



Research

Studies of the formation process of water-in-oil emulsions

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Abstract

This paper summarizes studies to determine the formation process of water-in-oil emulsions and the stability of such emulsions formed in the laboratory and in a large test tank. These studies have confirmed that water-in-oil mixtures can be grouped into four states: stable emulsions, unstable water-in-oil mixtures, mesostable emulsions, and entrained water. These states are differentiated by rheological properties as well as by differences in visual appearance. The viscosity of a stable emulsion at a shear rate of one reciprocal second is about three orders of magnitude greater than that of the starting oil. An unstable emulsion usually has a viscosity no more than about 20 times greater than that of the starting oil. A stable emulsion has a significant elasticity, whereas an unstable emulsion does not. A mesostable emulsion has properties between stable and unstable, but breaks down within a few days of standing. The usual situation is that emulsions are either obviously stable, mesostable, or unstable. Entrained water, water suspended in oil by viscous forces alone, is also evident. Very few emulsions have questionable stability. Analytical techniques were developed to test these observations.

The type of emulsion produced is determined primarily by the properties of the starting oil. The most important of these properties are the asphaltene and resin content and the viscosity of the oil. The composition and property ranges of the starting oil that would be required to form each of the water-in-oil states are discussed in this paper.

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1. Introduction

Emulsification is the process whereby water-in-oil emulsions are formed. These emulsions are often called “chocolate mousse” or “mousse” by oil spill workers. When emulsions form, the properties and characteristics of oil spills change significantly. For example, stable emulsions contain from 60% to 80% water, thus expanding the volume of the spilled material from two to five times the original volume. The density of the resulting emulsion can be as great as 1.03 g/ml compared to a starting density as low as 0.80 g/ml. Most significantly, the viscosity of the oil typically changes from a few 100 to about 100,000 mPa s, a typical increase of 1000. A liquid product is thereby changed to a heavy, semi-solid material.

Many researchers feel that emulsification is the second most important behavioural characteristic of oil after evaporation. Emulsification significantly affects the behaviour of oil spills at sea. As a result of emulsification, evaporation of oil spills slows by orders of magnitude, spreading slows by similar rates, and the oil rides lower in the water column, showing different drag with respect to the wind. Emulsification also significantly affects other aspects of a spill, such as cleanup response. Spill countermeasures are quite different for emulsions as they are hard to recover mechanically, to treat, or to burn.

The availability of methodologies to study emulsions is very important. In the past 10 years, both dielectric methods and rheological methods have been exploited to study formation mechanisms and stability of emulsions made from many different types of oils (Sjöblom et al., 1994; Fingas et al., 1998). Standard chemical techniques, including nuclear magnetic resonance, chemical analysis techniques, microscopy, interfacial pressure, and interfacial tension, are also being applied to emulsions. These

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techniques have largely confirmed findings noted in the dielectric and rheological mechanisms.

The mechanism and dynamics of emulsification were poorly understood until the 1990s. It was not recognized until recently that the basics of water-in-oil emulsification were understood in the surfactant industry, but not in the oil spill industry. In the late 1960s, Berridge et al. (1968) were the first to describe emulsification in detail and measured several physical properties of emulsions. Berridge described the emulsions as forming because of the asphaltene and resin content of the oil. Bridie et al. (1980) studied emulsions and proposed that the asphaltenes and waxes in the oil stabilized water-in-oil emulsions. The wax and asphaltene content of two test oils correlated with the formation of emulsions in a laboratory test. Mackay and coworkers hypothesized that emulsion stability was due to the formation of a film in oil that resisted water droplet coalescence (Mackay and Zagorski, 1982). The nature of these thin films was not described, but it was proposed that they were caused by the accumulation of certain types of compounds. Mackay and Nowak studied emulsions and found that stable emulsions had low conductivity and therefore a continuous phase of oil (Mackay and Nowak, 1984). Stability was discussed and it was proposed that it was a function of oil composition, particularly waxes and asphaltenes. It was proposed that a water droplet could be stabilized by waxes, asphaltenes, or a combination of both. The viscosity of the resulting emulsions was correlated with water content.

In 1992, Schramm reviewed the basics of emulsions and provided the oil spill industry with the basis for much subsequent understanding of water-in-oil emulsions (Schramm, 1992). In 1993, Becher reviewed emulsion stability in mathematical terms (Becher, 1993). Sjöblom and coworkers surveyed several oils from the Norwegian continental shelf. After the interfacially active fraction was removed from the oils, none would form water-in-oil emulsions (Sjöblom et al., 1992). Model emulsions could be made from the extracted interfacially active fractions. Stability was gauged by measuring the separation of water over time. Destabilization studies showed that the rigidity of the interfacial film or reaction with the film components are the principle methods of emulsion breakdown. Medium chain alcohols and amines destabilized emulsions the most.

In 1992, Friberg reviewed the stability of emulsions, noting that a primary measure of stability is the separation into two phases (Friberg, 1992). Friberg noted the focus on two factors, the rheology of the continuous phase and the barrier between the dispersed droplets. It was demonstrated that an increase in viscosity of the continuous phase of the emulsion is not a viable alternative to increasing the half-life of the emulsion. Friberg noted that the continuous phase must show a small yield value in order to demonstrate stability.

More than 30 years ago, it was found that asphaltenes were a major factor in emulsion stability (Berridge et al., 1968). Specific roles of emulsions have not been defined until recently. The Sjöblom group in Norway defined the interfacial properties of asphaltenes in several local offshore crudes (Nordli et al., 1991). Asphaltenes were separated from the oils using consecutive separations involving absorption to silica. Molecular weights ranged from 950 to 1450 Da. Elemental analysis revealed that 99 mol% of the asphaltenes was carbon and hydrogen, while up to 1% was nitrogen, oxygen, and/or sulphur. The films form monomolecular layers at the air/water interface. Aromatic solvents such as benzylalcohol have a strong influence on the asphaltenes and will destabilize water-in-oil emulsions. Asphaltenes were shown to be the agent responsible for stabilizing the Norwegian crudes tested.

Acevedo et al. (1993) studied the interfacial behaviour of a Cerro Negro crude by a planar rheology. Distilled water and salt water were used with a 30% and a 3.2% xylene-diluted crude. The elasticity and viscosity were obtained from creep compliance measurements. The high values of viscoelastic and elastic moduli were attributed to the flocculation of asphaltene:resin micelles at the interface. The high moduli were associated with the elastic interface. In the absence of resins, asphaltenes were not dispersed and did not form stable interface layers and then, by implication, stable emulsions.

Urdahl and Sjöblom (1995) studied stabilization and destabilization of water-in-crude oil emulsions. It was concluded that indigenous, interfacially active components in the crude oils are responsible for stabilization. These fractions would be the asphaltenes and resins. Model systems stabilized by extracted interfacially active components had stability properties similar to the crude oil emulsions. The same group studied the ageing of the interfacial components (Sjöblom et al., 1995). Resins and asphaltenes were extracted from North Sea crudes and exposed to ageing under normal atmospheric and ultraviolet conditions. The FT-IR spectra shows that the carbonyl peak grew significantly as indicated by the C=O mode. Spectra also showed that condensation was occurring. The interfacial activity increased in all fractions as the ageing process proceeded. In the case of two crude oils, the ageing was accompanied by an increase in the stability of the water/oil emulsion.

McLean and Kilpatrick (1997a) studied asphaltene aggregation in model emulsions made from heptane and toluene. The resins and asphaltenes were extracted from four different crude oils—two from Saudi Arabia, Alaskan North Slope, and San Joaquin Valley crudes. The asphaltenes were extracted using heptane and the resins were extracted using open-column silica columns. Asphaltenes dissolved in heptol consisting of only about 0.5% asphaltenes generated more stable emulsions than those generated by the originating crude oils. Although

some emulsions could be generated using resins, they were much less stable than those generated by asphaltenes. The model emulsions showed that the aromaticity of the crude medium was a prime factor. This was adjusted by varying the heptane:toluene ratio. It was also found that the concentration of asphaltenes and the availability of solvating resins were important. The model emulsions were most stable when the crude medium was between 30% and 40% toluene and with low resin:asphaltene ratios.

McLean and Kilpatrick (1997b) put forward the thesis that asphaltenes were the most effective in stabilizing emulsions when they are near the point of incipient precipitation. It was noted that there are specific resin–asphaltene interactions, as differing combinations yielded different results in the model emulsions. The resins and asphaltenes were characterized by elemental and neutron activation analyses. The most effective emulsion stabilizers of the resins and asphaltenes were the most polar and the most condensed. McLean and Kilpatrick concluded that the most significant factor in emulsion formation is the solubility state of asphaltenes.

McLean et al. (1998) subsequently reviewed emulsions and concluded that the asphaltene content is the single most important factor in the formation of emulsions. Even in the absence of any other synergistic compounds (i.e., resins, waxes, and aromatics), asphaltenes were found to be capable of forming rigid, cross-linked, elastic films which are the primary agents in stabilizing water-in-crude oil emulsions. It was noted that the exact conformations in which asphaltenes organize at oil–water interfaces and the corresponding intermolecular interactions have not been elucidated. McLean and colleagues suggest that the intermolecular interactions must be either π -bonds between fused aromatic sheets, H-bonds mediated by carboxyl, pyrrolic, and sulfoxide functional groups, or electron donor–acceptor interactions mediated by porphyrin rings, heavy metals, or heteroatomic functional groups.

Sjöblom et al. (1999) used dielectric spectroscopy to study emulsions over a period of years. They concluded that the asphaltenes, not the resins, are the stabilizing fraction in water-in-oil emulsions. It was noted, however, that some resins must be present to give rise to stability. It is suggested that the greater mobility of the resins is needed to stabilize the emulsions until the asphaltenes, which migrate slowly, can align at the interface and stabilize the emulsions.

Dielectric spectroscopy is one of the methods used to study emulsions. The permittivity of the emulsion can be used to characterize an emulsion and assign a stability (Sjöblom et al., 1999). The Sjöblom group has measured the dielectric spectra using the time domain spectroscopy technique. A sample is placed at the end of a coaxial line to measure total reflection. Reflected pulses are observed in time windows of 20 ns, Fourier transformed

in the frequency range from 50 MHz to 2 GHz, and the complex permittivity calculated. Water or air can be used as reference samples.

Skodvin and Sjöblom (1996) used dielectric spectroscopy in conjunction with rheology to study a series of emulsions. A close connection was found between the viscosity and dielectric properties of the emulsions. The large effects of shear on both the static permittivity and the dielectric relaxation time for the emulsion was ascribed, at least in part, to the degree of flocculation in the emulsion system. At high-shear rates, at which emulsions are expected to have a low degree of flocculation and high stability, the dielectric properties still varied from those expected from a theoretical model for spherical emulsion droplets.

Førdeidal and coworkers used dielectric spectroscopy to study several actual crude oil emulsions and model systems stabilized with either separated asphaltenes and resins from crude oil or commercial surfactants (Førdeidal and Sjöblom, 1996). Emulsions could be stabilized with the asphaltene fraction alone, but not with the resin fraction alone. A study of a combination of mixtures shows an important interaction between emulsifying components. Analysis showed that the choice of organic solvent and the amount of asphaltenes, as well as the interaction between these variables, were the most significant parameters for determining the stability of the emulsions.

Tadros (1994) summarized the fundamental principles of emulsion rheology. Emulsions stabilized by surfactant films (such as resins and asphaltenes) behave like hard sphere dispersions. These dispersions display viscoelastic behaviour. Water-in-oil emulsions show a transition from a predominantly viscous to a predominantly elastic response as the frequency of oscillation exceeds a critical value. Thus, a relaxation time, which increases with the volume fraction of the discontinuous phase, can be determined for the system. At the critical value, the system shows a transition from predominantly viscous to predominantly elastic response. This reflects the increasing steric interaction with increases in volume of the discontinuous phase.

Ese et al. (1998) studied the film-forming properties of asphaltenes and resins using a Langmuir trough. Asphaltenes and resins were separated from different crude oils. It was found that the asphaltenes appear to pack closer at the water surface and form a more rigid surface than the resins. The size of asphaltene aggregates appears to increase when the spreading solvent becomes more aliphatic and with increasing asphaltene bulk concentration. Resin films show high compressibility, which indicates a collapse of the monomolecular film. A comparison between asphaltenes and resins shows that resins are more polar and do not aggregate to the same extent as the asphaltenes. Resins also show a high degree of sensitivity to oxidation. When resins and asphaltenes

are mixed, resins begin to dominate the film properties when they exceed about 40 wt.%.

Eley et al. (1988) studied the size of water droplets in emulsions using optical microscopy and found that the droplet sizes followed a log-normal distribution. The number mean diameters of the droplets varied from about 1.4–5.6 µm. Paczynska-Lahme (1990) studied several mesophases in petroleum using optical microscopy. Petroleum resins showed highly organized laminar structures and water-in-oil emulsions were generally unstructured, but sometimes hexagonal.

