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The Physics and Chemistry of Emulsions

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SUMMARY

Studies on the formation and stability of emulsions have been conducted in the past four years. These studies have led to a relatively good understanding of why emulsions form and some insight into their stability. The formation of emulsions is due to the surfactant-like action of the polar and asphaltene components of oil. These compounds behave like low HLB surfactants and stabilize water droplets in the oil. The polars and asphaltenes are stabilized in many crude oils by the aromatic components, especially the BTEXs (benzene, toluene, ethylbenzene and xylenes). If these compounds are in low quantity or are lost through evaporation the polars (or resins) and asphaltenes can precipitate (or are no longer solvated) and thus can stabilize the water-in-oil droplets. A relatively large amount of energy is required to form these emulsions after the chemical conditions are correct. This mechanism of emulsion formation has been verified by several experiments including the creation of "artificial" crudes and the doping of crudes. The mechanism is sufficiently well understood that work can now proceed on the prediction of emulsion behaviour of crudes knowing the content of the resins, asphaltenes and the BTEXs.

Studies of the stability of emulsions have been initiated but further work is still necessary. The stability of emulsions can be measured by leaving prepared emulsions at room temperature for several days. Unstable emulsions will break down rapidly. Most emulsions are either stable or not and show this characteristic in a short time. Rapid methods for assaying stability are under development. These studies show that the droplet size of water in emulsions may be related to stability. A stable emulsion will have poly-disperse droplets (VMD of 5 and 20 microns), whereas an unstable emulsion will not. The characteristic red colour of an emulsion appears to be related to this poly-dispersability. The viscosity of an emulsion is correlated with the starting oil, however there exists high variation in this factor. The water content is again a characteristic of the oil and for stable emulsions vary from 50 to 80%. A loss of only about 10% water from a stable emulsion is a sign of break-down. However, apparently stable emulsions of some oils can be made with water contents varying from 10 to 80% water. Weathering effects on the oil are strong. This relates to the BTEX factor noted above. Many oils must lose sufficient BTEX which solvates the asphaltenes and resins of the oil, before they will form emulsions. There exists a point of weathering for many oils after which it will form an emulsion. This point is relatively sharp for most oils. Very few quasi-stable emulsions are formed. A study of the energy needed to form an emulsion has begun. It appears that although some emulsions are more stable when formed at high

energies, most emulsions simply require a "sufficient" amount, the latter is still high when compared to other processes such as chemical dispersion.

INTRODUCTION

Emulsification is the process of the formation of water-in-oil emulsions often called "chocolate mousse" or "mousse" among oil spill workers. These emulsions change the properties and characteristics of oil spills to a very large degree. Stable emulsions contain between 50 and 80% water thus expanding the volume of spilled material from 2 to 5 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 hundred cSt to about one hundred thousand cSt, a typical increase of 1000. This changes a liquid product to a heavy, semi-solid material. Emulsification is felt by many to be the second most important behavioral characteristic after evaporation. Emulsification has a very large effect on the behaviour of oil spills at sea. As a result of emulsification, evaporation 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 has significant effects on other spill aspects; spill countermeasures are quite different for emulsions. Emulsions are hard to recover mechanically, treat or burn.

PHYSICS OF EMULSIFICATION

The mechanism and dynamics of emulsification have been poorly understood. 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. Berridge and co-workers were the first to describe emulsification in detail and measured several physical properties (Berridge et al., 1968). Berridge described the emulsions as forming because of asphaltene and resin content. Workers in the 1970's concluded that emulsification occurred primarily with increased turbulence or mixing energy (Haegh and Ellingston, 1977; Wang and Huang, 1979). Composition of the oil was not felt to be a major factor. Some workers speculated that particulate matter in the oil may be a factor and others suggested it was viscosity. Evidence could be found for and against all these hypotheses. Twardus studied emulsions in 1980 and found that emulsion formation might be correlated with oil composition. Asphaltenes and metal porphyrins were suggested as contributing to emulsion stability. Bridie and coworkers studied emulsions in the same year and proposed that the asphaltenes and waxes 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 co-workers (Mackay and Zagorski, 1981a, 1982a, 1982b) hypothesized that emulsion stability was due to the formation of a film in oil that resisted water droplet coalescence. The nature of these thin films was not described, but was proposed to be due to the accumulation of certain types of compounds. Later work led to the conclusion that the compounds were asphaltenes and waxes. A standard procedure for making emulsions and measuring stability was devised.

