

**Studies of Water-in-Oil Emulsions:
Energy and Work Threshold for Emulsion Formation**

Merv Fingas and Ben Fieldhouse
Emergencies Science Division
Environmental Technology Centre
Environment Canada
Ottawa, Ontario
E mail: Fingas.Merv@etc.ec.gc.ca

James Lane and Joseph Mullin
U.S. Minerals Management Service
Hemdon, Virginia

Abstract

This paper summarizes studies to determine the energy and work onset of water-in-oil state formation. The total energy applied to the oil/water in the emulsion formation apparatus was varied from approximately 50 to 600,000 ergs (equivalent to 1×10^6 to 6×10^7 Joules). Work was varied from 1 to 5123 J.s. It was found that although a minimum energy threshold is necessary for most emulsion formation, only work correlates with the stability value. This has clear implications for the formation of emulsions at sea, where a given energy level corresponding to turbulent energy at sea would require a period of time before a given water-in-oil state would be produced.

Four clearly-defined states of water-in-oil have been characterized by a number of measurements and by their visual appearance, both on the day of formation and one week later, and in one case of some samples, one year later. It was found that one year later, the value of stability was generally slightly less than at the time of formation, but the stability class did not change.

It has also been noted that there is a progression in the formation of the emulsions. At the onset of agitation, a coarse mixture appearing like a sponge or foam, is formed. If a stable emulsion will be formed, this occurs quickly and was never observed to revert with the oils in this study. A meso-stable emulsion will form after about 20 minutes of agitation at low energy. In some cases, the meso-stable emulsion can change to a less stable 3-way, water-in-oil-in-water emulsion. Most often a meso-stable emulsion remains as meso-stable. The coarse mixture usually remains as such until mixing ceases, however, in the case of some oils it can also form a 3-way emulsion.

1.0 Introduction

Studies in the past year showed that the energy threshold for the onset of the two states known as stable emulsion and entrained water, is usually very low, 300 to about 1500 ergs, corresponding to a rotational rate in the formation apparatus of about 1 to 3 rpm (Fingas *et al.*, 1999). It was shown that for the one oil type, Bunker C, which forms an entrained water state, that there is no increase in stability with increasing energy input, after the initial formation point. An oil that forms a meso-stable emulsion, Prudhoe Bay, showed a similar tendency in that after the energy

onset, which occurs at a high level of about 25,000 ergs, there is no apparent increase in stability. Two oils that formed stable emulsions, Arabian Light and Sockeye showed an increasing stability with increasing energy, although the rate of increase was gradual with increasing energy. These stable emulsions actually undergo an increase in viscosity over time. Monitoring of these emulsions has been performed for as long as 6 years in the laboratory. Increasing viscosity may be caused by increasing alignment of asphaltenes at the oil-water interface (McLean and Kilpatrick, 1997a, 1997b; Sjoblom and Førdedal, 1996).

An important aspect of emulsions, that has not been studied extensively to date, is the kinetics of emulsion formation and the energy levels associated with the formation of emulsions. Such information is needed to understand the emulsification process and to model the process. The study presented last year, initiates the subject (Ingas *et al.*, 1999). This paper reports on further experiments to examine the kinetics and the formation energy of emulsions. It is important to note that turbulent energy is felt to be the most important form of energy related to emulsion formation. Turbulent energy could not be measured in this apparatus, so the total energy was used as an estimate of the energy available for emulsion formation.

2.0 Experimental

Water-in-oil emulsions were made in a rotary agitator and then the rheological characteristics of these emulsions studied over time. Oils were taken from the storage facilities at the Emergencies Science Division. Properties of these oils are given in standard references (Jokuty *et al.*, 1999).

This paper reports on two series of experiments, one to measure the work and energy threshold and a second set of experiments to measure the properties and stability of the emulsions formed in the study one year ago. The energy threshold measurements were conducted by varying the rotational rate, and hence the energy of the apparatus used to make the emulsions. Work was varied by using different time periods of agitation at the same rotational energy. Analysis of the emulsions was conducted using rheological measurements as described herein and visual observations.

Emulsion Formation General - Emulsions were made in an end-over-end rotary mixer (Associated Design). The apparatus was located in a temperature controlled room at a constant 15 °C. The mixing vessels were 2.2 L FLPE wide-mouthed bottles (Nalge). The mixing vessels were approximately one-quarter full, with 600 mL salt water (3.3% w/v NaCl) and 30 mL of the sample crude oil or petroleum product. The vessels were mounted into the rotary mixer, and allowed to stand for several hours (usually three) to thermally equilibrate. The vessels were then rotated for 12 hours at a rate between 1 and 55 rpm. The resulting emulsions were then collected into Fleaker jars, covered, and stored in the same 15 degree cold room. Analysis was performed on the day of collection a short time after formation.

Emulsion Formation - Effect of Work - For the first study, water-in-oil emulsions were formed in 2.2 L fluorinated vessels on an end-over-end rotary mixer. 600 mL of salt water (3.3% w/v NaCl) is placed in each mixing vessel and allowed to stand in a temperature-controlled room at 15 °C overnight. 30 mL of oil is added to each vessel for a 1:20 oil: water ratio. The exception was Bunker C, which was adjusted to 60 mL. This was due to the low water content of Bunker C emulsions,

which prematurely depletes the supply of emulsion as a result of successive sampling. The vessels were sealed and placed in the rotary mixer such that the cap of each mixing vessel follows, rather than leads, the direction of rotation. The entire system was allowed to thermally equilibrate for a period of at least 30 minutes. The mixing was initiated at the rotational rate indicated for each experiment, either 10, 30 or 50 RPM. The rotation was stopped at each of the indicated sampling times, the sample characteristics observed, and sufficient sample collected to perform water content analysis and rheological measurements. Rotation and timing was then resumed. The test period ran for a total of 24 hours or for the specified time period.

Rheology - The following apparatuses were used for rheological analysis: Haake RS100 RheoStress rheometer, IBM-compatible PC with RheoStress RS Ver. 2.10 P software, 35 mm parallel plates with corresponding base plates, and a circulating bath maintained at 15.0 °C. Analysis was performed on a sample spread onto the base plate and raised to 2.00 mm from the measuring plate, with the excess removed using a teflon spatula. This was left for 15 minutes to thermally equilibrate at 15 °C.

Forced Oscillation - A stress sweep at a frequency of 1 reciprocal second was performed first to determine the linear viscoelastic range (stress independent region) for frequency analysis. This also provides values for the complex modulus, the elasticity and viscosity moduli, the low shear dynamic viscosity, and the $\tan(\delta)$ value. A frequency sweep was then performed at a stress value within the linear viscoelastic range, ranging from 0.04 to 40 Hz. This provides the data for analysis to determine the constants of the Ostwald-de-Waele equation for the emulsion.

