obiafu - 24TBG	E2.000X	39	3.6	468	87	32	1232	517	715	58.0	0.79	644
10	Obiafu - 25SS	E2.000X	37	0.84	197	130	48	1167	537	630	54.0	0.70	598
11	Obiafu - 25LS	A9.210X	33	7.5	1362	87	16	830	780	50	6.0	0.68	825
12	Obiafu - 26LS	A9.200X	25	0.21	504	86	32	1406	872	534	38.0	0.83	590
13	Obiafu - 26SS	A9.200X	29	0.46	248	120	28	510	400	110	21.6	0.33	641
14	Obiafu - 28SS	A9.200X	31	3.35	1042	218	28	1347	1266	81	6.0	1.76	1310
15	Obiafu - 29SS	A9.200X	24	5.7	376	94	32	650	600	50	7.7	0.80	1230
16	Obiafu - 29LS	G9.300X	23	6.4	139	65	32	411	279	132	32.0	0.22	540
17	Obiafu - 30TBG	G9.300X	28	0.11	166	71	32	443	248	195	44.0	0.28	634
18	Obiafu - 31LS	G9.300X	40	0.33	331	98	16	234	225	9	3.8	0.15	657
19	Obiafu - 31SS	E2.000X	39	3.33	1300	305	28	1284	822	462	36.0	2.54	1980
20	Obiafu - 32LS	E2.000X	23	4.2	939	230	24	946	549	397	42.0	1.16	1230
21	Obiafu - 32SS	E2.000X	33	0.45	1340	412	28	1274	1124	150	11.8	2.68	2100

Table 5.4 Shearing Energy for the 21 wells in Obiafu

S/N	Well	Reservoir	API	BS&W %	Asphaltene (wt%)	Choke size 1/64 in	FTHP psia	FLP psia	Pressure drop psia	Shearing Energy Joules	Laboratory Scale Joules x E+6
1	Obiafu - 2LS	A9.200X	37	15.7	1.6	48	122	66	56	200,035	0.20
2	Obiafu - 2SS	A9.200X	24	5.2	0.2	32	387	110	277	1,633,001	1.63
3	Obiafu - 4SS	A9.210X	40	12.0	0.1	35	247	101	146	973,851	0.97
4	Obiafu - 3LS	A9.200X	38	20.0	0.21	33	453	88	365	2,746,222	2.75
5	Obiafu - 3SS	A9.200X	24	14.2	2.44	28	286	193	93	969,078	0.97
6	Obiafu - 6LS	E2.000X	20	52.0	5.9	28	176	66	110	1,147,815	1.15
7	Obiafu - 6SS	E2.000X	20	40.0	6.7	32	180	143	37	293,014	0.29
8	Obiafu - 9T	E2.000X	21	45.0	5.3	24	2640	305	2335	33,187,625	33.19
9	Obiafu - 24TBG	E2.000X	39	58.0	3.6	32	468	87	381	3,041,923	3.04
10	Obiafu - 25SS	E2.000X	37	54.0	0.84	48	197	130	67	237,752	0.24
11	Obiafu - 25LS	A9.210X	33	6.0	7.5	16	1362	87	1275	40,764,774	40.76
12	Obiafu - 26LS	A9.200X	25	38.0	0.21	32	504	86	418	3,341,751	3.34
13	Obiafu - 26SS	A9.200X	29	21.6	0.46	28	248	120	128	1,336,552	1.34
14	Obiafu - 28SS	A9.200X	31	6.0	3.35	28	1042	218	824	8,607,754	8.61
15	Obiafu - 29SS	A9.200X	24	7.7	5.7	32	376	94	282	2,251,414	2.25
16	Obiafu - 29LS	G9.300X	23	32.0	6.4	32	139	65	74	592,315	0.59
17	Obiafu - 30TBG	G9.300X	28	44.0	0.11	32	166	71	95	762,698	0.76
18	Obiafu - 31LS	G9.300X	40	3.8	0.33	16	331	98	233	7,454,276	7.45
19	Obiafu - 31SS	E2.000X	39	36.0	3.33	28	1300	305	995	10,385,720	10.39
20	Obiafu - 32LS	E2.000X	23	42.0	4.2	24	939	230	709	10,074,967	10.07
21	Obiafu - 32SS	E2.000X	33	11.8	0.45	28	1340	412	928	9,687,730	9.69

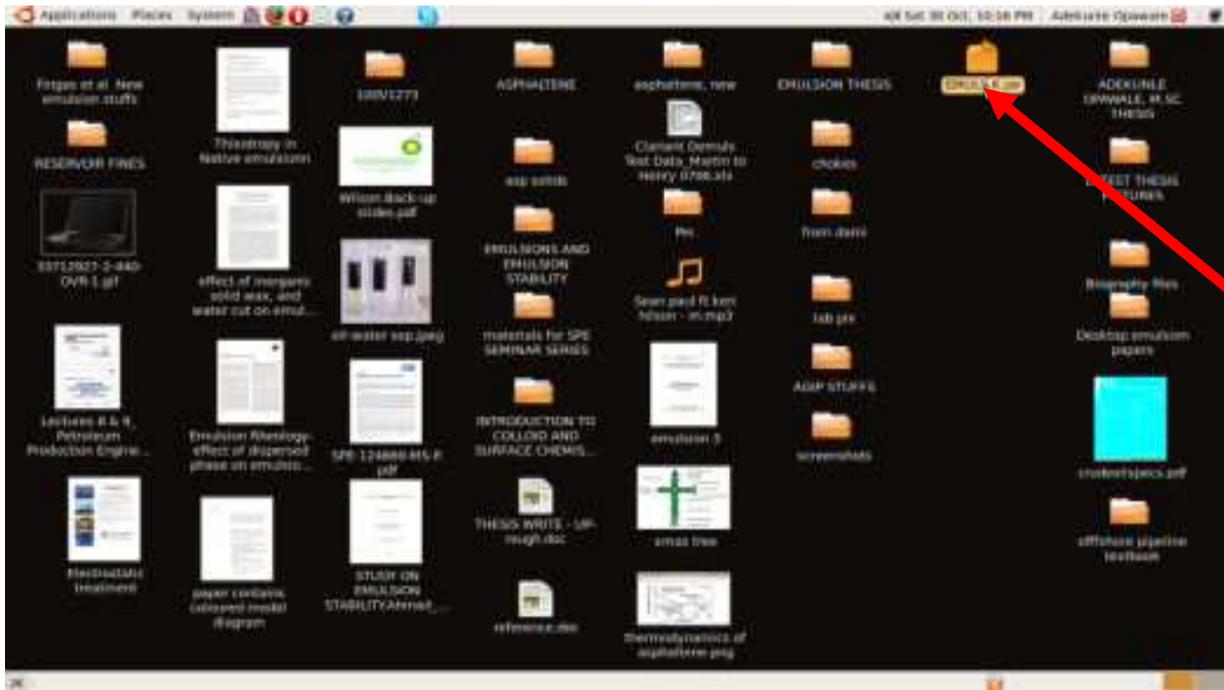


Figure 5.18: Desktop displaying icon of EMULS-K application



Figure 5.19: Inputting the name of the oilfield to be analysed



Figure 5.21: Inputting the location of field

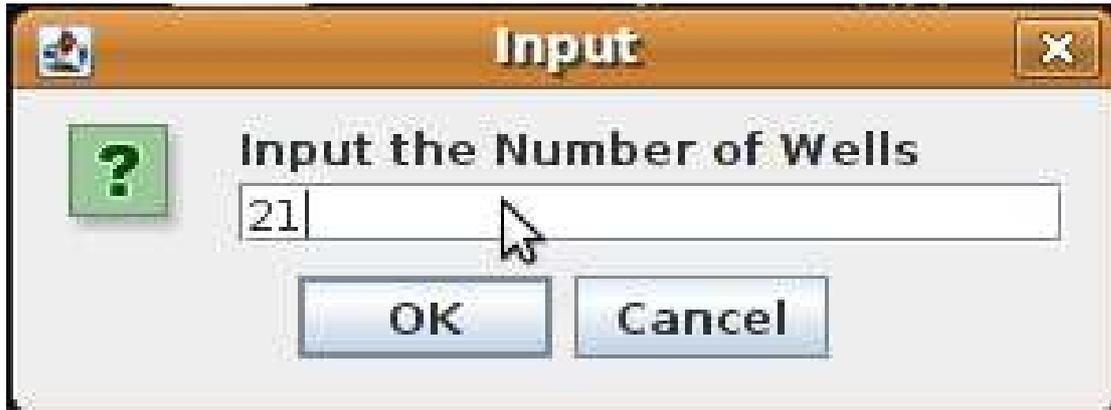


Figure 5.22: Inputting the number of wells on the field.

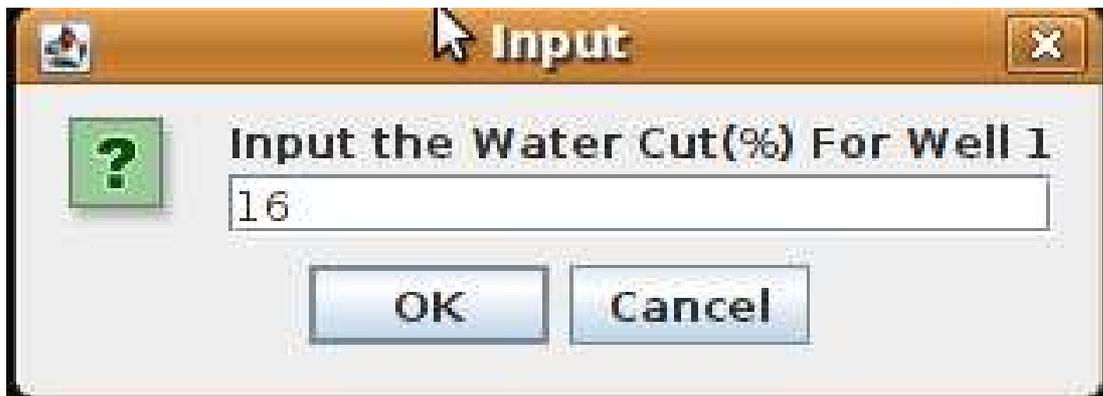


Figure 5.23: Inputting the watercut of the well



Figure 5.24: Inputting the asphaltene content of the well



Figure 5.25: Inputting the shearing energy estimated to be experienced at well1

PREDICTION OF OIL FIELD EMULSION TIGHTNESS AT WELLHEAD
 ADEKUNLE OPAWALE
 DEPARTMENT OF PETROLEUM ENGINEERING
 AFRICAN UNIVERSITY OF SCIENCE AND TECHNOLOGY. ABUJA NIGERIA
 Version 1.01: Copyright 2010, All rights

Name of Oil Field : AGIP, Ob-Ob (Obiafu Wells)
 Location of Oil Field : Portharcourt, Nigeria

Well	WaterCut(%)	Asph.Content(wt%)	ShearingEnergy(J)	EmulsionTightness
1	16	1.6	0.3	0.1699391129098038
2	5	0.2	1.63	0.05250981698367343
3	12	0.1	0.97	0.02208940907564455
4	20	0.21	2.75	0.2874647659482422
5	14	2.44	0.97	0.02858636030781303
6	52	5.9	1.15	1.648239683436408
7	40	6.7	0.29	0.4144739058322722
8	45	5.3	33.19	14.847904281699227
9	58	3.6	3.04	3.842581305691703
10	54	0.84	0.26	0.17389598489171987
11	6	7.5	40.76	5.257212384106894
12	38	0.21	3.34	0.3287138914921697
13	22	0.46	1.34	0.17064776934495463
14	6	3.35	8.61	1.300227628402126
15	8	5.7	2.25	0.2949561254242188
16	32	6.4	0.59	0.5526000643829286
17	44	0.11	0.76	0.29424947883984726
18	4	0.33	7.45	0.43700089842501416
19	36	3.33	10.39	3.52541575757461
20	42	4.2	10.07	7.897276341155961
21	12	0.45	9.69	0.61593164651766

Figure 5.26: Result of Emulsion Tightness from Emuls-K software

PREDICTION OF OIL FIELD EMULSION TIGHTNESS AT WELLHEAD
ADEKUNLE OPAWALE
DEPARTMENT OF PETROLEUM ENGINEERING
AFRICAN UNIVERSITY OF SCIENCE AND TECHNOLOGY. ABUJA NIGERIA
Version 1.01: Copyright 2010, All rights

Name of Oil Field : AGIP, Ob-Ob (Obiafu Wells)

Location of Oil Field : Portharcourt, Nigeria

Well	WaterCut(%)	Asph.Content(wt%)	ShearingEnergy(J)	EmulsionTightness
1	16	1.6	0.3	0.17
2	5	0.2	1.63	0.05
3	12	0.1	0.97	0.02
4	20	0.21	2.75	0.29
5	14	2.44	0.97	0.03
6	52	5.9	1.15	1.65
7	40	6.7	0.29	0.41
8	45	5.3	33.19	14.85
9	58	3.6	3.04	3.84
10	54	0.84	0.26	0.17
11	6	7.5	40.76	5.26
12	38	0.21	3.34	0.33
13	22	0.46	1.34	0.17
14	6	3.35	8.61	1.30
15	8	5.7	2.25	0.29
16	32	6.4	0.59	0.55
17	44	0.11	0.76	0.29
18	4	0.33	7.45	0.44
19	36	3.33	10.39	3.53
20	42	4.2	10.07	7.90
21	12	0.45	9.69	0.62

Figure 5.27: Excel refined Result from Emuls-K software

After a complete running of this program, a result of the emulsion tightness of all the wells are displayed and compared by visual inspection. Figure 5.26 and 5.27 displays the raw and excel refined result of the emulsion tightness respectively. Obiafu -9T and Obiafu - 32LS have the highest tightness of emulsion and hence tagged as the problematic wells in this field. Obiafu - 31SS and Obiafu - 25LS also shows some high degree of emulsion tightness followed by Obiafu - 24TBG and Obiafu – 6LS.

