

Formation of water-in-oil emulsions and application to oil spill modelling

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Abstract

Water-in-oil mixtures were grouped into four states or classes: stable, mesostable, unstable, and entrained water. Of these, only stable and mesostable states can be characterized as emulsions. These states were established according to lifetime, visual appearance, complex modulus, and differences in viscosity. Water content at formation was not an important factor. Water-in-oil emulsions made from crude oils have different classes of stability as a result of the asphaltene and resin contents, as well as differences in the viscosity of the starting oil. The different types of water-in-oil classes are readily distinguished simply by appearance, as well as by rheological properties.

A review of past modelling efforts to predict emulsion formation showed that these older schemes were based on first-order rate equations that were developed before extensive work on emulsion physics took place. These results do not correspond to either laboratory or field results. The present authors suggest that both the formation and characteristics of emulsions could be predicted using empirical data. If the same oil type as already studied is to be modelled, the laboratory data on the state and properties can be used directly.

In this paper, a new numerical modelling scheme is proposed and is based on empirical data and the corresponding physical knowledge of emulsion formation. The density, viscosity, saturate, asphaltene and resin contents are used to compute a class index which yields either an unstable or entrained water-in-oil state or a mesostable or stable emulsion. A prediction scheme is given to estimate the water content and viscosity of the resulting water-in-oil state and the time to formation with input of wave height.

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1. Introduction

Emulsification is the process whereby water-in-oil emulsions are formed. These emulsions are sometimes called “chocolate mousse” or “mousse” by oil spill workers. Emulsions change the properties and characteristics of oil spills to a very large degree. Stable emulsions contain between 60 and 80% 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 1.01 g/mL compared to a starting density as low as 0.80 g/mL [6,8]. Most significantly, the dynamic viscosity of the oil typically changes from a few hundred mPa·s to about one hundred thousand mPa·s, a typical increase of 1000. Thus, a liquid product is changed to a heavy, semi-solid material.

The most important characteristic of a water-in-oil emulsion is its stability. Properties change very significantly for

each type of emulsion. Studies have shown that the most important factor for emulsion stability relates to the asphaltene content [6,13,18,19,21].

Water-in-oil mixtures are grouped into four states or classes: stable, mesostable, unstable, and entrained water [6,9,10]. Of these, only stable and mesostable states can be characterized as emulsions. These states were established primarily by lifetime, but also by visual appearance, elasticity, and differences in viscosity. Water content at formation was not an important factor. Water-in-oil emulsions made from crude oils have different classes of stability as a result of the asphaltene and resin contents, as well as differences in the viscosity of the starting oil. The different types of emulsions are readily distinguished simply by appearance, as well as by their rheological properties.

Mesostable emulsions are emulsions that have properties between stable and unstable emulsions (really oil/water mixtures) [6]. It is thought that mesostable emulsions lack sufficient asphaltenes to render them completely stable. The viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Mesostable emulsions

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may degrade to form layers of oil and stable emulsions. Mesostable emulsions can be brown or black in appearance.

Unstable emulsions are those that largely decompose to water and oil rapidly after mixing, generally within a few hours. Some water (usually less than about 10%) may be retained by the oil, especially if the oil is viscous. Entrained water (typically 30–40%) may persist in viscous oils for a period of several hours. This ‘entrained’ class has a short life span, but residual water, typically about 10%, may persist for a long time.

Emulsification has been shown to be a very important part of oil behaviour and thus should be included into oil spill models [1]. The drastic changes in oil properties that occur after emulsification occurs, can result in very different behaviour and fate on the sea.

2. Traditional modelling of the process

The early emulsion formation modelling equations did not use specific knowledge of emulsion formation processes. The processes outlined above were not discovered until many years after the process equations were put forward. Furthermore, the presence of different water-in-oil states dictates that one simple equation is not adequate to predict emulsion formation.

Information on the kinetics of formation at sea and other modelling data was less abundant in the past. It is now known that emulsion formation is a result of surfactant-like behaviour of the polar asphaltene and resin compounds. While these are similar compounds that both behave like surfactants when they are not in solution, asphaltenes form much more stable emulsions [19]. Emulsions begin to form when the required chemical conditions are met and there is sufficient sea energy.

In the past, the rate of emulsion formation was assumed to be first-order with time. This could be approximated with a logarithmic (or exponential) curve. Although not consistent with the knowledge of how emulsions formed, this assumption has been used extensively in oil spill models. Most models that incorporate emulsification as an algorithm use the estimation technique of Mackay and co-workers or a variation of this technique [15–17].

Mackay proposed the following generic equation to model water uptake:

$$\Delta W = K_a(U + 1)^2(1 - K_b W)\Delta t, \quad (1)$$

where ΔW is 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, and t the time. Because Eq. (1) 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 [16] proposed two relationships to predict the formation of emulsions on the sea. They proposed

that the stability could be predicted as follows:

$$S = x_a \gamma_a \exp[k_{a0}(1 - x_a - x_w)^2 + K_{aw} x_w^2] \exp^{[-0.04(T-293)]}, \quad (2)$$

where S is the stability index in relative units, high numbers indicate stability, x_a the fraction of asphaltenes, γ_a the activity of asphaltenes, K_{a0} a constant (here 3.3), x_w the fraction of waxes, K_{aw} a constant which is 200 at 293 K, and T the temperature in Kelvin.

Water uptake was given as:

$$\Delta W_T = \Delta W_L + \Delta W_s = \Delta T[k_f - k_l W_l], \quad (3)$$

where ΔW_T is the total change in water content, ΔW_L the change in water content for large droplets, ΔW_s the change in water content for small droplets, ΔT the time, k_f the rate constant for formation, typically 1 h^{-1} , k_l the rate constant for large droplet formation and is about 3 h^{-1} , and W_l the fraction of large droplets, which is typically 3–4.

Kirstein and Redding [14] used a variation of the Mackay equation to predict emulsification:

$$(1 - k_2 W) \exp\left(\frac{-2.5 W}{1 - k_1 W}\right) = \exp(-k_5 k_3 t), \quad (4)$$

where k_2 is a coalescing constant which is the inverse of the maximum weight fraction water in the mixture, W the weight fraction water in the mixture, k_1 the Mooney constant which is 0.62–0.65, k_5 the increase in mousse formation due to weathering, k_3 the lumped water incorporation rate constant and is a function of wind speed in knots, and t the time in days. The change in viscosity due to mousse formation was given by:

$$\mu = \mu_0 \exp\left(\frac{2.5 W}{1 - k_1 W}\right), \quad (5)$$

where μ is the resulting viscosity, μ_0 the starting oil viscosity, and the remainder are identical to the above.

Reed [20] used the Mackay equations in a series of models. The constants were adjusted to match field observations:

$$\frac{dF_{wc}}{dt} = 2 \times 10^{-5} (W + 1)^2 \left(1 - \frac{F_{wc}}{C_3}\right), \quad (6)$$

where dF_{wc}/dt is the rate of water incorporation, W the wind speed in m/s, F_{wc} the fraction of water in oil, and C_3 the rate constant equal to 0.7 for crude oils and heavy fuel oils.

