INVERSION OF HEAVY CRUDE OIL-IN-BRINE EMULSIONS

A Thesis

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DEDICATION

This thesis is dedicated to Mrs. Mary E. Cornell and Mr. Richard J. Cornell who were willing to take a chance to support my unproven ability and made it possible with their love.

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ABSTRACT

A large portion of Canada's reserves of crude oil consists of extra heavy crude and natural bitumens. As the reserves of conventional crude oil continue to decline, heavy oil and bitumen are becoming increasingly important sources of hydrocarbon liquids. Oil-in-water emulsions provide an alternative to heating and dilution methods for transportation of these viscous heavy oils through conventional pipelines.

One of the most important preconditions for implementing this technology is prediction of the flow behavior and stability of the heavy oil-in-water emulsions. Inversion, a process by which one type of emulsion (such as oil-in-water) is converted to another (such as water-in-oil), is critical because it could cause a region of very high viscosity to form in the pipeline. This research attempts to investigate the causes of inversion, and to develop a simple and effective laboratory method for selecting suitable surfactants and their concentrations at the emulsion pipeline operation conditions.

The inversion of heavy crude oil-in-brine emulsions stabilized with non-ionic surfactants has been studied experimentally. Tests were carried out in beakers and in a cone and plate viscometer. The effects of shear rate, surfactant species and concentration, temperature, and oil fraction on emulsion inversion were studied. Toroid tests were carried out to compare the data generated from the cone and plate viscometer to that for a pipeline.

It was found that inversion of oil-in-brine emulsions was always associated with the disappearance of the non-ionic surfactant from the aqueous phase. The surfactant affinity (i.e., hydrophilic property) for the aqueous phase thus appeared to be critical in the stabilization of these emulsions. Increasing the number of ethylene oxide units increased the hydrophilic property of the non-ionic surfactant and the stability of the emulsion. The emulsion stability also depends on the strength of the interfacial adsorption film. High shear rates not only destroyed the film, but also displaced fragments of the film back to the aqueous phase. The emulsions remained stable only when the surfactant concentration in the aqueous phase was above the C.M.C. level, meaning there was enough surfactant stock to maintain the stability of the interfacial adsorption film. High temperatures reduced the physical strength of the interfacial adsorption film and the repulsive force between oil droplets, encouraging the flocculation and inversion.

The toroid tests indicated that the cone and plate viscometer is probably a good simulation of the emulsion flow behavior in pipelines. A laboratory method to select a suitable surfactant type and concentration has been developed using the cone and plate viscometer.

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NOMENCLATURE

Regular symbols:

C	Dispersed phase fraction, wt. %
C_E	Surfactant concentration in solution, mole
d	Gap distance between cone and plate in the viscometer, μm
g	The acceleration of gravity, m/s^2
K	Constant of power law equation
k_1	Parameter of Ellis model
k_2	Parameter of Sisko model
m	Number of alkyl groups in the nonionic ethylene oxide surfactant
n	Number of ethylene oxide units in the surfactant
n_p	Constant in power law equation
ΔP	Pipeline pressure drop
Q	Flowrate, m^3/s
q_1	Constant in Szyskowski equation
q_2	Constant in Szyskowski equation
R	Gas constant, 8.314 J/mole.K
R_d	Oil droplet radius, μm
r, r_1, r_2	Viscometer cone radial position, cm
T	Absolute temperature, K
T_v	Torque in the viscometer, dyne-cm
$\frac{dx}{dt}$	Rate of creaming, m/s
X_i	Surfactant concentration in the aqueous phase, ppm
Y_i	HPLC response, inches

Greek symbols:

α	Parameter of Ellis model
Γ	Emulsion interface coverage, mole/m ²
γ	Interfacial tension between two phases in the emulsion, J/m
γ_0	Initial interfacial tension between two pure phases, J/m
$\dot{\gamma}$	Shear rate, s ⁻¹
$\dot{\gamma}_{\max}$	Maximum shear rate, s ⁻¹
$\dot{\gamma}_{\min}$	Minimum shear rate, s ⁻¹
δ	Parameter of Sisko model
η_0	Viscosity at zero shear rate, mPa.s
η_{∞}	Viscosity at infinite shear rate, mPa.s
θ	Viscometer cone angle, degrees
μ_e	Viscosity of the emulsion, mPa.s
μ_{ext}	Viscosity of the external phase, mPa.s
μ_r	Relative viscosity of the emulsion
ρ_1	Density of the sphere, kg/m ³
ρ_2	Density of the liquid, kg/m ³
τ	Shear stress, dynes/cm ²
ω	Viscometer cone rotational speed, red/s

Abbreviations:

API	American Petroleum Institute
bpd	Barrels per day
C.M.C.	Critical micelle concentration
BS&W	Method of oil inner water determination
HPLC	High performance liquid chromatography
I.D.	Inner diameter of pipeline
N.D.	Not detected
MS	Mass spectrometry
MW	Molecular weight
O/W	Oil-in-water emulsion
ppm	Parts per million
PSA	Particle size analyzer
UV	Ultra violet
W/O	Water-in-oil emulsion
w/w	Weight/weight
v/v	Volume/volume

Subscripts

d	Droplet
E	Emulsion
ext	External
i	i th value
max	Maximum value
min	Minimum value
o	Initial value
p	Power law
r	Relative
v	Viscometer
∞	Infinite value

1.0 INTRODUCTION

1.1 Foreword

Heavy crude oils and natural bitumens account for a large fraction of Canada's oil reserves. As the reserves of conventional crude oil keep declining, heavy crude oil and bitumen are becoming increasingly important sources of hydrocarbon liquids. Generally, heavy crude oils and bitumens have viscosities ranging from 300 to several thousand centipoise at 30 °C. To transport these viscous heavy oils after production, many oil companies use trucks to collect the oil from the wells. This operation is often expensive because of the distances which are involved and the fact that direct road connections are not available. If conventional pipelines are used for transportation, heating or dilution methods are needed to reduce the viscosity of the oil. Heating often requires considerable amounts of energy and there are logistic problems in using diluents. For field production to be transported by pipeline using a diluent, two pipelines would be required (one for the oil and one for the diluent). It would thus be desirable to develop an alternative method of transportation.

A possible alternative is to use surfactant(s) to emulsify the heavy crude oil in water or brine and to transport the low viscosity emulsion in a pipeline. The viscosity of the emulsion is about 100 centipoise, much lower than that of heavy crude oil. This development has been studied extensively during the past two decades, and has led

to a vast literature on the topic. However, most of these studies have focused on the viscosity of the oil-in-water (o/w) emulsions. Demonstrations have been carried out in field scale trials and/or in laboratory pipeline loops but both types of test are fairly expensive, which limits the progress and application of this technology. To this date, there is no commercial use of this technology in Saskatchewan. Furthermore, there is still no simple and effective method for selecting suitable surfactant(s) and the appropriate concentration, using laboratory tests. Thus research is desirable to develop the technology and minimize expensive pipeline trials.

One of the most important preconditions to implement this technology is to be able to predict the flow behavior and stability of the heavy o/w emulsion in pipeline transportation. Inversion, a process by which one type of emulsion (such as o/w) is converted to another (such as water-in-oil (w/o) emulsion) is critical because it could cause the viscosity to change drastically. If inversion occurred in a pipeline, it must be considered a disaster because it would be very difficult to re-disperse and/or remove the inverted emulsion from the pipeline. The exact mechanism of inversion does not seem to have been reported in the published literature dealing with o/w emulsion transportation through pipelines. Thus lack of knowledge concerning emulsion inversion becomes a major obstacle to implementation of this technology. Obviously, one should be able to understand, predict and avoid inversion of emulsions in pipelines by all means.

1.2 Objectives

This study had two objectives. The first was to investigate the cause and mechanism of inversion. The second objective was to seek a simple and effective laboratory method for selecting suitable surfactants and their concentrations to prevent inversion at the lowest possible cost at the required test conditions. An actual heavy crude oil and brine were to be used in these investigations.

2.0 LITERATURE REVIEW

2.1 Rheological Research on Crude O/W Emulsions

In the past two decades, many studies have been carried out on the rheological behavior of o/w emulsions. These studies were mostly experimental in nature and very often refined mineral oil, deionized water and surfactant concentrations as high as 3000 - 5000 ppm were used to produce the emulsions [1-5]. Since the variation of composition of crude oil is vast, and emulsion behavior is dependent on many variables, it is almost impossible to globally extrapolate the results for a particular oil under specific flow conditions.

In the literature published to date, many workers have concentrated on the viscosities of emulsions. Theoretical and empirical viscosity equations have been developed to predict the flow behavior of the emulsions as a function of dispersed phase concentration and shear rate [1, 6-10].

A generalized mathematical model which describes the behavior of the emulsions is given by the Ostwald-de Waele equation [11], commonly known as the power law equation:

$$\tau = -K\dot{\gamma}[\dot{\gamma}]^{n-1} \quad (2.1)$$

where τ is the shear stress, $\dot{\gamma}$ is the shear rate, K and n are constants.

When $n=1$, the fluid is Newtonian. For a pseudo plastic fluid, n is less than unity. In the region where the power law is valid, a log-log plot of τ versus $\dot{\gamma}$ gives a straight line whose slope is n . To describe the extreme ends of the viscosity curve near $\dot{\gamma}=0$ and $\dot{\gamma} \rightarrow \infty$, the Ellis model at low shear rates and the Sisko model at high shear rates can be used [12]:

$$\text{Ellis: } \dot{\gamma} = - \tau \{ (1/\eta_0) + k_1 |\tau|^{\alpha-1} \} \quad (2.2)$$

$$\text{Sisko: } \tau = -\dot{\gamma} \{ \eta_{\infty} + k_2 |\dot{\gamma}|^{\delta-1} \} \quad (2.3)$$

where η_0 and η_{∞} are viscosities at zero shear rate and infinite shear rate respectively, k_1 , k_2 , α and δ are adjustable parameters. Both the Ellis and Sisko models contain Newton's law and the power law as limiting forms [11].

Basically, very dilute oil-in-water emulsions are Newtonian fluids. The relative viscosity μ_r of the emulsion (the ratio of the viscosity of the emulsion, μ_e , to that of the external phase, μ_{ext}) increases linearly with the dispersed phase fraction C . At moderate fractions, μ_r begin to increase non linearly with C , but the emulsions remain Newtonian. At higher fractions, emulsions become non-Newtonian. The non-Newtonian character is initially pseudo plastic, but in very concentrated emulsions ($C > 0.74$), it often becomes plastic and emulsions exhibit yield stresses [13-15].

