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RESEARCH

Agents Which Promote and Stabilize Water-in-Oil Emulsions

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A number of research groups have investigated the formation and stabilization of water-in-oil emulsions. A variety of compounds and mixtures have been shown to promote and stabilize these emulsions, including sea water particulates, as well as fractions or compounds found in crude oil. Asphaltenes, resins and waxes in crude oil contribute to the formation of stable oil-in-water emulsions. Within the asphaltene fraction, the nickel porphyrins appear to play an essential role in emulsion formation. The vanadium porphyrins, although more abundant than nickel porphyrins in most crude oils, do not play an important role in emulsion formation, possibly because of their higher polarity. It appears that compounds with higher solubility in the oil phase than in the aqueous phase are the emulsifying agents that can promote stable water-in-oil emulsions. Crude oils that form very unstable emulsions, e.g. Gullfaks crude oil from the North Sea, require weathering as well as the addition of nickel porphyrins before a stable emulsion will form. The weathering may cause the formation of colloidal asphaltene particles and highly polar compounds that contributes to emulsion stabilization. Essential to the formation of stable water-in-oil emulsions are sufficient amounts of certain polar compounds. If there are insufficient amounts of these compounds, then even the presence of particles and waxes will not lead to the formation of stable emulsions. © 1999 Elsevier Science Ltd. All rights reserved

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Introduction

Certain crude oils when mixed with seawater form water-in-oil emulsions which consist of droplets of water dispersed in the oil (Fig. 1). Mixing energy, required to form emulsions, is provided in the ocean by wind or wave induced turbulence. Stable water-in-oil emulsions are characterized by a high water content (50 to 90%), high viscosity, small water droplets and higher density than the original oil (Brandvik and Daling, 1991; Fingas *et al.*, 1994) Stable emulsions have been defined by Fingas *et al.* (1994) as emulsions in which the water persists for 5 days or longer. The high viscosity of stable emulsions results in a semi-solid or gel formed from the liquid crude oil. Brandvik and Daling (1991) found that water uptake was first order during the formation of a water-in-oil emulsions and most oils had taken up the maximum amount of water after 10 h of mixing.

Stable emulsions are characterized by properties which prevent the coalesce of their small water droplets (1 to 10 μm), while in unstable emulsions the larger water droplets quickly coalesce (Fig. 1). The size of water droplets in water-in-oil emulsions has been investigated by light and electron microscopy (Mikula, 1992). Crude oil from the Norwegian continental shelf formed emulsions containing water droplets with dimensions in the 10 to 30 μm range (Sjöblom *et al.*, 1990a). An emulsion of North Sea crude oil had water droplets with an average diameter of 10 μm (Thompson *et al.*, 1985).

A stable emulsion is composed of an aqueous phase, an oil phase and an emulsifying agent. Particles and surfactants found in crude oil can act as emulsifying agents and thus can promote and stabilize water-in-oil emulsions (Bobra, 1990, 1991; Brandvik and Daling,

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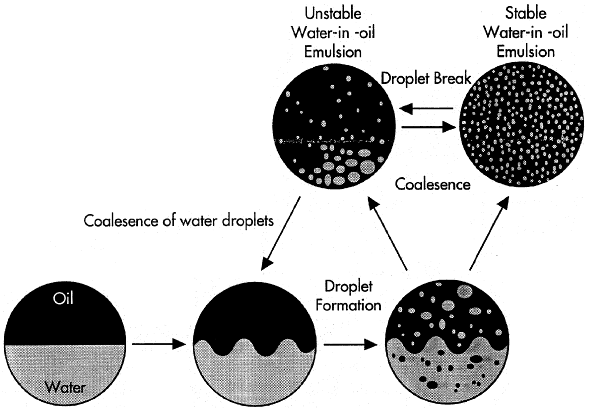


Fig. 1 Formation of water-in-oil emulsions. Modified from Lewis and Walker (1993).

1991; Canevari, 1987; Christopher, 1993; Durell *et al.*, 1994; Eley *et al.*, 1976, 1988; Fingas *et al.*, 1993, 1994, 1995; Gelot *et al.*, 1984; Graham, 1988; Isaacs and Chow, 1992; Johansen *et al.*, 1989; MacKay, 1987; MacKay *et al.*, 1973; Payne and Phillips, 1985; Sjöblom *et al.*, 1990a). If the concentrations of particles and surfactants are sufficiently high, then water droplet coalescence is prevented, leading to stable emulsions (Fig. 2). Particles in the ocean can enter an oil slick and act as emulsifying agents. Particles found in crude oils include waxes and asphaltenes, while particles found in sea water include suspended sediments and/or particulates. Dissolved surfactants which accumulate at the water–oil interface include metallic salts, organic acids, organic bases and organometallics.

Oxygenated compounds in the oil are thought to increase the solubility of water so that after turbulent mixing, water in the oil is in a supersaturated condition. This is followed by precipitation of water as small droplets in the oil (Fig. 1). Surfactants and particles accumulate at the interfacial film, stabilize the water droplets and thereby stabilize the emulsion. A schematic diagram by MacKay (1987) features a stabilized water droplet with associated asphaltenes and wax crystals (Fig. 3). This paper reviews the literature on chemicals and particulates which contribute to the formation and stabilization of water-in-oil emulsions. A number of review articles have been written summarizing the literature on water-in-oil emulsions. (Bobra, 1990; Bansback, 1970; Canevari and Fiocco, 1997; Christopher, 1993; Fingas *et al.*, 1993; Friberg, 1991; Graham, 1988; MacKay, 1987; Payne and Phillips, 1985; Schramm, 1992; Sjöblom *et al.*, 1996).

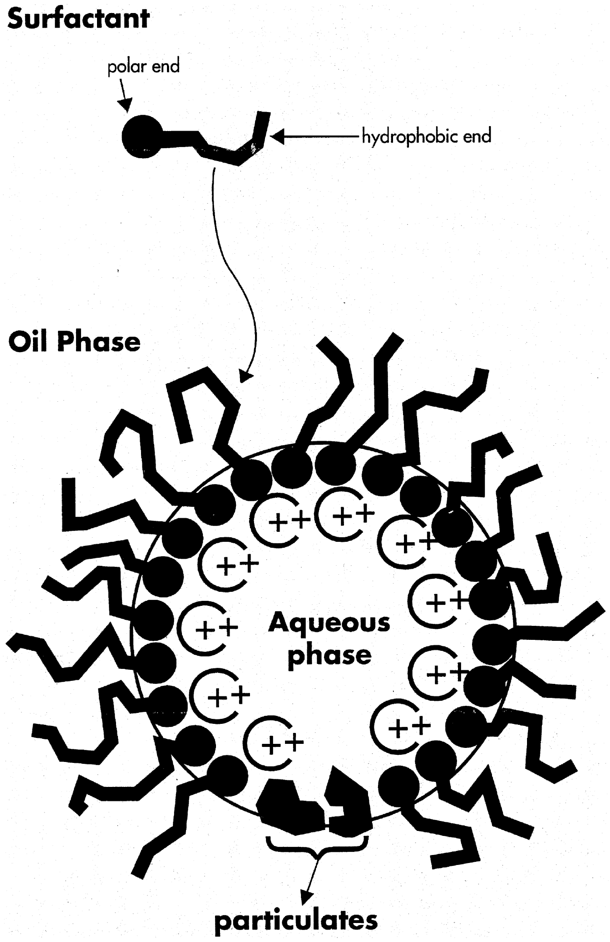


Fig. 2 Water-in-oil emulsions. Water droplet in oil showing stabilization by surfactants and particulates. Modified from Christopher (1993).