The viscosity of the emulsion was predicted using the following variant of the Mooney equation, similar to Eq. (5):

$$\frac{\mu}{\mu_0} = \exp\left(\frac{2.5 F_{wc}}{1 - 0.65 F_{wc}}\right), \quad (7)$$

where μ is the viscosity of the mixture, μ_0 the viscosity of the starting oil, and F_{wc} the fraction of water in oil.

The effect of evaporation on viscosity was modelled as:

$$\mu = \mu_0 \exp(C_4 F_{evap}), \quad (8)$$

where μ is the viscosity of the mixture, μ_0 the viscosity of the starting oil, C_4 a constant which is 1 for light fuels and 10 for heavy fuels, and F_{evap} the fraction evaporated from the slick.

All of the above work has a basis in the Mackay equations, which were developed before extensive work on emulsion physics took place. Using the old prediction schemes, most oils behave similarly and uptake a large percentage of water. This does not occur in nature. The present authors suggest that both the formation and the characteristics of emulsions could be predicted with accuracy using empirical data as described below.

3. New studies on stability

The rheometric studies on the water-in-oil states of over 200 oils show that there are large differences in the viscosities of unstable, mesostable and stable emulsions, and entrained water. The stability, rheological properties, and water content of the resulting water-in-oil state for the day after formation are given in Table 1. The second column of the table is the evaporation state of the oil in mass percent lost. Some physical properties of the starting oil are given in columns 3–7. The eighth column is the assessment of the stability of the emulsion based on water loss over a period of 1 week. The ninth column is a measure of the stability of the water-in-oil state after 1 week. This is the complex modulus divided by the starting oil viscosity. The 10th column is the viscosity of the emulsion and the 11th column is the complex modulus which is the complex sum of the viscous and the elastic components. 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). The water content of the water-in-oil state is presented in the 12th column.

Observations were made on the appearance of the emulsions and used to classify the water-in-oil classes. All the stable emulsions appeared to be stable and remained intact over 7 days in the laboratory. All the mesostable 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 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. Kinetic observations were also made in another study on the formation of emulsions [2]. These show that the emulsions are formed fairly rapidly and that there is neither a continuum of formation nor interconversion between types.

Table 1 can be used as a reference to decide if the selected oil will emulsify and what state is achieved. It can also be used to provide the oil properties, water content and complex modulus of the resulting water-in-oil states.

4. Summary of emulsion formation knowledge

Four clearly defined states of water-in-oil have been shown to exist [6,9]. The states are stable water-in-oil emulsions, mesostable water-in-oil emulsions, entrained water, and unstable water-in-oil. These are established by their stability over time, their appearance, and by rheological measurements.

Stable emulsions are brown or reddish, semi-solid materials with an average water content of about 80% on the first day of formation and about the same 1 week later. Stable emulsions remain stable for at least 4 weeks under laboratory and test tank conditions. Mesostable water-in-oil emulsions are brown or black viscous liquids with an average water content of 70% on the first day of formation and about 30% 1 week later. Mesostable emulsions remain as such less than 3 days under laboratory conditions.

Entrained water-in-oil states (and not emulsions) are black liquids with an average water content of about 40% on the first day of formation and about 15% 1 week later. Entrained water-in-oil remains as such for less than 1 day under laboratory conditions. Entrained water states are most often produced from heavier oils, that is those having a density greater than 0.92.

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

The stability of emulsions is due to the formation of asphaltene and resin films at the oil and water interface [2]. Asphaltenes form strong elastic films, which are largely responsible for the stability of emulsions. While there is clear evidence of interaction between resins and asphaltenes in forming emulsions, asphaltenes can form emulsions without resins.

Experiments show that asphaltenes migrate to the interface very slowly [6]. There is evidence that the migration can continue for longer than 1 month. This leads to the possibility that the resins migrate very quickly and temporarily stabilize water droplets before stronger asphaltene films form and displace the weaker resin films. Asphaltene films have been found to be a highly viscoelastic barrier to coalescence of water droplets. The films may be strengthened by H- or π -bonding between individual asphaltene molecules.

Oil viscosity alone may be a partial barrier to the re-coalescence of the water droplets. This mechanism is proposed as the primary stabilizer for entrained water and partially for mesostable emulsions. This may also explain why waxes are seen as important in certain circumstances. They may increase viscosity enough to allow the formation of entrained water states. Waxes are not a factor, however, in the formation of either stable or mesostable emulsions [2].

Table 1
Properties of oils and their water-in-oil classes

Oil	% evaporation	Oil properties					Water-in-oil class properties					
		Density (g/mL)	Viscosity (mPa. s)	Saturates (%)	Resins (%)	Asphaltenes (%)	Emulsion			Complex modulus (mPa)	Water content (%, w/w)	
							Visual stability	Stability (s)	Viscosity (mPa. s)			
Alaska North Slope (2002)	0.0	0.8663	12	75	6	4	Unstable	0				
Alaska North Slope (2002)	10.0	0.8940	32	72	7	4	Unstable	0				
Alaska North Slope (2002)	22.5	0.9189	152	69	9	5	Unstable	0				
Alaska North Slope (2002)	30.5	0.9340	625	65	10	6	Mesostable	100		6.47E+04	73	
Arabian Light	0.0	0.8658	14	51	6	3	Stable	33,570	2.30E+04	4.70E+05	87	
Arabian Light	12.0	0.8921	33	49	8	5	Stable	12,120	4.60E+04	4.00E+05	89	
Arabian Light	24.2	0.9111	94	46	10	6	Stable	5,430	4.80E+04	5.10E+05	85	
Arabian Light (2002)	0.0	0.8641	13	76	6	4	Mesostable	7,130		9.27E+04	91	
Arabian Light (2002)	9.0	0.8660	27	73	6	4	Mesostable	7,740		2.12E+05	89	
Arabian Light (2002)	17.0	0.9028	60	72	7	4	Stable	4,570		2.74E+05	84	
Arabian Light (2002)	26.0	0.9193	174	70	9	5	Stable	2,890		5.03E+05	84	
Arabian Medium	0.0	0.8783	29	54	7	6	Stable	18,900	4.10E+04	5.48E+05	85	
Arabian Medium	13.2	0.9102	91	42	7	7	Stable	1,650	2.00E+04	1.50E+05	77	
Arabian Medium	20.8	0.9263	275	40	8	7	Stable	270	2.10E+04	7.40E+04	73	
Arabian Medium	30.9	0.9495	2,155	33	9	7	Stable	90	4.60E+04	1.94E+05	65	
ASMB (std. #5)	0.0	0.8404	6	77	4	2	Mesostable	21,800		1.33E+05	90	
ASMB (std. #5)	12.0	0.8676	14	77	5	2	Mesostable	29,640		4.09E+05	93	
ASMB (std. #5)	24.0	0.8852	32	77	6	2	Stable	20,000		6.30E+05	88	
ASMB (std. #5)	36.0	0.9017	123	72	7	3	Stable	8,330		1.03E+06	86	
Aviation Gasoline 100LL	0.0	0.7143	1				Unstable	0				
Aviation Gasoline 100LL	32.7	0.7258	1				Unstable	0				
Aviation Gasoline 100LL	60.1	0.7292	1				Unstable	0				
Barrow Island	0.0	0.8410	2	64	4	0	Unstable	0				
Barrow Island	16.7	0.8700	4	66	4	0	Unstable	0				
Barrow Island	32.2	0.8906	11	61	4	0	Unstable	0				
Barrow Island	47.9	0.9075	23	59	6	0	Unstable	0				
Belridge Heavy	0.0	0.9746	12,610	28	30	3	Entrained	20	4.20E+04	2.96E+05	58	
Belridge Heavy	2.7	0.9770	17,105	29	30	4	Entrained	10	4.70E+04	1.95E+05	60	
Beta	0.0	0.9738	13,380	21	31	7	Entrained	0			37	
Bunker C (1987)	0.0	0.9830	45,030	24	15	7	Entrained	20	1.10E+05	8.11E+05	26	
Bunker C (Anchorage)	0.0	0.9891	8,710	25	17	11	Entrained	10	2.80E+04	1.26E+05	35	
Bunker C (Anchorage)	8.4	1.0050	280,000	23	20	15	Unstable	0			6	
California API 11.0	0.0	0.9882	34,000			16	Entrained	0			35	
California API 15.0	0.0	0.9770	6,400	19	23	22	Entrained	130		8.31E+05	39	
Carpenteria	0.0	0.9155	164	44	17	9	Unstable	0			9	
Carpenteria	10.3	0.9299	755	40	19	11	Mesostable	100	2.10E+04	7.30E+04	72	
Carpenteria	14.9	0.9482	3,430	31	22	11	Mesostable	40	2.90E+04	1.30E+05	54	
Coal Oil Point Seep Sample	0.0	0.9872	165,800	21	24	21	Stable ^a	10	2.80E+05	1.18E+06	32	
Cold Lake Bitumen	0.0	1.0166	825,000	46	13	17	Entrained	3		2.82E+06	17	
Cook Inlet—Granite Point	0.0	0.8293	4	72	5	1	Unstable	0				
Cook Inlet—Granite Point	45.3	0.9028	75	62	7	3	Mesostable	4,870	1.60E+04	3.65E+05	83	