A typical correlation describing Newtonian emulsion behavior is

the Richardson equation [16]:

$$\mu_e = \mu_{ext} e^{(KC)} \quad (2.4)$$

A semi-log plot of μ_e versus C gives K as the slope of the line and μ_{ext} as the intercept on the appropriate axis.

Simon and Poynter [17] have reported that for o/w emulsions, $K=7$ up to a fraction $C = 0.75$, and $K=8$ at higher fractions. Camy, et al. [18] reported K values of 6 to 7 for o/w emulsions and -3 to -4 for w/o emulsions. Mao and Marsden [19] reported K values of 3.5 and -4.4 for o/w and w/o emulsions respectively.

The flow behavior of emulsions also depends on the dispersed phase droplet size and size distribution. Oldroyd and Rajagopal [20-22] proposed viscosity correlations for dilute emulsions incorporating a particle size effect. Sherman [23-24] obtained a relationship between relative viscosity and inter particle distance. Sherman [25] also suggested that the non-Newtonian behavior and yield stress in emulsions were caused mainly by the formations of flocs of dispersed particles. Because the flocs immobilize a significant amount of the continuous phase, the effective dispersed phase fraction of a non-Newtonian emulsion is higher than its true fraction [4, 26].

2.2 Surfactant Effects on O/W Emulsion

Because oil droplets are hydrophobic, petroleum emulsions are thermodynamically unstable, and always have a tendency to form two separate layers. Without a surfactant, it is impossible to form a stable emulsion. In the formation and stabilization of o/w emulsion, the surfactant functions to lower the interfacial tension and introduce repulsive forces between oil droplets. This makes it easier to form smaller droplets and stabilizes them under shear. When oil droplets are deformed by shear, a new interface is created. The surfactant molecules in the aqueous phase move to the interface and form a surfactant interfacial film. This process will continue to establish the interface coverage Γ corresponding to the isothermal equation of Gibbs [27-28]:

$$\Gamma = -(1/RT)(d\gamma/d\ln C_{ext})_T \quad (2.5)$$

where Γ is the density of coverage (number of surfactant molecules per unit area, i.e., interface coverage), C_{ext} is the concentration of surfactant, γ is the interfacial tension, R is the universal gas constant, and T is the absolute temperature.

Equation (2.5) presupposes that the interfacial film is formed by a monolayer of surfactant, even at maximum coverage, and that the surfactant is insoluble in the oil phase. If the surfactant is a mixture of homologues, Γ will be the overall density of coverage, and C_E will be the overall surfactant concentration.

The interfacial tension γ decreases with increasing concentration of surfactant up to the Critical Micelle Concentration (C.M.C.), which can be expressed by the equation of Szyskowski [28]:

$$\gamma = \gamma_0 - q_1 \ln (1 + q_2 C_{\text{ext}}) \quad (2.6)$$

where γ_0 is the initial interfacial tension between the two pure phases, q_1 and q_2 are constants. Above the C.M.C., when the interface is completely covered by surfactant molecules, γ will be constant. Adding more surfactant can not lower γ further.

Above the C.M.C., the excess surfactant molecules form micelles of diameter of 5 nm to 40 nm [27]. Micelles are non-surface-active but can provide the emulsion with surfactant molecules so that micelles are an important source of stock of surface active substance. For non-ionic surfactants, the C.M.C. value at room temperature is in the range of 10^{-3} to 10^{-4} mole/liter, and for nonionic polyethylene oxide surfactants in aqueous solution, it is of the order of 10^{-4} mole/liter [29].

It was reported [30a] that the emulsion stability depends greatly on the strength and compactness of the interfacial film, and other factors of the emulsion are subsidiary except insofar as they affect the properties of the film. These factors include the concentration of the surfactant, which can significantly improve the strength of the interfacial film by providing electrolyte around the oil globule, thus improving the stability of the emulsion. Higher surfactant concentrations also reduce the interfacial tension, thus making the

deformation of the dispersed phase easier. However, it has been reported [30b] that the role of interfacial tension is rather doubtful in the stabilization of o/w emulsions.

The temperature of the emulsion system is important because it could affect the physical properties of the interfacial film [30a]. It also may affect the micelle formation and disaggregation processes [26]. Whether high temperatures could increase the solubility of nonionic surfactants in the oil phase is not clear because the opinions given by different literature sources are contradictory. Although it has been reported [31] that the nonionic surfactants are not soluble in oil, it has also been reported [26] that higher temperature may increase the solubility of the surfactant in the oil. Zakin, et al. [5] dissolved Triton X-114, a nonionic ethylene oxide surfactant in a refined mineral oil (i.e., using the agent-in-oil method) to prepare o/w emulsions. Description of their study will be given in section 2.5.

The stability of o/w emulsions also depends on the hydrophilic properties of the surfactant(s). It has long been recognized [32] that the emulsifying efficiency of a surfactant is related to the polarity of the molecule, i.e., the relation between the contribution of the polar hydrophilic head and the non polar hydrophobic tail. It has been reported [33-34] that when inversion occurs, the emulsion system is in a hydrophilic-hydrophobic balance and the more hydrophilic the surfactant, the more stable the o/w emulsion [32]. Ottewill [35] suggested that the longer ethylene oxide chains would enhance the hydrophilic property of the surfactant. Winsor and Shinoda [36-37]

reported that higher temperatures would reduce the hydrophilic property of ethylene oxide nonionic surfactant. Saito, et al. [38-39] reported that a wider distribution of the ethylene oxide units or alkyl chains even for the same number of ethylene oxide units or alkyl chain lengths of the ethylene oxide nonionic surfactants could improve the o/w emulsion stability because it expands the stable temperature region. However these conclusions were rather qualitative and so far there is no single quantitative equation to describe the relationship between emulsion stability and these variables.

There is no direct information reported so far concerning decreasing effectiveness of surfactants in the course of inversion. It has been suggested [26] that when a specific surfactant capable of stabilizing one type of emulsion is chemically changed to one of the opposite type, inversion may be expected to occur. However, to the author's knowledge, no literature exists concerning the mechanism, that the conditions or the manner in which surfactant changes its emulsifying capability.

An important factor determining the relationship between surfactant and emulsion stability is the kinetics of occupation of the interface. Schubert and Armbruster [27] suggested that when a fresh interface is formed, first the adsorption equilibrium and then the micellar equilibrium are disturbed. The emulsion system then reacts by recovering the momentarily undercovered interface to restore the adsorption equilibrium. During this process, the rate of occupation of the interface is important because rapid occupation can significantly

improve the stability of an emulsion.

2.3 Flocculation and O/W Emulsion Stability

When an o/w emulsion is formed, there is always a tendency for oil droplets to attract each other due to the universal van der Waals' force. To reduce the attractive force, i.e., to stabilize the emulsion, a repulsive force must be introduced between the droplets. Very often this can be achieved by adding surfactant(s) so the double layer force can balance the van der Waals' force. There are many variables which could affect the repulsive force in an emulsion system but the effectiveness of the surfactant and its concentration is primarily important, i.e., the strength of the interfacial film is predominant [30a].

If the emulsion is under shear and the repulsive force is weakened by reducing the surfactant concentration etc., collisions between droplets will occur. The collisions may result in flocculation or even coalescence of the droplets, so that large flocs and/or drops may form. If the collision is caused by the highly ordered flow fields, it is called orthokinetic flocculation, whereas collisions caused by random Brownian motion is termed as perikinetic flocculation [40].

Under perikinetic flocculation, there is no significant coalescence. The droplets form larger flocs which tend to rise in the emulsion due to the gravity difference. The process is referred to as creaming (i.e., the opposite process to sedimentation), which can be

described by Stokes' law [30]:

$$\frac{dx}{dt} = 2gR_d^2 (\rho_1 - \rho_2) / 9\mu_{ext} \quad (2.7)$$

where $\frac{dx}{dt}$ is the rate of creaming (or negative sedimentation), g is the acceleration of gravity, R_d is the droplet radius, ρ_1 is the density of the sphere, ρ_2 is that of the liquid, and μ_{ext} is the viscosity of the liquid. Equation (2.7) shows that creaming will increase when there is a larger density difference between the dispersed and continuous phases and/or when the oil droplets (or flocs) are large. However, Stokes' law may not strictly apply since emulsion droplets are not rigid spheres and can be deformed in a shear flow. Also, in the presence of surfactant molecules at the interface, the droplets will not be non-interacting as is assumed in Stokes' law [41].

Creaming will eventually result in two separate layers of emulsion which have different droplet concentrations. Since it occurs under perikinetic flocculation, creaming usually does not consume very much surfactant(s) because there is not much energy input to the emulsion system. Usually the creamed emulsion can be redispersed again with shear and thus can be restored as a good emulsion.

When orthokinetic flocculation occurs, the droplets' motion will determine the rate of collision. If the flow is laminar, the collision frequency will depend on the size of the droplets and the shear rate

[40]. If the flow is turbulent, a much enhanced collision rate could be encountered. Both laminar and turbulent flow conditions will affect the strength of the interfacial film (i.e., to reduce the repulsive force) but their rates will be different and so should be the tendencies to inversion.

2.4 Oil Polarity and Emulsion Type

It has been reported [42-43] that the polarity of an oil can affect the formation and the type of emulsion. The oil polarity values depend on the heteroatomic compounds which are concentrated in the heaviest fractions of the oils. It increases with nitrogen, sulfur, and asphaltene contents as well as specific gravity and acid number of the oil. High oil polarity always encourages the formation of a very stable water-in-oil emulsions, although the exact mechanism of this process has not been known. Usually the more polar crude oils will be the more interactive and the less valuable ones, so that treating and refining will be more difficult and costly.

2.5 Laboratory and Field Trials of O/W Emulsion Pipeline Transportation

Investigations of o/w emulsion pipeline transportation can be traced back as far as 1963 in Indonesia [44]. In 1968, Rose and Marsden [45-46] investigated the flow of emulsions of Prudhoe Bay

Oil in a 20% NaCl brine. Emulsions containing 25% to 60% oil were pumped through 6.25 mm copper tubing and Triton X-114 was used to emulsify the oil. The data were to be used in the design of the trans-Alaska pipeline. Some of their conclusions were: 1) isothermal viscosities and flow resistance factor ($\Delta p/Q$) increased exponentially with fractions of oil in the emulsion and the emulsions had much lower viscosities than the oil itself; 2) viscosity and flow resistance factor increased exponentially with decreasing temperature; 3) the viscosity versus oil fraction relationship for these emulsions were best described by the equation proposed by Richardson (2.4)[16] with the constant K equal to 4.08.

