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## Studies on crude oil and petroleum product emulsions: Water resolution and rheology

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### ABSTRACT

Water-in-oil mixtures from more than 300 crude oils and petroleum products were made in the laboratory and studied over time. More than 140 of these yielded products resembling emulsion. Water-in-oil types were characterized by resolution of water at 1 and 7 days, and some after 1 year. Rheology measurements were carried out at the same intervals. The objective of the study was to characterize the water-in-oil types and relate these to starting oil properties.

It was found that water-in-oil types can be grouped into four categories: stable, unstable, meso-stable and entrained. Each of these has distinct physical properties. A stable emulsion remains so for at least 30 days and takes up typically 80% water. The viscosity of a stable emulsion is at least two orders-of-magnitude greater than that of the starting oil. An unstable emulsion does not retain water volume greater than 10%. For an unstable emulsion, the viscosity is typically less than two times greater than the viscosity of the starting oil. A meso-stable emulsion has properties between unstable and stable emulsions and typically takes up 60% water, breaking down within 7 days, losing most of this water. A meso-stable emulsion usually has a viscosity no more than one order-of-magnitude greater than that of the starting oil. Another retention mechanism for water in oil is that of viscous entrainment of water droplets. This type of water uptake, not a true emulsion, has been called entrained. Entrained water to the extent of typically 45% is taken up initially and this water content declines slowly over a period of days.

A stability index was developed to characterize these water-in-oil types. This consists of the product of the ratio of viscosity increase and a ratio of the elasticity increase. This index was used to describe the water-in-oil types and to correlate stability with starting oil composition and properties.

A comparison of the properties of the starting oils before mixing with water shows that the most important factors for water uptake and emulsion formation are asphaltene and resin content, starting oil viscosity and density. Other factors that are shown to be important are the saturate content and asphaltene-to-resin ratio. The relationship between these factors and stability gives insights into the nature of water-in-oil types and emulsions.

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### 1. Introduction

Water-in-oil emulsions sometimes form after oil spills. These emulsions, often called “chocolate mousse” or “mousse” by oil spill workers, complicate the cleanup of oil spills [1]. When emulsions form, the physical properties and characteristics of oil spills change extensively. For example, stable emulsions contain from 65 to 85% water, thus expanding the spilled material from two to five times the original volume. Most significantly, the viscosity of the oil typically changes from a few hundred mPa s to about 100,000 mPa s, an increase of 500 or more. A liquid product is thereby changed into

a heavy, semi-solid material. These emulsions may not be recoverable by conventional spill equipment. The variability in stability of the water-in-oil types, lifetimes varying from minutes to years, has been noted for many years [2]. These emulsions, therefore, should be studied to ascertain what types form and how these might be predicted from the available starting oil properties.

More than 40 years ago, it was found that asphaltenes were a major factor in oil spill emulsions [2]. The specific roles of asphaltenes in emulsions have not been defined until recently. The basics of water-in-oil emulsification are now better understood [3–5]. The basic principle is that water-in-oil emulsions are stabilized by the formation of asphaltene layers around water droplets in oil. The layer or film is characterized by its high-strength viscoelastic properties. Resins also form emulsions, to a certain extent, but resins do not form stable emulsions, and may aid in asphaltene

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emulsion stability by acting as asphaltene solvents and by providing temporary stability during the time of slow asphaltene migration. The extent of knowledge on water-in-oil emulsion formation to this date is strongly limited by the amount of knowledge of asphaltenes and resins themselves [4,5].

McLean and Kilpatrick studied asphaltene aggregation in model emulsions made from heptane and toluene [6]. The resins and asphaltenes were extracted from four different crude oils—two from Saudia Arabia, Alaskan North Slope, and San Joaquin Valley crudes. The asphaltenes were extracted using heptane and the resins using open-column silica columns. Although some emulsions could be generated using resins, they were much less stable than those generated by asphaltenes. The model emulsions showed that the aromaticity of the crude medium was a prime factor. It was also found that the concentration of asphaltenes and the availability of solvating resins were important. McLean and Kilpatrick put forward the thesis that asphaltenes were most effective in stabilizing emulsions when they are near the point of incipient precipitation [7]. It was noted that there are specific resin–asphaltene interactions, as differing combinations yielded different results in the model emulsions. The most effective emulsion stabilizers of the resins and asphaltenes were the most polar and the most condensed. McLean and Kilpatrick concluded that the most significant factor in emulsion formation is the solubility state of asphaltenes.

Subsequently, several workers reviewed emulsions and concluded that the asphaltene content is the single most important factor in the formation of emulsions [3,8,9]. Even in the absence of any other possibly synergistic compounds (i.e., resins, waxes and aromatics), asphaltenes were found to be capable of forming rigid, cross-linked, elastic films which are the primary agents in stabilizing water-in-crude oil emulsions. It was noted that the exact conformations in which asphaltenes organize at oil–water interfaces and the corresponding intermolecular interactions have not been elucidated. McLean and colleagues suggest that the intermolecular interactions must be either  $\pi$ -bonds between fused aromatic sheets, H-bonds mediated by carboxyl, pyrrolic, and sulfoxide functional groups, or electron donor–acceptor interactions mediated by porphyrin rings, heavy metals, or heteroatomic functional groups [3]. Workers studying only crude oil emulsions, as opposed to studying bitumens which contain clay, concluded that water-in-oil emulsions are exclusively stabilized by asphaltenes [9]. Even though the emulsions contain inorganic solids, waxes and other organic solids, the main stabilization comes from asphaltenes. Other workers have noted that solid particles, such as clays, when present, can stabilize or contribute to the stabilization of emulsions [10].

It is noted that asphaltenes are defined by their precipitation from oil in pentane, hexane, or heptane. The specific structure of asphaltenes is unknown, however the molecular weight averages about 750 and there is a planar aromatic structure surrounded by alkane groups, some with heteroatoms, S, N and O [11]. Studies of the time dependency of film strength by viscosity measurements showed that the complex modulus increased by about 2-fold between 2 and 4 h. This indicates an increased film strength, probably due to asphaltene aggregation and cross-linking. The mechanism by which emulsions form begins when asphaltenes migrate to the oil–water interface, a process which is regulated by the diffusion of the soluble asphaltenes. At the interface, the asphaltenes self-assemble to produce a layer or film. The film that is formed is an elastic, rigid, stable film. Studies of the film strength of asphaltenes in Langmuir troughs shows that such films display high strength and elasticity [4,12,13].

The absorption of asphaltenes proceeds for a long time and may still align after a year [14]. This implies that the absorp-

tion at the interface, lowers the net energy of the system and thus this is favoured thermodynamically. The bulk concentration of asphaltenes is important and drives the amount that is absorbed at the interface. Asphaltenes have their greatest tendency to absorb and make the strongest interfacial film at their limit of solubility. The most polar and least soluble asphaltenes appear to make the strongest film. Studies of the mass of asphaltenes at the interface were carried out [15]. Several workers noted that there were differences in the stability of emulsions, depending on the fractions of asphaltenes taken and also by the amount of asphaltene aggregation present [16,17]. Asphaltene aggregation may be an important topic in emulsion stability. Gafonova and Yarranton noted that asphaltenes may self-associate in a manner that is oligimerization rather than simple stacking [18].

Kilpatrick and Spieker reviewed the role of resins in water-in-oil formation [9]. They noted that the main role appears to be solvation of the asphaltenes in the oil solution. They conducted experiments which showed that the addition of resins at ratios of 2:1 (resins:asphaltenes) or less could increase the stability of the water-in-oil emulsions by as much as twice. Others have noted that resins and asphaltenes are somehow tied together in emulsion stability. Ali and Alqam noted that with increasing asphaltene:resin ratio, the emulsions in well heads were more stable [19]. The Sjöblom group in Norway studied the interfacial properties of asphaltenes in several local offshore crude oils [20]. Asphaltenes were shown to be the agent responsible for stabilizing the Norwegian crude oils tested. Some effect from naphthenic acids was also noted [21].

Sjöblom et al. noted that much of the stability differences in emulsions can be explained by the interactions between asphaltenes and resins [5]. The authors noted that asphaltenes are believed to be suspended as colloids in the oil with some stabilization by resins. Each particle is believed to consist of one or more sheets of asphaltene monomers and absorbed resins to stabilize the suspension. Under certain conditions, the resins can desorb from the asphaltenes leading to increased asphaltene aggregation and precipitation of the larger asphaltene aggregates. Several workers then noted that there is significant interplay between asphaltenes and resins and that resins solvate the asphaltenes [22].

The availability of methodologies to study emulsions is very important. In the past 15 years, both dielectric methods and rheological methods have been exploited to study formation mechanisms and stability of emulsions made from many different types of oils [4,23]. Standard chemical techniques, including nuclear magnetic resonance (NMR), chemical analysis techniques, near-infrared spectroscopy (NIR), microscopy, interfacial pressure, and interfacial tension, are also being applied to emulsions. These techniques have largely confirmed findings noted in the dielectric and rheological mechanisms. The use of high pressure NIR has been used by one group to study asphaltene aggregation of live crude oils [5,24,25]. Further NIR information on the amount of asphaltenes and resins was tied to the emulsion stability [25]. Many of the measurements can be correlated.

Most researchers studied the stability of emulsions by measuring the amount of water resolved with time [8,9,26–30]. Some researchers also subjected the emulsions to centrifugation at various forces to assess stability. A variation on water resolution is the use of turbidity to measure emulsion stability [31].