2. Studies on stability classes of water-in-oil emulsions

This section summarizes studies to measure the stability of water-in-oil emulsions and define characteristics of different stability classes. Four ‘states’ in which water can exist in oil will be described. These include: stable emulsions, mesostable emulsions, unstable emulsions (or simply water and oil), and entrained water. These four ‘states’ are differentiated by visual appearance as well as by rheological measures.

The most important characteristic of a water-in-oil emulsion is its ‘stability’. The reason for this is that one must first characterize an emulsion as stable (or unstable) before one can identify its properties. Properties were found to change significantly for each type of emulsion.

Studies in the past eight years have identified a class of very ‘stable’ emulsions characterized by their persistence over several months. The viscosity of these stable emulsions actually increases over time. The viscosity increase for stable emulsions is at least three orders of magnitude more than the starting oil. These emulsions have been monitored for as long as nine years in the laboratory.

Emulsions have been studied for many years (Bobra et al., 1992; Fingas et al., 1993, 1995–1999, 2000a,b, 2001a,b, 2002; Fingas and Fieldhouse, 1994). Both on the basis of the literature and experimental evidence, it was concluded that certain emulsions can be classed as stable. Some (if not all or many) stable emulsions increase in apparent viscosity with time, i.e., their elasticity increases. It is suspected that the stability derives from the strong viscoelastic interface caused by asphaltenes, perhaps along with resins. Increasing viscosity may be caused by increasing alignment of asphaltenes at the oil–water interface.

Mesostable emulsions are emulsions that have properties between stable and unstable emulsions (really oil/water mixtures) (Fingas et al., 1995). It is suspected that mesostable emulsions either lack sufficient asphaltenes to render them completely stable or still contain too many destabilizing materials, perhaps some aromatics and aliphatics. The viscosity of the oil may be high en-

ough to stabilize some water droplets for a period of time. Mesostable emulsions may degrade to form layers of oil and stable emulsions. Mesostable emulsions can be red or black.

Unstable emulsions are those that decompose (largely) to water and oil rapidly after mixing, generally within a few hours. Some water (usually less than about 10%) may be retained by the oil, especially if the oil is viscous. Unstable emulsions do not show the same increase in viscosity as stable emulsions. Their viscosity is less than about 20 times greater than the starting oil.

Forced oscillation rheometry studies are the most important measurements to characterize emulsions. The presence of significant elasticity clearly defines whether a stable emulsion has been formed. The viscosity by itself can be an indicator of the stability of the emulsion, although it is not necessarily conclusive, unless one knows the exact viscosity of the starting oil. Colour is an indicator, but may not be definitive. This laboratory’s experience is that all stable emulsions were reddish. Some mesostable emulsions had a reddish colour and unstable emulsions were always the colour of the starting oil (brown or black). Water content is not an indicator of stability and is error-prone because of ‘excess’ water that may be present. It should be noted, however, that stable emulsions contain more than 70% water and unstable emulsions or entrained water-in-oil generally contain less than 50% water. Water content after a period of about one week is found to be more reliable than initial water content because emulsions that are less stable will separate.

2.1. Summary of laboratory experiments

Detailed experimental procedures are given in the literature (Fingas et al., 1998, 2000a). Water-in-oil emulsions were made in a rotary agitator and the rheometric characteristics of these emulsions were then studied over time. Two hundred and four oils were used, taken from the storage facilities at the Emergencies Science and Technology Division. Properties of these oils are given in standard references (Jokuty et al., 1999).

Emulsions were made in an end-over-end rotary mixer (Associated Design). The apparatus was located in a temperature-controlled cold room at a constant 15 °C. The mixing vessels were 2.2 l FLPE wide-mouthed bottles. The mixing vessels were approximately one-quarter full, with 600 ml of 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 3 h to thermally equilibrate. The vessels were then rotated for 12 h at a rate of 55 rpm. The vessels were approximately 20 cm in height. The radius of rotation was about 10 cm. The resulting emulsions were then collected into jars, covered, and stored in the same 15 °C cold room. Analysis was per-

formed on the day of collection and again one week later.

The following apparatuses were used for rheological analysis: Haake RS100 RheoStress rheometer, IBM-compatible PC with RheoStress RS Ver. 2.10 P software, 35- and 60-mm parallel plates with corresponding base plates, clean air supply at 40 p.s.i., and a circulating bath maintained at 15 °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 min to thermally equilibrate at 15 °C. 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 Metrohm 701 KF Titrino Karl–Fischer volumetric titrator and Metrohm 703 Ti Stand were used to measure water content. The reagent was Aquastar Comp 5 and the solvent, 1:1:2 methanol:chloroform:toluene.

2.2. Laboratory results and discussion

The rheological data on the emulsions produced in this series of experiments are given in Table 1. The second column of the table lists the evaporation state of the oil in mass percent lost. The third column lists the assessment of the stability of the emulsion based on both visual appearance and rheological properties. The fourth column gives the stability which is the complex modulus divided by the viscosity of the starting oil. It is noted from this table that this parameter correlates quite well with the assigned behaviour of the oils. High stability parameters imply stable emulsions and low ones imply unstable emulsions. Stability has nominally the units of mPa/mPa s or s^{-1} . The viscosity of the emulsion is next and in column 6, the complex modulus which is the vector sum of the viscosity and elasticity. Column 7 lists the elasticity modulus and column 8, the viscosity modulus. In column 9, the isolated, low-shear viscosity is given. This is the viscosity of emulsion at very low-shear rate. In column 10, the $\tan \delta$, the ratio of the viscosity to the elasticity component, is given. Finally, the water content of the emulsion is presented. The table then provides the same data for the water-in-oil state one week after formation.

Observations were made on the appearance of the emulsions and were used to classify the emulsions. All of the stable emulsions appeared to be stable and remained intact over seven days in the laboratory. All of the mesostable emulsions broke into water, free oil, and emulsion within about 1–3 days. The emulsion portion of these broken down fractions appears to be somewhat stable, although separate studies have not been performed on this portion because of the difficulty in sep-

arating them from the oil and water. All entrained water appeared to have larger suspended water droplets. 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 properties of the starting oil and the various water-in-oil states are shown in Table 2. This indicates that the factor defined as emulsion stability can be used to discriminate among the various states of water-in-oil studied here. Although there are overlapping ranges, the differences are generally sufficient to act as a single-value discriminator. It is noted that there are different viscosity ranges for the different states. This shows that viscous forces are responsible for part of the stability, but that after the viscosity of the starting oil rises to a given point (about 20,000 mPa s), mesostable or stable emulsions are no longer produced. This may also explain an outstanding mystery, that of why Bunker C generally does not form emulsions. Especially after a short period of weathering, Bunker C is too viscous to form either stable or mesostable emulsions.

Table 2 also illustrates that the deviation from Newtonian behaviour is greatest for the stable emulsions, then for mesostable emulsions, with almost no deviation noted for the entrained and unstable cases. This is the result of a high elastic component to the viscosity, as evidenced by the elastic modulus and $\tan \delta$ for the stable emulsions and slightly for the mesostable emulsions. As would be expected, the water content correlates very highly with the state after one week. This is accentuated by the fact that mesostable emulsions and entrained water-in-oil have separated to a significant degree after this time.

Table 3 summarizes the properties of the water-in-oil states studied here. As can be seen, the properties of the starting oil differ somewhat for oils that form the various states. The properties of oil that form stable and mesostable emulsions are similar. These are oils of medium viscosity that contain a significant amount of resins and asphaltenes. Mesostable emulsions may form from oils that have higher or lower viscosities than oils that might form stable emulsions. Stable emulsions are more likely to form from those oils containing more asphaltenes than resins. Entrained water is likely to form from more viscous oils with relatively high densities. Oils of very high or very low viscosities (and densities) are unlikely to uptake water in any form. These oils typically have no asphaltenes or resins (associated with low viscosity and density) or very high amounts of these.

Table 3 also illustrates that the differences between the four water-in-oil states are readily discernible by appearance and rheological properties. The reddish or brown colour on formation indicates either a stable or mesostable emulsion, although stable emulsions always have a more solid appearance. The increase in apparent

Dos Cuadras	11.17	Meso	0.09	8.0E+02	3.4E+03	1.3E+03	3.3E+03	5.0E+02	2.5	47.60	5.3E+02	4.6E+03	1.6E+03	4.2E+03	7.0E+02	3.0	29.49	
Dos Cuadras	20.30	Meso	0.02	9.8E+03	3.3E+04	2.3E+04	2.2E+04	3.6E+03	1.0	68.55	1.9E+03	1.7E+04	3.0E+03	1.3E+04	2.1E+03	4.2	28.72	
Fuel Oil #5 [2002]	0	Stable			1.6E+06	1.5E+06	4.6E+05		0.29	78.3								
Fuel Oil #5 [2002]	7.25	Stable			2.5E+06	2.4E+06	7.1E+05		0.30	72.8								
Garden Banks 387	0	No																
Garden Banks 387	7.07	No																
Garden Banks 387	15.14	No																
Garden Banks 387	23.3	Meso		6.8E+03	8.2E+03	4.0E+03	7.1E+03			1.80	36.52							
Garden Banks 426	0	No																
Garden Banks 426	0	No																
Garden Banks 426	12.28	No																
Garden Banks 426	24.75	No																
Garden Banks 426	37.72	Stable			9.2E+03	7.3E+04	6.5E+04	3.4E+04		0.53	64.67							
Genesis	0	No																
Genesis	8.11	No																
Genesis	15.14	No																
Genesis	23.06	Meso		1.1E+04	2.6E+04	8.1E+03	2.5E+04			3.10	61.51							
Green Canyon 184	0	No																
Green Canyon 184	12.12	No																
Green Canyon 184	26.03	No																
Green Canyon 184	38.21	Meso		8.3E+03	2.2E+04	1.3E+04	1.7E+04			1.34	69.48							
Heavy Fuel Oil [2002]	0	Entrained				7.5E+05	4.5E+05	6.0E+05			2.42	57.7						
Heavy Fuel Oil [2002]	2.5	Entrained				9.8E+05	3.0E+05	9.4E+05			3.16	24.1						
High Viscosity Fuel Oil	0	Entrained																
Hondo	0	Stable	0.02	1.1E+05	9.2E+05	9.1E+05	2.2E+05	3.6E+04	0.24	80.93	1.7E+05	8.8E+05	8.3E+05	2.5E+05	4.2E+04	0.32	79.96	
Hondo	16.67	Stable	0.00	1.9E+05	1.3E+06	1.1E+06	5.3E+05	8.4E+04	0.45	66.20	2.8E+05	8.4E+05	6.2E+05	6.1E+05	9.0E+04	0.96	64.23	
Hondo	32.29	No	0								5.24							
IFO-180	0	Entrained																
IFO-180	7.77	Entrained																
IFO-300	0	Entrained																
IFO-300	5.33	No																
Jet A1	0.00	No																
Jet A1	12.03	No																
Jet A1	23.21	No																
Jet A1	37.14	No																
Jet Fuel (Anchorage)	0	No	1,133,000								<1							
Jet Fuel (Anchorage)	52.72	No	1,651,000								<1							
Lago	0.00	No																
Lago	0.00	No																
Lago	10.54	Stable		1.0E+05	2.0E+05	1.8E+05	8.0E+04		0.44	63.72								
Lago	16.68	Stable		5.3E+05	1.1E+06	1.0E+06	2.9E+05		0.28	53.29								
Lucula	0.00	Stable		2.5E+04	8.0E+05	7.9E+05	1.1E+05		0.14	84.63								
Lucula	10.69	Stable		4.8E+04	6.9E+05	6.7E+05	1.7E+05		0.25	73.55								
Lucula	15.41	Stable		5.3E+04	1.5E+06	1.5E+06	3.1E+05		0.21	77.59								
Lucula	26.93	Entrained			1.1E+07	1.0E+07	3.6E+06		0.35	20.52								
Malongo	0.00	No																
Malongo	11.83	Stable		3.3E+04	7.4E+05	7.3E+05	1.5E+05		0.21	70.50								
Malongo	15.54	Entrained		5.6E+04	2.5E+06	2.3E+06	8.6E+05		0.37	50.59								
Malongo	21.74	Entrained		8.6E+04	3.3E+06	3.0E+06	9.9E+05		0.33	45.99								
MARS-TLP	0	No																
MARS-TLP	8.42	Meso		5.8E+03	1.1E+04	5.4E+03	9.0E+03		1.70	63.45								
MARS-TLP	17.21	Meso		1.1E+04	2.7E+04	5.7E+03	2.6E+04		5.50	64.85								
MARS-TLP	26.15	Meso		3.1E+04	9.5E+04	4.0E+04	8.6E+04		2.15	62.17								
Mississippi Canyon 72	0	No																
Mississippi Canyon 72	0	No																
Mississippi Canyon 72	9.41	No																
Mississippi Canyon 72	18.01	Meso		4.9E+03	7.6E+03	5.5E+03	5.1E+03		0.92	51.93								

