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RESEARCH

Water-in-oil Emulsions Results of Formation Studies and Applicability to Oil Spill Modelling

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This paper summarizes studies of water-in-oil emulsions, their stability, and modelling of their formation. Studies show that water-in-oil emulsions might be characterized into three categories (stable, mesostable and unstable). These categories were established by visual appearance, elasticity and viscosity differences. It was also shown that water content was not an important factor. A fourth category of water-in-oil exists, that of water entrainment, which is not an emulsion. Water-in-oil emulsions made from crude oils have different classes of stabilities as a result of the asphaltene and resin contents. The differences in the emulsion types are readily distinguished both by their rheological properties, and simply by appearance. The apparent viscosity of a stable emulsion at a shear rate of one reciprocal second, is at least three orders-of-magnitude greater than the starting oil. An unstable emulsion usually has a viscosity no more than one order-of-magnitude greater than that of the starting oil. A stable emulsion has a significant elasticity, whereas an unstable emulsion does not. Stable emulsions have sufficient asphaltenes ($> \sim 7\%$) to establish films of these compounds around water droplets. Mesostable emulsions have insufficient asphaltenes to render them completely stable. Stability is achieved by visco-elastic retention of water and secondarily by the presence of asphaltene or resin films. Mesostable emulsions display apparent viscosities of about 80–600 times that of the starting oil and true viscosities of 20–200 times that of the starting oil. Mesostable emulsions have an asphaltene and resin content greater than 3%. Entrained water occurs when a viscous oil retains larger water droplets, but conditions are not suitable for the formation of an emulsion. Entrained water may have a viscosity that is similar or slightly greater ($\sim$2–10 times) than the starting oil. It was found that emulsion formation occurs at a threshold energy, however this energy has not been accurately defined. Emulsions from many oils have been characterized. This information is used to describe how this process can be accurately modelled and what information gaps exist for complete description of the physical process. The modelling of emulsions is reviewed. A new modelling scheme based on the new physical findings, is suggested. © 1999 Elsevier Science Ltd. All rights reserved

Keywords: Water-in-oil emulsions, oil spill modelling, emulsion formation, stable emulsions, mesostable emulsions, unstable emulsions

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

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change the properties and characteristics of oil spills to a very large degree. Stable emulsions contain between 55 and 85% water thus expanding the volume of spilled material from two to five times the original volume. The density of the resulting emulsion can be as great as 1.03 g/ml compared to a starting density as low as 0.80 g/ml. Most significantly, the viscosity of the oil typically changes from a few hundred Centistokes (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 behavioural 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 (Mackay, 1980). Emulsification also has significant effects on other spill aspects; spill countermeasures are quite different for emulsions. Emulsions may be hard to recover mechanically, treat or burn.

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.*, 1995b). Therefore, studies were difficult because the end points of analysis were not defined. Relationships used in early models simply presumed one type of emulsion which was the result of a first-order water uptake.

It has been noted that the stability of emulsions can be grouped into three categories: stable, unstable and mesostable (Fingas *et al.*, 1997). These have been distinguished by physical properties. The viscosity of a stable emulsion at a low shear rate has been shown to be a particularly easy discriminating factor between various emulsions. The study of elasticity, a related property to viscosity, has also been shown to be very useful because stable emulsions show high elasticity and vice versa.

The present authors have studied emulsions for many years (Bobra *et al.*, 1992; Fingas *et al.*, 1993a,b,c, 1994a, 1995a,b, 1996, 1997; Fingas and Fieldhouse, 1994) The findings of these studies are summarized here and related to spill modelling. Studies in the past three years have shown that a class of 'very stable' emulsions exists, characterized by their persistence over several months (Fingas *et al.*, 1995b, 1996, 1997). These stable emulsions actually undergo an increase in viscosity over time. Monitoring of these emulsions has been performed over a period of weeks. 'Unstable' emulsions do not show this viscosity increase and their viscosity is less than two orders-of-magnitude greater than the starting oil. The viscosity increase for stable emulsions is at least three orders-of-magnitude greater than the starting oil. It was concluded, both on the basis of the literature and experimental evidence above, that certain emulsions can be classed as stable. Some (if not all or many) stable emulsions increase in apparent viscosity with time (i.e. their elasticity increases). The stability derives from the strong viscoelastic interface caused by asphaltenes, perhaps along with resins. Increasing viscosity may be caused by increasing alignment of asphaltenes at the oil–water interface (Fingas *et al.*, 1996).