Dielectric spectroscopy is one of the methods used to study emulsions. The permittivity of the emulsion can be used to characterize an emulsion and assign a stability [21,25,32,33]. The Sjöblom group has measured the dielectric spectra using the time domain spectroscopy (TDS) technique. A sample is placed at the end of

a coaxial line to measure total reflection. Reflected pulses are observed in time windows of 20 ns and Fourier transformed in the frequency range from 50 MHz to 2 GHz [5].

Extensive studies on the rheology of emulsions have been performed [34–36]. Emulsions stabilized by surfactant films (such as resins and asphaltenes) behave like hard sphere dispersions. These dispersions display viscoelastic behaviour. Water-in-oil emulsions show a transition from a predominantly viscous to a predominantly elastic response as the frequency of oscillation exceeds a critical value. Relaxation time can be determined for the system, which increases with the volume fraction of the discontinuous phase. It has been noted that the emulsion stability is highly dependent on the rheological properties of the water–oil interface and that a high elasticity will increase the level of stability [5].

Several workers in the field have used methods to study the interface forces on single droplets. Dropwise studies of emulsion stability have been extensively carried out and correlated to bulk properties. One group used an oscillating pendant drop apparatus and correlated this to asphaltene solubility as measured by NIR [37]. Yarranton et al. report on the use of interfacial rheology to study emulsion coalescence [29,30]. Asphaltenes from Athabasca Bitumen were mixed with a solvent and injected into an optical cuvette and the droplet monitored by camera. Interfacial tension was measured from static measurements on the droplet. Elasticity was measured by manipulating the droplet so that sinusoidal oscillations occurred and the elasticity measured using Fourier analysis. The findings were that the interfacial modulus was a function of asphaltene content and reached a maximum at an asphaltene concentration of about 1 kg/m<sup>3</sup>. The modulus increased as the interface aged. The data were found to be consistent with the gradual formation of a cross-linked asphaltene network on the interface. Moran et al. studied emulsions using a micropipette technique in which individual emulsion drops are elongated into a cantilever for force measurements [38]. The stress–strain measurements are converted to interfacial rheological behaviour. Khristov and co-workers studied emulsions as a film with toluene dilution and the thin liquid film–pressure balance technique [39].

Many researchers studied emulsification by using model oils or modified crude oils. Other researchers studied emulsions as thin layers or droplets [7,40]. Hemmingston et al. studied the water-in-oil emulsions formed from 27 crude oils of different origins [41]. They found that there is an increase in stability as viscosity increases. Viscosity also correlated with the SARA data taken on the crude oil. Sjöblom et al. studied 16 crudes from the North Sea and 5 from North Africa [33]. Stability was measured using the results from an electric field cell. A voltage was applied to the cell until coalescence was observed using a microscope. The value of the voltage at the critical point was taken as a measure of stability.

The objective of this work was to ascertain the types of water-in-oil products that are formed from many crude oils and petroleum products. These water-in-oil products will be characterized and indices developed to distinguish them. Further, this study will investigate how the type of water-in-oil product formed is related to the starting oil properties. The ultimate goal is to predict the types of emulsions which would be formed after a spill and their behaviour after formation, using only the starting oil properties and composition.

The crude oils and petroleum products were selected from oil companies to represent the highest volume products and thus those that pose the greatest spill potential. The water-in-oil type was studied from periods of time of 1–30 days and in some case up to 1 year. The emulsions were studied by examining water content and rheological properties.

## 2. Experimental

### 2.1. Materials

Water for emulsification was purified by reverse osmosis, it was mixed with salt to yield a 33 parts-per-thousand saline water to represent sea water. Fine granular sodium chloride was used for making the salt water. Oil and petroleum products were used as received from petroleum companies. Oils and petroleum products handling and source of origin are recorded; those with unusual characteristics or additives such as asphaltene suspenders, were not used for the study. Oils and petroleum products are taken from those with high volumes and those that would have a high spill potential. The same samples were analyzed for SARA, not as part of this study, and other properties and data posted on the internet [42]. Oils and petroleum products were stored in a refrigerated room at 5 °C when not in use. Before use oil samples were removed from the refrigerator and shaken for at least 30 min to ensure that they were homogeneous. Emulsions were stored in a refrigerated room at the same temperature until they were removed for further study.

### 2.2. Methods

#### 2.2.1. Mixing

Emulsions were made in an end-over-end rotary mixer (Associated Design). The apparatus was located in a temperature-controlled room at 15 °C. The mixing vessels were 2.2 L fluorinated HOPE wide-mouthed bottles (Nalge). The mixing vessels were approximately one-quarter full, with 600 mL salt water (3.3% (w/v) NaCl) and 30 mL of the sample crude oil or petroleum product. The vessels were mounted in the rotary mixer, and allowed to stand for several hours (usually 4) to thermally equilibrate. The vessels were placed in the rotary mixer such that the cap of each mixing vessel follows, rather than leads, the direction of rotation. The vessels were approximately 24 cm in height, with a radius of rotation of about 15 cm. At the conclusion of the mixing time, the emulsions were collected from the vessels for measurement of water content and rheology. Some studies were carried out on the effects of various factors of mixing [14].

For those oils that did not form any visible sign of emulsification, no further studies were carried out. All formation studies were carried out at least twice. Mixing was repeated if the analytical results noted below were not repeated within 10%. Few repeats were required.

#### 2.2.2. Sampling

Sampling was found in previous studies to be important to the variability of results as often excess water or oil are present along with the emulsified product [14]. The most continuous emulsion was sampled with a spatula and any excess oil or water, differing in appearance from the bulk, was removed. The sample was then immediately analyzed for viscosity or water content. If the sample showed no sign of emulsion or other product formation, samples were not taken for analysis. A study on sampling had shown that sampling is largely the source of error and variation, as one is prone to take excess water with the samples and samples are more heterogeneous as time progresses after mixing [14]. Excessive manipulation of the sample was found to change the measurements with some water-in-oil products, thus manipulation was minimized wherever possible. Further, once an emulsion was broken, it was very difficult to sample the product consistently. Most broken emulsions were not sampled and were simply noted as broken.

### 2.2.3. Rheological studies

The following apparatuses were used for rheological analysis: Haake RS100 RheoStress rheometer, RheoWin software, 35 mm parallel plate with corresponding base plate, and a circulating bath maintained at 15 °C. Analysis was performed on a sample spread onto the base plate and raised to 2.00 mm from the measuring plate, with the excess removed using a teflon spatula. This was left for 15 min to thermally equilibrate at 15 °C. A stress sweep from 100 to 10,000 mPa at a frequency of one reciprocal second was performed to determine the linear viscoelastic range. The rheological properties are reported for the linear viscoelastic range. The standard deviation of the viscosity and complex modulus has been measured in a previous study and found to be about 6.5% [14].

### 2.2.4. Water content

A Metrohm 784 KF Titrino Karl–Fischer volumetric titrator and Metrohm 703 Ti Stand were used to measure water content. Water content was reported as a weight percentage. If the samples visually did not form an emulsion or other water-in-oil type, the water was simply reported as less than 5%. In the latter case further analysis after a week or a year was not carried out. In a past study the repeatability of the water content measurement was found to be 3.4% [14].

## 3. Results and discussion

Rheological data and properties of samples which showed signs of emulsion formation are summarized in the supplementary data (Table S1). Oil property data are taken from a database on the internet and were taken from the same samples as used here for emulsion formation testing [42]. Table S2, also in the supplementary section, shows the oils and oil properties from those oils which showed no sign of emulsion formation. Information measured includes the water content of the oil phase just after mixing for 1 day. The water content is given as <5% if it was very small visually, in which case it was not measured. Samples which were not analyzed for water on the first day were not subsequently analyzed for water. The water content was also measured, where applicable, 1 week after the mixing. Physical and chemical properties of the starting oil include: density, viscosity, SARA content and wax content. Rheological measurements include the complex modulus of the water-in-oil product. The complex modulus is a measure of the overall resistance of the material to flow under an applied stress, in units of force per unit area. This combines the elements of viscosity and elasticity for viscoelastic materials such as water-in-oil emulsions [34]. Measurements also included the elasticity modulus, the viscosity modulus, and the  $\tan \delta$ , the viscosity:elasticity ratio of the complex modulus. All these data are derived from creep-recovery measurements on a cone-plate rheometer as described above.

Table 1 shows the same rheological data for water-in-oil types that showed stability 1 year after the products were made. It should be noted that water-in-oil mixtures that showed nearly complete breakdown or water loss, were not analyzed further.

These data show that the resulting water-in-oil products, fall into four categories. The most obvious is that of unstable products. A number of oils did not form any visible type of emulsion or stable product with the water. This group includes the majority of the oils. On the other side, there were oils that formed an emulsion which retained water for at least 1 year after formation. These will be referred to in this paper as 'stable' emulsions. These stable emulsions had a semi-solid appearance and were reddish in color. There is another grouping which had a similar appearance and retained about the same amount of water at the time of formation but within a week broke and little water was retained. These are called 'meso-

stable' emulsions in this paper. Finally, there is a fourth group of water-in-oil types characterized by the uptake of only a little water at the time of mixing, but display a slow loss of this water over time. These water-in-oil types did not resemble the stable or meso-stable emulsions in that they remained black in color as the starting oil. They are formed from viscous oils and apparently the water was entrained in them as a result of the mixing process. This group of products are called 'entrained' in this paper. These are not believed to be emulsions as there is apparently no chemical stabilization evident and water is lost from these progressively over the observation time of up to 1 week or 1 month.

