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

Merv Fingas*, Ben Fieldhouse

Emergencies Science and Technology Division, Environmental Technology Centre, Environment Canada, Ottawa, Ont., Canada K1A 0H3

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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Keywords: Emulsification; Oil spills; Water-in-oil; Emulsions; Crude oil; Rheology of emulsions; Water uptake

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 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...
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, asphaltene forms 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:

\[
\Delta W = K_b (U + 1)^2 \Delta t
\]

where \(\Delta W\) is the water uptake rate, \(W\) the fractional water content, \(K_b\) 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:

\[
S = x_a y_a \exp(\ln(1 - x_a - x_w) + K_{aw}^x w_a x_a \exp(-0.04(T - 293)))
\]

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

Water uptake was given as:

\[
\Delta W = \Delta W_L + \Delta W_s = \Delta T[k_t - k_t W]
\]

where \(\Delta W_L\) is the total change in water content, \(\Delta W_s\) the change in water content for large droplets, \(\Delta W_t\) the change in water content for small droplets, \(\Delta T\) the time, \(k_t\) the rate constant for formation, typically 1 h\(^{-1}\), \(k_t\) the rate constant for large droplet formation and is about 3 h\(^{-1}\), and \(W\) the fraction of large droplets, which is typically 3–4.

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

\[
(1 - k_t W) \exp \left( \frac{-2.5W}{1 - k_t W} \right) = \exp(-k_t k_t W)
\]

where \(k_t\) 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, \(k_t\) the Mooney constant which is 0.62–0.65, \(k_t\) the increase in mousse formation due to weathering, \(k_t\) 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:

\[
\mu = \mu_0 \exp \left( \frac{2.5W}{1 - k_t W} \right)
\]

where \(\mu\) is the resulting viscosity, \(\mu_0\) 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:

\[
\frac{dF_{wc}}{dt} = 2 \times 10^{-5}(W + 1)^2 \left(1 - \frac{F_{wc}}{C_1} \right)
\]

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 \(C_1\) 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):

\[
\frac{\mu}{\mu_0} = \exp \left( \frac{2.5F_{wc}}{1 - 0.65F_{wc}} \right)
\]

where \(\mu\) is the viscosity of the mixture, \(\mu_0\) the viscosity of the starting oil, and \(F_{wc}\) the fraction of water in oil.

The effect of evaporation on viscosity was modelled as:

\[
\frac{\mu}{\mu_0} = \exp \left( C_1 F_{evap} \right)
\]
where \( \mu \) is the viscosity of the mixture, \( \mu_0 \) the viscosity of the starting oil, \( C_i \) a constant which is 1 for light fuels and 10 for heavy fuels, and \( F_{\text{cap}} \) 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 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].
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<th>Resins (%)</th>
<th>Asphaltenes (%)</th>
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*Note: Data from different sources and years.*
| Location            | Occupancy | $X$ | $Z$ | $Y$ | $W$ | $V$ | $U$ | $T$ | $S$ | $R$ | $Q$ | $P$ | $O$ | $N$ | $M$ | $L$ | $K$ | $J$ | $I$ | $H$ | $G$ | $F$ | $E$ | $D$ | $C$ | $B$ | $A$ | $X$ | $Z$ |
|---------------------|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Cook Inlet—Swanson River | 0.0 | 0.8420 | 6 | 65 | 6 | 5 | Mesostable | 1,720 | 2.90E+03 | 1.01E+04 | 76 |
| Cook Inlet—Trading Bay | 0.0 | 0.9143 | 152 | 56 | 7 | 7 | Stable | 4,070 | 2.90E+04 | 6.19E+05 | 81 |
| Cook Inlet—Trading Bay | 0.0 | 0.9143 | 152 | 56 | 7 | 7 | Stable | 4,070 | 2.90E+04 | 6.19E+05 | 81 |
| Diesel (Anchorage) | 0.0 | 0.8300 | 2 | 74 | 1 | 0 | Unstable | 0 |
| Diesel (Anchorage) | 0.0 | 0.8300 | 2 | 74 | 1 | 0 | Unstable | 0 |
| Diesel (Mobile Burn #3) | 0.0 | 0.8389 | 5 | 76 | 2 | 0 | Unstable | 0 |
| Diesel (Mobile Burn #3) | 0.0 | 0.8389 | 5 | 76 | 2 | 0 | Unstable | 0 |
| Des Cuadras | 0.0 | 0.9000 | 51 | 48 | 17 | 6 | Unstable | 0 |
| Des Cuadras | 0.0 | 0.9000 | 51 | 48 | 17 | 6 | Unstable | 0 |
| Des Cuadras | 11.2 | 0.9270 | 187 | 42 | 20 | 7 | Mesostable | 20 | 8.00E+02 | 3.45E+03 | 48 |
| Fuel Oil #5 (2000) | 0.0 | 0.9803 | 1.410 | 44 | 8 | 8 | Stable | 1,310 | 9.80E+03 | 3.28E+04 | 69 |
| Garden Banks 387 | 0.0 | 0.8782 | 29 | 53 | 10 | 1 | Unstable | 0 |
| 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 | 7.1 | 0.8979 | 64 | 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 | 0.8963 | 136 | 56 | 10 | 3 | Stable | 590 | 9.14E+03 | 8.00E+04 | 65 |
| Genesis | 0.0 | 0.8841 | 26 | 59 | 10 | 2 | Unstable | 0 |
| Genesis | 0.0 | 0.8841 | 26 | 59 | 10 | 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 | 2.60E+04 | 62 |
| Green Canyon 184 | 0.0 | 0.8314 | 5 | 60 | 6 | 1 | Unstable | 0 |
| Green Canyon 184 | 12.1 | 0.8575 | 11 | 61 | 8 | 1 | Unstable | 0 |
| Green Canyon 184 | 26.9 | 0.8024 | 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 | 0.9599 | 457 | 38 | 15 | 5 | Stable | 300 | 1.38E+05 | 78 |
| Green Canyon 65 | 13.1 | 0.9559 | 880 | 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 #303 | 0.0 | 0.9888 | 22,800 | 43 | 16 | 13 | Entrained | 40 | 9.06E+05 | 57 |
| Heavy Fuel Oil #303 | 2.5 | 0.9998 | 149,000 | 39 | 17 | 18 | Entrained | 10 | 8.62E+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 | 40 | 12 | 14 | 1 | Stable | 410 | 5.80E+05 | 72 |
| Hebron M-04 | 22.6 | 0.8564 | 5,369 | 38 | 13 | 17 | Stable | 70 | 5.47E+05 | 57 |
| High Viscosity Fuel Oil | 0.0 | 1.0140 | 13,460 | 18 | 13 | 26 | Entrained | 20 | 7.30E+04 | 3.18E+05 | 48 |
| Honda | 0.0 | 0.9356 | 735 | 33 | 24 | 12 | Stable | 1,280 | 1.10E+05 | 9.39E+05 | 81 |
| Honda | 16.7 | 0.9674 | 9,580 | 27 | 29 | 12 | Stable | 130 | 1.90E+05 | 1.27E+06 | 66 |
| Honda | 32.3 | 0.9881 | 440,700 | 27 | 32 | 13 | Unstable | 0 |
| IFO—180 | 0.0 | 0.9670 | 2,320 | 20 | 10 | 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 | 5.3 | 0.9996 | 220,000 | 24 | 30 | 17 | Unstable | 0 |
| Jet A | 2.3 | 0.8216 | 2 | 96 | 1 | 0 | Unstable | 0 |
| Jet A | 2.3 | 0.8216 | 2 | 96 | 1 | 0 | Unstable | 0 |
Table 1 (Continued)

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<th>Water-in-oil class properties</th>
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<td>% evaporation</td>
<td>Oil properties</td>
<td>Water-in-oil class properties</td>
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* 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