Furthermore, the results obtained from this program are compared with the bottle test result reported by Clariant Oil services after their test in 2008. Good correlations are seen between the clariant bottle test analysis, and the EMULS-K application results. Both approaches presents Obiafu-9T, Obiafu 32LS, Obiafu-25LS and Obiafu 31SS as being problematic. Emuls-K further included Obiafu 24-TBG as well that needs to check as well. It has emulsion tightness of 3.84, which is relatively high compared to the other wells in the field.

CHAPTER 6

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary

The objectives of this study are as follows: (1) to develop a theoretical approach to analyse and quantify the agitation energy encountered at the wellhead. (2) To investigate the effect of water cut, inorganic solids, reservoir fines and asphaltenes on the stability of water-in-oil emulsions produced. (3) To develop an experimental approach to model the process of water-oil emulsion formation and its associated shearing energy. (4) To develop an index to compare emulsion tightness from individual wells in a field. (5) To develop an emulsion testing procedure based on a computer program and (6) To use all the techniques developed in this thesis to address the OB-OB Agip's emulsion problem.

In order to achieve these objectives, equation relating shearing energy to pressure drop at the wellhead was first established and detailed in Chapter Three. This approach tried to correlate the turbulence and shearing action at the well head to the pressure drop across it and the choke size. The concept of pressure drop in fluid flows over a surface area of characteristic length was used. Both the properties of the flowing fluid through the wellhead and the nature of the choke dictates the turbulence experienced in this region.

In chapter Four, two sets of experiments were carried out. The first sets of experiment were to identify the effects of Watercut, asphaltene content, Reservoir fines and inorganic solids on emulsion tightness. Several factors which include watercut, asphaltene content, reservoir fines and inorganic solids were studied. The second sets of experiments were to investigate the combined effect of water oil ratio, asphaltene concentrations and shearing energy on tightness of crude oil emulsions.

The technology developed in this thesis was applied to an emulsion problem encountered at the Ob-Ob field of National Agip Oil Company in 2006. This field has 21 wells. This issue was resolved by Clariant Oil Services after series of bottle test in July 2006. Identification of the problematic wells in this field was easily spotted out using the concept of Emulsion tightness, E_T developed. This was only with the set of equation developed, and no further laboratory bottle test were carried out. The results obtained from this study correlates perfectly well with those of Clariant in 2006 when this problem was encountered.

6.2 Conclusion

Based on the theoretical studies and experimental work from this study, the following conclusions were made.

1. A relationship that relates shearing energy, pressure drop, choke size was developed. This equation relates the production rate, type of the crude oil produced and the nature of the choke during production to shearing energy. Values of this shearing energy are used as the independent variable in the equations for calculating emulsion tightness, ET.
2. Increase in the fraction of the dispersed water phase in an oil-water mixture, leads to formation of tight emulsions. This relationship would exist until the point of inversion from water/oil emulsion to oil/water emulsion is reached, thereafter loose emulsions will start forming. The inversion point for the crude oils considered in this study was found to be approximately 60%.

Increase in the concentration of asphaltene significantly increases the tightness of an emulsion. By nature, reservoir fines and other inorganic solid tested are not good emulsifiers. However, in the presence of asphaltene, increasing the concentration of inorganic solids also contributes to emulsion stability. Hence asphaltene concentration is the major factor contributing to the formation of tight emulsion in this field.

3. A threshold shearing energy is needed to form emulsion. This energy varies with the nature of the fluid produced. Shearing energy and asphaltene concentrations determines the degree of emulsion tightness for all the water cuts studied. Tightness increases only after the threshold energy is reached.
4. An emulsion classification index was developed. It displays values of emulsion tightness (E_T) ranging from 0 to 100 percent. This range of emulsion tightness numbers is called Emulsion Classification Number, (ECN). Movement along the index from 0 to 100 classifies emulsion as unstable, very loose, medium, tight and very tight emulsion. Zero means emulsion is unstable and 100 mean emulsion is very tight.

5. A Java program has been written which inputs shearing energy at the wellhead, watercut and asphaltene contents for n-different number of wells and compares their tightness of emulsion. It automatically spots out the problematic well without any laboratory bottle test. The developed program was used to solve OB-OB emulsion upset problem, and the result obtained correlates very well with those obtained by a service company during their bottle trials.

6.3 Recommendation

Based on this study, the following recommendations are proposed.

1. More comprehensive study should be done on the thermodynamics of asphaltene precipitation.
2. The relationship between viscosity and shear rate for emulsion formation should be studied.
3. More research should be carried out on how the developed technology can be integrated into the development of an emulsion testing tool that uses probe technology.

Nomenclature

a	particle radius as used in Hamakar's equation
A	Hamakar's Constant
ΔA	Change in interfacial area between two surfaces
CPF	Central Processing Facilities
C_o	bulk concentration of ionic specie
D_o	Characteristic length of flow
EO	Ethylene oxide
ΔE	Change in activation energy
EDP	Emulsion Diagnostic Plots
ECN	Emulsion Classification Number
FTHP	Flow Tubing head pressure, psi
FLP	Flowline pressure, psi
GLR	Gas Liquid Ratio, scf/bbl
ΔG_{form}	Free energy of formation of droplets
h	Minimum distance between two approaching surfaces
H	Centre to centre separation distance between two approaching surfaces
HLB	Hydrophylic-Lipophylic balance
HMW	High molecular weight
K	Ratio of viscosity of the dispersed phase to that of the continuous phase
k^{-1}	Debye length
LMW	Low molecular weight
n	Empirical constant
N_A	Avogadro's Number, mol^{-1}
O/W	Oil in water
Δp	Pressure drop across the choke, psi

PO	Propylene oxide
PPM	Parts per Million
P_L	Laplace Pressure
PVT	Pressure Volume Temperature
r	Radius of the spherical particles according to stokes law.
S	Solubility fraction of Asphaltene
ΔS	Change in entropy of dispersed particles
T	Temperature, °F
U_{\max}	Maximum attraction energy of aggregation
U_A	London van-der-waals attraction energy of aggregation
U_E	Electrostatic Interaction energy
U_S	Additional contribution to attraction due to steric repulsion
V_a	Molar volume of asphaltene, $m^3/kgmol$.
V_o	Molar volume of oil, $m^3/kgmol$.
V_{eff}	Effective terminal sedimentation velocity
W_e	Weber's number
WCHF	Wet crude Handling Facility
W/O	Water in oil
W/O/W	Water in oil, and oil itself already dispersed in water (Multiple dispersion)
z	Magnitude of ion valence.

Greek Symbols

γ_{12}	Interfacial tension between two liquids
δ_a	Solubility parameter of the asphaltenes, $Mpa^{\frac{1}{2}}$
δ_o	Solubility parameter of the oil, $Mpa^{\frac{1}{2}}$
η_c	Viscosity of continuous phase

η_r	Relative viscosity of oil to emulsion
φ	Dispersed phase concentration
φ^*	Dispersed phase concentration at relative viscosity of 100
ρ_o	Electronic charge on dispersed particles.
ω	Angular Velocity

References

1. Kokal, S. "Crude Oil Emulsions: A state-of-the-art Review," SPE paper 77497 presented at the SPE Annual Technical Conference and Exhibition, San Antonio, 29 September – 2 October 2002.
2. Becker, J.R., Crude Oil Waxes, Emulsions, and Asphaltenes. 4th edition; Pennwell publishing company: Oklahoma, 1997.
3. Opawale, A.O., "Optimising the Demulsification of Heavy Crude Oil: A means of Improving its Flow through Flowlines, Manifolds and Processing Facilities", Proceedings of the 11th Offshore West Africa Conference and Exhibition, Abuja, 2009.
4. Schramm, L.L., "Emulsion: Fundamentals and Applications in the Petroleum Industry, Advances in Chemistry Series-231, Washington DC, 1992
5. Kokal, S.L. "Crude-Oil Emulsions," Petroleum Engineering Handbook, SPE, Richardson, Texas, 2005.
6. Gary, W.S., Moshen. Z. "The practised art of Emulsion Resolution in Electrostatic Processes" presented at Spring Meeting, Houston, 1999.
7. Kokal, S.L. and Wingrove, M., "Emulsion Separation Index: From Laboratory to Field Case Studies," SPE paper 63165 presented at the SPE annual conference and Exhibition, Dallas, October, 2000.
8. Treating Oilfield Emulsions, 4th edition; Petroleum Extension service at The University of Texas at Austin: Austin, 1990.
9. Clariant Oil Services, Oilfield Production Chemicals and Microbiology, 4th Edition, hts consultants, Aberdeen, 2007.
10. Opawale, A.O., "Oilfield Emulsion Control: A major issue during; A major issue during heavy crude oil production," SPE paper 128352 presented at the SPE annual conference and Exhibition, Abuja, August, 2009.
11. Kokal, S.L., Al-Ghamdi, A. and Meereanpillai, N.S., "An Investigative Study of Potential Emulsion Problems Before Field Development," SPE paper 102856 presented at the SPE Annual Technical Conference and Exhibition, San Antonio, September, 2006.

12. Fingas, W., Fieldhouse, B. and Mullin, J., "Water-in-Oil Emulsions: How they are Formed and Broken," Proceedings of the 17th Arctic and Marine Oil spill Program (AMOP) Technical Seminar, Ontario, 1994.
13. Fingas, M.F., Fieldhouse, B. and Mulin, J.V., "Studies of Water-in-Oil Emulsions: The Role of Asphaltene and Resins," Proceedings of Nineteenth Arctic and Marine oil spill program (AMOP) Technical Seminar Ontario, 1996
14. Fingas, M.F., Fieldhouse, B., Bier, I., Conrod, D., and Tennyson, E., "Development of a test for Water-In-Oil Emulsion Breakers", in proceedings of the Sixteenth Arctic and Marine Oil Spill Program Technical Seminar, Environment Canada, Ontario, 1993.
15. Fingas, M.F., Fieldhouse, B., Bier, I., Bora, M.A. and Tennyson. E., "The Physics and Chemistry of Emulsions", in proceedings of The Workshop on Emulsions, Marine Spill Response Corporation, Washington, D.C., 11p., 1993.
16. Bobra, M.A., "A Study of the Formation of Water-in-Oil Emulsions", in proceedings of the Thirteen Annual Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ontario, pp.87-117, 1990.
17. Bobra, M.A., " Water-in-Oil Emulsification: A physicochemical study", in Proceedings of the International Oil Spill Conference, American Petroleum Institute, Washington, D.C., pp.483-488, 1991.
18. Bobra, M.A., A Study of Water-in-Oil Emulsification, Environmental Canada Manuscript Report EE-132, 1992.
19. Sjoblom, J., Mingyuan-christy, A.A. and Ronningsen, H.P., "Water-in-Crude Oil Emulsions From the Norwegian Continental Shelf", Journal of Colloid and Interface Science. 220:329-337.
20. McLean, J.D., Spiecker, P.M., Sullivian, A.P., and kilapatric, P.K., " The Role of Petroleum Asphaltenes in the Stabilization of Water-in-oil Emulsions: Structure and Dynamics", Mullins.O.C Plenium Press, Newyork, 1998.
21. Yan, N., Gray, M.R., Masliyah, J.H., "Water-in-oil emulsions stabilized by fine solids," Colloids surface A, Physicochemical Eng. Aspects, 193, 97-107, 2001.
22. Cairns, R.J.R., Grist, D.M., and Neustadter, E.L., " The effect of Crude oil-water interfacial properties on Water-Crude Oil Emulsion Stability, " Symposium on Emulsion Technology, 1974, Academic Press inc., pp.135-151, 1996.