Mesostable emulsions are emulsions that have properties between stable and unstable emulsions (really oil/water mixtures) (Fingas *et al.*, 1995b). It is suspected that mesostable 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. Mesostable emulsions may degrade to form layers of oil and stable emulsions. Mesostable emulsions can be red in appearance or black. Mesostable 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 forced oscillation 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. All emulsions which test as stable were reddish. Some mesostable emulsions 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.

Extensive literature reviews have been carried out and summarized in the literature (Fingas *et al.*, 1995b, 1996, 1997). The consensus of the literature is as follows:

1. stable and less-stable emulsions exist,
2. emulsion stability results from the viscoelastic films formed by asphaltenes,
3. asphaltenes produce more rigid films than do resins,
4. stable emulsions might be classified by their dielectric and viscoelastic properties,
5. water content does not appear to relate to stability, however, very low or very high water contents (< 30 or > 90%) will not yield stable emulsions,

6. most researchers use visible phase separation to classify emulsions as stable or not and most concede that this is not an optimal technique.

Several other authors have published relevant papers and reviews (Aveyard *et al.*, 1991; Breen *et al.*, 1996; Førdedal and Sjöblom, 1996; Førdedal *et al.*, 1996a,b; Friberg, 1991; Friberg and Yang, 1996; Sjöblom and Førdedal, 1996).

Experimental

Emulsions have been studied extensively in the laboratory by the present authors and results reported in the literature (Bobra *et al.*, 1992; Fingas and Fieldhouse, 1994; Fingas *et al.*, 1993a,b,c, 1994a, 1995a,b, 1996, 1997). It is not the intent of this paper to provide details on all the experiments, but to provide a summary of these and relate these to spill modelling.

Water-in-oil emulsions were made in various agitators or devices and then the rheometric characteristics of these emulsions studied over time. The relative energy only of the devices was characterized. Differences were noted in the emulsion formation tendency of oils at different energy levels. Compared to other oil phenomena such as dispersion, the energy required to make an emulsion might be characterized as high. Work is now in progress to quantify the energy in these apparatuses.

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

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, 60 mm 4°cone with corresponding base plate, clean air supply at 40 p.s.i., and a circulation bath maintained at 15°C. Analysis was performed on a sample scooped onto the base plate and raised to the measuring cone. This was left for 15 min to thermally equilibrate at 15°C.

Forced oscillation – A stress sweep at a frequency of one 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.

Observations were made on the appearance of the emulsions. Some emulsions appeared to be stable and remained intact over several days in the laboratory. Some formed mesostable emulsions and broke after a few days into water, free oil and emulsion. The time for these emulsions to break down varied from about 1 to 3 days. The emulsion portion of these break-down emulsions appears to be somewhat stable, although studies on them have not been performed. Some emulsions were mesostable at formation ratios of 1:10 and 1:20 (O:W) and broke after about 1 day of sitting into water, oil and emulsion. Other emulsions formed at ratios of 1:30 (O:W) and higher were not stable and broke into water and oil within hours of mixing. It is suspected that the O:W ratio only relates to the shaking energy applied to the oil and may not be meaningful in itself.