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<th>Asphaltenes</th>
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<td>ln x</td>
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<td>S.E.</td>
<td>3.87</td>
<td>-0.031</td>
<td>0.0066</td>
<td>0.11</td>
<td>-4.07E-07</td>
<td>4.04</td>
<td></td>
</tr>
<tr>
<td>r-Ratio</td>
<td>1.26</td>
<td>-6.57</td>
<td>-2.71</td>
<td>0.37</td>
<td>-1.09</td>
<td>-0.89</td>
<td></td>
</tr>
<tr>
<td>Prob(r)</td>
<td>0.210</td>
<td>0.0</td>
<td>0.008</td>
<td>0.71</td>
<td>0.28</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Model C</td>
<td>0.38 (light oils only)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Value in model</td>
<td>-0.15</td>
<td>-0.14</td>
<td>0.00</td>
<td>0.03</td>
<td>-2.55E-07</td>
<td>Not used</td>
<td>Not used</td>
</tr>
<tr>
<td>S.E.</td>
<td>3.17</td>
<td>0.049</td>
<td>0.0070</td>
<td>0.08</td>
<td>8.56E-08</td>
<td>3.30</td>
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<tr>
<td>r-Ratio</td>
<td>-0.05</td>
<td>-2.89</td>
<td>-0.24</td>
<td>0.33</td>
<td>-2.98</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>Prob(r)</td>
<td>0.960</td>
<td>0.0</td>
<td>0.081</td>
<td>0.740</td>
<td>0.0036</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>Model D</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Value in model</td>
<td>3.03</td>
<td>-0.19</td>
<td>-0.01</td>
<td>0.04</td>
<td>-1.64E-07</td>
<td>-0.38</td>
<td>Not used</td>
</tr>
<tr>
<td>S.E.</td>
<td>2.02</td>
<td>0.028</td>
<td>0.0047</td>
<td>0.06</td>
<td>7.66E-08</td>
<td>2.12</td>
<td></td>
</tr>
<tr>
<td>r-Ratio</td>
<td>1.50</td>
<td>-6.93</td>
<td>-1.92</td>
<td>0.66</td>
<td>-2.11</td>
<td>-1.84</td>
<td>-0.83</td>
</tr>
<tr>
<td>Prob(r)</td>
<td>0.14</td>
<td>0.0</td>
<td>0.056</td>
<td>0.510</td>
<td>0.034</td>
<td>0.668</td>
<td>0.41</td>
</tr>
<tr>
<td>Model E</td>
<td>0.49</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Value in model</td>
<td>2.85</td>
<td>-0.19</td>
<td>-0.01</td>
<td>0.03</td>
<td>-1.53E-07</td>
<td>-0.36</td>
<td>-0.12</td>
</tr>
<tr>
<td>S.E.</td>
<td>2.03</td>
<td>0.028</td>
<td>0.0064</td>
<td>0.06</td>
<td>7.62E-08</td>
<td>0.21</td>
<td>0.11</td>
</tr>
<tr>
<td>r-Ratio</td>
<td>1.41</td>
<td>-6.87</td>
<td>-2.18</td>
<td>0.43</td>
<td>-2.01</td>
<td>-1.69</td>
<td>-1.10</td>
</tr>
<tr>
<td>Prob(r)</td>
<td>0.16</td>
<td>0.0</td>
<td>0.03</td>
<td>0.67</td>
<td>0.046</td>
<td>0.093</td>
<td>0.27</td>
</tr>
</tbody>
</table>

* If the transform parameter is less than value then the parameter becomes the original parameter less than the value.
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. 1. Illustration of the correlation of resins with stability before correction.

Fig. 2. Correlation of resins with stability after correction of 4.9.
are 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 was measured. 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 $1/(x^2)$, 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>
<thead>
<tr>
<th>Number of samples</th>
<th>Average (%)</th>
<th>Water content, S.D. (%)</th>
<th>Average ratio</th>
<th>Viscosity increase, S.D. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unstable</td>
<td>80</td>
<td>6.4</td>
<td>4.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Entrained</td>
<td>34</td>
<td>44</td>
<td>17</td>
<td>6.5</td>
</tr>
<tr>
<td>Mesostable</td>
<td>37</td>
<td>65</td>
<td>17</td>
<td>55</td>
</tr>
<tr>
<td>Stable</td>
<td>55</td>
<td>76</td>
<td>9</td>
<td>1200</td>
</tr>
<tr>
<td>Total</td>
<td>206</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
E is: 

after 10% is lost through evaporation. From the evaporating properties of the oil to be the state after the appropriate 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.

### Table 4: Wave height predictions

<table>
<thead>
<tr>
<th>Wave height predictions</th>
<th>Input data*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wave height</td>
<td>Stable</td>
</tr>
<tr>
<td>Test tank average</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td>Laboratory data</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>81</td>
</tr>
</tbody>
</table>

* Resulting equation is a predictor equation: $y = ax + by^2$, where $y$ is the wave height in centimetres and $x$ the time to formation in minutes.

### 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 mesostable emulsion formed at this time has a viscosity of

where

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

### Viscosity:

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

The value used in the equation is this transformed value.

### Saturate content (in percentage):

$$\text{saturate content parameter} = \begin{cases} 39 - \text{saturate content}, & \text{if saturate content} < 39 \\ \text{saturate content} - 39, & \text{if saturate content} > 39 \end{cases}$$

The value used in the equation is this transformed value.

### Resin content:

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

The value used in the equation is this transformed value.

### Asphaltene content:

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

The value used in the equation is this transformed value.

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

$$\text{Class} = -1.36 + 2.62D_i - 0.18V_i - 0.01S_i + 0.02R_i - 2.25 \times 10A_i,$$

where $D_i$ is the transformed density as calculated in Eq. (10), $V_i$ the transformed viscosity as calculated in Eq. (11), $S_i$ the transformed saturate content as calculated in Eq. (12), $R_i$ the transformed resin content as calculated in Eq. (13), $A_i$ 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 to 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 emulsion after weathering about 10%.

Comparing this to Table 1, Carpenteria would still form a mesostable emulsion at this length of time and increased weathering would have to be examined. As can be noted in Table 3.

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 $4 \times 10^4$. 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:

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

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 extensive 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.

**References**