Cook Inlet—Swanson River	0.0	0.8420	6	65	6	5	Mesostable	1,720	2.90E+03	1.03E+04	76
Cook Inlet—Swanson River	39.7	0.9143	152	56	7	7	Stable	4,070	2.90E+04	6.19E+05	81
Cook Inlet—Trading Bay	0.0	0.8602	10	62	7	5	Unstable	0			
Cook Inlet—Trading Bay	33.3	0.9242	278	51	9	8	Mesostable	1,330	2.40E+04	3.71E+05	76
Diesel (Anchorage)	0.0	0.8300	2	74	1	0	Unstable	0			
Diesel (Anchorage)	37.4	0.8515	5	75	1	0	Unstable	0			
Diesel (Mobile Burn #3)	0.0	0.8389	5	76	2	0	Unstable	0			
Diesel (Mobile Burn #3)	8.2	0.8427	5	78	2	0	Unstable	0			
Diesel (Mobile Burn #3)	16.3	0.8447	6	78	2	0	Unstable	0			
Dos Cuadras	0.0	0.9000	51	48	17	6	Unstable	0			
Dos Cuadras	11.2	0.9270	187	42	20	7	Mesostable	20	8.00E+02	3.45E+03	48
Dos Cuadras	20.3	0.9359	741	41	19	9	Mesostable	40	9.80E+03	3.28E+04	69
Fuel Oil #5 (2000)	0.0	0.9883	1,410	44	8	8	Stable	1,310		1.85E+06	76
Fuel Oil #5 (2000)	7.3	1.0032	4,530	40	8	13	Stable	590		2.67E+06	77
Garden Banks 387	0.0	0.8782	29	53	10	1	Unstable	0			
Garden Banks 387	7.1	0.8979	64	51	11	1	Unstable	0			
Garden Banks 387	15.1	0.9144	181	51	11	1	Unstable	0			
Garden Banks 387	23.3	0.9287	579	46	13	2	Mesostable	10	6.84E+03	8.15E+03	37
Garden Banks 426	0.0	0.8285	6	70	5	1	Unstable	0			
Garden Banks 426	12.3	0.8561	13	61	8	1	Unstable	0			
Garden Banks 426	24.8	0.8779	34	62	8	2	Unstable	0			
Garden Banks 426	37.7	0.8993	136	56	10	3	Stable	590	9.16E+03	8.00E+04	65
Genesis	0.0	0.8841	26	59	10	2	Unstable	0			
Genesis	8.1	0.9074	66	57	9	2	Unstable	0			
Genesis	15.1	0.9223	157	57	11	2	Unstable	0			
Genesis	23.1	0.9364	543	48	21	3	Mesostable	50	1.05E+04	2.65E+04	62
Green Canyon 184	0.0	0.8314	5	69	6	1	Unstable	0			
Green Canyon 184	12.1	0.8575	11	61	8	1	Unstable	0			
Green Canyon 184	26.0	0.8824	31	58	8	1	Unstable	0			
Green Canyon 184	38.2	0.9043	117	54	11	1	Mesostable	190	8.25E+03	2.18E+04	69
Green Canyon 65	7.7	0.9509	457	38	15	5	Stable	300		1.38E+05	78
Green Canyon 65	13.1	0.9559	800	36	15	4	Stable	140		1.14E+05	73
Green Canyon 65	22.9	0.9716	4,250	32	16	8	Stable	40		1.56E+05	57
Heavy Fuel Oil 6303	0.0	0.9888	22,800	43	16	13	Entrained	40		9.06E+05	57
Heavy Fuel Oil 6303	2.5	0.9988	149,000	39	17	18	Entrained	10		8.65E+05	21
Hebron M-04	8.8	0.9344	676	46	9	13	Stable	330		2.25E+05	75
Hebron M-04	16.4	0.9423	1,440	40	12	14	Stable	410		5.89E+05	72
Hebron M-04	22.6	0.9564	7,369	38	13	17	Stable	70		5.47E+05	57
High Viscosity Fuel Oil	0.0	1.0140	13,460	18	13	26	Entrained	20	7.36E+04	3.18E+05	48
Hondo	0.0	0.9356	735	33	24	12	Stable	1,280	1.10E+05	9.39E+05	81
Hondo	16.7	0.9674	9,580	27	29	12	Stable	130	1.90E+05	1.27E+06	66
Hondo	32.3	0.9881	449,700	27	32	13	Unstable	0			5
IFO—180	0.0	0.9670	2,320	29	11	10	Entrained	100	5.29E+04	2.41E+05	69
IFO—180	7.8	0.9840	27,280	28	17	15	Entrained	20	1.50E+05	6.06E+05	58
IFO—300	0.0	0.9859	14,500	26	12	10	Entrained	30	9.66E+04	3.93E+05	52
IFO—300	5.3	0.9996	220,000	24	30	17	Unstable	0			11
Jet A1	0.0	0.8159	2	94	0	0	Unstable	0			
Jet A1	12.0	0.8193	2	98	0	0	Unstable	0			
Jet A1	23.2	0.8216	2	96	1	0	Unstable	0			