Stabilization of water-in-oil emulsions by sea water particles

High concentrations of sea water particulates occur in high latitude waters when there is glacial runoff. Clay particles have been shown to stabilize water-in-oil emulsions (Menon and Wasan (1988)). An X-ray

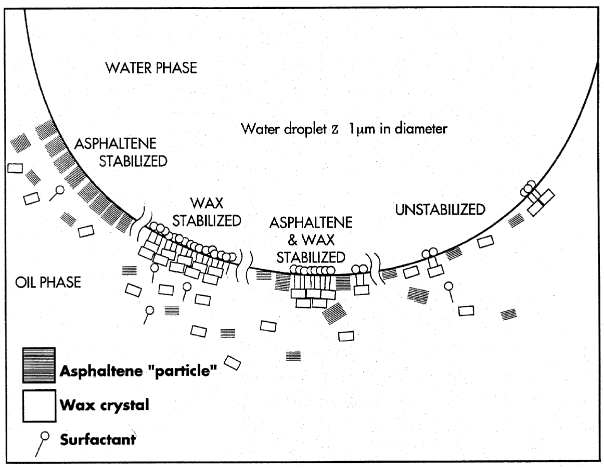


Fig. 3 Schematic diagram showing a water emulsion droplet in oil which is stabilized by asphaltenes, surfactants and waxes. An unstabilized region is shown where there is formation of an incomplete barrier. Modified from MacKay (1987).

detector coupled to an electron microscope was used to show clays at the water–oil interface in a water-in-oil emulsion (Mikula, 1987). Clays present at the interface were shown by the presence of clay-derived silicon. Large phytoplankton blooms result in high concentrations of organic particulates. Clay particles and the organic-clay particulates found in coastal ocean waters have both hydrophobic and hydrophilic regions so that such particles would be located at the oil–water interface and would be expected to stabilize emulsions (Tsugita *et al.*, 1983). Menon and Wasan (1988) have suggested that asphaltene particles after binding to clay are highly hydrophobic and can better stabilize water-in-oil emulsions. For particles to act as emulsifying agents, the particles must be much smaller than the water droplets, collect at the water–oil interface and have regions which can enter the oil and aqueous phase (Bobra, 1991). For the particles to contribute to emulsion stabilization, the particles should be no more than 1 μm in size, since the size of the water droplets in stable emulsions are generally 10 μm or less (Graham, 1988). The importance of seawater particulates in the formation of oil-in-water emulsions can be seen in the formation of emulsions of Alaska North Slope crude oil (Fig. 4, Lee, 1995). Filtered estuary water formed unstable emulsions whereas unfiltered water formed stable emulsions. Such results were not found with other crude oils.

Crude oil fractions that promote and stabilize water-in-oil emulsions

Certain fractions of crude oil have been identified as contributing to the formation of water-in-oil emulsions. These fractions include waxes, asphaltenes and resins and can exist in both the dissolved and particulate form. Waxes are high-molecular-weight alkanes. Asphaltenes are defined as the solid material precipitating from crude oil after the addition of a low-boiling liquid hydrocarbon such as heptane or pentane. The resins are defined as the pentane-soluble but methanol-insoluble fraction of crude oil.

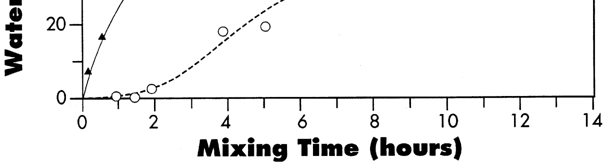


Fig. 4 Effect of seawater particulates on formation of water-in-oil emulsion by Alaska North Slope crude oil. Seawater (300 ml) either filtered (0.45 μm filter) or unfiltered was mixed with 30 ml of oil on a rotating apparatus and the water content of the emulsion formed was noted at the different times.

Since the classification of asphaltenes and resins is an operational term, i.e. solubility in different solvents, there is not a clear distinction between the compounds found in the two fractions. Resin particles are generally smaller than asphaltene particles and most of the metal porphyrins are in the asphaltene fraction. Asphaltenes tend to have higher-molecular-weight compounds and to be more polar than resins (Filby, 1975).

A number of studies have demonstrated the importance of asphaltenes, resins and waxes in promoting and stabilizing water-in-oil emulsions. Brandvik and Daling (1991) found that the stability of a water-in-oil emulsion was positively correlated with the resin, wax and asphaltene content of the original crude oil. Removal of asphaltenes from crude oils by silica columns produced oils that did not form water-in-oil emulsions (Ebeltoft *et al.*, 1992; Sjöblom *et al.*, 1990b, 1992; Urdahl *et al.*, 1992). Bridie *et al.* (1980) found that after the removal of asphaltenes from Kuwait crude oil, very unstable emulsions were produced. When wax crystals and asphaltenes were added back to the treated oil, a stable water-in-oil emulsion was formed. Waxes cannot act as emulsifying agents by themselves but can act in combination with resins or asphaltenes to produce stable oil-in-water emulsions. Thus, a concentration of 0.01 g/ml of asphaltenes did not produce a stable water-in-oil emulsion, but when waxes were added (0.05 g/ml), stable emulsions were formed (Bobra *et al.*, 1992). An asphaltene concentration of 0.03 g/ml, with no wax added, produced a stable emulsion. Bobra (1991) found that resins alone could act as effective emulsifiers, but the most stable emulsions were formed when both asphaltenes and resins were present. It was suggested that waxes could interact with asphaltenes and resins to stabilize emulsions.

