Characterization Of Crude Oil Emulsion

by

Muhammad Waseem

12954

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Mechanical Engineering)

MAY 2012

Universiti Teknologi PETRONAS Bandar Seri Iskandar 31750 Tronoh Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Characterization Of Crude Oil Emulsion

by

Muhammad Waseem

A project dissertation submitted to the Mechanical Engineering Programme Universiti Teknologi PETRONAS in partial fulfilment of the requirement for the BACHELOR OF ENGINEERING (Hons) (MECHANICAL ENGINEERING)

Approved by,

Dr.Azuraien Japper.

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

CERTIFICATION OF ORIGINALITY

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

MUHAMMAD WASEEM

ABSTRACT

Crude oil emulsification happens at all stages of crude oil production and processing creating operational problems such as pressure drops in flow lines, corrosion, catalyst poisoning, increase in demulsifier usage and trips in crude oil handling facilities. In order to demulsify the crude oil aptly in-depth analysis of the characteristics of the crude oil is inevitable. This report presents the findings of a series of experiments performed to analyze the oil/ water separation in the presence of varying amounts and types of brine and emulsifiers respectively by using crude oil /water ratios of 70/30, 80/20 and 90/10. The results show the existence of an optimal salinity at which full or partial separation can be achieved without utilizing demulsifiers which can reduce considerable amounts of costs in terms of demulsifiers and other techniques for separation.

ACKNOWLEDGEMENTS

My deepest gratitude and appreciation goes to my supervisor, Dr. Azuraien Japper for her help and limitless guidance throughout this work. And finally a humble acknowledgment goes to my grand campus "Universiti Teknologi PETRONAS" for providing the facilities.

TABLE OF CONTENTS

	iv
INTRODUCTION	1
1.1 Background of Study	- 1
1.2 Problem Statement	- 1
1.3 Objectives and Scope of Study	1
1.4 The Relevancy of the Project	- 1
1.5 Feasibility of the Project within the Scope and	
Time frame	1
LITERATURE REVIEW	2
2.1 Emulsions	2
2.2 Types of Emulsions	2
2.3 Formation of Emulsions	3
2.4 Emulsifiers	3
2.5 Interfacial Film	4
2.6 Characteristics and Physical Properties of	
Crude Oil Emulsions	- 5
2.7 Factors affecting Interfacial Film	7
2.8 Demulsification	12
2.9 Mechanisms involved in Demulsification	12
2.10 Sedimentation and Creaming	12
METHODOLOGY 3.1 Research Methodology	14 - 14 14 15 15 15 - 17
RESULTS AND DISCUSSIONS 4.1 Using Oil/Brine (90%/ 10%) ratio with Surfactant -1 4.2 Using Oil/Brine (80%/ 20%) ratio with Surfactant-1 4.3 Using Oil/Brine (70%/ 30%) ratio with Surfactant-2 4.4 Using Oil/Brine (90%/ 10%) ratio with Surfactant-2 4.5 Using Oil/Brine (80%/ 20%) ratio with Surfactant-2 4.6 Using Oil/Brine (70%/ 30%) ratio with Surfactant-2 4.7 Using Oil/Brine (90%/ 10%) ratio with Surfactant -3- 4.8 Using Oil/Brine (80%/ 20%) ratio with Surfactant -3- 4.9 Using Oil/Brine (70%/ 30%) ratio with Surfactant -3- 4.9 Using Oil/Brine (70%/ 30%) ratio with Surfactant -3-	- 18 - 18 22 - 23 23 25 25 25 25 26
	INTRODUCTION

4.10.1 Surfactant -1 (Sodium Stearate) 33
4.10.2 Surfactant -2 (Alkylbenzenesulphonate) 33
4.10.3 Surfactant -3(Sodium lauryl sulphate) 35
4.11 Surfactant Type Variation (Surfactant-1: Sodium Stearate,)
Surfactant-2: Alkylbenzenesulphonate, Surfactant-3: Sodium lauryl
Sulphate) 37
4.11.1 Oil/Brine Ratio 90/10 37
4.11.2 Oil/Brine Ratio 80/20 39
4.11.3 Oil/Brine Ratio 70/30 41
4.12 Surfactant Amount Variation (Surfactant-1: Sodium
Stearate, Surfactant-2: Alkylbenzenesulphonate, Surfactant-3: Sodium
lauryl Sulphate) 43
4.12.1 Surfactant-1 (Sodium Stearate) 43
4.12.2 Surfactant -2 (Alkylbenzenesulphonate) 45
4.12.3 Surfactant -3 (Sodium lauryl sulphate) 47

CHAPTER 5:	CONCLUSION AND RECOMMENDATION	49
REFERENCES		50

LIST OF FIGURES

Fig 1: Water in Oil emulsion	2
Fig 2: Oil in Water emulsion	2
Fig 3: Water in Oil in Water	3
Fig 4: Droplets surrounded by Interfacial Film	5
Fig 5: Droplet size Distribution	5
Fig 6: Viscosities of very tight emulsions at 125° F	6
Fig7: Viscosities of very tight emulsions at shear rate of 0.1 (1/s)	6
Fig 8: Relative viscosities of emulsions	7
Fig 9: Mechanism of emulsion stabilization by asphaltenes	8
Fig 10: 3D representation of Asphaltene molecule	8
Fig 11: Steric repulsion between two water droplets	9
Fig 12: Effect of asphaltenes on emulsion stability	9
Fig13: Wetting behaviour of solids at oil/water interface	10
Fig 14: Droplet stabilization by solids	10
Fig 15: Effect of pH and Demulsifier on emulsion stability	11
Fig 16: Effect of brine and pH on emulsion stability	11
Fig 17: Emulsion by Mechanical Stirrer	15
Fig 18: Experimental Planning for each Surfactant	16
Fig 19: Oil 75%, Surfactant 15%, Brine 10%	18
Fig 20: Oil 70%, Surfactant 10%, Brine 20%	19
Fig 21: Oil 65%, Surfactant 15%, Brine 20%	20
Fig 22: Oil 65%, Surfactant 5%, Brine 30%	22
Fig 23: Oil 55%, Surfactant 15%, Brine 30%	23
Fig 24: Oil 65%, Surfactant 5%, Brine 30%	28
Fig 25: Oil 60%, Surfactant 10%, Brine 30%	29