Table 1 (continued)

Oil	% Evap.	Visual stability	Stability	Day of formation							One week after formation						
				Viscosity (mPa s)	Complex modulus (mPa)	Elasticity modulus (mPa)	Viscosity modulus (mPa)	Isolated low-shear viscosity (mPa s)	$\tan \delta (V/E)$	Water content (% w/w)	Viscosity (mPa s)	Complex modulus (mPa)	Elasticity modulus (mPa)	Viscosity (mPa)	Isolated low-shear viscosity (mPa s)	$\tan \delta (V/E)$	Water content (% w/w)
Mississippi Canyon 72	26.15	Stable		3.3E+04	2.2E+05	2.0E+05	1.0E+05		0.51	74.36							
Mississippi Canyon 807	0	Meso		6.2E+03	1.0E+04	7.7E+03	5.6E+03		0.72	59.98							
Mississippi Canyon 807	8.67	Meso		1.0E+04	1.9E+04	5.5E+03	1.9E+04		3.38	68.38							
Mississippi Canyon 807	16.44	Stable		1.8E+04	5.4E+04	2.7E+04	4.6E+04		1.74	67.51							
Mississippi Canyon 807	25.51	Stable		3.4E+04	1.6E+05	8.0E+04	1.4E+05		1.69	65.44							
Neptune Spar (Viosca Knoll 826)	0	No															
Neptune Spar (Viosca Knoll 826)	7.92	No															
Neptune Spar (Viosca Knoll 826)	15.41	Meso		1.4E+04	5.5E+05	5.4E+05	1.1E+05		0.19	47.86							
Neptune Spar (Viosca Knoll 826)	22.62	Stable		3.1E+04	9.3E+05	9.1E+05	2.1E+05		0.23	62.52							
North Slope (Middle Pipeline)	0	No	1062.5							<1							
North Slope (Middle Pipeline)	0	No	367,000							1.00							
North Slope (Middle Pipeline)	30.54	Meso	14.78	6.8E+03	1.2E+05	1.0E+05	4.8E+04	7.6E+03	0.52	61.92	1.8E+03	1.1E+04	1.3E+03	1.1E+04	1.7E+03	8.4	21.76
North Slope (Northern Pipeline)	31.14	Meso	55.45	2.6E+03	1.1E+05	9.6E+04	4.7E+04	7.4E+03	0.50	69.82	1.7E+03	9.8E+03	2.2E+03	9.6E+03	1.5E+03	4.2	15.00
North Slope (Southern Pipeline)	0	No								<1							
North Slope (Southern Pipeline)	29.62	Meso	0.19	8.7E+03	1.9E+05	1.7E+05	8.1E+04	1.3E+04	0.46	53.47	2.2E+03	2.0E+04	7.7E+03	1.8E+04	2.8E+03	2.2	21.14
Pitas Point	0	No	1.5							<1							
Pitas Point	23.56	No	2.5							<1							
Platform Gail (Sockeye)	0	Stable		3.6E+04	1.2E+05	8.3E+04	8.8E+04		1.06	75.78							
Platform Gail (Sockeye)	7.34	Stable		7.0E+04	2.0E+05	1.2E+05	1.6E+05		1.25	75.06							
Platform Gail (Sockeye)	13.33	Stable		1.1E+05	3.4E+05	2.2E+05	2.6E+05		1.20	67.10							
Platform Gail (Sockeye)	20.63	Entrained		4.0E+05	1.2E+06	7.3E+05	9.6E+05		1.34	44.41							
Platform Holly	0	Same ^a															
Platform Holly	24.24	Same ^a															
Platform Holly	53.87	Same ^a															
Platform Holly	78.47	Same ^a															
Platform Holly	78.47	Same ^a															
Platform Irene	0	Entrained	0	3.9E+05	1.4E+06	7.6E+05	1.2E+06	1.9E+05	1.52	62.22	5.4E+05	3.3E+06	2.1E+06	2.5E+06	4.0E+05	1.20	34.94
Point Arguello Comingled	0	Stable	0.01	1.8E+05	7.8E+05	7.2E+05	3.2E+05	5.0E+04	0.43	82.31	1.8E+05	1.1E+06	1.0E+06	4.1E+05	6.4E+04	0.36	82.19
Point Arguello Comingled	9.05	Stable	0.00	1.5E+05	8.5E+05	7.9E+05	3.0E+05	4.7E+04	0.38	67.92	1.5E+05	6.2E+05	4.7E+05	4.3E+05	7.0E+04	0.95	69.41
Point Arguello Comingled	15.19	Entrained	0.65	1.4E+05	6.1E+05	2.7E+05	5.5E+05	8.7E+04	2.0	30.15	1.6E+05	8.0E+05	3.5E+05	7.0E+05	1.1E+05	2.10	28.42
Point Arguello Comingled	22.12	No	0							4.96							
Point Arguello Heavy	0	Stable	163.08	1.5E+05	4.9E+05	4.0E+05	2.8E+05	4.5E+04	0.71	72.95	1.8E+05	7.2E+05	5.8E+05	3.9E+05	6.6E+04	0.72	74.97
Point Arguello Heavy	8.88	Entrained	4.88														
Point Arguello Heavy	17.78	No	0.24							<1							
Point Arguello Light	0	Stable	11,818.18	6.7E+04	6.5E+05	6.4E+05	6.8E+04	1.0E+04	0.11	93.14	9.6E+04	8.3E+05	8.2E+05	1.4E+05	2.2E+04	0.17	93.79

Point Arguello Light	10.19	Stable	473.68	2.8E+05	3.3E+06	3.3E+06	1.7E+05	2.6E+04	0.05	88.84	2.5E+05	2.8E+06	2.8E+06	3.3E+05	5.2E+04	0.12	87.78
Point Arguello Light	19.04	Stable	409.84	2.7E+05	3.4E+06	3.4E+06	2.8E+05	4.3E+04	0.08	85.50	3.1E+05	3.5E+06	3.6E+06	4.2E+05	7.2E+04	0.13	85.63
Point Arguello Light	28.33	Stable	6.86	1.4E+05	9.8E+05	9.6E+05	2.5E+05	4.0E+04	0.26	79.80	1.6E+05	1.5E+06	1.4E+06	4.2E+05	6.6E+04	0.28	75.89
Port Hueneme	0	Entrained	38.73	1.6E+04	6.4E+04	2.4E+04	6.1E+04	8.8E+03	2.6	37.97	8.8E+03	4.3E+04	4.8E+03	4.1E+04	6.9E+03	9.4	20.06
Port Hueneme	3.14	Entrained	2.17	4.6E+04	1.7E+05	8.2E+04	1.5E+05	2.3E+04	1.7	45.33	2.7E+04	1.3E+05	2.1E+04	1.2E+05	2.0E+04	5.7	29.20
Port Hueneme	6.37	Entrained	17.63	7.1E+04	2.7E+05	1.4E+05	2.3E+05	3.6E+04	1.7	43.37	5.4E+04	2.6E+05	6.4E+04	2.4E+05	4.0E+04	3.9	26.42
Prudhoe Bay	0	Meso															
Prudhoe Bay	9.32	Stable															
Prudhoe Bay	18.12	No															
Prudhoe Bay	27.25	Meso?															
Santa Clara	0	Meso	592.11	2.1E+04	1.8E+04	2.2E+03	1.8E+04	2.8E+03	6.5	60.63	2.6E+03	2.9E+04	1.7E+04	2.4E+04	3.9E+03	1.4	12.75
Santa Clara	11.40	Meso	59.17	2.0E+04	7.0E+05	6.9E+05	1.0E+05	1.5E+04	0.15	50.43	1.5E+04	7.5E+04	2.0E+04	7.3E+04	1.1E+04	3.5	38.72
Santa Clara	21.63	Meso	0	1.0E+05	3.6E+05	2.0E+05	2.9E+05	4.7E+04	1.4	38.99	9.2E+04	3.7E+05	2.0E+05	3.3E+05	5.0E+04	1.65	40.15
Sockeye	0	Stable	73,333.33	6.9E+05	6.4E+06	6.3E+06	4.0E+05	6.2E+04	0.06	87.12	6.9E+05	4.3E+06	1.0E+06	3.1E+05	8.8E+04	0.11	86.87
Sockeye	12.50	Stable	4907.98	1.7E+05	9.3E+05	8.9E+05	2.4E+05	3.9E+04	0.27	80.05	2.2E+05	1.1E+06	4.3E+06	4.9E+05	5.0E+04	0.31	74.35
Sockeye	22.10	Stable	207.01	2.6E+05	1.4E+06	1.3E+06	3.9E+05	9.8E+04	0.30	77.94	3.1E+05	1.5E+06	1.4E+06	5.0E+05	7.8E+04	0.35	70.39
Sockeye [2002]	0	Meso															
Sockeye [2002]	6	Meso															
Sockeye [2002]	13	Entrained															
Sockeye [2002]	19	Entrained															
Sockeye Comingled	0	Stable															
Sockeye Sour	0	Stable															
Sockeye Sour	9.55	Stable/ meso															
Sockeye Sour	18.52	No															
Sockeye Sweet	0	Webby															
Sockeye Sweet	8.13	Webby															
Sockeye Sweet	17.46	Inversion															
Sockeye Sweet	26.91	Stable															
South Louisiana [2002]	0	Unstable															
South Louisiana [2002]	10	Unstable															
South Louisiana [2002]	19	Unstable															
South Louisiana [2002]	27	Unstable															
Sumatran Heavy	0	No	10.53														12.73
Sumatran Heavy	5.26	No	38.24														
Sumatran Light	0	No	6.27														11.20
Taching	0	No	0.01														
Takula	0	Stable	136.36	8.9E+04	1.1E+06	1.1E+06	1.6E+05	2.5E+04	0.14	86.40	1.2E+05	1.2E+06	1.2E+06	2.1E+05	3.1E+04	0.15	84.18
Takula	8.31	Stable	15.85	1.1E+05	1.1E+06	1.0E+06	2.1E+05	3.0E+04	0.21	82.21	1.3E+05	1.2E+06	1.1E+06	2.3E+05	3.6E+04	0.20	81.08
Takula	15.88	Stable	10.8	1.5E+05	1.1E+06	1.1E+06	2.5E+05	4.0E+04	0.23	75.56	1.7E+05	1.2E+06	1.2E+06	2.8E+05	4.4E+04	0.24	73.83
Tapis	0	No															9.06
Tapis	13.90	No															20.03
Tapis	28.62	No															
Tapis	43.43	No															
Thevenard Island	0.00	No															
Udang	0	Entrained	0.6	3.2E+04	1.3E+05	5.6E+04	1.1E+05	1.8E+04	2.00	37.05							19.65
Viosca Knoll 826	0	No															
Viosca Knoll 826	0	No															
Viosca Knoll 826	8.14	No															
Viosca Knoll 826	16.89	No															
Viosca Knoll 826	23.97	Stable		1.4E+04	3.4E+05	3.3E+05	8.8E+04		0.27	64.14							
Viosca Knoll 990	0	No															
Viosca Knoll 990	0	No															
Viosca Knoll 990	12.32	No															
Viosca Knoll 990	24.4	No															
Viosca Knoll 990	35.15	Stable		9.3E+03	1.0E+05	9.8E+04	3.4E+04		0.38	63.93							

Table 1 (continued)

Oil	% Evap.	Visual stability	Stability	Day of formation							One week after formation						
				Viscosity (mPa s)	Complex modulus (mPa)	Elasticity modulus (mPa)	Viscosity modulus (mPa)	Isolated low-shear viscosity (mPa s)	$\tan \delta (V/E)$	Water content (% w/w)	Viscosity (mPa s)	Complex modulus (mPa)	Elasticity modulus (mPa)	Viscosity (mPa)	Isolated low-shear viscosity (mPa s)	$\tan \delta (V/E)$	Water content (% w/w)
Waxy Light Heavy Blend	0	No	23,369.57							4.11							
Waxy Light Heavy Blend	12.00	Entrained	5.34	6.0E+03	3.1E+04	1.0E+04	3.0E+04	4.6E+03	2.80	33.97	3.7E+03	1.5E+04	2.4E+03	1.5E+04	2.4E+03	6.2	12.21
Waxy Light Heavy Blend	19.60	Meso	3.44	4.5E+04	1.9E+05	9.6E+04	1.6E+05	2.7E+04	1.70	34.65	3.7E+04	1.1E+05	5.3E+04	1.0E+05	1.6E+04	2.1	33.58
West Texas Intermediate [2002]	0	Unstable															
West Texas Intermediate [2002]	10	Unstable															
West Texas Intermediate [2002]	21	Meso			1.9E+04	1.7E+04	9.6E+03		0.61	82.7							
West Texas Intermediate [2002]	31	Meso			8.4E+04	7.8E+04	2.9E+04		0.38	83.6							

^a Starting oil also had a significant water content.