Table 2 summarizes the studied oils by the average, maximum and minimum properties. Entrained types take up an average of 45% water on the first day and within a week lose water down to about 28%. Meso-stable emulsions take up an average of 64% on the first day, lose a significant amount down to less than 30% within a week. They appear to be entirely broken by this time. It should be noted that the values of water after a week are an average of those where measurements were taken. Water-in-oil mixtures that were largely broken and would not result in water contents over about 5%, were not measured. The actual averages of the water content 1 week later may be at least under half of the stated value if actual measurements were taken. Measurements could not be taken in many cases because of the high errors and fragility of sampling an unstable product. Stable emulsions uptake an average of 81% water on the first day, and retain about 77% in a week and about 68% in a year. Unstable types uptake only about 6–7% water and seemingly retain this over the week period. Table 2 also highlights other differences, such as rheological properties, among the four categories of water-in-oil types. Several of these will be highlighted graphically in this paper. In every category of measurement, extensive differences are displayed among the four water-in-oil types, although there also is overlap between the minimum and maximum values of the points of comparison.

Fig. 1 shows the differences among the four categories of water-in-oil types. Fig. 1A shows the difference in average water retention over 1 year. Only stable emulsions retain most of their water. Meso-stable emulsions lose the greatest percentage of water in 1 week. After 1 week, meso-stable emulsions have, on average, less water than the entrained types. The presentation in Fig. 1A is somewhat effected by the fact that many meso-stable and entrained types did not have sufficient water content to enable re-measuring at the 1 week and later intervals. Thus the average water contents for these two types would actually be lower than shown. Fig. 1B shows the apparent viscosity of the four types. The apparent viscosity of the stable emulsions increases substantially from that of the starting oil, and is the highest of all four types. The entrained and meso-stable increase in apparent viscosity somewhat, however this may also be the result of losing volatile components by evaporation (weathering) during the year. Fig. 1C shows the  $\tan \delta$ , the ratio of viscous to elastic modulus, change over the year. Stable emulsions show little change in their  $\tan \delta$  of about 0.75, whereas the meso-stable product initially goes up and then falls, unstable shows a slow rise in  $\tan \delta$  and entrained a slow fall in 1 year. Fig. 1D shows the change in the viscosity modulus over 1 year. Stable types show a slow increase in the viscosity modulus, the entrained and meso-stable types increases sharply. In all illustrations, there are major differences shown between the four water-in-oil types.

Fig. 2 includes two photographs that show the very dramatic difference between a meso-stable and stable emulsion in 1 week. Fig. 2A shows a stable emulsion after 1 week, its appearance is very similar to that upon formation. Fig. 2B shows a meso-stable emulsion after 1 week. The meso-stable emulsion appeared very similar to that of the stable emulsion at formation, but obviously broke after 1 week.



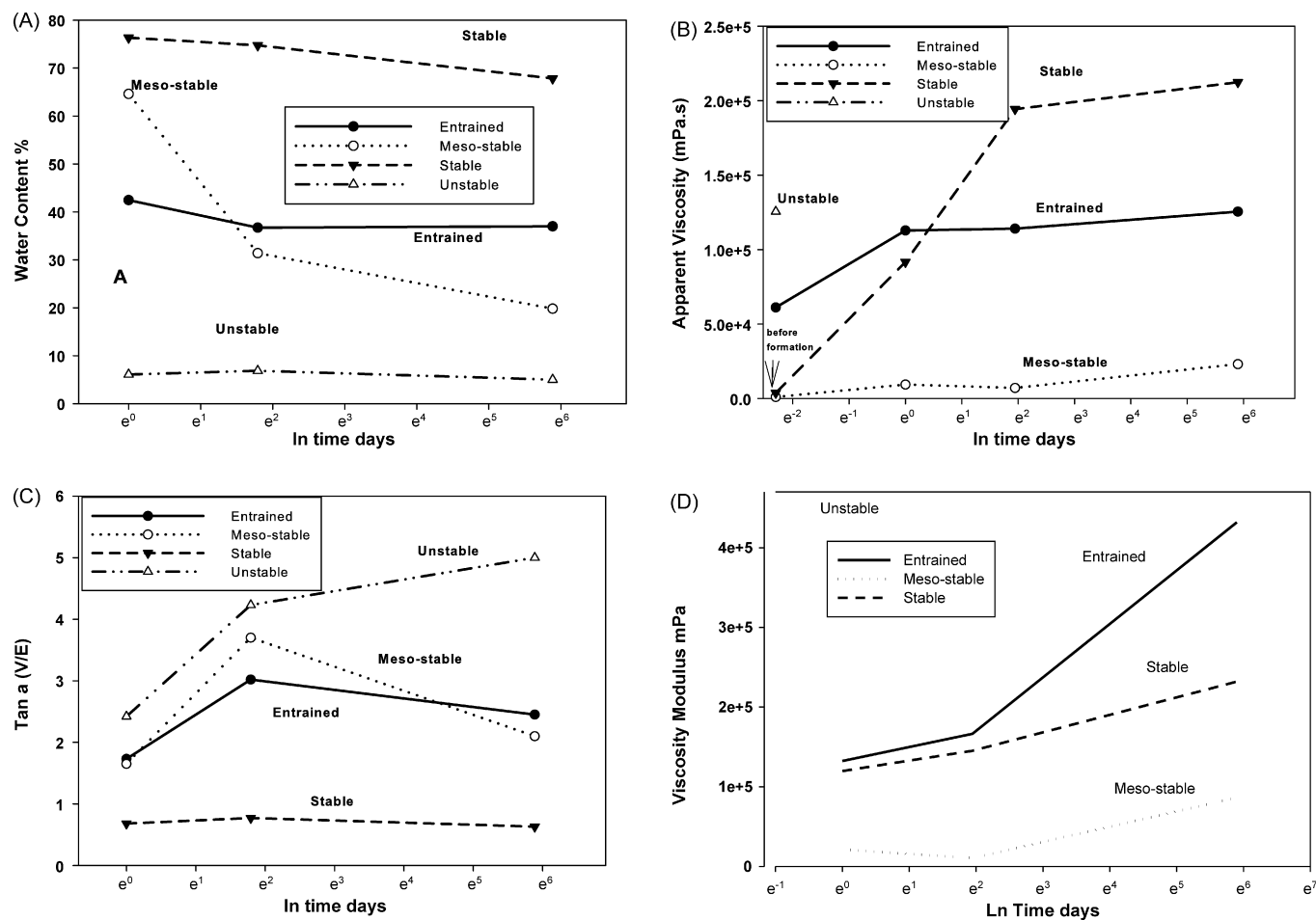
**Table 1**  
Long-term data on the emulsions produced from the oils.