Fig 26: Surfactant -1 (Sodium Stearate, 5%), Settling time (5 mins) 31

Fig 27: Surfactant -1 (Sodium Stearate, 10%), Settling time (5 mins)	31
Fig 28: Surfactant -1 (Sodium Stearate, 15%), Settling time (5 mins)	32
Fig 29: Surfactant -2 (Alkylbenzenesulphonate, 5%), Settling time (5 mins)	33
Fig 30: Surfactant -2 (Alkylbenzenesulphonate, 10%), Settling time (5min)	33
Fig 31: Surfactant -2 (Alkylbenzenesulphonate, 15%), Settling time (5mins)	34
Fig 32: Surfactant -3 (Sodium lauryl sulfate, 5%), Settling time (5 mins)	35
Fig 33: Surfactant -3 (Sodium lauryl sulfate, 10%), Settling time (5 mins)	35
Fig 34: Surfactant -3 (Sodium lauryl sulfate, 15%), Settling time (5 mins)	36
Fig 35: Oil/Brine Ratio 90/10, Surfactant Ratio 5%, Settling time (5 mins)	37
Fig 36: Oil/Brine Ratio 90/10, Surfactant Ratio 10%, Settling time (5 mins)	37
Fig 37: Oil/Brine Ratio 90/10, Surfactant Ratio 15%, Settling time (5mins)	38
Fig 38: Oil/Brine Ratio 80/20, Surfactant Ratio 5%, Settling time (5 mins)	39
Fig 39: Oil/Brine Ratio 80/20, Surfactant Ratio10%, Settling time (5 mins)	39
Fig 40: Oil/Brine Ratio 80/20, Surfactant Ratio 15%, Settling time (5 mins)	40
Fig 41: Oil/Brine Ratio 70/30, Surfactant Ratio 5%, Settling time (5 mins)	41
Fig 42: Oil/Brine Ratio 70/30, Surfactant Ratio 10%, Settling time (5 mins)	41
Fig 43: Oil/Brine Ratio 70/30, Surfactant Ratio 15%, Settling time (5 mins)	42
Fig 44: Oil/Brine Ratio 90/10, Surfactant -1 (Sodium Stearate), Settling time (5 mins)	43
Fig 45: Oil/Brine Ratio 80/20, Surfactant -1 (Sodium Stearate), Settling time (5 mins)	43
Fig 46: Oil/Brine Ratio 70/30, Surfactant -1 (Sodium Stearate), Settling time (5 mins)	44
Fig 47: Oil/Brine Ratio 90/10, Surfactant -2 (Alkylbenzenesulphonate), Settling time (5 mins)	45
Fig 48: Oil/Brine Ratio 80/20, Surfactant -2 (Alkylbenzenesulphonate), Settling time (5 mins)	45
Fig 49: Oil/Brine Ratio 70/30, Surfactant -2 (Alkylbenzenesulphonate), Settling time (5 min)	46

viii

Fig 50: Oil/Brine Ratio 90/10, Surfactant -3 (Sodium lauryl sulfate), Settling 47 time (5 mins)

Fig 51: Oil/Brine Ratio 80/20, Surfactant -3 (Sodium lauryl sulfate), Settling 47 time (5 mins)

Fig 52: Oil/Brine Ratio 70/30, Surfactant -3 (Sodium lauryl sulfate), Settling 48 time (5 mins)

LIST OF TABLES

Table 1: Resins and Asphaltenes contents of various	4
crude oils	
Table 2: Saturated, Aromatic, Resin and Asphaltene	4
analysis of crude oil	
Table-3: Oil/ Water Ratio (90%/10%) with surfactant -1	21
Table-4: Oil/ Water Ratio (80%/20%) with surfactant -1	21
Table-5: Oil/ Water Ratio (70%/30%) with surfactant -1	24
Table-6: Oil/ Water Ratio (90%/10%) with surfactant -2	24
Table-7: Oil/ Water Ratio (80%/20%) with surfactant -2	26
Table-8: Oil/ Water Ratio (70%/30%) with surfactant -2	26
Table-9: Oil/ Water Ratio (90%/10%) with surfactant -3	27
Table-10: Oil/ Water Ratio (80%/20%) with surfactant -3	27
Table-11: Oil/ Water Ratio (70%/30%) with surfactant -3	30

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Heavy crude oil contains natural surfactants like (asphaltenes, and resins) and in the presence of water forms an emulsion. In order to comply with the crude oil specifications (water content < 1%) and environmental regulations (oil content < 10 ppm) the water needs to be separated, treated and disposed of properly (DOE, Malaysia). Crude oil emulsion leads to pressure drops in flow lines, corrosion, catalyst poisoning, increase in demulsifier usage and trips in crude handling facilities thus requiring an in-depth analysis to tackle the stated issues. Hence, understanding the characteristics of crude oil emulsion is inevitable in order to address the problems.

1.2 PROBLEM STATEMENT

The composition of heavy crude oil is unique at each location thus emulsion formation and stability varies accordingly and cannot be eliminated by a single solution. Crude oil emulsions create numerous problems at crude oil handling facilities such as pressure drops in flow lines, corrosion, catalyst poisoning, increase in demulsifier usage and trips. Feasible and eco-friendly ways to breakup the crude oil emulsion are required at all stages of crude oil processing.

1.3 OBJECTIVE AND SCOPE OF STUDY

The objective is to study,

1. The effect of salinity on heavy crude oil emulsion using oil/water ratios of 90/10, 80/20 and 70/30.

- 2. The factors affecting the making and breaking up of crude oil emulsion.
- 3. The effect of salinity on crude oil emulsion breakup.

The scope of the study is far reaching as every oil well has a unique crude oil emulsion and any effort towards understanding the behaviour of crude oil emulsion at one field will ultimately assist the analysis of the crude oil emulsion at other fields.

1.4 THE RELEVANCY OF THE PROJECT

The study is a part of the project to find solutions for emulsion related issues at crude oil handling facilities operated by Petronas Carigali.

1.5 FEASIBILITY OF THE PROJECT WITHIN THE SCOPE AND TIME FRAME

Angsi-C crude oil will be characterized as specified in the Gantt chart.

CHAPTER 2

LITERATURE REVIEW / THEORY

2.1 EMULSION

Emulsion is the dispersion of one liquid in the form of droplets in another immiscible liquid. The phase in droplets form is called the dispersed or internal phase whereas the phase in which the droplets are suspended is called the continuous or external phase. (Narve Aske, 2002, p.15). The amount of water emulsifying crude oil varies regionally, ranging from less than 1% to greater than 80%. (Kokal, 2006, p.534).

2.2 TYPES OF EMULSION

Produced oilfield emulsions can be categorised in three types:

- water in oil, droplets of water suspended in oil. .(Mehta S, 2005, p.13).



Fig 1: Water in Oil emulsion(Mehta S, 2005, p.13).

- oil in water, droplets of oil suspended in water.(Mehta S, 2005, p.13).



Fig 2: Oil in Water emulsion (Mehta S, 2005, p.13).

- **multiple or complex emulsions**, droplets of water suspended in oil drops which in turn are suspended in water or droplets of oil suspended in water drops which in turn are suspended in oil. (Pal R, 2010, p.1).



Fig 3: Water in Oil in Water (Pal R, 2010, p.1).

Emulsions are also classified according to the size of droplets. If the size of the droplets dispersed in the external phase is larger than 0.1 micrometer, the emulsion is called a 'macroemulsion' which is thermodynamically unstable and is rife among oilfields whereas if the droplets size is smaller than 0.1 micrometer then the emulsion is called a 'microemulsion' which is thermodynamically stable.(Kokal, 2006,p.534). The effects of droplet size on the rheology of water-in-oil emulsions become significant only at high values of dispersed phase concentration greater than 60%. (Rajinder Pal, 1998, p.1).

2.3 FORMATION OF EMULSIONS

Crude oil emulsions are formed when oil and water are mixed with sufficient mixing energy, in the presence of natural emulsifiers (asphaltenes and resins), via various sources such as flow through reservoir rock, bottomhole perforations/pump, flow through tubing, flow lines, production headers, valves, fittings, chokes, surface equipment and gas bubbles.(Spiecker P and Kilpatrick K, 2004, p.2).

Bancroft proposed that upon mixing oil, water and surfactant the external phase forms out of the phase in which the surfactant is more soluble. (Poteau S, 2004, p.515).

2.4 EMULSIFIERS

Emulsifiers are agents that stabilize emulsions and are of two types,

- **Surface-** Active agents or surfactants are compounds that are partly soluble in both oil and water and due to this nature form interfacial films at the oil/water interface thus inhibiting the water droplets to combine and settle down.(Kokal, 2006,p.536). Emulsifiers that occur naturally are Asphaltenens, Resins, organic acids and bases.

Heavy crude oils contain huge amounts of asphaltenes. Components such as resins, waxes, naphthenic acids etc. are also present but are unable to produce stable

emulsions alone. However, these components effect the stability of the emulsion by associating with asphaltenes. (Poteau S, 2004, p.512).