Thingstand and Pengerud (1983) conducted photooxidation experiments and found that photooxidized oil formed emulsions. Nesterova and co-workers studied

emulsion formation and concluded that it was strongly correlated with both the asphaltene and tar content of oil and also the salinity of the water with which it was formed (Nesterova et al., 1983). Mackay and Novak (1984, Mackay, 1984) studied emulsions and found that stable emulsions had low conductivity and therefore a continuous phase of oil. Stability was discussed and proposed to be 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. Viscosity of the resulting emulsions was correlated with water content. Later work by the same group reported examination of Russian hypotheses that emulsions are stabilized by colloidal particles which gather at the oil-water interface and may combine to form a near-solid barrier that resists deformation and thus water-water coalescence (Stiver et al., 1983). These particles, it was said, could be mineral, wax crystals, aggregates of tar and asphaltenes or mixtures of these. Asphaltenes were felt to be the most important of these particles and controlled the formation of all particles. A formation equation relating the asphaltene, paraffin, aromatic and silica gel (resin) content was proposed. This was later shown to be a poor predictor of oil emulsion tendencies.

Desmaison and co-workers conducted studies on Arabian crudes and noted that emulsion formation was correlated with two factors, photooxidation exposure and amount of asphaltenes (Desmaison et al. 1984). The photooxidation was found to occur on the aromatic fractions of the oil. Asphaltenes were found to become structured with time and this was associated with emulsion formation. Miyahara (1985) reported that the stability of emulsions was primarily controlled by the composition of the oil, specifically that which resided in the hexane-insoluble fraction of the oil. He did not define what this content was. Miyahara also reported that salt and freshwater emulsions showed relatively similar stabilities, although in one case the salt water emulsion appeared to be more stable. Payne and Philips (1985) reviewed the subject in detail and reported on their own experiments of emulsification with Alaskan crudes in the presence and absence of ice. Their studies showed that emulsion formation can occur in an ice field, thus indicating that there was sufficient energy in this environment and that the process could occur at relatively low temperatures.

Environment Canada conducted a series of studies which focussed on the physics of emulsion formation (Bobra, 1992). This study provided experimental results that show, rather conclusively, that emulsion formation is a result of surfactant-like behaviour of the polar and asphaltene compounds. The latter are similar compounds and both behave like surfactants when they are not in solution. The aromatic components of oil solubilize asphaltene and polar compounds. When there are insufficient amounts of these components to solubilize the asphaltenes and polars, these precipitate and are available to stabilize water droplets in the oil mass. These studies are confirmed by a large number of similar studies in the surfactant sciences.

Formation of Emulsions

Environment Canada and Minerals Management Service conducted extensive studies on the formation of emulsions (Bobra, 1992). These studies show clearly that the formation of emulsions are due to the stabilization of water droplets in the oil

mass by the surfactant action of the asphaltenes and resins in the oil. This is confirmed by numerous studies in surfactant literature.

The quantity of asphaltenes or resins required to produce a stable emulsions is determined to be 0.03 g/mL (approximately 3%). The equivalency of asphaltenes and resins confirms the theory that both of these materials are approximately equivalent. Polars or resins are smaller compounds of asphaltene materials. Both materials are defined by precipitation techniques. The findings of the study show that these materials are soluble in aromatic solvents such as benzene, toluene and xylenes. There the quantity of these solvents are insufficient to maintain them in solution, they precipitate and then act as surfactants. A water-in-oil emulsion then results. This explains why some oils require weathering before emulsions form. The BTEX (benzene, toluene, ethylbenzene and xylene) solvents evaporate rapidly from oil. The required quantity of 0.03 mg/L also explains why some oils never form emulsions, many oils do not contain this quantity of resins and asphaltenes.

Water Droplet Size

Two sub-studies on water droplet sizes in emulsion were conducted. The maximum content of one liquid in another with uniform particle size is 70%. This is simply a function of geometric packing constraints. This limit can be increased by poly-dispersability, or by having particles of different sizes. This has been found to be the case for many of the emulsions tested.

Two techniques were used to estimate water droplet sizes in emulsions - optical microscopy and laser diffraction. Both techniques have limitations in current instrumentation, however these preliminary studies agree that the droplets cluster bimodal around 5 and 20 microns. Unstable emulsions have droplets with large droplets, often as large as 250 microns. Further work and correlation on droplet size is required.