In another study Shah et al. [46-47] assessed the effects of salts and various surfactants on Mississippi crude oil-in-water emulsions of various phase volume ratios using electrical resistance and viscosity measurements. They concluded that in the absence of added surfactants, the maximum viscosity occurred at 50% oil fraction. The maximum viscosity almost doubled in the presence of sea water. The maximum viscosity and the minimum interfacial tension occurred in the presence of 1% NaCl in water. Mao and Marsden [19] studied the rheological properties of emulsions containing different amounts of crude oil at different temperatures. The emulsions were prepared with a California waxy crude oil, tap water and Triton X-114. Some of their conclusions were: 1) The rheology of both o/w and w/o emulsions over the temperature range from 24 °C to 82 °C can be described adequately by the power-law relationship in the laminar flow region. 2) Both the consistency, K and the apparent viscosity, $\tau/\dot{\gamma}$, increase with

the volumetric fraction of the dispersed phase. 3) Apparent viscosity of emulsions depends not only on the temperature and the overall composition, but also on the emulsion type, i.e., w/o or o/w. 4) Increasing the shear stress by increasing the pumping rate also causes inversion of o/w emulsions to w/o ones.

Zakin, et al. [5] studied concentrated o/w emulsions in turbulent flow. Refined mineral oils were used, which were emulsified at fractions of 50% and 75% by weight with tap water in a Morehouse mill. Triton X-114 was used as the surfactant at a concentration of 5000 ppm. The emulsification method was the agent-in-oil method. The study was aimed at investigating the effects of viscosity, temperature and oil fractions on the flow characteristics of the o/w emulsions in a 25 mm diameter pipe. The oil viscosity showed no significant effect on the pressure drops, nor did the fluid temperature (up to 45 °C). Surprisingly, oil fraction did not affect the pressure drop significantly either. In 1973 Marsden and Raghavan [48] transported a 50% emulsion of highly viscous 13.5 API gravity crude for a distance of 21 km in an 200 mm diameter pipeline in California. Marsden and Ozarar [49] also carried out an experiment on the Sadlerochit crude oil-in-brine (10% NaCl) emulsions which were prepared by an ultrasonic emulsifier in 1991. Other workers have generated dozens of patents for heavy crude o/w emulsions in the past two decades [31,50-53].

In Canada, Parker, et al. [54] investigated the flow behavior in a laboratory viscometer in 1985. Subsequently, Gillies, et al. [55] carried out pipeline flow tests on emulsions prepared with Saskatchewan

heavy crude oil. Wyslouzil, et al. [56] reported a closed loop test on Cold Lake crude oil emulsified by 0.1% NaOH in 1987. Hardy, et al. [57] carried out a 27 km, 114 mm I.D. pipeline trials on the emulsions prepared from Canadian Wolf Lake bitumen in 1989. In 1992 Gillies and Shook [58] reported a study of the laminar flow behavior of o/w emulsions in a recirculating pipeline loop with 53 mm I.D. In this investigation they also studied the effects of temperature and sand content on the flow resistance of high fraction emulsions.

The largest scale of pipeline trial conducted so far is probably the B.P. Transoil project [59-61]. From 1981 to 1985, the British Petroleum Company p.l.c. (BP) and INTERVEP, Petroleos de Venezuela jointly developed the Transoil technology, which produced the emulsion of very viscous 8 API extra heavy crude oil from the Orinoco Oil Belt and Boscan field in Venezuela. Sodium hydroxide, nonylphenol and octylphenol ethylene surfactant were used as emulsifiers at concentrations of 3000 ppm. The crude contained less than 1% water, the dispersed phase fractions were from 40% to 80%. Some of their conclusions were: 1) Emulsion stability, as well as distribution and mean droplet size, was greatly influenced by the physicochemical composition of the crude oil. 2) Nonionic and natural surfactants seemed to be the most appropriate surfactants for the stabilization of crude o/w emulsions. 3) When using nonionic surfactants, the number of ethylene oxide groups per molecule in the surfactant, was of paramount importance in finding the optimal hydrophilic-lipophylic balance required for stabilizing emulsions for a given crude. Temperature and aqueous phase salinity modify this

optimum balance. 4) Distribution and mean droplet size in crude o/w emulsion, and hence stability, were influenced significantly by the type of mixer, speed and time of mixing used in emulsion preparation. 5) Crude o/w emulsions containing high dispersed phase volumes ($C > 0.70$) behave as pseudo plastic fluids which obey a power law equation. For more dilute emulsions, the behavior is Newtonian at the shear rate range studied. 6) The viscosity of crude o/w emulsions is directly influenced by droplet size distribution, but does not depend on the type of oil used. After completion of the emulsion formulation and formation investigations in the laboratory, a production of 14,000 bpd scale field trial was also completed.

3.0 EQUIPMENT AND PROCEDURES

3.1 Emulsion Materials

The oil used in this investigation was collected from Wascana Energy wells (a mixture of crudes from four wells) near Luseland, Saskatchewan on May 13, 1993. It contained 11% (v/v) internal brine. At low surfactant concentration, it was more difficult to prepare stable oil-in-brine emulsions with this oil than with oil from another well near Lloydminster, Saskatchewan. The latter oil contained only 1% (v/v) internal brine. This difficulty may be caused by the salinity of the high brine content which would tend to increase the polarity of the oil.

The brine used as the continuous phase of emulsions in this investigation was obtained from the same wells at the same time. The properties of oil and brine used in this investigation are given in Appendices A and B.

The two surfactants used in this investigation were Rexol 25/10 and Rexol 25/307, manufactured by Hart Chemicals Ltd., Guelph, Ontario, Canada. These were used as received. Both of the surfactants are nonionic ethoxylated alkylphenol surfactants. Nonionic surfactants were used because they are relatively cheap and are apparently not affected by the salinity of the brine [31].

Depending upon the etherification process and/or conditions,

possible molecular structure of the surfactants are:

A third possibility is that the surfactant has an ester linkage:

In these formulas m is the number of alkyl groups and n is the number of ethylene oxide units.

3.2 Surfactant Characterization

In this investigation, High Performance Liquid Chromatography was used to determine the surfactant concentration changes associated with shear flow. Mass spectrometry was used to determine the surfactant molecular weight(s).

3.2.1 High Performance Liquid Chromatography (HPLC)

High Performance Liquid Chromatography (HPLC) is a useful

analytical technique for the identification and quantification of analytes. The HPLC method is based on the partitioning of the analytes between two immiscible phases which move relative to one another through a column. Usually one phase is packed in the column, such as octyldecyl (C-18) bonded on the silica particles of diameter of 3 to 5 μm , to form the stationary phase. The analytes are carried through the column with the mobile phase. As they pass through the column the analytes are partly retained, depending on their interaction with the stationary phase, and even small differences in the distribution coefficients will eventually cause the components to be separated (Fig. 3.1). By altering the nature of the stationary and mobile phases or by changing the experimental conditions, such as the mobile phase composition and/or its flow rate, the degree of separation and its selectivity can be altered. Once the components have been separated, they can be detected by a detector such as an Ultraviolet (UV) detector to give a chromatogram. By comparing the elution time and the peak area (or height) with the chromatogram and the calibration curve prepared for an external standard, one can qualitatively identify and quantitatively determine the analytes. A Waters 510 HPLC pump and a Waters 484 absorbancy detector were used in this investigation, which were manufactured by the Millipore Corporation, Waters Chromatography Division, Milford, MA, U.S.A. The column was Supelcosil LC-18 with 5 μm octyldecyl group packing which was manufactured by Supelco Canada Ltd., Oakville, Ontario, Canada.

Figure 3.1: Chromatographic separation on a column [after 62]

3.2.2 Operation of the HPLC

3.2.2.1 Mobile Phase and Its Flow Rate

To choose the correct mobile phase is critical because it must satisfy the balance of the intermolecular forces among analytes, the mobile phase and the stationary phase. As a rule, the polarity of the analytes and the stationary phase should be matched, and a mobile

phase of considerably different polarity is used [62]. The separation method used in this investigation was reversed-phase separation, meaning that the stationary phase is a non-polar alkyl substituent and the mobile phase is a polar eluent. In this investigation, methanol, acetonitrile and water were used as mobile phases. It was found that a methanol-water solution of 90:10 (v/v) was the best composition for quantitative determination of the surfactant used in this investigation. 100% acetonitrile was appropriate for qualitative identification. These three solvents are inexpensive but good ventilation is required when using acetonitrile because its vapors are toxic.

The mobile phase flow rate can affect the resolution of chromatogram. Higher flow rates may not permit separation while lower flow rates may cause band broadening. The optimized flow rate in this investigation was 2 mL/min.

3.2.2.2 Selection of Detector

UV/visible Absorption Spectroscopy analysis (Table 3.1) revealed the preferred absorption wavelengths for the surfactants used in this investigation. Three peaks were observed in both cases. 215 nm and 226 nm were chosen as appropriate wavelengths for the two surfactants (Rexol 25/307 and Rexol 25/10) respectively.

The Lambda 4B UV/Visible Spectrophotometer was manufactured by Perkin Elmer Co., Norwalk, Connecticut, U.S.A. It is located in the Department of Chemistry, University of Saskatchewan.

Table 3.1: 'Absorption' wavelength for surfactant solutions

surfactants	wavelength (nm)	Absorbance
Rexol 25/10	282.8	0.707
	276.3	1.094
	225.9	1.565
Rexol 25/307	267.8	0.679
	214.1	2.922
	196.4	2.978

3.2.2.3 Qualitative Identification by HPLC

Fig. 3.2 shows the separation chromatogram of one of the surfactants (Rexol 25/10) at different concentrations, suggesting that Rexol 25/10 is a mixture of homologues. Although it might be possible to identify the peaks (i.e., the components of the surfactant mixture) which disappeared most quickly during shearing of the emulsion, this was found to be impractical because the analysis required fairly high concentrations (i.e., over 400 ppm).

The HPLC column failed to separate Rexol 25/307 qualitatively in this investigation. The lower sensitivity of the UV detector was also a limiting factor in the procession of the measurement.

Figure 3.2: Chromatogram of Rexol 25/10 surfactant

Injection: (1) 4000 ppm (2) 1000 ppm (3) 400 ppm (4) 80 ppm

Mobile phase: 100% MeCN. Flow rate: 2 mL/min

UV detector wavelength: 226 nm.