Table 1 (Continued)

Oil	% evaporation	Oil properties					Water-in-oil class properties				
		Density (g/mL)	Viscosity (mPa. s)	Saturates (%)	Resins (%)	Asphaltenes (%)	Emulsion		Complex modulus (mPa)	Water content (%, w/w)	
Visual stability	Stability (s)	Viscosity (mPa. s)									
Jet A1	37.1	0.8244	2	98	0	0	Unstable	0			
Jet Fuel (Anchorage)	0.0	0.8111	2	81	0	0	Unstable	0			
Jet Fuel (Anchorage)	52.7	0.8354	3	80	0	0	Unstable	0			
Lago	0.0	0.8907	153	56	11	3	Unstable	0			
Lago	10.5	0.9128	7,820	51	14	2	Stable	20		1.76E+05	71
Lago	16.7	0.9230	39,300	53	14	3	Stable	10		5.08E+05	61
Lago Treco	0.0	0.9230	272	38	14	11	Stable	1,760		4.80E+05	83
Lago Treco	16.0	0.9661	16,200	32	15	15	Entrained	30		5.35E+05	63
Lucula	0.0	0.8574	43	67	8	4	Stable	18,530		7.97E+05	85
Lucula	10.7	0.8821	5,210	64	8	4	Mesostable	80		4.41E+05	70
Lucula	15.4	0.8904	6,120	62	9	4	Stable	250		1.52E+06	78
Lucula	26.9	0.9050	32,600	59	12	4	Entrained	60		2.07E+06	13
Malongo	0.0	0.8701	63	62	9	4	Unstable	0			
Malongo	11.8	0.8970	6,360	60	10	3	Stable	120		7.41E+05	71
Malongo	15.5	0.9026	10,950	55	13	3	Entrained	230		2.50E+06	51
Malongo	21.7	0.9141	25,600	54	15	4	Entrained	120		3.18E+06	46
MARS—TLP	0.0	0.8883	33	60	11	6	Unstable	0			
MARS—TLP	8.4	0.9122	93	55	11	6	Mesostable	140	5.84E+03	1.30E+04	63
MARS—TLP	17.2	0.9331	400	50	13	7	Mesostable	80	1.05E+04	3.10E+04	65
MARS—TLP	26.2	0.9520	2,240	49	13	10	Mesostable	40	3.07E+04	9.45E+04	62
Maya	15.0	0.9657	8,670	31	10	17	Entrained	50		4.53E+05	55
Maya	22.0	0.9868	405,000	28	11	22	Unstable	0		2.05E+03	2
Mississippi Canyon 72	0.0	0.8649	16	64	7	2	Unstable	0			
Mississippi Canyon 72	9.4	0.8827	34	57	8	2	Unstable	0			
Mississippi Canyon 72	18.0	0.8966	76	58	9	2	Mesostable	90	4.90E+03	7.00E+03	52
Mississippi Canyon 72	26.2	0.9095	195	52	11	3	Stable	1,130	3.30E+04	2.20E+05	74
Mississippi Canyon 807	0.0	0.8894	41	47	12	6	Mesostable	250	6.20E+03	1.02E+04	60
Mississippi Canyon 807	8.7	0.9187	127	39	13	7	Mesostable	150	1.01E+04	1.95E+04	68
Mississippi Canyon 807	16.4	0.9375	490	39	13	7	Stable	110	1.79E+04	5.45E+04	68
Mississippi Canyon 807	25.5	0.9582	3,450	31	18	8	Stable	50	3.36E+04	1.60E+05	65
Neptune Spar (Viosca Knoll 826)	0.0	0.8687	17	65	6	1	Unstable	0			
Neptune Spar (Viosca Knoll 826)	7.9	0.8826	42	63	6	2	Unstable	0			
Neptune Spar (Viosca Knoll 826)	15.4	0.8925	84	62	7	2	Mesostable	6,490	1.41E+04	5.45E+05	48
Neptune Spar (Viosca Knoll 826)	22.6	0.8986	187	61	8	2	Stable	4,950	3.12E+04	9.25E+05	63
North Slope (Middle Pipeline)	0.0	0.8761	16	52	9	5	Unstable	0			
North Slope (Middle Pipeline)	30.5	0.9418	900	42	12	7	Mesostable	120	2.60E+03	1.12E+05	62
North Slope (Northern Pipeline)	0.0	0.8719	14	51	9	5	Unstable	0			
North Slope (Northern Pipeline)	31.1	0.9402	748	44	12	7	Mesostable	140	1.40E+03	1.06E+05	70
North Slope (Southern Pipeline)	0.0	0.8766	18	54	8	6	Unstable	0			
North Slope (Southern Pipeline)	29.6	0.9431	960	42	13	7	Mesostable	200	1.90E+03	1.89E+05	53
Oriente	29.0	0.9426	6,120	41	11	15	Entrained	120		7.60E+05	56