Stability Criteria For Emulsions

A study on emulsion stability was started. Initial results show that if emulsions are stable at room temperature for 5 days, they will not break down after this time. Further oils should be tested to confirm this finding. Initial results indicate that most unstable emulsions will show breakdown, strongly indicated visually, before a 24-hour time period. Work on developing a stability test continues, however, results indicate that very few quasi- or semi-stable emulsions are formed.

Emulsion Stability With Varying Water Content

A study on the stability of emulsions was initiated to identify the regions of instability related to water content. The test method was mixing oil with water in a blender at a specific ratio of oil-to-water. The water content is measured daily for a week to monitor water content changes. The ratios chosen range from 10% water to 90%, in increments of 10%. The 90% mixture did not form a stable emulsion. For the blend of 30% California Crude API=11.0 and 70% Alberta Sweet Mixed, the water content did not change in any of the emulsions over the 7 days, except for the 90% mixture. This oil, the standard for mousse formation used throughout the studies on emulsion breakers, is a very stable emulsion requiring physical or chemical

factors to destabilize it. This test also shows that the use of a high energy device such as a blender, results in the formation of a very stable emulsion. Table 1 shows the water contents of the emulsions over time. All emulsions irrespective of the water content were stable.

Table 1 **Emulsion Stability Tests**
Blender and California Crude/ASMB Mix

Time (Days)	10	20	30	Approximate Water Content 40	50	60	70	80
0	13.56	25.58	35.16	44.11	54.04	61.35	71.74	79.73
1	13.68	25.40	35.56	44.47	54.10	61.75	72.36	79.31
2	14.54	26.01	35.72	44.76	54.47	61.93	71.77	78.45
3	14.83	25.69	35.98	43.59	54.42	61.19	71.74	78.04
4	13.64	25.45	35.59	44.05	54.46	61.30	71.96	78.98
5	14.24	24.86	35.43	45.40	54.80	61.49	71.87	77.97
6	13.40	25.52	35.25	43.55	54.55	60.35	70.76	79.62
7	13.45	25.06	34.50	44.79	55.21	60.20	71.20	77.10
Avg.	13.92	25.45	35.40	44.34	54.51	61.20	71.68	78.65
Std.Dev.	0.54	0.36	0.45	0.64	0.37	0.62	0.49	0.92

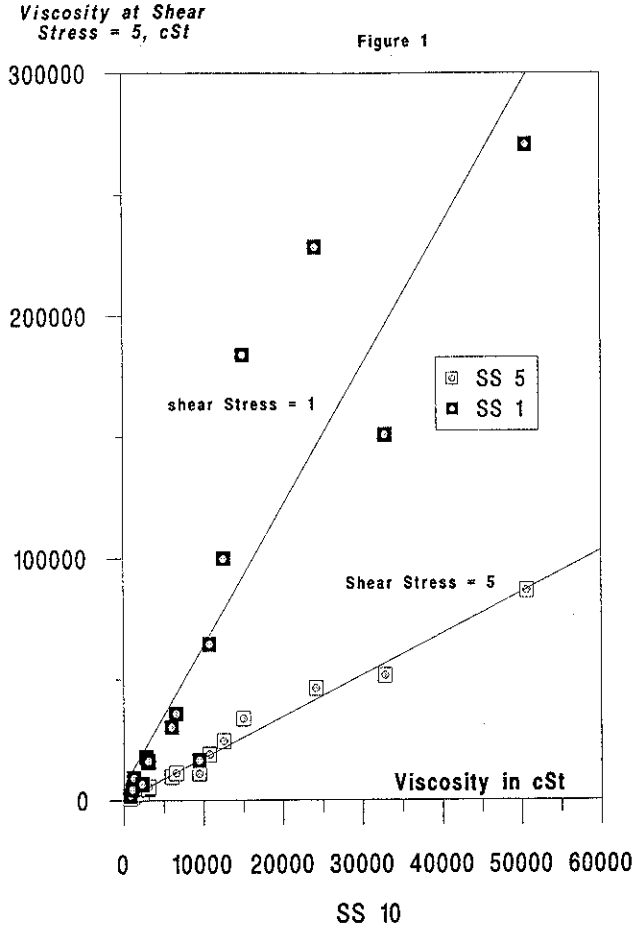
Energy of Emulsification

The energy of emulsification of different oils was studied using a low-energy shaker. The method makes use of the Turbula Shaker-Mixer, a 1 L teflon bottle, 800 mL salt water and 15 mL of oil. The oil and water are mixed for a specific time, then transferred to a separatory funnel for a 30-minute settling time, the water is separated and the water content is measured. The water content is measured again a few days after the run is complete to verify stability. The data produced to date are on the standard 30/70 Blend and Iranian Heavy Crude. The highest water contents are often produced with the lowest mixing energy, but instability has been noted with these emulsions. These show that the lower-energy device, the Turbula, will often not form stable emulsions. As energy is increased, the emulsions become increasingly stable.