23. Singh, B.P. and Pandey, B.P., "Physical Characteristics of Natural Films formed at Crude Oil-Water interfaces, Indian Journal of Technology, Vol. 29, pp.443-447, 1991.
24. Fingas, M.F., Fieldhouse, B., "How to Model Water-in-Oil ", in proceedings of The Workshop on Emulsions, Marine Spill Response Corporation, Washington, D.C., 123p., 2001.
25. Kotlar, H.Kr., Selle, O.M., And Kristensen, M.H., "Formation damage Due to Fine Stabilized Water-in-Oil Emulsions: A Possible Mechanism of Plugging in the Near Well Bore Area," SPE paper 31117 presented at the SPE International Symposium on Formation Damage Control, Lafayette, 14-15 February, 1998.
26. Kokal, S.L. and Al-Juraid, J., "Quantification of factors Affecting Emulsion Stability: Watercut, Temperature, Shear, Asphaltene Content, Demulsifier Dosage and Mixing Different Crudes," SPE paper 56641 presented at the SPE annual conference and Exhibition, Houston, October 1999.
27. Omole, O., Falode, O.A., "Effects of Mixing Conditions, Oil Type and aqueous phase composition on some Crude oil Emulsion," Journal of Applied Sciences, 873-877, 2005.
28. Kokal, S.L. and Al-Dokhi, M., "Case Studies of Emulsion Behaviour at Reservoir Conditions", SPE paper 105534 presented at the SPE Middle East Oil Show, Bahrain, March, 2006.
29. Peña, A.A., Dynamic aspects of emulsion stability, Ph.D thesis. Houston: Rice University, 2004.
30. Miller, C.A., "Spontaneous emulsification produced by diffusion - a review", Colloids and Surfaces, 29 (1988) 89-102.
31. Nishimi, T. and Miller, C.A., "Spontaneous emulsification produced by chemical reactions", J. Colloid Interface Sci., 237 (2001) 259-266.
32. Schubert, H., and Armbruster, H., "Principles of Formation and Stability of Emulsions," International Chemical Engineering Series, No. 1, 14-28, 1992
33. Jan, O., Particle-Stabilized Emulsion and Heavy Crude Oil, Ph.D thesis. Norwegian University of Science and Technology, 2004.

34. Becher, P., "Emulsions: theory and practice," 3rd Ed.; Washington, D.C., American Chemical Society; New York: Oxford University Press, 2001.
35. Sjöblom, J., "Encyclopedic Handbook of Emulsion Technology," 5th Ed, Marcel Dekker, Newyork City , 2001
36. Shaw, D.J., "Introduction to Colloid and Surface Chemistry," 3rd Ed., Elsevier Science, New York, 1992.
37. Berryman, J.G., "Random close packing of hard spheres and disks", Phys. Rev. A, 27 (1983) 1053-1061.
38. Arirachakaran, S., Oglesby, K.D., Malinowsky, M. S., Shoham, O. and Brill, J.P., "An Analysis Of Oil-Water Flow Phenomena In Horizontal Pipes ", SPE paper 1883, presented at the SPE Annual Conference and Exhibition, Oklahoma October, 1989.
39. Becher, P., Principles of Emulsion Technology, Reinhold Pilot Book -5, Chapman & Hall, 1955.
40. Salager, J.L., "Emulsion Phase Inversion Phenomena", in Emulsions and emulsion stability, Sjöblom J., Editor, Surfactant science series, Vol.132. CRC Press, Taylor & Francis Group, 2006.
41. Vaessen, G.E.J., Visschers M., and H.N. Stein, "Predicting Catastrophic Phase Inversion on the Basis of Droplet Coalescence Kinetics", American Chemical Society, Langmuir, Vol. 12, No. 4, 1996.
42. Barnes, H. A., "Barnes, "Rheology of emulsions - a review", Colloids Surf. A, 89-95, 1994.
43. Tadros, T.F., "Fundamental principles of emulsion rheology and their applications", Colloids Surf. A, 91, 39-55, 1994.
44. Taylor, G.I., "The viscosity of a fluid containing small drops of another liquid". Prec. R. Soc. A, 41-48, 1932.
45. Pal, R. and Rhodes, E., "Viscosity-concentration relationships for emulsions", J. Rheol., 1021-1045, 1989.
46. Peña, A.A., Hirasaki, G.J. and Miller, C.A., "Solubilisation rates of oils in surfactant solutions and their relationship to mass transport in emulsions", Adv. Colloid Interface Sci., 241-257, 2006.

47. Weiss, J., Cancelliere, C. and McClements D.J., “Mass Transport Phenomena in Oil-in-Water Emulsions Containing Surfactant Micelles: Ostwald Ripening”, *Langmuir*, Vol. 16, No. 17, 2000.
48. Derjaguin B.V. and Landau, L., “Theory of the stability of strongly charged Lyophobic sols and of the adhesion of strongly charged particles in solution of electrolytes”, *.Acta Physicochem. URSS*, 633, 1998.
49. Verwey, E.J.W. and Overbeek, J.T.G., Theory of the Stability of Lyophobic Colloids, Elsevier: Amsterdam, 1948.
50. Hamaker, H.C., “The London-van der Waals attraction between spherical particles”, *Physical*, 1058-1072, 1997.
51. Israelachvili, J., “Intermolecular & Surface Forces,” 2nd Ed., Academic Press, London, 1992.
52. Miller, C.A. and Neogi, P., *Interfacial Phenomena: Equilibrium and Dynamic Effects*, 2nd Ed., CRC Press: Houston, 2008.
53. Walstra, P., “Emulsion stability”, in Encyclopedia of Emulsion Technology’’, Becher, P., Editor. Vol.4. Marcel Dekker, Inc.: New York, 1990.
54. Tadros, T.F. and Vincent, B., Emulsion stability, in “Encyclopedia of Emulsion Technology”, Marcel Dekker, Inc., New York, 1983.
55. Richardson, J.F. and Zaki, W.N., “Sedimentation and fluidisation: Part I”, *Trans. Inst. Chem. Eng.*, 32, 1954.
56. Pal R., “Techniques for measuring the composition (oil and water content) of emulsions — a state of the art review”, *Colloids Surfaces A.*, 1994.
57. Lissant, K.J., “Demulsification: Industrial Application; Surfactant science series vol.13, Marcel Dekker: New York, 1993.
58. Wang, Y., Zhang, L., Sun, T. Sun, Zhao, S. and Yu, J., “A study of interfacial dilational properties of two different structure demulsifiers at oil–water interfaces”, *J. Colloid Interface Sci.*, 270, 2004.
59. Kim, Y.H. and Wasan, D.T., “Effect of Demulsifier Partitioning on the Destabilization of Water-in-Oil Emulsions”, *Ind. Eng. Chem. Res.*, 1996.
60. Kang, W., Jing, G., Zhang, H., Li, M. and Z. Wu, “Influence of demulsifier on interfacial film between oil and water”, *Colloids Surf. A*, 2006.

61. Sjöblom, J., Sounderlund, H., Lindblad, S., Johansen, E.J. and Skjarvo, I M., "Water-in-crude oil emulsions from the Norwegian continental shelf Part II: Chemical destabilization and interfacial tensions", *Colloid Polym. Sci.*, 1990.
62. Sjöblom, J., Johnsen, E.E., Westvik, A., Ese, M.-H., Djuve, J., Auflem, I.H. and Kallevik H., "Demulsifiers in the oil industry", in *Encyclopedia handbook of emulsion technology*, Sjöblom J., Editor, Marcel Dekker: New York, 2001,
63. Peña, A.A., Hirasaki G.J. and Miller C.A., "Chemically Induced Destabilization of Water-in-Crude Oil Emulsions", *Ind. Eng. Chem. Res.*, (2005).
64. Breen P.J., Yen, A. and Tapp, J., "Demulsification of asphaltene-stabilized emulsions-correlation of demulsifier performance with crude oil composition", *Proceedings of the 3rd International Conference on Petroleum Phase Behaviour and Fouling*, New Orleans, 2002.
65. Angle, C. W., "Chemical demulsification of stable crude oil and bitumen emulsions in petroleum recovery -A review", In *Encyclopaedic handbook of emulsion technology*; Sjöblom, J., Ed.; Marcel Dekker: New York, 2001,
66. Abdel-Azim, A.A., Zaki, N.N. and Maysour, N.E.S., "Polyalkoxylated amines for breaking water-in-oil emulsions: effect of structural variations on the demulsification efficiency", *Polym. Adv. Technol.*, 1998.
67. Abdel-Aal, H.K., Mohamed, A. And Fahim, M.A., "Petroleum and Gas Field Processing, " 3rd Ed., Mercel Dekker, New York, 2003.
68. Byung, K.H., Chong, B.K., and Choul-Gyun, L., "Functional Relationship between Volume Concentration of Dispersed Phase and Relative Viscosity in a Liquid-Liquid Dispersion and Emulsion, " *Journal of Industrial and Engineering Chemistry*, Vol. 6, No. 5, 318-324, September 2000.
69. El-Gamel, M., Mohamed, A.O., and Zekri, A.Y., "Effect of Asphaltene, Carbonates and clay mineral contents on water cut determination in water-in-oil Emulsions," *Journal of Petroleum science and Engineering.*, 46,209-234, 2005.
70. Benayonne, M., Khezzar, L., Al-Rumhy, M., "Viscosity of Water in oil emulsions," *Journal of petroleum Science Technology*, 767-784, 1998.
71. Elsharkawy, A.M., Al-sahhaf, T.A., Fahim, M.," Effect of Inorganic solids, Wax to asphaltene ratio, and water cut on the stability of Water-in-Crude Oil Emulsions,

Journal of Petroleum science and Engineering., 46,623-2634, 2008.

72. Kokal, S.L. and Al-Juraid, J., "Reducing Emulsion Problems By Controlling Asphaltene Solubility and Precipitation" SPE paper 48995 presented at the SPE annual conference and Exhibition, New Orleans, September 1998.
73. Khadim, M.A., Sarbar, M.A., "Role of Asphaltene and Resins in Oilfield Emulsions," Journal of Petroleum Science and Engineering, 213 – 222, 1999
74. Sarbar, M., and Wingrove, M.D., "Physical and Chemical Characterization of Saudi Arabian crude oil emulsions," SPE paper 38817 presented at the SPE annual conference and Exhibition, San Antonia, October5-8, 1997.
75. Gu, G., Xu, Z., Nandakumar, K., and Masliyah, J.K., "Influence of water-Soluble and Water –Insoluble natural surface active components on the stability of water-in-toluene-diluted bitumen emulsion," Journal of Colloidal Chemistry, 1859-1869, 2002.
76. Michael, B., Senegy, S., Waggoner, S., Hess, C., "Fines Migration in a High Temperature Gas Reservoir- Laboratory Simulation and Implications for Completion Design," SPE paper 121897 presented at the SPE European Formation damage conference , Scheveningen, May 27-29, 2009.
77. Cengel, Y.A., Cimbala, J.M., "Fluid Mechanics: Fundamentals and Applications," 1st Edition, MCGraw-Hill Publisher, New York, 2006.
78. Guo, B., Lyons, W.C., Ghalambor, A., "Petroleum Production Engineering: A Computer-Assisted Approach," 3rd Edition, Elsevier Science, New York, 2007.
79. Boar, R.B., Leoloyer, K., EIgner, M.R.P. and Bergen, A.R.D., "Screening of crude oils for Asphalt Precipitation: Theory, Practice and the Selection of Inhibitors," SPE Production and Facilities, PP.555-61, 1995.

APPENDIX A – DATA SPREADSHEETS

Table A.1: Effect of Watercut on emulsion Tightness

WATER CUT		
WATER BLENDED %	SEPARATION AFTER 20 MIN	ET %
10.00	9.4	6.01
20.00	18.1	9.40
30.00	24.0	19.98
40.00	28.8	28.10
50.00	32.9	34.21
60.00	38.8	35.32
70.00	47.5	32.20
80.00	64.4	19.50
90.00	79.1	12.16

Table A.2: Effect of Asphaltene on Emulsion Tightness

ASPHALTENE		
ASPHALTENE CONC (wt%)	WATER SEP AFTER 20 MIN	ET %
0.05	29.3	2.3
0.50	27.5	8.20
1.30	25.4	15.21
2.90	24.5	18.20
4.80	17.0	43.20
9.40	9.8	67.32
14.80	6.0	80.00
21.00	2.9	90.30

Table A.3: Effect of Reservoir fines on Emulsion Tightness

RESERVOIR FINES		
FINES (wt%)	WATER SEP AFTER 20 MIN	ET %
0.05	29.7	1.01
0.50	29.3	2.28
1.30	28.8	3.915
2.90	28.8	4.005
4.80	28.7	4.315
9.40	28.5	4.94
14.80	28.4	5.32
21.00	27.8	7.18

Table A.4: Effect of Inorganic Solids on Emulsion Tightness

INORGANIC SOLIDS, CaCO₃		
CaCO ₃ (wt %)	WATER SEP AFTER 20 MIN	ET %
0.05	29.6	1.3
0.50	28.8	4.11
1.30	27.2	9.34
2.90	26.1	13.05
4.80	25.4	15.32
9.40	25.2	16.00
14.80	24.8	17.48
21.00	23.1	23.00

Table A.5: Effect of Asphaltene and fines on Emulsion Tightness

ASPHALTENE + FINE		
(ASPH + FINE) CONC (wt%)	WATER SEP AFTER 20 MIN	ET %
0.05	29.0	3.21
0.50	28.6	4.70
1.30	27.2	9.30
2.90	21.3	29.10
4.80	16.7	44.30
9.40	10.2	66.00
14.80	4.8	84.00
21.00	2.4	92.00

Table A.6: Effect of Asphaltene and calcite on Emulsion Tightness

ASPHALTENE + CaCO₃		
(ASPH + CaCO ₃) CONC (wt%)	WATER SEP AFTER 20 MIN	ET %
0.05	29.0	3.21
0.50	27.1	9.65
1.30	23.0	23.30
2.90	19.4	35.50
4.80	13.8	54.00
9.40	7.8	74.00
14.80	4.8	84.00
21.00	0.6	98.00

Table A.7: Effect of Calcite and reservoir fines on Emulsion tightness

CaCo₃ + FINES		
(ASPH + CaCo ₃ +FINE) CONC (wt%)	WATER SEP AFTER 20 MIN	ET %
0.05	29.4	1.92
0.50	28.8	3.86
1.30	27.3	8.98
2.90	26.6	11.32
4.80	25.7	14.30
9.40	26.1	13.00
14.80	25.8	14.12
21.00	23.5	21.70

Table A.8: Effect of Asphaltene, calcite and reservoir fines on emulsion tightness

ASPHALTENE + CaCo₃ + FINES		
(ASPH +CaCo ₃ +FINE) CONC (wt%)	WATER SEP AFTER 20 MIN	ET %
0.05	29.1	2.98
0.50	25.7	14.45
1.30	23.1	23.10
2.90	20.4	32.00
4.80	13.7	54.21
9.40	6.6	78.00
14.80	4.8	84.00
21.00	1.8	94.00

Table A.9: Combined effect of shearing energy and asphaltene on emulsion tightness at 5% Watercut.