Orinoco	0.0	1.0166	10,200,000	41	17	21	Unstable	0		3.55E+07	8
Pitas Point	0.0	0.8341	2	80	3	0	Unstable	0			
Pitas Point	23.6	0.8537	2	62	0	0	Unstable	0			
Platform Gail (Sockeye)	0.0	0.9297	406	39	21	12	Stable	300	3.58E+04	1.20E+05	76
Platform Gail (Sockeye)	7.3	0.9489	1,450	35	21	13	Stable	140	6.95E+04	2.02E+05	75
Platform Gail (Sockeye)	13.3	0.9645	7,090	32	25	15	Stable	50	1.13E+05	3.38E+05	67
Platform Gail (Sockeye)	20.6	0.9810	161,500	27	25	19	Entrained	10	3.98E+05	1.21E+06	44
Platform Holly	0.0	0.9928	3,310	54	15	17	Stable ^a	130	1.53E+05	4.4E+05	77
Platform Holly	24.2	1.0003	150,200	29	19	24	Stable ^a	10	3.62E+05	1.6E+06	60
Platform Holly	53.9	1.0066	399,700	36	17	22	Stable ^a	10	6.67E+05	3.5E+06	49
Platform Holly	78.5	1.0705	304,600	19	19	36	Stable ^a	10	8.04E+05	3.4E+06	34
Platform Irene	0.0	0.9907	76,000	26	22	22	Entrained	20	3.90E+05	1.39E+06	62
Point Arguello Comingled	0.0	0.9248	533	36	23	16	Stable	1,470	1.80E+05	7.86E+05	82
Point Arguello Comingled	9.1	0.9528	4,988	31	19	17	Stable	170	1.50E+05	8.53E+05	68
Point Arguello Comingled	15.2	0.9688	41,900	27	21	19	Entrained	10	1.40E+05	6.16E+05	30
Point Arguello Comingled	22.1	0.9853	2,266,000	24	21	22	Unstable	0		6.12E+06	2
Point Arguello Heavy	0.0	0.9447	3,250	32	17	19	Stable	160	1.50E+05	5.12E+05	73
Point Arguello Heavy	8.9	0.9706	59,400	26	18	20	Entrained	10		8.49E+05	17
Point Arguello Heavy	17.8	0.9914	4,953,000	25	21	22	Unstable	0			
Point Arguello Light	0.0	0.8739	22	57	9	7	Stable	29,320	6.70E+04	6.45E+05	93
Point Arguello Light	10.2	0.8979	76	54	9	8	Stable	44,080	2.80E+05	3.35E+06	89
Point Arguello Light	19.0	0.9132	183	48	12	9	Stable	18,740	2.70E+05	3.43E+06	86
Point Arguello Light	28.3	0.9289	670	45	12	11	Stable	1,470	1.40E+05	9.85E+05	80
Port Hueneme	0.0	0.9662	4,130	24	20	12	Entrained	20	1.60E+04	6.32E+04	38
Port Hueneme	3.1	0.9745	7,830	23	21	14	Entrained	20	4.60E+04	1.67E+05	45
Port Hueneme	6.4	0.9787	20,990	23	28	13	Entrained	10	7.10E+04	2.68E+05	43
Prudhoe Bay (1995)	0.0	0.8837	22	53	10	4	Mesostable	310	5.00E+02	6.81E+03	43
Prudhoe Bay (1995)	9.3	0.9048	55	51	10	3	Stable	11,710	4.61E+04	6.44E+05	85
Prudhoe Bay (1995)	18.1	0.9204	148	52	12	4	Unstable	0			
Prudhoe Bay (1995)	27.3	0.9352	623	43	15	5	Mesostable	250	1.55E+03	1.58E+05	20
Santa Clara	0.0	0.9202	304	36	29	13	Mesostable	50	2.70E+03	1.65E+04	61
Santa Clara	11.4	0.9479	1,860	32	27	13	Mesostable	380	2.00E+04	6.98E+05	50
Santa Clara	21.6	0.9672	22,800	28	23	17	Mesostable	20	1.00E+05	3.56E+05	39
Sockeye	0.0	0.8965	45	48	13	8	Stable	144,440	6.85E+05	6.50E+06	87
Sockeye	12.5	0.9166	163	44	15	9	Stable	7,760	2.02E+05	1.27E+06	81
Sockeye	22.1	0.9264	628	39	15	11	Stable	2,230	2.49E+05	1.40E+06	79
Sockeye (2000)	0.0	0.9354	760	50	18	15	Mesostable	240		1.83E+05	76
Sockeye (2000)	7.0	0.9537	2,720	47	19	16	Mesostable	90		2.51E+05	73
Sockeye (2000)	13.0	0.9692	15,100	45	19	18	Entrained	30		3.91E+05	53
Sockeye (2000)	20.0	0.9839	274,000	42	20	20	Entrained	5		1.30E+06	18
Sockeye Comingled	0.0	0.9350	550	34	21	13	Stable	210	3.87E+04	1.13E+05	74
Sockeye Sour	0.0	0.9409	820	38	20	13	Stable	150	3.20E+04	1.19E+05	74
Sockeye Sour	9.6	0.9682	8,710	29	22	17	Stable	40	7.91E+04	3.12E+05	60
Sockeye Sour	18.5	0.9838	475,000	26	22	24	Unstable	0			10
Sockeye Sweet	0.0	0.8792	20	55	10	4	Unstable	0			5
Sockeye Sweet	8.1	0.8945	39	56	10	4	Unstable	0			1
Sockeye Sweet	17.5	0.9089	103	50	13	5	Mesostable	310	8.18E+03	3.15E+04	82
Sockeye Sweet	26.9	0.9229	320	48	14	6	Stable	1,600	4.80E+04	5.13E+05	75
South Louisiana (2001)	0.0	0.8562	10	81	6	1	Unstable	0			

Table 1 (Continued)

Oil	% evaporation	Oil properties					Water-in-oil class properties				
		Density (g/mL)	Viscosity (mPa. s)	Saturates (%)	Resins (%)	Asphaltenes (%)	Emulsion			Complex modulus (mPa)	Water content (%, w/w)
							Visual stability	Stability (s)	Viscosity (mPa. s)		
South Louisiana (2001)	11.0	0.8770	24	80	6	1	Unstable	0			
South Louisiana (2001)	20.0	0.8906	49	78	8	1	Unstable	0			
South Louisiana (2001)	28.0	0.9018	141	77	8	2	Unstable	0			
Sumatran Heavy	0.0	0.9312	13,300	46	13	10	Entrained	0			21
Sumatran Heavy	5.3	0.9374	12,900	45	16	8	Unstable	0			2
Sumatran Light	0.0	0.8600	41,500	70	6	8	Unstable	0			13
Taching	0.0	0.8700	5,138,000	74	9	6	Unstable	0			4
Takula	0.0	0.8637	110	65	8	2	Stable	8,590	4.47E+04	9.45E+05	85
Takula	11.0	0.8860	844	62	10	4	Stable	1,420	8.32E+04	1.20E+06	81
Takula	18.0	0.8961	3,150	60	11	4	Stable	370	1.12E+05	1.15E+06	75
Tapis	0.0	0.8020	8	81	2	2	Unstable	0			16
Tapis	13.9	0.8237	57	77	3	1	Entrained	0			23
Tapis	28.6	0.8396	800	80	3	2	Unstable	0			9
Tapis	43.4	0.8552	1,440	79	4	3	Unstable	0			8
Thevenard Island	0.0	0.7855	1	85	2	0	Unstable	0			
Udang	0.0	0.9701	10,700	32	24	3	Entrained	20		1.91E+05	39
Viosca Knoll 826	0.0	0.8668	16	66	6	2	Unstable	0			2
Viosca Knoll 826	8.1	0.8842	43	61	7	3	Unstable	0			
Viosca Knoll 826	16.9	0.8970	132	62	6	3	Unstable	0			
Viosca Knoll 826	24.0	0.9067	325	59	8	3	Stable	1,050	1.37E+04	3.40E+05	64
Viosca Knoll 990	0.0	0.8337	7	73	4	1	Unstable	0			0
Viosca Knoll 990	12.3	0.8585	12	69	6	1	Unstable	0			
Viosca Knoll 990	24.4	0.8752	31	66	6	1	Unstable	0			
Viosca Knoll 990	35.2	0.8905	91	62	8	2	Stable	1,070	9.34E+03	9.8E+04	64
Waxy Light Heavy Blend	0.0	0.9311	184	39	21	5	Unstable	0			4
Waxy Light Heavy Blend	12.0	0.9582	2,000	32	24	6	Mesostable	20	6.16E+03	3.05E+04	50
Waxy Light Heavy Blend	19.6	0.9749	17,300	30	28	6	Mesostable	10	4.39E+04	1.90E+05	55
West Texas (2000)	0.0	0.8474	9	79	6	1	Unstable	0			
West Texas (2000)	10.0	0.8665	16	79	7	1	Unstable	0			
West Texas (2000)	21.0	0.8827	38	76	8	1	Mesostable	510		1.91E+04	83
West Texas (2000)	31.0	0.8973	112	75	10	2	Mesostable	730		8.19E+04	84
Zaire	0.0	0.8720	15,100	64	9	5	Entrained	30		5.10E+05	76
Zaire	6.0	0.8872	52,800	61	9	5	Entrained	10		7.53E+05	65
Zaire	14.0	0.9015	94,600	59	10	5	Entrained	10		1.15E+06	61
Zaire	23.0	0.9020	533,000	53	16	5	Unstable	0		2.27E+06	5

^a Oils contained water when received and were the water-in-oil class noted.