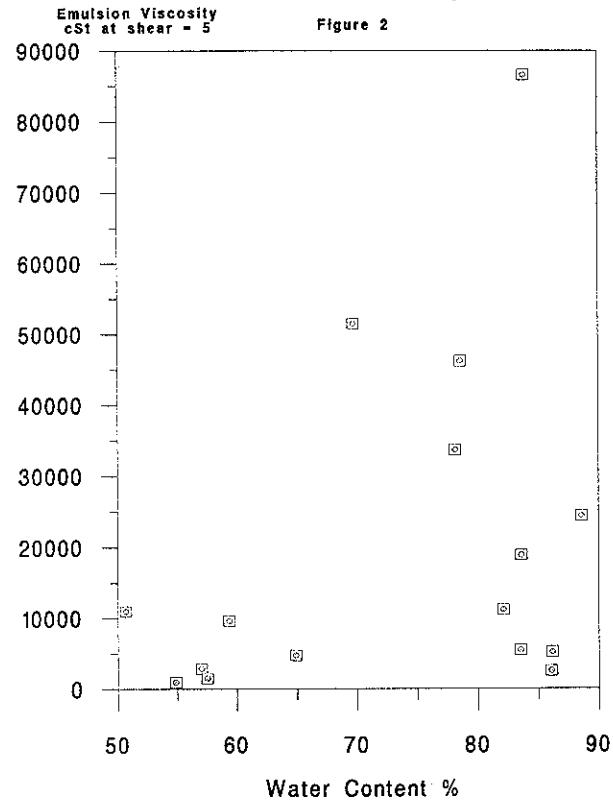
Study of Emulsion Viscosities

An initial study of the variance of emulsion viscosity was performed. The results are summarized in Table 2. The findings are also illustrated in Figures 1 to 4. Figure 1 shows that the viscosity of emulsion is strongly correlated at different shear rates. Figure 2 shows that water content and viscosity of emulsion is not correlated simply, but as Figure 3 shows, there is a correlation in the blender, but not in the Mackay apparatus. The emulsion in the Mackay apparatus often contains an excess of water and this may be skewing results. Figure 4 shows that there is a poor correlation between the starting oil viscosity and the viscosity of the resulting emulsion.

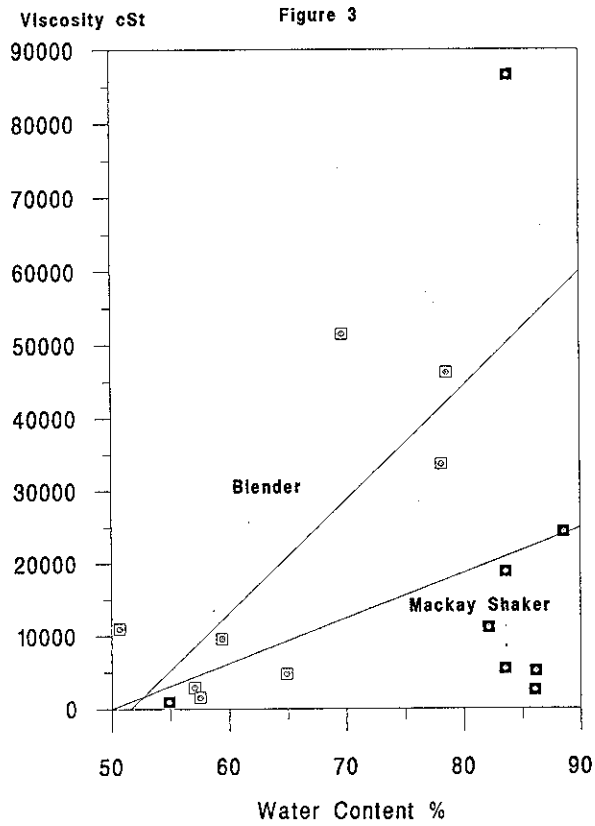
Comparison of Viscosity Taken at Different Shear Rates