RPM	Kinetic Energy		Emulsion Tightness							
	CGS(ergs)	S(Joules)	ASPHALTENE CONCENTRATIONS, WT%							
			0.5	2.1	5.4	14.8	21.1			
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	101999.20	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20	407996.79	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	917992.79	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40	1631987.18	0.16	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
50	2549979.96	0.25	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.02
60	3671971.14	0.37	0.00	0.01	0.00	0.01	0.01	0.01	0.02	0.03
70	4997960.72	0.50	0.00	0.01	0.01	0.01	0.01	0.01	0.02	0.03
80	6527948.70	0.65	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.05
90	8261935.07	0.83	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.06
100	10199919.84	1.02	0.01	0.02	0.02	0.02	0.02	0.02	0.10	0.11
200	40799679.38	4.08	0.09	0.11	0.21	0.28	0.28	0.28	0.28	0.43
300	91799278.60	9.18	0.64	0.67	1.37	2.09	2.09	2.09	2.09	2.32
400	163198717.52	16.32	1.19	1.83	2.53	3.89	3.89	3.89	3.89	4.21
500	254997996.12	25.50	1.74	2.99	3.69	5.70	5.70	5.70	5.70	6.10
600	367197114.41	36.72	2.29	4.14	4.85	7.50	7.50	7.50	7.50	7.99
700	499796072.40	49.98	2.84	5.30	6.01	9.31	9.31	9.31	9.31	9.88
800	652794870.07	65.28	3.39	6.46	9.10	12.20	12.20	12.20	12.20	15.40
900	826193507.43	82.62	3.94	6.72	8.88	14.30	14.30	14.30	14.30	16.98
1000	1019991984.48	102.00	6.30	8.18	14.30	20.87	20.87	20.87	20.87	21.32

Table A11: Combined effect of shearing energy and asphaltene on emulsion tightness at 30% Watercut.

RPM	Kinetic Energy		Emulsion Tightness						
	CGS(ergs)	SI(Joules)	ASPHALTENE CONCENTRATIONS,WT%						
			0.5	2.1	5.4	14.8	21.1		
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
10	101999.20	0.01	0.00	0.00	0.00	0.00	0.00	0.00	
20	407996.79	0.04	0.00	0.00	0.00	0.00	0.00	0.00	
30	917992.79	0.09	0.00	0.00	0.00	0.00	0.00	0.00	
40	1631987.18	0.16	0.00	0.00	0.00	0.03	0.03	0.00	
50	2549979.96	0.25	0.03	0.02	0.03	0.02	0.02	0.01	
60	3671971.14	0.37	0.05	0.03	0.04	0.03	0.03	0.02	
70	4997960.72	0.50	0.04	0.03	0.00	0.15	0.15	0.18	
80	6527948.70	0.65	0.01	0.09	0.45	1.13	1.13	1.39	
90	8261935.07	0.83	0.17	0.56	1.41	3.31	3.31	4.80	
100	10199919.84	1.02	0.46	1.36	2.79	6.62	6.62	9.12	
200	40799679.38	4.08	0.48	1.50	2.63	6.74	6.74	9.86	
300	91799278.60	9.18	0.52	1.69	3.15	7.27	7.27	10.73	
400	163198717.52	16.32	0.61	2.55	4.00	8.28	8.28	15.51	
500	254997996.12	25.50	0.87	4.74	6.16	14.28	14.28	18.49	
600	367197114.41	36.72	1.94	7.42	10.29	22.87	22.87	28.50	
700	499796072.40	49.98	4.18	11.59	16.23	38.18	38.18	47.95	
800	652794870.07	65.28	7.58	16.57	24.63	64.14	64.14	82.55	
900	826193507.43	82.62	12.15	23.86	35.96	89.20	89.20	97.00	
1000	1019991984.48	102.00	18.52	32.95	49.43	94.20	94.20	100.00	

Table A.12: Combined effect of shearing energy and asphaltene on emulsion tightness at 55% Watercut.

RPM	Kinetic Energy		Emulsion Tightness							
	CGS(ergs)	S(Joules)	ASPHALTENE CONCENTRATIONS,WT%							
			0.5	2.1	5.4	14.8	21.1			
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	101999.20	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20	407996.79	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	917992.79	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40	1631987.18	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	2549979.96	0.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
60	3671971.14	0.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
70	4997960.72	0.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	6527948.70	0.65	0.00	0.02	0.03	0.08	0.19	0.30	0.19	0.19
90	8261935.07	0.83	0.36	1.04	1.26	2.16	3.30	4.76	3.30	3.30
100	10199919.84	1.02	1.21	2.26	4.07	10.32	12.56	14.17	10.32	12.56
200	40799679.38	4.08	2.06	4.90	5.94	10.90	14.17	14.17	10.90	14.17
300	91799278.60	9.18	2.23	5.23	6.61	11.10	19.12	19.12	11.10	19.12
400	163198717.52	16.32	2.89	6.04	8.61	12.51	23.47	23.47	12.51	23.47
500	254997996.12	25.50	4.46	7.91	12.10	17.08	29.11	29.11	17.08	29.11
600	367197114.41	36.72	6.60	10.76	16.66	22.64	38.55	38.55	22.64	38.55
700	499796072.40	49.98	9.90	15.58	25.27	33.27	60.92	60.92	33.27	60.92
800	652794870.07	65.28	12.37	22.19	35.93	47.66	86.00	86.00	47.66	86.00
900	826193507.43	82.62	20.61	30.60	49.00	67.12	99.00	99.00	67.12	99.00
1000	1019991984.48	102.00	28.51	40.96	66.83	90.51	100.00	100.00	90.51	100.00

