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"Studies of Water-in-Oil Emulsions: Stability Classes and Measurement", in Proceedings of the Eighteenth Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ontario, pp 21-42,1995.

STUDIES OF WATER-IN-OIL EMULSIONS: STABILITY CLASSES AND MEASUREMENT

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ABSTRACT

This paper summarizes studies to determine the stability of water-in-oil emulsions and the measurement of emulsion stability. The most important question related to emulsion analysis is whether they are stable. In the strict thermodynamic sense, all emulsions are unstable; however, experimental evidence has shown that some emulsions will persist over a matter of months. A commonly-accepted definition is that an emulsion is considered stable if it persists at least five days at 15°C. An assessment of several tests for stability has been correlated to the basic definition. These tests include: observation of the colour of the emulsion, viscosity, elasticity, zero-shear rate viscosity, water content, and conductivity. The latter two measures are not, in themselves, reliable indicators of emulsion stability. It has been noted that most, if not all, emulsions that are stable are reddish in appearance and those that are not are black. The viscosity of a stable emulsion at a shear rate of one reciprocal second, is at least three orders-of-magnitude greater than that of the starting oil. An unstable emulsion usually has a viscosity no more than two orders-of-magnitude greater than that of the starting oil. The zero-shear-rate viscosity is at least six orders-of-magnitude greater than the starting oil for a stable emulsion. For an unstable emulsion, it is usually less than two or three orders-of-magnitude greater than the viscosity of the starting oil. A stable emulsion has a significant elasticity, whereas an unstable emulsion does not. These measures can then be used in the design of any emulsion-breaking test as a quick analytical tool. It should be noted that very few emulsions have questionable stability. The usual situation is that emulsions are obviously either stable or unstable. Analytical techniques are then largely required to test the few questionable emulsions or to rapidly confirm the stability of the others.

Studies have shown that a class of 'very stable' emulsions exists, characterized by their persistence over several days. These stable emulsions actually undergo an increase in viscosity over time. Monitoring of these emulsions has been performed for over two weeks and new studies over much longer times are being conducted. 'Unstable' emulsions do not show this viscosity increase. A class of emulsions between stable and un-stable has been proposed. These ‘meso-stable’ emulsions have properties between the stable and unstable and decay within a few months to either two or three phases. In the case of the latter, one of the phases is a stable emulsion.

Introduction

The most important characteristic of a water-in-oil emulsion is its "stability". The reason for this importance is that one must first characterize an emulsion as stable (or unstable) before one can characterize the properties. Properties change very significantly for each type of emulsion. The major problem is, however, that the types or stabilities of emulsions have not been defined. Therefore, studies are difficult because the end points of analysis are not defined. The purpose of this paper will be to propose a definition of stability for water-in-oil emulsions and characteristics of different stability classes.

The 'stability' of an emulsion itself might be a question. Historically, emulsions were thought of as unstable, therefore any discussion of 'stability' would be considered trivial at best, and irrelevant at worst. This has changed in recent years. Many commercial products resembling water-in-oil emulsions made from crude oil, have been shown to be stable, especially as it relates to their production, sale, storage and use as consumer products. A quick scan at the references in this paper shows that most workers in the field, now discuss the 'stability' of water-in-oil emulsions.

Given that stability exists, how does one define stability? One solution that has been proposed is that an emulsion that does not lose more than 20% of its water over five days, might be said to be stable (proposed at the emulsion workshop held in Kananaskis, 1993). Another definition at the same workshop proposed that the same definition be altered to reflect 10% water loss. Still another suggested 10% oil loss. The problem with these definitions is that they may not relate to the actual situation. In fact, observations by the present authors are that 'stable' emulsions do not lose any measurable water or oil in five days. Furthermore, there may be more than one class of stable emulsions. Both the loss percentage of the above proposals and the number of days should be called into question. This paper will present stability definitions which relate to the intrinsic properties of the emulsions rather than *pro forma* definitions.

The present authors have studied emulsions for many years (Bobra, 1992; Fingas, Fieldhouse et al., 1993a, 1993b, 1993c, 1994a, 1994b, 1995). Reviews of the physical characteristics of emulsions formed during these years of study and in the past year are used to classify emulsion behaviour. These data are largely taken from laboratory measurements, however, the group has analysed several emulsions from field trials and actual spills during this time. No major differences have been observed.

Literature Review

An extensive literature search was performed specifically of topics that related to the stability of water-in-oil emulsions and measurements of stability. This includes the sub-topics of causative agents to stability, techniques to characterize emulsions (ie. stability) and descriptions of measurement apparatus.

Berridge, Dean and co-workers (1968) were the first to publish a paper that referred to the water-in-oil emulsions as highly stable and stated that this stability must be derived from 'external agents'.

Jones, Neustadter and Wittingham (1978) studied the stability of crude oil emulsions of several types. They measured stability by phase separation. They noted that much of the contemporary instrumentation was incapable of providing accurate prediction of emulsion stability. Interfacial tension and rheometry on the starting oils were not found to be useful predictors of resulting emulsion stability. A dilational modulus apparatus was proposed to provide a reliable emulsion stability prediction measurement.

Fogler, Reddy and colleagues (1979) studied the properties and stabilities of a variety of fuel emulsions, noting stability only in number 4 and 6 fuels. Stability was monitored by viscosity and was attributed to the viscosity of the product, which slowed water droplet coalescence.

Bridie, Wanders and co-workers (1980) studied the stability and de-stabilization of emulsions. The workers noted that viscosity and thixotropic properties could be associated with stability.

Neuman and Paczynska-Lahme (1981, 1988) reviewed the properties of crude oil emulsions noting that the emulsions are often very stable. They pointed out that the emulsions are stabilized by the surfactant effects of asphaltenes and resins. Stability is associated with unusually high viscosities - higher than predicted by viscosity equations such as the Einstein equation.

