Studies of Water-in-Oil Emulsions: Long-Term Stability, Oil Properties, and Emulsions Formed at Sea

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ABSTRACT

This paper summarizes studies to determine the stability of water-in-oil emulsions of over 100 oils, including one emulsion from the ERIKA spill. Emulsions were analysed after one year of storage to examine the change in properties after that time.

These studies have confirmed that the stability of emulsions can be grouped into three categories: stable, unstable and meso-stable. Water can also reside in oil as 'entrained water', in which larger droplets of water are temporarily suspended by viscous forces. These have been distinguished by physical measures as well as visual differences. 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 meso-stable 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, meso-stable 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 properties of the starting oil are the important factor in determining what type of water-in-oil state is produced. Composition and property ranges are given for the starting oil to form each of the water-in-oil states. Important property factors are the asphaltene content, resin content, and starting oil viscosity.

1.0 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. Until recently, emulsion stability has not been defined (Fingas *et al.* 1998). Therefore, studies were difficult because the end points of analysis were not defined. This paper continues studies of the stability of water-in-oil emulsions and defines characteristics of different stability classes. Four 'states' that water can exist in oil will be described. These include: stable emulsions, mesoble emulsions, unstable emulsions (or simply water and oil) and entrained water. se four 'states' are discriminated by visual appearance as well as by rheological asures.

Mesostable emulsions are emulsions that have properties between stable and table emulsions (really oil/water mixtures) (Fingas *et al.* 1998). It is suspected mesostable emulsions lack sufficient asphaltenes to render them completely le or still contain too many de-stabilizing materials such as smaller aromatics. viscosity of the oil may be high enough to stabilize some water droplets for a iod of time. Mesostable emulsions may degrade to form layers of oil and stable lsions. Mesostable emulsions can be red in appearance or black.

Unstable emulsions are those that decompose (largely) to water and oil dly after mixing, generally within a few hours. Some water (usually less than ut 10%) may be retained by the oil, especially if the oil is viscous. Entrained er may persist in viscous oils for a period of time. This 'entrained' stage has a r life span, but residual water, typically about 10%, may persist for a long time.

The most important measurements to characterize emulsions are forced illation rheometry studies. The presence of significant elasticity clearly defines ther or not a stable emulsion has been formed. The viscosity by itself can be an icator (not necessarily conclusive, unless one is fully certain of the starting oil osity) of the stability of the emulsion. Colour is an indicator, but may not be initive. This laboratory's experience is that all stable emulsions were reddish. he meso-emulsions also had a reddish colour, but unstable emulsions were always olour of the starting oil. Water content is not an indicator of stability and is r-prone because of 'excess' water that may be present. It should be noted ever that stable emulsions have water contents greater than 70% and that unstable lsions or entrained water-in-oil generally have water contents less than 50%. ter content after a period of about one week is found to be more reliable than nediate water content. This is because separation will occur in those emulsions are less stable.

This paper reports on studies of the states of new oils from a previous study gas *et al.*, 1998) and reports on the analysis of some of the water-in-oil states e than one year after their initial formation. Over 100 oils have been studied to

Experimental

Water-in-oil emulsions were made in a rotary agitator and then the rheometric acteristics of these emulsions studied over time. Over 100 oils were used. Oils taken from the storage facilities at the Emergencies Science Division. erties of these oils are given in standard references and will be summarized later is paper (Jokuty *et al.*, 1999). A sample of the oil spilled from the ERIKA, a ple of the emulsion formed in a test tank and a sample of the emulsion recovered a approximately two weeks after the spill, were provided by CEDRE, Brest, ice

Emulsion Formation - Emulsions were made in an end-over-end rotary mixer sociated Design). The apparatus was located in a temperature controlled room at egrees Celsius. The mixing vessels were 2.2 L FLPE wide-mouthed bottles ne) The mixing vessels were approximately one-quarter full, with 600 mL salt

water (3.3% w/v NaCl) and 30 mL of the sample crude oil or petroleum product. The vessels were mounted into the rotary mixer, and allowed to stand for several hours (usually four) to thermally equilibrate. The vessels were placed in the rotary mixer such that the cap of each mixing vessel follows, rather than leads, the direction of rotation. The vessels were then rotated for a period of 12 hours at a rate of 55 RPM, or at the specified rate of rotation for the specified time. The vessels were approximately 20 cm in height, providing a radius of rotation of about 10 cm. At the conclusion of the mixing time, the emulsions are collected from the vessels for measurement of water content, viscosity and the complex modulus. The emulsions were stored in the cold room at 15°C for one week, then measured again. The emulsions continue to be stored until measured at a time greater than one year from the time of formation.

Rheology - The following apparatuses were used for rheological analysis: Haake RS100 RheoStress rheometer, IBM-compatible PC with RheoStress RS Ver. 2.10 P software, 35 mm and 60 mm parallel plates with corresponding base plates, and a circulating bath maintained at 15.0 °C. Analysis was performed on a sample spread onto the base plate and raised to 2.00 mm from the measuring plate, with the excess removed using a teflon spatula. This was left for 15 minutes to thermally equilibrate at 15 °C.

Viscosity denoted as "RS100" was measured on an RS100 RheoStress rheometer using a 35 mm plate-plate geometry. The shear rate was nominally 1 reciprocal second, and corrected by the Weissenberg equation: corrected viscosity = measured viscosity * (3+n)/4 where n is the power-law exponent, determined by a frequency sweep in the oscillation mode.