APPENDIX B
TRENDLINE PLOTS FROM REGRESSION ANALYSIS

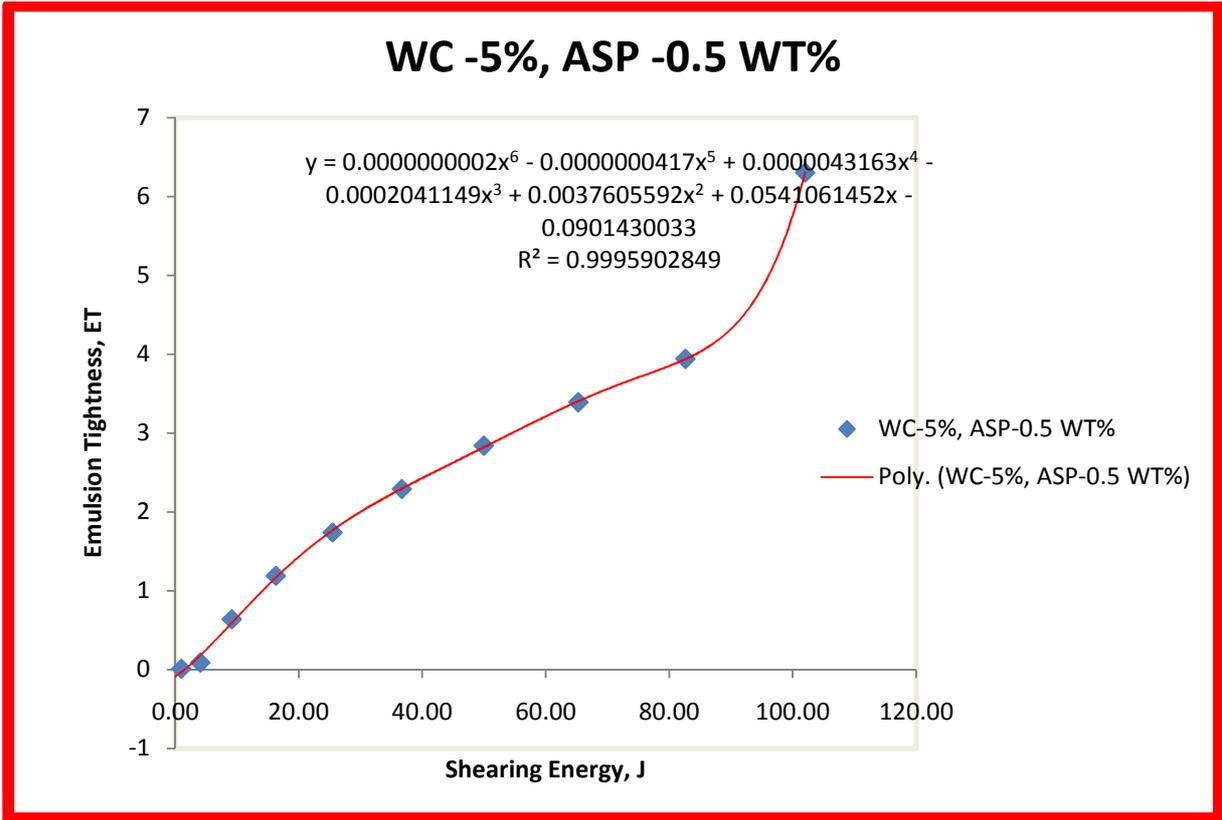


Figure B.1: Regression analysis of 5% Watercut and 0.5% asphaltene plot

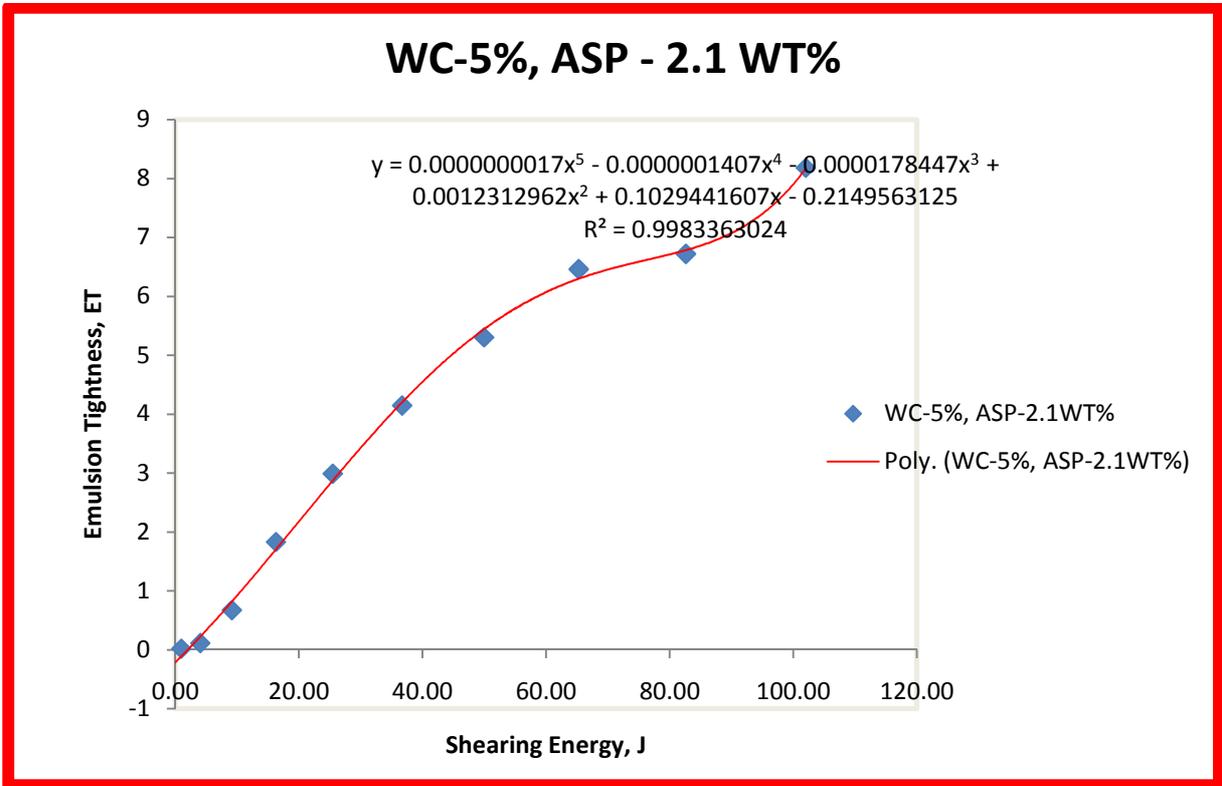


Figure B.2: Regression analysis of 5% Watercut and 2.1% asphaltene plot

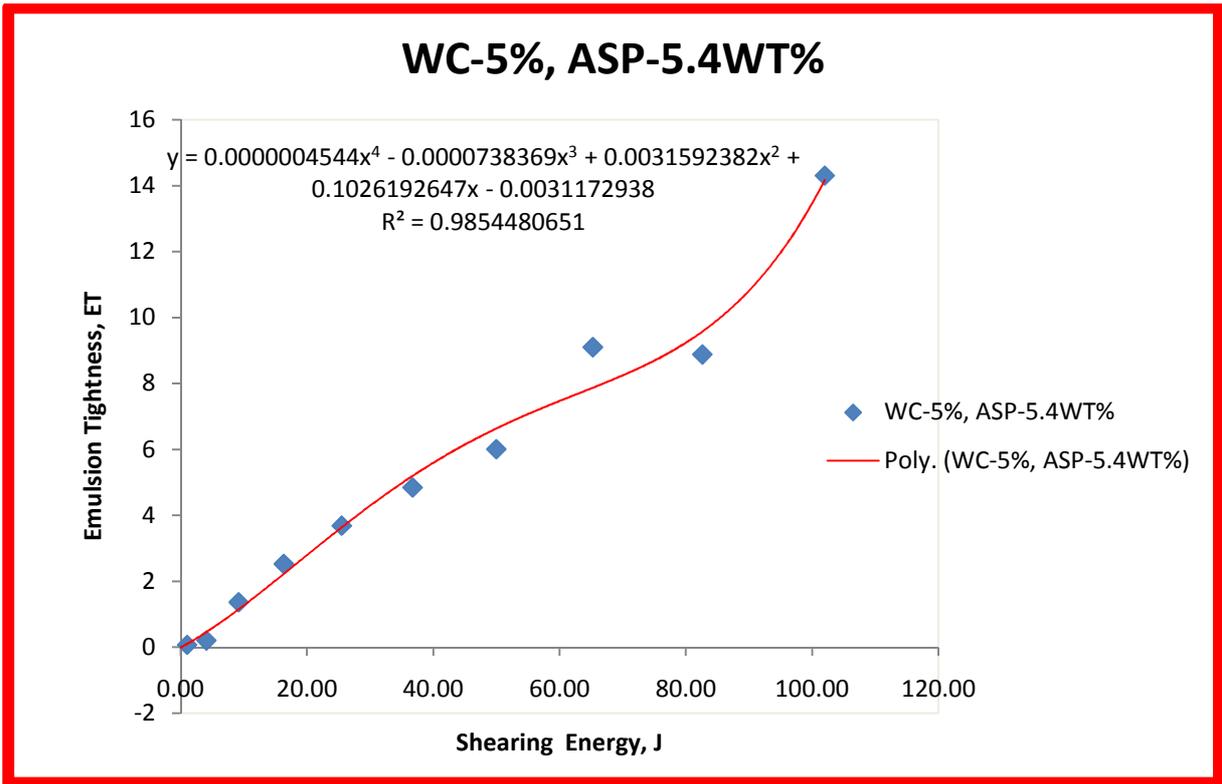


Figure B.3: Regression analysis of 5% Watercut and 5.4% asphaltene plot

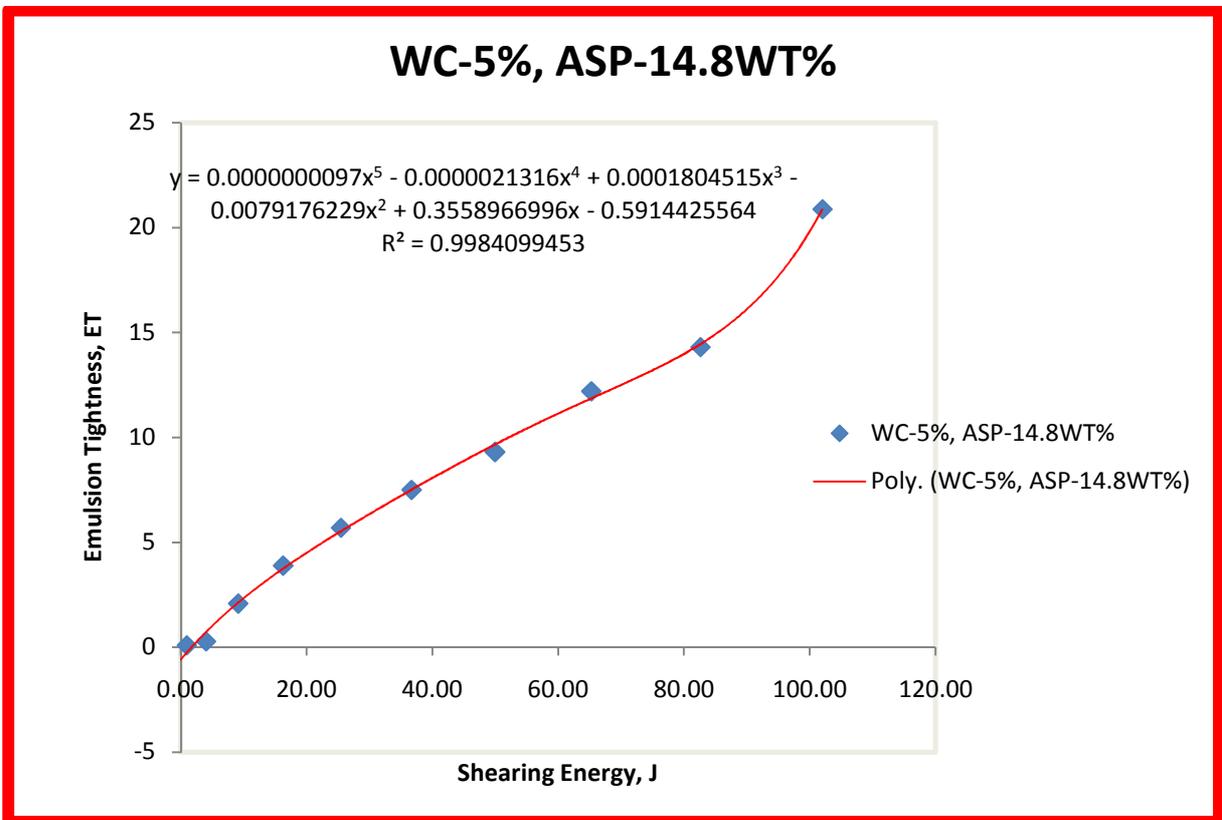


Figure B.4: Regression analysis of 5% Watercut and 14.8% asphaltene plot

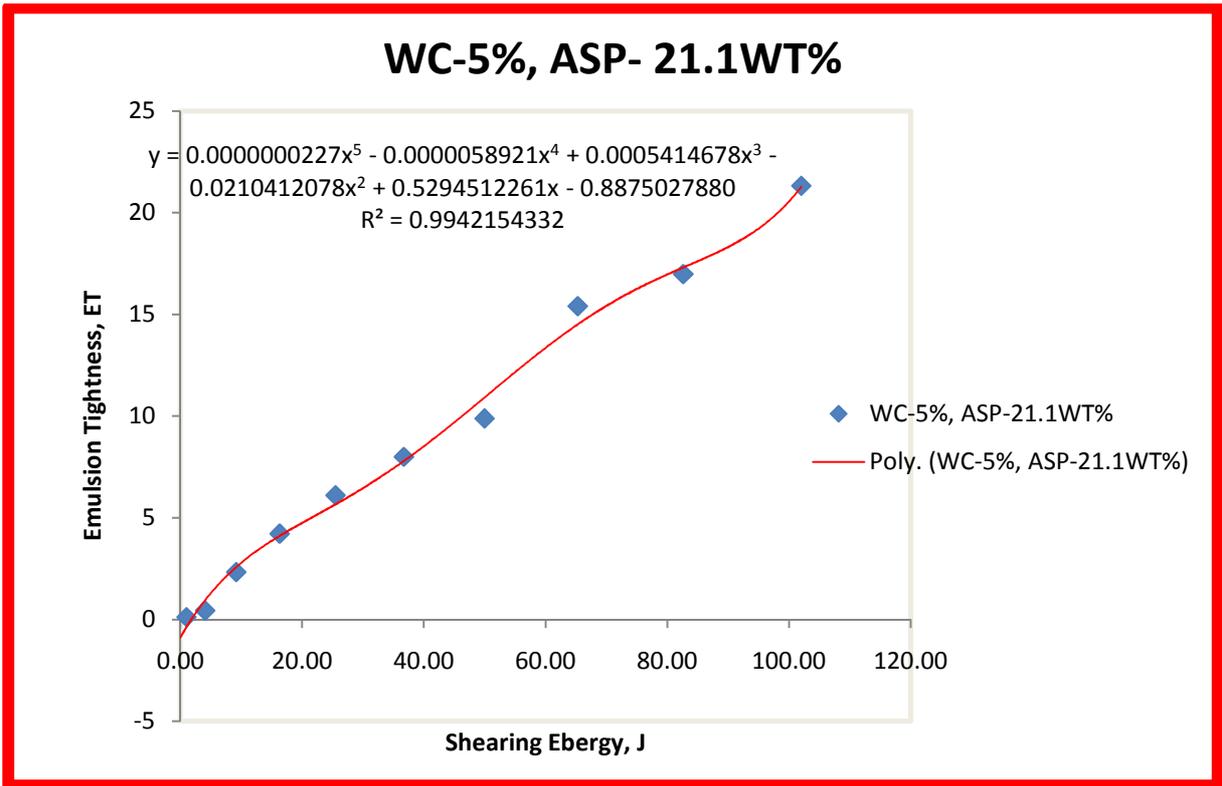


Figure B.5: Regression analysis of 5% Watercut and 21.1% asphaltene plot

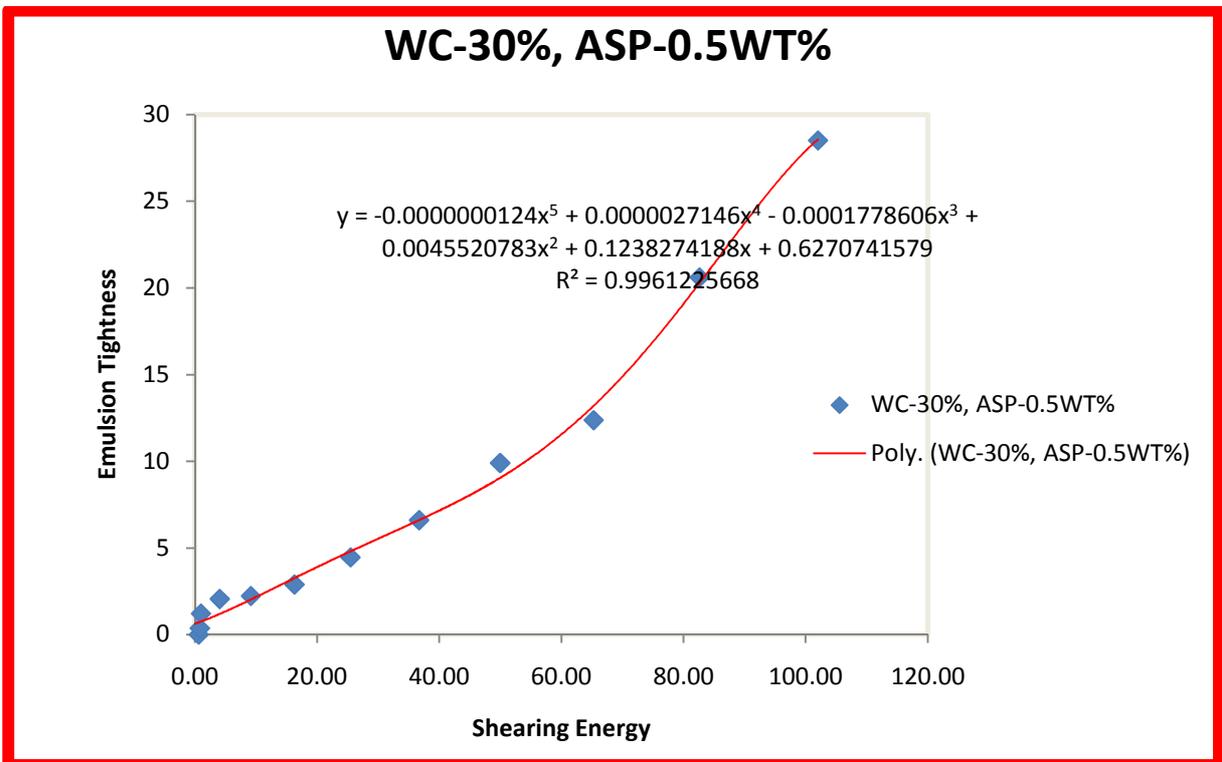


Figure B.6: Regression analysis of 30% Watercut and 0.5% asphaltene plot

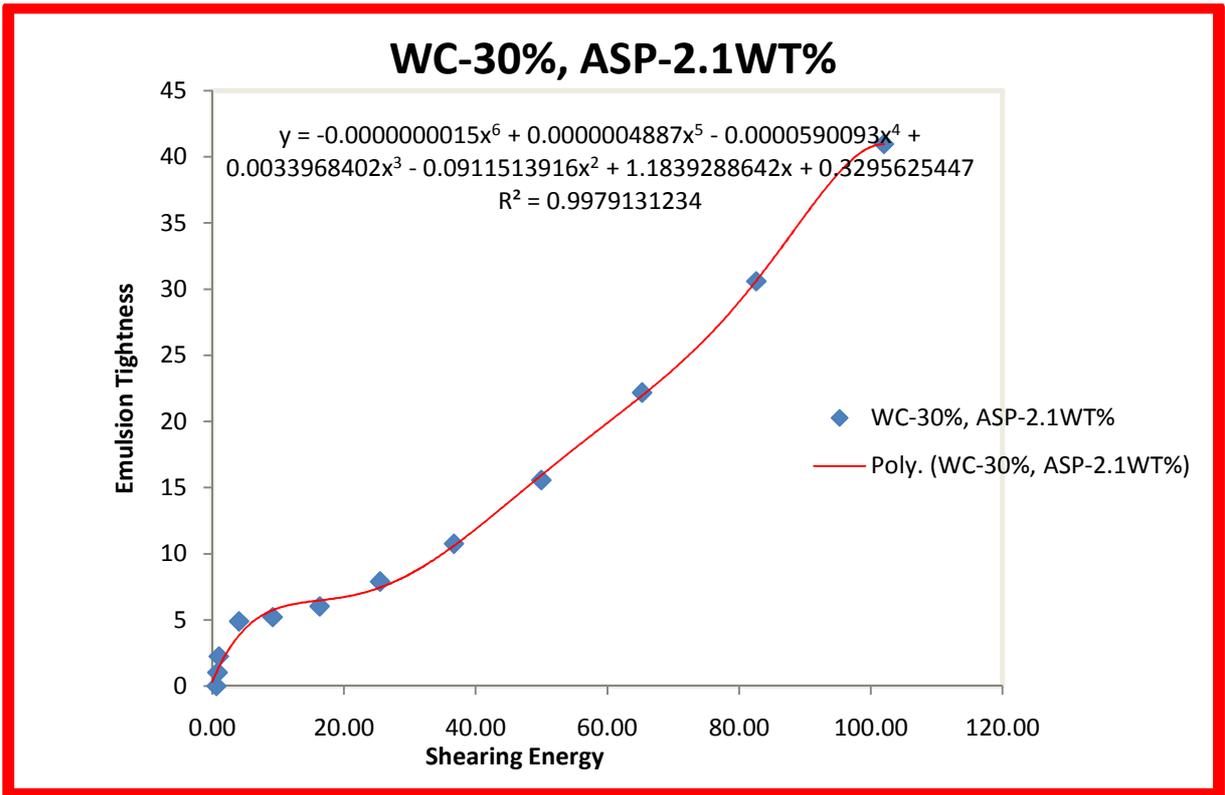


Figure B.7: Regression analysis of 30% Watercut and 2.1% asphaltene plot

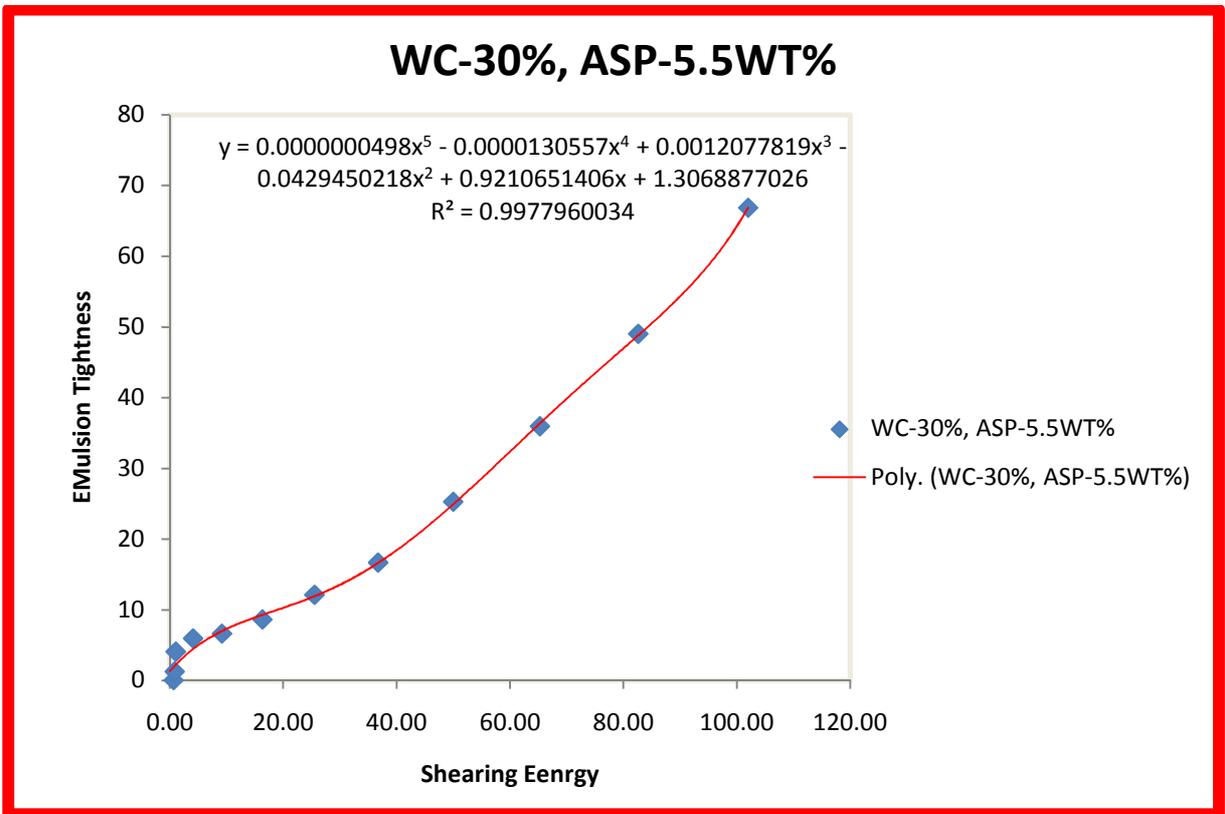


Figure B.8: Regression analysis of 30% Watercut and 5.4% asphaltene plot

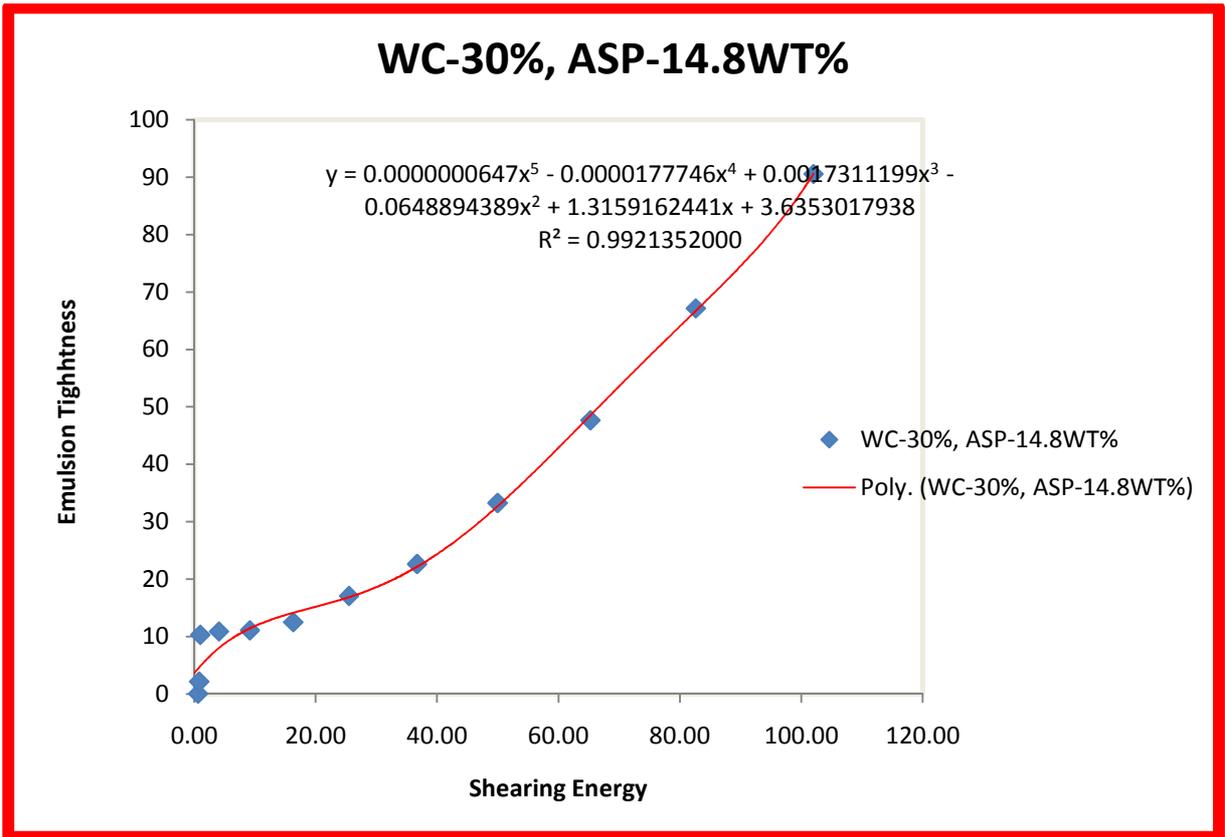


Figure B.9: Regression analysis of 30% Watercut and 14.8% asphaltene plot

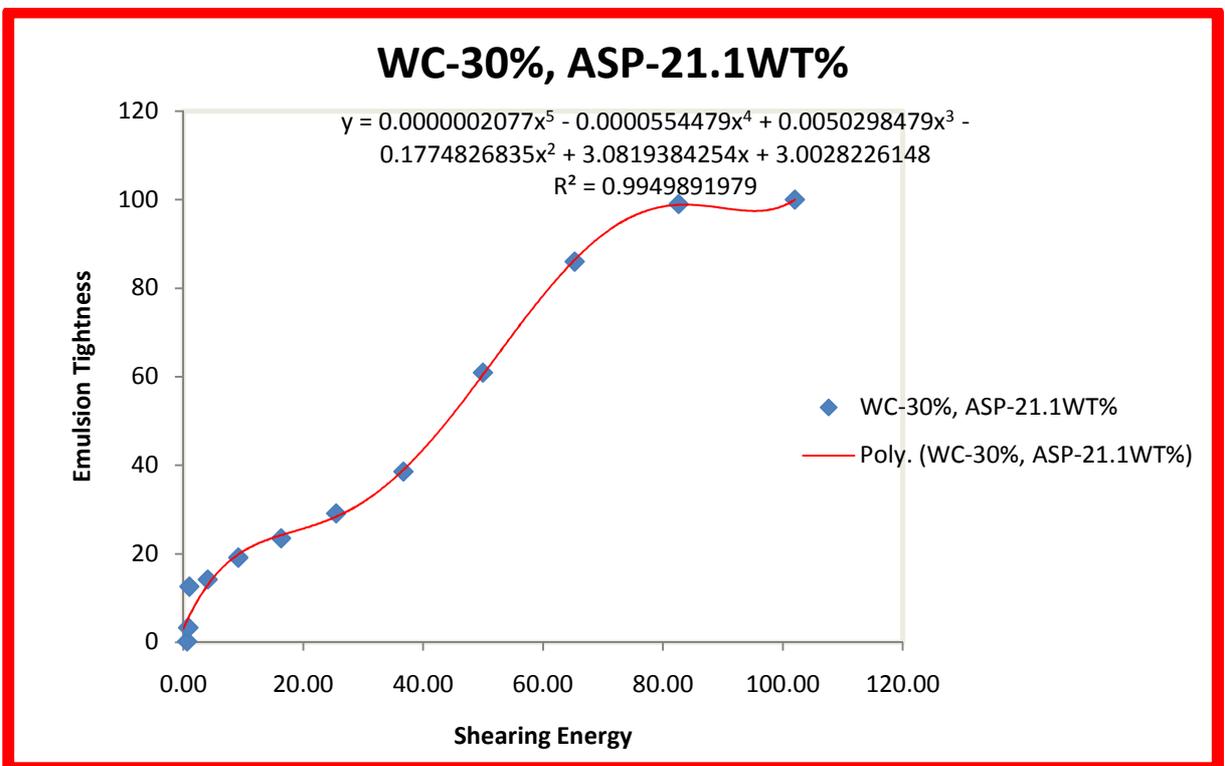


Figure B.11: Regression analysis of 30% Watercut and 21.1% asphaltene plot

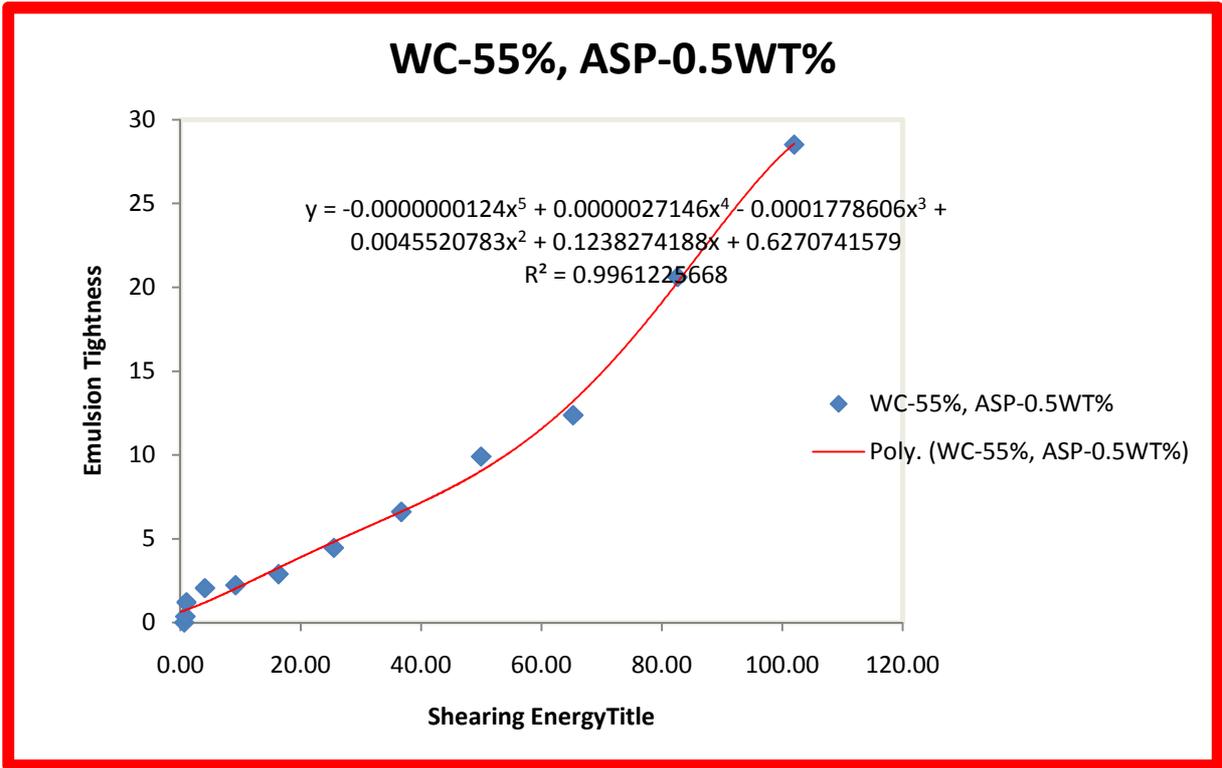


Figure B.12: Regression analysis of 55% Watercut and 0.5% asphaltene plot

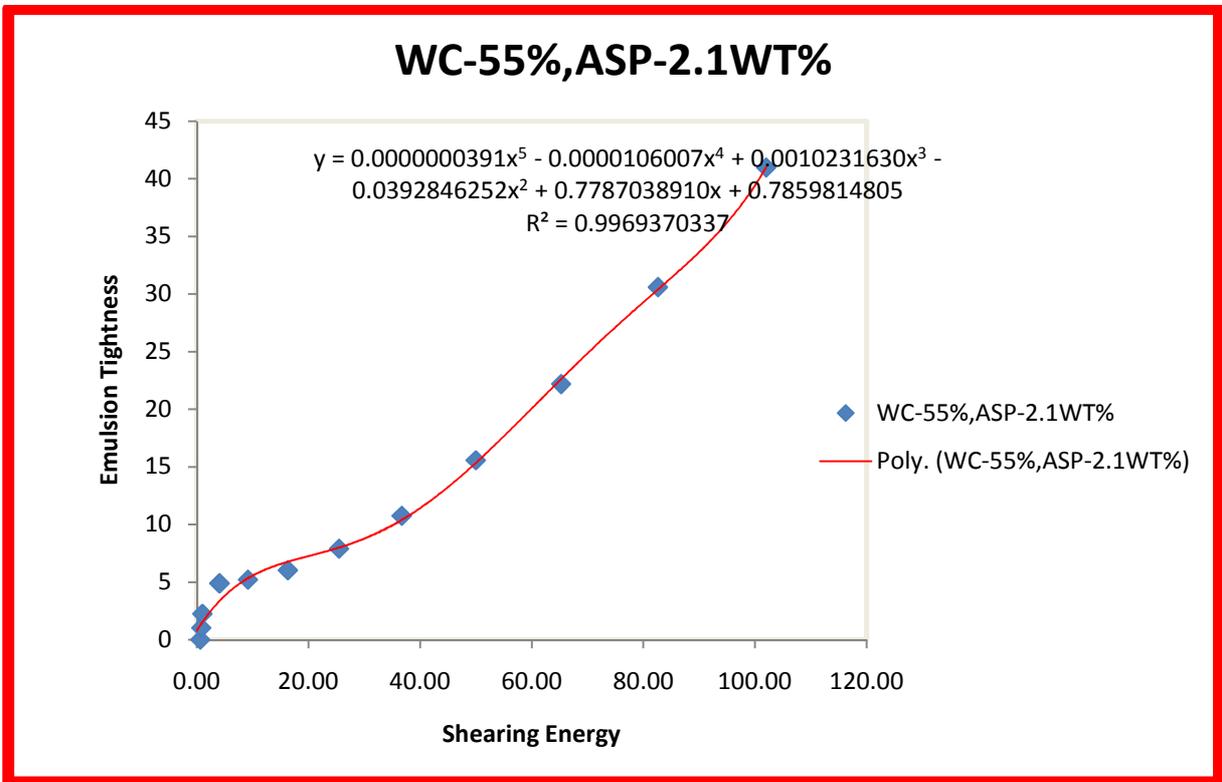


Figure B.13: Regression analysis of 55% Watercut and 2.1 % asphaltene plot

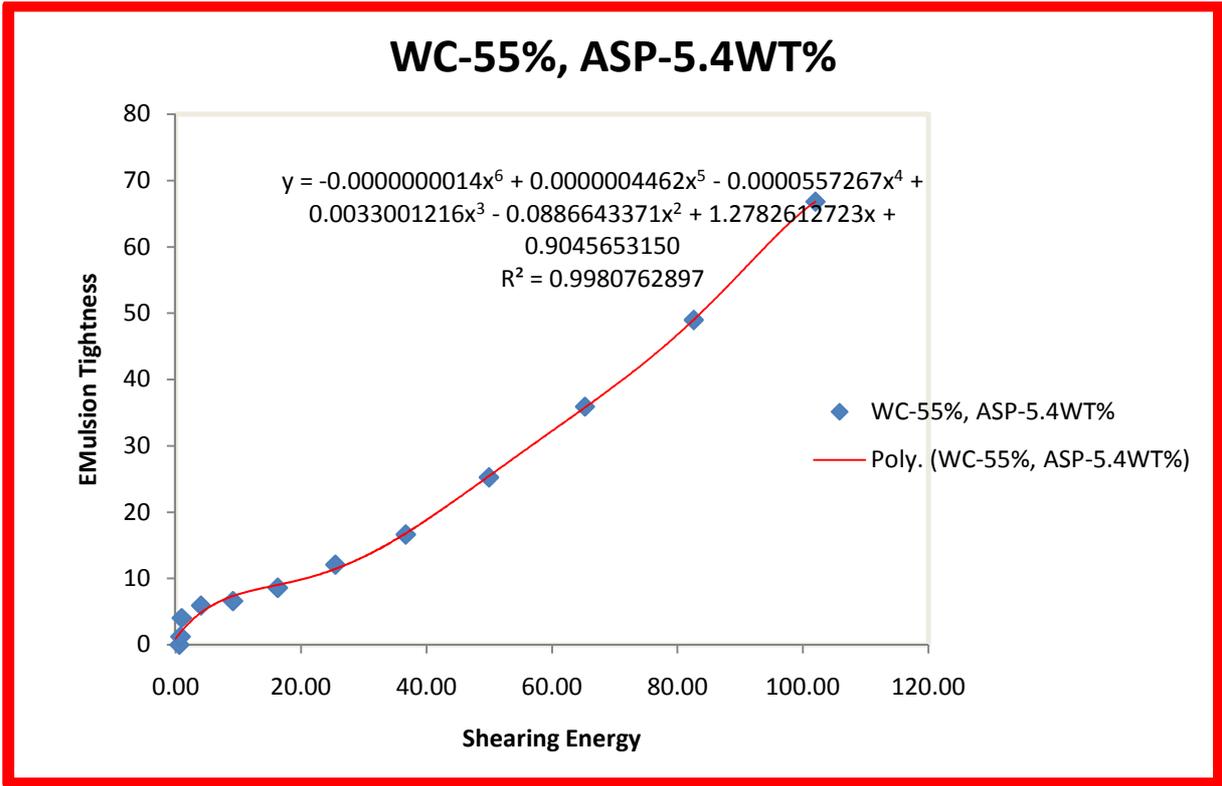


Figure B.14: Regression analysis of 55% Watercut and 5.4% asphaltene plot

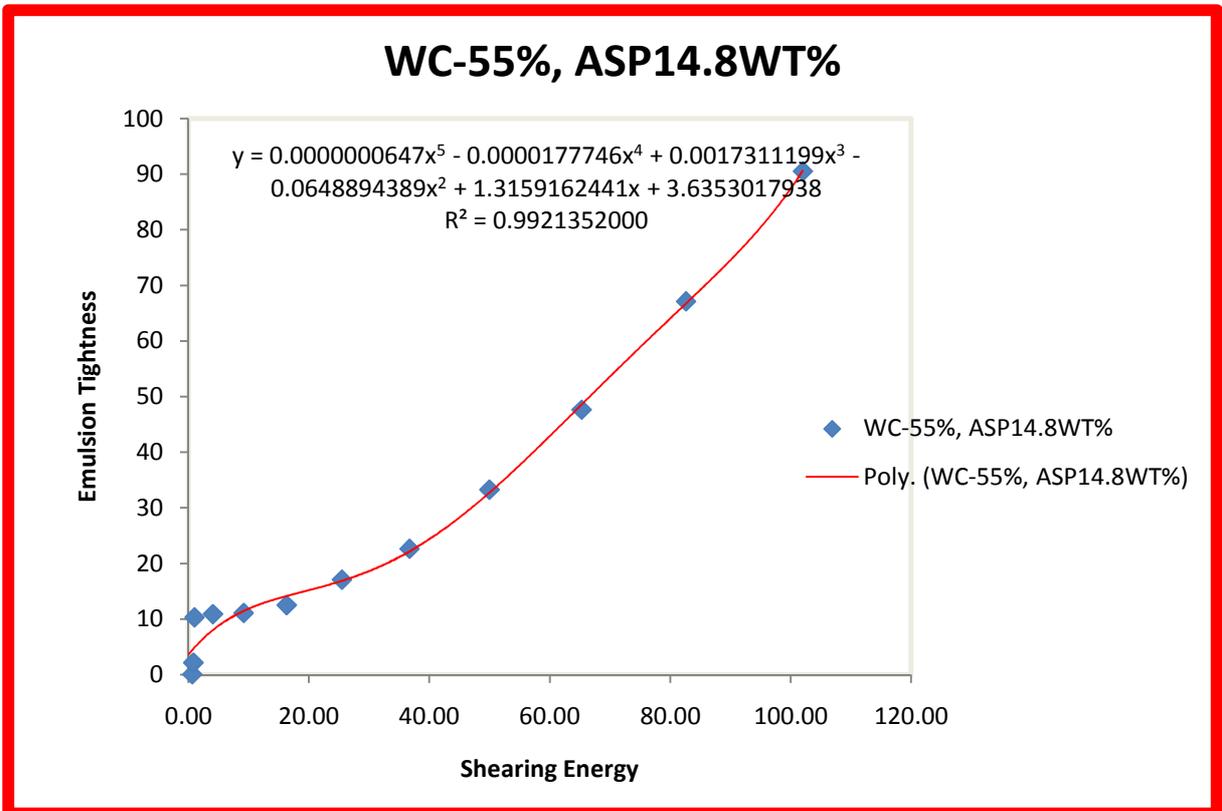


Figure B.15: Regression analysis of 55% Watercut and 14.8% asphaltene plot

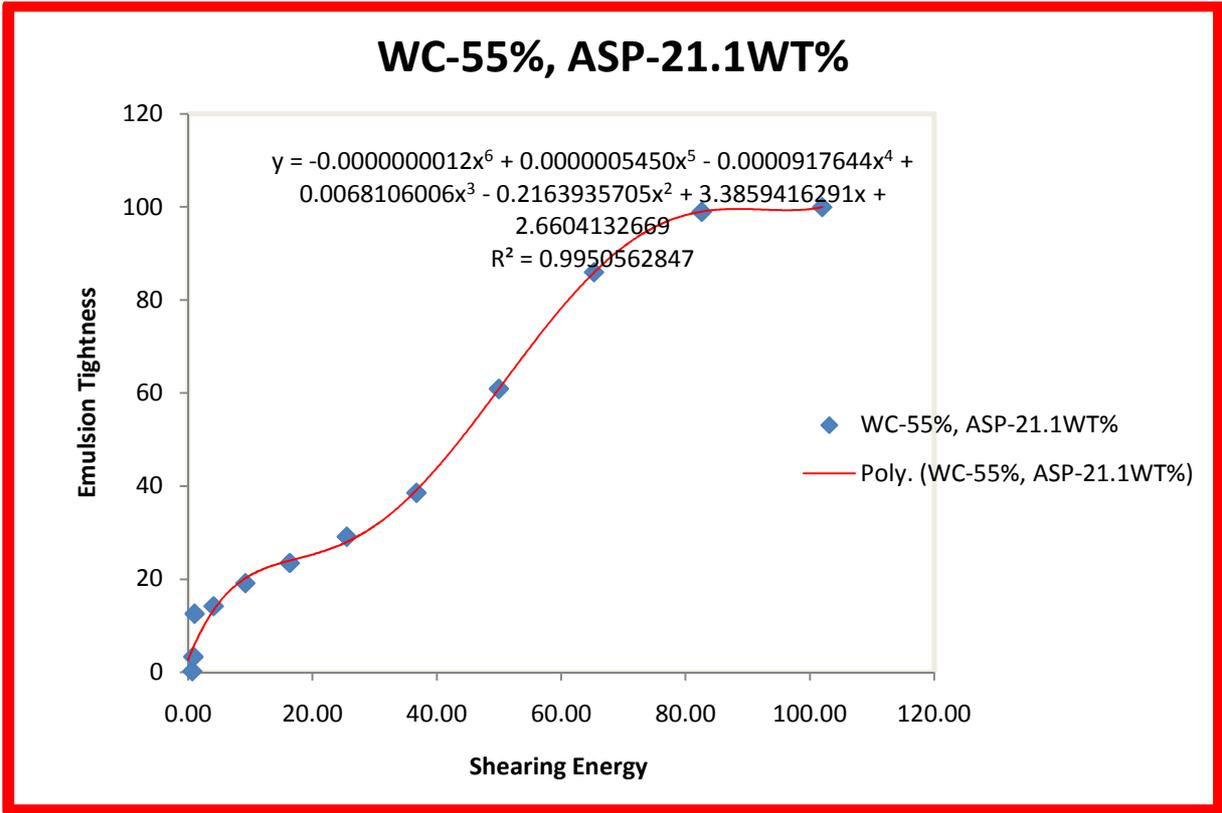


Figure B.16: Regression analysis of 55% Watercut and 21.1% asphaltene plot

APPENDIX C

Java Codes for Emulsion Tightness Program

```

import java.awt.BorderLayout;
import java.awt.Color;
import java.awt.Dimension;
import java.awt.Font;
import java.util.ArrayList;
import javax.swing.JFrame;
import javax.swing.JOptionPane;
import javax.swing.JTextArea;

public class Emulsion {
    JFrame myFrame;
    static JTextArea results;
    double emulsionTight;
    static double asphat;
    static double x;
    static int waterContent;
    static int numberOfWells,index;
    static ArrayList<String> myList;
    static String field;
    static String loc;

    public Emulsion(){
        myList=new ArrayList<String>();
    }
    public void execute(){