Graham, Stockwell and Thompson (1983, also Graham, 1988) studied the stability of crude oil emulsions using viscosity measurements, interfacial film pressures and phase separation. It was noted that the thermal history of oil production affected emulsion stability. Rapid chilling was felt to decrease wax particle size which was proposed to have a direct effect on emulsion stability.

Steinborn and Flock (1983) studied the viscosity of oils and emulsions. They found that water-in-oil emulsions display a pseudoplastic characteristic.

Desmaison, Desmarquest and co-workers (1984) studied the stability of water-in-oil emulsions formed from weathered Arabian crude oil using an interfacial viscosity apparatus. They found that the interfacial viscosity increases with time and this was attributed to the increasing aggregation of asphaltenes.

Friberg and Solans (1986) reviewed the stability of emulsions and noted that liquid crystals (here: surfactant association structures) gave enhanced stability to emulsions.

Davies, Graham and Vincent (1988) studied the stability of water-in-oil emulsions using pure components as a surrogate. The stability was measured by using light-scattering.

Eley, Hey and Symonds (1988) studied emulsions using crude oil and crude oil surrogates. Stability was determined by phase separation observation, but also correlated to droplet size distributions, which were found to follow log-normal distributions, and to interfacial area, which is calculated from the volume of water uptake in a given amount of time. The most stable emulsions were found to be formed from oils where the aliphatic/aromatic ratio is such that the asphaltenes are at the point of precipitation.

Johansen, Skjärvö and co-workers (1988) studied the stability of 32 emulsified oils from Norway. They studied stability primarily by using normal phase separation, but also by separation using ultra-centrifugation at 650-30,000 g. These two measures correlated well. Viscosity of the resulting emulsion correlated well with the stability. Emulsion stability was given a numeric value by taking the separation time at which 20% of the water was lost. A three-parameter model was created which could predict emulsion stability with a correlation coefficient of 0.7. Input parameters to this equation included emulsion viscosity, starting oil viscosity and wax content. Interfacial tension, measured using a DeNouy ring, did not correlate well with emulsion stability.

Sax, Schön and co-workers (1988) studied model water-in-oil emulsions using dielectric spectroscopy between 5 Hz and 13 MHZ. They concluded that the complex dielectric constants calculated from the spectroscopic data could clearly distinguish between stable and unstable emulsions.

Aveyard, Binks and co-workers (1990, 1992) studied the stability and breakdown of water-in-oil emulsions. They concluded that the stability of emulsions was achieved by a low HLB surfactant or material acting as a surfactant. In their tests, they used artificial surfactants, but they noted that natural products could perform the same role. Emulsion stability was measured by using visual appearance on separation and by conductivity.

Chen and Ruckenstein (1990) studied the stability of concentrated pure-hydrocarbon emulsions and rated the stability of the emulsions by visible phase separation. They concluded that the larger the interfacial free energy between water and oil phases and the more non-polar the oil phase, the more stable the emulsion will be.

Paczynska-Lahme (1990) examined oil and emulsions and proposed that water-in-oil emulsions are stable because of the elastic interfacial films formed by the resins and asphaltenes. It was also noted that multiple types of emulsions could apparently coexist in petroleum.

Sjöblom, Urdahl and co-workers (1990a, 1990b) studied several crude oils from Norway and measured emulsion stability by examining phase separation. Asphaltenes were removed and it was found that no oils would produce stable emulsions. The asphaltenic and resinic fraction was analyzed by FTIR and palmitic acid was identified. Addition of the asphaltenes and resins back to oils rendered stable emulsions.

Brandvik and Daling (1991, also Daling and Brandvik, 1988) studied the stability of several Norwegian crude oil emulsions by measuring the water settled out after 24 hours. Stability was assigned a numerical value of one less the fraction of water lost after the 24-hour settling period. Stability correlated most with the viscosity of the oil, then the amount of resins and then the amount of asphaltenes in the oil.

Nordli, Sjöblom et al. (1991) separated interfacially-active components in six different North Sea oils and measured their film properties. The fractions form monomolecular films at the air/water interface and were relatively stable, but could be fractured with surface pressures between 10 and 29 nNm^{-1}. Aromatic solvents were found to interact strongly with the film and modify film properties. The interfacially-active components were asphaltenes and resins and are attributed to be the cause of emulsion stability. The researchers proposed the strength of the surface film they measured is responsible for water-in-oil emulsion stability.

Omar, Desouky and Kamara (1991) used viscometry to study water-in-oil emulsions made from Saudi Arabian crudes. They noted that stable emulsions displayed non-Newtonian characteristics and exhibited pseudoplastic behaviour.

Darkisov and Faitel'son (1991) studied water-in-oil emulsions and noted that more concentrated and stable emulsions had higher viscosity and displayed elastic properties.

Reddy (1991) presented an overview of emulsion stability and theoretical calculations associated with de-stabilizing processes including flocculation and creaming.

Ebeltoft, Børve and co-workers (1992) studied the interactions between poly(styrene-allyl alcohol) monolayers and a surfactant in a Langmuir trough to apply this to crude oil emulsion stability and stabilization. This study points to the oleophilicity of the natural oil surfactants as being a primary factor to stability.

Friberg (1992) reviewed the stability of emulsions and noted that although viscosity is a stabilizing influence in that it slows coalescence, surfactants are generally necessary to form a truly stable product.

Hill and Cooper (1992) studied the use of dielectric spectroscopy to study emulsions. In this method electric response of the sample is measured as a function of the frequency of the applied AC voltage. Frequencies ranging from milliHertz to megaHertz were found to be useful in studying emulsion stability.

McMahon (1992) studied emulsion stability by observing phase separation or by measuring residual water in the oil phase by Karl-Fischer titration. The hypothesis that wax content influences stability was tested. It was found that the wax influence on stability was present, but not as strong as the asphaltene and resin influence and that the wax influence may not be through action at the interface. It was proposed that the wax influence on stability was exerted by inhibiting film thinning between approaching droplets.