Crude	°API	Resin (wt%)	Asphaltene (wt%)	Asph./Resin
Canada, Atabasca	8.3	14.0	15.0	1.07
Venezuela, Boscan	10.2	29.4	17.2	0.58
Canada, Cold Lake	10.2	25.0	13.0	0.52
Mexico, Panucon	11.7	26.0	12.5	0.48

Table 1: Resins and Asphaltenes contents of various crude oils (Poteau S, 2004,p.512).

- **Finely Divided Solids** are submicron fine solid particles comprising of clay, sand, waxes, corrosion products, mineral scales and drilling muds that collect at oil/water interface and stabilize emulsions.(Kokal, 2006,p.536). Particles like silica, iron oxides, clay, etc. are hydrophilic by nature but become hydrophobic after continuous long term exposure to crude oil and lack of water. (Poteau S, 2004, p.512).

Table 2: Saturated, Aromatic, Resin and Asphaltene analysis of crude oil (Poteau S, 2004, p.512).

(% weight)	SARA pentane	SARA heptane	h	(% eptane s	6 weigh SARA f	t) ractions	1
			С	Н	Ν	0	S
Asphaltenes	17	14.1	83.8	7.5	1.3	1.7	4.8
Resins	33	37.3	82.8	8.9	1.5	2.0	4.3
Aromatics	37	37.2	84.3	10	<0.3	1.1	4.0
Saturated	12	11.4	86.6	13	<0.3	<0.2	<0.1

2.5 INTERFACIAL FILM

The adsorption of emulsifiers around the droplets at the oil/water interface creates a film that stabilizes the emulsion. The interfacial film increases the interfacial viscosity which reduces the water drainage rate from the droplets during coalescence thus inhibiting the emulsion breakup. There are 2 types of interfacial films,

- Rigid or solid films are like insoluble solid skins covering the droplets with high interfacial viscosities and are stabilized by fine solid particles thus hindering coalescence and discouraging emulsion breakup.

- Mobile or liquid films have low interfacial viscosities and are formed by the addition of demulsifiers thus promote coalescence.



Fig 4: Droplets surrounded by Interfacial Film (Pal R, 2010, p.1).

2.6 CHARACTERISTICS AND PHYSICAL PROPERTIES OF CRUDE OIL EMULSIONS

- **Appearance and colour.** Dark reddish, brown, gray, or blackish brown are the common colours of crude oil emulsions, emulsions with light colour have small diameter droplets and those with dark colour have large diameter droplets. (Ivanov Bl, 1999).

- **Droplet size and Droplet-size distribution.** The smaller the dispersed water droplet size the more tighter is the emulsion. Droplet size distribution plays an important role in emulsion stability and can be represented by a distribution function. (Kokal, 2006,p.537).



Fig 5: Droplet size Distribution (Kokal, 2006, p. 537).

- **Basic Sediment and Water.** BS&W constitutes the solids and aqueous portion of the emulsion and numerous techniques are used for BS&W removal. (Kokal, 2006,p.537). The most common technique for the determination of solids, water and oil is slightly overdosing the emulsion with a demulsifier in a specially designed

centrifuge tube, letting it stand for some time after centrifuging and directly measuring the amount of water and solids. (Kokal, 2006,p.537)..

- **Bulk viscosity.** Upto a water content of 40%, water in oil emulsion exhibits Newtonian behaviour and above 40%, emulsion exhibits non –Newtonian behaviour as shown in Fig.6. (Kokal, 2006,p.538). Fig.6 shows slopes of curves above water cuts of 40% deviating from zero indicating non-Newtonian behaviour. Viscosity decreases with increasing temperature and must be considered at respective temperature during experimentations.(Kokal, 2006,p.538).



Fig 6: Viscosities of very tight emulsions at 125° F (Kokal, 2006, p. 538).

It has been observed that an emulsion remains a water in oil emulsion upto a water cut of 80%, at 80% the water in oil emulsion 'inverts' and becomes an oil in water emulsion as shown in Fig. 7 (Kokal, 2006,p.538). Water which was the dispersed phase previously now becomes the continuous phase. (Kokal, 2006,p.538). Temperature plays an important role in emulsion viscosity. Fig.7 shows that increasing temperature decreases emulsion viscosity.



Fig:7 Viscosities of very tight emulsions at shear rate of 0.1 (1/s) (Kokal, 2006,p.538).

The following equation presents the ratio of the viscosity of virgin crude oil to the viscosity of an emulsion at the same temperature,

$$\mu_{e} / \mu_{o} = e^{(5\varphi)} x (1-3\varphi + a\varphi^{2})$$
 (Kokal, 2006, p. 538).

Where, μ_e = Emulsion viscosity, μ_o = Clean oil viscosity, ϕ = Water cut and a = 7.3 for very tight emulsion, 5.5 for tight emulsion, a = 4.5 for medium emulsion, 3.8 for loose emulsion, 3.0 for very loose emulsion.

- **Interfacial Viscosity.** The interfacial viscosity is the viscosity of the fluid at the oil/water interface. The interfacial films increase the interfacial viscosity and lower the drainage rate of water, inhibiting coalescence for emulsion breakup. (Kokal, 2006,p.540).



Fig 8: Relative viscosities of emulsions (Kokal, 2006, p.540).

Properties of interfacial rheology can be measured through interfacial dilatational modulus, ε , which measures the resistance of the creation of the interfacial tension gradients and the rate at which such gradients disappear after deformation. (Narve Aske, 2002, p.22).

$$\mathcal{E} = d \gamma / d \ln A$$
 (Narve Aske, 2002, p.22).

where,

 γ = Interfacial tension

A = Interfacial area

2.7 FACTORS AFFECTING INTERFACIAL FILMS

Emulsion stability is primarily dependent upon interfacial films and the factors affecting interfacial films are,

- Asphaltenes. Asphaltenes are complex polyaromatic molecules (C_{75} H_{90}) that have an affinity for both oil and water and form a rigid interfacial film around the droplet thus inhibiting coalescence and stabilising the emulsion as shown in Fig. 9. Carbon numbers in asphaltene molecules can be from 30 and above with molecular weights from 500 to above 10000. (Kokal, 2006,p.544). Asphaltenes have a hydrogen/carbon ratio of 1.15 with a specific gravity close to 1. (Kokal, 2006,p.544).



Fig 9: Mechanism of emulsion stabilization by asphaltenes (Kokal, 2006, p. 544).



Fig 10: 3D Representation of Asphaltene molecule (Courtesy of J. Murgich and A. Mansoori)

Fig. 11 shows steric repulsion between hydrophobic groups of the surfactant molecules causing inhibition to coalescence. Asphaltenes making up greater than 10% of crude oil composition result in tight emulsions by forming rigid films as shown in Fig 12. (Kokal, 2006,p.544).



Fig 11: Steric repulsion between two water droplets (Kokal, 2006, p.545)



Fig 12: Effect of asphaltenes on emulsion stability (Kokal, 2006, p.545)

- **Resins.** Resins, like asphaltenes are complex molecules with molecular weight ranging from 500 to 2000 and have a tendency to bond with asphaltenes forming a micelle. It has been observed that the ratio of asphaltene and resin in crude oil determines the type of interfacial film, solid or mobile. (Kokal, 2006,p.545).

- Waxes. Waxes ($C_{16}H_{32}$) only stabilize emulsions in the presence of Asphaltenes or as fine solid particles at low temperatures. (Kokal, 2006,p.545). There are two kinds of petroleum waxes, paraffins which are high-molecular-weight normal alkanes and microcrystalline waxes which are high-molecular-weight iso-alkanes. (Kokal, 2006,p.545).