Comparison of Water Content and Viscosity



Correlation of Water Content and Viscosity in Separate Apparatus



Correlation Between Starting Oil and Emulsion Viscosities

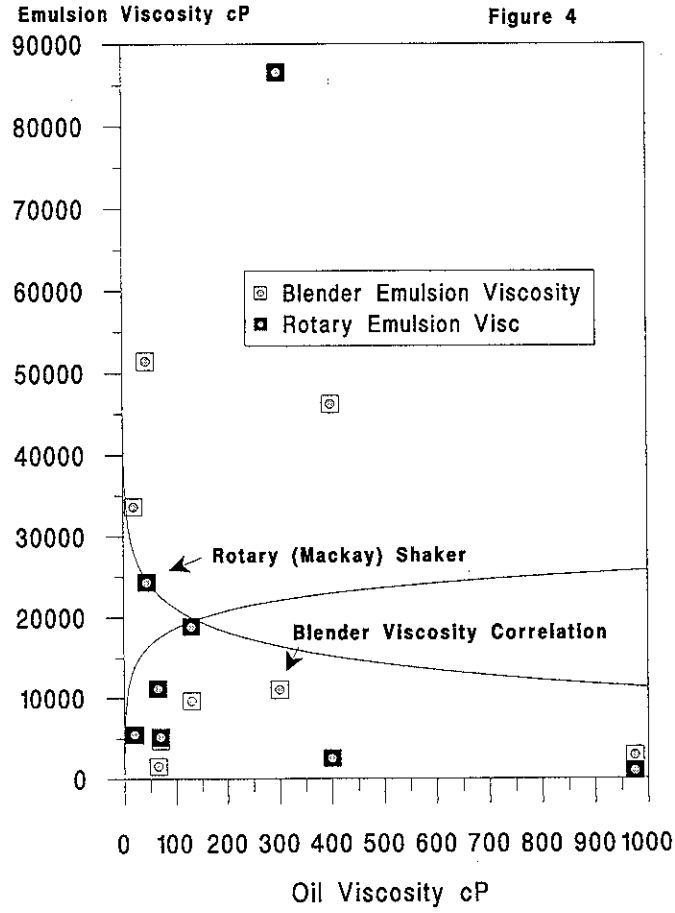


Table 2 **Studies of Emulsion Viscosity Behaviour**

Name of Crude Oil	% weathered	Emulsion Viscosities - cP Shear = 10/s	Shear - 5/s	Shear - 1/s	Method	Water %	Viscosity Original Oil
Alberta Sweet Mixed Blend	36	5997	9587	30070	b	59.39	130
Atkinson	0	1105	1491	4372	b	57.51	65
Iranian Heavy	0	14990	33630	183850	b	78.16	20
Lubricating Oil (Gear Oil)	0	2311	2855	6597	b	57.02	975
Maya	0	9465	10950	16390	b	50.67	300
Oseberg	28	3032	4722	15650	b	64.89	70
Point Arguiello Light	0	24130	46160	228400	b	78.59	400
Sockeye	0	32810	51460	150550	b	69.73	45
Alberta Sweet Mixed Blend	36	10755	18830	64535	m	83.60	130
Atkinson	0	6576	11140	35795	m	82.12	65
Iranian Heavy	0	3104	5450	15965	m	83.52	20
Lubricating Oil (Gear Oil)	0	815	950	2004	m	54.87	975
Maya	0	50620	86535	270600	m	83.87	300
Oseberg	28	2832	5147	17715	m	86.15	70
Point Arguello Light	0	1301	2499	9094	m	86.06	400
Sockeye	0	12525	24325	99825	m	88.60	45

b=blender, m=Mackay or rotary

FURTHER WORK

Further work on emulsion formation continues. A series of five studies have begun. The first is a comparison of end-point using viscosity and water content. A method to remove the large water droplets is being developed. The second study is a study of emulsions in a new shaker to replace the Mackay shaker. The new shaker is a standard for several EPA extraction methods and would represent a potential standard. The shaker has an analogous motion (rotation) and has a two-litre vessel available in glass or teflon. The standard rotational speed is 30 rpm, but variable versions are available. The third study is comparison of emulsions made in several different shakers. The fourth study is a study of the properties of several different emulsions and the fifth study, a completion of emulsion data measurement for oils not tested in the above two studies, but listed in the oil properties catalogue.

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