Mingyuan, Christy and Sjøblom (1992) studied emulsion stability as it related to asphaltene and resin content. The authors concluded that asphaltenes yielded more stable emulsions than resins. They also noted that water-in-oil emulsion stability is a function of aromaticity, polarity, molecular size, and type of functionality in the stabilizing fraction (asphaltenes and resins).

Ponton, Nozaki and Bose (1992) studied pure compound water-in-oil emulsions using dielectric relaxation. This technique provided differentiation between types and characteristics of emulsions.

Sjöblom, Urdahl and co-workers (1992a, 1992b) studied the stability of Norwegian oil emulsions and concluded that stability is the result of the asphaltene/resin fraction. Dielectric spectroscopy was also thought to be a useful means of studying stability in addition to phase separation. The interfacial pressure of asphaltenic- and resinic-stabilized emulsions was shown to correlate with stability.

Tambe and Sharma (1992, 1993, 1994) studied colloid-stabilized emulsions and noted that stability was largely achieved by the presence of a visco-elastic interface. This interface affects stability by retarding the rate of film drainage between coalescing emulsion droplets and by increasing the energy required to displace particles from the contact region between droplets (or described in a different way - by increasing the steric hindrance).

Urdahl, Brekke and Sjöblom (1992) studied the silica-absorbed fractions of crude oil (traditionally taken as resins and asphaltenes) and found that the bulk of the stabilizing fraction consisted of long, straight-chain aliphatic compounds containing a heteroatom substituent.

Acevedo, Escobar and co-workers (1993) studied the rheological properties of heavy crude oils and oils to which resins and asphaltenes were added. A planar surface rheological study of a Cerro Negro crude oil, its emulsions and dilutions of emulsions and its asphaltenes, was conducted. The interfacial moduli instantaneous (Eo) and retarded (E_1) elasticities, as well as the associated (η_1) and Newtonian (η_n) viscosities were determined from creep compliance experiments. High values were obtained for viscoelastic parameters for 'stable' emulsions. The researchers noted that these findings agree with the general view that during adsorption at the oil-water interface, the natural surfactants (asphaltenes and resins) form a three-dimensional cross-linked network leading to strong interfacial films. These interfacial films cause the stability of the w/o emulsions

Aronson and Petko (1993) studied concentrated emulsions with over 95% water prepared from refined mineral oil and commercial low HLB surfactants. Emulsions prepared when electrolytes were present were more stable than those prepared from de-ionized water. Stability was noted by high yield stress. Destabilization was noted by droplet size increases up to the phase separation of the oil and water and by decreases in yield stress.

Becher (1993) reviewed the stability of water-in-oil emulsions and noted that some emulsions formed from crudes at sea may be classified as 'very stable'. This stability is attributed to 'steric stabilization'. Steric stabilization is the stabilization resulting from the presence of many smaller chain surfactants at an interface, thus preventing re-coalescence. Becher points out that 100 times more smaller surfactants (which could include resins and smaller asphaltenes) can be placed at an interface compared to some polymer systems studied.

Miller and Böhm (1993) studied coalescence in crude oil emulsions using optical methods. The researchers found that they could use either transmitted light through a cuvette or back-scattered light using a fibre optic reflection probe. It is questionable whether these techniques could be applied in reverse, that is to examine fully emulsified oil.

Mohammed, Bailey and co-workers (1993a, 1993b, 1994a, 1994b) studied several aspects of water-in-oil emulsion stability. A rheological study using free oscillation and creep models showed a strong correlation of elasticity with stability. One study also showed that the viscous interfacial films formed between crude oil and water became more elastic and viscous with time, thus increasing the emulsion stability further. In another study, a Langmuir trough was used to study the surface pressure versus area (interfacial tension curves) of resin and asphaltene mixtures. These studies indicate that strong films (and hence stable emulsions) are a result of the flocculation of asphaltene-resin micelles at the interface. In the absence of resins, the asphaltenes behaved differently and were not dispersed but precipitated and formed multiple layers. This could produce a less stable emulsion. All the studies pointed out that the interfacial film ages and becomes stronger and thus the emulsion becomes more stable with time. This is also evidenced in an increasing difficulty breaking the emulsion.

Solans, Pons and co-workers (1993) studied model emulsion systems. They concluded that highly concentrated emulsions can be classified as stable or as highly unstable.

Tadros (1993) reviewed the rheology of emulsions noting that stable water-in-oil emulsions can be characterised by their viscoelastic properties. Unstable emulsions show low or decreasing amounts of elasticity.

Barnes (1994) reviewed the rheology of emulsions and noted that the specific characteristics of an emulsion strongly affects the rheological properties. Increasing phase volume and particle sizes influence the rheology greatly.

Bhardwaj and Hartland (1994a) studied emulsion coalescence. Destabilization of emulsions was studied by examining drop size during coalescence. It was found that coalescence rate was very fast and binary coalescence occurred after 5.4 seconds from the first minute after the addition of a chemical demulsifier. A further study by

Bhardwaj and Hartland (1994b) focussed on the study of the aging of the crude oil/water interface of emulsions. This was studied with interfacial tension data and microvideography. The researchers found that the accumulation of natural surfactants (resins and asphaltenes) occurred slowly and that after 60 hours accumulation at the interface was still in progress. Accumulation occurred over the minimum stabilization and continued until a large 'excess' was achieved. The area occupied by a natural surfactant molecule was calculated to be about 366 $Å^2$.

Brooks and Richmond (1994a, 1994b) have studied the inversion of simple systems and noted the effects of droplet size and mixing energy. Droplet sizes appear to be controlled by their area of surfactant coverage (and hence the amount of surfactants).