Table 2
Ranges of properties for the various emulsion stabilities

Emulsion stability	Property range	Starting oil properties												
		Density (g/ml)	Viscosity (mPa s)	Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)	Waxes (%)	Emulsion stability ^a	Viscosity (mPa s)	Complex modulus (mPa)	Elasticity modulus (mPa)	Viscosity modulus (mPa)	Water content (% w/w)
Stable	High	0.9674	9580	65	54	29	19	8	95,600	6.9E+05	4.3E+06	4.3E+06	6.1E+05	93.79
	Low	0.8637	14	27	22	6	3	4	88	2.3E+04	1.0E+05	5.0E+04	2.7E+04	64.23
	High difference from unstable	-0.0376	-5,128,000	-16	12	-3	-3	-16	95,400	687,400	-838,000	4,130,000	536,000	69.31
	Low difference from unstable	0.0527	12	4	10	6	3	4	87	23,000	99,998	50,000	27,000	64.23
	High difference from mesostable	-0.0096	-13,200	0	15	-1	2	0	93,700	520,000	3,100,000	3,100,000	280,000	32.36
	Low difference from mesostable	0.0217	8	-1	-3	0	0	3	87	22,470	99,990	48,400	22,800	62.34
Meso	High	0.977	22,760	65	39	30	17	8	1900	1.7E+05	1.2E+06	1.2E+06	3.3E+05	61.43
	Low	0.842	6	28	25	6	3	1	1	5.3E+02	10	1.6E+03	4.2E+03	1.89
	High difference from unstable	-0.028	-5,120,000	-16	-3	-2	-5	-16	1700	167,400	-3,938,000	1,030,000	256,000	36.95
	Low difference from unstable	0.031	4	5	13	6	3	1	0	530	8	1600	4200	1.89
Entrained	High	0.9907	59,390	32	55	31	22	12	430	5.4E+05	3.3E+06	6.2E+05	7.0E+05	34.94
	Low	0.9688	2002	19	29	15	3	1	1	3.7E+03	6400	2.4E+03	1.5E+04	12.21
	High difference from unstable	-0.0143	-5,080,000	-49	13	-1	0	-12	230	537,400	-1,838,000	450,000	626,000	10.46
	Low difference from unstable	0.1578	2000	-4	17	15	3	1	0	3700	6398	2400	15,000	12.21
Unstable	High	1.005	5,138,000	81	42	32	22	24	198	2.6E+03	5,138,000	1.7E+05	7.4E+04	24.48
	Low	0.811	2	23	12	0	0	0	1	0.0E+00	2	0.0E+00	0.0E+00	0.00

^a Starting oil also had a significant water content.

Table 3

Summary of properties of the water-in-oil states

	Stable		Meso		Entrained		Unstable	
	High	Low	High	Low	High	Low	High	Low
<i>Starting oil</i>								
Property								
Density (g/ml)	0.9674	0.8637	0.977	0.842	0.9907	0.9688	1.005	0.811
Viscosity (mPa s)	9580	14	22,800	6	59,400	2002	5,140,000	2
Saturates (%)	65	27	65	28	32	19	81	23
Aromatics (%)	54	22	39	25	55	29	42	12
Resins (%)	29	6	30	6	31	15	32	0
Asphaltenes (%)	19	3	17	3	22	3	22	0
Waxes (%)	8	4	8	1	12	1	24	0
Asphaltene-resin ratio	1.12	0.4	0.89	0.1	1.11	0.13	1.17	0
<i>Properties on day of formation</i>								
Appearance	Brown solid		Brown viscous liquid		Black with large droplets		Like oil	
Average ratio of viscosity increase	1100		45		13		1	
Range	15,000	14	250	2	70	1	8	1
Average water content	80		62		42		5	
Range	93	65	83	35	62	26	23	1
Stability ^a	15,000	20	400	1	50	1	60	1
<i>Properties after one week</i>								
Appearance	Brown solid		Broken, two or three phases		Separated oil and water		Like oil	
Average ratio of viscosity increase	1500		30		2		1	
Range	15,000	20	150	1	3	1	2	1
Average water content	79		38		15		2	
Range	94	64	61	2	35	12	24	0
Stability ^a	95,000	88	1900	1	434	1	198	1
Viscosity (mPa s)	6.9E+05	2.3E+04	1.7E+05	5.3E+02	5.4E+05	3.7E+03	2.6E+03	0.0E+00
Complex modulus (mPa)	4.3E+06	1.0E+05	1.2E+06	10	3.3E+06	6400	5,138,000	2
Elasticity modulus (mPa)	4.3E+06	5.0E+04	1.2E+06	1.6E+03	6.2E+05	2.4E+03	1.7E+05	0.0E+00
Modulus (mPa)	6.1E+05	2.7E+04	3.3E+05	4.2E+03	7.0E+05	1.5E+04	7.4E+04	0.0E+00
Shear viscosity (mPa s)	9.0E+04	1.1E+04	5.0E+04	7.0E+02	4.0E+05	2.4E+03	1.2E+04	0.0E+00
Delta (V/E)	1.8	0.11	12	0.24	9.4	1.0	1.4	0.00
Water-content (% w/w)	93.79	64.23	61.43	1.89	34.94	12.21	24.48	0.00

^a Complex modulus/viscosity of starting oil.

viscosity (from the starting oil) on formation averages about 1100 for a stable emulsion, 45 for a mesostable emulsion, 13 for entrained water-in-oil, and an unstable emulsion shows little or no increase. This difference increases after one week. The increase in apparent viscosity after one week averages about 1500 for a stable emulsion, 30 for a mesostable emulsion, three for entrained water-in-oil, and an unstable emulsion shows little or no increase. It is noted that, for stable emulsions only, apparent viscosity does not decrease after one week.

There are several other features noted in the summary data presented in Table 3. The wax content shows that, while there may be some correlation to viscosity, the specific wax content is not associated with the formation of any state. It is noted that density is associated with the viscosity and somewhat with the state. It is also noted that the water content correlates somewhat with the state. The average water content of stable emulsions

is 80% on the day of formation, of mesostable emulsions is 62%, of entrained water is 42%, and is 5% for unstable emulsions. One must be cautious in using this as a sole discriminator, however, because of overlapping ranges. As would be expected, the water content after one week correlates very highly with the state. As already noted, this is accentuated by the fact that mesostable emulsions and entrained water-in-oil have separated to a significant degree.

These data indicate that there are ‘windows’ of composition and viscosity which result in the formation of each of the types of water-in-oil states. The important factors in terms of oil composition are the asphaltene and resin contents. While asphaltenes are responsible for the formation of stable emulsions, a high asphaltene content can also result in a viscosity that is higher than the region in which stable emulsions form. The asphaltene/resin ratio is higher for stable emulsions. In a previous work by the present author, it was shown that the

Table 4
Typical properties of the water-in-oil states

	Stable	Meso	Entrained	Unstable
Day of formation appearance	Brown solid	Brown viscous liquid	Black with large droplets	Like oil
Water content on first day (%)	80	62	42	5
Appearance after one week	Brown solid	Broken, two or three phases	Separated oil and water	Like oil
Water content after one week (%)	79	38	15	2
Stable time (days)	>30	<3	<0.5	Not
<i>Starting oil</i>				
Density (g/ml)	0.85–0.97	0.84–0.98	0.97–0.99	0.8–1.03
Viscosity (mPa s)	15–10,000	6–23,000	2000–60,000	2–5.1 × 10 ⁶
Saturates (%)	25–65	25–65	19–32	23–80
Aromatics (%)	20–55	25–40	30–55	5–12
Resins (%)	5–30	6–30	15–30	0–32
Asphaltenes (%)	3–20	3–17	3–22	0–32
Asphaltenes/resins	0.74	0.47	0.62	0.45
<i>Properties on day of formation</i>				
Average ratio of viscosity increase	1100	45	13	1
<i>Properties after one week</i>				
Average ratio of viscosity increase	1500	30	2	1

migration rate of asphaltenes in emulsions is very slow (Fingas et al., 1996). This indicates that in very viscous oils, asphaltenes may migrate too slowly to allow emulsions to stabilize.

Four clearly defined states of water-in-oil have been shown to be characterized by a number of measurements as well as by their visual appearance, both on the day of formation and one week later. The differences between these states and the oils that form them are summarized in Table 4.

The results of this study indicate that both stable and mesostable emulsions form due to the combination of surface-active forces from resins and asphaltenes and from viscous forces. Each type of water-in-oil state exists in a range of compositions and viscosities. There is a small difference in composition between stable and mesostable emulsions. Stable emulsions have more asphaltenes and less resins and a narrow viscosity window. Instability results when the oil has a high viscosity (over about 50,000 mPa s) or a very low viscosity (under about 6 mPa s) and when the oil contains less than about 3% of resins and asphaltenes. Water entrainment, rather than emulsion formation, occurs when the viscosity is from about 2000 to 50,000 mPa s. Stable or mesostable emulsions may not form in highly viscous oils because the migration of asphaltenes (and resins) is too slow to allow droplets to stabilize. Water droplets simply cannot penetrate the oil when the viscosity is too high.

The role of other components of the oil is still unclear at this time. Aromatics dissolve asphaltenes and there is a small correlation observed with the stabilities. Waxes appear to have no role in emulsion formation. The density of the starting oil is highly correlated with viscosity and thus shows a correlation with stability.

The state of the final water-in-oil emulsion can be correlated with the single parameter of the complex modulus divided by the viscosity of the starting oil. This stability parameter also correlates somewhat with the non-Newtonian behaviour of the resulting water-in-oil mixture, the elasticity of the emulsion, and the water content. These properties are more decisive in defining the state one week after formation because all states have largely separated into oil and water except for stable emulsions. The water content retained one week after the formation process is a very clear discriminator of state.

3. Studies on energy threshold of formation

The kinetics of emulsion formation and the energy levels associated with their formation are important aspects of emulsions. Information in these areas is needed to understand and model the emulsification process. This section reports on initial experiments to examine the kinetics and the formation energy of emulsions. It is important to note that turbulent energy is thought to be the most important form of energy related to emulsion formation. Turbulent energy could not be measured in the experiment described here, so the total energy was used as an estimate of the energy available for emulsion formation.

3.1. Experimental summary on energy threshold studies

Details of the experimental work are given in Fingas et al. (1999). Water-in-oil emulsions were made in a rotary agitator and the rheometric characteristics of

these emulsions studied over time. Oils were taken from the storage facilities at the Emergencies Science and Technology Division. Properties of these oils are given in standard references (Jokuty et al., 1999).

The energy threshold measurements were taken by varying the rotational rate and hence the energy of the apparatus used to make the emulsions. The emulsions were analyzed using rheological measurements as described in this paper and using standard visual observations.

Emulsions were made in an end-over-end rotary mixer as noted above. After temperature equilibration, the vessels were rotated for 12 h at between 1 and 55 rpm, with sampling at specified intervals. The resulting emulsions were then collected into jars, covered, and stored in a 15 °C cold room. Analysis was performed on the day of collection a short time after formation.

Rheology and water content were measured in the same manner as noted above.

Energy calculation was related to the total kinetic energy exerted on the oil/water in the device. The total kinetic energy in each bottle is given by:

$$KE = \frac{1}{2}MV^2 \quad (1)$$

where KE is the energy in ergs, M is the mass in grams, here approximately 620 g of water and oil, and V is the velocity in cm/s which is $2\pi r$ —which is $\text{rpm}/60 \times 7.5 \text{ cm}$.

By this formula, kinetic energy is then $196 \times \text{rpm}^2$ ergs. Ergs were used in this study because they are a much more convenient unit than the SI Joules at these low energy levels. This simple formulation was 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.

Since

$$F = ma \quad (2)$$

where F is the force applied to the system in newtons, m is the mass which here is 0.62 kg, and a is the acceleration of gravity which is 9.8 m/s^2 .

Thus $F = 6.08$ newtons

$$\text{Work} = F \times D \quad (3)$$

where F is the force in newtons = 6.08; D is the distance through which the force moves, which 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.

3.2. Results and discussion of the kinetic studies

The rheological data associated with the energy threshold experiments are given in Table 5. The second column of Table 5 is the rotational rate of the formation

vessel (mixing energy). The third column is the time from mixing until when 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 viscosity of the starting oil. The seventh column is the calculated kinetic energy applied to the system in ergs and the eighth column gives the work applied to the emulsions in J.