Complex Modulus - The complex modulus is a measure of the overall resistance of the material to flow under an applied stress, in units of force per unit area. This combines the elements of viscosity and elasticity for a viscoelastic material such as water-in-oil emulsions. The complex modulus is measured on an RS100 RheoStress rheometer using a 35 mm plate-plate geometry. A stress sweep is performed in the range 25 to 1,000,000 mPa in the oscillation mode at a frequency of 1 Hz. The resulting complex modulus in the linear portion of the range is reported.

Viscosities - The apparent dynamic viscosity was determined on the plate-plate apparatus as well in some cases, and corrected for their non-Newtonian behaviour using the Weissenberg equation. A shear rate of 1 reciprocal second was employed for a period of one minute, without ramping.

For characterization of apparent viscosity, the concentric cylinder geometry was used. This consisted of the Haake Roto visco RV20 with M5 measuring system, Haake Rheocontroller RC20 and PC with dedicated software package Roto Visco 2.2. The spindle and cup used were the SVI spindle and SV cup. The shear rate was one reciprocal second. The viscometer was operated with the following ramp times: one minute to target shear rate (1/s), one minute at target shear rate (1/s). The temperature was maintained at 15 °C. Fifteen minutes was allowed for the sample to thermally equilibrate.

Water Content - A Metrohm 701 KF Titrino Karl-Fischer volumetric titrator and Metrohm 703 Ti Stand were used. The reagent was Aquastar Comp 5 and the solvent, 1:1:2 Methanol:Chloroform:Toluene. The titre was standardized according to the written procedure and the solvent blanked. The emulsion sample was stirred to achieve a relatively homogeneous mixture. A 1 mL plastic syringe was filled with

emulsion, while avoiding free water pockets present in the sample. All but 0.1 mL of sample was ejected. This removed most of the free water from the more viscous emulsion. The sample syringe was weighed and injected into the reaction vessel, being careful the sample went into the solution and not onto the vessel walls. The syringe was reweighed and the difference of weight entered into the titrator. Titration was then initiated and then weight percentage of water was displayed.

3.0 Energy and Work Calculations

The general layout of the rotational device is shown in Figure 1.

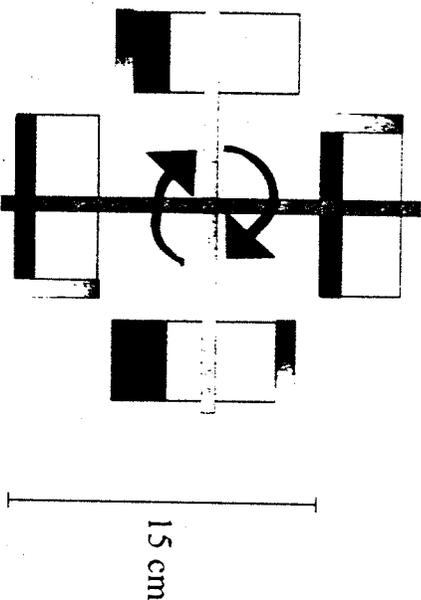


Figure 1 Diagram of the Emulsion Formation Device

The simple way to calculate the total energy exerted on the oil/water in the device is to calculate the total kinetic energy of the system.

The total kinetic energy in each bottle is given by:

$$KE = \frac{1}{2} MV^2$$

Where: KE is the energy in ergs

M is the mass in grams, here approximately 620 g of water and oil

V is the velocity in cm/s which is $2\pi r$ - which is $\text{rpm}/60 \times 7.5 \text{ cm}$

(1)

Kinetic energy by this formula is then $196 \times \text{rpm}^2$ ergs. Ergs were used in this study because they are a much more convenient unit than the SIU Joules at these low energy levels. This simple formulation will be used to assign an energy level to each rotational velocity. Again, it is important to note that the energy estimated here is the total energy input to the system, and not turbulent energy which is the prime factor in emulsion formation.

Work can be defined by looking at the force applied to the system by gravity.

Since $F = ma$

where F = force applied to the system in newtons

m = mass which here is 0.62 kg

(2)

a = the acceleration of gravity which is 9.8 m/s^2
thus $F = 6.08 \text{ newtons}$

$$\text{Work} = F \times D$$

(3)

Where F = the force in newtons = 6.08

D = distance through which the force moves, here is the average height through which the water falls, which is $15/2 \text{ cm}$ or 0.075 m

Thus, work is $6.08 \times 0.075 \text{ J}$ per revolution of the apparatus or 0.456 J per revolution of the apparatus

4.0 Results and Discussion

The first part of this study involved measuring the emulsion formation thresholds at various rotational energies and various times. The rheological data associated with the energy and work threshold experiments are given in Table 1. The second column of Table 1 is the rotational rate of the formation vessel. The third column is the time of mixing until the measurement was taken. The fourth column is the complex modulus which is the vector sum of the viscosity and elasticity. The fifth column gives the water content of the emulsion. The sixth column shows stability of the emulsion which is the complex modulus divided by the starting oil viscosity (Fingas *et al.* 1998). The seventh column is the calculated kinetic energy applied to the system in ergs. The eighth column gives the work applied to the emulsions in J.

Observations were made on the appearance of the emulsions and were used to classify the emulsions. All of the stable emulsions remained intact over seven days in the laboratory. All of the meso-stable emulsions broke within three days into water, free oil and emulsion. The emulsion portion of these break-down fractions appears to be somewhat stable, although separate studies on this portion have not been performed because of the difficulty in separating these portions from the oil and water.

All entrained water mixtures appeared to have larger suspended water droplets initially. The appearance of non-stable water in oil was just that, the oil appeared to be unchanged and a water layer was clearly visible.

The appearance of the oil/water through the process is very important in terms of understanding the process. Table 2 gives the observations reported for each series of experiments. It has also been noted that there is a progression in the formation of the emulsions. At the onset of agitation, a coarse mixture appearing like a sponge or foam, is formed. If a stable emulsion will be formed, this occurs quickly and did not appear to revert with the oils in this study. A meso-stable emulsion will form after about 20 minutes of agitation at low energy. In some cases, the meso-stable emulsion can change to a less stable 3-way, water-in-oil-in-water emulsion. Most often a meso-emulsion would remain as meso-stable. The coarse mixture often remains as such. In summary, a 'coarse mixture' is often formed near the beginning before any other type of water-in-oil state is observed. Stable emulsions, usually appear very rapidly and the coarse mixture is sometimes not observed, probably because it is only apparent for a very short period of time. Meso-stable emulsions appear about 20 minutes later and may stay as meso-stable emulsions, but some oils, under high energy, may break back down into a coarse mixture. The coarse mixture may convert into a 3-way water-in-oil-in-water emulsion which is not stable for longer than about one day until mixing ceases. The 3-way emulsions retain some of the characteristics of the