- **Fine Solid Particles.** Fine solids form rigid interfacial films at oil water interface by diffusion and inhibit coalescence as shown in Fig. 14. Effectiveness of fine solids in emulsion stabilization is dependent upon electrical charge, inter-particle interactions, particle size and wettability. The degree to which a solid particle is wetted by oil or water is called "wettability". For a particle to act as a stabilizer it has to be wetted by both water and oil at the oil/water interface. (Kokal, 2006,p.546). If the contact angle in the fig.13 is <90° the solid is oil- wet whereas angle >90° results in solid being water-wet as shown in Fig. 13. (Kokal, 2006,p.546). Contact angles near 90° form intermediately wetted solid particles which results in the tightest emulsions as shown in Fig. 13. (Kokal, 2006,p.546).



Fig 13: Wetting behaviour of solids at oil/water interface (Kokal, 2006,p.546).



Fig 14: Droplet stabilization by solids (Kokal, 2006,p.546).

- **Temperature**. Temperature affects the emulsion stability as increasing temperature decreases viscosity of the system, re-dissolves the waxes, increases thermal energy of droplets and reduces interfacial viscosity. (Kokal, 2006,p.547). A kinetic barrier still exists at high temperatures to drop coalescence as high temperatures change the characteristics of the interfacial film and at a point emulsion resolution remains unaffected. (Kokal, 2006,p.547).

- **Drop size**. The smaller the droplet size the more stable is the emulsion. Small droplets also increase emulsion viscosity and the time for separation. Droplets size distribution is presented in Fig 5. (Kokal, 2006,p.548).

- **pH**. The ionization of organic acids and bases contained in the interfacial films is affected by the addition of inorganic acids and bases which in turn changes the physical properties of the interfacial films. Interfacial films formed by asphaltenes are weakest if pH is high whereas interfacial films formed by resins are weakest if pH is low. (Kokal, 2006,p.549). It has been observed that an optimum pH exists for crude oil/brine systems at which maximum emulsion breakup takes place depending upon the crude oil and brine compositions as shown in Fig 15. (Kokal, 2006,p.549).



Fig 15: Effect of pH and Demulsifier on emulsion stability (Kokal, 2006, p. 549).

- **Brine Composition.** In determining the stabilizing properties of films pH and Brine are inter-related. The rigid films covering the water droplets are formed due to brines with a high ratio of Ca/Mg and Ca ions thus creating stable emulsions. Emulsion stability decreases due to high concentrations of divalent ions and high pH. (Kokal, 2006,p.549).Water in crude oil contains a variety of ions especially high concentrations of sodium and chloride that form insoluble salts by reacting with hydrophilic groups. (Kokal, 2006,p.549). Fig. 16 shows maximum separation occurs at a particular pH value.



Fig 16: Effect of brine and pH on emulsion stability (Kokal, 2006, p. 549).

Water from petroleum formations usually contain Sodium and Chloride ions in high concentrations which react at the interface with hydrophilic groups forming insoluble salts. (Kokal, 2006,p.549). Some general trends that have been noted are,

- Brine composition and pH determine the stabilizing properties of the interfacial films. . (Kokal, 2006,p.549).

- Brines with high Ca/Mg ratio and high Ca ions form rigid films resulting in stabkeemulsions. (Kokal, 2006,p.549).

2.8 DEMULSIFICATION

The breaking of crude oil emulsion into oil and water phases is called demuslification (Pierre C, 2004). Fast rate of breakup, least residual oil in water and least residual water in oil is required depending upon the oil specifications and environmental regulations. In order for the demulsification to occur interfacial films must be ruptured and droplets coalesced. Factors that enhance demulsification are,

- **Temperature**. High temperatures increase the water expansion inside the droplet and rupture the interfacial film thus causing water droplets to coalesce.

- **Agitation**. A small amount of shear is required to aptly mix the demulsifier for emulsion breakup.

- Retention Time. Increase in retention time increases oil/water separation

- **Solids Removal**. Fine solids may enhance emulsion stability and should be removed by dispersion or water wetting. Adsorption of solid particle is irreversible if contact angle is near to 90 $^{\circ}$. (Pierre C, 2004, p.511).

- **Control of emulsifying agents**. The chemicals injected in the well may have the tendency to stabilize emulsions and should be tested for compatibility before injection.

- **Retrofitting.** Field aging can create problems with equipments handling the separation and therefore should be reengineered from time to time for proper demulsification.

2.9 MECHANISMS INVOLVED IN DEMULSIFICATION

Demulsification is a two step process,

- **Flocculation**. During this process the water droplets clump together or aggregate whilst retaining the interfacial film. (Ivanov B, 1999, p.20).

- **Coalescence**. During this process the interfacial film ruptures and droplets fuse or coalesce to form larger drops. (Ivanov B, 1999, p.2).

2.10 SEDIMENTATION OR CREAMING

'Sedimentation' is the process in which the water droplets settle down whereas 'Creaming' is the process in which oil droplets rise up to the surface. An emulsion pad is created at the oil water interface due to the accumulation of unresolved emulsion droplets resulting in operational problems and should be removed. Emulsions with small drops having radius, ($R < 1 \mu m$), are insensitive to sedimentation or creaming. (Langevin D, 2004, p.517).

Methods for demulsification are dependent upon the crude oil composition, brines, separation equipment, chemical demulsifiers, and product specifications and include any or combination of the following methods,

- Addition of chemical demulsifiers.
- Increasing the emulsion temperature.
- Application of electrostatic fields to promote coalescence.

- Gravitational separation of oil, gas and water in large volume separators and desalters.

It is difficult to eliminate emulsification completely but it can be minimised by following good operational practices. Acid jobs should be performed with care as precipitation occurs during acidization resulting in tight emulsions. Mixing at chokes and pumps should be optimized as severe mixing contributes to stability of emulsions. As numerous chemicals are utilized during crude processing, compatibility studies should be conducted and the tendency to form emulsion should be evaluated in order to avoid emulsification. Every producing stream is unique and requires a different separation strategy based upon the composition of crude oil. Demulsifier overdosing can result in rag layers or pads inside separators and is difficult to detect on time. With the installation of automated or semi-automated control systems, that can control grid voltage in the dehydrator and desalter, emulsion layer inside the separator, crude quality, water quality and operating temperature, overdosing can be checked and demulsifier usage can be optimized. An optimization program for emulsion treatment can reduce the costs and detect the flaws on time to keep the performance of the crude handling facilities at its peak.

CHAPTER 3

METHODOLOGY

3.1 RESEARCH METHODOLOGY



3.2 EMULSION PREPARATION METHOD

- Mechanical Stirrer

Macro-eddies or macro turbulences are generated by mechanical stirrers in the oil/water mixture. Macro-eddies are decomposed in micro-eddies with a characteristic length known as Kolmogorov Length. Micro-eddies are responsible for energy transfer and macroscopic phase breakage. The drops split into smaller droplets as the shear exerted by the turbulence exceeds the bonding forces of the liquids. (Tauer, Kalus, 2005).