3.2.2.4 Calibration and Aqueous Sample Preparation

Calibration curves were made for Rexol 25/10 and Rexol 25/307 in the concentration range from 0 ppm to 1000 ppm, the range used most frequently in this investigation (Figs. 3.3 and 3.4). Both visual inspection and linear regression show that the calibration curve for Rexol 25/10 is close to linear ($R_r^2 > 0.998$) (Table 3.2). However the normal linear regression analysis assumes that the standard deviation for Y is constant throughout the whole calibration range and this is not true at the extreme ends of the concentration range. This can be seen by plotting (Y_i/X_i) , where Y_i is the peak height and X_i is the concentration (Fig. 3.5). Restricting the data to the region above 32 ppm and below 500 ppm and repeating the regression analysis, one obtains new coefficients and the resulting curve is very nearly linear (Fig. 3.6). The error limit is reduced to $\pm 0.86\%$ compared to $\pm 6.96\%$ with the original correlation.

The aqueous phases from a centrifuged emulsion or from the separated layer of an emulsion before inversion were prepared for determination of the surfactant concentration by the HPLC. The aqueous phase was first filtered to remove the oil droplets. Nylon-66 filters with pore sizes of $0.45\ \mu\text{m}$ were used in this step, the filters were manufactured by Supelco Canada Ltd. The pore size was chosen to be ten times that of the estimated maximum micelle diameter [27], so that the filtration would not affect the surfactant concentration in the aqueous phase. However, it was observed that smaller pore size (i.e., $0.20\ \mu\text{m}$) did result in a difference in surfactant concentration in

Figure 3.3: HPLC calibration curve for Rexol 25/10 & brine solution
HPLC mobile phase: methanol:water, 90:10. Flow rate: 2 mL/min.
UV detector wavelength: 226 nm.

Figure 3.4: HPLC calibration curve for Rexol 25/307 & brine solution
HPLC mobile phase: methanol:water, 90:10. Flow rate: 2mL/min.
UV detector wavelength: 215 nm.

Figure 3.5: Linearity analysis for original Rexol 25/10 calibration in Figure 3.3.

Figure 3.6: Linearity analysis for modified Rexol 25/10 calibration in Fig. 3.3. Points at 1000, 16 and 8 ppm were discarded.

Table 3.2: Regression analysis for Rexol 25/10 calibration curves

Regression output	Before modification	After modification
Constant	- 9.821	- 0.387
Std. Err. of Y Set	15.396	1.314
R^2 Squared	0.998	0.999
No. of Observations	10	7
Degrees of Freedom	8	5
X Coefficient(s)	52.978	49.801
Std. Err. of Coef.	0.910	0.138
Regression Formula	$X=52.98Y-9.82$	$X=49.80Y-0.39$

some samples during the course of inversion. This will be discussed later in section 4.6.

3.2.3 Mass Spectrometry

Mass Spectrometry can determine an analyte's molecular weight distribution. This determination was made using the VG BIO-Q Dedicated Electrospray Triple Quadrupole Mass Spectrometer, which was manufactured by VG Biotech, Altrincham, England. The mobile phase was 50% CH₃CN and 50% Water. Flow rate was 7 μ L/min. The MS is located in the College of Pharmacy, University of Saskatchewan.

3.2.4 Operation of the Mass Spectrometry

3.2.4.1 Determination Procedure

The sample in solution is introduced into the atmospheric pressure ion source through a stainless steel capillary. The capillary, typically at 4 KV, is situated a few millimeters from the counter electrode which is typically at 1 KV. As a consequence of this potential difference, an electric field is created and the sample emerging from the capillary is nebulised and ionized. The aerosol of highly charged droplets is then dried by a flow of warm nitrogen gas flowing through the source resulting in singly charged gas phase ions free of solvent. Before entering the high vacuum of the mass analyzer, the ions pass through a two stage momentum separator. The first separation stage occurs through the sampling cone orifice into a pumped intermediate vacuum region at about 1 MBar pressure. This is followed by the second stage, the skimmer. The voltage of the sampling cone can be varied to optimize the analysis. A low cone voltage produces a spectrum dominated by quasi molecular ions, and a high cone voltage induces fragmentation.

3.2.4.2 Identification of the Surfactant Structure

The HPLC results suggested that Rexol 25/10 is a mixture of homologues. Mass Spectrometry results (Fig. 3.7) suggest that these homologues might be due to the different numbers of ethylene oxide units (i.e. $(-\text{CH}_2-\text{CH}_2-\text{O}-)$ units), each of which has a molecular weight

of 44. The major component in Rexol 25/10 has a molecular weight of 706, which has a possible molecular formula:

containing 12 ethylene oxide units. If Rexol 25/10 has a molecular formula as (3.C), the number of ethylene oxide units would be 8:

The Mass Spectrometry results (Fig. 3.8) showed that Rexol 25/307 may be a mixture of two major components, containing 13 and 23 ethylene oxide units respectively, provided they all have a molecular structure similar to (3.A), or containing 7 and 26 ethylene oxide units based on the formula (3.C). It seems not to be possible to determine the exact molecular formula without more information. However, it is certain that Rexol 25/307 has more ethylene oxide units and a broader distribution than Rexol 25/10. Obviously Rexol 25/307 is more hydrophilic.

Figure 3.7: Mass spectrogram of Rexol 25/10 surfactant
Rexol 25/10 used as received

Figure 3.8: Mass spectrogram of Rexol 25/307 surfactant
Rexol 25/307 used as received

3.3 Oil Droplet Size Determination

It has been reported that emulsion stability is dependent on oil droplet size and size distribution and can be affected by surfactant concentration and shear rate [4, 63]. The oil droplet size and size distribution was determined by the Brinkmann Particle Size Analyzer (PSA), which was manufactured by the Brinkmann Instruments (Canada) Ltd., Rexdale, Ontario, Canada.

3.3.1 Description of the Particle Size Analyzer (PSA)

The PSA is a comprehensive particle analysis system, which can provide particle size and particle shape data. For particle size analysis, it is based on the time-of-transition. This is the time it takes a laser beam moving at a fixed velocity to cross a particle. Particle-laser interactions can then be processed to produce diameter size. Algorithms which reject particles measured off their centre increase data accuracy. The PSA can provide statistical data on the particle diameter, area and volume, number of particles sampled and even their concentration. However the concentration must always be very dilute.

3.3.2 Operation of the PSA

Although the PSA was originally designed to determine the size and size distribution of solid particles, in this investigation the oil droplet size and size distribution of emulsions were determined.

The operation of the PSA is simple because the instructions are provided on the computer screen. The data are processed automatically. There are two sample preparation procedures. The first procedure, using a transparent cuvette as the sample container, was developed by Sumner and was reported elsewhere [64]. The second procedure uses a glass tube so the sample can pass through it continuously. This procedure was developed by the pipeline group, Saskatchewan Research Council.

Very often the emulsions were close to inversion so the droplets were large. In the cuvette, larger oil droplets tended to float upward so that the laser beam counted the smaller droplets near the center of the cuvette. This caused the measured data to deviate considerably from the actual size.

For the procedure using the continuous flow-through method, the larger droplets were easily broken by passing through the various connections because of the weakened interfacial film. Thus the droplet sizes given by this procedure were also much smaller than those observed visually. These two sample preparation procedures are evidently not satisfactory for very large droplets. Notwithstanding these shortcomings, data were generated by using a modified method based on the first procedure to compare the trend of droplet size variation with test conditions.

3.4 Emulsion Sample Preparation

3.4.1 The Stirred Beaker Tests

The emulsion was prepared by the agent-in-water method [65]. In this method the surfactant was first dissolved in brine at a designated concentration by weight. The solution was warmed during dissolution. A known amount of oil was then added to the surfactant solution while it was stirred in an 800 mL beaker. The impeller was a "high-shear" impeller with a diameter of 4.375 cm. It consisted essentially of a flat disc, 2 mm in thickness with twelve 6.25 mm $\times$ 5.00 mm peripheral projections normal to the plane of the disc. The mean shear rate in the beaker was governed by the rotational speed of the impeller which was monitored constantly. The temperature was controlled with a thermal bath.

3.4.2 The Dispersed Oil Phase Fraction

Two dispersed oil phase fractions were investigated in this study. The first one contained 73.0% oil w/w, meaning that the free brine and total brine in the emulsion were 27.0% w/w and 35.0% w/w respectively. A 65.0% oil w/w emulsion was also used whose free brine and total brine contents were 35.0% w/w and 42.2% w/w respectively.

The internal brine in the oil was very stable as a brine-in-oil

emulsion, so that even centrifuging at 2000 rpm or heating to 80 °C could not demulsify it. When it was used to prepare oil-in-brine emulsions, at least part of the oil and brine formed a brine-in-oil-in-brine emulsion, commonly known as a w/o/w emulsion. This makes the emulsion formation and inversion mechanism somewhat more complicated.

3.4.3 Brine Content Determination

The free brine content of the emulsion was determined by centrifuging the emulsion at 2000 rpm and 20 °C for 10 minutes in a graduated centrifuge tube. The total brine content of the emulsion and the internal brine of the crude oil were determined by the BS&W method [66].

3.4.4 Surfactant Concentration and the C.M.C Value

The surfactant concentrations are reported in parts per million parts of oil (w/w oil). Various surfactant concentrations both for Rexol 25/10 and Rexol 25/307 were tested, but the investigation focused mainly on the low concentrations for the practical consideration of meeting the requirements of industrial applications. A low surfactant concentration would also speed up droplet coalescence in emulsions so that the experiments could be carried out in a reasonable period of time in the laboratory. According to Becher [29], the C.M.C. values of nonionic polyethylene oxide surfactant are on the order of 10^{-4} mole/liter, so for Rexol 25/10 which has an average molecular weight

of 706, its C.M.C value should be around 70 ppm. Similarly, Rexol 25/307 should have a C.M.C value of 130 ppm, which is higher than Rexol 25/10 because of its higher average molecular weight (MW=1340).

3.4.5 Emulsion Aging and Inversion

Inversion was almost invariably observed in the beaker tests after emulsions had been stirred for a sufficiently long time. That is, the oil-in-brine emulsions eventually inverted to brine-in-oil emulsions. It was found that the time for a stable emulsion to invert depended on the shear rate (i.e., the stirring speed), temperature, the surfactant species and its concentration. It was also found that when a stable emulsion was stirred, the droplet size increased with stirring time (Fig. 3.9). This process was defined as emulsion aging. When the droplet size increased dramatically just before inversion in a beaker, brine was centrifuged out of the stirred emulsion and the emulsion often remained stirrable with no significant increase in effective viscosity. The apparent increase in the volume of the aqueous phase was due to the release of the water molecules which had previously been immobilized by the oil droplets in the stable emulsion. This change is defined as emulsion failure. Beyond emulsion failure, inversion could occur any time when suddenly all the brine entered the oil to produce a brine-in-oil emulsion with very high viscosity.