The appearance of the oil/water throughout the process is very important in terms of understanding the process (Fingas et al., 1999). It has also been noted that there is a progression in the formation of the emulsions. At the onset of agitation, a coarse mixture is formed, which looks like a sponge or foam. If a stable emulsion is to be formed, this occurs quickly and did not appear to revert with the oils in this study. A mesostable emulsion forms after about 20 min of agitation at low energy. In some cases, the mesostable emulsion can change to a less stable, three-way, water-in-oil-in-water emulsion. Most often, a mesostable emulsion would remain as mesostable. The coarse mixture often remains as such.

In summary, a coarse mixture is often formed at 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 time. Mesostable emulsions appear about 20 min later and may stay as mesostable emulsions, but under high energy, some oils may break back down into a coarse mixture. The coarse mixture may convert into a three-way, water-in-oil-in-water emulsion which is not stable for longer than about one day until mixing ceases. The three-way emulsions retain some of the characteristics of the emulsion from which they are formed, either a mesostable or coarse mixture. Three-way emulsions do not convert into other water-in-oil states and break down after mixing ceases.

The stability and energy of formation are plotted for the four types of water-in-oil states in Fig. 1. The stability in these figures is the complex modulus divided by the viscosity of the starting oil. It was found that the ‘stability’, as here defined, was 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 1 indicates that for Arabian Light oil, the onset of stability is rapid and stability increases somewhat after onset. Stability is generally taken as the point at which the stability is approximately 1000 and this is achieved at a very low energy level corresponding to a rotational rate of about 5 rpm.

The uptake of water by one sample of Bunker C is also shown in Fig. 1. The Bunker C takes up water very

Table 5
Summary of kinetic results

Mixing energy (rpm)	Time (min)	Complex modulus (mPa)	Water content (% w/w)	Stability (s ⁻¹)	Energy (ergs)	Work (J)
<i>Sockeye</i>						
10	10	9.3E+03	73.6	210	19,600	2700
	20	2.5E+04	79.8	540	19,600	5500
	30	1.4E+05	83.9	3160	19,600	8200
	60	1.7E+05	89.3	3870	19,600	16,400
	120	2.7E+05	90.1	6070	19,600	32,800
	360	3.8E+05	89.8	8500	19,600	98,500
	1440	9.7E+05	88.2	21,440	19,600	394,000
30	10	1.3E+05	85.1	2790	176,400	8200
	20	3.0E+05	85.7	6670	176,400	16,400
	30	4.2E+05	85.7	9220	176,400	24,600
	60	3.8E+05	86.1	8330	176,400	49,200
	120	4.5E+05	86.7	9890	176,400	98,500
	360	5.9E+05	87.8	13,110	176,400	295,500
	1440	8.0E+05	87.9	17,670	176,400	1,182,000
55	10	2.7E+05	82.2	6000	592,900	15,000
	20	6.6E+05	84.6	14,670	592,900	30,100
	30	7.9E+05	85.3	17,440	592,900	45,100
	60	1.2E+06	86.1	25,780	592,900	90,300
	120	1.9E+06	85.6	41,330	592,900	180,600
	360	2.9E+06	83.5	63,330	592,900	541,700
	1440	4.7E+06	82.8	103,330	592,900	2,166,900
<i>Point arguello light</i>						
10	10	1.3E+04	78.5	570	19,600	2700
	20	3.7E+04	83.7	1680	19,600	5500
	30	4.7E+04	86.6	2110	19,600	8200
	60	1.3E+05	93.5	6110	19,600	16,400
	120	3.7E+05	92.1	16,820	19,600	32,800
	360	5.2E+05	91.8	23,640	19,600	98,500
	1440	7.9E+05	91.7	35,680	19,600	394,000
30	10	5.5E+04	82.9	2500	176,400	8200
	20	2.3E+05	92.2	10,230	176,400	16,400
	30	5.1E+05	92.0	23,180	176,400	24,600
	60	8.6E+05	91.8	39,090	176,400	49,200
	120	7.8E+05	92.0	35,230	176,400	98,500
	360	6.6E+05	91.7	30,000	176,400	295,500
	1440	8.2E+05	91.2	37,050	176,400	1,182,000
55	10	5.3E+05	90.9	23,860	592,900	15,000
	20	5.7E+05	91.0	25,680	592,900	30,100
	30	5.8E+05	90.9	26,360	592,900	45,100
	60	6.5E+05	91.3	29,320	592,900	90,300
	120	6.4E+05	91.0	28,860	592,900	180,600
	360	8.6E+05	90.5	39,090	592,900	541,700
	1440	2.1E+06	89.8	97,500	592,900	2,166,900
<i>Arabian light</i>						
10	10	NM	73.4	NM	19,600	2700
	20	NM	86.0	NM	19,600	5500
	30	NM	NM	NM	19,600	8200
	60	4.5E+03	83.6	320	19,600	16,400
	120	NM	76.4	NM	19,600	32,800
	360	NM	76.6	NM	19,600	98,500
	1440	8.0E+03	77.0	570	19,600	394,000
30	10	NM	79.3	NM	176,400	8200
	20	2.1E+04	83.8	1460	176,400	16,400
	30	1.4E+04	84.1	1020	176,400	24,600

(continued on next page)

Table 5 (continued)

Mixing energy (rpm)	Time (min)	Complex modulus (mPa)	Water content (% w/w)	Stability (s ⁻¹)	Energy (ergs)	Work (J)
55	60	1.8E+04	83.0	1250	176,400	49,200
	120	4.7E+04	83.5	3360	176,400	98,500
	360	8.6E+04	86.8	6140	176,400	295,500
	1440	1.0E+05	85.9	7210	176,400	1,182,000
	10	3.0E+04	80.6	2130	592,900	15,000
	20	5.8E+04	90.0	4110	592,900	30,100
	30	5.8E+04	90.2	4110	592,900	45,100
55	60	1.8E+05	89.4	13,180	592,900	90,300
	120	1.9E+05	90.9	13,360	592,900	180,600
	360	1.8E+05	89.1	12,640	592,900	541,700
	1440	2.0E+05	87.3	14,110	592,900	2,166,900
<i>Green canyon 65, 7.7% weathered</i>						
10	10	1.1E+04	62.8	20	19,600	2700
	20	2.0E+04	73.2	40	19,600	5500
	30	2.8E+04	74.1	60	19,600	8200
	60	4.5E+04	83.1	100	19,600	16,400
	120	5.0E+04	80.5	110	19,600	32,800
	360	7.0E+04	82.7	150	19,600	98,500
	1440	1.1E+05	86.6	240	19,600	394,000
30	10	1.1E+04	53.0	20	176,400	8200
	20	2.0E+04	70.2	40	176,400	16,400
	30	NM	NM	NM	176,400	24,600
	60	3.2E+04	70.3	70	176,400	49,200
	120	4.6E+04	72.4	100	176,400	98,500
	360	3.9E+04	69.6	90	176,400	295,500
	1440	3.5E+04	62.2	80	176,400	1,182,000
55	10	1.3E+04	62.6	30	592,900	15,000
	20	2.0E+04	58.6	40	592,900	30,100
	30	2.3E+04	61.9	50	592,900	45,100
	60	3.5E+04	59.7	80	592,900	90,300
	120	1.5E+04	52.7	30	592,900	180,600
	360	2.1E+04	56.4	50	592,900	541,700
	1440	1.8E+04	63.4	40	592,900	2,166,900
<i>Sockeye sweet, 17% weathered</i>						
10	10	8.2E+03	67.7	80	19,600	2700
	20	1.2E+04	72.4	110	19,600	5500
	30	2.0E+04	76.9	200	19,600	8200
	60	4.4E+04	88.9	420	19,600	16,400
	120	6.4E+04	90.3	620	19,600	32,800
	360	9.0E+04	91.5	870	19,600	98,500
	1440	1.0E+05	95.2	1000	19,600	394,000
30	10	1.1E+04	64.3	110	176,400	8200
	20	2.1E+04	75.7	210	176,400	16,400
	30	2.9E+04	76.6	280	176,400	24,600
	60	4.1E+04	79.7	400	176,400	49,200
	120	8.0E+04	87.7	780	176,400	98,500
	360	9.0E+04	90.1	870	176,400	295,500
	1440	9.4E+04	93.0	910	176,400	1,182,000
55	10	3.8E+04	78.2	370	592,900	15,000
	20	5.4E+04	79.2	520	592,900	30,100
	30	6.2E+04	82.4	600	592,900	45,100
	60	7.8E+04	82.8	750	592,900	90,300
	120	9.0E+04	81.0	870	592,900	180,600
	360	9.0E+04	80.4	870	592,900	541,700
	1440	8.4E+04	83.8	820	592,900	2,166,900

Table 5 (continued)

Mixing energy (rpm)	Time (min)	Complex modulus (mPa)	Water content (% w/w)	Stability (s^{-1})	Energy (ergs)	Work (J)
<i>Bunker C (1987)</i>						
10	10	NM	2.3	NM	19,600	2700
	20	NM	3.2	NM	19,600	5500
	30	NM	2.6	NM	19,600	8200
	60	NM	6.8	NM	19,600	16,400
	60	NM	6.8	NM	19,600	16,400
	120	NM	6.3	NM	19,600	32,800
	360	NM	9.6	NM	19,600	98,500
	1440	4.5E+05	31.9	10	19,600	394,000
30	10	4.5E+05	4.4	10	176,400	8200
	20	NM	4.1	NM	176,400	16,400
	30	NM	9.4	NM	176,400	24,600
	60	NM	8.9	NM	176,400	49,200
	120	3.8E+05	12.4	10	176,400	98,500
	360	4.0E+05	20.6	10	176,400	295,500
	1440	5.5E+05	36.7	10	176,400	1,182,000
55	10	4.5E+05	5.7	10	592,900	15,000
	20	NM	4.2	NM	592,900	30,100
	30	NM	NM	NM	592,900	45,100
	60	NM	5.8	NM	592,900	90,300
	120	NM	5.8	NM	592,900	180,600
	360	3.9E+05	12.0	10	592,900	541,700
	1440	6.2E+05	24.7	10	592,900	2,166,900

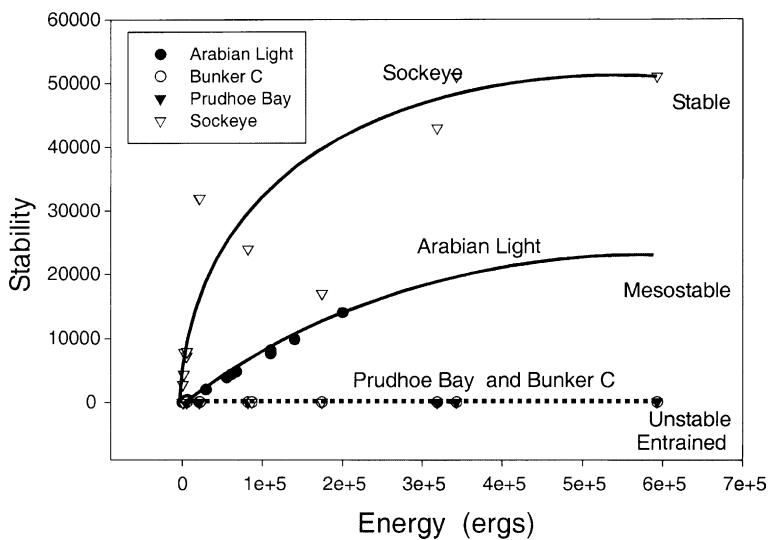


Fig. 1. Stability versus energy for four oils after one year.

rapidly between 200 and 300 ergs (1–1.3 rpm). After the rapid initial uptake, the stability of the water–oil mixtures remains the same and is typical of entrained water in oil. This study also shows that, for Bunker C, which forms an entrained water state, there is no increase in stability with increasing energy input after the initial formation point. The oil that forms a mesostable emulsion, Prudhoe Bay, shows 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. Both oils that form stable emulsions, Arabian Light and Sockeye, show an increasing stability with increasing energy, although the rate of increase is gradual with increasing energy.

Figure 1 also illustrates the relationship of stability of Prudhoe Bay with increasing energy. Water uptake is again rapid as in Bunker C, but at a higher energy threshold and a mesostable emulsion is formed. The

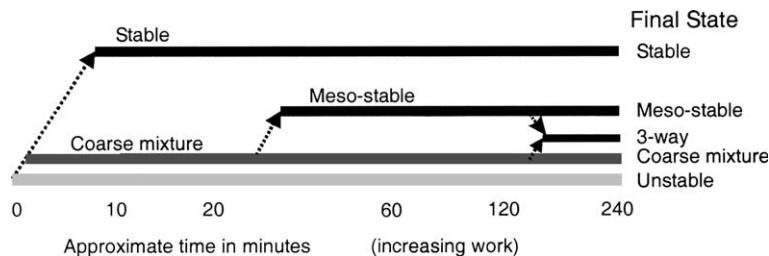


Fig. 2. The overall concept of state and approximate kinetics in emulsion and water-in-oil state formation.

uptake of water for Sockeye is very rapid at first, between the energy levels of 300–1500 ergs (1.3–2.8 rpm), and after this point stability increases slowly with increasing energy.