Fig 17: Emulsion by Mechanical Stirrer (Tauer, Kalus, 2005)

3.3 PROJECT ACTIVITIES FOR THE EXPERIMENT

Three brine solutions containing salinity of 2%, 5% and 8% by weight were prepared by mixing Sodium Chloride in distilled water in a mechanical stirrer at 500 rpm for 3 hours. A total of 81 heavy crude oil emulsion samples were prepared by using a mechanical stirrer at 1000 rpm for 5 minutes and using oil/brine ratios of 90/10, 80/20 and 70/30. 3 different types of surfactants (Surfactant 1: Sodium Stearate, Surfactant 2: Akylbenzenesulphonate and Surfactant 3: Sodium lauryl Sulfate) were used and for each surfactant type 27 emulsion samples were prepared by varying the salinity of the brine by 2%, 5% and 8% and the amount of surfactant by 5%, 10% and 15% by volume. The surfactant replaced the equivalent percentage of oil within a specific oil/brine ratio, for eg. 5% surfactant in oil/brine ratio of 90/10 containing 90% oil and 10% brine means the emulsion constituted 85% oil, 5% surfactant and 10% brine. Each sample was observed over the course of 4 hours to observe the effect of salinity, in combination with surfactant, on oil/water separation. Fig.18 shows the different ratios of oil/water and amounts of surfactant and brines used for the preparation of emulsions for each surfactant at room temperature.

3.4 KEY MILESTONE

To observe the effect of varying salinity on heavy crude oil emulsion using 3 ratios of oil/brine, 70/30, 80/20, 90/10 with different types and varying amounts of surfactants.

3.5 TOOLS REQUIRED

- Flask, Mechanical Stirrer, Test tubes, Droppers and Beaker.

- Oil/Water Ratio by % Volume



- Salinity Ratio by % weight



Fig 18: Experimental Planning for each Surfactant

3.6 GANTT CHART



CHAPTER 4

RESULTS AND DISCUSSION

4.1 USING OIL / BRINE (90%/10%) RATIO WITH SURFACTANT -1 (Sodium Stearate)

As the salinity was increased 80% of the water got separated after 5 minutes in the emulsions containing Surfactant-1 at 15% by volume as shown in Fig. 19. No further separation was observed till the end of the observation time of 4 hours. The emulsions containing 5% and 10% of Surfactant-1 resulted in stable emulsions as shown in Table-3.. However the salinities used for these emulsions were uptil 8%. Stability of the emulsion decreases with increasing salinity only when the amount of Surfactant -1 is 15%. The optimal salinity at which maximum separation takes place is 8% when the amount of Surfactant -1 is 15%. Surfactant-2 and Surfactant-3 did not showed any water separation at oil/brine ratio of 90/10 which also reveals that only surfactant-1 affects the stability of the emulsion at this oil/brine ratio.



Fig 19: Oil 75%, Surfactant 15%, Brine 10%

4.2 USING OIL / BRINE (80%/20%) RATIO WITH SURFACTANT -1 (Sodium Stearate)

At oil/brine ratio of 80/20 adjusting the salinity led to both an increase and a decrease in the stability of the emulsions containing Surfactant -1 at 10% and 15%. Fig. 20 shows an increase in the stability of the emulsion as the salinity is increased when the amount of Surfactant-1 used is 10%. The optimum salinity at this amount is 2% showing the maximum water separation. The settling time was 5 minutes after which no further emulsion breakup was observed till the end of the observation time of 4 hours.



Fig 20: Oil 70%, Surfactant 10%, Brine 20%

Fig. 21 shows a decrease in the stability of the emulsion as the salinity is increased with complete separation occurring at a salinity of 8% when the amount of Surfactant-1 used is 15%. Hence the optimal salinity at this oil/brine ratio is 8% when the amount of Surfactant -1 is 15%. Settling time was 5 minutes as shown in Table-4. Surfactant-2 also showed a complete separation when the amount of Surfactant used was 15%. Hence, the best surfactants to achieve full water separation at oil/brine ratio of 80/20 are Surfactant-1 and Surfactant-2 with optimum salinities of 2% and 8% respectively. Emulsions at oil/brine ratio of 80/20 form loose emulsions as compared to emulsions at oil/brine ratio of 90/10 as the water molecules are closer to each other due to a higher percentage of water resulting in easy coalescence.



Fig 21: Oil 65%, Surfactant 15%, Brine 20%

10%)	
/%06)	
IATIO	
ATER F	
il/Wi	
E3:0	
TABL	

Emulsion 1	formed at 100	0 rpm				SURFACTANT -1				
					6	0% /10% (o/w ratio	()			
	oil %	85	85	85	80	80	80	75	75	75
Min/Hr	brine %	10 (NACL 2%)	10(NACL 5%)	10(NACL 8%)	10 (NACL 2%)	10(NACL 5%)	10(NACL 8%)	10 (NACL 2%)	10(NACL 5%)	10(NACL 8%)
	surfactant %	5	5	5	10	10	10	15	15	15
					O/W SEP	ARATION (%)				
	5 m	0	0	0	0	0	0	97/3	95/5	92/8
1	15 m	0	0	0	0	0	0	97/3	95/5	92/8
3	0 m	0	0	0	0	0	0	97/3	95/5	92/8
	1 hr	0	0	0	0	0	0	97/3	95/5	92/8
	2 hr	0	0	0	0	0	0	97/3	95/5	92/8
	3 hr	0	0	0	0	0	0	97/3	95/5	92/8
	4hr	0	0	0	0	0	0	97/3	95/5	92/8

TABLE 4 : OIL/WATER RATIO (80%/ 20%)

		65	20(NACL 8%)	15		80/20	80/20	80/20	80/20	80/20	80/20	80/20
		65	20(NACL 5%)	15		95/5	95/5	95/5	95/5	95/5	95/5	95/5
		65	20(NACL 2%)	15		98/2	98/2	98/2	98/2	98/2	98/2	98/2
	2	70	20(NACL 8%)	10		0	0	0	0	0	0	0
SURFACTANT -1	0% /20% (o/w ratio	70	20(NACL 5%)	10	ARATION (%)	5/86	98/2	2/86	98/2	98/2	2/86	5/86
	80	70	20(NACL 2%)	10	O/W SEP/	95/5	95/5	95/5	95/5	95/5	95/5	95/5
		75	20(NACL 8%)	5		0	0	0	0	0	0	0
		75	20(NACL 5%)	S		0	0	0	0	0	0	0
) rpm		75	20(NACL 2%)	S		97/3	97/3	97/3	97/3	97/3	97/3	97/3
formed at 100		oil %	brine %	surfactant %		5 m	15 m	30 m	1 hr	2 hr	3 hr	4hr
Emulsion			Min/Hr									

4.3 USING OIL / BRINE (70%/30%) RATIO WITH SURFACTANT -1 (Sodium Stearate)

A decrease in emulsion stability was observed with increasing salinity when the amount of Surfactant-1 used was 5% at oil/brine ratio of 70/30 as shown in Fig. 22. The optimum salinity at this amount of surfactant is 8% displaying the maximum water separation. As the amount of surfactant was increased to 10% and 15% the stability of emulsions increased with increasing salinity. Fig. 23 shows the increasing stability with increasing salinity when the amount of surfactant used is 15%. Despite that the water ratio has increased the water separation is not plausible as compared to Surfactant-2 and Surfactant-3 which show a higher water separation at the same oil/brine ratio. The optimum oil/brine ratio for Surfactant-1 as observed from the experiments is 80/20 at which full separation was achieved at 15% of Surfactant-1 and 8% of salinity.



Fig 22: Oil 65%, Surfactant 5%, Brine 30%



Fig 23: Oil 55%, Surfactant 15%, Brine 30%

4.4 USING OIL / BRINE (90%/10%) RATIO WITH SURFACTANT -2 (Alkylbenzenesulphonate)

At all amounts of surfactant and varying salinity, Surfactant-2 did not affected the stability of emulsions in any way. All the emulsions remained stable and no water separation took place till the end of the observation time as shown in Table-6. Similar results were achieved with Surfactant-3. The results show that the best surfactant for maximum separation at oil/brine ratio of 90/10 is Surfactant-1.