Table 1 Summary of Kinetic Results

Oil	Mixing Time Energy (min)	Complex Modulus (mPa)	Water Content (% w/w)	Stability (s)	Energy (ergs)	Work (J)
Sockeye	10	9.3E+03	73.6	210	19600	2700
	20	2.5E+04	79.8	540	19600	5500
	30	1.4E+05	83.9	3160	19600	8200
	60	1.7E+05	89.3	3870	19600	16400
	120	2.7E+05	90.1	6070	19600	32800
	360	3.8E+05	89.8	8500	19600	98500
	1440	9.7E+05	88.2	21440	19600	394000
	30	1.3E+05	85.1	2790	176400	8200
	20	3.0E+05	85.7	6670	176400	16400
	30	4.2E+05	85.7	9220	176400	24600
Punt Arguello Light	60	3.8E+05	86.1	8330	176400	49200
	120	4.5E+05	86.7	9890	176400	98500
	360	5.9E+05	87.8	13110	176400	295500
	1440	8.0E+05	87.9	17670	176400	1182000
	55	10 2.7E+05	82.2	6000	592900	15000
	20 6.6E+05	84.6	14670	592900	30100	
	30 7.9E+05	85.3	17440	592900	45100	
	60 1.2E+06	86.1	25780	592900	90300	
	120 1.9E+06	85.6	41330	592900	180600	
	360 2.9E+06	83.5	63330	592900	541700	
1440 4.7E+06	82.8	103330	592900	2166900		

Table 1 Summary of Kinetic Results

Oil	Mixing Time Energy (min)	Complex Modulus (mPa)	Water Content (% w/w)	Stability (s)	Energy (ergs)	Work (J)
Arabian Light	10	NM	73.4	NM	19600	2700
	20	NM	86.0	NM	19600	5500
	30	NM	NM	NM	19600	8200
	60	4.5E+03	83.6	320	19600	16400
	120	NM	76.4	NM	19600	32800
	360	NM	76.6	NM	19600	98500
	1440	8.0E+03	77.0	570	19600	394000
	30	NM	79.3	NM	176400	8200
	20 2.1E+04	83.8	1460	176400	16400	
	30 1.4E+04	84.1	1020	176400	24600	
Green Canyon 65, 7.7% weathered	60 1.8E+04	83.0	1250	176400	49200	
	120 4.7E+04	83.5	3360	176400	98500	
	360 8.6E+04	86.8	6140	176400	295500	
	1440 1.0E+05	85.9	7210	176400	1182000	
	55	10 3.0E+04	80.6	2130	592900	15000
	20 5.8E+04	90.0	4110	592900	30100	
	30 5.8E+04	90.2	4110	592900	45100	
	60 1.8E+05	89.4	13180	592900	90300	
	120 1.9E+05	90.9	13360	592900	180600	
	360 1.8E+05	89.1	12640	592900	541700	
1440 2.0E+05	87.3	14110	592900	2166900		

Table 1 Summary of Kinetic Results

Oil	Mixing Time Energy (min)	Complex Modulus (mPa)	Water Content (% w/w)	Stability (s ⁻¹)	Energy (ergs)	Work (J)
Sockeye Sweet, 17% weathered	10	10 8.2E+03	67.7	80	19600	2700
		20 1.2E+04	72.4	110	19600	5500
		30 2.0E+04	76.9	200	19600	8200
		60 4.4E+04	88.9	420	19600	16400
		120 6.4E+04	90.3	620	19600	32800
		360 9.0E+04	91.5	870	19600	98500
	30	1440 1.0E+05	95.2	1000	19600	394000
		10 1.1E+04	64.3	110	176400	8200
		20 2.1E+04	75.7	210	176400	16400
		30 2.9E+04	76.6	280	176400	24600
		60 4.1E+04	79.7	400	176400	49200
		120 8.0E+04	87.7	780	176400	98500
Bunker C (1987)	55	360 9.0E+04	90.1	870	176400	295500
		1440 9.4E+04	93.0	910	176400	1182000
		10 3.8E+04	78.2	370	592900	15000
		20 5.4E+04	79.2	520	592900	30100
		30 6.2E+04	82.4	600	592900	45100
		60 7.8E+04	82.8	750	592900	90300
	10	120 9.0E+04	81.0	870	592900	180800
		360 9.0E+04	80.4	870	592900	541700
		1440 8.4E+04	83.8	820	592900	2166900
		10 NM	2.3	NM	19600	2700
		20 NM	3.2	NM	19600	5500
		30 NM	2.6	NM	19600	8200
30	60 NM	6.8	NM	19600	16400	
	120 NM	6.3	NM	19600	32800	
	360 NM	9.6	NM	19600	98500	
	1440 4.5E+05	31.9	10	19600	394000	
	10 4.5E+05	4.4	10	176400	8200	
	20 NM	4.1	NM	176400	16400	
	30 NM	9.4	NM	176400	24600	
	60 NM	8.9	NM	176400	49200	
	120 3.8E+05	12.4	10	176400	98500	
	360 4.0E+05	20.6	10	176400	295500	
	1440 5.5E+05	36.7	10	176400	1182000	
	55	10 4.5E+05	5.7	10	592900	15000
20 NM		4.2	NM	592900	30100	
30 NM		NM	NM	592900	45100	
60 NM		5.8	NM	592900	90300	
120 NM		5.8	NM	592900	180800	
360 3.9E+05		12.0	10	592900	541700	
1440 6.2E+05		24.7	10	592900	2166900	

Table 2

General Observations of the Emulsion Formation Over Time at Three Rates of Mixing

Stable Emulsions

Sockeye

55 RPM
The oil rapidly emulsified and attained elastic properties in less than five minutes. By 30 minutes, it was characterized by a pasty quality, turning to a reddish brown by 60 minutes. At the 6 hour mark, it was a lighter brown and was segregating into smaller clumps. By 24 hours the mass consisted of small (about 1 cm), semi-solid pellets.

30 RPM

The emulsion formed at the 10 minute observation time consisted of large water droplets surrounded by a web of emulsion, described here as "coarse" emulsion due to its wide range of particle size distribution up to 3 mm diameter size. This quickly changed by the 20 minute mark to demonstrate more elastic properties. The colour was lighter at 30 minutes, and the emulsion resided primarily on the vessel walls. At 2 hours, there were small batches of emulsion in the water. The completion of the experiment at 24 hours revealed a mix of light reddish brown emulsion in the water, and darker patches of emulsion on the walls.

10 RPM

A coarse emulsion, as described above, formed within 10 minutes. Elasticity was observed at 30 minutes. By 60 minutes the emulsion was chocolate brown, moderately stable with some water resolution. The colour was lighter at 6 hours, and by the end of the 24 hour period there was a ball of light brown semi-solid emulsion in the water, with dark smears of emulsion on the walls.