All four oils have several similar features: initial water uptake occurs very rapidly over a short energy range; the energy threshold for initial water uptake is very low, typically around 300 ergs, except for that of Prudhoe Bay which is about 250,000 ergs; there is no stability increase for the Bunker C in which the water is entrained and for the Prudhoe Bay which forms a mesostable emulsion; and there is a slow increase in stability with increasing energy for the oils, Sockeye and Arabian Light, which form stable emulsions.

The energy threshold at the onset of the two states known as stable and entrained water is very low, 300 to about 1500 ergs, which corresponds to a rotational rate of about 1–3 rpm in the formation apparatus. Total energy applied to the system was used as an indicator value. Turbulent energy could not be measured. The kinetics are summarized in Fig. 2.

4. Studies on migration of asphaltenes and resins

A series of studies was conducted to indicate the rate of asphaltene and resin migration in emulsions. Basically, the technique was to measure the asphaltene and resin content of the starting oil, in the bulk emulsion, and at the oil–water interface in the emulsion.

4.1. Experimental summary

Emulsions were formed using the specified crude oil either according to selected standard emulsion formation procedures outlined in the experimental sections above or in a blender. The emulsion was then placed in a large beaker and allowed to stand in a 10 °C cold room for one week. The oil layer on top was removed using a syringe with a large-gauge needle. The oil was collected as close to the surface as possible, with care taken to avoid the emulsion below. This sample was called the “free oil”.

If the emulsion was semi-solid, the beaker was tipped to concentrate the oil at one end. Oil remaining on top

of the emulsion was collected later and discarded. The emulsion remaining after the free oil was removed constituted the emulsion layer. The emulsion was broken using freeze/thaw cycles from −36 °C to room temperature. The thawed emulsion was then centrifuged at >2500 rpm for 30 min to separate as much water as possible.

After several cycles, the water content was minimal. It has been shown that the method of analysis of the oil for asphaltenes, saturates, aromatics, and resins is able to tolerate a small quantity of water without significantly affecting the results. This method was therefore deemed acceptable for the given application.

The asphaltene content of the oil sample was determined by asphaltene precipitation according to ASTM Standard Method D 2007. The eluted maltenes were blown dry using compressed air. The maltenes components of the oil were then determined. Only the non-volatile portions of the oil were analyzed.

For the long-term experiment, 1000 ml of emulsion was then placed in a large beaker and allowed to stand in a 10 °C cold room for three months. The layer of oil was removed using a syringe with a large-gauge needle. The oil was collected as close to the surface as possible, with care taken to avoid the emulsion below. If the emulsion was semi-solid, the beaker was tipped to concentrate the oil at one end. Oil remaining on top of the emulsion was collected after and discarded. It was found that an emulsion that has survived three months has elasticity, giving the emulsion some rigidity. The top 20% of the emulsion could therefore be collected using a spatula. The top layer of the emulsion was scooped up in small quantities covering the surface of the emulsion and placed in a graduated cylinder until 200 ml had been collected. The middle layer of emulsion between the top and bottom 20% was removed in the same manner as the top portion. It was not possible to collect a full 600 ml as coalesced water on the bottom distorted the proportion. An estimation was made to leave approximately 200 ml of emulsion, which was collected for extraction.

The extraction procedure was used on both of the emulsion layers from the experiment, as well as on the oil layer. The sampling procedure collected approximately 10 ml of oil. The sample was homogenized by simple mixing/stirring and an estimated amount of

emulsion sampled to yield 10–15 ml of oil. In the case of the oil layer, 10 ml of mixed oil was sampled for extraction using a 10-ml disposable plastic syringe. The sample was put into a 500-ml glass separatory funnel and 100 ml of dichloromethane (DCM) and 50 ml of salt water (3.3% NaCl) were added to the sample. The separatory funnel was shaken for 1 min and allowed to settle until most of the water and DCM had separated. The DCM layer was drained off to the turbid layer between the water and DCM phases and collected into a 500-ml beaker. Care was taken to ensure that there were no water droplets in the DCM layer, as the dark colour makes it difficult to determine the presence of water. A 70/30 mixture of DCM and pentane, respectively, was added to the separatory funnel. This was again shaken for 1 min and allowed to settle until most of the water and DCM phases had separated and the DCM layer was drained off into the 500-ml beaker. The rinsing of the sample with 50-ml aliquots of DCM/pentane was continued until the DCM layer was clear, usually between 4 and 6 rinse cycles, depending on the oil. When the DCM layer was clear and most of the DCM/pentane removed, 50 ml of benzene was added. The separatory funnel was shaken for 1 min and allowed to settle. The water layer was then drained off, down to the turbid layer, into a separate beaker to be discarded.

Two rinses of de-ionized water in the amount of 100 ml were performed, discarding the water from each rinse. The remaining benzene layer and the turbid layer containing water were both collected in the 500-ml beaker containing the rest of the effluent. The contents of the 500-ml collection beaker were evaporated down in a 100-ml boiling flask until the oil sample was obtained. The oil sample was then placed under a blow-down apparatus and blown with compressed air until the remaining solvent was driven off.

The asphaltene content of the oil sample was determined by asphaltene precipitation according to ASTM Standard Method D 2007. The maltenes were blown dry using compressed air. Weight difference was used in both instances to determine quantities. Only the non-volatile portions of the oil were analyzed.

Centrifuging was used to extract oil for analysis for some experiments. Salt water (2 ml of 3.3% NaCl) was poured into a 15-ml disposable centrifuge tube. Oil (10 ml) was injected over the water from a 10-ml disposable plastic syringe. A total of six tubes were filled in this manner. The centrifuge tubes were then placed into a centrifuge and spun at 3300 rpm for 2.5 h. The tubes were not moved from their places in the centrifuge as 2 ml of oil was removed from each tube by a syringe with a large-gauge needle, keeping the tip as close to the surface as possible. The oil was collected for later analysis.

One series of experiments consisted of placing oil and emulsion side by side to measure the migration of asphaltenes and resins without the influence of gravity.

Emulsion (120 ml) was placed into a 125-ml, wide-mouthed bottle. Teflon tape was wound around the threads of the bottle and upper rim. The mouth of the bottle was covered with a 10 × 10 cm square of 105-µm nylon mesh. A 60-mm ID Teflon collar was forcefully inserted over the mouth of the bottle to make a firm seal between the mesh and the rim of the bottle, aided by Teflon tape. An aliquot of 120 ml of the crude oil was added into another 125-ml, wide-mouthed bottle and used to form the emulsion. Teflon tape was wound around the threads and rim of the bottle and covered with a 10 × 10 cm square of 105-µm nylon mesh. The first bottle was placed over the second and inserted into the Teflon collar, using the necessary force to complete the union. The bottles in the collar were laid on their sides and clamped into place with a C-clamp. Neoprene spacers were used to protect the bottles from the contact pressure of the C-clamp. The bottles remained horizontal for one week in a 10 °C cold room.

The extraction procedure was used on both the emulsion side of the experiment and the source oil side. The procedure varied, depending on the quantity of oil expected to be contained in the emulsion. If 25 ml or less of oil was expected in the emulsion, the entire sample was extracted. If there was more oil present, then the sample was homogenized by simple mixing/stirring and an estimated amount of emulsion sampled to yield 10–15 ml of oil. In the case of the oil layer, 10 ml of mixed oil was sampled for extraction using a 10-ml disposable plastic syringe, using the liquid extraction procedure described above.

4.2. Results of the asphaltene migration experiments

The summary results of all four series of experiments are shown in Table 6. The experiments described as “one-week standing” in the table were designed to determine if there was a separation of asphaltenes between the top oil layer and the lower emulsion layer. Table 6 shows that there is a concentration of both asphaltenes and resins in the emulsion layer. While one particular experiment shows low concentration (−0.04%), this result is felt to be anomalous.

It is interesting to note that both the resins and asphaltenes are concentrated in the emulsion layer. In terms of relative percent, asphaltenes are concentrated an average of 18% and resins an average of 10%. When the emulsions were formed in the blender, perhaps leading to a more stable emulsion, asphaltenes are concentrated an average of 32% and resins an average of 1%. This appears to indicate that asphaltenes move downward to the emulsion layer, whereas a lesser amount of resins migrate. Because the emulsion layer is underneath the oil layer in this case, at least part of this migration may be due to gravity separation of the heavier asphaltenes.

Table 6

Summary of asphaltene and resin partitioning studies (Arabian light crude and emulsion)

Location	% Absolute change from starting oil		Asphaltenes	Resins now	Asphaltenes starting	Resins				
	Asphaltenes	Resins								
<i>Separation following one-week standing</i>										
Rotary shaker										
Free oil layer	0.16	0.3	4.01	8.34	3.85	8.04				
Free oil layer	0.07	0.3	3.92	8.34	3.85	8.04				
Emulsion layer	-0.04	0.9	3.81	8.94	3.85	8.04				
Emulsion layer	1.31	0.73	5.16	8.77	3.85	8.04				
Blender formation										
Emulsion layer	1.25	0.11	5.1	8.15	3.85	8.04				
<i>Long-term standing (three months)</i>										
Free oil layer	-0.23		3.62		3.85					
Top 20% of emulsion	0.56		4.41		3.85					
Bottom 20% of emulsion	2.86		6.71		3.85					
<i>Centrifuging oil over salt water</i>										
Top 20% of oil layer	0.71		4.56		3.85					
Bottom 20% of oil layer	1.8		5.65		3.85					
<i>Side-by-side experiment (one week)</i>										
Oil side	0.7		4.55		3.85					
Emulsion side	1.48		5.33		3.85					
Transmountain blend oil										
Oil side	0		4.55		4.55					
Emulsion side	0.85		5.4		4.55					
 % Relative change from starting oil										
Location	Asphaltenes		Asphaltenes	Resins						
	Asphaltenes	Resins								
<i>Separation following one-week standing</i>										
Rotary shaker										
Free oil layer	4.2	3.7								
Free oil layer	1.8	3.7								
Emulsion layer	-1	11.2								
Emulsion layer	34	9.1								
Blender formation										
Emulsion layer	32.5	1.4								
<i>Long-term standing (three months)</i>										
Free oil layer	-6									
Top 20% of emulsion	14.5									
Bottom 20% of emulsion	74.3									
<i>Centrifuging oil over salt water</i>										
Top 20% of oil layer	18.4									
Bottom 20% of oil layer	46.8									
<i>Side-by-side experiment (one week)</i>										
Oil side	18.2									
Emulsion side	38.4									
Transmountain blend oil										
Oil side	0									
Emulsion side	18.7									

The second set of experiments involved the testing of an emulsion that had been standing for three months. Three layers were sampled, a free oil layer from the top,

the top 20% (by height measurement) of the emulsion, and the lower 20% of the emulsion. As shown in Table 6, the oil layer is depleted 0.23% in asphaltene content in

absolute terms or 6% in relative terms. The top 20% is enriched by 15% in asphaltenes (relative percent) and the bottom by 74%, which indicates a strong partitioning of asphaltenes to the lower part of the emulsion system. Again, part of this may be due to gravitational settling of the asphaltenes.

A third experiment measured the asphaltene content of a salt water–emulsion–oil system in a centrifuge tube. This experiment was designed to measure whether asphaltenes would migrate to the oil–water interface. Gravity might be a factor, because the centrifugal force should move the heavier asphaltenes to the bottom. In fact, the results as shown in Table 6, indicate that there is a greater concentration of asphaltenes at the oil–water interface (47% relative). This shows that the asphaltenes will move to the oil–water interface and will be influenced by gravity.

A fourth series of experiments was conducted to examine how asphaltenes would migrate in the absence of a strong gravity effect. Two vessels were placed side by side, one with oil and the other with emulsion, with only a mesh separating the two materials. Sampling after one week showed an increase of 38% (relative) in asphaltenes in the emulsion formed from Arabian light crude and an increase of 17% in the emulsion formed from Transmountain blend oil.

These experiments show that asphaltenes migrate to the oil–water interface from the oil, which explains why an emulsion that sits for a period of time may become more viscous and stable as time progresses. During this time, asphaltenes are still migrating to the oil–water interface, thus rendering the emulsion more stable. The experiments show that migration still occurs after one or more weeks of contact. Furthermore, these experiments provide evidence that asphaltenes are the primary hydrocarbon group responsible for emulsion stability.

5. Tank tests

The relationship of the emulsions formed during the laboratory studies noted above to emulsions actually formed at sea is an important consideration. There are some concerns that laboratory studies may not be relevant to emulsions formed at actual spills. These concerns are based on the fact that there are major wall effects in laboratory vessels and the energy level may be undefined, as well as several other factors in the field that may not be accounted for in laboratory experiments.