Oil name	Evaporated (% w/w)	Day water content (% w/w)	Week water content (% w/w)	>1 year after formation						
				Viscosity (mPa s)	Complex modulus (mPa)	Elasticity modulus (mPa)	Viscosity modulus (mPa)	Tan $\delta$ (V/E)	Complex viscosity (mPa s)	Water content (% w/w)
Arabian Light	0	87.4	86.9	1.0E+04	8.6E+04	7.8E+04	3.7E+04	0.48	1.4E+04	76
Arabian Light	12.04	88.9	85.8	4.9E+03	1.4E+04	8.5E+03	1.1E+04	1.24	2.2E+03	59
Arabian Light	24.2	84.7	83.6	4.5E+03	2.2E+04	1.4E+04	1.7E+04	1.23	3.5E+03	48
Arabian Medium	0	84.7	84.4	4.3E+04	2.9E+05	2.9E+05	6.2E+04	0.22	4.7E+04	84
Arabian Medium	13.15	76.5	77.1	5.6E+04	4.4E+05	4.3E+05	1.1E+05	0.27	7.0E+04	77
Belridge Heavy	0	57.9	44.4	6.1E+04	1.6E+05	7.0E+04	1.4E+05	2.01	2.5E+04	35
Belridge Heavy	2.74	59.6	45.2	7.1E+04	2.1E+05	8.8E+04	1.9E+05	2.18	3.4E+04	33
Bunker C (1987)	0	26.4	24.0	3.9E+05	3.5E+06	1.8E+06	3.0E+06	1.63	5.5E+05	23
Bunker C (Anchorage)	0	34.7	31.0	3.9E+04	4.2E+05	3.7E+05	1.9E+05	0.52	6.6E+04	18
California API 15.0	0	39.0	22.0		2.3E+06	1.3E+06	1.9E+06	1.49	3.6E+05	44
Carpenteria	10.31	71.8	28.2	NM	2.4E+05	1.4E+05	2.0E+05	1.46	3.8E+04	23
Carpenteria	14.87	54.3	30.9	3.6E+04	7.5E+05	6.6E+05	3.5E+05	0.53	1.2E+05	18
Cook Inlet—Granite Point	45.32	83.1	57.6	5.6E+03	4.3E+05	3.9E+05	1.4E+05	0.35	6.8E+04	21
Cook Inlet—Swanson River	0	76.0	57.5	1.1E+04	4.5E+05			0.37		61
Cook Inlet—Swanson River	39.69	81.5	80.8	3.5E+05	2.8E+06	2.7E+06	8.1E+05	0.30	4.4E+05	79
Cook Inlet—Trading Bay	33.3	76.2	61.4	6.7E+04	1.8E+06	1.7E+06	5.8E+05	0.33	2.9E+05	53
Dos Cuadras	11.17	47.6	29.5	NM	5.3E+04	3.0E+04	4.3E+04	1.43	8.4E+03	7
Dos Cuadras	20.3	68.6	28.7	1.3E+04	3.1E+04	5.8E+03	3.0E+04	5.22	4.9E+03	20
High Viscosity Fuel Oil	0	47.6	42.2	2.0E+05	6.6E+05	3.7E+05	5.4E+05	1.46	1.1E+05	48
Hondo	0	80.9	80.0	1.9E+05	9.5E+05	8.9E+05	3.2E+05	0.36	1.5E+05	77
IFO—180	0	69.4	22.0	1.4E+05	3.9E+05	2.3E+05	3.2E+05	1.41	6.3E+04	66
IFO—180	7.77	58.4	37.0	2.7E+05	6.7E+05	4.4E+05	5.1E+05	1.14	1.1E+05	58
IFO—300	0	52.3	32.0	1.8E+05	5.8E+05	3.1E+05	4.9E+05	1.58	9.2E+04	45
Lago Treco	16	62.6	32.0		8.1E+05	5.4E+05	6.0E+05	1.11	1.3E+05	63
Lucula	10.69	70.4			3.6E+06	3.4E+06	1.2E+06	0.36	5.8E+05	44
Lucula	26.93	13.4	13.0		3.0E+07	2.8E+07	1.0E+07	0.37	4.8E+06	8
Maya	15	54.9	25.0		7.7E+05	4.8E+05	6.0E+05	1.26	1.2E+05	57
Mississippi Canyon 807	0	60.0			1.2E+04	4.9E+03	1.1E+04	2.21	1.9E+03	44
North Slope (Middle Pipeline)	30.54	61.9	21.8							10
North Slope (Northern Pipeline)	31.14	69.8	15.0							6
North Slope (Southern Pipeline)	29.62	53.5	21.1							10
Oriente	21	55.7	16.0		6.4E+05	4.5E+05	4.6E+05	1.02	1.0E+05	56
Platform Irene	0	62.2	34.9		9.8E+06	7.5E+06	6.4E+06	0.85	1.6E+06	53
Point Arguello Comingled	0	82.3	82.2	3.9E+05	1.7E+06	1.6E+06	5.1E+05	0.32	2.7E+05	82
Point Arguello Comingled	15.19	30.2	28.4		1.7E+06	1.2E+06	2.3E+05	1.30	2.8E+05	30
Point Arguello Light	0	93.1	93.8	1.6E+05	1.1E+06	1.1E+06	2.3E+05	0.21	1.8E+05	90
Point Arguello Light	10.19	88.8	87.8	5.2E+05	2.7E+06	2.7E+06	4.3E+05	0.16	4.4E+05	86
Point Arguello Light	19.04	85.5	85.6	7.9E+05	3.7E+06	3.7E+06	6.8E+05	0.19	6.0E+05	88
Point Arguello Light	28.33	79.8	75.9	3.7E+05	2.3E+06	2.2E+06	6.5E+05	0.29	3.7E+05	78
Port Hueneme	0	38.0	20.1	1.5E+04	4.8E+04	4.8E+03	4.8E+04	9.93	7.7E+03	10
Port Hueneme	3.14	45.3	29.2	3.6E+04	2.6E+05	7.4E+04	2.5E+05	3.38	4.1E+04	23
Port Hueneme	6.37	43.4	26.4	6.4E+04	1.3E+05	3.0E+04	1.3E+05	4.30	2.1E+04	24
Prudhoe Bay (1995)	0	43.1	39.4	3.9E+03	9.1E+03	5.7E+03	7.1E+03	1.24	1.5E+03	38
Prudhoe Bay (1995)	9.32	85.1	85.1	1.7E+04	5.1E+04	3.7E+04	3.5E+04	0.95	8.1E+03	71
Prudhoe Bay (1995)	27.25	20.4	18.8		3.3E+04	1.5E+04	2.9E+04	1.98	5.3E+03	12
Santa Clara	0	60.6	12.8							7
Santa Clara	11.4	50.4	38.7	3.9E+04	1.3E+05	2.9E+04	1.3E+05	4.45	2.1E+04	19
Santa Clara	21.63	39.0	40.2	1.6E+05	1.2E+06	1.0E+06	6.0E+05	0.59	1.9E+05	33
Sockeye	0	86.5	87.0	8.1E+05	3.7E+06	3.6E+06	8.4E+05	0.24	5.8E+05	83
Sockeye	12.5	80.7	76.8	3.1E+05	1.8E+06	1.7E+06	6.6E+05	0.40	2.9E+05	69
Sockeye	22.1	79.1	74.8	3.9E+05	2.2E+06	2.0E+06	8.6E+05	0.43	3.4E+05	66
Sockeye Comingled	0	73.6	46.2	5.2E+04	1.3E+05	4.7E+04	1.2E+05	2.49	2.0E+04	71
Sockeye Sour	0	73.6	53.1	5.2E+04	1.5E+05	5.6E+04	1.4E+05	2.48	2.4E+04	49
Sockeye Sour	9.6	59.9	30.2	1.3E+05	3.9E+05	2.1E+05	3.2E+05	1.49	6.1E+04	54
Sockeye Sweet	17.46	81.8		4.8E+03	8.6E+04	7.2E+04	4.7E+04	0.66	1.4E+04	34
Sockeye Sweet	26.91	75.5	72.3	3.1E+04	2.7E+05	2.2E+05	1.6E+05	0.73	4.3E+04	59
Takula	0	84.8	83.8	1.5E+05	3.1E+06	3.1E+06	5.8E+05	0.19	5.0E+05	81
Takula	11	81.3	81.4	2.5E+05	1.9E+06	1.8E+06	4.1E+05	0.22	3.0E+05	78
Waxy Light Heavy Blend	19.6	54.6	39.2	6.9E+03	9.7E+04	8.4E+03	9.7E+04	11.50	1.5E+04	59

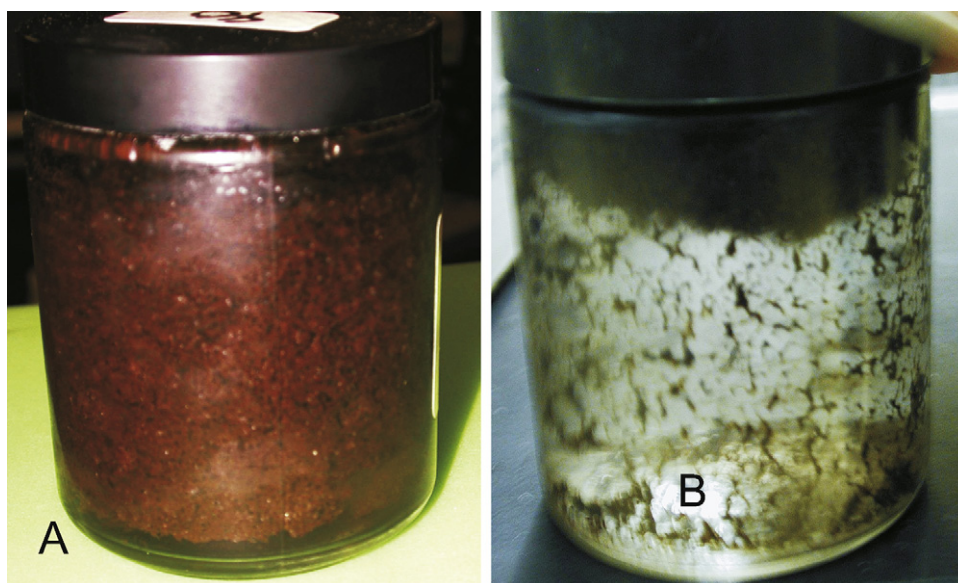
NM: not measured.

*M. Fingas, B. Fieldhouse / Colloids and Surfaces A: Physicochem. Eng. Aspects 333 (2009) 67–81*

<sup>a</sup> These water content values are high as most were not measured as they were obviously low.



**Fig. 1.** Comparison of properties of water-in-oil types over 1 year. (A) Comparison of water content, (B) comparison of apparent viscosity, (C) comparison of  $\tan \delta$  and (D) comparison of viscosity modulus.