Chaala, Benallai and Hachelef (1994) studied the stability of crude oils with varying asphaltene and wax components. This group has developed a method of rating emulsion stability based on the difference in optical densities of samples, before and after centrifugation. Emulsions are rated on a stability basis of zero to one based on the ratio of the optical density. Studies showed that emulsion stability is decreased by increasing quantities of waxes and aromatics.

Hartland and Jeelani (1994) show, using mathematical models, that emulsion stability can be explained by the concept of surface mobility which is proportional to surface velocity. If the interfacial gradient is negative, the surface mobility is negative and thus drainage is reduced and the emulsion is stable.

Pal (1994) reviewed techniques for measuring the composition of emulsions. Water content was suggested as best performed by Karl Fischer titrations. Other methods have difficulties when stable emulsions are being studied. Differential Scanning Calorimetry may be the only technique capable of distinguishing free from bound water, however, evaporation of volatile oil components may be a problem. Capacitance and conductivity measurements may have applications, however, the variance in salinity of the water may confound measurements. Viscosity has similar limitations in that the nature of the emulsion changes the results.

Sjöblom, Skodvin and Jakobsen (1994) studied the application of dielectric spectroscopy to the stability characteristics of emulsions. The results appear to indicate that the dielectric constants may correlate with stability of emulsions, however further work was suggested.

Skodvin, Jakobsen and Sjöblom (1994) and Skodvin, Sjöblom and co-workers (1994) continued the study of the application of dielectric spectroscopy to emulsion stability. In one study, emulsions were studied under flow conditions in the frequency range 50 MHz to 2 Ghz. The flowing emulsions show lower static permittivities than those at rest. Dielectric data were explained by flocculation of the aqueous droplets. Theoretical data was not found to be useful to explain results. Dielectric spectroscopy was said to have potential for emulsion characterization.

The consensus of the literature is as follows:

1. Stable emulsions exist,
2. Emulsion stability results from the viscoelastic films formed by asphaltenes and resins at the oil-water interface,
3. Asphaltenes produce more rigid films than do resins,
4. Stable emulsions might be classified by their visco-elastic properties derived

from the stable film - stable emulsions show elasticity, unstable do not.

5. Stable emulsions also show high viscosities associated with the viscoelastic nature of the product,
6. Water content does not appear to relate to stability, however, very low or very high water contents (<30 or >90%) are generally conceded not to yield stable emulsions.
7. The role of water droplet size is unclear, there may be a weak association to the presence of 1-20 μ droplet sizes (versus much larger) in stable emulsions.
8. Dielectric spectroscopy might be a useful tool to explore emulsion properties and stability, however the technique requires much more work.
9. Most researchers use visible phase separation to classify emulsions as stable or not and most concede that this is not an optimal technique.
10. Standard conductivity measurements, particle size measurement and interfacial tensions measurements on bulk emulsion, do not show promise for studying or classifying emulsions.

Experimental

Methods of Analysis

Precise measurement techniques are essential to the study of emulsions. The measurement currently of prime utility is that of viscosity. Because of the nature of the emulsion, non-Newtonian and subject to shear breaking, the equipment and techniques must be modified from those used to measure regular oil viscosity. The next most important measurement is that of water content. Commercial instrumentation and standard techniques exist for this purpose. No current instrumentation or methodology exists to measure water droplet size in the emulsions except for optical microscopes.

A major drawback with emulsions is that certain formation techniques result in heterogeneous emulsions. These usually consist of emulsions with large droplets of water adhering or partially trapped. This "excess" water must be dealt with before analysis for viscosity or water content. The excess water can cause very large errors, especially in viscometers. The free water can become entrained in the spindle path of a cup and spindle viscometer. This can result in readings as low as two orders-of-magnitude lower than the actual emulsion viscosity value (Fingas, Fieldhouse et al., 1994). This laboratory has examined some techniques for dealing with this excess water. The following are detailed descriptions of analytical techniques developed by and used in this laboratory for characterizing emulsions.

Viscosity - This laboratory uses the following apparatuses: Haake Rotovisco RV20 with M5 measuring system, Haake Rheocontroller RC20 and PC with dedicated software package Rotovisco 2.2. The sensors and vessels used are: high viscosity - SVI spindle and SV cup; low viscosity- NV spindle and cup. The shear rates used are one and five reciprocal seconds. The viscometer is operated with the following ramp times: five minutes to target shear rate 1/s; 5 minutes at target shear rate 1/s; return to stationary 5 minutes to target shear rate 5/s; and 5 minutes at target shear rate 5/s. The temperature is maintained at 15 degrees Celsius. The method steps are as follows: set circulating bath at 15 degrees Celsius. Scoop or syringe 9 mL sample into the cup. Screw spindle into the M5 sensor system. Slowly raise cup up to the spindle. Secure in place. Program shear ramps. Allow 15 minutes to thermally equilibrate. Initiate program. Maximum viscosity values at each shear rate are selected.

Rheology - The following apparatuses were used for rheological analysis: Haake RS100 RheoStress rheometer, IBM-compatible PC with RS100-CS Ver. 1.28 Controlled Stress Software and RS100-OSC Ver. 1.1.4 Oscillation Software, 35 mm parallel plate and 60 mm 4-degree cone with corresponding base plate, clean air supply at 40 p.s.i., and a circulation bath maintained at 15.0 degrees Celsius. Analysis was performed on a sample scooped onto the base plate and raised to the measuring plate or cone. This was left for 15 minutes to thermally equilibrate at 15 degrees Celsius.

Controlled Stress - this was used for determining the linear viscoelastic range (stress independent region) and the creep and recovery analysis. The linear viscoelastic range (LVER) was determined first for all samples, as all measurements must be made in the LVER to be valid. It was determined by making a stress sweep over the stress range to identify the break point (estimates will speed this process). After identifying the stress independent range, two stress values were chosen for subsequent analysis - one close to the break point, and one other. These stress values were used in the creep and recovery analysis, and the oscillation procedures.