Weathering of oil is a factor in the stability of emulsions. First, the elimination of saturates and smaller aromatic compounds aids the formation of emulsions by reducing the amount of solvating material. Second, the viscosity increases as oil weathers, inhibiting the re-coalescence of water droplets. Third, oxidation and photooxidation create more polar compounds, some of which may be regarded as resins.

The energy required to form emulsions is quite low in most cases [4,5].

5. Model development

Two approaches to model development were implemented and are detailed in a current paper [12]. The approaches were to use the empirical data as presented in Table 1. One approach was to curve fit the physical and content data to the 'stability' index as noted in Table 1. Then this stability factor was used in turn to predict a class (stable, mesostable,

entrained or unstable). Another approach was to predict the class directly from the data. This latter approach will be summarized and applied in this paper.

The data in Table 1 were used to develop specific equations. The correlation for each parameter, as listed in Table 2, was correlated in a series of models using DataFit (Oakdale Engineering), which calculates linear models. The two-step process is necessary as DataFit is not able to calculate the specific mathematical function with more than two variables, due to the large number of possibilities. Thus, the function, e.g., linear, square, log, were calculated using a two-way regression (TableCurve) and these functions were in turn used in developing a predictor model for emulsification. The model that predicts class directly will be summarized here.

The steps to produce the model are summarized in Table 2. First the parameters available were correlated one at a time with the class criteria. Regression coefficients were optimized by adjusting the class criteria from a starting value of 1–4 to a logarithm of this value. This was performed on

Table 2
Model development process summary

	Value density	Viscosity	Saturates	Resins	Asphaltenes	a/r	Aromatics	Constant
Starting R^2	0.24	0.24	0.2	0.18	0.2	0.11	0.1	
Simplest function	1/x	ln x	x^3	ln	1/x	1/x		
First transform	None	None	None	If 0, 20	If 0, 30	Eliminate 0	none	
Second transform value ^a	0.96	ln 7.7	39	2.4	15.4	0.96	7	
Second R^2	0.32	0.43	0.27	0.15	0.32	0.11	0.09	
Third R^2	0.29	0.43	0.27	0.13	0.32	0.11	0.09	
Function used	exp	x	x	ln	exp	x^3	ln	d
Linear R^2	0.29	0.42	0.26	0.13	0.32	0.1	0.09	
Model R^2	0.51 (recommended model)							
Value in model	2.62	-0.18	-0.01	0.02	-2.25E-07	Not used	Not used	-1.36
S.E.	2.02	0.027	0.0047	0.06	6.77E-08			2.12
t-Ratio	1.30	-6.64	-1.71	0.29	-3.32			-0.64
Prob(t)	0.197	0.0	0.089	0.774	0.0011			0.52
Model R^2	0.39 (heavy oils only)							
Value in model	4.88	-0.20	-0.02	0.04	-4.43E-07	Not used	Not used	-3.61
S.E.	3.87	0.031	0.0066	0.11	4.07E-07			4.04
t-Ratio	1.26	-6.57	-2.71	0.37	-1.09			-0.89
Prob(t)	0.210	0.0	0.008	0.71	0.28			0.37
Model R^2	0.38 (light oils only)							
Value in model	-0.15	-0.14	0.00	0.03	-2.55E-07	Not used	Not used	1.35
S.E.	3.17	0.049	0.0070	0.08	8.56E-08			3.30
t-Ratio	-0.05	-2.89	-0.24	0.33	-2.98			0.41
Prob(t)	0.960	0.00	0.810	0.740	0.0036			0.68
Model R^2	0.5							
Value in model	3.03	-0.19	-0.01	0.04	-1.6E-07	-0.38	Not used	-1.75
S.E.	2.02	0.028	0.0047	0.06	7.6E-08	0.21		2.12
t-Ratio	1.50	-6.93	-1.92	0.66	-2.11	-1.84		-0.83
Prob(t)	0.14	0.0	0.056	0.510	0.036	0.068		0.41
Model R^2	0.49							
Value in model	2.85	-0.19	-0.01	0.03	-1.53E-07	-0.36	-0.12	-1.13
S.E.	2.03	0.028	0.0061	0.06	7.62E-08	0.21	0.11	2.19
t-Ratio	1.41	-6.87	-2.18	0.43	-2.01	-1.69	-1.10	-0.52
Prob(t)	0.16	0.0	0.03	0.67	0.046	0.093	0.27	0.61

^a If the transform parameter is less than value then the parameter becomes the original parameter less than the value.

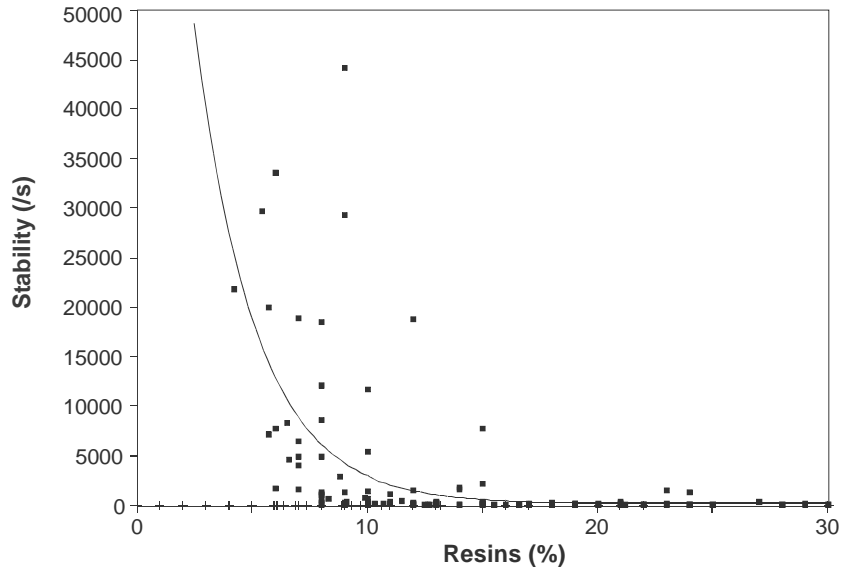


Fig. 1. Illustration of the correlation of resins with stability before correction.