Point Arguello Light

55 RPM
The oil rapidly emulsified and attained elastic properties in less than 10 minutes, becoming pasty in quality. This appeared essentially the same for the first 2 hours, becoming lighter in colour at the 6 hour mark, and at the end of the experiment. The changes in appearance were only small.

30 RPM

The emulsion formed at the 10 minute observation time was coarse, as described above. There was water resolved to yield foam over water. The emulsion improved until at 30 minutes it possessed a pasty quality. The colour became lighter by the 6 hour observation, and ended essentially the same in appearance.

10 RPM

The coarse emulsion generated at the 10 minute observation point rapidly resolved to water. The droplet size visibly decreases by the 30 minute mark, but still resolves water. At 60 minutes, all water was trapped into the emulsion, with no excess water present in the vessel. By the end of the experiment, excess water had reappeared in small quantity - perhaps 100 of the original 600 mL - but the appearance of the emulsion had not changed except for a lighter brown colour.

Emulsions Difficult to Classify

Arabian Light

55 RPM

The initial observation at 10 minutes revealed a very fluid, coarse black emulsion. The colour lightened by the 20 minute point, and became more elastic at 30 minutes. The emulsion was distributed about the walls, very

Table 2 - continued

little in the water. At 60 minutes the reddish brown colour had appeared, and remained essentially the same to the end. There was some water resolution from the emulsion at all sampling times, but the character of the emulsion that remains did not appear to change with the water loss. The second experiment under the same conditions was essentially the same until the final observation and sampling, at which point the emulsion was darker and seemed more fluid, qualitatively indicating a stability reversal. The measurements indicated similar complex modulus to the first experiment, but the water content had decreased. It had been observed in the past that Arabian Light can have dramatically different results between runs under the same test conditions, in those instances over a 12 hour mixing time. It would appear that there was an as yet unidentified process that was causing these variances.

30 RPM
The first observation at 10 minutes revealed a coarse emulsion that quickly broke to rag. This was the observed up until the 2 hour point, when the coarse emulsion decays to water and emulsion. At the end of experimentation, the emulsion was a dark brown but water was still gradually resolved. The second experiment under the same conditions showed essentially the same results up to the 2 hour mark, at which point the emulsion seemed to reverse, completely breaking by the end of the experiment. This appeared similar to, yet more dramatic, than the 55 RPM run.

10 RPM
The emulsion formed was essentially the same throughout the experiment, not changing from a coarse black emulsion that quickly resolved water, leaving rag over a layer of water.

Meso-stable Emulsions

(Green Canyon 7.7% (w/w) weathered

55 RPM
The emulsion formed was smeared on the walls, this was generally a coarse emulsion, decaying to water and emulsion. By 1 hour, there was a brownish colouration, but at the 2 hour observation point, the emulsion appears "fatigued". The emulsion had lost its ability to retain the large droplets characteristic of the coarse emulsion initially formed. The emulsion was mostly at the water surface, very little on the vessel walls. By 6 hours it was obvious that the emulsified layer on the surface was coming from droplets in the water. The system was a water-in-oil-in-water (w/o/w) emulsion. The analysis supports these observations, as the peak in the complex modulus was reached at the 1 hour sampling time, and drops thereafter. There was not a huge magnitude change in the complex modulus from the 10 minute to 60 minute to 2 hour fluctuation, but was lends support to the qualitative changes noted.

30 RPM
The coarse emulsion that was formed up to the 60 minute mark, had rapid resolution of water. At 60 minutes there was a brownish colouration to the emulsion smeared on the walls. By 2 hours, the emulsion on the walls was becoming pasty. At 6 hours there was a divergence by distribution, with the emulsion on the walls being a pasty smear, while the emulsion in the water can be characterized as a w/o/w emulsion. By the end of the experiment, all the emulsion resides in the water column as a w/o/w emulsion.

10 RPM
The initial observation at 10 minutes revealed a coarse mixture smeared on the vessel walls. This was consistent until the 1 hour observation, at which point the emulsion had a brown colouration, and appeared thicker and more

Table 2 continued

elastic. This was maintained until the end. At all sampling times, the emulsion decayed to water and emulsion upon standing.

Sockeye Sweet 17.7% (w/w) weathered

55 RPM
The emulsion formed was smeared on the walls, this was generally a coarse mixture, decaying to water and rag. By 30 minutes, there was a brownish colouration, but at the 2 hour observation point, the emulsion appeared "fatigued". The emulsion had lost its ability to retain the large droplets characteristic of the coarse emulsion initially formed. The emulsion was mostly in the water, very little on the vessel walls. By 6 hours it was obvious that the emulsified layer on the surface was coming from droplets in the water. The system was a water-in-oil-in-water (w/o/w) emulsion. The complex modulus did not change throughout this transition, indicating the water-in-oil emulsion in the water was not undergoing further change.

30 RPM
The initial observation at 10 minutes revealed a coarse emulsion smeared on the vessel walls. Beyond 60 minutes, the emulsion appears to become more elastic, although there was decay of the emulsion to water and emulsion at all sampling times.

10 RPM
The emulsion formed was smeared on the walls, this was generally a coarse mixture. By the 60 minute observation, it had become more elastic, appearing like a meringue. At the 2 hour mark, all water was entrapped in the emulsion. This remains the same to the end of the experiment. At all sampling times, there was water resolved from the emulsion.

Entrained Water

Bunker C

All RPM
A 60 mL sample was used for this oil, as the sampling regime would quickly deplete the supply due to the low water content of the samples. In all cases, the visual character of the sample did not change from the beginning to the 6 hour observation point. At the end of the experiments, there was a slight change in the malleability of the sample, as it was easier to cleave rather than spread like taffy.

emulsion from which they are formed, either a meso-stable or coarse mixture. 3-way emulsions do not convert into other water-in-oil states and break down after mixing ceases.

The stability and work of formation are plotted for the four oils in Figure 2. The stability in these figures is the complex modulus divided by the starting oil viscosity (Fingas *et al.* 1998). The latter reference traces the development of this index. In summary, the 'stability', as here defined, was found to be the only single parameter that could be used to describe the emulsions mathematically. Furthermore, stability was found to correlate very highly with other indices related to the formation of emulsions. Figure 2 corresponds to the previous figure in a paper one year ago, where only energy was varied (Fingas *et al.*, 1999). Because the time was not varied in the previous year's study, the energy was equivalent to the work applied to the oil. Thus essentially the same result was obtained.

Figure 3 shows the result of plotting the stability versus the energy. Only a scatter of points is obtained along a given energy level. Figure 3 was drawn using the data from Table 1 for Sockeye oil. Figure 4 shows the same data, however, stability is plotted against work. Figure 4 clearly shows the consistent relationship between stability and work. It is still clear, however, that a minimum energy level is necessary to produce the emulsion in the first instance. Increasing work then increases the stability of the emulsion, past the point of initiation. This effect can be seen especially in Arabian Light oil in Table 1. At the lowest energy level of 10 rpm, the complex modulus is too low to be measured in most instances and no increase with the amount of work is seen. At 55 rpm, the stability of the water-in-oil increases as work increases.