Viscosity denoted as "RV20" is measured on an RV20 with RheoController and M5 measuring head. The concentric cylinder geometry is used, specifically the SV and SV1 cup and spindle combination, at a controlled shear rate of 1 reciprocal second.

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

Water Content - A Metrohm 701 KF Titrino Karl-Fischer volumetric titrator and Metrohm 703 Ti Stand were used. The reagent was Aquastar Comp 5 and the solvent, 1:1:2 methanol:chloroform:toluene. The specific method used was as follows: standardize the titre and blank the solvent. The sample emulsion was stirred to get a relatively homogeneous mixture. A 1 mL plastic syringe was filled with emulsion, trying to avoid free water pockets present in the sample. All but 0.1 mL was ejected; this should have removed most of the free water from the more viscous emulsion. The sample syringe was weighed and injected into the reaction vessel, being careful the sample went into the solution and not onto the vessel walls. The syringe was reweighed and the mass difference entered into the titrator. Titration was initiated. Weight percentage of water was displayed.

Complex Modulus - The complex modulus is a measure of the overall resistance of the material to flow under an applied stress, in units of force per unit area. This combines the elements of viscosity and elasticity for viscoelastic materials such as water-in-oil emulsions. Since crude oils generally do not possess significant elasticity, it has been found that dividing the complex modulus of the emulsion by the viscosity of the fresh oil is a useful indicator of the stability of the emulsion, as a value greater than 200 generally indicates a stable emulsion.

The complex modulus was measured on an RS100 RheoStress rheometer using a 35 mm plate-plate geometry. A stress sweep was performed in the range 25 to 1,000,000 mPa in the oscillation mode at a frequency of 1 Hz. The resulting complex modulus in the linear portion of the range was reported.

3.0 Results and Discussion

The emulsions and mixtures formed in a previous study (Fingas *et al.*, 1998) were stored in a cold room and the rheological properties were re-measured after at least one year had passed. The rheological data for over 100 oils are given in Table 1. The second column of the table is the evaporation state of the oil in mass percent lost. The third column is the assessment of the stability of the emulsion based on both visual appearance and rheological properties. The fourth column is the viscosity of the emulsion and the fifth column is the complex modulus which is the vector sum of the viscosity and elasticity. The complex modulus represents the total resistance of a substance against the applied stress, combining elements of viscosity and elasticity, in units of force per area (Pa). Column 6 is the tan delta, the ratio of the viscosity to the elasticity component. Tan(delta) is the tangent to the phase angle of response to the applied stress, providing a relative ratio of the elastic response to the viscous response. An in-phase response (phase angle = 0) is wholly elastic, while an out-of-phase response (phase angle = 90) is wholly viscous. A phase angle between 0 and 90 shows elements of both, with the relative ratio provided by the tangent. Finally, the water content of the water-in-oil state is presented. This is repeated for the measurements taken at one week and for those taken at least one year later.

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 meso-stable emulsions broke after a few days into water, free oil and emulsion. The time for these emulsions to break down varies from about 1 to 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 some 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.*, 2000). These show that the emulsions are formed fairly rapidly and that there is not a continuum of formations.

Table 2 shows the summary of the property changes for the different types of emulsions over the three time periods. The most obvious, and largest change is that of water content, and other properties for the meso-stable emulsions between the day of formation and one week later. These values are highlighted in the table. These emulsions break down between these two times, thus all properties are drastically different. The complex modulus stayed about the same or went up for all states between the one week time period and one year. The value of stability would do so as

well. Other values in the table show changes for the different types, for example, the water content of the unstable mixtures went up between one week and one year. This latter example is based only on a few values and the standard deviation is very high. Overall, the water-in-oil states gained viscosity, values of complex modulus and lost water between each time period. Stable emulsions lost the least amount of water. Only one oil, Arabian Light, refer to Table 1, appeared to lose some stability during the year time period. Its characteristics are now more similar to that a meso-stable emulsion than of a stable, after one year. This is the first and only case of a high decrease in both stability and water content observed for a stable emulsion over a one-year time period.

The oils that were reported in the earlier study (Fingas *et al.*, 1998) were re-assessed and Table 3 summarizes the data on these. Table 3 provides the data on the oil properties as well as the parameter called '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.

Table 4 summarizes the data from Table 3. Table 4 shows that all classes of water-in-oil states (except unstable, which was not included here) increased in stability over the year time period. All lost some amount of water as well during the year time period. Stable emulsions showed the least increase in stability and the least loss of water, probably because these values were both the highest to begin with. Water loss, very slight in the case of stable emulsions, is probably due to drainage of excess water and loss of water during each subsequent analysis procedure. The Arabian Light emulsions were separated from the stable emulsions in calculating the data from Table 4 because their stability after one year was in question.

Table 5 shows properties of the oils in various classes and the properties of the resulting water-in-oil state. Data were averaged from this paper and the previous work (Fingas *et al.*, 1998). This shows that the factor, stability, is capable of discriminating 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 viscosity of the starting oil rises to a given point, about 20,000 mPa.s, that meso-stable or stable emulsions are no longer produced.