a trial and error basis to yield the highest regression coefficient. The resulting criteria are: -0.22 , unstable; 0.69 , entrained; 1.1 , mesostable and 1.38 , stable. The regression coefficients (R^2) for each of the correlations are shown in Table 2 for the input parameters of density, viscosity, saturates, resins, asphaltenes, a/r —the asphaltene–resin ratio and the aromatic content. Several of these parameters can have a zero value which causes calculation problems. If this is the case, the 0 is adjusted to either delete these values or to adjust it to the typical high value for the parameter. This is shown as the ‘first transform’ in Table 2. A second transformation is performed to adjust the data to a singular

increasing or decreasing function. Most parameters have an optimal value with respect to class, that is the values have a peak function with respect to stability or class. This is illustrated in Figs. 1 and 2. The resin content without any adjustment is plotted against the stability in Fig. 1. As can be seen in this figure, the values of stability peak at about 5% resins. After this correction is made to the values, the regression coefficient increases. The modified distribution is shown in Fig. 2. The arithmetic converts values in front of the peak to values behind the peak, thus yielding a singular declining or increasing function. The optimal value of this manipulation is found by trial and error, beginning with the

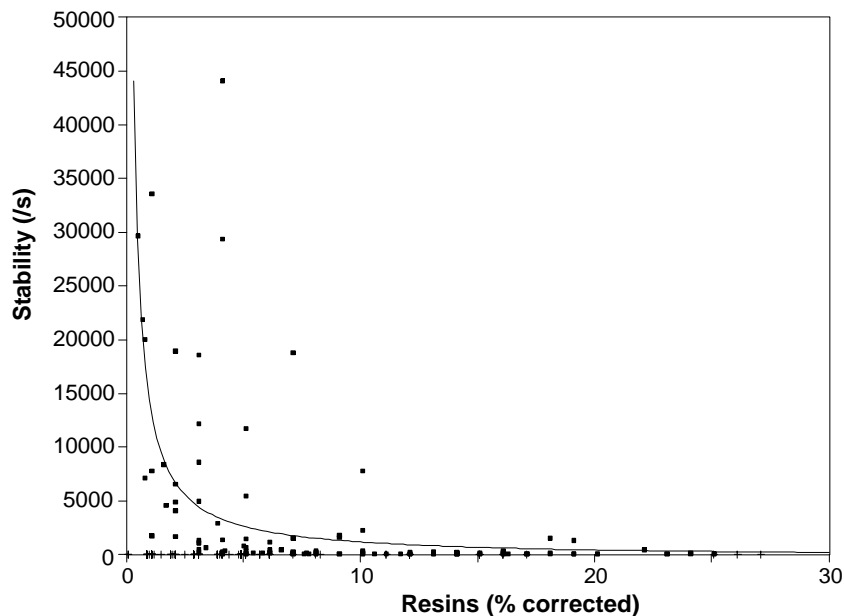


Fig. 2. Correlation of resins with stability after correction of 4.9.

estimated peak from the first correlation such as can be seen in Fig. 1. The arithmetic to perform this manipulation is: if the initial value is less than the peak value, then the adjusted value is the peak value less the initial value; and if the initial value is more than the peak value, the adjusted value is the initial value less the peak value. The peak values are shown as the second transform value in Table 2. The corresponding regression coefficients are also shown in Table 2.

The values of the second correction were then correlated using the package DataFit. Several models were developed as noted in Table 2. It had been noted in earlier work that heavy oils were somewhat different in emulsion formation than were light oils [11]. For this reason, models were created separately for light and heavy oils. These were actually poorer than the other models and so were not used. The best model was one that included only five parameters, density, viscosity, saturates, resins and asphaltenes. It was found that the regression coefficients of class with aromatic content, asphaltene/resin ratio and waxes were too low to include in the model. The relation between the categories and model outputs as well as the fit statistics for this model are shown in Table 3. The categorizations were optimized by trial and error. As can be seen in Table 3, the fit of the class is over 50% correct and most mis-categorizations are only one level different. It should be noted that there are some problems with the fundamental process of categorizing water-in-oil states at the onset. Some crude oils are enhanced by the addition of emulsion preventors (also called asphaltene suspenders) directly at the well-head; this is because they are very emulsion-prone. Thus, some emulsion-prone oils may not form emulsions during the laboratory or field tests because of the addition of these emulsion-preventing materials. Although attempts are made to receive oils that do not contain these emulsion-preventing materials, it is impossible to know this fact in every case.

The models are presented in Table 2, along with the parameters and relevant statistics. The summary statistics given are the R^2 or regression coefficient. The higher this value, the higher the predicted value relates to the actual data. The other test that is given in Table 2 is the Prob(t) or probability associated with the t -test. This value gives the importance of the particular variable in the model at hand. The higher the value of the Prob(t), the more the probability that the variable could be eliminated from the model with minimal

loss to its prediction capability or conversely, the lesser importance that parameter has to the model.

The oils and resulting water-in-oil states used for this correlation were studied to yield the average water content and increase in the viscosity from the starting oil to the water-in-oil class. This is shown in Table 3. This can be used to predict the water content and the viscosity given the known class of water-in-oil formed.

6. Development of emulsion kinetics estimator

The kinetics of emulsion formation have been studied and data are available to compute the time to formation. A kinetics study has shown the time to formation for stable emulsions is particularly rapid and that of entrainment is also rapid—both in a matter of minutes [3]. This study yields data in terms of relative formation time and energy (rpm) of the mixing apparatus. This particular data set is thought to be particularly accurate. A study in a large test tank has yielded data on the formation time of the various water-in-oil states [7]. The data are available of the relative formation times and the wave height. This data set is more noisy than the previously described data set, particularly because of long intervals between sample times. The average data over 25 runs is shown in Table 4. The formation time is taken as that time at which 75% of the maximum stability measured occurs. The conditions under which these tests took place and the measurements taken are described in the literature [7]. The wave height for each experiment was measured and used to indicate relative sea energy, taken for a fully developed sea. The laboratory data was converted from relative rotational energy to wave height by equating formation times and then using this multiplier to calculate the equivalent wave height. Formulae were fitted to each of the three categories and the common formula among all three relevant classes was found to be $1/x^{1.5}$, as detailed in Table 4. The regression coefficients for this formula are also given. It should be noted that it was possible to fit each curve with formulae having regression coefficients of about 0.99, however, the one noted was the highest one common to all three water-in-oil categories. Application of the equations in Table 4 will then provide a user with a time to formation of a particular water-in-oil state, given the wave height.

Table 3
Properties of the water-in-oil classes

	Number of samples	Average (%)	Water content, S.D. (%)	Average ratio	Viscosity increase, S.D. (%)
Unstable	80	6.4	4.1	1.7	1.6
Entrained	34	44	17	6.5	8.0
Mesostable	37	65	17	55	98
Stable	55	76	9	1200	3300
Total	206				

Table 4
Wave height prediction

	Input data ^a			
	Wave height	Stable	Mesostable	Entrained
Test tank average	15	110	865	720
	24	150	300	140
	25	140	247	60
Laboratory data conversions	48	30	153	20
	77	20	60	10
	81	10	35	8

^a Resulting equation is a predictor equation: $y = a + b/x^{1.5}$, where x is the wave height in centimetres and y the time to formation in minutes. Stable: $a, 27.1; b, 7,520; R^2, 0.51$. Mesostable: $a, 47; b, 49,100; R^2, 0.95$. Entrained: $a, 30.8; b, 18,300; R^2, 0.94$.