A practical way to approach this study is to conduct parallel studies on real spills in the field and in the laboratory. The opportunities for studying the formation of emulsions at real spills, however, are very limited. Most oil spills do not result in the formation of stable emulsions that can be transported back to the

laboratory. The water in oil from spills often changes significantly before it can be measured.

In order to study emulsions on a larger scale, the OHMSETT facility of the US Minerals Management Service (MSS) in New Jersey was used. It should be added, however, that using this facility does not preclude the problems of wall effects, energy, and possible other factors. The test slicks at OHMSETT must be contained and the energy levels are still unknown, as are the wave regime relationships to those of the open ocean.

5.1. Methodology for tank tests

The tests were conducted in a manner similar to the laboratory tests described above, although using the features of the OHMSETT tank. To compare the OHMSETT results to those of the laboratory, the same oils were run through the standard laboratory tests. Detailed methodology and results are given in Fingas et al. (2001b, 2002).

The OHMSETT facility has an above-ground concrete tank measuring 203 m long, 20 m wide, and 3.4 m deep. The tank is filled with 9.84 million l of brackish water from nearby Sandy Hook Bay. Salt is occasionally added to the tank to make the water more saline, although this is diluted by rain water over time. The facility has a tow bridge capable of towing test equipment at speeds of up to 6.5 knots, which was used in these tests to anchor circular containment booms approximately 5 m in diameter. An auxiliary bridge provided an additional anchor point. A wave generator at one end of the tank can be set to four different stroke lengths and a relatively continuous variation in frequency of up to about 0.5 Hz.

The test oils were obtained by Mars through MMS regional contacts or contacts with refineries in the New Jersey area. Oils were poured from drums into smaller containers and enough oil was added to create the desired nominal slick thickness, calculated to be 20 l/mm. At the start of an experiment, the oil was placed in each of the four boom containment areas. A sample of the starting oil was taken and its properties measured. Samples were taken at intervals such as 1, 4, 7, 11, and 22 h.

The rheological properties of emulsions were measured using the Haake RS100 RheoStress rheometer, IBM-compatible PC with RheoStress RS Ver. 2.10 P software, 35-mm parallel plate spindle with corresponding base plate, and a circulating bath maintained at 15 °C. Analysis was performed on a sample spread onto the base plate and raised 2 mm from the measuring plate, with the excess removed using a Teflon spatula.

The sample was thermally equilibrated for only 5 min so that all four samples could be analyzed quickly, thus

limiting decomposition of the emulsion. As a result, thermal equilibration was incomplete, with a corresponding impact on data values. This compromise is necessary, however, to avoid further decomposition of the emulsions over time. A stress sweep at a frequency of one reciprocal second was performed first to determine the linear viscoelastic range (stress-independent region).

The viscosity of the starting oil was measured using an RV20 with RheoController, M5 measuring head, and NV cup and spindle with concentric cylinder geometry. The measurement protocol was a 5-min ramp up to a shear rate of 100 l/s, holding for 5 min, then ramping back down to zero. The reported value for the oil is the average viscosity over the 5 min at 100 l/s.

Water content was measured using a Metrohm 701 KF Titrino Karl–Fischer volumetric titrator and Metrohm 703 Ti stand. The sample was dissolved in a 1:1:2 solution of methanol, chloroform, and toluene and titrated with the single component Karl–Fischer reagent, Aquastar Comp 5. Water content is reported as percentage water by mass.

The results and test conditions of the first round of OHMSETT tests are summarized in Table 7. This shows that entrained water and mesostable states were produced in these tests. During the second series of tests, all states were categorized as unstable. This is probably a result of residual dispersant in the water from dispersant tests held in the tank two weeks earlier. The water

content and complex modulus of the oils were measured both at the OHMSETT facility and in the laboratory.

Observations were made on the appearance of the emulsions and used to classify the emulsions. All the stable emulsions appeared to be stable and remained intact over seven days in the laboratory. All the mesostable emulsions broke down into water, free oil, and emulsion in about 1–3 days. All entrained water mixtures appeared to have larger suspended water droplets and broke down within hours to an oil and water layer, with retention of some water. The appearance of non-stable water in oil was just that—the oil appeared to be unchanged and a water layer was clearly visible. Observations were also made in another study on the formation of emulsions (Fingas et al., 2000a). These show that the emulsions are formed fairly rapidly and that there is not a continuum of formation.

The stability over time for the oils tested both in the OHMSETT facility and in the laboratory is compared in Table 8. Stability is the complex modulus divided by the viscosity of the starting oil. While stability has units of s^{-1} , since the viscosity is measured at a shear rate of 1 s, it can be taken as unitless here. The emulsions formed in the first series of OHMSETT tests are typically more stable than those formed in the laboratory. In the second series of tests, the emulsions were about equally stable, but generally the emulsions formed in the laboratory results were more stable.

Table 7
Summary of tests and conditions—first round of OHMSETT tests

	First series—July			Second series—November		
	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
Start date	18 July	19 July	20 July	28 November	29 November	30 November
Oil boom 1	Sockeye	Sockeye	Sockeye	Fuel Oil #6	Arabian Light	Sockeye
Nominal thickness (mm)	1	2	4	2	2	2
Final result	Entrained	Entrained	Entrained	Unstable	Unstable	Unstable
Oil boom 2	Sockeye	Sockeye	Sockeye	Fuel Oil #6	Arabian Light	Sockeye
Nominal thickness (mm)	3	2	0.5	2	2	2
Final result	Entrained	Entrained	Entrained	Unstable	Unstable	Unstable
Oil boom 3	Fuel Oil #6	Fuel Oil #6	Fuel Oil #6	Arabian medium	Mars	Fuel Oil #6
Nominal thickness (mm)	1	2	4	2	2	2
Final result	Entrained	Meso	Meso	Unstable	Unstable	Unstable
Oil boom 4	Fuel Oil #6	Fuel Oil #6	Fuel Oil #6	Arabian light	Rock	Arabian light
Nominal thickness (mm)	3	2	0.5	2	2	2
Final result	Entrained	Meso	Meso	Unstable	Unstable	Unstable
Water temperature (°C)	27	27	27	3	3	3
Salinity (‰)	38	38	38	26	26	26
Water condition	Clear	Clear	Clear	Turbid/low ST	Turbid/low ST	Turbid/low ST
Average wave height (cm)	25	27.6	28.1	18.3	19.4	11.8
Average wave deviation (cm)	9	7.9	6.7	10.2	10.8	4.1
Average wave period (s)	2	1.9	1.92	1.8	1.8	1.4

Table 8

Comparision of stability of emulsions in OHMSETT tests and in the laboratory^a (first round)

Hours	OHMSETT emulsions				Laboratory emulsions		
	Original oil thickness				Second round average	Mixing speed (rpm)	
	1 mm	2 mm	4 mm	0.5		30	55
<i>Sockeye</i>							
0.17						1.0E+02	3.0E+02
0.5						1.0E+02	4.0E+02
1	4.0E+02	2.0E+02	1.0E+02	3.0E+02	4.0E+01	1.0E+02	3.0E+02
2						4.0E+01	3.0E+02
3			3.0E+02	1.0E+03	1.0E+02	2.0E+01	3.0E+02
4	6.0E+02	4.0E+02			1.0E+02		1.0E+02
6							
7	1.0E+03	7.0E+02	7.0E+02	1.6E+03			
10					2.0E+02		
11	2.3E+03	1.0E+03	1.1E+03	1.9E+03			
22	4.4E+03	1.5E+03	3.7E+03	4.0E+03	3.0E+02		
24						3.0E+02	1.0E+02
<i>Fuel Oil #6</i>							
0.17						2.0E+01	
0.5						3.0E+01	3.0E+01
1	4.4E+02		8.5E+02	4.4E+02	1.5E+02	6.0E+01	7.0E+01
2						4.2E+02	1.9E+02
3			4.2E+02	5.3E+02	9.0E+01	1.0E+01	5.1E+02
4	6.0E+02	5.1E+02			1.1E+02	2.0E+01	
6							
7	5.0E+02	5.6E+02	5.6E+02	6.2E+02		2.0E+01	
10					8.0E+01		
11	5.7E+02		6.2E+02			2.5E+04	
22	7.3E+02	7.8E+02	1.5E+03	7.7E+02	9.0E+01		
24						8.8E+02	1.4E+03
<i>Arabian light</i>							
0.17						9.0E+02	4.6E+03
0.5						1.6E+03	5.9E+03
1	1.0E+02	1.0E+02				9.0E+02	4.1E+03
2						6.0E+02	3.9E+03
3	4.0E+02	1.0E+02	5.0E+02			3.0E+02	4.6E+03
6	5.0E+02	6.0E+02	3.0E+02	1.0E+02			
10	2.0E+02	1.0E+02	5.0E+02	3.0E+02			
22	2.0E+02	2.0E+02	2.0E+02	7.0E+02			
24						4.0E+03	1.4E+03
<i>Arabian medium</i>							
6		1.0E+02					
10		2.0E+02					
22		5.0E+02					
24						3.0E+02	
<i>Rock</i>							
0.17						1.0E+01	
1		1.0E+01				1.0E+01	
2						3.0E+01	
3		1.0E+01				4.0E+01	
7		1.0E+01					
11		1.0E+01					
22		2.0E+01					
24						4.0E+01	
<i>Mars</i>							
0.17						dispersed in lab	
6		2.6E+02					
10		3.2E+02					
22		2.2E+02					

^a Stability is the complex modulus divided by starting viscosity.

5.2. Second round of tank tests

The second round of OHMSETT tests consisted of two series of tests, each conducted over two-week periods. The first series of tests took place in July and August, 2001 and consisted of testing nine oils and mixtures through a series of 12 experiments. The oils were sometimes tested over longer periods of time and one was tested for the full period of the experiment. During the second series of tests in November, 2002, eight oils were used in eight experiments. Two oils were tested for the entire period of the experiment. The rheological properties of the oils were measured and compared to the same oils undergoing emulsification in the laboratory. Some weathering studies were conducted in conjunction with the emulsification tests.

The tests were conducted in a manner similar to the laboratory tests described above. The rheological properties and viscosity of the oil were measured as described above.

Results and test conditions of the second round of OHMSETT tests (first and second series) are summarized in Table 9. This shows that stable, entrained, and mesostable states were produced in both series of tests. The relative wave energy varied in the OHMSETT tank, despite identical settings, probably because of differences in wind direction and velocity. This does not appear to have affected the results.

The stability of the water-in-oil states from the third and fourth series of the second round of OHMSETT tests is compared in Table 10. The ‘stability’ noted in these tables is the complex modulus (G^*) divided by the

viscosity of the starting oil. A slight problem noted in the 2001 OHMSETT tests was that the stability of emulsions formed from heavy oils is lower than those from light oils and in some cases is not necessarily a positive indicator of water-in-oil state. It is still useful, however, and the development of an absolute indicator may be a worthwhile project in the future. For diagnostic purposes, it is useful to group the more viscous oils together and the less viscous oils together. Stability then becomes a better discriminator. The overall average of ratio between the stability in the OHMSETT tank and the laboratory is about 0.6. This indicates that, overall, the ratio of energy in the OHMSETT tank during these tests and in the lab was about 0.6. As shown in Table 10, the stability of the particular oil or mixture during the OHMSETT test is about the same as at a later point in time.

Figure 3 indicates that the emulsions formed from the Sockeye and a mixture of Sockeye and Rock are about the same stability as those formed in the OHMSETT 3, 4, and laboratory trials. Similarly, Fig. 4 shows that the same stabilities are achieved in the OHMSETT 3 trials as achieved in the laboratory for two batches of Mars oil. It was noted in these trials that the stability of emulsions formed from heavier oils is indicated better by the complex modulus than the ‘stability’ index used throughout this paper. This will be further investigated in the future.