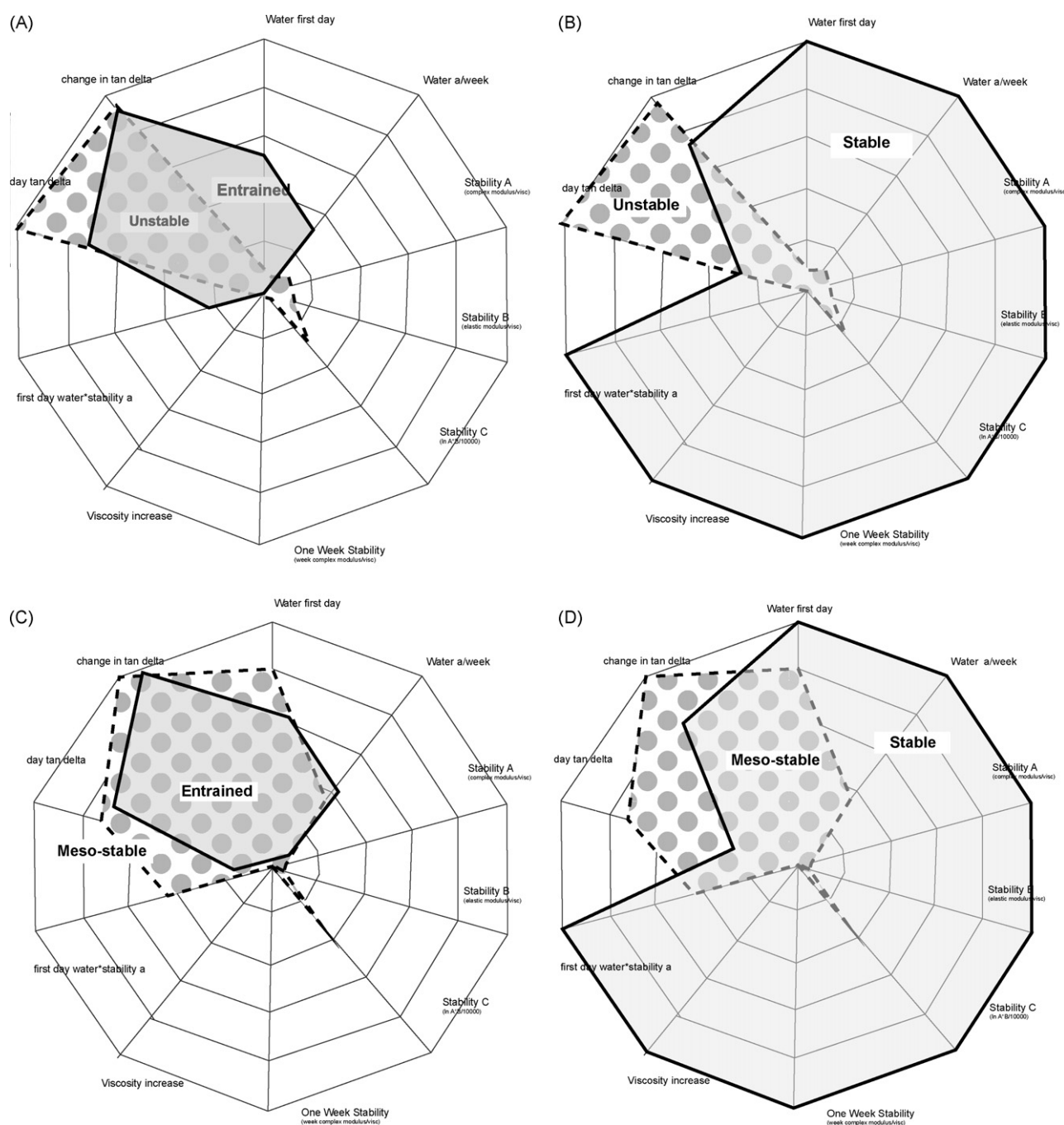


**Fig. 2.** Photographs of emulsions after 1 week. (A) shows a stable emulsion 1 week after formation. (B) shows a meso-stable emulsion after 1 week. This latter emulsion was similar in appearance to A upon formation and obviously has broken in 1 week.



In order to correlate oil properties and the resulting water-in-oil types, a single measure of stability is required. The water content measurements are different on the first day for all water-in-oil products except for the difference between meso-stable and stable emulsions. A series of measures, mostly based on the rheological measures, were evaluated. These measures were compared to that of water resolution, that is water uptake on the first day and water remaining in the oil mass within 1 week. These measures employ the major differences in the four water-in-oil types noted in Table 2, particularly the rheological properties. The first measure to be studied was the ratio of the complex modulus of the product on the first day divided by the starting oil viscosity. The measure

may be viewed as an indication of the elastic and viscosity modulus increases over the formation period. This index is named 'stability A' in this paper. Similarly it was noted that the elastic modulus by itself, also provided differentiation between types. Thus a 'stability B' was tested which is the elastic modulus on the first day divided by the starting oil viscosity. A combination of these two indices, the log of the cross-product of stabilities A and B was evaluated. This was called 'stability C'. Other measures include a '1 week stability', the complex modulus after 1 week divided by oil starting viscosity. The 'viscosity increase', the ratio of the oil viscosity after mixing divided by the starting oil viscosity was another measure. Another test, 'first day water  $\times$  stability A' was a simple composite of the



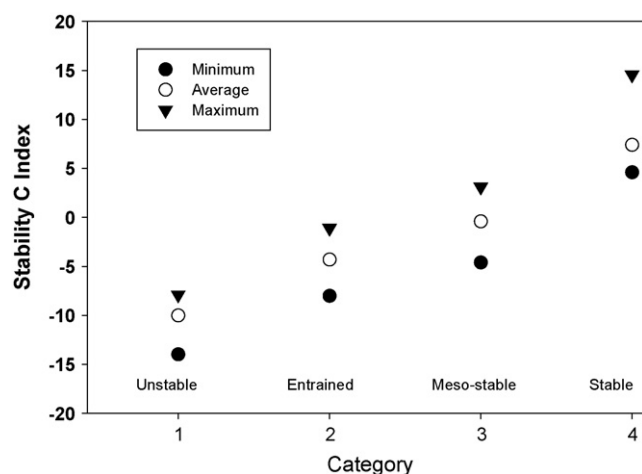
**Fig. 3.** Comparison of stability indices for the four water-in-oil types. All parameters are scaled from 0 to 10. (A) shows a comparison between unstable (patterned area) and entrained (shaded area) types, (B) a comparison between the unstable (patterned area) and stable (shaded area) types, (C) between meso-stable (patterned area) and entrained (shaded area) types and (D) between meso-stable (patterned area) and stable (shaded area) types.

**Table 3**  
Indices for stability.

Water-in-oil type	Statistic	Stability A (complex modulus/starting viscosity)	Stability B (elastic modulus/starting viscosity)	Cross-product/10,000	Stability C (ln cross-product)
Entrained	Average	11.7	6.6	0.0	−4.3
Meso-stable	Average	81.7	58.8	0.5	−0.4
Stable	Average	3867.8	3779.1	1461.7	7.4
Unstable	Average	96.6	27.1	0.3	−10.0
Entrained	Average	8.4	8.0	0.0	−4.3
Entrained	Maximum	63.4	53.7	0.3	−1.1
Entrained	Minimum	0.0	0.0	0.0	−8.0
Meso-stable	Average	81.7	58.8	0.5	−0.4
Meso-stable	Maximum	846.2	769.2	65.1	3.1
Meso-stable	Minimum	14.1	4.0	0.0	−4.6
Stable	Average	3.9E+03	3.8E+03	1.5E+03	7.4
Stable	Maximum	1.4E+05	1.4E+05	2.1E+06	14.5
Stable	Minimum	1046.2	857.1	89.7	4.6
Unstable	Average	96.6	27.1	0.3	−10.0
Unstable	Maximum	4.3	1.7	0.0	−7.9
Unstable	Minimum	0.0	0.8	0.0	−14.0

first day water content times stability A. The last two parameters evaluated were the 'day  $\tan \delta$ ' or the  $\tan \delta$  on the day of formation and the 'change in  $\tan \delta$ ' which is the ratio of the change in  $\tan \delta$  over 1 week.

Fig. 3 shows the comparison of the indices with the four water-in-oil types using umbrella or spider graphs. These were drawn without specialized software and all values on these charts were scaled by simple mathematics to a 1–10 scale. Further, only two types of water-in-oil mixtures are displayed at one time to avoid confusion. In this discussion, water resolution will not be mentioned, as it is the basis of comparison. Fig. 3A shows the tested indices for the unstable and entrained types. Differentiation between these two water-in-oil types is provided clearly by stability C and by  $\tan \delta$ . Fig. 3B shows the stable and unstable types. Differentiation is best shown by  $\tan \delta$  on day of formation and by stability C. Fig. 3C shows a comparison of the indices for the meso-stable and entrained types. Differentiation is provided by stabilities A, B, C, and to a lesser degree the other indicators. Fig. 3D shows the indices for stable and meso-stable states. Differentiation is again provided by stabilities A, B, C, and to a lesser degree the other indicators. The index which provides the most differentiation among all the water-in-oil types is stability C, which here is stability A times stability B. Mathematically, stability C is defined as natural



**Fig. 4.** A plot of the minimum, average and maximum stability C index values for each water-in-oil type. Figure shows that averages are different and there is overlap between minimum and maximum values.