In the second part of the study, the emulsions formed during a study one year ago were re-analyzed to determine whether or not the parameters are the same one year later. The data from this study are given in Table 3. The differences in the stability between the one-week time and the one-year time are highlighted. These differences are generally within 10%, but for some mixtures can be significantly greater. The stability of the emulsions one week after the time of formation is shown in Figure 5. Figure 6 shows the corresponding values one year later. As can be seen from these figures, the situation with the emulsions remains relatively the same. Stable emulsions remain stable emulsions and so on. The emulsions of water-in-oil states lose water and some stability over the year, but do not change state. Arabian Light emulsion loses enough stability that it may be unstable after one year. This is the only oil that showed this effect.

5.0 Conclusions

Four, clearly-defined states of water-in-oil have been shown to be defined by a number of measurements and by their visual appearance, on the day of formation, one week later, and one year later. This study shows that the energy to the onset of the three states known as stable, meso-stable and entrained water, is very low, 300 to about 1500 ergs, corresponding to a rotational rate in the formation apparatus of about 1 to 3 rpm. Turbulent energy could not be measured. Work was varied from 1 to 5123 J.s. It was found that although a minimum energy threshold is necessary for most emulsion formation, that only work correlates with the value of stability. This has clear implications for the formation of emulsions at sea, where a given energy