Bobra *et al.* (1992) has suggested that asphaltenes, resins and waxes must be in the form of finely divided submicrometer particles to act as emulsifying agents. Several studies support the importance of wax, asphaltene, and resin particles in emulsion formation and stability. Centrifugation of a North Sea crude to remove wax crystals resulted in an oil which formed a less stable emulsion (Graham, 1988). It should be noted that such centrifugation could also remove some colloidal asphaltene particles. Electron micrographs of frozen water-in-oil emulsions showed granules on the oil side of the droplet interface and these were suggested to be composed of finely divided asphaltene particles (Eley *et al.*, 1976, 1988). In emulsions made with Brega crude, which is high in waxes, wax crystals were observed along the oil–water interface (Eley *et al.*, 1976). Wax particles were also found in microscope studies of emulsions produced by North Sea crude oil (Thompson *et al.*, 1985). The asphaltenes are soluble in aromatic solvents, e.g. xylene, and insoluble in alkane solvents. Thus, the alkane/aromatic ratio in an oil is important in determining the size of the asphaltene particles. If the alkane/aromatic ratio is high, then the asphaltenes will be in the form of particles in the oil, with the size of the particles determined by the ratio. After weathering, lighter hydrocarbons are lost and the weathered oil generally forms a more stable emulsion than the one formed with the original crude. The formation of stable emulsions with weathered oil may be due to the formation of more asphaltenes particles because of the loss of solvents (low-weight aromatics).

The solubility behavior of asphaltenes and their precipitation in crude oil has been described by Bobra *et al.* (1992) and Griffith and Siegmund (1985) using the solubility theory described by the Hilderand–Scatchard equation. Oil is assumed to be composed of a solute (asphaltenes) and solvent (compounds in oil other than asphaltenes). Thus, the lighter weight aromatics, e.g. toluene, xylene, of crude oil act as solvents for the heavier asphaltenes. The application of the Hildebrand–Scatchard equation for describing asphaltene solubility is as follows:

$$RT \ln \left(\frac{A_a}{X_a}\right) = \frac{M_a \phi_s^2}{\rho_a} (\sigma_a - \sigma_s)^2$$

where

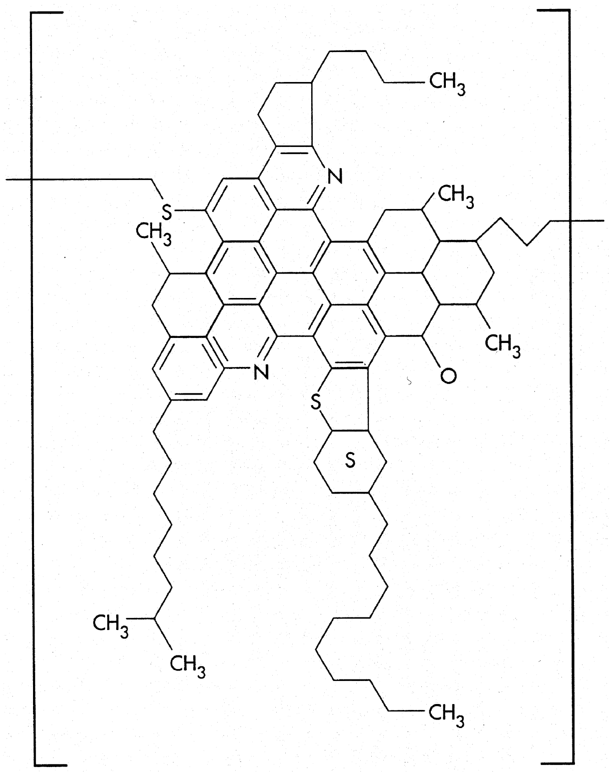
A_a = activity coefficient of asphaltenes
X_a = mole fraction of asphaltenes
M_a = molecular weight of asphaltenes
ϕ_s = volume fraction of solvent
σ_a = Hildebrand solubility parameter of the asphaltenes
σ_s = Hildebrand solubility parameter of the solvent
ρ_a = density of asphaltenes
R = gas constant
T = temperature

When the amount of asphaltenes present in the oil exceeds X_a, the excess asphaltenes precipitate. Assuming asphaltenes are homogeneous and $A = 1$, the equation can be rewritten in terms of maximum amount of asphaltenes soluble in oil:

$$\ln X_a = \frac{M_a \phi_s^2}{\rho_a RT} (\sigma_a - \sigma_s)^2$$

The amount of asphaltenes soluble in oil, X_a, is controlled by the solubility parameters of the asphaltenes (σ_a) and the oil (σ_s). As $(\sigma_a - \sigma_s)^2$ increases, the amount of asphaltenes soluble in oil decreases and the excess asphaltenes precipitate.

A study of the structure of asphaltenes may give some insight into why asphaltenes play such an important role in promoting and stabilizing emulsions. The structure of asphaltenes is not well understood, but several possible structures have been proposed to explain the composition and properties of the asphaltene fraction. In addition to carbon and hydrogen, other elements found in asphaltenes include nitrogen, oxygen, sulfur and metals (primarily vanadium and nickel). Asphaltene properties include high molecular weight, solubility in aromatic solvents and very low solubility in *n*-alkane solvents. One proposed structure for asphaltene is shown in Fig. 5 which accounts for the nitrogen, sulfur and oxygen in asphaltenes, but does not include the organometallic compounds. Figure 6 shows an asphaltene micelle showing a flat central region consisting of fused aromatic rings with a corrugated periphery made up of naphthenic rings and aliphatic chains. An organometallic complex is also shown which is assumed to complex other asphaltene compounds in the micelle. Such asphaltene sheets



$(C_{79}H_{92}N_2S_2O_3)_3$
mol wt. 3449

Fig. 5 Hypothetical structure of a petroleum asphaltene. Modified from Speight and Moschopedis (1981).

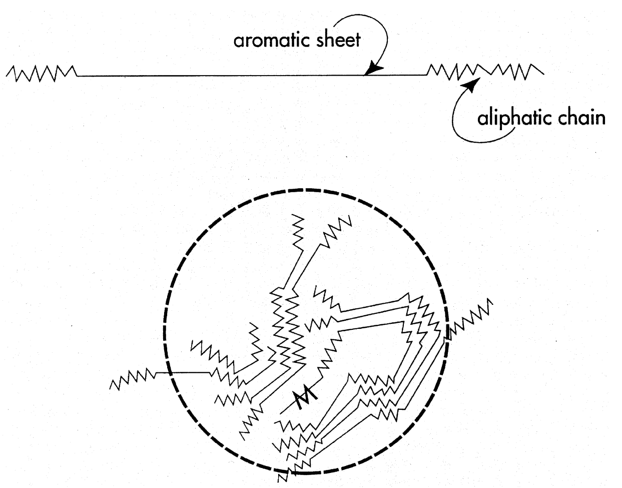


Fig. 6 Asphaltene micelle. Metal porphyrin (M) is a coordination center for several clusters. Modified from Yen (1981) and Speight and Moschopedis (1981).

appear to be regularly stacked in lamellar structures and such structures, which are found in other surfactant systems, are known to enhance emulsion stability (Johansen *et al.*, 1989).