Table 5 shows that the starting oil properties differ somewhat for oils that form the various states. The oil properties for stable and meso stable are similar. These are oils of medium viscosity that contain a significant amount of resins and asphaltenes. Meso-stable emulsions may form from oils that have higher or lower viscosities than those that might form stable emulsions. Stable emulsions are more likely to form from those oils having 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 5 also shows that the differences between the four water-in-oil states is readily discernible by appearance and rheological properties. The reddish or brown colour on formation indicates either a stable or meso-stable emulsion, however,

Oil	% evap.	Visual Stability	Day of Formation Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)	One Week After Formation Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)	>1 Year After Formation Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)
Arabian Light	0	Stable	2 3E+04	4.7E+05	0.11	87 42	2 3E+04	4 6E+05	0 14	86 93	1 0E+04	7 6E+04	0.48	76.20
Arabian Light	12 04	Stable	4.6E+04	4.0E+05	0.1	88 86	3.1E+04	2.0E+05	0 13	85.82	4 9E+03	5.5E+04	1 0	59.06
Arabian Light	24 2	Stable	4 8E+04	5.1E+05	0.11	84 71	4.3E+04	3 6E+05	0 2	83 62	4.5E+03	5.4E+03	0.30	47.60
Arabian Medium	0	Stable	4 1E+04	5.5E+05	0 09	84 68	4.2E+04	6 8E+05	0 11	84.36	4 3E+04	3.2E+05	0 20	83.81
Arabian Medium	13.15	Stable	2 0E+04	1.5E+05	0 9	76 52	2.4E+04	2 1E+05	0 64	77 06	5 6E+04	4.4E+05	0.26	77.05
Arabian Medium	20.77	Stable	2.1E+04	7.4E+04	2.9	73.10	2.2E+04	1 0E+05	1.8	72.86	5.2E+04	5.1E+05	0.31	73.32
Arabian Medium	30.93	Stable	4.6E+04	1.9E+05	1.7	64 92	4.6E+04	4.0E+05	0 7	65.60	8.8E+04	5.8E+05	0 63	65.26
Belridge Heavy	0	Entrained	4.2E+04	1.4E+05	1.5	54.23	5.0E+04	1.6E+05	1 6	44.39	6.1E+04	1.6E+05	2.0	35.25
Belridge Heavy	2.74	Entrained	4.7E+04	2.0E+05	1.4	59.55	5.6E+04	1 8E+05	1.44	45.19	7.1E+04	2.1E+05	2.2	33.26
Bunker C (Anchorage)	0	Entrained	2.8E+04	1.3E+05	2.8	34 74	1.5E+05	1 4E+05	4	30.96	3.9E+04	4.2E+05	0 48	17.86
Bunker C (Anchorage)	8.41	No				5 83								
Bunker C (1987)	0	Entrained	1.1E+05	7.2E+05	.1.3	26.44	1.4E+05	6.5E+05	1	24.02	3 9E+05	3.5E+06	1.6	23.42
Carpenteria	0	No				8.73								
Carpenteria	10.31	Meso	2.1E+04	7.3E+04	1.2	71.80	2.3E+04	3 6E+04	.12	28.19	NM	2.5E+05	1.4	22.97
Carpenteria	14.87	Meso	2.9E+04	1.3E+05	1.2	54.26	2.0E+04	2.9E+05	0.57	30.87	3.6E+04	7.5E+05	0.47	18.02
Coal Oil Point Seep Sample	0	*Same	2.8E+05	1.2E+06	1.8	32.15	3.7E+05	1 5E+06	2	39.24	2.4E+05	1.7E+06	3.0	22.76
Cook Inlet - Granite Point	0	No												
Cook Inlet - Granite Point	45.32	Meso	1.6E+04	3.4E+05	0.3	83 05	7.9E+02	2 6E+05	0 3	57.58	5 6E+03	4.1E+05	0.18	21.17
Cook Inlet - Swanson River	0	Meso	2.9E+03	1.0E+04	0.8	75 95	0 0E+00	2.7E+04	0 8	57.50	1 1E+04	4.5E+05	0.37	60.82
Cook Inlet - Swanson River	39.69	Stable	2.9E+04	2.9E+05	0.3	81.48	1.4E+05	8 2E+05	0 43	80.76	3 5E+05	2.4E+06	0.30	78.75
Cook Inlet - Trading Bay	0	Meso				80.63				1.89				
Cook Inlet - Trading Bay	33.3	Meso	2.4E+04	4.5E+05	0.34	76.22	4.3E+04	5 3E+05	0 27	61.43	6 7E+04	1.9E+06	0.35	52.65
Diesel (Anchorage)	0	No												
Diesel (Anchorage)	37.44	No												
Diesel (Mobile Burn #3)	0	No												
Diesel (Mobile Burn #3)	8 21	No												
Diesel (Mobile Burn #3)	16.32	No												
Dos Cuadras	0	No												
Dos Cuadras	11.17	Meso	8.0E+02	3.4E+03	2.5	47.60	7.0E+02	4 6E+03	3	29.49	NM	5.3E+04	1.4	7.34
Dos Cuadras	20.3	Meso	9.8E+03	3.3E+04	1	68.55	2.5E+03	1.7E+04	4 2	28.72	1.3E+04	3.1E+04	5.0	19.86