Creep and recovery provides the zero shear viscosity, and was performed in two phases; first the creep for 240 seconds at the designated stress, followed by the recovery for 60 seconds. An analysis of the resulting curve provides the zero shear viscosity.

Oscillation - this was used for determining the tan(δ) (ratio of viscous to elastic components) and G* (total resistance to flow). Both values were obtained from a frequency sweep of the sample from 0.1 to 25 Hz, at the designated stress values. Mathematical treatment provides the G* and tan(δ) values.

Water Content - A Metrohm 701 KF Titrino Karl-Fischer volumetric titrator and Metrohm 703 Ti Stand are used. The reagent is Aquastar Comp 5 and the solvent, 1:1:2 Methanol:Chloroform:Toluene. The specific method used is as follows: standardize the titre and blank the solvent. Stir the sample to get a relatively homogeneous emulsion. Fill a 1 mL plastic syringe with emulsion, avoiding free water pockets present in the sample. Eject all but 0.1 mL; this will remove most of the free water from the more viscous emulsion. Weigh the sample syringe and inject into the reaction vessel, being careful the sample goes into the solution and not onto the vessel walls. Reweigh the syringe and enter the difference into the titrator. Initiate titration. Weight percentage of water is displayed.

Laboratory Formation Techniques

One of the objectives of the investigation into emulsions is to have a standard method of forming the emulsion from a given oil. To compare various means of forming an emulsion and their ability to create emulsions, formation methods for three different apparatuses were developed. Each uses a different means of supplying energy to the oil/water system, and all are all commercially available.

Rotary Agitator

This apparatus imparts energy to the oil/water by an end-over-end rotation of glass cylinders. The apparatus has an advantage in that it is a standard extraction apparatus specified in an EPA standard, unrelated to oil emulsions. The major differences between this and previous rotary apparatuses are the increased height and volume of the bottles and the speed of rotation. The standard motor of the rotary agitator drives the apparatus at 30 rpm. However, a variable speed motor is also available for this apparatus, capable of up to 56 rpm. A rotation speed of 50 rpm has been chosen for the general method to give a high rotation rate. As well, the increased height of the bottles increases the distance through which the contents fall during rotation. The combination of increased height and higher rotational speed, increases the energy applied.

A 1:25 oil-to-water ratio is now used for stability studies and emulsion inhibitor tests.

An observation of note is that emulsions of higher viscosity are formed when the vessels are inserted such that the capped end leads into the direction of rotation. The reason for this may be the added turbulence created by the neck region of the bottle as the oil falls, as opposed to falling on the smooth bottom end.

The currently used procedure is summarized in the following paragraph:

The apparatus is an 8-place Rotary Agitator from Associated Design and is equipped with a variable speed motor from 1.5 to 56 rpm. The mixing vessels are Wheaton 2.2 litre wide mouth glass bottles. The fill is 500 mL salt water (3.3% w/v NaCl) and 20 mL oil. This yields an oil-water-ratio of 1:25. Stability studies are performed at 50 rpm, which is set using a tachometer. The mixture is rotated for 3 hours. The specific method is as follows: place rubber collars on glass bottles at the midway point. Add 500 mL salt water and 20 mL oil to the mixing vessel. Place Teflon lid liners on the bottles and cap. These steps should be performed as quickly as possible to reduce exposure of the oil. Insert the bottles into the rotary agitator at the rubber collars, such that the cap is leading into the direction of rotation. Rotate at 50 rpm for 3 hours. Remove the bottles and pour off the water. Collect the emulsion in an appropriately sized beaker. Analyze for water content and viscosity.

Blender

The use of a blender for making emulsions was first used in early emulsion-breaker testing, for creating the most-stable emulsion possible. The method is simple and quick, has the highest energy available, and generates the highest-viscosity and most stable emulsions. The method employed in our laboratory is as follows:

The Waring 1 litre Duo Speed Commercial Blender is used with Eberbach 1 litre borosilicate container with stainless steel blender assembly. The fill is 70 mL salt water (3.3% w/v NaCl), additional 25 mL aliquots as needed and 30 mL oil. The starting oil-to-water ratio is generally 1:4, but variable as noted. The mixture is stirred with 15,500 rpm blade rotation. The mixture is agitated for 30-second intervals until a stable (as determined visually) emulsion forms. The specific methodology is as follows: combine 70 mL salt water with 30 mL of oil in the blender vessel. Turn blender on at low setting for 30 seconds. Stir with a rubber policeman and add 25 mL salt water. Turn on blender again for 30 s. Stop, stir and repeat. If an excess of at least 2 mL water is not present, add another 25 mL aliquot of salt water. Continue to blend, stir and add water until an excess of water is obtained. Additional water is not normally required. When emulsion formation is complete, pour off the excess water and pour/scoop the emulsion into an appropriately sized beaker.

Wrist-Action Shaker

The Burrell wrist action shaker had been utilized in the past for its emulsion breaking ability. It was used specifically to relate the energy of the emulsion breaking test to the energy of formation. At that time, it was found that the Burrell would not always form a stable emulsion. The detailed method for using the wrist action shaker in this laboratory is as follows:

The specific device used is the Burrell wrist action shaker model 75. This unit is equipped with a top platform mount with large separatory funnel clamps. The vessels used are Nalgene 1 litre Teflon separatory funnels with screw-cap lids. In the stability studies, 800 mL salt water (3.3% w/v NaCl) is used with 32 mL oil, yielding an oil-to-water ratio of 1:25. The oscillation is set at a 5 degree arc at a 20 cm radius. The agitation time was 30 minutes. The specific experimental procedures are: measure salt water into the separatory funnel. Add oil using a plastic syringe. Mount the separatory funnels into the funnel clamps on the top platform; be sure all apparatus are at 90 degree angles. Move adjustment arm on the Burrell shaker until an arc of 5 degrees is obtained. Shake for 2 hours. Remove from the shaker and allow emulsion to settle to the top. Drain the water and pour/scoop the emulsion into an appropriately sized beaker.