There is not always a direct correlation between the concentration of asphaltenes in a crude oil and the formation of a water-in-oil emulsion. For example, while Kuwait crude oil is 1.4% asphaltenes and TiaJuana crude oil is 3.1% asphaltenes, the Kuwait crude forms a more stable emulsion than the TiaJuana crude (Lee, 1995). Jenkins *et al.* (1991) found that one crude (identified as crude A) had 1.6% asphaltenes and formed a very stable emulsion while a second crude (crude B) had 1.03% asphaltenes and did not form stable emulsions. Thus, certain components of the asphaltenes may play a critical role in emulsion formation. The amounts of these emulsifying agents in asphaltenes are likely to vary for asphaltenes from different crude oils. Asphaltenes are composed of neutral, acidic and basic components. Siffert *et al.* (1984) found that stable emulsions were formed with crude oils containing asphaltenes with an imbalance between the proportion of acidic and basic groups. Much more work will be necessary to better define which compounds in asphaltenes and resins make major contributions to emulsion stability.

Promotion and stabilization of water-in-oil emulsions by photo-oxidation products of oil

Klein and Pilpel (1974) found that photo-oxidation of oil resulted in stabilized water-in-oil emulsions. Bocard and Gatellier (1981) found that emulsions formed with fresh crude were unstable, while after exposure to light, these crudes formed stable emulsions. Thingstad and Pengerud (1983) found that a Norwegian crude oil (Statfjord crude) did not form stable water-in-oil emulsions in the dark. When this oil was illuminated for 3 to 4 days before mixing with seawater a stable emulsion was formed. Crude oils exposed to simulated sunlight produced stable water-in-oil emulsions, and the suggestion has been made that photo-oxidation products with surfactant properties acted as emulsifying agents (Brandvik and Daling, 1991). Lamathe (1982) found that carboxylic-sulfonated acids, produced during the photo-oxidation of asphaltene fraction of oil, were important in the formation of water-in-oil emulsions. It seems likely that some photo-oxidation products of asphaltenes have surfactant properties.

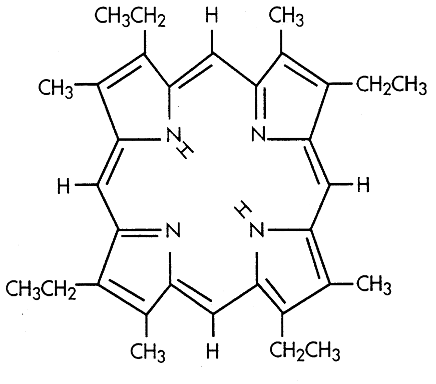
The addition of a model photo-oxidation product, tetradecanal (n-C_{14} aldehyde), to a Statfjord crude produced a stable emulsion. The tetradecanal was required to be above 10% in the oil before water was taken into the emulsion. Beta-carotene, an inhibitor of photo-oxidation, prevented the formation of water-in-oil emulsions during light exposure. Thus, Thingstad and Pengerud (1983) concluded that some of the products of oil photo-oxidation, e.g. acids, aldehydes, were surfactants that facilitated the formation of water-in-oil emulsions. In general, tertiary free radicals are more stable than those formed from primary or second carbons, so that isoprenoids with tertiary carbons are more susceptible to photo-oxidation than *n*-alkanes. Thus, there should be a predominance of products derived from tertiary carbons after photo-oxidation.

Compounds that promote and stabilize water-in-oil emulsions

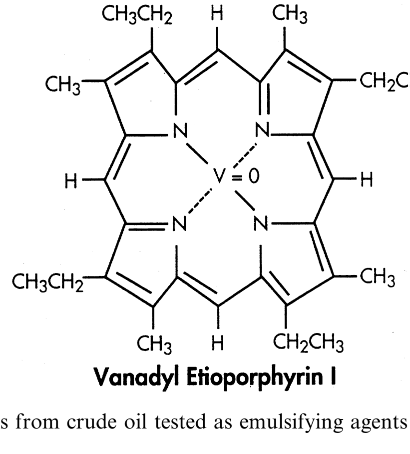
Few studies have demonstrated that pure compounds isolated from crude oil can promote and stabilize water-in-oil emulsions. Compounds with surfactant properties in crude oil can be expected to promote and stabilize water-in-oil emulsions since surfactants are associated with the water–oil interface. As shown in Fig. 2, surfactants surround the water droplets and the polar-hydrophilic end is in the aqueous phase while the hydrophobic end is in the oil phase. To form stable water-in-oil emulsions, the surfactant should have a large hydrophobic region and a smaller hydrophilic region. The surfactants are likely to influence the viscosity of the emulsion. MacKay *et al.* (1973) concluded that each water droplet was encapsulated in an envelope of surfactants with a plastic nature that prevented coalescence of the water droplets due to altered interfacial oil–water tensions.

Canevari (1987) extracted high-molecular-weight surfactant residues from various crude oils and the amount of surfactant residue correlated with the emulsion forming tendency of the crude oil. The relative amount of surfactant residues found in various crude oils included 19.5% in Kuwait crude, 1.1% in Ekofish, 2.8% in South Louisiana and 16.8% in La Rosa. Examples of compounds found in crude oil having surfactant properties include carboxylic acids and porphyrins. Porphyrins in crude oil contain four indole nuclei and a metal, generally nickel or vanadium (Fig. 7). Fingas *et al.* (1994) noted that most stable emulsions are reddish in appearance. The addition of nickel porphyrins to non-emulsion-forming crude oils followed by mixing with seawater resulted in the formation of a stable reddish-brown water-in-oil emulsion (Lee, 1995). Based on studies with Kuwait crude oil, it was suggested that porphyrins and metal porphyrins play a major role in the emulsification of oil (Canevari, 1982). These porphyrins are thought to orient at the oil–water interface forming a film which is a barrier for coalescence of water droplets.