4.5 USING OIL / BRINE (80%/20%) RATIO WITH SURFACTANT -2

(Alkylbenzenesulphonate)

Surfactant-2 showed a 50% and 100% water separation in 5minutes at amounts of 10% and 15% respectively. In both the amounts the salinity was constant at 2% as shown in Table-7. Surfactant-3 showed no separation at this oil/brine ratio whereas Surfactant-1 also showed a 100% separation at this ratio. The best surfactants to achieve maximum water separation at oil/brine ratio of 80/20 are Surfactant-1 and Surfactant-2.

Emulsion	formed at 100	0 rpm				SURFACTANT -1				
					JT I	0% /30% (o/w ratio	(0			
	oil %	65	65	65	60	60	60	22	55	55
Min/Hr	brine %	30(NACL2%)	30(NACL5%)	30(NACL8%)	30(NACL2%)	30(NACL5%)	30(NACL8%)	30(NACL2%)	30(NACL5%)	30(NACL8%)
	surfactant %	5	5	5	10	10	10	15	15	15
					O/W SEP	ARATION (%)				
	5 m	98/2	97/3	95/5	90/10	0	0	90/10	99/1	0
	15 m	98/2	97/3	95/5	90/10	0	0	90/10	99/1	0
	30 m	98/2	97/3	95/5	90/10	0	0	90/10	99/1	0
	1 hr	98/2	97/3	95/5	90/10	0	0	90/10	99/1	0
	2 hr	98/2	97/3	95/5	90/10	0	0	90/10	99/1	0
	3 hr	98/2	97/3	95/5	90/10	0	0	90/10	99/1	0
	4hr	98/2	97/3	95/5	90/10	0	0	90/10	99/1	0

TABLE 5 : OIL/WATER RATIO (70%/ 30%)

TABLE 6 : OIL/WATER RATIO (90%/ 10%)

Emulsion	formed at 100	0 rpm				SURFACTANT -2				
)6	0% /10% (o/w ratio	(0			
	oil %	85	85	85	80	80	80	75	75	75
Min/Hr	brine %	10 (NACL 2%)	10(NACL 5%)	10(NACL 8%)	10 (NACL 2%)	10(NACL 5%)	10(NACL 8%)	10 (NACL 2%)	10(NACL 5%)	10(NACL 8%)
	surfactant %	5	S	5	10	10	10	15	15	15
					O/W SEPAR	ATION TIME IN %				
	5 m	0	0	0	0	0	0	0	0	0
	15 m	0	0	0	0	0	0	0	0	0
	0 m	0	0	0	0	0	0	0	0	0
	30 m	0	0	0	0	0	0	0	0	0
	1 hr	0	0	0	0	0	0	0	0	0
	2 hr	0	0	0	0	0	0	0	0	0
	3 hr	0	0	0	0	0	0	0	0	0
	4hr	0	0	0	0	0	0	0	0	0

4.6 USING OIL / BRINE (70%/30%) RATIO WITH SURFACTANT -2 (Alkylbenzenesulphonate)

All emulsions except for two showed a complete water separation in 5 minutes as showed in Table-8. The salinity affected the stability of the emulsion only when amount of surfactant used was 10%. Surfactant-2 also gives the highest number of complete water separations at the oil/brine ratio of 70/30 as compared to other surfactants making it the best surfactant at this oil/brine ratio and among other oil/ brine ratios.

4.7 USING OIL / BRINE (90%/10%) RATIO WITH SURFACTANT -3 (Sodium lauryl sulfate)

At all amounts of surfactant and varying salinity, Surfactant-3 did not affected the stability of emulsions in any way. All the emulsions remained stable and no water separation took place till the end of the observation time as shown in Table-9. Similar results were achieved with Surfactant-2. The results show that the best surfactant for maximum separation at oil/brine ratio of 90/10 is Surfactant-1.

4.8 USING OIL / BRINE (80%/20%) RATIO WITH SURFACTANT -3 (Sodium lauryl sulfate)

At all amounts of surfactant and varying salinity, Surfactant-3 did not affected the stability of emulsions in any way. All the emulsions remained stable and no water separation took place till the end of the observation time as shown in Table-10. The best surfactants to achieve maximum water separation at oil/brine ratio of 80/20 are Surfactant-1 and Surfactant-2.

(80%/20%)
/WATER RATIO
TABLE 7 : OIL

Emulsion	formed at 100	0 rpm				SURFACTANT -2				
					8(3% /20% (o/w ratio	()			
	oil %	75	75	75	70	70	70	65	65	65
Min/Hr	brine %	20(NACL 2%)	20(NACL 5%)	20(NACL 8%)	20(NACL 2%)	20(NACL 5%)	20(NACL 8%)	20(NACL 2%)	20(NACL 5%)	20(NACL 8%)
	surfactant %	2	5	5	10	10	10	15	15	15
					O/W SEP	ARATION (%)				
	5 m	0	0	0	90/10	0	0	80/20	0	0
	15 m	0	0	0	90/10	0	0	80/20	0	0
	30 m	0	0	0	90/10	0	0	80/20	0	0
	1 hr	0	0	0	90/10	0	0	80/20	0	0
	2 hr	0	0	0	90/10	0	0	80/20	0	0
	3 hr	0	0	0	90/10	0	0	80/20	0	0
	4hr	0	0	0	90/10	0	0	80/20	0	0

TABLE 8 : OIL/WATER RATIO (70%/30%)

Emulsion	formed at 100	0 rpm				SURFACTANT -2				
					70	0% /30% (o/w ratic	()			
	oil %	65	65	65	60	60	60	55	55	55
Min/Hr	brine %	30(NACL2%)	30(NACL5%)	30(NACL8%)	30(NACL2%)	30(NACL5%)	30(NACL8%)	30(NACL2%)	30(NACL5%)	30(NACL8%)
	surfactant %	5	S	5	10	10	10	15	15	15
					O/W SEP	ARATION (%)				
	5 m	70/30	70/30	70/30	70/30	0	80/20	70/30	70/30	70/30
	10 m	70/30	70/30	70/30	70/30	0	80/20	70/30	70/30	70/30
	30 m	70/30	70/30	70/30	70/30	0	80/20	70/30	70/30	70/30
	1 hr	70/30	70/30	70/30	70/30	0	80/20	70/30	70/30	70/30
	2 hr	70/30	70/30	70/30	70/30	0	80/20	70/30	70/30	70/30
	3 hr	70/30	70/30	70/30	70/30	0	80/20	70/30	70/30	70/30
	4hr	70/30	70/30	70/30	70/30	0	80/20	70/30	70/30	70/30

			~										
		75	10(NACL 8%	15		0	0	0	0	0	0	0	
		75	10(NACL 5%)	15		0	0	0	0	0	0	0	
		75	10 (NACL 2%)	15		0	0	0	0	0	0	0	
		80	10(NACL 8%)	10		0	0	0	0	0	0	0	
SURFACTANT-3	0% /10% (o/w ratio	80	10(NACL 5%)	10	ARATION (%)	0	0	0	0	0	0	0	
)6	80	10 (NACL 2%)	10	O/W SEP	0	0	0	0	0	0	0	
		85	10(NACL 8%)	5		0	0	0	0	0	0	0	
		85	10(NACL 5%)	5		0	0	0	0	0	0	0	
) rpm		85	10 (NACL 2%)	2		0	0	0	0	0	0	0	
formed at 1000		oil %	brine %	surfactant %		5 m	15 m	30 m	1 hr	2 hr	3 hr	4hr	
Emulsion			Min/Hr										

TABLE 9 : OIL/WATER RATIO (90%/ 10%)

TABLE 10 : OIL/WATER RATIO (80%/20%)