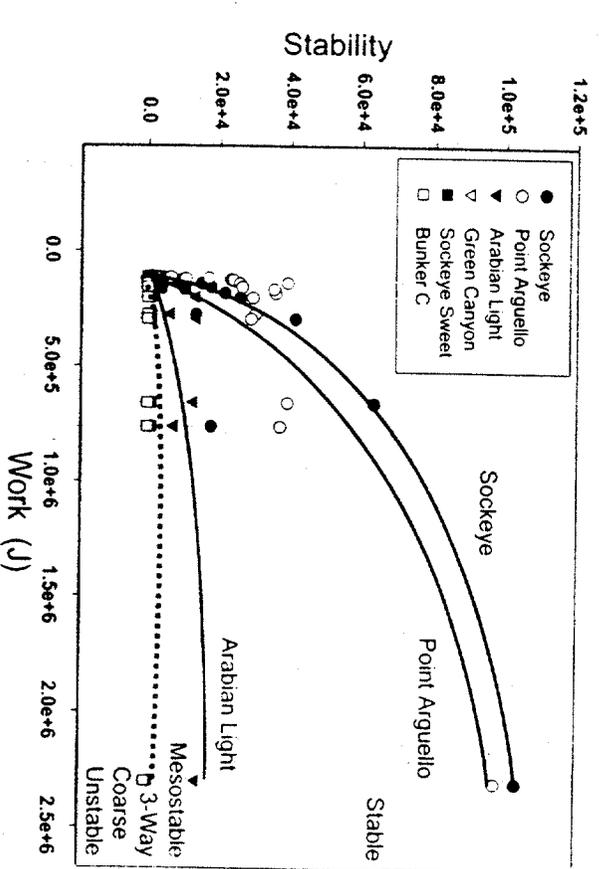


Figure 2 Stability versus Work for Six Oils

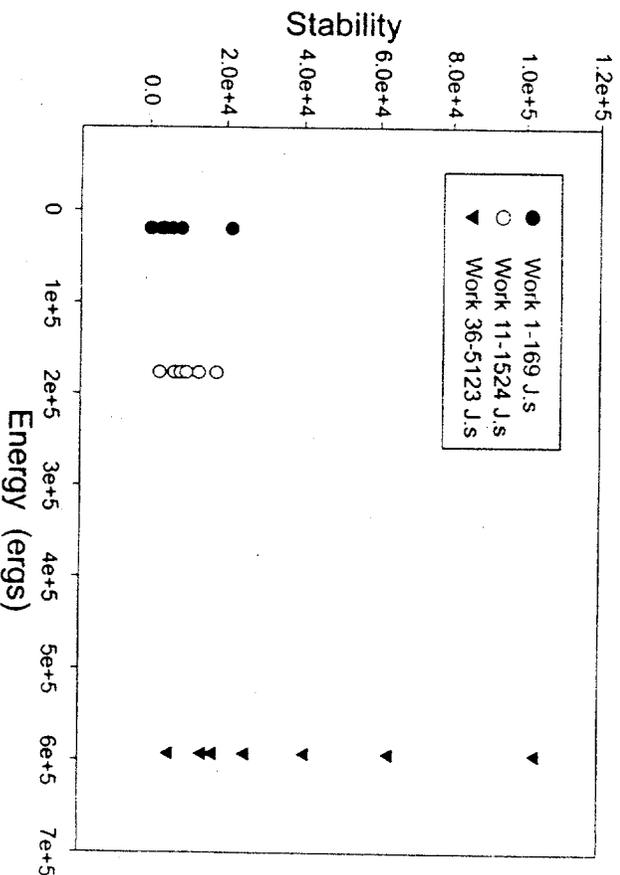


Figure 3 Stability versus Energy for Sockeye

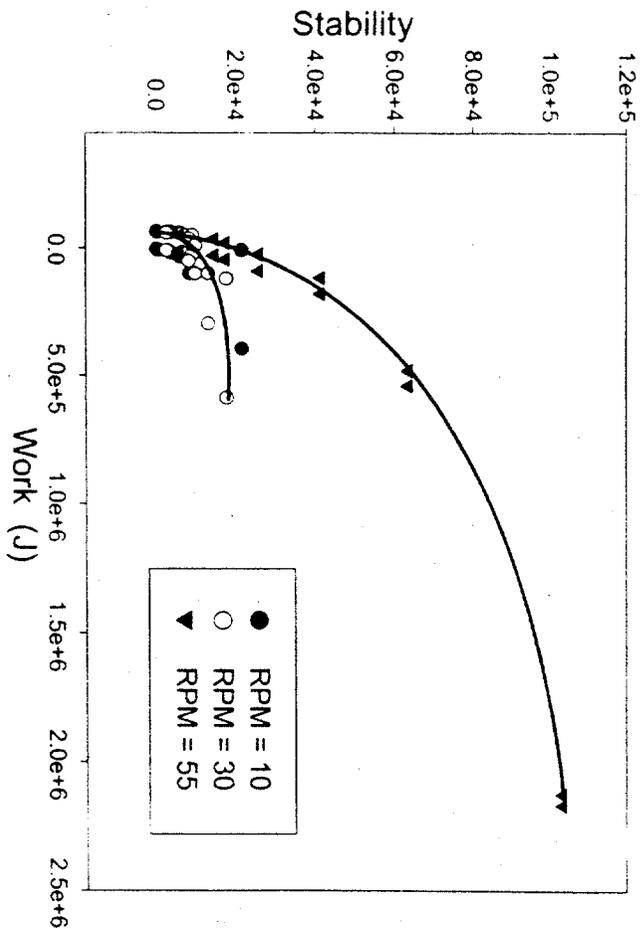


Figure 4 Stability versus Work for Sockeye

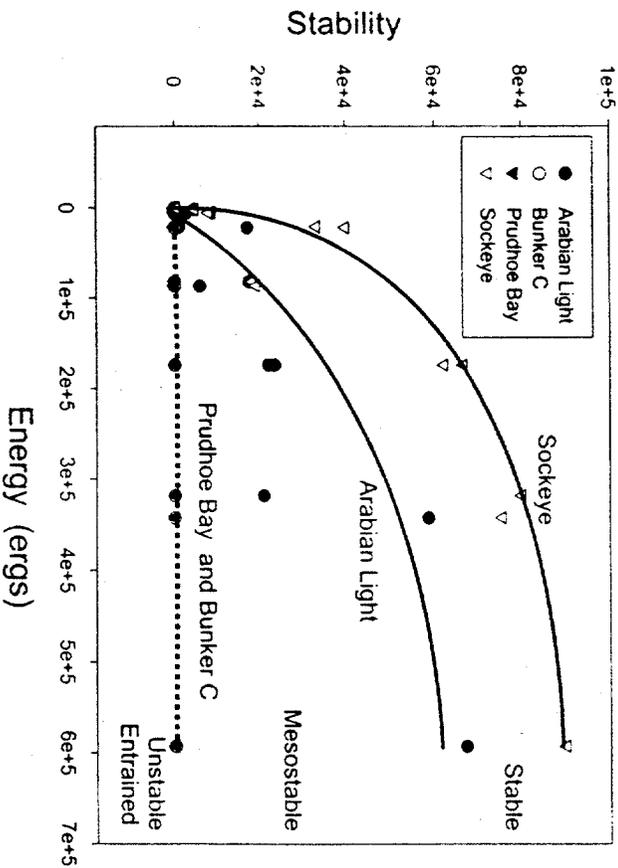


Figure 5 Stability versus Energy for Four Oils

Table 3 Results of Kinetic Studies

Oil	RPM	Energy ergs	Visual Stability	Properties at Formation			Properties One Year Later					Oil		
				Complex Modulus mPa	H ₂ O %(w/w)	Viscosity RV20 RS100	Stability s ⁻¹	Complex Modulus mPa	H ₂ O %(w/w)	Viscosity RV20	Stability s ⁻¹		Stability Difference	
Arabian Light	1.0	200	Unstable											
Arabian Light	1.3	330	Unstable				0.0E+00				0.0E+00	0.0E+00	14	
Arabian Light	2.8	1540	Unstable				0.0E+00				0.0E+00	0.0E+00	14	
Arabian Light	3.1	1880	Unstable				0.0E+00				0.0E+00	0.0E+00	14	
Arabian Light	5.1	5100	Stable	4.0E+04	84.73	4.9E+03	5.5E+03	6.7E+03	5.8E+03	0.58	3.5E+03	4.1E+02	-6.3E+03	14
Arabian Light	5.3	5510	Stable	8.2E+03	81.82		1.5E+03	1.4E+03	2.1E+03	2.29	4.4E+03	1.5E+02	-1.2E+03	14
Arabian Light	10.3	20790	Stable	1.5E+04	85.60	7.0E+03	4.2E+03	2.5E+03	5.5E+04	81.35	1.4E+04	3.9E+03	1.4E+03	14
Arabian Light	10.5	21610	Stable	2.4E+05	90.31		1.1E+03	4.0E+04	6.1E+04	34.98	5.1E+03	4.4E+03	-3.6E+04	14
Arabian Light	20.4	81570	Stable	2.5E+05	93.22	5.9E+04		4.1E+04	2.1E+03	0.27	4.9E+03	1.5E+02	-4.1E+04	14
Arabian Light	21.0	86440	Stable	8.3E+04	85.06		1.2E+04	1.4E+04	1.1E+05	80.47	1.9E+04	7.6E+03	-6.2E+03	14
Arabian Light	29.8	174060	Stable	3.1E+05	92.3		4.0E+04	5.2E+04	2.9E+04	73.08	1.7E+04	2.0E+03	-5.0E+04	14
Arabian Light	29.8	174060	Stable	3.3E+05	92.56	6.0E+04	5.0E+04	5.5E+04	1.1E+05	80.71	2.6E+04	8.1E+03	-4.7E+04	14
Arabian Light	39.8	310470	Stable	7.9E+05	91.58	9.1E+04		1.3E+05				0.0E+00	-1.3E+05	14
Arabian Light	39.8	310470	Stable	6.6E+05	90.73	1.0E+05		1.1E+05				0.0E+00	-1.1E+05	14
Arabian Light	40.3	318320	Stable	3.0E+05	92.06	5.9E+04	7.0E+04	4.9E+04	1.4E+05	81.16	2.4E+04	9.8E+03	-3.9E+04	14
Arabian Light	41.8	342460	Stable	8.2E+05	90.4		3.0E+04	1.4E+05	6.7E+04	80.39	1.9E+04	4.8E+03	-1.3E+05	14
Arabian Light	55	592900	Stable	9.4E+05	88.71	1.4E+05	5.0E+04	1.6E+05	2.0E+05	79.51	2.5E+04	1.4E+04	-1.4E+05	14
Bunker C	1.0	200	Entrained	2.2E+05	46.83		6.5E+04	3.7E+04	2.5E+05	21.87	1.0E+05	1.0E+01	-3.7E+04	45030
Bunker C	1.3	330	Entrained	2.4E+05	49.91	9.7E+04	9.0E+04	4.0E+04	4.4E+05	55.72	1.8E+05	1.0E+01	-4.0E+04	45030
Bunker C	2.8	1540	Entrained	3.6E+05	58.22		1.2E+05	6.0E+04	5.2E+05	57.81	2.1E+05	1.0E+01	-6.0E+04	45030
Bunker C	3.1	1880	Entrained	3.6E+05	61.72	1.5E+05	1.3E+05	6.0E+04	5.2E+05	64.14	1.9E+05	1.0E+01	-6.0E+04	45030
Bunker C	5.1	5100	Entrained	4.0E+05	60.32	1.7E+05	1.3E+05	6.7E+04	5.8E+05	61.86	2.4E+05	1.0E+01	-6.7E+04	45030
Bunker C	5.3	5510	Entrained	4.4E+05	62.96		1.3E+05	7.3E+04	6.2E+05	63.32	2.5E+05	1.0E+01	-7.3E+04	45030
Bunker C	10.3	20790	Entrained	2.9E+05	49.91	1.2E+05	1.0E+05	4.8E+04	4.8E+05	56.49	1.9E+05	1.0E+01	-4.8E+04	45030
Bunker C	10.5	21610	Entrained	3.6E+05	54.71		1.3E+05	6.0E+04	5.6E+05	64.59	2.3E+05	1.0E+01	-6.0E+04	45030
Bunker C	20.4	81570	Entrained	5.1E+05	64.80	1.7E+05		8.5E+04	7.1E+05	62.46	2.3E+05	2.0E+01	-8.5E+04	45030
Bunker C	21.0	86440	Entrained	4.5E+05	54.16		1.2E+05	7.5E+04	5.3E+05	54.39	3.0E+05	1.0E+01	-7.5E+04	45030
Bunker C	29.8	174060	Entrained	3.4E+05	48.89		9.5E+04	5.7E+04	4.7E+05	48.62	1.3E+05	1.0E+01	-5.7E+04	45030
Bunker C	29.8	174060	Entrained	3.5E+05	45.82	9.1E+04	8.5E+04	5.8E+04	4.7E+05	49.03	1.8E+05	1.0E+01	-5.8E+04	45030
Bunker C	40.3	318320	Entrained	3.8E+05	49.18	1.1E+05	9.5E+04	6.3E+04	5.4E+05	54.25	2.2E+05	1.0E+01	-6.3E+04	45030
Bunker C	41.8	342460	Entrained		47.46		1.1E+05	0.0E+00	5.7E+05	56.41	2.0E+05	1.0E+01	-1.0E+01	45030
Bunker C	55	592900	Entrained	3.9E+05	49.27	1.1E+05	1.1E+05	6.5E+04	7.4E+05	45.58	2.5E+05	2.0E+01	-6.5E+04	45030
Prudhoe Bay	1.0	200	Unstable				0.0E+00					0.0E+00	0.0E+00	900
Prudhoe Bay	1.3	330	Unstable				0.0E+00					0.0E+00	0.0E+00	900