        if(waterContent>0 && waterContent<=15 ){
            if(x>=0.5 && x<=70){
                fiveEmulsion(asphat);
            }
            else{
                JOptionPane.showMessageDialog(null, "Shearing Energy is
out of Range");
            }
        }
        else if(waterContent>=16 && waterContent<=40 ){
            if(x>=0.2 && x<=70){
                thirtyEmulsion(asphat);
            }
            else{
                JOptionPane.showMessageDialog(null, "Shearing Energy is
out of Range");
            }
        }
    }
}

```

```

else if(waterContent>=41 && waterContent<=59 ){
    if(x>=0.25 && x<=70){
        fiftyEmulsion(asphat);
    }
    else{
        JOptionPane.showMessageDialog(null, "Shearing Energy is
out of Range");
    }
}
else {
    JOptionPane.showMessageDialog(null, "Water Content Value out of
Range !!!: Enter Values 1-59");
}
}

```

```

public void showMessage(){
    results.append("    PREDICTION OF OIL FIELD EMULSION
TIGHTNESS AT WELLHEAD\n");
    results.append("    ADEKUNLE OPAWALE \n");
    results.append("    DEPARTMENT OF PETROLEUM
ENGINEERING\n");
    results.append("    AFRICAN UNIVERSITY OF SCIENCE AND
TECHNOLOGY. ABUJA NIGERIA \n");
    results.append("    Version 1.01: Copyright 2010, All rights \n");

    results.append("_____ \n");
}

```

```

public void showList(){
    myFrame=new JFrame(" EMULSION TIGHTNESS RESULTS ");
    Font font= new Font("Verdana",Font.BOLD,12);
    results=new JTextArea();
    results.setFont(font);
    results.setEditable(false);
    results.setForeground(Color.BLUE);
    myFrame.setDefaultCloseOperation(JFrame.EXIT_ON_CLOSE);
    myFrame.setLayout(new BorderLayout());
    myFrame.getContentPane().add(results);
    myFrame.pack();
    myFrame.setSize(new Dimension(700,700));
    myFrame.setLocationRelativeTo(null);
    showMessage();
    results.append("                Name of Oil Field : "+ field +" \n");
    results.append("                Location of Oil Field : "+ loc +" \n");
}

```

```

        results.append("*****\n");
        results.append("Well" + " " + WaterCut("%)" + " " + Asph.Content(wt%) + "
+" ShearingEnergy(J)" + " "+"EmulsionTightness \n");
        results.append("----- \n");
        for(int i=0;i<myList.size();i++){
            results.append(myList.get(i)+"\n");
            System.out.println(myList.get(i));
        }
        myFrame.setVisible(true);
    }

    public void fiveEmulsion(double as){
        if(as>=0.1 && as<=1.3){
            emulsionTight=(1*Math.pow(10,-10)*Math.pow(x,6))-