Figure 3.9: Effect of stirring speed on oil droplet size
Emulsions prepared with 400 ppm Rexol 25/10 (w/w oil), 73%
oil, stirred at 20 °C.

3.5 Cone and Plate Viscometer

3.5.1 Description of Cone and Plate Viscometer

To simulate a pipeline transportation process, a cone and plate viscometer was used in this investigation (Fig. 3.10). The viscometer resembles the pipeline in that the shear increases from zero at the axis to a maximum value at the wall of pipeline or tip of the cone. Thus the cone and plate viscometer can simulate the shear and flow conditions in a pipeline.

Figure 3.10: Comparison of cone and plate viscometer and pipeline flows. (a) $\dot{\gamma}_{\max}$ (b) $\dot{\gamma}_{\min}$

The viscometer was manufactured by Brookfield Engineering Laboratories, Inc., Stoughton, MA, U.S.A. The cone, which has a diameter of 48 mm, was rotated at a constant speed. Although a parallel plate would have been desirable, the smallest cone angle manufactured by Brookfield is 0.8 degrees, and this cone angle was used throughout the investigation. Because the torque of the emulsions ranged widely with different test conditions, two different viscometers (LVTDV-IICP and RVTDV-IICP) had to be used but their features were identical except for different torque ranges.

For true cone and plate geometry (Fig. 3.11), with the apex of the cone touching the plate, the shear stress and shear rate relationships are calculated from the measured torque and cone rotational speed by Equations (3.1) and (3.2):

$$\text{Shear Stress } \tau \text{ (dynes/cm}^2\text{)} = \frac{T_v}{\frac{2}{3} \pi r_1^3} \quad (3.1)$$

$$\text{Shear Rate } \dot{\gamma} \text{ (s}^{-1}\text{)} = \frac{2 \pi \omega}{\tan \theta} \quad (3.2)$$

where T_v is the torque, r_1 is the cone radius, ω is the cone speed and θ is the cone angle. Both r_1 and θ are constants. However, because most of the emulsions prepared by the stirring process had mean initial droplet sizes of 150-200 μm (Fig. 3.9) and these sizes increased with shear, a gap was introduced between the cone and the plate. The shear rate is then given by Equations (3.3):

Figure 3.11: Geometry of cone and plate viscometer

$$\text{Shear Rate } \dot{\gamma} \text{ (s}^{-1}\text{)} = \frac{2 \pi r \omega}{(d + r \tan \theta)} \quad (3.3)$$

where d is the gap distance between the cone and the plate, r is the cone radial position which is a variable.

3.5.2 Operation of Cone and Plate Viscometer

The emulsion sample, prepared by stirring in a beaker, was placed in the cup of the viscometer whose lower surface formed the plate. It was then sheared at a constant rotational speed. By adjusting the cone rotational speed, one could produce a range of maximum shear rates. By measuring the torque applied to the sample, one can obtain a measure of the shear stress required to overcome the cohesive forces between the molecules of a liquid at a given shear rate.

Since $\tan \theta$ is very small in this viscometer, Equation (3.3) shows that $\dot{\gamma}$ is very nearly a linear function of r , as it is in laminar pipe flow. Thus the viscometer provides a useful simulation of pipe flow for an emulsion.

The effect of gap distance (d) on the torque for an emulsion can be seen in Fig. 3.12. For an emulsion stabilized by 1500 ppm Rexol 25/10 surfactant, the largest torque was observed at a gap distance of 125 μm and this decreased rapidly at 250 μm . Considering the droplet sizes shown in Fig. 3.9, it is concluded that at the gap distance of 125 μm , the oil droplets were sheared by the viscometer. Above 625 μm , the torque seemed to become insensitive to gap distance. However, it was observed that when emulsions close to inversion, some droplet size could be as large as 1200 μm . In order to minimize the influence of larger droplet, a gap distance of 1250 μm was chosen in this investigation.

Figure 3.12: Effect of viscometer gap distance on torque (I)
Emulsions prepared with 1500 ppm Rexol 25/10 (w/w oil), 73%
oil, sheared at 0.3 rpm and 20 °C.

The variation of the torque with shearing time was frequently substantial and required interpretation. Very often the torque reading increased with time, especially at lower shear rates (Fig. 3.13). This was attributed to the formation of flocs or large drops during shear, which eventually linked the cone and plate as a "bridge", so that the viscometer sheared oil flocs or drops instead of o/w emulsion. This is defined as the "bridging" effect. It was considered to result from the flocculation and/or coalescence processes which are functions of shear rate, temperature, surfactant species and concentration. Obviously, "bridging" would occur more easily at a smaller gap distance.

Inversion was also observed in the viscometer at high shear rates. Fig. 3.14 shows that an emulsion stabilized at 30 °C by 60 ppm Rexol 25/307 inverted at 19 minutes at a higher shear rate of 80 s⁻¹. The sharp increase and fluctuation of torque implied that a lump of very high viscosity was formed. Sometimes one also could observe emulsion failure. Fig. 3.15 shows that the torque decreased drastically after shearing at 80 s⁻¹ and 20 °C for 30 minutes, meaning that a layer of very low viscosity was formed, probably caused by the release of aqueous phase fluid.

Figure 3.13: Effect of viscometer gap distance (II)

Emulsions prepared with 420 ppm Rexol 25/10 (w/w oil), 73% oil, sheared at 1.0 s^{-1} ($\dot{\gamma}_{\text{max}}$) and 20°C .

Figure 3.14: Emulsion inversion at the viscometer (gap 1250 μm)
 Emulsions prepared with 60 ppm Rexol 25/307 (w/w oil), 73% oil,
 sheared at 80 s^{-1} ($\dot{\gamma}_{\text{max}}$) and 30°C .

Figure 3.15: Emulsion failure at the viscometer (gap 1250 μm)
 Emulsions prepared with 60 ppm Rexol 25/307 (w/w oil), 73% oil,
 sheared at 80 s^{-1} ($\dot{\gamma}_{\text{max}}$) and 20°C .

3.6 The Toroid Tests

To determine how well the cone and plate viscometer can simulate the pipeline flow conditions, emulsions should be transported through a pipeline. However it had been found by Gillies and Shook [58] that pipeline loop tests are unreliable simulations of emulsion behavior because of the effect of repeated passages through the pump. To overcome this effect, a toroid test apparatus was used.

The toroid equipment is shown schematically in Fig. 3.16. It consists of a pipe with diameter of 0.0525 m. The radius of the pipe hoop is 2.315 m and the length of pipe section containing emulsion is 7.28 m. The toroid was rotated at a fixed speed after 8 liters of emulsion were placed in the pipe. The emulsion bulk velocity in the test was 1.5 m/s so it produced a wall shear rate of 230 s^{-1} .

An 100 mL emulsion sample was removed after a predetermined time interval to check the emulsion state and surfactant concentration in the aqueous phase. This emulsion sample was first centrifuged at 1000 rpm and 20°C for 5 minutes. The separated aqueous sample was then used to determine the surfactant concentration by HPLC.

Figure 3.16: Schematic representation of Toroid and comparison with pipeline flow

4.0 RESULTS AND DISCUSSION

4.1 Effect of Surfactant Concentration

Figs. 4.1, 4.2 and 4.3 show the surfactant concentrations given by the HPLC analysis of the aqueous phase vs. stirring time in the beaker at 800 rpm. It was invariably observed that when inversion occurred, there was a very low surfactant concentration remaining in the aqueous phase (only few ppm), no matter what the initial concentration, oil fraction or stirring speed. This disappearance suggests that most of the surfactant had left the aqueous phase and entered the oil, since there was no evidence of broken surfactant fragments in the HPLC results. Thus the affinity of the surfactant for the aqueous phase (i.e., the hydrophilic property) must be a controlling parameter in resisting inversion especially at low surfactant concentrations.

Fig. 4.4 shows that the torque change vs. shearing time in the cone and plate viscometer. At a very low shear rate, the lower the surfactant concentration, the higher the torque and the greater the slope of the torque vs. shearing time plots. This difference is probably related to the fact that at the low surfactant concentrations, which do not provide enough repulsive force to keep droplets apart because of the poor surfactant coverage of the interface, droplets tend to flocculate or coalesce together to produce the "bridging" effect.

Of the two surfactants used in this investigation, Rexol 25/307

Figure 4.1: Effect of stirring speed at high oil fraction

Emulsions prepared with 1200 ppm Rexol 25/10 (w/w oil), 73% oil, stirred at 20°C.

Figure 4.2: Effect of surfactant concentration on inversion
Emulsions prepared with Rexol 25/10 (w/w oil), 65% oil,
stirred at 800 rpm and 20°C.

Figure 4.3: Effect of stirring speed at low oil fraction
Emulsions prepared with 1200 ppm Rexol 25/10 (w/w oil), 65% oil, stirred at 20°C.

Figure 4.4: Effect of surfactant concentration on torque
Emulsions prepared with Rexol 25/10 (w/w oil), 73% oil,
sheared at 1.0 s^{-1} ($\dot{\gamma}_{\max}$) and 20°C .

has more ethylene oxide units than Rexol 25/10 so it has the greater affinity for the aqueous phase. Comparing Fig. 4.5 and Fig. 4.6, it can be observed that at low shear rates, the emulsion made with 90 ppm Rexol 25/307 "bridged" only slightly while the emulsion made with 420 ppm Rexol 25/10 "bridged" considerably. It was found throughout this investigation that Rexol 25/307 was about six times as effective as Rexol 25/10. It is possible that Rexol 25/307 can provide a better coverage of the interface and form a stronger interfacial film because it has more ethylene oxide units [28], so it has more resistance to the shear-induced collisions.

Evidence given by the PSA measurements (Fig. 4.7) showed that the higher the surfactant concentration, the smaller the initial oil droplet size and the longer the emulsion could be stabilized. This is probably an interfacial tension effect. However, the primary role of the surfactant is to prevent the immediate flocculation and coalescence of the newly formed emulsions [63], i.e., to provide enough repulsive force between oil droplets. It seems that of the emulsions produced in this investigation, the droplet size and size distribution are not as critical as the interfacial film in the course of emulsion stabilization.

It is also seen (Figs. 4.1 and 4.2) that at moderate stirring speeds (i.e., 800 rpm), there is a period of quasi-steady surfactant concentration. The mechanism which produces this period will be discussed later in section 4.6.

Figure 4.5: Bridging effect of Rexol 25/307 at low shear rates
Emulsions prepared with 90 ppm Rexol 25/307 (w/w oil), 73% oil,
sheared at 30°C.

Figure 4.6: Bridging effect of Rexol 25/10 at low shear rates
Emulsions prepared with 420 ppm Rexol 25/10 (w/w oil), 73% oil, sheared at 30°C.