Results and discussion on emulsion laboratory studies

The rheometric studies on the emulsions of over eighty oils shows that there exist large differences in the viscosities (both apparent and true) of unstable, mesostable and stable emulsions and entrained water. Table 1 shows the summary results of the analysis of over 80 oils. Column 2 of Table 1 is the evaporation state of the oil in mass percent lost. Column 3 is the assessment of the stability of the emulsion based on both visual appearance and rheological properties. The power law constants, k and n, are given next. These are parameters from the Ostwald de Waele equation which describes the Newtonian (or non-Newtonian) characteristics of the material. The viscosity of the emulsion is next and in column 7, the complex modulus which is the vector sum of the viscosity and elasticity. Column 8 lists the elasticity modulus and column 9, the viscosity modulus. In column 10, the isolated, low-shear viscosity is given. This is the viscosity of emulsion at very low shear rate. In column 9 tanδ, the ratio of the viscosity to the elasticity component, is given. Finally, the water content of the emulsion, after 1 week, is presented.

Table 1 Oil properties and comparison to the one-week emulsion properties

Oil	Starting oil properties									Emulsion stability*	Emulsion rheological properties – one week after formation								
	Evap. (%)	Visual stability	Density	Viscosity	Saturates	Aromatics	Resins	Asphalt-enes	Waxes		Power Law (K)	Constants (n)	Viscosity (mPa.s)	Complex modulus (mPa)	Elasticity modulus (mPa)	Viscosity modulus (mPa)	Isolated low shear viscosity (mPa.s)	Tax delta (V/E)	Water content (%w/w)
Sockeye	0	Stable	0.897	45	48	31	13	8	6	95555.56	8.596E+05	0.0544	6.9E+05	4.3E+06	1.0E+06	3.1E+05	8.8E+04	0.11	86.87
Point Arguello Light	0	Stable	0.874	22	57	27	9	6	6	37727.27	9.671E+04	0.0581	9.6E+04	8.3E+05	8.2E+05	1.4E+05	2.2E+04	0.17	93.79
Point Arguello Light	10.19	Stable	0.898	76	54	30	9	8	6	36842.11	4.167E+05	0.0372	2.5E+05	2.8E+06	2.8E+06	3.3E+05	5.2E+04	0.12	87.78
Arabian Light	0	Stable	0.866	14	51	39	6	3	5	32857.14	3.537E+04	0.0860	2.3E+04	4.6E+05	4.6E+05	4.0E+04	6.3E+04	0.14	86.93
Arabian Medium	0	Stable	0.878	29	54	32	7	6	6	23448.28	8.828E+04	0.0944	5.5E+04	6.8E+04	7.7E+05	7.9E+04	1.2E+04	0.11	84.36
Point Arguello Light	19.04	Stable	0.913	183	48	31	12	9	7	19125.68	5.054E+05	0.0539	3.1E+05	3.5E+06	3.6E+06	4.2E+05	7.2E+04	0.13	85.63
Takula	0	Stable	0.864	110	65	22	8	5	8	10909.09	1.609E+05	0.1371	1.2E+05	1.2E+06	1.2E+06	2.1E+05	3.1E+04	0.15	84.18
Sockeye	12.50	Stable	0.917	163	44	32	15	9	5	6748.47	1.806E+05	0.1871	2.2E+05	1.1E+06	4.3E+06	4.9E+06	5.0E+04	0.31	74.35
Arabian Light	12.04	Stable	0.892	33	49	37	8	5	5	6060.61	3.596E+04	0.0957	3.1E+04	2.0E+05	2.0E+05	2.7E+04	4.2E+04	0.13	85.82
Cook Inlet-Swanson River	39.69	Stable	0.914	152	56	29	7	7		5394.74				8.2E+05	7.4E+05	3.3E+05	5.2E+04	0.43	80.76
Arabian Light	24.20	Stable	0.911	94	46	39	10	6	5	3829.79	4.091E+04	0.1226	4.3E+04	3.6E+05	3.5E+05	7.3E+04	1.1E+04	0.20	83.62
Sockeye	22.10	Stable	0.926	628	39	34	15	15	5	2388.54	2.396E+05	0.1948	3.1E+05	1.5E+06	1.4E+06	5.0E+05	7.8E+04	0.35	70.39
Arabian Medium	13.15	Stable	0.91	91	42	44	7	7	5	2307.69	2.663E+04	0.4521	2.8E+04	2.1E+05	1.8E+05	1.2E+05	1.9E+04	0.64	77.06
Point Arguello Light	28.33	Stable	0.929	671	45	32	12	11	8	2235.47	1.920E+05	0.1723	1.6E+05	1.5E+06	1.4E+06	4.2E+05	6.6E+04	0.28	75.89
Point Arguello Comingled	0	Stable	0.925	533	36	25	23	16	8	2063.79	1.493E+05	0.2883	1.8E+05	1.1E+06	1.0E+06	4.1E+05	6.4E+04	0.36	82.19
Takula	8.31	Stable	0.886	844	62	24	10	4	8	1421.80	1.528E+05	0.1744	1.3E+05	1.2E+06	1.1E+06	2.3E+05	3.6E+04	0.20	77.18
Hondo	0	Stable	0.936	735	33	31	24	12	4	1197.28	1.665E+05	0.1825	1.7E+05	8.8E+05	8.3E+05	2.5E+05	4.2E+04	0.32	79.96
Arabian Medium	20.77	Stable	0.926	275	40	46	8	7	5	363.64	1.117E+04	0.8129	2.3E+04	1.0E+05	5.0E+04	9.2E+04	1.5E+04	1.8	72.86
Point Arguello Heavy	0	Stable	0.945	3250	32	32	17	19	6	221.54	8.767E+04	0.4322	1.8E+05	7.2E+05	5.8E+05	3.9E+05	6.6E+04	0.72	74.97