Table 1

Rheological Data on Water-in-Oil States

Oil	% evap.	Visual Stability	Day of Formation Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)	One Week After Formation Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)	>1 Year After Formation Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)
Garden Banks 426	0	No												
High Viscosity Fuel Oil	0	Entrained	7.4E+04	3.1E+05	1.8	47.63	8.3E+04	3.7E+05	1.8	49.80	2.0E+05	6.6E+05	1.5	47.70
Hondo	0	Stable	1.1E+05	9.2E+05	0.24	80.93	1.4E+05	8.8E+05	0.32	79.96	1.9E+05	9.5E+05	0.36	76.77
Hondo	16.67	Stable	1.9E+05	1.3E+06	0.45	66.20	2.5E+05	8.4E+05	0.96	64.23	4.6E+05	2.0E+06	0.53	61.19
Hondo	32.29	No				5.24								5.52
IFO - 180	0	Entrained	5.3E+04	2.4E+05	1.5	69.41	5.9E+04	2.4E+05	1.7	68.42	1.4E+05	3.9E+05	1.4	65.74
IFO - 180	7.77	Entrained	1.5E+05	6.1E+05	1	58.40	1.5E+05	5.8E+05	1.1	58.78	2.7E+05	6.8E+05	1.1	58.21
IFO - 300	0	Entrained	9.7E+04	3.9E+05	1.8	52.33	9.7E+04	4.2E+05	1.7	52.19	1.8E+05	5.8E+05	1.6	45.38
IFO - 300	5.33	No				11.18								
Jet Fuel (Anchorage)	0	No												
Jet Fuel (Anchorage)	52.72	No												
Mississippi Canyon 72	0	No												
North Slope (Middle Pipeline)	0	No												
North Slope (Middle Pipeline)	30.54	Meso	2.6E+03	1.2E+05	0.52	61.92	1.8E+03	1.1E+04	8.4	21.76				9.58
North Slope (Northern Pipelir	0	No												
North Slope (Northern Pipelir	31.14	Meso	1.4E+03	1.1E+05	0.5	69.82	1.6E+03	9.8E+03	4.2	15.00				5.66
North Slope (Southern Pipeli	0	No												
North Slope (Southern Pipeli	29.62	Meso	1.9E+03	1.9E+05	0.46	53.47	2.0E+03	2.0E+04	2.2	21.14				9.55
Pitas Point	0	No												
Pitas Point	23.56	No												
Platform Holly	0	Same*	1.5E+05	4.4E+05	1.1	77.12	1.8E+05	5.3E+05	1	75.64	NM	Insufficient quantities		
Platform Holly	24.24	Same*	3.6E+05	1.6E+06	1	59.60	3.8E+05	1.6E+06	1	59.30	NM	Insufficient quantities		
Platform Holly	53.87	Same*	6.7E+05	3.3E+06	1.2	48.55	7.1E+05	3.3E+06	1.1	46.75	NM	Insufficient quantities		
Platform Holly	78.47	Same*	8.0E+05	3.3E+06	1.3	34.49	8 9E+05	4.0E+06	1.3	33.94	NM	Insufficient quantities		
Platform Irene (Emulsion)	0	Entrained	3.9E+05	1.4E+06	1.52	62.22	5.4E+05	3.3E+06	1.2	34.94	NM	Insufficient quantities		
Point Arguello Comingled	0	Stable	1.8E+05	7.8E+05	0.43	82.31	1.8E+05	1.1E+06	0.36	82.19	3.9E+05	1.7E+06	0.30	82.21
Point Arguello Comingled	9.05	Stable	1.5E+05	8.5E+05	0.38	67.92	1.5E+05	6.2E+05	0.95	69.41	3.4E+05	1.7E+06	0.41	67.39
Point Arguello Comingled	15.19	Entrained	1.4E+05	6.1E+05	2	30.15	1.6E+05	8.0E+05	2.1	28.42	NM	1.8E+06	1.3	30.18
Point Arguello Comingled	22.12	No												
Point Arguello Heavy	0	Stable	1.5E+05	4.9E+05	0.71	72.95	1.8E+05	7.2E+05	0.72	74.97	3.6E+05	1.1E+06	0.60	70.19