Figure 4.7: Effect of surfactant concentration on droplet size
Emulsions prepared with Rexol 25/10, 73% oil, stirred at 800 rpm and 20 °C.

4.2 Effect of Temperature

An interfacial film is required to maintain a stable emulsion. However, this film is sensitive to disturbances such as those produced by elevated temperatures and shear rates. As indicated in Figs. 4.8, 4.9 and 4.10, at a low temperature (i.e., 10 °C), the torque vs. shearing time plots were fairly stable. At the intermediate temperature (i.e., 20°C) and at a high temperature (i.e., 28 °C) "bridging" occurred at low shear rates (i.e., 0.5 s⁻¹). The same trend can be seen in Fig. 4.11. This suggests that a high temperature increases the solubility of surfactant in the oil and the rate of surfactant consumption, thus encouraging the interface to adsorb more surfactant. It is also possible that the higher temperature increases the micelle disaggregation rate and diffusion rate from the aqueous phase to the interface. Also at higher temperatures, the oil droplets are no longer as rigid as at low temperature so they may be distorted and deformed more easily under shear to create new interface. The higher temperature would reduce the hydrophilic property of the nonionic ethylene oxide surfactant [37], further encouraging the formation of w/o emulsion. All of these processes contribute to rapid flocculation or coalescence and eventually to inversion.

Comparing Figs. 4.5 and 4.6 again, it was found that the sensitivity of surfactant to the temperature also depends on its hydrophilic property. If the surfactant is more hydrophilic, i.e., it has more ethylene oxide units (as in the case of Rexol 25/307), it should

Figure 4.8: Effect of shear rates and time at 10 °C

Emulsions prepared with 400 ppm Rexol 25/10 (w/w oil), 73% oil.

Figure 4.9: Effect of low shear rates and time at 20 °C

Emulsions prepared with 425 ppm Rexol 25/10 (w/w oil), 73% oil.

Figure 4.10: Effect of low shear rates and time at 28 °C
Emulsions prepared with 445 ppm Rexol 25/10 (w/w oil), 73% oil.

Figure 4.11: Effect of temperatures at low shear rate

Emulsions prepared with 500 ppm Rexol 25/10 (w/w oil), 73% oil, sheared at 1.0 s^{-1} ($\dot{\gamma}_{\text{max}}$).

be less soluble in the oil. At higher temperatures, it would have more resistance to the reduction of its hydrophilic property so the time to reach the emulsion hydrophilic-hydrophobic balance (i.e, emulsion inversion) can be prolonged. Thus should be less sensitive to the temperature increase.

4.3 Effect of Shear Rate

Basically, high concentration oil-in-brine emulsions are thixotropic fluids. Figs. 4.8, 4.12 and 4.13 are shear diagrams of torque vs. shearing time at temperatures of 10, 20 and 28 °C for emulsions containing 73% oil with Rexol 25/10 surfactant. It was observed that at high shear rates (i.e, 30 s^{-1} - 80 s^{-1}), the torque decreased with shearing time at a constant shear rate and a fixed temperature. The higher the shear rate, the more obvious the downward trend of the torque vs. shearing time plots. This change could result from the high shear rate deflocculating more oil droplets per unit time than the flocculation process can produce, releasing some of the continuous phase originally immobilized within the flocs. Alternatively, it could be due to droplet migration from regions of high shear rate to those of low shear rate, as described by Leighton and Acrivos [67]. This migration would reduce the dispersed phase fraction in the region of high shear rate which contributes most to the torque. As the effective dispersed phase fraction decreases, this would lead to a decreased torque. A third possibility reported in the literature [4] is that the thixotropic behaviour of emulsion is caused by the migration of surfactant from the

Figure 4.12: Effect of shear rate and time at 20 °C

Emulsions prepared with 420 ppm Rexol 25/10 (w/w oil), 73% oil.

Figure 4.13: Effect of shear rate and time at 28 °C

Emulsions prepared with 445 ppm Rexol 25/10 (w/w oil), 73% oil.

continuous phase to the interface of the oil droplets. This then could lead to a decrease of viscosity of the continuous phase so that the torque of emulsion decreased with shearing time. However this seems unlikely in this case since this process would be significant only at the moment when the surfactant solution contacts the fresh oil. Once the aqueous surfactant concentration reaches equilibrium, the influence of the continuous phase viscosity should vanish. Furthermore, the effect of surfactant on continuous phase viscosity at 400-450 ppm is very small.

At medium shear rates (i.e., 4.0 s^{-1} - 8.0 s^{-1}), the rate of deflocculation tends to equilibrate with the rate of flocculation so that the torque vs. shearing time plots become level. At low shear rates (i.e., 0.5 s^{-1} - 2.5 s^{-1} in Fig. 4.13), visual observations showed that very large droplets formed throughout the sheared sample. Bridging was also observed at the higher temperatures (i.e., 20°C and 28°C) and low shear rates.

Fig. 4.1 shows that an emulsion stirred at 2000 rpm inverted in about 90 minutes while the same emulsion lasted about 280 minutes at 800 rpm. This difference occurs because at the high shear rate, new interface was formed continuously by the distortion and deformation of the dispersed phase, consuming more surfactant.

High shear rates also produced finer droplets, as shown in Fig. 3.9. It is seen that stirring at 1200 rpm produced an average droplet size of $200 \mu\text{m}$ initially while 400 rpm produced an average size of

250 μm . These results were obtained with 400 ppm surfactant (w/w oil) at 20 °C. It is possible that the smaller droplet sizes produced by high shear rates could improve the emulsion stability by extending the flocculation and coalescence processes. However the emulsion stability does not depend directly on the droplet size and size distribution. This is true because to produce smaller droplets, higher shear forces (i.e., energy) will be needed, which would increase the droplet velocity and momentum of the droplets. This would increase the probability of collisions and distortion, tending to destroy the interfacial film. Also the smaller droplet sizes would increase the total interfacial area, reducing the average adsorbed surfactant concentration per unit area (if the original surfactant concentration in the solution is below the C.M.C.) or reducing the micelle stock in the solution (if the original surfactant concentration is above the C.M.C.). As observed in this investigation, inversion was associated with the disappearance of surfactant from the aqueous phase, so that any direct or indirect influence on the decrease of the surfactant stock from the aqueous phase would encourage quick inversion.

Fig. 4.14 gives the rheogram for emulsions sheared for 15 min, showing that at this condition the emulsions are pseudo plastic fluids, whose rheograms can be described by the power law (2.1). However n is close to unity so that the degree of pseudo plastic character is small at all three temperatures. With shear, flocculation is much faster at the higher temperature, as indicated in Fig. 4.14, so that only a small apparent yield stress was observed.

Figure 4.14: Shear diagram at different temperatures
Emulsions prepared with 400 ppm Rexol 25/10 (w/w oil).

4.4 Effect of Oil Fraction

Theoretically, the dispersed oil phase volume fraction can be increased up to 74% for uniform rigid spherical droplets and above this fraction, it is often very difficult to form a stable oil-in-brine emulsion. However it is still possible to prepare emulsions having dispersed fractions more than 90% because of the deformable nature of the dispersed phase.

In this investigation, dispersed oil phase fractions of 65% and 73% were used, which provided a 12.3% difference in total interfacial area. Fig. 4.15 shows that for the emulsions stabilized by 600 ppm Rexol 25/10 (w/w oil), and stirred at 800 rpm and 20 °C, the emulsion with 73% oil inverted at 80 minutes while that with 65% oil lasted 195 minutes. Thus the oil fraction had a very important influence on the emulsion stability and rheological behaviour, especially when the surfactant concentration in solution is low (i.e, well below the C.M.C value). This occurs because only single molecular layer is formed at the C.M.C., and any increase of the total interfacial area would affect the coverage and strength of the interfacial film, thus affecting the stability of the emulsion.

Fig. 4.16 verifies this trend, which shows that under shear, the surfactant concentration in the aqueous phase of emulsions with 73% oil always decreased somewhat more rapidly than those with 65% oil, no matter what the initial surfactant concentration or how high the shear rate (i.e, stirring speed).

Figure 4.15: Effect of oil fractions (I)

Emulsions prepared with 600 ppm Rexol 25/10 (w/w oil), stirred at 800 rpm and 20 °C.

Figure 4.16: Effect of oil fractions (II)

Emulsions prepared with 1200 ppm Rexol 25/10 (w/w oil), stirred at 2000 rpm and 20 °C.

The effect of oil fraction also can be seen in the torque vs. viscometer shearing time plots. In Figs. 4.17 and 4.18, the 73% oil not only has a higher torque, indicating that the increasing oil fraction increased the viscosity of the emulsion, but it also inverts more rapidly. This indicates that at a given surfactant concentration and shear rate, the larger the interfacial area, the more rapid the inversion. It is thus clear that emulsion stability is closely related to the coverage of interfacial area by surfactant molecules and the strength of the interfacial film.

The 12.3% difference of the total interfacial area in these two oil fractions resulted in a nearly constant factor of two in the inversion times, which was indicated by either the Rexol 25/10 concentration or the sudden change in the torque. This might provide a useful correlation for subsequent work.

4.5 The Toroid Tests

Toroid tests were conducted in this investigation to compare the emulsion data generated from the cone and plate viscometer and that for a pipeline. Figs. 4.19 and 4.20 show the comparison of the inversion times indicated by the sharp decrease of the surfactant concentration in the toroid and the rapid deviation of the torque in the viscometer respectively. The emulsion was prepared with 1200 ppm Rexol 25/10 (w/w oil), and the oil fractions were 65% and 73% respectively. The shear rate in the viscometer was 220 s^{-1} and 230 s^{-1}

Figure 4.17: Effect of oil fractions (III)

Emulsions prepared with 1200 ppm Rexol 25/10 (w/w oil), sheared at 220 s^{-1} ($\dot{\gamma}_{\text{max}}$) and 25°C .

Figure 4.18: Effect of oil fractions (IV)

Emulsions prepared with 600 ppm Rexol 25/10 (w/w oil), sheared at 160 s^{-1} ($\dot{\gamma}_{\text{max}}$) and 20°C .

Figure 4.19: Comparison of emulsion behaviour in the viscometer and the toroid (I)

Emulsions prepared with 1200 ppm Rexol 25/10 (w/w oil), 73% oil, sheared at 25 °C.

Figure 4.20: Comparison of emulsion behaviour in the viscometer and the toroid (II)

Emulsions prepared with 1200 ppm Rexol 25/10 (w/w oil), 65% oil, sheared at 25 °C.

in the toroid test. It can be seen that the time for emulsion inversion (or failure) in the toroid and in the viscometer were very close under these test conditions for both the 65% oil and 73% oil fractions, indicating that the cone and plate viscometer gives a good simulation of the o/w emulsion pipe flow and inversion processes.