7. Modelling emulsification

Two ways are available to predict the emulsification of oil on the sea. First, one can use the exact data on specific oils as presented in Table 1. Second, one can use the specific algorithm as described above.

In the first method, using the data from Table 1, one examines the water-in-oil state that the oil will form and then the weathering percentage of the oil at which the formation occurs. One then models the evaporation and assigns the properties of the oil to be the state after the appropriate weathering percentage is obtained. The energy level at which this occurs could be set at a threshold of about that corresponding to a wind speed of approximately 5–10 m/s. An example of this is the prediction of the emulsification of Carpenteria crude oil. From Table 1, we see that Carpenteria does not form any type of emulsion or entrained water at 0% evaporation, but forms a mesostable emulsion after 10% is lost through evaporation. From the evaporation data published [8], we see that the evaporation equation is:

$$\%E_v = (1.68 + 0.045T) \ln(t), \quad (9)$$

where $\%E_v$ is the percent evaporated, T the temperature in degrees Celsius, and t the time in minutes.

By using Eq. (9) and taking the temperature to be 15 °C, it is found that the time until 10% weathering is reached, is $\ln(t) = 10/[1.68 + 0.045(15)]$ or 68 min. The mesostable emulsion formed at this time has a viscosity of 2.1×10^4 mPa.s and a water content of about 72%. These latter data are obtained directly from Table 1.

The second way to model emulsion formation is to use the newly developed model as presented here. The first step is to obtain or estimate the oil properties as they are at the weathering condition of concern. The properties needed are the density, viscosity, and saturate, resin and asphaltene contents. These values require transformation as noted in Table 2 and summarized below.

Density:

$$\text{density parameter} = \begin{cases} 0.96 - \text{density}, & \text{if density} < 0.96 \\ \text{density} - 0.96, & \text{if density} > 0.96 \end{cases} \quad (10)$$

The value used in the equation is then the exponential of this transformed value.

Viscosity:

$$\begin{aligned} & \ln(\text{viscosity parameter}) \\ & = \begin{cases} 7.7 - \text{viscosity}, & \text{if } \ln(\text{viscosity parameter}) < 7.7 \\ \text{viscosity} - 7.7, & \text{if } \ln(\text{viscosity parameter}) > 7.7 \end{cases} \end{aligned} \quad (11)$$

The value used in the equation is this transformed value.

Saturate content (in percentage):

$$\begin{aligned} & \text{saturate content parameter} \\ & = \begin{cases} 39 - \text{saturate content}, & \text{if saturate content} < 39 \\ \text{saturate content} - 39, & \text{if saturate content} > 39 \end{cases} \end{aligned} \quad (12)$$

The value used in the equation is transformed value.

Resin content:

$$\begin{aligned} & \text{resin content parameter} \\ & = \begin{cases} 20, & \text{if resin content} = 0 \\ 2.4 - \text{resin content}, & \text{if resin content} < 2.4 \\ \text{resin content} - 2.4, & \text{if resin content} > 2.4 \end{cases} \end{aligned} \quad (13)$$

The value used in the equation is the natural logarithm of this transformed value.

Asphaltene content:

$$\begin{aligned} & \text{asphaltene content parameter} \\ & = \begin{cases} 30, & \text{if asphaltene content} = 0 \\ 15.4 - \text{asphaltene content}, & \text{if asphaltene content} < 15.4 \\ \text{asphaltene content} - 15.4, & \text{if asphaltene content} > 15.4 \end{cases} \end{aligned} \quad (14)$$

The value used in the equation is then the exponential of this transformed value.

The class of the resulting emulsion is then calculated as follows:

$$\begin{aligned} \text{Class} = & -1.36 + 2.62D_t - 0.18V_t - 0.01S_t \\ & + 0.02R_t - 2.25 \times 10A_t, \end{aligned} \quad (15)$$

where class is the numerical index of classification, D_t the transformed density as calculated in Eq. (10), V_t the transformed viscosity as calculated in Eq. (11), S_t the transformed saturate content as calculated in Eq. (12), R_t the transformed resin content as calculated in Eq. (13), A_t the transformed asphaltene content as calculated in Eq. (14).

The oil above, *Carpenteria* weathered about 10%, can be used to illustrate how this method functions. The density, viscosity, saturate, resin and asphaltene contents are 0.9299, 755, 40, 19, and 11, respectively, and the transformed values are 1.03, 1.07, 1, 2.81, 81, respectively. Applying these values in Eq. (15) yields a class of 1.1.

The second step to calculation of the emulsion formation and its properties is to apply the numeric class value as yielded from Eq. (15). This is simply accomplished by using Table 2. In the *Carpenteria* example, the value of 1.1 implies that *Carpenteria* will form a mesostable emulsion after weathering about 10%. Comparing this to Table 1, we see that this is also the case in controlled studies.

The third step is to predict the properties of the resulting water-in-oil emulsion. Table 3 gives the average water content and increase in viscosity. For a mesostable emulsion, such as would be formed by *Carpenteria* crude, the water content is 65% and the viscosity increase is 55 times, or 755×55 or 4×10^4 . These values compare favourably to those listed in Table 1 and are within the standard deviations noted in Table 3.

The fourth step is to predict the time to formation after the oil is weathered to the stated percentage. This calculation can be made using the equations in Table 4:

$$\text{Time to formation (min)} = \frac{a + b}{W_h^{1.5}}, \quad (16)$$

where a is a constant and is 27.1 for a stable emulsion formation, 47 for mesostable and 30.8 for an entrained water-in-oil class; b a constant and is 7,520 for a stable emulsion formation, 49,100 for mesostable and 18,300 for an entrained water-in-oil class; W_h the wave height in centimetres.

In the case of a mesostable emulsion, like our example of *Carpenteria*, and for a wave height of 10 cm, the prediction yields a time to formation of 900 min, or 15 h. If the wave height of 10 cm did not persist that long, the emulsion would not be formed. Further, after this length of time the oil could have weathered to a greater degree and this increased weathering would have to be examined. As can be seen from Table 1, *Carpenteria* would still form a mesostable emulsion at this length of time and increased weathering stage, so the longer time on the sea is not important in this case.

8. Conclusions

Water-in-oil mixtures can be grouped into four states or classes: stable, mesostable, unstable, and entrained water. Only stable and mesostable states can be characterized as emulsions. These states were established by lifetime, visual appearance, complex modulus, and differences in viscosity.

Past modelling of emulsion formation was based on first-order rate equations that were developed before ex-

tensive work on emulsion physics took place. These old predictions have not correlated well to either laboratory or field results. The present authors suggest that both the formation and characteristics of emulsions could be predicted using empirical data. If the same oil type is studied in the field, the laboratory data on the state and properties can be used directly.

In this paper, a new modelling scheme is proposed and is based entirely on empirical data. The density, viscosity, saturate, asphaltene and resin contents are used to compute a class index, which predicts either an unstable or entrained water-in-oil state or a mesostable or stable emulsion. A prediction scheme is also given to estimate the water content and viscosity of the resulting water-in-oil state and the time to formation given a sea wave height.

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