Oil	% evap.	Visual Stability	Day of Formation: Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)	One Week After Formation: Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)	>1 Year After Formation: Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)
Point Arguello Heavy	8.88	Entrained				27.58								
Point Arguello Heavy	17.78	No												
Point Arguello Light	0	Stable	6.7E+04	6.5E+05	0.11	93.14	9.6E+04	8.3E+05	0.17	93.79	1.6E+05	1.1E+06	0.20	90.20
Point Arguello Light	10.19	Stable	2.8E+05	3.3E+06	0.05	88.84	2.5E+05	2.8E+06	0.12	87.78	5.2E+05	2.7E+06	0.16	86.37
Point Arguello Light	19.04	Stable	2.7E+05	3.4E+06	0.08	85.50	3.1E+05	3.5E+06	0.13	85.63	7.9E+05	3.7E+06	0.19	87.55
Point Arguello Light	28.33	Stable	1.4E+05	9.8E+05	0.26	79.80	1.6E+05	1.5E+06	0.28	75.89	3.7E+05	2.3E+06	0.28	78.29
Port Hueneme	0	Entrained	1.6E+04	6.4E+04	2.6	37.97	8.7E+03	4.3E+04	9.4	20.06	1.5E+04	4.8E+04	10	9.82
Port Hueneme	3.14	Entrained	4.6E+04	1.7E+05	1.7	45.33	2.6E+04	1.3E+05	5.7	29.20	3.6E+04	2.6E+05	3.4	23.03
Port Hueneme	6.37	Entrained	7.1E+04	2.7E+05	1.7	43.37	5.1E+04	2.6E+05	3.9	26.42	6.4E+04	2.7E+06	2.8	24.20
Prudhoe Bay	0	Meso	5.0E+02	6.8E+03	0.1	43.06	5.3E+02	4.4E+03	0.3	39.37	3.9E+03	9.8E+03	1.2	38.05
Prudhoe Bay	9.32	Stable	4.6E+04	6.4E+05	0.11	85.07	3.2E+04	3.4E+05	0.2	85.13	1.7E+04	5.1E+04	0.90	71.03
Prudhoe Bay	18.12	No												
Prudhoe Bay	27.25	Meso?	1.6E+03	2.3E+05	0.3	20.37				18.76				12.12
Santa Clara	0	Meso	2.7E+03	1.8E+04	6.5	60.63	2.6E+03	2.9E+04	1.4	12.75				7.04
Santa Clara	11.4	Meso	2.0E+04	7.0E+05	0.15	50.43	1.5E+04	7.5E+04	3.5	38.72	3.9E+04	1.4E+05	5.0	18.73
Santa Clara	21.63	Meso	1.0E+05	3.6E+05	1.4	38.99	9.2E+04	3.7E+05	1.65	40.15	1.6E+05	1.2E+06	0.55	33.26
Sockeye	0	Stable	6.9E+05	6.5E+06	0.065	86.51	2.8E+06	4.7E+06	0.105	87.02	8.1E+05	3.5E+06	0.23	83.04
Sockeye	12.5	Stable	2.0E+05	1.3E+06	0.235	80.71	2.5E+05	1.2E+06	0.305	76.78	3.1E+05	1.8E+06	0.40	69.14
Sockeye	22.1	Stable	2.5E+05	1.4E+06	0.25	79.10	3.1E+05	1.4E+06	0.325	74.75	3.9E+05	2.1E+06	0.43	66.26
Sockeye Comingled	0	Stable	3.9E+04	1.1E+05	1.2	73.62	2.4E+04	8.5E+04	2.2	66.16	5.2E+04	1.3E+05	2.3	70.79
Sockeye Sour	0	Stable	3.2E+04	1.2E+05	1.3	73.64	2.5E+04	1.1E+05	1.7	53.12	5.2E+04	1.5E+05	2.5	48.75
Sockeye Sour	9.55	Stable/meso	7.9E+04	3.0E+05	1.3	59.93	8.5E+04	3.2E+05	1.3	60.19	1.3E+05	3.8E+05	1.5	53.66
Sockeye Sour	18.52	No				9.89								
Sockeye Sweet	0	Webby				5.04								
Sockeye Sweet	8.13	Webby				0.78								
Sockeye Sweet	17.46	Inversion	8.2E+03	3.1E+04	0.4	81.75	4.3E+03	2.0E+04	0.5	76.81	4.8E+03	8.7E+04	0.66	34.09
Sockeye Sweet	26.91	Stable	4.8E+04	5.1E+05	0.3	75.47	3.6E+04	1.3E+05	0.6	72.28	3.1E+04	2.7E+05	0.72	59.44
Sumatran Heavy	0	No				20.97				12.73				
Sumatran Heavy	5.26	No				2.35								
Sumatran Light	0	No				12.54				11.20				

able 1

Rheological Data on Water-in-Oil States

Oil	% evap.	Visual Stability	Day of Formation: Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)	One Week After Formation: Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)	>1 Year After Formation: Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)
aching	0	No				3.53								
akula	0	Stable	4.5E+04	9.5E+05	0.17	84.76	8.7E+04	8.9E+05	0.175	83.81	1.5E+05	3.3E+06	0.20	81.26
akula	8.31	Stable	8.3E+04	1.2E+06	0.205	81.34	1.1E+05	1.2E+06	0.2	81.41	2.5E+05	1.9E+06	0.22	78.44
akula	15.88	Stable	1.1E+05	1.2E+06	0.265	75.00	1.5E+05	6.0E+05	0.26	73.94	3.2E+05	9.7E+06	0.23	71.80
apis	0	No				15.87				9.06				
apis	13.9	No				22.68				20.03				
apis	28.62	No				9.02								
apis	43.43	No				7.75								
dang	0	Entrained	3.2E+04	1.3E+05	2	37.05				19.65				
osca Knoll 826	0	No				1.69								
osca Knoll 990	0	No				0.18								
axy Light Heavy Blend	0	No				4.11								
axy Light Heavy Blend	12	Meso	6.2E+03	4.1E+04	1.7	49.72				14.43				
axy Light Heavy Blend	19.6	Meso	4.4E+04	2.3E+05	1.1	54.57	3.3E+04	1.2E+05	1.2	59.19	6.9E+03	1.7E+05	10	59.06