**Table 4**  
Average properties of the four water-in-oil types.

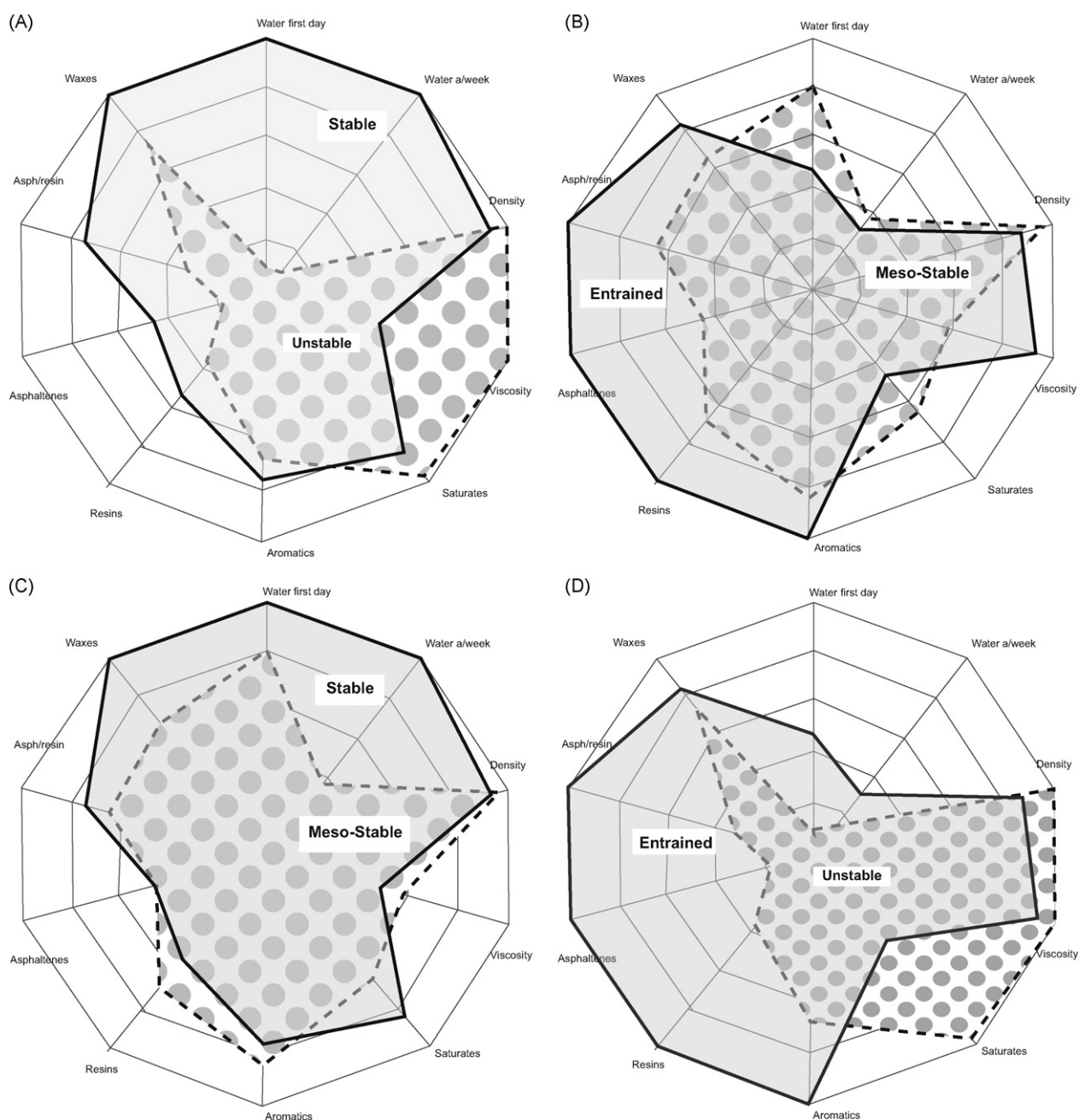
Averages	Appearance	Day water content (% w/w)	Week water content (% w/w)	Rheological properties on day of formation				
				Viscosity increase from starting	Complex modulus (mPa)	Elasticity modulus (mPa)	$\tan \delta$ (V/E)	Complex viscosity (mPa s)
Entrained	Viscous black	44.5	27.5 <sup>a</sup>	1.9	8.30E+05	5.14E+05	1.73	1.3E+05
Meso-stable	Viscous reddish	64.3	29.6 <sup>a</sup>	7.2	1.33E+05	1.07E+05	1.7	2.1E+04
Stable	Solid reddish	80.7	77.4	405	7.50E+05	7.10E+05	0.7	1.2E+05
Unstable	Oil-like	6.1	6.85 <sup>a</sup>	0.0	1.10E+07	3.37E+06	2.4	1.8E+06
	Appearance	Rheological properties 1 week after formation						
		Viscosity increase from starting	Complex modulus change	Elasticity modulus change	$\tan \delta$ change	Complex viscosity change		
Entrained	Viscous black	1.9	0.8	0.6	1.7	1.3		
Meso-stable	Broken	5.4	0.6	0.5	2.2	0.5		
Stable	Solid reddish	859	1.1	1.1	1.1	1.2		
Unstable	Oil-like	0.0	3.8	2.9	1.7	3.6		

Increase is shown as number larger than 1.00.

<sup>a</sup> These water content values are high as most were not measured as they were obviously low.

**Table 5**  
Correlation of variables.

	Correlation coefficient ( $r^2$ )			Log viscosity	Saturates	Aromatics	Resins	Asphaltenes	A/R	Waxes	Stability C
	Day water	Week water	Density								
Day water	1.00	<b>0.82</b>	−0.28	−0.57	0.29	−0.14	−0.29	−0.31	−0.13	−0.05	0.70
Week water	0.82	1.00	−0.48	−0.62	0.39	−0.18	−0.41	−0.34	−0.08	0.12	<b>0.86</b>
Density	−0.28	−0.48	1.00	<b>0.84</b>	<b>−0.84</b>	0.56	<b>0.81</b>	<b>0.77</b>	0.54	−0.06	−0.09
Log viscosity	−0.57	−0.62	0.84	1.00	−0.73	0.40	<b>0.75</b>	<b>0.78</b>	0.59	0.21	−0.20
Saturates	0.29	0.39	−0.84	−0.73	1.00	<b>−0.83</b>	<b>−0.86</b>	<b>−0.77</b>	−0.51	0.13	0.09
Aromatics	−0.14	−0.18	0.56	0.40	−0.83	1.00	0.50	0.36	0.24	−0.10	−0.04
Resins	−0.29	−0.41	0.81	0.75	−0.86	0.50	1.00	0.72	0.35	−0.14	−0.13
Asphaltenes	−0.31	−0.34	0.77	0.78	−0.77	0.36	0.72	1.00	<b>0.81</b>	−0.09	−0.06
A/R	−0.13	−0.08	0.54	0.59	−0.51	0.24	0.35	0.81	1.00	0.03	0.15
Waxes	−0.05	0.12	−0.06	0.21	0.13	−0.10	−0.14	−0.09	0.03	1.00	0.12
Stability C	0.70	0.86	−0.09	−0.20	0.09	−0.04	−0.13	−0.06	0.15	0.12	1.00



**Fig. 5.** Comparison of SARA and physical properties for the four water-in-oil types. All parameters are scaled from 0 to 10. (A) shows a comparison between the unstable (patterned area) and stable types (shaded area), (B) a comparison between meso-stable (patterned area) and entrained (shaded area) types, (C) between meso-stable (patterned area) and stable (shaded area) types and (D) a comparison between unstable (patterned area) and entrained (shaded area) types.

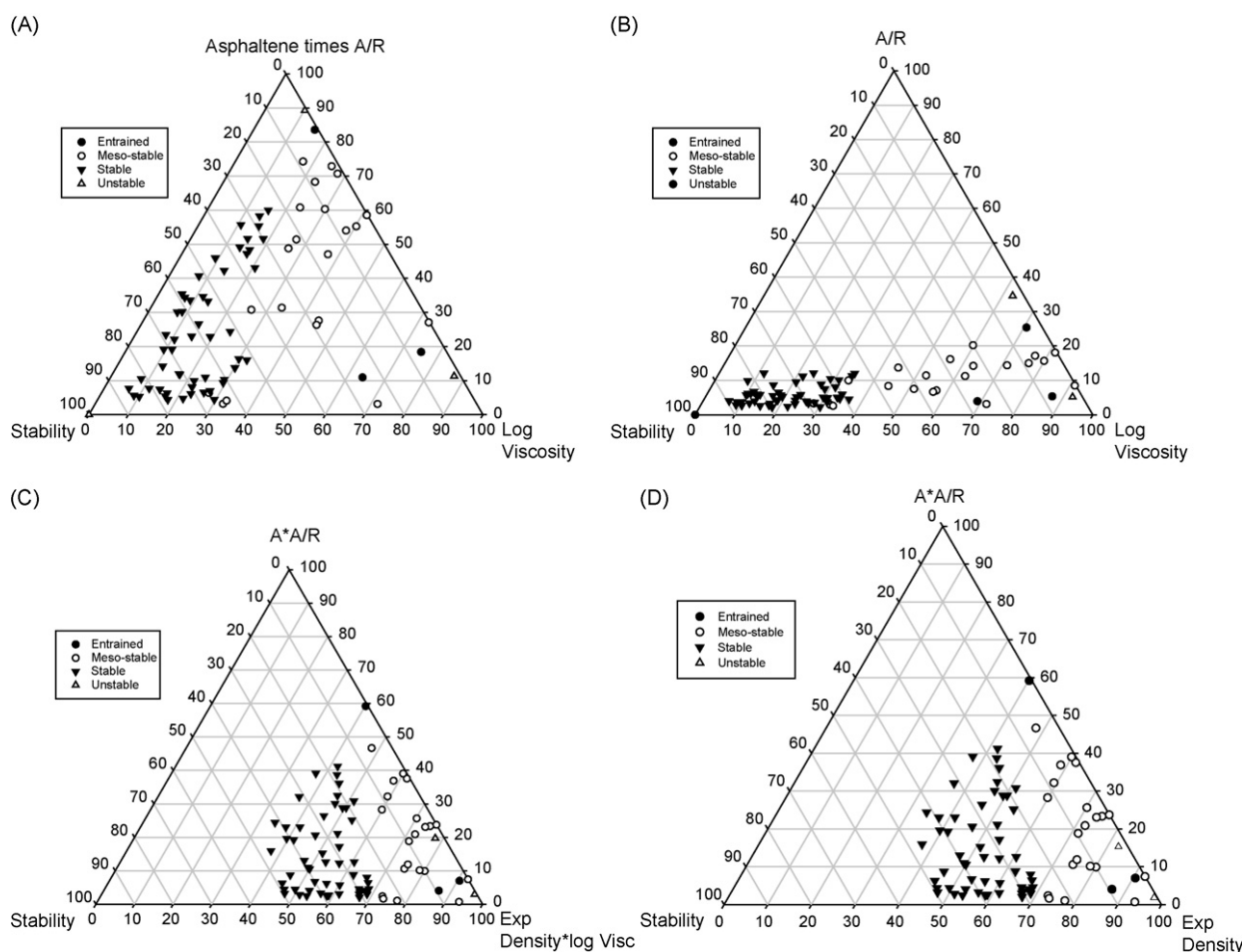
$\log(\ln)$  of the cross-product of the complex modulus on the first day of formation divided by the starting oil viscosity times the elastic modulus divided by the starting oil viscosity. The latter cross product was divided by 10,000 to yield a simple number. The statistical values of the stability indices, A, B, and C are given in Table 3. This table shows that there is some overlap of the indices A and B, and some overlap for index C. In particular, the cross-product between the two indices, index C, shows the least overlap in the categories. Examination of the data showed that there are a few outliers which would show more overlap than is actually the case. Those oils that showed stability indices greater than twice the standard deviation were removed from statistical analysis only. These oils are indicated in Table S1. These oils will be studied further in the future. Fig. 4 shows the minimums, maximums and averages for all four categories of water-in-oil types. This shows that index C has very little overlap, and does provide significant differentiation between water-in-oil types. This index would be useful for discrimination on the first day of emulsion formation as well as for further correlation of starting oil properties.