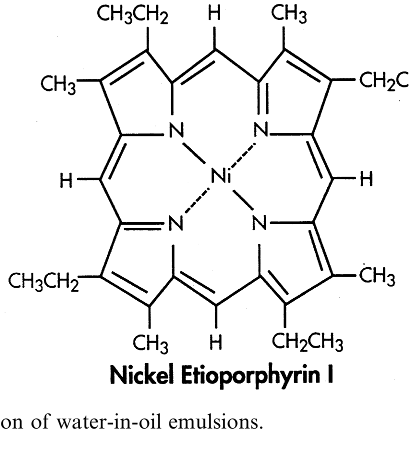
Following up on the work of Canevari (1987), we added asphaltene bases and nickel porphyrins isolated from an emulsifying crude (Monterey crude) oil to South Louisiana crude, a crude oil which does not form strong water-in-oil emulsions (Fig. 8, Lee, 1995). While vanadium porphyrins are in higher concentrations than nickel porphyrins in most crude oils (Baker and Louda, 1986; Filby and Van Berkel, 1987; Hirner, 1987), vanadium porphyrins are generally not effective emulsifying agents (Fig. 9, Lee, 1995). Strong emulsifying agents in water-in-oil emulsions should have a large hydrophobic region and a smaller hydrophilic region. The oxygenated vanadyl moiety found in vanadium porphyrins is more polar than the nickel ion found in nickel porphyrins, so vanadium porphyrins are more hydrophilic than nickel porphyrins and presumably vanadium porphyrins are less able to stabilize emulsions. The emulsifying properties of porphyrins were in the order of nickel porphyrins, non-metal porphyrins and vanadium porphyrins (Fig. 9). The structure of these porphyrins are shown in Fig. 7. An interesting experiment was carried with Gullfaks crude oil where an emulsion was not formed by itself or after the addition of nickel porphyrins, but only after the Gullfaks oil was first weathered by exposure to sunlight for 2 days (Fig. 10). Two-day-weathered oil without nickel porphyrins did not form stable emulsions. These results suggest that nickel



Etioporphyrin I



Vanadyl Etioporphyrin I



Nickel Etioporphyrin I

Fig. 7 Porphyrins from crude oil tested as emulsifying agents in the formation of water-in-oil emulsions.

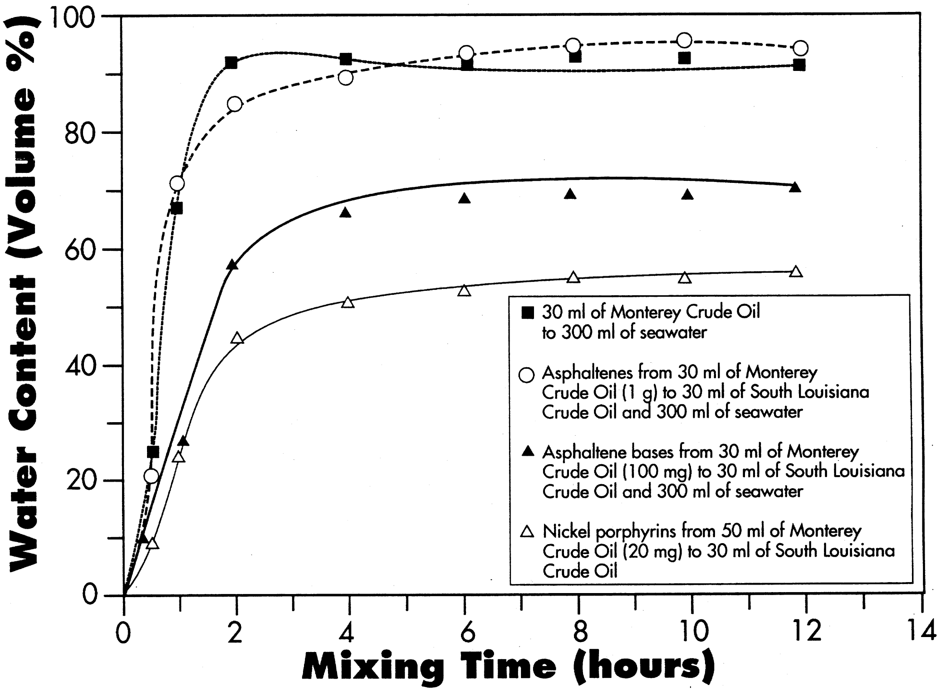


Fig. 8 Emulsion formation by monterey crude oil and by addition of various fractions of monterey crude oil to south Louisiana crude oil (non-emulsion forming oil). Sea water (300 ml) was mixed with oil, oil fraction and/or porphyrins on a rotating apparatus and the water content of the emulsion formed was noted at the different times.

porphyrins are unable to promote and stabilize emulsions by themselves but require other surfactants and/or particulates in the oil. Similarly, adding nickel porphyrins to fuel oil, which lacks asphaltenes, results in unstable oil-in-water emulsions (Lee, 1995). Crude oil with low vanadium and nickel concentrations (less than 15 ppm) will not emulsify even with extensive mixing with water (Canevari and Fiocco, 1997).

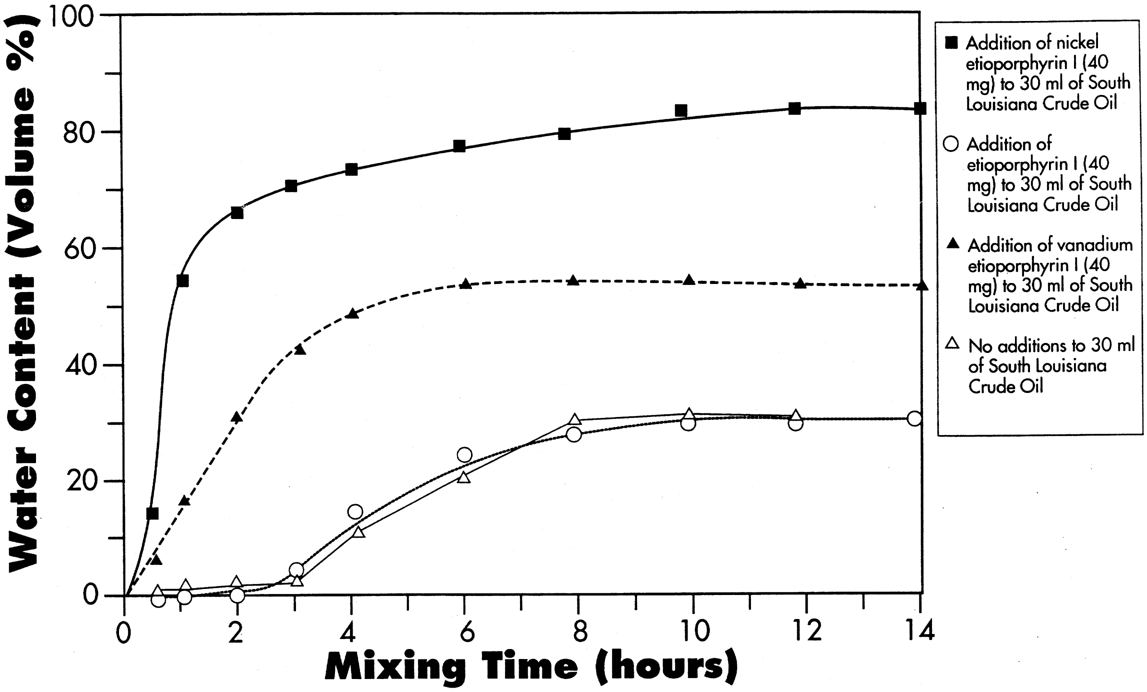


Fig. 9 Effect of porphyrin additions on the formation of oil-in-water emulsions. Seawater (300 ml) was mixed with 30 ml of South Louisiana crude oil (non-emulsion forming oil) and 40 mg of one of the porphyrins. The mixture was placed on a rotating apparatus and the water content of the emulsion formed was noted at the different times.