Type	Parameter	Day of Formation Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)	One Week After Formation Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)	>1 Year After Formation Viscosity (mPa.s)	Complex Modulus (mPa)	tan delta (V/E)	Water Content (%w/w)
Entrained	Average	1.0E+05	4.3E+05	1.7E+00	4.9E+01	1.3E+05	6.0E+05	2.3E+00	4.1E+01	1.5E+05	1.0E+06	1.8E+00	3.7E+01
	Std. Dev	9.6E+04	3.6E+05	4.3E-01	1.4E+01	1.4E+05	8.8E+05	1.5E+00	1.5E+01	1.2E+05	1.1E+06	8.1E-01	1.6E+01
Mesostable	Average	1.7E+04	1.8E+05	1.2E+00	5.9E+01	1.6E+04	1.2E+05	2.9E+00	3.2E+01	3.8E+04	4.9E+05	2.4E+00	2.5E+01
	Std. Dev	2.5E+04	1.9E+05	1.5E+00	1.6E+01	2.5E+04	1.6E+05	3.3E+00	1.8E+01	5.0E+04	5.9E+05	3.1E+00	1.3E+01
Unstable	Average	NR	NR	NR	NR	NR	NR	NR	1.3E+01	NR	NR	NR	5.5E+00
	Std. Dev	NR	NR	NR	NR	NR	NR	NR	4.8E+00	NR	NR	NR	NR
Stable	Average	1.2E+05	1.1E+06	4.8E-01	8.0E+01	2.2E+05	9.9E+05	5.3E-01	7.8E+01	2.4E+05	1.6E+06	5.4E-01	7.3E+01
	Std. Dev	1.4E+05	1.4E+06	6.4E-01	7.2E+00	5.3E+05	1.1E+06	5.6E-01	9.0E+00	2.3E+05	2.0E+06	5.8E-01	1.1E+01
Stable without breakage	Average	1.4E+05	1.2E+06	4.9E-01	8.0E+01	2.5E+05	1.1E+06	4.8E-01	7.9E+01	2.7E+05	1.9E+06	4.3E-01	7.7E+01
	Std. Dev	1.5E+05	1.5E+06	6.8E-01	6.9E+00	5.9E+05	1.1E+06	5.4E-01	7.3E+00	2.3E+05	2.1E+06	4.5E-01	7.2E+00

Differences (In percent compared to the longest time)		Overall Differences			
Entrained	Between Day of Formation and One Week	-20.8	-28.2	-26.5	18.5
	Between One Week and One Year	-9.6	-41.3	28.8	11.7
Mesostable	Between Day of Formation and One Week	5.8	**49.0**	**-59.7**	**83.9**
	Between One Week and One Year	-58.0	-75.5	24.5	29.5
Unstable	Between Day of Formation and One Week	NR	NR	NR	NR
	Between One Week and One Year	NR	NR	NR	140.1
Stable	Between Day of Formation and One Week	-43.7	9.3	-8.5	2.3
	Between One Week and One Year	-9.6	-40.1	-2.8	7.4
Average	Overall Average	-22.6	-21.1	-7.4	41.9

Table 3

Oil	evap. %	Visual stability	Starting Oil Properties Density	Viscosity	Saturates	Aromatics	Resins	Asphaltenes	Waxes	One-Week Emulsion Stability*	One-Year Emulsion Stability*	Ratio Initial/One Year Stability	Ratio Initial/ One Year Water Content	Water Content (%w/w)	Water Content (%w/w)
Arabian Light	0	Stable-?	0.866	14	51	39	6	3	5	32857	5429	6	1.1	75.20	86.93
Arabian Light	12.04	Stable-?	0.892	33	49	37	8	5	5	6061	1667	4	1.5	59.06	85.82
Arabian Light	24.20	Stable-?	0.911	94	46	39	10	6	5	3830	57	67	1.8	47.60	83.62
Arabian Medium	0	Stable	0.878	29	54	32	7	6	6	23448	11034	2	1.0	83.81	84.36
Arabian Medium	13.15	Stable	0.91	91	42	44	7	7	5	2308	4857	1	1.0	77.05	77.06
Arabian Medium	20.77	Stable	0.926	275	40	46	8	7	5	364	1836	0	1.0	73.32	72.86
Arabian Medium	30.93	Stable	0.95	2155	33	54	9	7	5	186	270	1	1.0	65.26	65.60
Belridge Heavy	0	Meso	0.975	12610	28	39	30	3	1	13	13	1	0.8	35.25	27.16
Belridge Heavy	2.74	Meso	0.977	17105	29	38	30	4	1	11	12	1	0.9	33.26	29.47
Bunker C (1987)	0	Entrained	0.983	45030	24	55	15	7	12	14	77	0	1.0	23.42	24.02
Bunker C (Anchorage)	0	Entrained	0.989	8706	25	47	17	11	2	16	48	0	1.7	17.86	30.96
Carpenteria	10.31	Meso	0.93	755	40	30	19	11	5	48	331	0	0.6	22.37	13.82
Carpenteria	14.87	Meso	0.948	3426	31	36	22	11	4	85	219	0	0.9	18.02	16.04
Cook Inlet - Granite Point	45.32	Meso	0.903	4119	62	28	7	3		63	100	1	2.7	21.17	57.58
Cook Inlet - Swanson River	0	Meso	0.842	6	65	25	6	5		4500	75000	0	1.0	60.82	57.50
Cook Inlet - Swanson River	39.69	Stable	0.914	152	56	29	7	7		5395	15789	0	1.0	78.75	80.76
Cook Inlet - Trading Bay	33.30	Meso	0.924	278	51	32	9	8		1906	6835	0	1.2	52.65	61.43
Dos Cuadras	11.17	Meso	0.927	187	42	31	20	7	4	25	283	0	4.0	7.34	29.49
Dos Cuadras	20.30	Meso	0.947	741	41	31	19	9	6	23	41	1	1.5	19.86	28.72
Hondo	0	Stable	0.936	735	33	31	24	12	4	1197	1293	1	1.0	76.77	79.96
Hondo	16.67	Stable	0.967	9583	27	33	29	12	4	88	207	0	1.1	61.19	64.23
Point Arguello Comingled	0	Stable	0.925	533	36	25	23	16	8	2064	3152	1	1.0	82.21	82.19
Point Arguello Comingled	9.05	Stable	0.953	4988	31	33	19	17	4	124	334	0	1.0	67.39	69.41
Point Arguello Comingled	15.19	Entrained	0.969	41860	27	33	21	19	4	19	42	1	0.9	30.18	28.42
Point Arguello Heavy	0	Stable	0.945	3250	32	32	17	19	6	222	338	1	1.1	70.19	74.97
Point Arguello Light	0	Stable	0.874	22	57	27	9	6	6	37727	50455	1	1.0	90.20	93.79
Point Arguello Light	10.19	Stable	0.898	76	54	30	9	8	6	36842	35987	1	1.0	86.37	87.78
Point Arguello Light	19.04	Stable	0.913	183	48	31	12	9	7	19126	20328	1	1.0	87.55	85.63
Point Arguello Light	28.33	Stable	0.929	671	45	32	12	11	8	2235	3428	1	1.0	78.29	75.89
Port Hueneme	0	Entrained	0.966	4131	24	43	20	12	5	10	12	1	2.0	9.82	20.06
Port Hueneme	3.14	Entrained	0.975	7833	23	41	21	14	3	17	33	1	1.3	23.03	29.20
Port Hueneme	6.37	Entrained	0.979	20990	23	37	28	13	3	12	129	0	1.1	24.20	26.42
Santa Clara	11.40	Meso	0.948	1859	32	28	27	13	4	40	75	1	2.1	18.73	38.72
Santa Clara	21.63	Meso	0.967	22760	28	32	23	17	5	16	54	0	1.2	33.26	40.15
Sockeye	0	Stable	0.897	45	48	31	13	8	6	95556	77111	1	1.1	83.04	86.87
Sockeye	12.50	Stable	0.917	163	44	32	15	9	5	6748	11156	1	1.1	69.14	74.35
Sockeye	22.10	Stable	0.926	628	39	34	15	15	5	2389	3344	1	1.1	66.26	70.39
Takula	0	Stable	0.864	110	65	22	8	5	8	10909	30000	0	1.0	81.26	84.18
Takula	8.31	Stable	0.885	844	62	24	10	4	8	1422	2222	1	1.0	78.44	77.18
Takula	15.88	Meso	0.896	3148	60	25	11	4	8	381	3081	0	0.8	71.80	60.22
Waxy Light Heavy Blend	19.60	Meso	0.975	17280	30	35	28	6	1	6	10	1	0.6	59.06	33.58
											Average	2.40	1.2		