Emulsion fo			Min/Hr	VI		5	10	30	1	2	3	4
ormed at 100(oil %	brine %	surfactant %		Е	m	m	hr	hr	hr	hr
0 rpm		75	20(NACL 2%)	5		0	0	0	0	0	0	0
		75	20(NACL 5%)	5		0	0	0	0	0	0	0
		75	20(NACL 8%)	S		0	0	0	0	0	0	0
	8	02	20(NACL 2%)	10	O/W SEP	0	0	0	0	0	0	0
SURFACTANT-3	0% /20% (o/w ratio	70	20(NACL 5%)	10	ARATION (%)	0	0	0	0	0	0	0
	()	70	20(NACL 8%)	10		0	0	0	0	0	0	0
		65	20(NACL 2%)	15		0	0	0	0	0	0	0
		65	20(NACL 5%)	15		0	0	0	0	0	0	0
		65	20(NACL 8%)	15		0	0	0	0	0	0	0

4.9 USING OIL / BRINE (70%/30%) RATIO WITH SURFACTANT -3 (Sodium lauryl sulfate)

At all amounts of surfactants, Surfactant-3 showed decreasing stability of emulsion with increasing salinity as shown in Table -11. Fig. 24 and Fig. 25 show a decreasing stability of emulsion with increasing salinity in 5 minutes. Since the percentage of brine in oil/brine ratio of 70/30 is highest among all the oil/brine ratios it's easier for water molecules to flocculate and coalesce. Surfactant-2 and Surfactant-3 show high percentages of water separation as compared with Surfactant-1at oil/brine ratio of 70/30. Surfactant-1 should also show higher percentage of water separation at oil/brine ratio of 70/30 however the amount of salinity that has so far displayed any affect on the stability of the emulsions was uptil 8%. Higher amounts of salinities might deliver better conclusions.



Fig 24: Oil 65%, Surfactant 5%, Brine 30%



Fig 25: Oil 60%, Surfactant 10%, Brine 30%

DISCUSSION

A general trend has been observed that adjusting the salinity of the emulsions affects the stability of the emulsions at room temperature. In emulsions where separation didn't occurred further increasing the salinity needs to be tested since the limit of the salinity for the experiments performed was uptil 8%. At oil/brine ratios of 90/10 all the emulsions except for one remained stable as compared to oil/brine ratios of 80/20 and 70/30 where the stability of the majority of the emulsions was affected by salinity adjustment. At oil/brine ratios of 70/30 majority of the emulsions showed complete water separation which reveals that the optimal salinities to achieve maximum separation for oil/brine ratios of 70/30 are uptil or around 8%. The emulsions constituting Surfactant-3 were less affected by change in oil/water ratios and salinities as compared to emulsions constituting Surfactant-1. Testing at higher salinities, greater than 8%, for emulsions displaying partial or no separation can deliver better results.

Emulsion	formed at 1000) rpm				SURFACTANT-3				
					7(0% /30% (o/w ratic	()			
	oil %	65	65	65	09	60	60	55	55	55
Min/Hr	brine %	30(NACL2%)	30(NACL5%)	30(NACL8%)	30(NACL2%)	30(NACL5%)	30(NACL8%)	30(NACL2%)	30(NACL5%)	30(NACL8%)
	surfactant %	S	5	5	10	10	10	15	15	15
					O/W SEP	ARATION (%)				
	5 m	0	90/10	80/20	0	90/10	70/30	90/10	70/30	70/30
	10 m	0	90/10	80/20	0	90/10	70/30	90/10	70/30	70/30
	30 m	0	90/10	80/20	0	90/10	70/30	90/10	70/30	70/30
	1 hr	0	90/10	80/20	0	90/10	70/30	90/10	70/30	70/30
	2 hr	0	90/10	80/20	0	90/10	70/30	90/10	70/30	70/30
	3 hr	0	90/10	80/20	0	90/10	70/30	90/10	70/30	70/30
	4hr	0	90/10	00/08	U	01/06	0£/02	90/10	02/02	70/30

TABLE 11 : OIL/WATER RATIO (70%/30%)

4.10 Volume fraction Variation





Fig 26: Surfactant -1 (Sodium Stearate, 5%), Settling time (5 mins)



Fig 27: Surfactant -1 (Sodium Stearate, 10%), Settling time (5 mins)



Fig 28: Surfactant -1 (Sodium Stearate, 15%), Settling time (5 mins)

Figures 26-28 show the affect of different oil/water ratios with increasing amounts of Surfactant-1 (Sodium Stearate) on emulsion stability. The stability of the emulsions is most affected by Surfactant-1 at oil/water ratios of 80/20 and 70/30. The optimum salinity for Surfactant-1 to achieve a complete separation at oil/water ratio of 80/20 is 8% and the optimum surfactant amount is 15%.





Fig 29: Surfactant -2 (Alkylbenzenesulphonate, 5%), Settling time (5 mins)



Fig 30: Surfactant -2 (Alkylbenzenesulphonate, 10%), Settling time (5 mins)



Fig 31: Surfactant -2 (Alkylbenzenesulphonate, 15%), Settling time (5 mins)

Figures 29-31 show the affect of different oil/water ratios with increasing amounts of Surfactant-2 (Alkylbenzenesulphonate) on emulsion stability. The stability of the emulsions is most affected by Surfactant-2 at oil/water ratios of 80/20 and 70/30. At oil/water ratio of 90/10, Surfactant-2 and the varying salinities have no effect on the stability of the emulsions. At oil/water ratio of 70/30 the amount of Surfactant-2 has no effect on the emulsion stability as complete separation can be achieved by adjusting the salinity only.

4.10.3 Surfactant -3 (Sodium lauryl sulphate)



Fig 32: Surfactant -3 (Sodium lauryl sulfate, 5%), Settling time (5 mins)



Fig 33: Surfactant -3 (Sodium lauryl sulfate, 10%), Settling time (5 mins)



Fig 34: Surfactant -3 (Sodium lauryl sulfate, 15%), Settling time (5 mins)

Figures 32-34 show the affect of different oil/water ratios with increasing amounts of Surfactant-3 (Sodium lauryl sulfate) on emulsion stability. Surfactant amount snd salinity has no effect on the stability of the emulsions at oil/water ratios of 90/10 and 80/20. The stability of the emulsions is affected only at oil/water ratio of 70/30. The optimum salinity to achieve maximum separation at all amounts of surfactant-3 is 8%.

4.11 Surfactant Type Variation (Surfactant-1: Sodium Stearate, Surfactant-2: Alkylbenzenesulphonate, Surfactant-3: Sodium lauryl Sulphate)





Fig 35: Oil/Brine Ratio 90/10, Surfactant Ratio 5%, Settling time (5 mins)



Fig 36: Oil/Brine Ratio 90/10, Surfactant Ratio 10%, Settling time (5 mins)



Fig 37: Oil/Brine Ratio 90/10, Surfactant Ratio 15%, Settling time (5 mins)

Figures 35-37 show the affect of different types of surfactants with increasing amounts at oil/water ratio of 90/10 on the stability of the emulsion. The emulsion stability was affected only by Surfactant-1 when the amount used was 15%. The optimum Surfactant type and amount to achieve maximum separation at oil/water ratio of 90/10 is Surfactant-1 (Sodium Stearate) at an amount of 15% and optimum salinity of 8%.