(3.71*Math.pow(10,-8)*Math.pow(x,5))+4.37*Math.pow(10,-6)*Math.pow(x,4)-
(2.334*Math.pow(10,-4)*Math.pow(x,3)) + (0.0051*Math.pow(x,2)) + (0.034*x)-0.01548 ;
        }
        else if(as>=1.4 && as<=3.0){
            emulsionTight=(2.8*Math.pow(10,-
9)*Math.pow(x,5))+8.96*Math.pow(10,-7)*Math.pow(x,4)-(1.03*Math.pow(10,-
4)*Math.pow(x,3))+0.0043*Math.pow(x,2) + (0.05791*x)-0.031539 ;
        }
        else if(as>=3.1 && as<=9.0){
            emulsionTight=(-2.7*Math.pow(10,-
8)*Math.pow(x,4))+5.1291*Math.pow(10,-6)*Math.pow(x,3)-(0.0011137*Math.pow(x,2))
+ (0.169674*x)-0.08123 ;
        }
        else if(as>=10.0 && as<=19){
            emulsionTight=(-5.1*Math.pow(10,-
9)*Math.pow(x,5))+1.376*Math.pow(10,-6)*Math.pow(x,4)-
(0.00012851*Math.pow(x,3))+0.003303*Math.pow(x,2)+(0.2044*x)-0.09431 ;
        }
        else if(as>19 && as<=25){
            emulsionTight=(-1*Math.pow(10,-
9)*Math.pow(x,5))+3.06*Math.pow(10,-7)*Math.pow(x,4)-(3.279*Math.pow(10,-
5)*Math.pow(x,3)-(0.0001546*Math.pow(x,2))+0.260769*x)-0.1146055 ;
        }
        String message=index+1
+"t"+waterContent+"t"+asphat+"t"+x+"t"+emulsionTight;
        myList.add(message);
    }

```

```

public void thirtyEmulsion(double as){
    if(as>=0.1 && as<=1.3){
        emulsionTight=(1.14*Math.pow(10,-8)*Math.pow(x,5))-
(3.013*Math.pow(10,-6)*Math.pow(x,4)) + (2.778481*Math.pow(10,-4)*Math.pow(x,3)) -
(0.0084198*Math.pow(x,2)) + (0.113776*x)+0.032647656 ;
    }
    else if(as>=1.4 && as<=3.0){
        emulsionTight=(-8*Math.pow(10,-
10)*Math.pow(x,6))+2.409*Math.pow(10,-7)*Math.pow(x,5)-(2.675*Math.pow(10,-
5)*Math.pow(x,4))+0.001367*Math.pow(x,3)-(0.029562*Math.pow(x,2)) +
(0.38553*x)+0.056904 ;
    }
    else if(as>=3.1 && as<=9.0){
        emulsionTight=(2.6*Math.pow(10,-8)*Math.pow(x,5))-
(7.0597*Math.pow(10,-6)*Math.pow(x,4))+6.6774*Math.pow(10,-4)*Math.pow(x,3)-
(0.022278*Math.pow(x,2))+0.479625*x)+0.27724 ;
    }
    else if(as>=10.0 && as<=19){
        emulsionTight=(5.5*Math.pow(10,-8)*Math.pow(x,5))-
(1.85*Math.pow(10,-5)*Math.pow(x,4))+0.00194*Math.pow(x,3)-
(0.06787*Math.pow(x,2))+1.26232*x)+0.6247884 ;
    }
    else if(as>19 && as<=25){
        emulsionTight=(2.19*Math.pow(10,-7)*Math.pow(x,5))-
(5.896*Math.pow(10,-5)*Math.pow(x,4))+0.0053456*Math.pow(x,3)-
(0.181068915*Math.pow(x,2))+2.6954*x)+0.410177166;
    }
    String message=index+1
+"t"+waterContent+"t"+asphat+"t"+x+"t"+emulsionTight;
    myList.add(message);
}

```

```

public void fiftyEmulsion(double as){