* emulsion stability is the complex viscosity of the emulsion divided by the starting oil viscosity

Table 4 Summary of the Properties of Water-in-Oil States After One Year

Oil	Visual stability	Starting Oil Properties: Density	Viscosity	Saturates	Aromatics	Resins	Asphaltenes	Waxes	Asphaltene Resin Ratio	One-Week Emulsion Stability*	One-Year Emulsion Stability*	Ratio Initial/One Year Stability	Ratio Initial/One Year Water Content	One Year Water Content (%w/w)	One-Week Water Content (%w/w)
Entrained	Average	0.977	21425	24.3	42.7	20.3	12.7	4.8	0.6	14.7	56.8	0.4	1.4	21.4	26.5
	Std. Dev.	0.009	18003.2	1.5	7.7	4.5	3.9	3.7	0.2	3.3	41.2	0.3	0.4	6.9	4
Meso-Stable	Average	0.935	6482.62	41.5	31.5	19.3	7.8	3.9	0.5	547.5	6619.5	0.4	1.4	34.9	38
	Std. Dev.	0.039	7985.37	13.7	4.5	8.6	4.3	2.3	0.2	1295.8	20639.4	0.3	1	20	16.4
Stable	Average	0.916	1291.21	44.5	32.7	13.3	9.7	5.9	0.8	13071.1	14376.4	0.7	1	76.7	78.3
	Std. Dev	0.028	2389.94	11.2	7.7	6.5	4.3	1.4	0.2	23331.7	20730.7	0.4	0	8.2	7.9

* emulsion stability is the complex viscosity of the emulsion divided by the starting oil viscosity

stable emulsions always have a more solid appearance. The increase in apparent viscosity (from the starting oil) on formation averages about 1,100 for a stable emulsion, 45 for a meso-stable emulsion, 13 for entrained water-in-oil and unstable show little or no increase. This difference increases after one week. The increase in apparent viscosity after one week averages about 1,500 for a stable emulsion, 30 for a meso-stable emulsion, 3 for entrained water-in-oil and unstable show little or no increase. It is noted that apparent viscosity for stable emulsions only, does not decrease after one-week.

There are several other features noted in the summary data presented in Table 5. An examination of the wax content shows that wax content has no relation to the formation of any of these states. There may be some correlation to viscosity but 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 to 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 meso-stable - 62, of entrained - 42 and 5 for unstable. One must be cautious on using this as a sole discriminator because of over-lapping ranges. The water content after one week, as would be expected, correlates very highly with the state. This, as was noted above, is accentuated by the fact that meso-stable and entrained water-in-oil have separated to a significant degree.

These data indicate that there are 'windows' of composition and viscosity which results in the formation of each of the types of water-in-oil states. The important composition factors are the asphaltene and resin contents. Asphaltenes are responsible for the formation of stable emulsions, however, a high asphaltene content can also result in a high viscosity, one that is above the region where stable emulsions form. The asphaltene/resin ratio is generally higher for stable emulsions. In a previous work by the present author, it was shown that the migration rate of asphaltenes in emulsions is very slow (Fingas *et al.* 1996). This indicates that in very viscous oils, the migration of asphaltenes may be too slow to allow for the stabilization of emulsions.