Arabian Medium	30.93	Stable	0.95	2155	33	54	9	7	5	185.61	5.757E+04	0.4417	5.4E+04	4.0E+05	3.2E+05	2.2E+05	3.6E+04	0.70	65.60
Point Arguello Comingled	9.05	Stable	0.953	4988	31	33	19	17	4	124.30	1.651E+05	0.3100	1.5E+05	6.2E+05	4.7E+05	4.3E+05	7.0E+04	0.95	69.41
Hondo	16.67	Stable	0.967	9583	27	33	29	12	4	87.66	1.537E+05	0.5753	2.8E+05	8.4E+05	6.2E+05	6.1E+05	9.0E+04	0.96	64.23
North Slope (Southern Pipeline)	29.62	No	0.943	961	42	39	13	7		197.71	N/M	N/M	1.5E+03	1.9E+05	1.7E+05	7.4E+04	1.2E+04	0. 42	24.48
North Slope (Northern Pipeline)	31.14	No	0.94	748	44	37	12	7		147.06	N/M	N/M	1.2E+03	1.1E+05	9.4E+04	4.7E+04	7.6E+03	0.50	12.60
North Slope (Middle Pipeline)	30.54	No	0.942	900	42	38	12	7		122.22	N/M	N/M	1.4E+03	1.1E+05	1.0E+05	4.8E+04	7.4E+03	0.49	19.67
Santa Clara	0	No	0.92	304	36	22	29	13	6	95.39	2.125E+03	0.9800	2.6E+03	2.9E+04	1.7E+04	2.4E+04	3.9E+03	1.4	12.75
Bunker C (Anchorage)	8.41	No	1.005	280000	23	42	20	15	2	1				280000					
Carpenteria	0	No	0.916	164	44	30	17	9	7	1				164					
Hondo	32.29	No	0.988	449700	27	28	32	13	4	1				449700					
Jet Fuel (Anchorage)	0	No	0.811	2	81	19	0	0	0	1				2					
Jet Fuel (Anchorage)	52.72	No	0.835	3	80	19	0	0	0	1				3					
North Slope (Middle Pipeline)	0	No	0.876	16	52	35	9	5		1				16					
North Slope (Northern Pipeline)	0	No	0.872	14	51	34	9	5		1				14					
North Slope (Southern Pipeline)	0	No	0.877	18	54	32	8	6		1				18					
Pitas Point	0	No	0.834	2	80	18	3	0	0	1				2					
Pitas Point	23.56	No	0.854	2	62	35	0	0	0	1				2					
Point Arguello Comingled	22.12	No	0.985	2E+06	24	33	21	22	5	1				2266000					
Point Arguello Heavy	17.78	No	0.991	5E+06	25	34	21	22	4	1				4953000					
Sumatran Heavy	0	No	0.931	13300	46	30	13	8	5	1				13300					12.73