The question of the differentiation of the water-in-oil types is readily answered by water and rheological measurements on the first day and 1 week later as summarized in Table 4. There are sufficient differences in properties to be a clear differentiation between types, in addition, the appearance of the types is sufficiently different. On the first day, there may only be confusion between

meso-stable and stable when examined visually. However, within 1 week, the meso-stable will break and that difference will be clear. The use of the indices, especially index C, can provide differentiation on the first day as well.

The next question is that of the relationship of the four types of water-in-oil types to the SARA and physical oil properties. Several workers in the field have noted strong correlations of stability to SARA by PCA or Principle Component Analysis [5]. PCA analysis performed here (UnScrambler Version 8.05, Oslo, Norway) shows some differences between types. This analysis shows that there are large overlaps between the various types and that differentiation between types is complex. The most important factors found by PCA, in order of importance, are: resins, asphaltenes, viscosity, stability C and saturate content.

A multi-variate analysis was performed on the factors versus the index of stability C using SPSS (Version 13, Chicago, IL). Results are shown in Table 5. High correlation coefficients are in bold and significant ones are outlined. The first item noted is that there is a high correlation among density, viscosity, resin and asphaltene content. This correlation among the SARA contents would be expected as there are only four components and these total to 100%. Thus it is difficult to separate specific SARA components in some analyses. Stability C correlates best with the day and week water content, as one would hope. The importance of variables is similar to that found by PCA as noted above. The correlation shows that there are



**Fig. 6.** Ternary diagrams showing stability C against log of viscosity of the starting oil and other components. Fig. 6A shows the asphaltene content times the ratio of asphaltenes/resins and Fig. 6B the ratio of asphaltenes/resins. Fig. 6C shows the stability plotted against the asphaltenes times the asphaltene/resin ratio and the exponential of the density times the logarithm of the viscosity. Fig. 6D shows the stability plotted versus the asphaltenes times the asphaltene/resin ratio and the exponential of the density.



complex interactions among density, viscosity, resin and asphaltene content, thus an analysis with single values will not show strong correlation. Further analysis in this paper will illustrate this point.

Fig. 5 shows a comparison of the averages of SARA and physical properties, all parameters are scaled between 0 and 10, between the four water-in-oil types. Fig. 5A shows a comparison of stable and unstable emulsions. This figure shows that viscosity, resins, asphaltenes and asphaltene/resin ratio are the best discriminators. Fig. 5B shows the same comparison for meso-stable and

entrained types. In this comparison, viscosity of the starting oil, resins, asphaltenes and asphaltene/resin ratio are the best parameters to differentiate the types. Fig. 5C shows a comparison between stable and meso-stable emulsions. The differentiation between the two types is not as clear as for the other types, and saturate content, and resin content are the best discriminators. The asphaltene/resin ratio and waxes show slight differences. Finally, Fig. 5D shows a comparison between the entrained and unstable water-in-oil types. Here, the saturate content, resin and asphaltene contents as well as the asphaltene/resin ratio show good differentiation between the

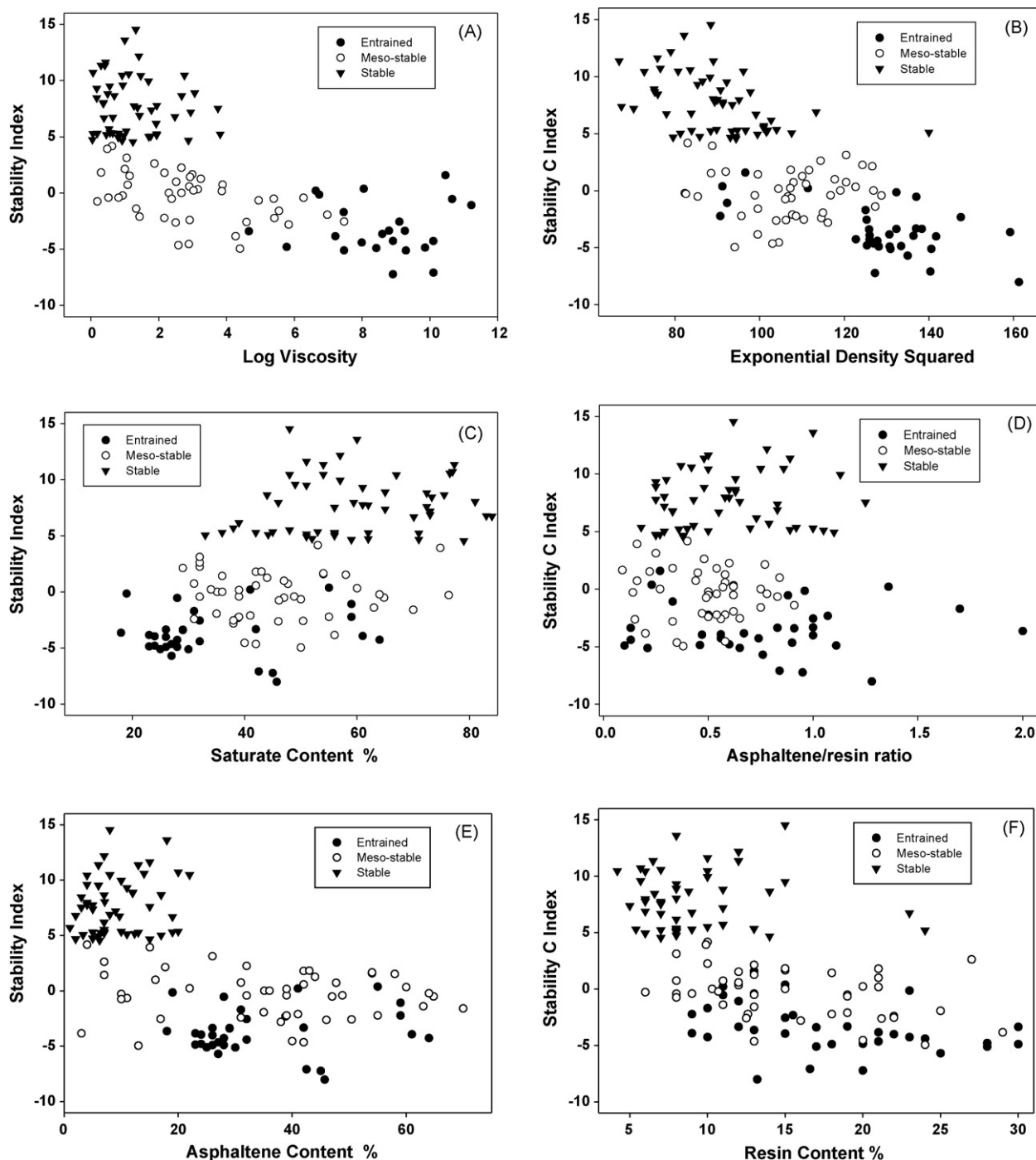


Fig. 7. Stability C plots versus various starting oil parameters. (A) log viscosity, (B) the square of the exponential of density, (C) the saturate content, (D) the asphaltene/resin ratio, (E) asphaltene content, and (F) resin content.



two types. Overall the best differentiation between any two types is shown by the asphaltene/resin ratio and the resin content. The asphaltene and saturate content, and the starting oil viscosity also show some differences. Unfortunately there appears to be no simple cut-offs, rather complex interactions between SARA contents and the physical parameters, appear to be operative.