The mixtures of Arabian light and heavy crude oils were more stable in the laboratory than in the test tank. This may be due to the unique emulsions formed by these two oils. It was noted that both of these oils form a

Table 9
Summary of tests and conditions—second round of OHMSETT tests

	First series—July–August				Second series—October		
	Test 1	Test 2	Test 3	Test 4	Test 1	Test 2	Test 3
Start date	July 24	July 25	July 30	August 1	October 2	October 3	October 5–11
Oil boom 1	Sockeye	Same oil	Same oil	Same oil	Sockeye/rock	Same oil	Same oil
Final result	In formation	Stable	Stable	Stable	Stable	Stable	Stable
Oil boom 2	Sockeye	Arabian me- dium	Mix-rock/ sock	Mix-FO#6/ sockeye	Sockeye	Same oil	Same oil
Final result	Mesostable	Mesostable	Entrained	Stable	Stable	Stable	Stable
Oil boom 3	Fuel Oil #6	Rock	Mars	Bunker C	Mars	Rock	FO#6/sock
Final result	Stable	Entrained	Stable	Entrained	Stable	Entrained	Stable
Oil boom 4	Fuel Oil #6	Arabian light	Mix-rock/ sock	Same oil	Arabian medium	Arabian light	Mars
Final result	Stable	Meso-stable	Entrained	Entrained	Meso-stable	Meso-stable	Stable
Water temperature (°C)	27.2	28	28	25	14	17	11–17
Salinity (‰)	28	28	28	28	23	23	23
Water condition	Clear	Clear	Clear	Clear	Clear	Clear	Clear
Average wave height (cm)	25.1	25.3	24	22.5	15.2	23.6	16.1
Average wave deviation (cm)	6	7.8	8.7	8.4	9.4	8.5	9.6
Average wave period (s)	1.7	1.5	1.9	1.9	2	1.9	2
Relative wave energy (cm ² /s)	1	0.9	0.8	0.7	0.5	0.8	0.6

Table 10

Comparison of emulsion stability between the laboratory and third and fourth series of OHMSETT tests (second round)

Time (h)	Rock/sock			Sockeye			Fuel Oil #6		Mars		Rock		
	OHM 3	OHM 4	Lab	OHM 3	OHM 4	Lab	OHM 3	Lab	OHM 3	Lab	OHM 3	OHM 4	Lab
0.17			0			100		300		600			0
0.5			0			300		100		1900			0
1	100	0	0	100	0	400	100	100	1100	2200	0	0	0
3	100	0	100	300	100	700	600	600	2200	2400	0	0	100
6	100	0		600	300		1000		3000		0	0	
10.5	200	0	100	1200	500	1000	1400	1200	4200	5000	0	0	100
11										0			
22										0	100		
24	200	200	200	2100	1400	1500	2200	2500	5100	4300	0		100
25													
28.5											100		
30	300								5300				
37		100			1800			1000					
44													
47	300	300			2400				5600			100	
50						900							
	Fuel #6/sock		Mars			Arabian medium			Arabian light				
	OHM 3	Lab	OHM 3	OHM 4	Lab	OHM 3	OHM 4	Lab	OHM 3	OHM 4	Lab		
0.17		100			600			2300			9300		
0.5		200			1900			4700			14,600		
1	400	400	1100	100	2200	600	100	6200	300	100	14,100		
3	500	700	2200	100	2400	1600	100	7900	300	300	12,900		
6	400		3000	100		1500	200		600	400			
10.5	600	1300	4200	600	5000	2700	500		500	500	15,400		
11													
22													
24	500	3900	5100		4300	3000	3300		2700	8100	15,100		
25				2000									
28.5			5300										
30													
37													
44													
47			5600										
50													

mesostable emulsion which is interwoven with threads of 'rag'. Rag is the standard industry terminology for the remnants of a broken emulsion. Preliminary investigations into the nature of rag in the Environment Canada laboratory shows that it has many of the characteristics of a stable emulsion. The Arabian light and Arabian medium crude oils form a mesostable emulsion interlaced with the rag material. This shows a higher stability than normal because of the presence of the rag. The mesostable emulsion, however, breaks down in about one day, leaving the rag material.

5.3. Summary and conclusions

It has been shown that there are four clearly defined states of water-in-oil. These are established by their stability over time, their appearance, and by rheological measurements. The states are stable water-in-oil emulsions, mesostable water-in-oil emulsions, entrained water, and unstable water-in-oil emulsions.

Stable emulsions are reddish to brown solid materials with an average water content of about 80% on the first day of formation and about the same one week later. Stable emulsions remain stable for at least four weeks under laboratory conditions. The properties of the starting oil required to form a stable emulsion are: density 0.85–0.97 g/ml; viscosity 15–10,000 mPa s; resin content 5–30%; asphaltene content 3–20%; asphaltene-to-resin ratio 0.74; and average increase in viscosity, 1100 at day of formation and 1500 one week later.

Mesostable water-in-oil emulsions are reddish brown or black viscous liquids with an average water content of 62% on the first day of formation and about 38% one week later. Mesostable emulsions remain so less than three days under laboratory conditions. The properties of the starting oil required to form a mesostable emulsion are: density 0.84–0.98 g/ml; viscosity 6–23,000 mPa s; resin content 6–30%; asphaltene content 3–17%; asphaltene-to-resin ratio 0.47; and average increase in viscosity, 45 at day of formation and 3 one week later.

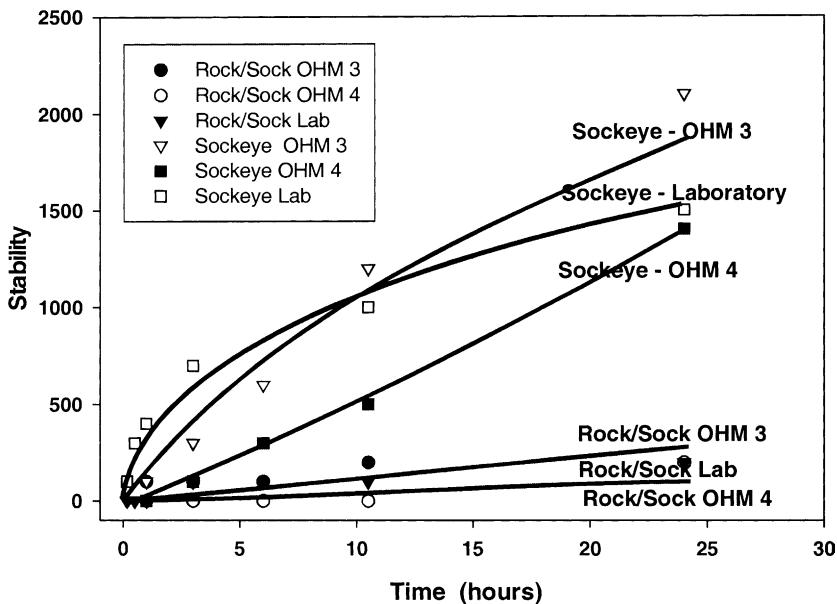


Fig. 3. Stability of Sockeye and rock/Sockeye mixture in various trials.

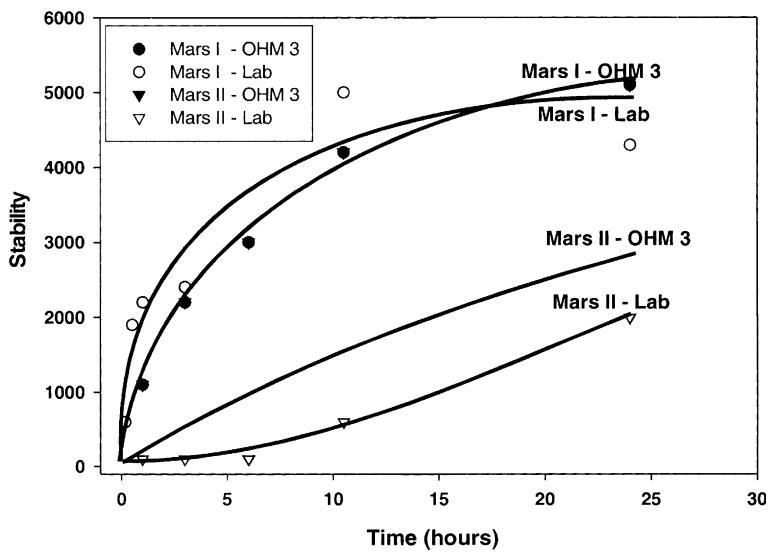


Fig. 4. Stability of two batches of Mars in various trials.

The greatest difference between the starting oils required to form stable and mesostable emulsions is the asphaltene-to-resin ratio (stable=0.74; mesostable=0.47) and the ratio of viscosity increase (stable 1100, first day and 1500 in one week; mesostable 45, first day and 30 in one week).

Entrained water-in-oil states are black liquids with an average water content of 42% on the first day of formation and about 15% one week later. Entrained water-in-oil states remain so less than one day under laboratory conditions. The average properties of the starting oil required to form entrained water are: density 0.97–0.99 g/ml; viscosity 2000–60,000 mPa s; resin content 15–30%; asphaltene content 3–22%; asphaltene-

to-resin ratio 0.62; and average increase in viscosity, 45 at day of formation and 30 one week later.

The greatest differences between the starting oils required to form entrained water-in-oil and those required for stable and mesostable emulsions are the narrow density range (entrained=0.97–99; stable=0.85–0.99; mesostable=about the same as stable) and the ratio of viscosity increase (entrained=13, first day and two in one week; stable 1100, first day and 1500 in one week; mesostable 45, first day and 30 in one week). Furthermore, the viscosity of the starting oil is 2000–60,000 mPa s compared to 15–10,000 mPa s for stable emulsions and 6–23,000 mPa s for mesostable emulsions.

Unstable water-in-oil emulsions are characterized by the fact that the oil does not hold significant amounts of water and, when it does, the water remains for only a short time. There is a much broader range of required properties for the starting oil than for the other three water-in-oil states. For example, viscosities are very low or very high. Included in this group are light fuels such as diesel fuel and very heavy, viscous oil products.

The stability of emulsions is due to the formation of asphaltene and resin films at the oil and water interface. Asphaltenes form strong, elastic films, which are largely responsible for the stability of emulsions. While there is clear evidence of interaction between resins and asphaltenes in forming emulsions, asphaltenes can form emulsions without resins. The most stable emulsions are formed when the asphaltene-to-resin ratio is about 0.75. The migration experiments show that asphaltenes migrate to the interface very slowly and that this process can continue for longer than one month. This leads to the possibility that the resins migrate very quickly and temporarily stabilize water droplets before stronger asphaltene films form and displace the weaker resin films.

It has been found that asphaltene films are a highly viscoelastic barrier to coalescence of water droplets. The films may be strengthened by H- or π -bonding between individual asphaltene molecules. Oil viscosity alone may be a partial barrier to re-coalescence of water droplets. This mechanism is proposed as the primary stabilizer for entrained water and partially for mesostable emulsions. This may also explain why waxes are seen as important in certain circumstances as they may increase viscosity enough to allow entrained water states to form. Waxes are not a factor in the formation of either stable or mesostable emulsions.

Weathering of oil is a factor in determining the stability of emulsions in a number of ways. First, the elimination of saturates and smaller aromatic compounds leads to the formation of emulsions. Second, viscosity increases as oil weathers, inhibiting the re-coalescence of water droplets. Finally, oxidation and photooxidation create more polar compounds, some of which may be regarded as resins.

The energy required to form emulsions is quite low in most cases. Further study is required on a wide variety of emulsions to determine if there is a relationship to oil properties or to emulsion types.

The properties and stability of emulsions can be measured by rheological studies, which include forced oscillation experiments and dielectric spectroscopy. The formation of stable emulsions is marked by a sharp increase in the elastic modulus. Water content is not a good indicator of emulsion characteristics other than that low water contents (<50%) indicate that an emulsion has not been formed and that the product is entrained water-in-oil. Interfacial measurements are useful for measuring the film strength of asphaltene and resin

components. It should be noted that initial water content is higher than water content after a period of time. Generally, a stable emulsion might lose up to 10% of its water content after about one year. This loss occurs both as a result of evaporation and water separation. The water separation appears to be largely 'excess water' and not breakdown of the emulsion structure.

The state of the final water-in-oil mixture can be correlated with the single parameter of the complex modulus divided by the viscosity of the starting oil (Fingas et al., 2000a,b). This stability parameter has been used to indicate the final stability of a given emulsion and thus its state. It was noted in these series of experiments that stability may not provide a definitive indication of the state for heavier oils. Mars and Fuel Oil #6 yielded stable emulsions at relatively low values of stability. Other parameters should be further investigated.

Many mesostable emulsions degrade into 'rag', which is the standard industrial term for the remnants of an emulsion. While it appears that rag may be large asphaltene–resin aggregates with trapped emulsion, further work is needed in this area.

The testing shows that the conditions for emulsion formation are similar in the OHMSETT tank and in the laboratory tests. Initially it was thought that energy level was the prime variant. With the exception of the Arabian crude oils, nearly identical water-in-oil states with similar stability are produced in similar times. The energy levels used in the laboratory for this set of experiments were high and thus the levels in the OHMSETT tank appear lower. The stability of emulsions formed in the OHMSETT tank lagged behind the laboratory ones in time, although similar stabilities were achieved in about 24 h. This also indicates that, if there is an energy threshold, both the laboratory and OHMSETT conditions are above that energy threshold required to produce emulsions.

All four states were produced during these experiments. Identical states were produced in the OHMSETT and laboratory experiments. The energy levels in the laboratory tests and those in the OHMSETT tank are similar. The test results indicate that the OHMSETT levels are similar to those conducted in the laboratory at between 50% and 70% of maximum energy.

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