— continued overleaf

Table 1 *(continued)*

Oil	Starting oil properties									Emulsion stability[a]	Emulsion rheological properties – one week after formation								
	Evap. (%)	Visual stability	Density	Viscosity	Saturates	Aromatics	Resins	Asphalt-enes	Waxes		Power Law (K)	Constants (n)	Viscosity (mPa.s)	Complex modulus (mPa)	Elasticity modulus (mPa)	Viscosity modulus (mPa)	Isolated low shear viscosity (mPa.s)	Tax delta (V/E)	Water content (%w/w)
Sumatran Heavy	5.26	No	0.937	17000	45	32	16	8	4	1				17000					
Sumatran Light	0	No	0.86	41480	70	15	6	7	24	1				41480					11.20
Taching	0	No	0.87	5E+06	74	12	9	4	23	1				5138000					
Waxy Light Heavy Blend	0	No	0.931	184	39	35	21	5	4	1				184					
Cook Inlet – Granite Point	0	No	0.829	4	72	22	5	1		1				4					
Diesel (Anchorage)	0	No	0.83	3	74	24	1	0	0	1				3					
Diesel (Anchorage)	37.44	No	0.862	5	75	23	1	0	0	1				5					
Diesel (Mobile Burn #3)	0	No	0.839	4	76	22	2	0	0	1				4					
Diesel (Mobile Burn #3)	8.21	No	0.843	5	78	20	2	0	0	1				5					
Diesel (Mobile Burn #3)	16.32	No	0.845	6	78	20	2	0	0	1				6					
Dos Cuadras	0	No	0.9	51	48	30	17	6	6	1				51					
Cook Inlet – Swanson River	0	Meso	0.842	6	65	25	6	5		4500	4.376E+02	0.4120	1.9E+03	2.7E+04	2.2E+04	1.7E+04	2.6E+03	0.80	57.50
Cook Inlet – Trading Bay	33.30	Meso	0.924	278	51	32	9	8		1906.47	1.361E+05	0.1861	4.3E+04	5.3E+05	4.9E+05	1.5E+05	2.6E+04	0.27	61.43
Takula	15.88	Meso	0.896	3148	60	25	11	4	8	381.19	1.877E+05	0.1791	1.7E+05	1.2E+06	1.2E+06	2.8E+05	4.4E+04	0.24	60.22
Carpenteria	14.87	Meso	0.948	3426	31	36	22	11	4	84.65	9.734E+03	0.8845	2.1E+04	2.9E+05	2.6E+05	1.5E+05	2.3E+04	0.57	16.04
Cook Inlet – Granite Point	45.32	Meso	0.903	4119	62	28	7	3		63.12	7.725E+04	0.1401	8.5E+03	2.6E+05	2.6E+05	7.4E+04	1.2E+04	0.30	57.58