The four types can be understood further using the inputs of oil properties such as the viscosity and the asphaltene/resin ratio as shown in Fig. 6. This figure was drawn with SigmaPlot using the built-in ternary transformation. Fig. 6A shows that the best separation of types occurs when the log viscosity is plotted against the asphaltene times the asphaltene/resin ratio and stability C. This confirms the above analysis that the asphaltene/resin ratio and viscosity were the best indicators of the four different water-in-oil types. It should be noted that because the stability C of unstable is either defaulted to the average of  $-4.3$  or the three values from which this average was calculated, these points are difficult to find on the graph as points are frequently overlaid. Several other points are also overlaid. Some separation of water-in-oil types is achieved as shown in Fig. 6B when the viscosity and asphaltene/resin ratio are plotted against the stability C. Fig. 6C repeats this analysis with the asphaltene content times the asphaltene/resin ratio, the exponential of the density times the log of the viscosity and stability C. Fig. 6D shows this analysis using only the exponential of the density. These latter two figures show that the density of the starting oil contains similar information to the viscosity of the oil and will graphically yield similar results. It also again confirms that the stability of the emulsions is strongly related to the asphaltene content, the asphaltene/resin ratio and the starting oil viscosity and density. This figure confirms that correlations with multiple factors of viscosity, density and chemical composition are better than with single factors. This indicates that there are complex interactions in emulsion formation involving the viscosity and SARA composition of the oil.

An examination of the stability (as shown by stability C) versus a number of starting oil parameters is given in Fig. 7. Fig. 7 shows the entrained, meso-stable and stable oil types and the unstable was not included. Fig. 7A shows the stability C versus the log of viscosity. A relatively clear separation is shown between the stable and meso-stable types with some overlap with the entrained types. Fig. 7B shows a similar situation with the square of the exponential of density. In the latter figure, there is slightly more overlap of the entrained and meso-stable states. Fig. 7C shows the stability versus the saturate content of the starting oil. This shows similar overlap as the density and the next Fig. 7D, which shows the asphaltene/resin ratio. Fig. 7E shows the stability versus the asphaltene content. There is relatively good separation between water-in-oil types shown here. Fig. 7F shows the stability versus resin content. There is some overlap between the entrained and meso-stable types. Overall, the stability, as represented here by the stability C, shows high differentiation between the stable and other water-in-oil types. There is some overlap between the meso-stable and entrained oil types. Differentiation between oil types is shown best when the viscosity, asphaltene/resin ratio and the asphaltene content are used as indicators. Fig. 7 again shows that the emulsion formation is a complex interplay of viscosity, asphaltene and resin contents and the interaction between these factors. Further, it appears that excess resin content ( $A/R > \text{about } 0.6$ ) is, in fact, a de-stabilizer.

Several oils do not form water-in-oil types until they lose a certain amount of volatile compounds through evaporation. A study of this phenomenon was carried out by examining the SARA and physical properties when the oils evaporate and the resulting water-in-oil type. This analysis again shows a broad range of viscosity, asphaltene and resin contents over which the transitions take

place. There is no simple cut-off for SARA or physical properties to form certain water-in-oil types.

These analyses show some fundamental differences in the formation of emulsions. Figs. 5 and 6 highlight some of these differences. Although stable and meso-stable show some similarities, such as similar asphaltene content, and somewhat similar density and viscosity, meso-stables have a lower asphaltene:resin ratio and thus more resins. This resin-content factor appears to destabilize the emulsions after time. Further, the viscosity of the starting oil is an average of about five times larger for the meso-stable emulsions. The entrained types result from viscous oils with large amounts of both resins and asphaltenes. The mechanism of water retention appears to be viscous entrainment as water is continually lost from these entrained types. Unstable water-in-oil types are produced from two types of oils; those very light oils with little asphaltenes or resins or highly viscous, heavy oils. The lighter oils have no asphaltenes or resins to chemically stabilize water. The very heavy oils may be too viscous to allow water droplets to penetrate.

Since in every form of analysis here, the asphaltene and resin contents were very important as was the viscosity, it confirms many of the previous analysis that water is retained in oils by two mechanisms, chemically by asphaltenes and resins and by viscous retention of droplets [5]. The water-in-oil type formed is a result of the combinations of these mechanisms and the factors forming products. This consideration does not include the fact that there are many types of asphaltenes and resins and that future analysis may show that these sub-classes of asphaltenes or resins may influence the type of water-in-oil emulsion formed [5].

#### 4. Conclusions

Four clearly defined water-in-oil types are formed by oil and petroleum products when mixed with water. This is shown by water resolution over time, by a number of rheological measurements, and by their visual appearance, both on the day of formation and 1 week later. Some emulsions were observed for over a year, with the same results. The types are named stable water-in-oil emulsions, meso-stable water-in-oil emulsions, entrained, and unstable water-in-oil emulsions. The differences among the four types are quite large and are based on at least two water content measurements and five rheological measurements. More than 300 oils or petroleum products were studied.

Tests of several indices of stability, a single value that could provide good discrimination between water-in-oil types even on day 1, were carried out. It was found that all of these indices could be used to some extent to differentiate the four water-in-oil types. One index of stability was the ratio of the complex modulus of the product on the first day divided by the starting oil viscosity. This index was named stability A. Stability B was the elastic modulus on the first day divided by the starting oil viscosity. Stability C was combination of these two indices, the log of the cross-product of stabilities A and B. Another index, the viscosity increase, the ratio of the oil viscosity after mixing divided by the starting oil viscosity was also evaluated. Another test, first day water times stability A was a simple composite of the first day water content times stability A. The last two parameters evaluated were the  $\tan \delta$  on the day of formation and the change in  $\tan \delta$  over 1 week. The index called stability C, proved to be the index that best differentiated all four water-in-oil types.

Stable emulsions are reddish-brown solid-like 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 conditions. All of the stable emul-

sions studied remained so for at least 1 year. The viscosity increase over the day of formation averages a factor of 400 and 1 week later averages 850. The average properties of the starting oil required to form a stable emulsion are: density 0.90 g/mL; viscosity 300 mPa s; resin content 9%; asphaltene content 5%; and asphaltene-to-resin ratio 0.6.

Meso-stable water-in-oil emulsions are reddish-brown viscous liquids with an average water content of 64% on the first day of formation and less than 30% 1 week later. Meso-stable emulsions generally break down fairly completely within 1 week. The viscosity increase over the day of formation averages a factor of 7 and 1 week later averages 5. The average properties of the starting oil required to form a meso-stable emulsion are: density 0.9 g/mL; viscosity 1300 mPa s; resin content 16%; and asphaltene content 8%; asphaltene-to-resin ratio 0.5. The greatest difference between the starting oils for stable and meso-stable emulsions are the ratio of viscosity increase (stable 400, first day and 850 in 1 week; meso-stable 7, first day and 5 in 1 week) and resin content (stable, 9%; meso-stable, 16%).

Entrained water-in-oil types are black viscous liquids with an average water content of 45% on the first day of formation and less than 28% 1 week later. The viscosity increase over the day of formation averages a factor of 2 and 1 week later still averages 2. The average properties of the starting oil required to form entrained water are: density 0.97 g/mL; viscosity 60,000 mPa s; resin content 18%; asphaltene content 12%; and asphaltene-to-resin ratio 0.75. The greatest differences between the starting oils for entrained water-in-oil compared to stable and meso-stable emulsions are the viscosity of the starting oil (entrained averages 60,000 mPa s compared to 200 mPa s for stable emulsions and 1300 mPa s for meso-stable emulsions and the ratio of viscosity increase (entrained = 2, first day and 2 in 1 week; stable 400, first day and 850 in 1 week; meso-stable 7, first day and 5 in 1 week).

Unstable water-in-oil emulsions are characterized by the fact that the oil does not hold significant amounts of water. There is a much broader range of properties of the starting oil 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 and very heavy, viscous oil products.

The stability of an emulsion, as represented by stability C, was correlated with starting oil properties. The different water-in-oil types could be differentiated by correlating individually with starting oil viscosity, density, saturate content, asphaltene content, resin content or asphaltene/resin ratio. Combinations of these oil properties yielded even greater differentiation between water-in-oil types. Examples of good separation of water-in-oil types was achieved by plotting asphaltene content times asphaltene/resin ratio, along with starting oil viscosity and stability. Other correlations with similar input also yielded differentiation between water-in-oil types.

The data strongly suggest that the water-in-oil types are stabilized by both asphaltenes and resins, but that, for greater stability, resin content should exceed the asphaltene content slightly. Excess resin content ( $A/R > \text{about } 0.6$ ) apparently destabilizes the emulsion. This does not consider the question of different types of asphaltenes or resins. A high asphaltene content (typically  $>10\%$ ) increases the viscosity of the oil such that a stable emulsion will not form. Viscous oils will only uptake water as entrained water and will slowly lose much of this water over a period of about 1 week. Viscous oils (typically  $>1000$  mPa s) will not form stable or meso-stable emulsions. Oils or low viscosity or without significant amounts of asphaltenes and resins will not form any water-in-oil type and will retain less than about 6% water. Oils of very high viscosity (typically  $>10,000$  mPa s) will not form any of these water-in-oil types. This is proba-

bly due to the inability of water droplets to penetrate the oil mass.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.colsurfa.2008.09.029.

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