Table 3 Results of Kinetic Studies

Oil	RPM	Energy ergs	Visual Stability	Properties at Formation				Properties One Year Later				Oil		
				Complex Modulus mPa	H ₂ O %(w/w)	Viscosity RV20 RS100		Stability s ⁻¹	Complex Modulus mPa	H ₂ O %(w/w)	Viscosity RV20		Stability s ⁻¹	Stability Difference
Prudhoe Bay	2.8	1540	Unstable					0.0E+00				0.0E+00	0.0E+00	900
Prudhoe Bay	3.1	1880	Unstable					0.0E+00				0.0E+00	0.0E+00	900
Prudhoe Bay	5.1	5100	Unstable					0.0E+00				0.0E+00	0.0E+00	900
Prudhoe Bay	5.3	5510	Unstable					0.0E+00				0.0E+00	0.0E+00	900
Prudhoe Bay	10.3	20790	Unstable					0.0E+00				0.0E+00	0.0E+00	900
Prudhoe Bay	10.5	21610	Unstable					0.0E+00				0.0E+00	0.0E+00	900
Prudhoe Bay	20.4	81570	Unstable					0.0E+00				0.0E+00	0.0E+00	900
Prudhoe Bay	21.0	86440	Unstable					0.0E+00				0.0E+00	0.0E+00	900
Prudhoe Bay	29.8	174060	Unstable					0.0E+00				0.0E+00	0.0E+00	900
Prudhoe Bay	29.8	174060	Unstable					0.0E+00				0.0E+00	0.0E+00	900
Prudhoe Bay	40.3	318320	Meso	8.8E+03	28.49	5.1E+03		1.5E+03	4.0E+03	16.23	6.0E+03	0.0E+00	-1.5E+03	900
Prudhoe Bay	41.8	342460	Meso	8.2E+03	72.52		1.3E+03	1.4E+03	3.8E+03	14.94	4.7E+03	0.0E+00	-1.4E+03	900
Prudhoe Bay	55	592900	Meso	4.2E+03	55.81	6.7E+03	4.0E+02	7.0E+02	2.7E+04	37.35		3.0E+01	-6.7E+02	900
Sockeye	1.0	200	Unstable					0.0E+00				0.0E+00	0.0E+00	45
Sockeye	1.3	330	Stable	1.4E+04	82.39	7.6E+03	3.0E+04	2.3E+03	1.3E+05	69.48	5.5E+04	2.8E+03	4.5E+02	45
Sockeye	2.8	1540	Stable	1.7E+05	89.45		2.5E+05	2.8E+04	2.0E+05	80.57	5.0E+04	4.4E+03	-2.4E+04	45
Sockeye	3.1	1880	Stable	2.1E+05	90.92	2.7E+04	2.0E+04	3.5E+04	3.5E+05	80.69	7.6E+04	7.8E+03	-2.7E+04	45
Sockeye	5.1	5100	Stable	3.9E+05	92.60	5.4E+04	7.0E+04	6.5E+04	3.3E+05	80.59	6.1E+04	7.2E+03	-5.8E+04	45
Sockeye	5.3	5510	Stable	3.6E+05	92.50		5.0E+04	6.0E+04	3.6E+05	81.71	1.1E+05	7.9E+03	-5.2E+04	45
Sockeye	10.3	20790	Stable	1.5E+06	90.57	4.0E+05	3.0E+05	2.5E+05	1.5E+06	81.38	3.5E+05	3.2E+04	-2.2E+05	45
Sockeye	10.5	21610	Stable	1.8E+06	90.56		2.8E+05	3.0E+05	1.5E+06	81.41	3.1E+05	3.2E+04	-2.7E+05	45
Sockeye	20.4	81570	Stable	8.3E+05	92.03	2.3E+05		1.4E+05	1.1E+06	81.48	2.2E+05	2.4E+04	-1.1E+05	45
Sockeye	20.7	83980	Stable	1.2E+06	90.51	2.8E+05		2.0E+05				0.0E+00	-2.0E+05	45
Sockeye	20.7	83980	Stable	7.6E+05	91.23	2.1E+05		1.3E+05				0.0E+00	-1.3E+05	45
Sockeye	21.0	86440	Stable	8.7E+05	91.31		1.6E+05	1.5E+05	7.7E+05	80.88	1.7E+05	1.7E+04	-1.3E+05	45
Sockeye	29.8	174060	Stable	2.8E+06	89.12		3.5E+05	4.7E+05	2.0E+06	81.48	5.2E+05	4.3E+04	-4.2E+05	45
Sockeye	29.8	174060	Stable	3.0E+06	88.17	6.6E+05	5.0E+05	5.0E+05	2.3E+06	82.38	4.5E+05	5.1E+04	-4.5E+05	45
Sockeye	40.3	318320	Stable	3.6E+06	88.95	9.2E+05	3.0E+05	6.0E+05	2.3E+06	83.49	4.4E+05	5.1E+04	-5.5E+05	45
Sockeye	41.8	342460	Stable	3.4E+06	87.95		4.0E+05	5.7E+05	2.6E+06	83.69	4.7E+05	5.7E+04	-5.1E+05	45
Sockeye	55	592900	Stable	4.1E+06	86.44	7.6E+05	5.8E+05	6.8E+05	3.3E+06	80.22	7.7E+05	7.3E+04	-6.0E+05	45
Sockeye 1:30	3.1		Stable	3.9E+05	91.99	1.0E+05	7.5E+04		5.5E+05	78.12	7.6E+04			
Sockeye 1:30	5.1		Stable	8.4E+05	92.15	1.5E+05	1.5E+05		1.2E+06	79.76	1.1E+05			

level corresponding to turbulent energy at sea would sometimes require a period of time before a given water-in-oil state would be produced. Importantly, the work (energy expended over time) correlates most closely with the stability of the emulsion or water-in-oil state.