Carpenteria	10.31	Meso	0.93	755	40	30	19	11	5	47.68	4.815E+03	0.9765	2.3E+04	3.6E+04	3.2E+03	3.6E+04	5.8E+03	12	13.82
Santa Clara	11.40	Meso	0.948	1859	32	28	27	13	4	40.34	1.087E+05	0.1688	1.5E+04	7.5E+04	2.0E+04	7.3E+04	1.1E+04	3.5	38.72
Dos Cuadras	11.17	Meso	0.927	187	42	31	20	7	4	24.6	N/M	N/M	5.3E+02	4.6E+03	1.6E+03	4.2E+03	7.0E+02	3.0	29.49
Dos Cuadras	20.30	Meso	0.947	741	41	31	19	9	6	22.94	N/M	N/M	1.9E+03	1.7E+04	3.0E+03	1.3E+04	2.1E+03	4.2	28.72
Santa Clara	21.63	Meso	0.967	22760	28	32	23	17	5	16.26	5.794E+04	0.6751	9.2E+04	3.7E+05	2.0E+05	3.3E+05	5.0E+04	1.65	40.15
Belridge Heavy	0	Meso	0.975	12610	28	39	30	3	1	12.69	2.638E+04	0.6938	5.4E+04	1.6E+05	8.2E+04	1.2E+05	2.2E+04	1.6	27.16
Belridge Heavy	2.74	Meso	0.977	17105	29	38	30	4	1	10.52	2.779E+04	0.6374	6.2E+04	1.8E+05	1.0E+05	1.4E+05	2.4E+04	1.4	29.47
Waxy Light Heavy Blend	19.60	Meso	0.975	17280	30	35	28	6	1	6.37	1.884E+04	0.7088	3.7E+04	1.1E+05	5.3E+04	1.0E+05	1.6E+04	2.1	33.58
Cook Inlet – Trading Bay	0	Meso	0.86	10	62	26	7	5		1				10					1.89
Platform Irene	0	Entrained	0.991	7600	26	29	22	22	2	434.21	2.744E+05	0.6255	5.4E+05	3.3E+06			4.0E+05	1.20	34.94
Point Arguello Comingled	15.19	Entrained	0.969	41860	27	33	21	19	4	19.11	9.211E+04	0.7623	1.6E+05	8.0E+05	3.5E+05	7.0E+05	1.1E+05	2.10	28.42
Port Hueneme	3.14	Entrained	0.975	7833	23	41	21	14	3	16.6	1.918E+04	0.8713	2.7E+04	1.3E+05	2.1E+04	1.2E+05	2.0E+04	5.7	29.20
Bunker C (Anchorage)	0	Entrained	0.989	8706	25	47	17	11	2	16.08	1.903E+04	0.8567	1.5E+05	1.4E+05	3.2E+04	1.3E+05	2.1E+04	4.0	30.96
Bunker C (1987)	0	Entrained	0.983	45030	24	55	15	7	12	14.43	9.818E+04	0.8336	1.4E+05	6.5E+05	6.2E+05	5.6E+05	8.4E+04	1.0	24.02
Port Hueneme	6.37	Entrained	0.979	20990	23	37	28	13	3	12.39	3.438E+04	0.8070	5.4E+04	2.6E+05	6.4E+04	2.4E+05	4.0E+04	3.9	26.42
Port Hueneme	0	Entrained	0.966	4131	24	43	20	12	5	10.41	7.253E+03	0.9633	8.8E+03	4.3E+04	4.8E+03	4.1E+04	6.9E+03	9.4	20.06
Waxy Light Heavy Blend	12.00	Entrained	0.958	2002	32	38	24	6	1	7.49	2.763E+03	0.9194	3.7E+03	1.5E+04	2.4E+03	1.5E+04	2.4E+03	6.2	12.21
Beta	0	Entrained	0.974	13380	21	39	31	7	3	1				13380					20.74
Calfornia API 11.0	0	Entrained	0.988	34000				16	1	1				34000					29.72
California API 15.0	0	Entrained	0.977	6400	19	35	23	22	1	1				6400					34.62

— continued overleaf

Table 1 *(continued)*

Oil	Starting oil properties									Emulsion stability*	Emulsion rheological properties – one week after formation								
	Evap. (%)	Visual stability	Density	Viscosity	Saturates	Aromatics	Resins	Asphalt-enes	Waxes		Power Law (K)	Constants (n)	Viscosity (mPa.s)	Complex modulus (mPa)	Elasticity modulus (mPa)	Viscosity modulus (mPa)	Isolated low shear viscosity (mPa.s)	Tax delta (V/E)	Water content (%w/w)
Point Arguello	8.88	Entrained	0.971	59390	26	35	18	20	4	1				59390					
Heavy Udang	0	Entrained	0.97	10700	32	41	24	3	1	1				10700					19.65