Results and Discussion

Table 1 shows the properties of several emulsions produced using the above methods. The emulsions were classified as being of three classes; stable, meso-stable or unstable (entrained water). The data show that there exist clear differences between the various subclasses of emulsions. Table 2 shows rheological studies on stable and meso-stable emulsions. A proposed division of these emulsions is shown in Table 3. This highlights the differences between the stable emulsions and those that are either meso-stable or unstable. Differences can be highlighted in terms of:

1. elasticity, meso-stable and unstable emulsions show less elasticity (.1 or higher)
2. viscosity differences from starting oil, meso stable typically show only two orders-of-magnitude increase above that of the starting oil; unstable emulsions, much less than that; whereas stable emulsions show viscosities of at least three orders-of-magnitude above that of the starting oil, and
3. zero-shear viscosity is 10^5 or higher for stable emulsions and much lower for meso-stable emulsions
4. appearance and longevity.

Furthermore, these differences are readily measurable or discernable. Table 1 shows that many of the meso-stable emulsions decay to oil, water and stable emulsion - indicated by the 'meso-3' in the emulsion type column. Less frequently, emulsions decay to oil and water, two phases, as indicated by the 'meso-2' in the emulsion column. The most obvious difference shown in Table 1 is the large difference in the ratio of the viscosity of the emulsion to that of the starting oil. Stable emulsions show a difference of at least 2000 times that of the starting oil. Also notable in the table is that water content does not correlate to viscosity or stability. The energy of formation is also important and it can be noted in Table 1 that the Burrell shaker never does create a stable emulsion, while the highest energy device, the blender, will succeed in many cases. The rotary agitator (R/A) appears to fall about intermediate in energy.

Table 2 shows that the zero-shear viscosity is clearly a discriminating parameter for stability. A zero-shear viscosity of above 10^5 is an indicator of stability. The elasticity is also a discriminator, however, is not clear in all cases. Values lower than

Table 1

Properties of Emulsions

Oil	Formation Method	Per Cent Weathered	Water Content Average (wt. %)	Viscosity (@ 15C, $1s^{-1}$)			Colour	Type
				Starting Oil* (cP)	Emulsion Average (cP)	Ratio Emulsion to Oil		
Point Arguello Light	R/A	Fresh	90.6	22	235050	10684	Brown	Stable
	R/A	Fresh	91.1	22	188000	8545	Brown	Stable
	Blender	Fresh	71.6	22	197500	8977	Brown	Stable
	Burrell	Fresh	89.8	22	24600	1118	Black	Meso-3
Arabian Light	R/A	Fresh	90.1	14	35295	2521	Brown	Stable
	R/A	Fresh	84.9	14	19750	1411	Black	Meso-3
	Blender	Fresh	75.5	14	44820	3201	Brown	Stable
	Burrell	Fresh	80.8	14	7640	546	Black	Meso-3
Iranian Heavy	R/A	Fresh	88.2	20	79975	3999	Brown	Stable
	R/A	Fresh	86.6	20	38110	1906	Black	Meso-3
	Blender	Fresh	74.1	20	160200	8010	Brown	Stable
	Burrell	Fresh	86.2	20	37570	1879	Black	Meso-3
Sockeye	R/A	Fresh	88.9	45	258550	5746	Brown	Stable
	R/A	Fresh	85.0	45	160900	3576	Brown	Stable
	Blender	Fresh	70.3	45	272550	6057	Brown	Stable
	Burrell	Fresh	87.4	45	134200	2982	Black	Meso-3
70/30 ASMB/California	R/A	Fresh	79.9	38	167700	4413	Brown	Stable
	Blender	Fresh	75.9	38	377400	9932	Brown	Stable
	Burrell	Fresh	74.9	38	1509	40	Black	Meso-3
Endicott	Blender	Fresh	57.3	84	7425	88	Brown	Meso-3
West Texas Intermediate	Blender	Fresh	80.7	7	850	121	Brown	Meso-3
South Louisiana	Blender	Fresh	50.1	8	350	44	Yellow	Meso-2
Arabian Medium	R/A	21	73.9	275	20400	74	Brown	Meso-3
Hondo	R/A	Fresh	81.0	735	116000	158	Brown	Meso-3
Atkinson	R/A	Fresh	78.5	65	16230	250	Brown	Meso-3
ASMB	R/A	35	87.3	48	53840	1122	Brown	Meso-3
Transmountain Blend	R/A	Fresh	81.9	4	7512	1878	Black	Meso-2
Oseberg	R/A	23	85.9	70	23655	338	Brown	Meso-3
North Slope	R/A	Fresh	88.9	23	N/M	0	Brown	Meso-3
Rangely	R/A	21	77.2	173	24385	141	Brown	Meso-3
Extreme Pressure Gear Oil	R/A	Fresh	15.7	975	N/M	0	Yellow	Meso-3
Green Canyon 65	R/A	Fresh	51.0	177	2581	15	Brown	Meso-3
	R/A	7.7	56.5	457	6119	13	Brown	Meso-3
	R/A	13.13	49.8	800	4861	6	Brown	Meso-3
	R/A	22.91	31.8	4250	11341	3	Brown	Meso-3
South Pass 67	R/A	Fresh	63.9	39	281	7	Black	Meso-3
	R/A	22.17	59.5	110		-	Black	Meso-3
	R/A	44.56	71.2	108	4846	45	Black	Meso-3
	R/A	63.99	68.4	236	9523	40	Black	Meso-3
West Delta 30	R/A	Fresh	77.6	1180	N/M **	0	Black	Meso-2
	R/A	23.76	34.1	1350	4031	3	Black	Meso-2
	R/A	42.16	32.3	1560	4450	3	Black	Meso-2
	R/A	61.34	37.2	4970	15370	3	Black	Meso-2
South Pass 60	R/A	Fresh	1.7	9		-	Black	Unstable
	R/A	16.51	0.6	22		-	Black	Unstable
	R/A	24.61	4.2	41		-	Black	Unstable
	R/A	38.12	68.5	161	9414	58	Black	Meso-3
South Pass 93	R/A	Fresh	27.0	19		-	Black	Unstable

Table 1 Ctd.