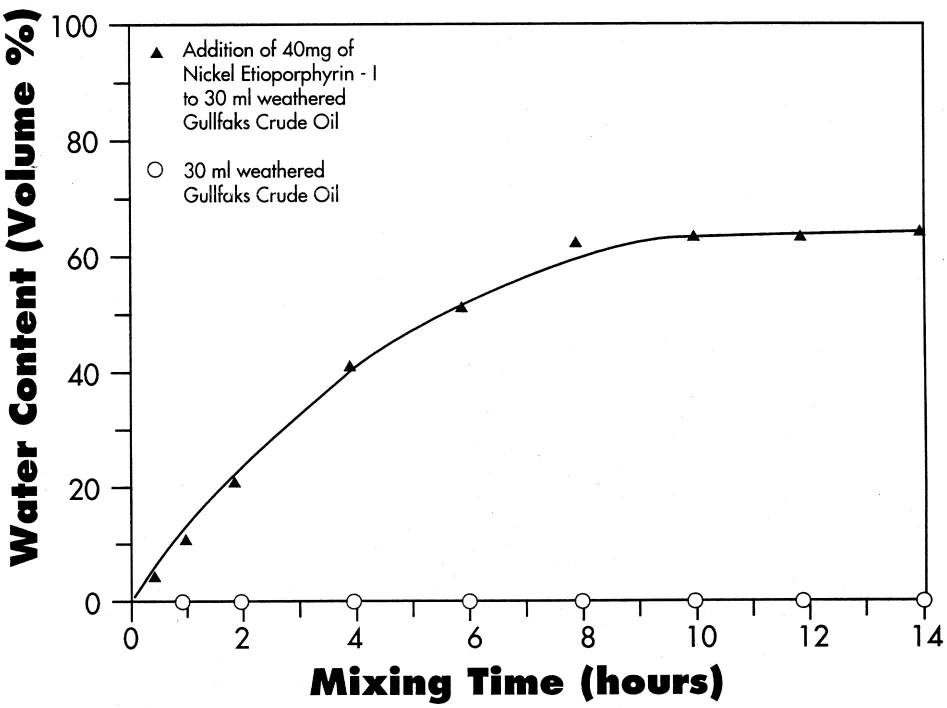


Fig. 10 Effect of nickel porphyrin to weathered Gullfaks crude oil. Seawater (300 ml) was mixed with 30 ml of weathered Gullfaks crude oil (non-emulsion forming oil) and 40 mg of nickel porphyrin. No emulsion was formed when nickel porphyrin was added to non-weathered oil. Oil was weathered by setting it outside in a beaker for 3 days before use.

Carboxylic acids with surfactant properties are found in crude oil and include fatty acids, both straight chain and branched, and naphthenic acids (Fig. 11). Naphthenic acids are saturated cyclic acids and can account for up to 3% of some crude oils. A tricyclic naphthenic acid found in many oils is shown in Fig. 11 (Green *et al.*, 1985; Koike *et al.*, 1992). Sjöblom *et al.* (1990a) have shown that fatty acids can stabilize water-in-oil emulsions. Gelot *et al.* (1984) produced a model water-in-oil emulsion with water, toluene, carbon black, bentonite and naphthenic acids. In our studies, naphthenic acids isolated from crude oil did not stabilize oil-in-water emulsions (Lee, 1995).

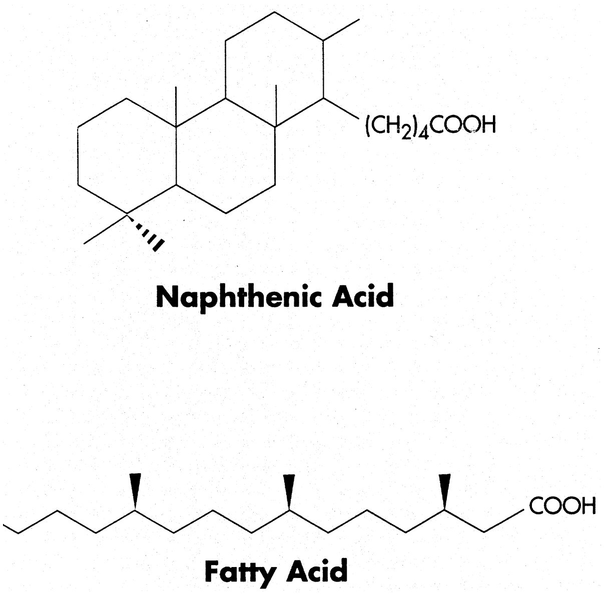


Fig. 11 Carboxylic acids found in crude oil.

Water-in-oil emulsions formed at sea

Payne *et al.* (1983) added Prudhoe Bay crude oil to a large wave tank and found that emulsification did not occur until a significant amount of evaporation had taken place to remove lower-molecular-weight compounds. Payne and Phillips (1985) in a review of oil spills noted which oils formed water-in-oil emulsions. Most of the oils that formed emulsions in real spill events also formed stable emulsions in the laboratory. Spills involving oils with relatively high asphaltene concentrations, such as the Torry Canyon spill, Tanker Arrow, and IXTOC-I, produced stable water-in-oil emulsions (Payne and Phillips, 1985). In contrast, the Ekofish Bravo blowout involving Ekofish crude, which is low in asphaltene (0.03%), formed very unstable emulsions (Audunson, 1978). Canevari and Fiocco (1997) have shown that the extent of emulsification after an oil spill could be predicted based on the vanadium and nickel content of the oil.

Conclusions

Based on the research done to date, stable water-in-oil emulsions can be produced by a variety of compounds and mixtures. While asphaltenes and resins clearly play an important role in the formation of stable emulsions, there are oils with significant amounts of asphaltenes which do not produce stable emulsions. Certain types of compounds in the asphaltenes and resins with surfactant properties likely play a major role in producing stable emulsions. Compounds with higher solubility in the oil phase than in the aqueous phase are the most likely emulsifying agents to produce stable water-in-oil emulsions. Waxes and sea water particles, such as clays, can contribute to the stability of water-in-oil emulsions, but cannot by themselves produce stable emulsions. Similarly, surfactants produced during the photo-oxidation of oil are assumed to still require the presence of asphaltenes and resins to produce stable water-in-oil emulsions. Thus, essential to the formation of stable water-in-oil emulsion are sufficient amounts of certain polar compounds, such as nickel porphyrins, found in the asphaltenes and resins of crude oil. If insufficient amounts of these polar compounds are present in the oil, then the presence of waxes and other particles will not lead to the formation of stable emulsions.