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

Table 2 Classes of water uptake in crude and refined oils

Property	Unstable emulsions no water uptake	Entrained water	Mesostable emulsions	Stable emulsions
Appearance	Same as the oil	Large droplets in oil	Black to brown	Red to brown
Typical water content at formation	Little	30–50%	75–85%	75–85%
Water content range at formation	Little	0–90%	30–95%	70–90%
Water content in oil after 1 week	Same as the oil	0–30%	0–10 or 75–85%	75–85%
Ratio of apparent viscosity to original oil (D = 1/s)	Same as starting oil	Same to slightly higher (1 or >1)	×75–200	×2000–3000
Ratio of true viscosity to original oil (D = 1/s)	Same as starting oil	Same to slightly higher (1 or >1)	×20–200	×500–800
Stiffness modulus (frequency of 1 Hz)	Same as starting oil	Same	Increase (×1000)	Greatest increase (×100,000)
Ratio viscosity/elasticity ($\tan\delta$ – forced oscillation, 1 Hz)	Same as starting oil	>5	0.5–5	<0.5
Non-Newtonian behaviour (exponent of Ostwald de Waele power law model)	Same as starting oil	>0.75	0.15–0.25	<0.1
Stability	None	Short term, hours	Mid term, days	Long term, years
Breakage	Immediate	Oil and Water	2 or 3 phases	Not relevant
Stabilizing force	None	Kinetic (viscosity)	Kinetic (viscosity and surfactant interaction	Natural surfactant interaction
Asphaltene percentage	Very high or low	<3%	>3%	>7%
Resin percentage	Very high or low	?	>3%	Not highly correlated
Waxes	No correlationn	Slight correlation	Not correlated	Not correlated

Table 2 summarizes the differences between the various oil-in-water states studied here. The results presented are consistent with previous results from the present authors and the literature (Fingas *et al.*, 1997). It was suggested that mesostable 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. Mesostable emulsions are probably the most commonly-formed emulsions in the field. It was noted that stable emulsions derive from oils that have asphaltene contents greater than 3–5% and a lower (as yet undefined) aromatic content. Further work on the interaction of these components is necessary before exact prediction of emulsion formation can occur, however predictions based on the physics noted above will be much more accurate than those in the past.

Modelling of the process

The early emulsion formation theories were translated into modelling equations at that time. Unfortunately, the processes described above were not apparent until 5 years ago and have not yet been translated into modelling equations. Information on the kinetics of formation at sea and other modelling data is less abundant in the past and in recent times. It is now known that emulsion formation is a result of surfactant-like behaviour of the polar and asphaltene compounds. These are similar compounds and both behave like surfactants when they are not in solution. When there are insufficient amounts of aromatic components to solubilize the asphaltenes and polars, these precipitate and are available to stabilize water droplets in the oil mass. The minimum mass percentage of either asphaltenes or resins to stabilize an emulsion is about 3%. This will form a mesostable emulsion. Stable emulsions form when the asphaltene content of the oil rises above 7%. Emulsions begin to form when the above chemical conditions are met and when there is sufficient sea energy. This energy is not measurable and its relative amount is not known in terms of emulsion onset. Literature indicates that relative energy required to form emulsion varies, but is not high.

In the past, the rate of emulsion formation was assumed to be first-order with time. This can be approximated with a logarithmic (or exponential) curve. This assumption, although not consistent with the knowledge of how emulsions formed, has been used extensively in oil spill models. Most models that incorporate the phenomenon use the Mackay and co-workers (Mackay, 1980; Mackay *et al.*, 1980) estimation technique or a variation of this. Mackay proposed a differential equation for the formation of emulsions. Mackay suggested that this equation not be used since it can only be solved for $k_2 = 0$ or a very large number. This corresponds to a very stable or unstable emulsion. This equation was fitted to some data from sea experiments and found to fit adequately. A simpler equation was proposed as well:

$$\Delta W = K_a (U + 1)^2 (1 - K_{bW}) \Delta t \tag{1}$$

where:

ΔW = the water uptake rate
W = the fractional water content
K_a = an empirical constant
U = the wind speed
K_b = a constant with the value of approximately 1.33
t = time

This equation is used in most models where emulsification is incorporated. Because the equation predicts that most oils will form emulsions rapidly given a high wind speed, most users have adjusted the equation by changing constants or the form slightly.