It has also been noted that there is a progression in the formation of the emulsions. At the onset of agitation, a coarse mixture appearing like a sponge, is formed. If a stable emulsion will be formed, this occurs quickly and was not observed to revert with the oils in this study. A meso-stable emulsion will form after about 20 minutes of agitation at low energy. In some cases, the meso-stable emulsion can change to a 3-way, water-in-oil-in water emulsion. Most often a meso-emulsion would remain as meso-stable. The coarse mixture usually remains as such until mixing ceases, however, in the case of some oils it also forms a 3-way emulsion. The possible pathways and approximate timing are illustrated in Figure 7.

6.0 References

Fingas, M.F., B. Fieldhouse and J.V. Mullin, "Studies of Water-in-Oil Emulsions: Energy Threshold of Emulsion Formation", in *Proceedings of the Twenty-Second Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 57-68, 1999.

Jokuty, P., S. Whittier, Z. Wang, M.F. Fingas, B. Fieldhouse, P. Lambert and J. Mullin, *Properties of Crude Oils and Oil Products*, (Volume 1, A-K; Volume 2, L-Z), Environment Canada Manuscript Report Number EE-165, Ottawa, Ontario, 1999.

McLean, J.D. and P.K. Kilpatrick, "Effects of Asphaltene Solvency on Stability of Water-in-Oil Emulsions", *Journal of Colloid and Interface Science*, Vol. 189, pp. 242-253, 1997a.

McLean, J.D. and P.K. Kilpatrick, "Effects of Asphaltene Aggregation in Model Heptane-Toluene Mixtures on Stability of Water-in-Oil Emulsions", *Journal of Colloid and Interface Science*, Vol. 196, pp. 23-34, 1997b.

Sjöblom, J., and H. Færdedal, "Flocculation and Coalescence in Emulsions as Studied by Dielectric Spectroscopy", in *Emulsions and Emulsion Stability*, ed. Johan Sjöblom, Marcel Dekker, New York, pp. 393-435, 1996.

**Methodology for Assessing Oil W
Evolution of the Phy
Dispersibili**

Julien Guyom

29604 Bre
Julien Gu

Abstract

When spilled at sea, crude oil evaporation, emulsification, dispersion under natural conditions due to sea surface and exposure of the oil to solar light, properties of the oil are constantly changing. Understanding these changes is a key to optimizing the response options, and preventing an oil spill.

The objective of this study was to simulate the evolution of crude oils from different oil fields, realistically simulated in Cedre's hydrodynamic conditions: wind, waves, and currents. The parameters measured or assessed were: density, viscosity, emulsification, chemical composition, emulsion stability, oil adhesion, and oil degradation.

1.0 Introduction

Various weathering processes (photo-oxidation) occur under natural conditions at sea. The chemical composition and physical properties of the oil change gradually, its density increases, and its viscosity decreases. The oil remaining on the water surface is oxidized by solar UV. Oil can get incorporated into the environment. The behavior of the oil in the environment is a function of that of the original oil.

- Understanding these changes is a key to optimizing the emergency response. Each spill entails a series of questions:
- What is the fate of the pollutant at sea?
 - Is natural dispersion possible?
 - Does the oil emulsify? What is the emulsion stability?
 - Is the oil chemically dispersible?
 - Is the oil likely to be mechanically dispersed?

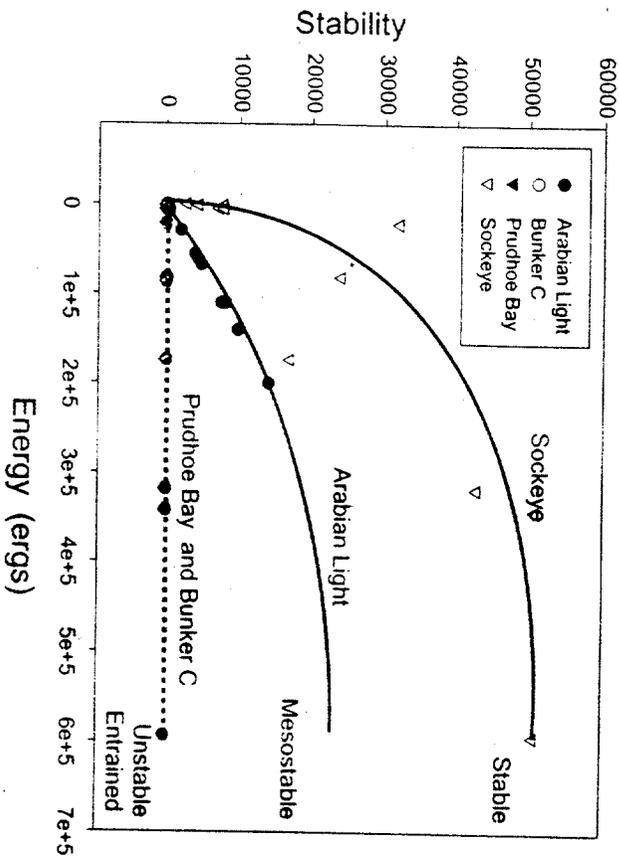


Figure 6 Stability versus Energy for Four Oils After One Year

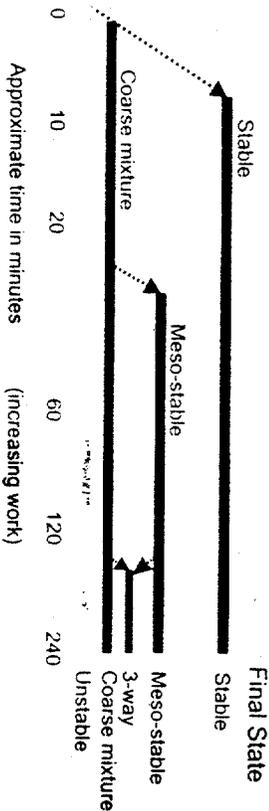


Figure 7 The Overall Concept of State and Approximate Kinetics in Emulsion and Water-in-oil State Formation