    if(as>=0.1 && as<=1.3 ){
        emulsionTight=(-5.6*Math.pow(10,-9)*Math.pow(x,5))+
(8.79*Math.pow(10,-7)*Math.pow(x,4)) - (1.3381*Math.pow(10,-6)*Math.pow(x,3))-
(0.00274*Math.pow(x,2))+0.24350234*x)+0.11077062 ;
    }
    else if(as>=1.4 && as<=3.0){

```

```

        emulsionTight=(4.84*Math.pow(10,-8)*Math.pow(x,5))-
(1.31*Math.pow(10,-5)*Math.pow(x,4))+(0.0012645*Math.pow(x,3))-
(0.04929732*Math.pow(x,2))+(0.9442998*x) +0.05632010 ;
    }

    else if(as>=3.1 && as<=9.0){
        emulsionTight=(-1.9*Math.pow(10,-
9)*Math.pow(x,6))+(6.12*Math.pow(10,-7)*Math.pow(x,5))-(7.51*Math.pow(10,-
5)*Math.pow(x,4))+(0.004374*Math.pow(x,3))-(0.117*Math.pow(x,2))+(1.593*x)-0.0355;

    }

    else if(as>=10.0 && as<=19){
        emulsionTight=(1.051*Math.pow(10,-7)*Math.pow(x,5))-
(2.86*Math.pow(10,-5)*Math.pow(x,4))+(0.00278*Math.pow(x,3))-
(0.108*Math.pow(x,2))+(2.024*x)+0.5651 ;
    }
    else if(as>19 && as<=25){
        emulsionTight=(-2.7*Math.pow(10,-
9)*Math.pow(x,6))+(1.028*Math.pow(10,-6)*Math.pow(x,5))-(1.482*Math.pow(10,-
4)*Math.pow(x,4))+(9.9368*Math.pow(10,-3)*Math.pow(x,3))-
(0.2991*Math.pow(x,2))+(4.2989*x)-0.0544;

    }
    String message=index+1
+"\\t"+waterContent+"\\t"+asphat+"\\t"+x+"\\t"+emulsionTight;
    myList.add(message);
}

public ArrayList<String> getMyList(){
    return myList;
}

public static void main(String args[]){
    field=JOptionPane.showInputDialog("Input Name of Oil Field");
    loc=JOptionPane.showInputDialog("Input Name Location");
    String wellValue=JOptionPane.showInputDialog("Input the Number of
Wells");
    numberOfWells=Integer.parseInt(wellValue);
    for(index=0;index<numberOfWells;index++){
        String emul=JOptionPane.showInputDialog("Input the Water Cut(%
For Well "+ (index+1));
        waterContent=Integer.parseInt(emul);

```

```
        String as=JOptionPane.showInputDialog("Input the Asphaltene  
Content(wt%) For Well "+ (index+1));  
        asphat=Double.parseDouble(as);  
        String se=JOptionPane.showInputDialog("Input WellHead Shearing  
Energy(J) For Well "+ (index+1));  
        x=Double.parseDouble(se);  
    }  
}  
}
```

APPENDIX D

Laboratory pictures gallery



Figure D.1: Myself in the Laboratory



Figure D.2: Mixing of water, crude oil and other ingredients to form emulsion



Figure D.3: Some set of samples arranged in a heated water bath



Figure D.4: Some set of emulsions created with different conditions



Figure D.5: Demulsification of emulsions showing different rates of resolution