4.6 Mechanism of Inversion

With the data collected so far, it is possible to discuss the mechanism of inversion of heavy crude oil-in-brine emulsions.

In the course of emulsion formation and stabilization, several processes occur simultaneously: disaggregation of micelles in the aqueous phase, diffusion of the surfactant molecules from the aqueous phase to the droplet interface and adsorption on the interface, as well as some other processes as the following discussion will suggest.

Initially (i.e., at time zero) most of the surfactant molecules in the aqueous phase exist in the form of micelles (provided the surfactant concentration in the aqueous phase is above the C.M.C.). When oil is added to the solution with stirring, the dispersed phase is distorted and fresh interface forms. However the fresh interface is only partly covered by the free surfactant molecules in the solution, i.e., the equilibrium of adsorption has not been achieved. The micelles in the aqueous phase start to disaggregate and release single surfactant molecules which diffuse to the fresh interface to be adsorbed. This

causes the initial decline of the total surfactant concentration in the aqueous phase, as indicated in Figs. 4.1, 4.21 and 4.22.

At the end of this initial decline, the interface is probably more or less substantially covered by the surfactant molecules. The coverage depends on the nature of the surfactant and the total interfacial area, which is related to the droplet size and dispersed phase fraction. The droplet size, in turn, is a function of shear rate and interfacial tension (i.e., surfactant concentration). Comparing the curves in Fig. 4.1, the initial decline for the 2000 rpm curve was 140 ppm more than that for the 800 rpm curve. Also in Fig. 4.21, the initial decline for 73% oil was 60 ppm more than that for the 65% oil. So for a given surfactant concentration, the smaller the droplet size and the larger the total interfacial area, the greater the number of surfactant molecules adsorbed in the interface, and the greater the consumption of the micelle stock from the aqueous phase.

It was observed that the initial decline rates of surfactant concentration were very high, no matter what the surfactant concentration, oil fraction or stirring speed. This similarity was probably due to the fact that the initial interfacial areas are large and the initial droplet sizes do not change drastically with these parameters. Similarly, rates of diffusion at a given temperature should not vary widely. Thus although adsorption occurs during this period, it is difficult to determine which process, if any, controls the rate. However this period is relatively short, i.e., three or four minutes in all cases. This is probably coincident with the period of emulsion formation.

Figure 4.21: Effect of oil fraction (V)

Emulsions prepared with 1200 ppm Rexol 25/10 (w/w oil), stirred at 800 rpm and 20 °C.

Figure 4.22: Effect of surfactant concentration

Emulsions prepared with Rexol 25/10 (w/w oil), 73% oil, stirred at 800 rpm and 20 °C. (a) initial decline (b) second decline (c) first lowest concentration (d) quasi steady state (e) final stage

The micelle stock in the aqueous phase probably plays an important role in the emulsion formation. It is a continuous source of surfactant molecules to replenish those diffusing from the aqueous phase to the interface, so that the micelle stock and the rate of micelle disaggregation could influence the coverage (i.e., adsorption) on the interface. Fig. 4.22 showed that for the emulsions prepared with the same stirring speed, the initial decline was 800 ppm for the 1640 ppm curve, while it was 460 ppm for the 560 ppm curve, meaning a less substantial adsorption.

The adsorption, which results in a formation of an interfacial film, is critical in the emulsion stabilization. After this initial decline new interface is constantly created by shear deformation and droplet collisions. At a given shear rate, if the interfacial adsorption is substantial, the decreased interfacial tension may make it easier to deform the dispersed phase into smaller droplets and thus increase the total interfacial area. This increased area can adsorb more surfactant molecules (provided there is enough surfactant stock in the aqueous phase). This is a possible cause of the second decline in the 1640 ppm curve in Fig. 4.22 (between 10 and 50 minutes). The decreased droplet size in fact would help to stabilize the emulsion. If the interfacial adsorption is not substantial, the interfacial tension is not decreased sufficiently so that further deformation will be difficult. It was observed that the second decline period was either very short or completely absent in the 840 ppm and 560 ppm curves in Fig. 4.22.

Each curve in Figs. 4.1, 4.21 and 4.22 has a first lowest value in

terms of surfactant concentration (i.e., point c in Fig. 4.22) which could be considered as an adsorption equilibrium. This equilibrium could arise because the droplet collisions, will lead to coalescence to form larger drops and reduce the total interfacial area causing less adsorption. In addition, the collisions may also displace surfactant molecules back to the aqueous phase.

The displaced surfactant molecules may be different from their original form. One possibility is that the surfactant molecules carried oil molecules with them. Because of the droplet collisions and deformation (both occur at a high frequency under shear), the interfacial film is deformed and some of it could be displaced back into the aqueous phase in the form of tiny fragments. The mechanism is schematically shown in Fig. 4.23.

Fig. 4.24 shows that for the same aqueous phase obtained from the emulsion stabilized by 1200 ppm Rexol 25/10 (w/w oil), after filtration by Nylon-66 filters with 0.45 μm and 0.20 μm pore sizes respectively, there was a concentration difference. This should not have been due to the filtration of micelles but was probably caused by the removal of tiny surfactant-oil fragments in this size range, five to ten times larger than the maximum micelle size. The chromatogram (2) of HPLC chart records (Fig. 4.25) showed that during this quasi steady state, it had a long extended band after the Rexol 25/10 peak. It will be recalled that in the reversed-phase separation method of the HPLC used in this investigation, the retention of an analyte depends on the degree to which it is partitioned into the non-polar

Figure 4.23: Processes of o/w emulsion formation and stabilization

(a) micelle formation (b) micelle disaggregation (c) surfactant molecules diffuse to oil interface (d) surfactant molecules adsorbed on the interface (e) surfactant-oil fragments diffuse back to the aqueous phase.

stationary phase and large non-polar molecules are the most highly retained. The extended band following the Rexol 25/10 peak then could be considered as something which is less polar or more hydrophobic than the original surfactant molecules. This should not have been due to the emulsion oil droplets because the $0.45\ \mu\text{m}$ pore size should effectively remove all of the initial oil droplets formed at this surfactant concentration (i.e., size of $200\text{-}250\ \mu\text{m}$). It is thus

Figure 4.24: Effect of filter pore size

Emulsions prepared with 1200 ppm Rexol 25/10 (w/w oil), 73% oil, stirred at 800 rpm and 20 °C. Filtered by Nylon-66 filter.

Figure 4.25: HPLC chart record corresponding to Fig. 4.24

Chromatogram: (1) stirred for 45 min (2) stirred for 135 min

(3) stirred for 210 min

Emulsion prepared with 1200 ppm Rexol 25/10 (w/w oil), stirred at 800 rpm, 20 °C. Samples filtered with 0.45 μ m pore size filter.

suggested that these are the surfactant-oil fragments. In these fragments the attached oil molecules cause the surfactant to gradually increase its hydrophobic property, disabling its effectiveness.

Evidence for these surfactant-oil fragments was also given by the period of a quasi steady state of surfactant concentration as indicated in Figs. 4.21 and 4.22, and observations of a yellow color in the aqueous phase during this period. During this period, micelles disaggregate and the net surfactant concentration decrease constantly due to the fresh interface created by shearing. It is suggested that most of the surfactant molecules adsorbed were in the interface, so the surfactant-oil fragments are saturated with surfactant. With shearing, the quantity of surfactant-oil fragments constantly increase and the apparent mass of surfactant in the fragments also increase. Two competing processes, surfactant molecules adsorption on the new interface and displacement of surfactant-oil fragments back to the aqueous phase, can exist simultaneously, which are balanced at a constant shearing rate (i.e., stirring speed). Thus the HPLC analysis indicate a nearly constant surfactant concentration in the aqueous phase in this region (Fig 4.26). The emulsions were stable during this period as long as the aqueous phase had enough surfactant molecules to maintain the adsorption on the new interface.

It is thus important to have a large micelle stock in the aqueous phase to ensure emulsion stability. If no micelle stock is left after the initial coverage, and no surfactant can be supplied to offset that forming the adsorption film and displaced, the interfacial surfactant

Figure 4.26: Mechanism of quasi steady state

- (a) Micelle and surfactant concentration
- (b) Surfactant-oil fragments concentration
- (c) Surfactant concentration determined by HPLC

concentration falls quickly below the value which had been maintained by the surfactant concentration in the aqueous phase, then a quick inversion is very likely. This can be seen from the curves of 840 ppm and 560 ppm in Fig. 4.22.

Once most of the original surfactant molecules in the aqueous phase have been replaced by the surfactant-oil fragments after the micelle stock is exhausted, the quasi steady state then ends, as the surfactant and the extended band diminished together (chromatogram (3), Fig. 4.25). This indicated that the surfactant-oil fragments disappear quickly if the interface is not covered by the surfactant molecules. It seems that these surfactant-oil fragments have more affinity for the oil than the original surfactant molecules because the attached oil makes the fragments more hydrophobic. When these fragments collide with the bare emulsion oil drops, they should be more easily scavenged, even penetrating inside the oil drops under shear, taking the surfactant with them. This would cause the rapid decrease of the surfactant concentration in the aqueous phase as the emulsion proceeded to inversion, which was invariably observed in the final stages, as shown by Figs. 4.21 and 4.22.

After all the surfactant-oil fragments penetrated inside the oil, water molecules from the bulk aqueous phase would also enter the oil drops with the ethylene oxide units.. In contrast to the o/w emulsions, the enlarged hydrophobic groups could form the outer shell and the hydrophilic units the core of these fine drops. In this way, water molecules could be stabilized into a w/o emulsion.

Fig. 4.1 showed the effect of shear rate on the interfacial adsorption and displacement. If the shear rates are moderate, the limited new interfacial area will not adsorb much of the micelle stock in the aqueous phase, so that the quasi steady state can endure a long time, i.e., more than 100 minutes (from 60 minute to 180 minute) under stirring at 800 rpm. If very intense shear rates are provided, i.e., if the emulsion system is stirred very strongly, the droplets are distorted and deformed so quickly that a very large fresh interface is constantly being formed. In this case there will be no equilibrium between adsorption and displacement so that surfactant molecules from the micelle stock will be adsorbed continuously on the interface until they are exhausted and inversion occurs. This is indicated in the curve for 2000 rpm in Fig. 4.1. The higher shear rate may also accelerate the surfactant convective and diffusive rates, thus increasing the collision probability.