Oil	Formation Method	Per Cent Weathered	Water Content Average (wt. %)	Viscosity (@ 15C, $1s^{-1}$)			Colour	Type
				Starting Oil* (cP)	Emulsion Average (cP)	Ratio Emulsion to Oil		
	R/A	11.03	26.4	23		-	Black	Unstable
	R/A	21.38	27.1	32	900	28	Black	Unstable
	R/A	33.7	31.9	80	3106	39	Black	Meso-2
Main Pass 37	R/A	Fresh	3.6	7		-	Black	Unstable
	R/A	16.22	2.2	16		-	Black	Unstable
	R/A	30.27	5.5	36	1547	43	Black	Unstable
	R/A	50.19	38.6	115	4757	41	Black	Meso-2
Ship Shoal 239	R/A	Fresh	2.4	34		-	Black	Unstable
	R/A	16.75	1.4	70		-	Black	Unstable
	R/A	42.57	4.0	74		-	Black	Unstable
	R/A	53.15	50.1	194	1036	5	Black	Meso-3
Green Canyon Block 109	R/A	Fresh	1.9	39		-	Black	Unstable
	R/A	7.63	7.0	98		-	Black	Unstable
	R/A	14.01	8.7	225		-	Black	Unstable
	R/A	22.11	36.1	690	3107	5	Black	Meso-3
Eugene Island 43	R/A	Fresh	1.4	13		-	Black	Unstable
	R/A	7.4	2.4	21		-	Black	Unstable
	R/A	15.66	4.8	36		-	Black	Unstable
	R/A	23.65	10.8	65	2561	39	Black	Meso-2
Eugene Island 32	R/A	Fresh	3.7	10		-	Black	Unstable
	R/A	6	< 0.1	9		-	Black	Unstable
	R/A	13.18	7.8	16		-	Black	Unstable
	R/A	20.04	8.1	21		-	Black	Unstable
Ship Shoal 269	R/A	Fresh	0.2	5		-	Black	Unstable
	R/A	13.23	10.1	7		-	Black	Unstable
	R/A	26.27	0.1	18		-	Black	Unstable
	R/A	38.95	0.6	44		-	Black	Unstable
South Timbalier Block 130	R/A	Fresh	0.5	7		-	Black	Unstable
	R/A	11.11	0.1	10		-	Black	Unstable
	R/A	21.98	0.1	19		-	Black	Unstable
	R/A	35.07	22.5	48		-	Black	Unstable
West Delta 97	R/A	Fresh	0.1	1		-	Black	Unstable
	R/A	23.38	< 0.1	1		-	Black	Unstable
	R/A	47.99	< 0.1	3		-	Black	Unstable
	R/A	73.68	< 0.1	7		-	Black	Unstable
Mississippi Canyon 194	R/A	Fresh	0.3	7		-	Black	Unstable
	R/A	10.47	0.2	11		-	Black	Unstable
	R/A	21.49	0.5	21		-	Black	Unstable
	R/A	35.06	0.9	51		-	Black	Unstable
Main Pass 306	R/A	Fresh	3.0	9		-	Black	Unstable
	R/A	11.84	0.7	19		-	Black	Unstable
	R/A	24.15	2.3	54		-	Black	Unstable
	R/A	37.04	3.8	219		-	Black	Unstable