References

Audunson, T., 1978. The fate and weathering of surface oil from the Brovo blowout. In: Proceedings of the Conference on Assessment of Ecological Impacts of Oil Spills. American Institute of Biological Sciences, Washington, DC, pp. 445–475.

Baker, E.W., Louda, J.W. 1986. Porphyrins in the geological record. In: Johns, R.B. (Ed.), Biological Markers in the Sedimentary Record. Elsevier, Amsterdam, pp. 125–225.

Bansback, P.L., 1970. The how and why of emulsions. Oil and Gas Journal 68, 87–93.

Bobra, M., 1990. A study of the formation of water-in-oil emulsions. In: Proceedings of Arctic and Marine Oil Spill Program (AMOP) Technical Seminar, 6–8 June. Environment Canada, Minister of Supply and Services, Ottawa, Ontario, Canada, pp. 37–117.

Bobra, M., 1991. Water-in-oil emulsification: a physicochemical study. In: Proceedings of 1991 International Oil Spill Conference. American Petroleum Institute, Washington, DC, pp. 483–488.

Bobra, M., Fingas, M., Tennyson, E., 1992. When oil spills emulsify. Chemtech 22, 236–241.

Bocard, C., Gatellier, C., 1981. Breaking of fresh and weathered emulsions by chemicals. In: Proceedings of 1981 Oil Spill Conference. American Petroleum Institute, Washington, DC, pp. 601–607.

Brandvik, P.J., Daling, P.S., 1991. W/o-emulsion formation and w/o-emulsion stability testing – an extended study with eight oil types. DIWO Report No. 10, IKU Sintef Group, Trondheim, Norway, p. 48.

Bridie, A.L., Wanders, T.H., Zegveld, W., Van Der Heijde, H.B., 1980. Formation, prevention and breaking of sea water in crude oil emulsions 'chocolate mousse'. Marine Pollution Bulletin 11, 343–348.

Canevari, G.P., 1982. The formulation of an effective emulsifier for oil spill emulsions. Marine Pollution Bulletin 13, 49–54.

Canevari, G.P., 1987. Basic study reveals how different crude oils influence dispersant performance. In: Proceedings 1987 Oil Spill Conference. American Petroleum Institute, Washington, DC, pp. 293–296.

Canevari, G.P. and Fiocco, R.J., 1997. Crude oil vanadium and nickel content can predict emulsification tendency. In: Proceedings 1997 Oil Spill Conference. American Petroleum Institute, Washington, DC, pp. 309–314.

Christopher, C.A., 1993. Fundamentals of emulsions. In: Walker, A.H., Ducey, D.L. Gould J.R., Nordvik, A.B. (Eds.), Formation and Breaking of Water-in-Oil Emulsions: Workshop Proceedings. MSRC Technical Report Series 93-018. Marine Spill Response Corporation, Washington, DC, pp. 63–79.

Durell, G.S., Ostazeski, S.A., Uhler, A.D., Almas, I.J., Daling, P.S., Strom-Kristiansen, T., Nordvik, A.B., 1994. Evaluation of the transfer of crude oil weathering technology. In: Proceedings of the Seventeenth Arctic and Marine Oil Spill Program (AMOP) Technical Seminar, vol. 1. Environment Canada, Ottawa, Ontario, pp. 39–76.

Ebeltoft, H., Borve, K.G.N., Sjöblom, J., Stenius, P., 1992. Interactions between poly(styrene–allylalcohol) monolayers and surfactants: correlations to water-in-crude oil emulsion stability. Progress in Colloids and Polymer Science 88, 131–139.

Eley, D.D., Hey, M.J., Symonds, J.D., Willison, J.H.M., 1976. Electron micrography of emulsions of water in crude petroleum. Journal of Colloid and Interface Science 54, 462–466.

Eley, D.D., Hey, M.J., Symonds, J.D., 1988. Emulsions of water in asphaltene-containing oils. 1. Droplet size distribution and emulsification rates. Colloids and Surfaces 32, 87–101.

Filby, R.H. (1975) The nature of metals in petroleum. In: Yen T.F. (Ed.), The Role of Trace Metals in Petroleum. Ann Arbor Science Publishers, Ann Arbor, MI, pp. 31–58.

Filby, R.H., Van Berkel, G.J., 1987. Geochemistry of metal complexes in petroleum, source rocks, and coals: an overview. In: Filby R.H., Branthaver J.F. (Eds.), Metal Complexes in Fossil Fuels. American Chemical Society, Washington, DC, pp. 1–39.

Fingas, M., Fieldhouse, B., Bobra, M., Tennyson, E., 1993. The physics and chemistry of emulsions. In: Walker, A.H., Ducey, D.L., Gould, J.R., Nordvik, A.B. (Eds.), Formation and Breaking of Water-in-Oil Emulsions: Workshop Proceedings. MSRC Corporation, Washington, DC, pp. 97–104.

Fingas, M., Fieldhouse, B., Mullin, J., 1994. Studies of water-in-oil emulsions and techniques to measure emulsion treating agents. In: Proceedings of the Arctic Marine Oilspill Program Technical Seminar. Environment Canada, Ottawa, Ontario, pp. 213–244.

Fingas, M., Fieldhouse, B., Mullin, J., 1995. Water-in-oil emulsions: how they are formed and broken. In: Proceedings of 1995 Oil Spill Conference. American Petroleum Institute, Washington, DC, pp. 829–830.

Friberg, S., 1991. Emulsion stability. In: J. Sjöblom (Ed.), Emulsions – A Fundamental and Practical Approach. Kluwer Academic Publisher, Dordrecht, Netherlands, pp. 1–24.

Gelot, A., Friesen, W., Hamza, H.A., 1984. Emulsification of oil and water in the presence of finely divided solids and surface active agents. Colloids and Surfaces 12, 271–303.

Graham, D.E., 1988. Crude oil emulsions; their stability and resolution. In: Ogden P.H. (Ed.), Chemicals in the Oil Industry. Special Publication No. 67, Royal Society of Chemistry, London, pp. 155–175.

Green, J.B., Stierwalt, B.K., Thomson, J.S., Treese, C.A., 1985. Rapid isolation of carboyxlic acids from petroleum using high-performance liquid chromatography. Anal. Chem. 57, 2207–2211.

Griffith, M.G., Siegmund, C.W., 1985. Controlling compatibility of residual fuel oils. In: Jones C.H. (Ed.), Marine Fuels. ASTM STP878. American Society for Testing and Materials, Philadelphia, pp. 227–247.