Mackay and Zagorski (1982) proposed two relationships to predict the formation of emulsions on the sea. They proposed that the stability could be predicted as follows with an equation that related asphaltenes and their activities as well as other factors such as waxes.

Kirstein and Redding (1988) used a variation of the Mackay equation to predict emulsification. The major difference being the addition of a 'coalescing constant' which is the inverse of the water constant. All of the above work is based on the Mackay equations which were developed before extensive work on emulsion physics took place. They have not been well correlated to either laboratory or field results. The present authors suggest that both the tendency and the formation of emulsions could be predicted with a degree of accuracy using empirical data (Fingas *et al.*, 1997, 1996, 1995b; Friberg, 1991; Aveyard *et al.*, 1991; Sjöblom *et al.*, 1992). The formation of mesostable emulsions is known to occur when the asphaltenic and resin fraction combined goes over 3% and the amount of the BTEX (benzene, toluene, ethylbenzene, and xylene) is less than this amount. Stable emulsions form when the asphaltene content is greater than 7%. Since evaporation on the sea rapidly removes the BTEX component, predication of formation could be approximated by predicted evaporative loss and the weight fraction of the asphaltenes and resins. When the latter rises over the requisite amount and there is sufficient sea energy, an emulsion will form. There is insufficient empirical or theoretical information to predict the requirement for energy. Observations in the literature suggest that the energy requirement is variable, but that some oils will form emulsions at apparently moderate sea energies, others at higher turbulent levels. The change in viscosity is indicated as that of Table 1.

Literature shows that emulsion formation is relatively rapid and in the laboratory occurs fully – at moderate energies – in 0.1–3 h. A simplified approximation is that emulsions form immediately given the correct oil composition and minimum energy.

Conclusions

The stability of emulsions can be classified into three categories: stable, mesostable and unstable. A fourth state, that of entrained water, which occurs as a result of viscosity retention of water droplets, has also been noted. The differences in the emulsion types are readily distinguished both by their rheological properties, and simply by appearance. The apparent viscosity of a stable emulsion at a shear rate of one reciprocal second, is at least three orders-of-magnitude greater than the fresh oil. An unstable emulsion usually has a viscosity no more than one order-of-magnitude greater than that of the starting oil. A stable emulsion has a significant elasticity, whereas an unstable emulsion does not. It should be noted that very few emulsions have questionable stability. Stable emulsions have sufficient asphaltenes (> ~7%) to establish films of these compounds around water droplets.

Mesostable emulsions have insufficient asphaltenes to render them completely stable. Stability is achieved by viscoelastic retention of water and secondarily by the presence of asphaltene or resin films. Mesostable emulsions display apparent viscosities of about 80–600 times that of the starting oil and true viscosities of 20–200 times that of the starting oil. Past emulsion-formation modelling was based on first-order rate equations which were developed before extensive work on emulsion physics took place. They have not been well correlated to either laboratory or field results. The present authors suggest that both the tendency and the formation of emulsions could be predicted using empirical data. The formation of mesostable emulsions is known to occur when the asphaltenic and resin fraction combined goes over 3% and the amount of the BTEX (benzene, toluene, ethylbenzene, and xylene) is less than this amount. Stable emulsions form when the asphaltene content is greater than 7%. Since evaporation on the sea increases the amount of resins and asphaltenes by loss of other components, predication of formation could be approximated by predicted evaporative loss and the weight fraction of the asphaltenes and resins. When the latter rises over the requisite amount and there is sufficient sea energy, an emulsion will form. Observations reported in the literature suggest that the energy requirement is variable, but that some oils will form emulsions at apparently moderate sea energies, others at higher turbulent levels. The change in viscosity is predictable using values reported here.

Literature shows that emulsion formation is relatively rapid and in the laboratory occurs fully – at moderate energies – in 0.1–3 h. A simplified approximation is that emulsions form immediately given the correct oil composition and minimum energy.

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