One very important question was whether actual emulsions formed at sea would fit this scheme. Emulsion formed in the lab, starting oil and an emulsion formed at sea in the recent ERIKA spill were analysed. The emulsion was stable. The water content was 57.2%, the complex modulus was 480,000 kPa and the tan delta was 1. The asphaltene content was 7 % and the resin content was 16 %, yielding an asphaltene/resin ratio of 0.4. The data from this emulsion fit the parameters of Table 5. Thus, this real world emulsion fits the same parameters as the laboratory emulsions. Further work will be done to ensure that the laboratory findings are relevant to those emulsions produced at spills in the real world.

5.0 Conclusions

Four, clearly-defined states of water-in-oil have been shown to be defined by a number of measurements and by their visual appearance, both on the day of formation and one week later. The difference between these states and the oils that form them are summarized in Table 6.

The results of this study indicate that the formation of both stable and meso-stable emulsions is due to the combination of surface-active forces from resins and

		Stable		Meso		Entrained		Unstable	
Starting Oil									
Property		high	low	high	low	high	low	high	low
Density	g/mL	0 9674	0 8637	0 977	0 842	0 9907	0 9688	1 005	0 811
Viscosity	(mPa s)	9583	14	22760	6	59390	2002	5138000	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
Properties on day of formation									
Appearance		brown solid		brown viscous liquid		black with large droplets		like oil	
Average Ratio of Viscosity Increase		1100		45		13		1	
range		15000	14	250	2	70	1	8	1
Average Water Content		80		62		42		5	
range		93	65	83	35	62	26	23	1
Stability*		15000	20	400	1	50	1	60	1
Properties after one Week									
Appearance		brown solid		broken, 2 or 3 phases		separated oil and water		like oil	
Average Ratio of Viscosity Increase		1500		30		2		1	
range		15000	20	150	1	3	1	2	1
Average Water Content		79		38		15		2	
range		94	64	61	2	35	12	24	0
Stability*		95000	88	1900	1	434	1	198	1
Power Law Constants	K	8 596E+05	1 117E+04	1 877E+05	4 376E+02	2 744E+05	2 763E+03	2 125E+03	0 000E+00
	n	0 8129	0 0372	0 9765	0 1401	0 9633	0 6255	0 9800	0
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
ComplexModulus	(mPa)	4.3E+06	1 0E+05	1 2E+06	10	3 3E+06	6400	5138000	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

* complex modulus/viscosity of starting oil

Table 6

Typical Properties for 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, 2 or 3 phases	separated oil and water	like oil
Water Content after week	%	79	38	15	2
Stable time	days	>30	<3	<0.5	not
Starting Oil					
Density	g/mL	0.85-0.97	0.84-0.98	0.97-0.99	0.8-1.03
Viscosity	(mPa s)	15-10000	6-23000	2000-60000	$2 - 5.1 \times 10^6$
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
Properties on day of formation					
Average Ratio of Viscosity Increase		1100	45	13	1
Properties after one Week					
Average Ratio of Viscosity Increase		1500	30	2	1
Properties after one Year					
Average Ratio of Viscosity Increase		1400	15	1	1

asphaltenes and from viscous forces. There exists a range of compositions and viscosities in which each type of water-in-oil state exist. The difference in composition between stable and meso-stable emulsions is small. Stable emulsions have more asphaltenes and less resins and have 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 resins and asphaltenes are less than about 3% each. Water entrainment occurs rather than emulsion formation when the viscosity is between about 2000 and about 50,000 mPa.s. The formation of stable or meso-stable emulsions may not occur in highly viscous oils because the migration of asphaltenes (and resins) is too slow to permit droplet stabilization.

The role of other components is still unclear at this time. Aromatics dissolve asphaltenes and there is a small correlation observed with the stabilities. Waxes have no role in emulsion formation. 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 mixture can be correlated with the single parameter of the complex modulus divided by the starting oil viscosity. This stability parameter also correlates somewhat with the non-Newtonian behaviour of the resulting water-in-oil mixture, with the elasticity of the emulsion and also the water content. These properties are more decisive in defining the state one-week after formation. This is because in this interval, 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.

All water-in-oil water states gain some stability after one year. All lose some water, but generally this is only a small percentage. There appears to be no change in state after one year, with the exception of Arabian light emulsions which lost significant stability indicating that the 'stable' emulsion may be breaking down in about one year.

6.0 References

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Worldwide Analysis (

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Abstract

Contingency planners, re
transporters share a keen interest
planning purposes. Oil spill clea
most notably, location, oil type,
develop a universal per-unit cost

This study analyzes mari
proximity to shoreline, spill size,
methodology to determine how c

The results show that oil
the world vary considerably in th
values, socio-economic factors, a
factor heavily in determining cle
times as expensive to clean up as
are more than ten times as expen
fuels. Spill responses for spills u
on a per-unit basis, as for spills o

The paper describes a cle
applied to marine spills of differe
data collected from case studies
account oil type, location, spill si
deduce a per-unit cleanup cost fi

1.0 Introduction

The entire cast of players
pipeline operators, insurers, spill
government officials – would all
cleanup costs. Many would like t
even in advance of spill incidents
that might be required to remove
like to develop a universal per-un
attempted to do this, the results h
cleanup cost factor does not take
and the fact that no two spills are
cleanup costs (Etkin, 1998b; 199
some extent.

One approach to predictin
to rely on "hindsight," i.e., exami
past spills based on important fac
to shoreline, location, cleanup m