Hirner, A.V., 1987. Metals in crude oils, asphaltenes, bitumen, and kerogen in Molasse Basin, southern Germany. In: Filby R.H., Branthaver, J.F. (Eds.), Metal Complexes in Fossil Fuels. American Chemical Society, Washington, DC, pp. 146–153.

Isaacs, E.E. and Chow, R.S., 1992. Practical aspects of emulsion stability. In: Schramm, L.L. (Ed.), Emulsions – Fundamentals and Applications in the Petroleum Industry. Advances in Chemistry Series 231. American Chemical Society, Washington, DC, pp. 51-77.

Jenkins, R.H., Grigson, S.J.W., McDougall, J., 1991. The formation of emulsions at marine oil spills and the implications for response strategies. Proceedings of the Society of Petroleum Engineers 2, 437–443.

Johansen, E.J., Skjarvo, I.M., Lund, T., Sjoblom, J., Soderlund, H., Bostrom, G., 1989. Water-in-crude oil emulsions from the Norwegian continental shelf. Part I. Formation, characterization and stability correlations. Colloids and Surfaces 34, 353–370.

Klein, A.E., Pilpel, N., 1974. The effect of artificial sunlight upon floating oils. Water Res. 8, 79–83.

Koike, L., Reboucas, L.C.M., Reis, F.A.M., Marsaioli, A.J., Richnow, H.H., Michaelis, W., 1992. Naphthenic acids from crude oils of Compos Basin. Org. Geochem. 18, 851–860.

Lamathe, J., 1982. Sur le mé canisme de formation des emulsions d'eau de mer dans le p é trole lors des mar é es noires . Comptes Rendus des Seances Academie des Sciences 295, 301–304.

Lee, R.F., 1995. Isolation and identification of compounds and mixture which promote and stabilize water-in-oil emulsions. Marine Spill Response Corporation, Washington, DC, MSRC Technical Report Series 95-002, p. 62.

Lewis, A. and Walker, M., 1993. A review of the process of emulsification and demulsification. In: Walker, A.H. Ducey, D.L. Gould, J.R., Nordnik, A.B. (Eds.), Formation and Breaking of Water-in-Oil Emulsions: Workshop Proceedings. MSRC Technical Report Series 93-018. Marine Spill Response Corporation, Washington, DC, pp. 223–238.

MacKay, D., 1987. Formation and stability of water-in-oil emulsions. Report EE-93, Environment Canada, Ottawa, Ontario, p. 42.

MacKay, G.D.M., Mclean, A.Y., Betancourt, O.J., Johnson, B.D., 1973. The formation of water-in-oil emulsions subsequent to an oil spill. Journal of the Institute of Petroleum 59, 164–172.

Menon, V.B., Wasan, D.T., 1988. Characterization of oil–water interfaces containing finely divided solids with applications to the coalescence of water-in-oil emulsions: a review. Colloids and Surfaces 29, 7–27.

Mikula, R.J., 1987. Application of X-ray microanalysis to tar sands emulsions. Colloids and Surfaces 23, 267–271.

Mikula, R.J., 1992. Emulsion characterization. In: L.L. Shramm (Ed.), Emulsions Fundamentals and Applications in the Petroleum Industry. Advances in Chemistry Series 231. American Chemical Society, Washington, DC, pp. 79–129.

Payne, J.R., Phillips, C.R., 1985. Petroleum spills in the marine environment. In: The Chemistry and Formation of Water-in-Oil Emulsions and Tar Balls. Lewis Publishers, Chelsea, Michigan, p. 148.

Payne, J.R., Kirsten, B.E., McNabb, G.D., Lamback, J.L., De Oliveira, L., Jordan, R.E. and Hom, W., 1983. Multivariate analysis of petroleum hydrocarbon weathering in the subarctic marine environment. In: Proceedings of the 1983 Oil Spill Conference. American Petroleum Institute, Washington, DC, pp. 423–434.

Schramm, L.L., 1992. Petroleum emulsions – basic principles. In: Schramm, L. (Ed.), Emulsions: Fundamentals and Applications in the Petroleum Industry. American Chemical Society, Washington, DC, pp. 1–49.

Siffert, B., Bourgeois, C., Papirer, E., 1984. Structure and water–oil emulsifying properties of asphaltenes. Fuel 63, 834–837.

Sjöblom, J., Sönderlund, H., Lindblad, S., Johansen, E.J., Skjärvö, I.M., 1990a. Water-in-crude oil emulsions from the Norwegian continental shelf. Part II. Chemical destabilization and interfacial tensions. Colloid and Polymer Science 268, 389–398.

Sjöblom, J., Urdahl, O., Borve, K.G.N., Mingyuan, L., Saeten, J.O., Christy, A.A., Gu, T., 1990b. Stabilization and destabilization of water-in-oil emulsions from the Norwegian continental shelf: correlation with model systems. Advances in Colloids and Polymer Science 82, 131–139.

Sjöblom, J., Mingyuan, L., Christy, A.A., Gu, T., 1992. Water-in-crude-oil emulsions from the Norwegian continental shelf. 7. Interfacial pressure and emulsion stability. Colloids and Surfaces 66, 55–62.

Sjöblom, J., Fordedal, H., Skodvin, T., 1996. Flocculation and coalescence in emulsions as studied by dielectric spectroscopy. In: Sjöblom, J. (Ed.), Emulsions and Emulsion Stability. Marcel Dekker, New York, pp. 393–435.

Speight, J.G., Moschopedis, S.E., 1981. On the molecular nature of petroleum asphaltenes. In: Bunger, J.W., Li, N.C. (Eds.), Chemistry of Asphaltenes. Advances in Chemistry Series 195. American Chemical Society, Washington, DC, pp. 1–15.

Thingstad, T., Pengerud, B., 1983. The formation of 'chocolate mousse' from Statfjord crude oil and seawater. Mar. Pollut. Bull. 14, 214–216.

Thompson, D.G., Taylor, A.S., Graham, D.E., 1985. Emulsification and demulsification related to crude oil production. Colloids and Surfaces 15, 175–189.

Tsugita, A., Takemoto, S., Mori, K., Yoneya, T., Otani, Y., 1983. Studies on o/w emulsions stabilized with insoluble montmorillonite–organic complexes. Journal of Colloid and Interface Science 95, 551–560.

Urdahl, O., Brekke, T., Sjöblom, J., 1992. C13 NMR and multivariate statistical analysis of adsorbed surface-active crude oil fractions and the corresponding crude oils . Fuel 71, 739–746.

Yen, T.F., 1981. Structural differences between asphaltenes isolated from petroleum and from coal liquid. In: Bunder, J.W., Li, N.C. (Eds.), Chemistry of Asphaltenes. Advances in Chemistry Series 195. American Chemical Society, Washington, DC, pp. 39–51.