*** Note - Oil samples are Newtonian at 15C**

number refers
to the number
of phases
after 4 months

**** Not Measurable - No response at 15C, shear rate of 1 s-1**

Table 2 Rheological Data

Oil Name	Water Content (%)	Viscosity (cP)	Viscosity Ratio (Emulsion/ Oil)	Elasticity (15°C)			Viscosity Ratio (Emulsion/ Oil)	Stability Class
				zero-shear viscosity (cP)	Tan(delta) (Viscous/ Elastic)	G* (Total Flow Resistance)		
Point Arguello Light		22						
Initial	90.6	235050	10782	3.33E+06	0.07	1.00E+03	152523	Stable
14 Days	89.9	311150	14273	6.88E+06	0.13	1.05E+03	315505	
8 Weeks	90.5	332150	15236	1.58E+06	0.10	1.23E+03	72569	
Arabian Light		14						
Initial	90.1	35295	2613	1.81E+05	0.10	3.05E+02	13420	Stable
14 Days	85.1	20180	1494	5.56E+05	0.10	1.40E+02	41184	
8 Weeks	84.8	9846	729	1.29E+05	0.19	9.40E+01	9563	
Arabian Medium 21% Wthrd.		275						
Initial	73.9	20400	74	4.22E+02	4.00	2.13E+01	2	Meso-3
14 Days	73.7	26210	95	2.08E+02	5.00	2.20E+01	1	
8 Weeks	74.5	35260	128	1.66E+02	6.75	1.83E+01	1	
Hondo		735						
Initial	81.0	116000	158	1.44E+04	0.55	3.40E+02	20	Meso-3
14 Days	78.9	136400	186	1.11E+03	1.45	1.50E+02	2	
8 Weeks	80.5	167200	227	6.91E+03	0.82	3.03E+02	9	
Atkinson		65						
Initial	78.5	16230	249	1.04E+02	1.65	9.53E+00	2	Meso-3
14 Days	78.8	11670	179	6.00E+01	2.63	6.88E+00	1	
8 Weeks	77.7	6871	106	N/M	6.18	6.18E+00	-	
ASMB 35% Weathered		48						
Initial	87.3			5.04E+05	0.16	6.68E+02	10504	Meso-3
14 Days	87.1	53840	1122	1.56E+05	0.23	2.98E+02	3250	
8 Weeks	88.2	54720	1140	5.75E+04	0.23	3.25E+02	1198	
Transmountain Blend		11						
Initial	81.9	7512	715	1.40E+04	1.78	6.73E+01	1331	Meso-2
14 Days	85.5	4678	446	4.79E+03	3.13	3.15E+01	456	
8 Weeks	93.5	1171	112	2.05E+01	9.80	9.80E+00	2	
Iranian Heavy		20						
Initial	88.2	79975	3926	6.57E+05	0.13	4.73E+02	32229	Stable
14 Days	84.0	62790	3082	8.75E+05	0.15	2.83E+02	42960	
8 Weeks	82.9	49875	2448	2.65E+05	0.30	2.45E+02	13024	
Oseberg 23% Weathered		70						
Initial	85.9	23655	339	1.90E+05	0.18	2.95E+02	2725	Meso-3
14 Days	85.7	20550	295	2.92E+04	0.23	1.15E+02	419	
8 Weeks	79.0	7479	107	4.57E+03	17.30	1.73E+01	66	
North Slope		23						
Initial	76.3	N/M		2.65E+02	1.25	2.93E+01	12	Meso-3
14 Days	45.7	N/M		1.99E+01	2.85	5.63E+00	1	
8 Weeks	44.4	N/M		2.38E+01	3.05	5.60E+00	1	
Sockeye		45						
Initial	88.9	258550	5733	6.14E+05	0.11	9.90E+02	13612	Stable
14 Days	86.4	199750	4429	8.82E+05	0.18	7.33E+02	19548	
8 Weeks	86.9	225450	4999	4.47E+05	0.21	7.25E+02	9902	
Rangely 21% Weathered		173						
Initial	77.2	24385	141	7.01E+04	0.23	2.43E+02	405	Meso-3
14 Days	73.1	15800	91	1.71E+04	0.47	8.35E+01	99	
8 Weeks	69.7	31270	181	1.61E+05	0.33	4.53E+02	927	
Extreme Pressure Gear Oil		975						
Initial	15.7	N/M		3.05E+00	35.00	3.38E+00	0	Meso-3
14 Days	7.1	N/M		1.99E+00	40.50	2.25E+00	0	
8 Weeks	2.1	N/M		1.86E+00	21.75	1.80E+00	0	

number refers
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of phases
after 4 months

Table 3

Water Content in Oils/Emulsions

Type ITEM	Soluble Water	Entrained Water	Emulsions	
			meso-stable	Stable
Maximum life time	infinite	< 1 day	<7 days	infinite
Note:		lifetime can be extended by high viscosity of the starting oils		
Typical water content	1-5%	0-50%	30-90%	70-75%
Appearance	like oil	can see water in black oil	black to brown	reddish brown
Viscosity compared to original oil	same	same - may be higher	X 100	X 1000
Viscoelasticity	viscous	viscous	mostly viscous	viscoelastic
Zero shear viscosity	low	low	slight	high
Long term viscosity	same	same	goes down	goes up/same
Water droplet sizes	<1μ	>50μ	10-50μ ?	1-50μ ?
Ease of water removal	very difficult	easy by gravity	relatively easy with surfactants	difficult
Stability driving force	solubility	coalesence retardation by viscosity	coalesence retardation by viscosity and natural surfactant interaction	natural surfactant interaction
		may degrade to oil and water or to stable emulsion, oil and water		

0.1 are stable, however there are some oils that cluster around this value.

Table 3 shows the classification of emulsions based on the experimental findings above, the literature search and the interpretation of the data.

Conclusions

It is clear from both the literature and experimental evidence above, that certain emulsions can be classed as stable. It is further proposed by the present authors that three stability classes of emulsions exist, unstable, meso-stable and stable. The differences between these are fairly easily measured. Stable emulsions will persist for days, weeks and longer. They show viscoelastic rheological properties and zero-shear viscosities of at least 10^5. Their viscosities are at least three orders-of-magnitude greater than that of the starting oil (greater than 2000 times). Some (if not all or many) stable emulsions increase in viscosity after time. The stability derives from the strong visco-elastic interface cause by asphaltenes, perhaps along with resins. Increasing viscosity may be caused by increasing alignment of asphaltenes at the oil-water interface.

Meso-stable emulsions, first proposed in this paper, are emulsions that have properties between stable and unstable emulsions (really oil/water mixtures). It is suspected that these emulsions lack sufficient asphaltenes to render them completely stable or still contain too many de-stabilizing materials such as smaller aromatics. The viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Meso-stable emulsions may degrade to form layers of oil and stable emulsions. Meso-stable emulsions can be red in appearance or black. Meso-stable emulsions are probably the most commonly-formed emulsions in the field.

Unstable emulsions are those that decompose (largely) to water and oil rapidly after mixing, generally within a few hours. Some water may be retained by the oil, especially if the oil is viscous.

The most important measurements taken on emulsions are creep and recovery rheometry studies. The presence of elasticity clearly defines whether or not a stable emulsion has been formed. The viscosity by itself can be an indicator (not necessarily conclusive, unless one is fully certain of the starting oil viscosity) of the stability of the emulsion. Colour is not a reliable indicator. This laboratory's experience is that all stable emulsions were reddish. Some meso-emulsions also had a reddish colour and unstable emulsions were always the colour of the starting oil. Water content is not an indicator of stability and is error-prone because of 'excess' water that may be present. At this time, water droplet size is not understood and does not appear to be a strong indicator. Dielectric spectroscopy may be a useful tool to explore emulsions, however much work is required.

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