4.11.2 Oil/Brine Ratio 80/20



Fig 38: Oil/Brine Ratio 80/20, Surfactant Ratio 5%, Settling time (5 mins)



Fig 39: Oil/Brine Ratio 80/20, Surfactant Ratio10%, Settling time (5 mins)



Fig 40: Oil/Brine Ratio 80/20, Surfactant Ratio 15%, Settling time (5 mins)

Figures 38-40 show the affect of different types of surfactants with increasing amounts, at oil/water ratio of 80/20, on the stability of the emulsion. Surfactant-3 has no effect on the stability of the emulsions at all amounts. Surfactant-1 and Surfactamt-2 affect the stability of the emulsions with increasing amounts. Salinity of 2% affects the stability of the emulsions at all amounts.

4.11.3 Oil/Brine Ratio 70/30



Fig 41: Oil/Brine Ratio 70/30, Surfactant Ratio 5%, Settling time (5 mins)



Fig 42: Oil/Brine Ratio 70/30, Surfactant Ratio 10%, Settling time (5 mins)



Fig 43: Oil/Brine Ratio 70/30, Surfactant Ratio 15%, Settling time (5 mins)

Figures 41-43 show the affect of different types of surfactants with increasing amounts, at oil/water ratio of 70/30, on the stability of the emulsion. Surfactant-2 and Surfactant-3 are showing the maximum separation as compared to Surfactant-1. Surfactant-2 is showing complete separation at all amounts at a salinity of 2% making it the optimum surfactant at oil/water ratio of 70/30.

4.12 Surfactant Amount Variation (Surfactant-1: Sodium Stearate, Surfactant-2: Alkylbenzenesulphonate, Surfactant-3: Sodium lauryl Sulphate)



4.12.1 Surfactant-1 (Sodium Stearate)





Fig 45: Oil/Brine Ratio 80/20, Surfactant -1 (Sodium Stearate), Settling time (5 mins)



Fig 46: Oil/Brine Ratio 70/30, Surfactant -1 (Sodium Stearate), Settling time (5 mins)

Figures 44-46 show the affect of different amounts of Surfactant-1 (Sodium Stearate) at different oil/water ratios on emulsion stability. The maximum separation at all oil/water ratios occurs when the amount of Surfactant-1 is 15% making it the optimum amount for Surfactant-1 (Sodium Stearate).

4.12.2 Surfactant -2 (Alkylbenzenesulphonate)







Fig 48: Oil/Brine Ratio 80/20, Surfactant -2 (Alkylbenzenesulphonate), Settling time (5 mins)



Fig 49: Oil/Brine Ratio 70/30, Surfactant -2 (Alkylbenzenesulphonate), Settling time (5 min)

Figures 47-49 show the affect of different amounts of Surfactant-2 (Alkylbenzenesulphonate) at different oil/water ratios on emulsion stability.. Surfactant-2 doesn't affects the stability of the emulsion at oil/water ratio of 90/10 at any amount. Maximum separation occurs at the amounts of 5% and 15% at oil/water ratios of 80/20and 70/30. Hence, the optimum amounts to achieve maximum separation are 5% and 15%.

4.12.3 Surfactant -3 (Sodium lauryl sulphate)



Fig 50: Oil/Brine Ratio 90/10, Surfactant -3 (Sodium lauryl sulfate), Settling time (5 mins)



Fig 51: Oil/Brine Ratio 80/20, Surfactant -3 (Sodium lauryl sulfate), Settling time (5 mins)



Fig 52: Oil/Brine Ratio 70/30, Surfactant -3 (Sodium lauryl sulfate), Settling time (5 mins)

Figures 50-52 show the affect of different amounts of Surfactant-3 (Sodium lauryl sulfate) at different oil/water ratios on emulsion stability. Surfactant-3 doesn't affects the stability of the emulsion at oil/water ratios of 90/10 and 80/20 at any amount. Complete water separation is achieved at oil/water ratio of 70/30 at amounts of 10% and 15% . Hence, the optimum amounts of Surfactant-3 at oil/water ratio of 70/30 is 10% and 15%.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The results showed that at Oil/Brine ratio of 70/30 majority of the emulsions achieved complete separation making it the optimum Oil/Water ratio as compared to other ratios. The optimum surfactant, presence of which showed complete separation in the majority of the emulsions, was Surfactant-2, Sodium Lauryl Sulphate. And the optimum amount of surfactant at which the majority of the emulsions showed complete separation was 15%.

The results revealed that oil/ water separation for Angsi-C crude oil emulsion was easier at oil/brine ratios of 70%/30% as compared with oil/brine ratios of 80%/20% and 90%/10%. At Oil/Brine ratio of 90%/10%, tight emulsions were formed as all the emulsions remained stable except for one that showed a decreasing stability of emulsion with increasing salinity. At Oil/Brine ratio of 80%/20%, medium emulsions were formed as varying salinity affected the stability of the majority of the emulsions. At Oil/Brine ratio of 70%/30%, loose emulsions were formed as majority of the emulsions achieved complete separation.

The results also showed that there exists an optimal salinity at which full or partial separation can be achieved without utilizing demulsifiers. The optimal salinity for an emulsion with a specific oil/brine ratio and specific amount of surfactant, resulting in complete or partial separation, may not be the same for another emulsion with a different combination of oil/brine and surfactant. Hence, individual analysis is required for each combination.

Apart from salinity, surfactant type, surfactant amount and oil/brine ratio also affected the stability of the emulsions but the most feasible way that has been observed to decrease the emulsion stability and achieve maximum oil/water separation is by adjusting the salinity of the emulsion.

Due to the lack of resources and time, limited numbers of tests were performed however it has been observed that adjusting the salinity of the emulsion can increase the oil/water separation which can reduce considerable amounts of costs in terms of demulsifier usage and other techniques for separation. Furthermore, emulsions that remained stable during the experiment need to be tested at salinities higher than 8% for better results. Further research is required to determine the optimal salinity for various combinations of oil/brine, together with surfactants, and the tabulation of the data can be extremely beneficial for the petroleum industry.

REFERENCES

- Kokal S ,2006, *Petroleum Engineering Handbook Vol. 1*, Texas, Society of Petroleum Engineers

- Narve Aske, 2002, *Characterisation of Crude Oil Components*, Ph.D, Thesis, Norwegian University of Science and Technology, Norway

- Pierre C, 2004, *Oil & Gas Science and Technology*, Cedex, Institut français du pétrole

- Rajinder Pal, 1998, *Effects of Droplet Size and Droplet Size Distribution on the Rheology of Oil-in-Water Emulsion*, Report Number 1998.053, University of Waterloo, Waterloo, Ontario, Canada

- Spiecker P and Kilpatrick K, 2004, "Interfacial Rheology of Petroleum Asphaltenes at the Oil-Water Interface," *Langmuir 20: 4022-4032*

- Mehta S, 2005, *Making and breaking of water in crude oil emulsions*, MSc. Thesis, Texas A&M University, USA

- Mason T, 1999, New fundamental concepts in emulsion rheology, New Jersey, Elsevier

- Pal R, 2010, "*Rheology of simple and multiple emulsions*," Current Opinion in Colloid & Interface Science 16: 41-60

- Langevin D, Poteau S, Hénaut I and J.F. Argillier, 2004, *Oil & Gas Science and Technology*, Cedex, Institut français du pétrole

- Ivanov B, 1999, *Flocculation and coalescence of micron-size emulsion droplets*, New Jersey, Elsevier

-Department of Energy, Malaysia, 2008, *Cleaner Production Tips for Small and Medium Industries*, Kuala Lumpur, DOE

- Tauer, Klaus, Kolloid Chemie, Micelles and Emulsions, Texas, Elsevier

- David McClements, 1999, Food Emulsions, Florida, CRC

- Mackosco, Christopher, 1994, *Rheology*, *Principles, Measurements and Applications*, New York, Wiley.

- Chhabra R and Richardson J, 2008, *Non Newtonian Flow and Applied Rheology*, New York, BH