The interfacial adsorption film may also be displaced back to the aqueous phase to form the surfactant-oil fragments at high shear rates, but the capture rate by the droplets is so high that these fragments can only exist a short time in the aqueous phase. It was also observed in Fig. 4.16 that under the high stirring speed of 2000 rpm, increasing the total interfacial area (i.e., 73% oil) resulted in a quick inversion. It is thus reasonable to assume that the absence of the quasi steady state was due to the large interfacial area generated at high shear rates. Thus the displacement of the interfacial adsorption film and penetration of the surfactant-oil fragments are critical in the stabilization of emulsion.

This mechanism is consistent with other phenomena observed in

this investigation. The greater effectiveness of Rexol 25/307 probably arises from the fact that it has more ethylene oxide groups and a wider molecular weight distribution. The increased hydrophilic tendency of the ethylene oxide group strengthens the interfacial adsorption film and resists the collision, deformation and coalescence of oil droplets, and the displacement of the interfacial adsorption film. High temperatures can reduce the physical strength of the interfacial adsorption film. Alternatively the solubility of the non polar alkyl group in the surfactant tail could be increased with temperature so reduce the hydrophilic property of the molecule, resulting in a rapid coalescence or inversion. In any event, the rate of displacement and penetration of surfactant-oil fragments is of primary importance in the course of inversion, because it weakens the strength of the interfacial adsorption film. This is in general agreement with the conclusions proposed by other workers [30a] in which the strength of the interfacial film was considered to be the most important variable in the stabilization of emulsions.

5.0 LABORATORY METHOD FOR SELECTING SURFACTANT SPECIES AND CONCENTRATION

5.1 Concept of the Method

As discussed previously, at extremely low shear rates, an emulsion always has a tendency to flocculate and cream because of the gravity difference. If the surfactant concentration is low, i.e., if there is not enough repulsive force between droplets, the flocs will coalesce and form large drops. For a given shear rate, whether and/or how much an emulsion flocculates depends on the repulsive force and the strength of the interfacial film.

The viscometer torque reading will be affected by the flocs or drops because they will bridge the cone and the plate. How soon the torque reading starts to increase and the magnitude of the subsequent rates of increase should be a measure of the repulsive force and the strength of the interfacial film, which in turn is related to the effectiveness of the surfactant and its concentration, as well as the test conditions such as temperature. The stirring rate in the beaker and the shear rate in the viscometer can also be related to the pipeline flowrate. If all these variables could be related to the pipeline operation conditions, one could further predict and/or simulate the emulsion flow behavior during pipeline transportation using laboratory apparatus.

5.2 Selection of a Suitable Surfactant and Concentration

A laboratory method for selecting the best surfactant species and concentration follows from the results obtained in this investigation. The emulsion is prepared in a beaker at a particular surfactant concentration. This emulsion is then stirred at a given speed and temperature until inversion occurs. The stirring speed and temperature can be adjusted but in a given test they are kept constant.

During the stirring process, i.e., at successive times, a 2 mL emulsion aliquot is removed into the cup of the viscometer. This sample is then sheared at 1.0 s^{-1} for about 20 minutes or until the torque limit is exceeded. For each aliquot, the slope of the torque vs. shearing time plots, or the "bridging" curve is different because of the different emulsion droplet size and interfacial film strength. The slope of these plots can be related to the rate of change of the emulsion stage. This is called the slope of the "bridging curve".

The slope of the "bridging curve" is then plotted vs. stirring time. Figs. 5.1 and 5.2 show that when inversion occurred in the cone and plate viscometer, the torque increased sharply to 670 dyne-cm in less than 1 minute, the slope of the "bridging curve" exceeded 740. This slope is considered to be the end point of a stable emulsion. Clearly, the more concentrated the surfactant, and/or the more effective the surfactant species, the slower the flocculation and coalescence processes and the less the change in the slope of the "bridging curve" and the longer the emulsion can be maintained in a stable state.

For example, for stirring at 800 rpm and 20 °C, an emulsion prepared with 600 ppm Rexol 25/10 (w/w oil) was close to inversion after being stirred for 35 minutes. Three bridging curves are shown plotted in Fig. 5.1. For 600 ppm Rexol 25/10 (w/w oil), it is seen that bridging occurs for mixtures stirred between 5 and 29 minutes. However an emulsion with 1200 ppm Rexol 25/10 (w/w oil) lasted 200 minutes, allowing generation of thirteen bridging curves (only six curves were plotted in Fig. 5.2). When the slopes of these bridging curves are plotted against the corresponding stirring time (Fig. 5.3), it can be seen clearly how the emulsion stability increases with surfactant concentration. At this stirring speed (i.e., 800 rpm), a surfactant concentration (i.e., 600 ppm w/w oil) which was obviously well below the C.M.C. value (i.e., 700 ppm) after the initial coverage, can maintain a stable emulsion only for about 30 minutes. Beyond 30 minutes, a separate oil layer will start to form, as indicated by emulsion failure .

If the initial surfactant concentration is well above the C.M.C. value, the emulsion stability is improved significantly by the increased surfactant stock in the aqueous phase. This suggests that above the C.M.C. value, the excess surfactant molecules function so as to "recover" a newly deformed interfacial film created by shear. This process appears to be much easier thermodynamically than to establish a new interfacial film. Below the C.M.C. value, the interfacial film is always incomplete, i.e., the interface is not substantially covered by the surfactant molecules and the film strength is weaker. This is why doubling the surfactant concentration and raising it above the C.M.C.

Figure 5.1: Bridging curves at different stirring time (I)
Emulsions prepared with 600 ppm Rexol 25/10 (w/w oil), stirred at 800 rpm, sheared at 1.0 s^{-1} ($\dot{\gamma}_{\text{max}}$) and 20°C .

Figure 5.2: Bridging curves at different stirring time (II)
 Emulsion prepared with 1200 ppm Rexol 25/10 (w/w oil), stirred
 at 800 rpm, sheared at 1.0 s^{-1} ($\dot{\gamma}_{\max}$) and 20°C .

Figure 5.3: Effectiveness of Rexol 25/10 surfactant concentration

Emulsions prepared with Rexol 25/10 (w/w oil), stirred at 800 rpm, sheared at 1.0 s^{-1} ($\dot{\gamma}_{\text{max}}$) and 20°C .

value, can increase the emulsion stability by a factor more than four (Fig. 5.3).

It was observed in this investigation that emulsion flocculation and coalescence not only depend on surfactant concentration but also on the surfactant species. Using the same procedure to determine the effectiveness of Rexol 25/307, it was found to be about six times more effective than Rexol 25/10 with this oil (Fig. 5.4).

Figure 5.4: Effectiveness of Rexol 25/307 surfactant concentration

Emulsions prepared with Rexol 25/307 (w/w oil), stirred at 800 rpm, sheared at 1.0 s^{-1} ($\dot{\gamma}_{\text{max}}$) 20°C .

6.0 CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

The following conclusions can be drawn from this investigation:

1. Inversion of oil-in-brine emulsions to brine-in-oil emulsions was always associated with the disappearance of the non-ionic ethylene oxide surfactant from the aqueous phase. The surfactant concentration in the aqueous phase is thus a measure of the emulsion stability.
2. The ineffectiveness of the surfactant occurs concurrently with displacement of the interfacial adsorption film. This process results in the formation of surfactant-oil fragments in the aqueous phase. The surfactant-oil fragments are more hydrophobic than the original surfactant molecules, so they can be scavenged easily by the oil droplets under shear.
3. The oil-in-brine emulsions are stable when two processes, the adsorption and the displacement of the interfacial adsorption film are balanced.
4. Once the surfactant molecules in the aqueous phase are all replaced by the surfactant-oil fragments, oil-in-brine emulsions are not stable. When most of the surfactant-oil fragments have

penetrated inside the oil, inversion occurs.

5. The hydrophilic property of the surfactant, which is proportional to the number of alkyl and ethylene oxide units and their distribution, is critical to the strength of the interfacial adsorption film. Inversion depends on the effectiveness of the surfactant and its concentration.
6. Micelles are required to maintain the balance of the adsorption and displacement of the interfacial adsorption film, because they can provide the continuous source of surfactant molecules to replenish the loss in the displacement.
7. External conditions, such as shear rates and temperatures, can influence the strength of the interfacial adsorption film and the stability of emulsions.
8. The results of toroid tests showed that the times for the shear-induced inversion in the cone and plate viscometer and in the toroid were very similar at a given shear rate. The cone and plate viscometer is thus suitable to simulate emulsion flow conditions in a pipeline.
9. A method to select a suitable surfactant and its concentration has been developed. The method is based on the concept that the interfacial tension and the strength of the droplet interfacial film, can affect the droplet size and the rate the droplet size changes.

These changes affect the torque reading in the cone and plate viscometer.

6.2 Future Work

Based on the results and experiences from this investigation, the following recommendations are made for future work:

1. More research needs to be done to identify the rate controlling process(s) in the course of inversion, and to obtain a mathematical relationship between o/w emulsion stability, shear rate and surfactant concentration for a designated oil and brine.
2. The method to select a suitable surfactant and its concentration needs to be improved by relating the shear rate in the stirred beaker to the pipeline flowrate.
3. A data base also should be set up to correlate the inversion characteristics of different oils with operating conditions. These inversion characteristics should then be related to oil and surfactant composition.

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APPENDICES

A. Properties of Luseland crude oil:

Density @ 15 °C, kg/m ³	985.9
Relative Density (15 °C/15 °C)	0.9868
API Gravity (15 °C/15 °C), °API	11.9
Sulfur Content, wt %	3.14
Acid Number: mg KOH/gram oil	
Very Strong	0.07
Strong	1.22
Weak	0.19
Total	1.48
(Asphaltenes) n-C ₅ insolubles, wt. %	12.0
Viscosity @ 20 °C, cP	-
@ 40 °C, cP	1930
@ 60 °C, cP	-
Water Content, wt. %	11.0

B. Properties of Luseland brine:

Cations (mg/L)	Na	Ca	Mg	K	Fe	Mn
	6040	201	122	52.8	<0.1	<0.03

Conductivity @ 25 °C, ms/cm ²	pH @ 22 °C	Alkalinity (mg/L) (as CaCO ₃)
24.0	7.59	710

Sulfate (mg/L)	Chloride (mg/L)	Carbonate (mg/L)	Bicarbonate (mg/L)	OH ⁻ (mg/L)
212	9520	N.D.	866	N.D.

Acetic (mg/L)	Propanoic (mg/L)	I-Butyric (mg/L)	Butyric (mg/L)	I-Valeric (mg/L)	Valeric (mg/L)
N.D.	N.D.	N.D.	N.D.	N.D.	N.D.