## 24

# Chemical Demulsification of Stable Crude Oil and Bitumen Emulsions in Petroleum Recovery—A Review

**Chandra W. Angle**
*Natural Resources Canada, Devon, Alberta, Canada*

## I. INTRODUCTION

The presence of emulsions in petroleum recovery operations is generally undesirable. Dehydration of the oil is demanded for various reasons. Among the foremost reasons are the high costs associated with transportation, corrosion, and heat demands, in addition to the problems caused by the presence of water/ solids in the refining of crudes or in the upgrading of heavy oils and bitumen. This chapter reviews the chemical dehydration of crudes, heavy oils, and bitumen. First, we present a brief introduction on the extraction processes and the emulsions involved, followed by an outline of the scope of this review.

Emulsions formed in crude oil and bitumen during extraction operations are usually water-in-oil (W/O) macroemulsions (>0.1 to 100 μm in diameter). Macroemulsions are kinetically stable, unlike microe-mulsions, which are thermodynamically stable. In conventional oil recovery (high-energy process), the crude is often in contact with formation water or injection water, as in secondary recovery. In tertiary or enhanced oil recovery, surfactants are used purposely in water floods to make microemulsions for enhancing the flowability of the crude. Crude-oil macroemulsions are produced when two immiscible liquid phases such as oil and water are mixed via the input of mechanical or thermal energy into the processes. Conventional crudes held under high pressures and temperatures amidst porous rocks are recovered by drilling. Emulsions in these oils form mainly through contact with formation water. As crude oil is pumped through various pipes, valves, chokes, etc., under high pressure and/or high temperature, fine water droplets are formed, producing macroemulsions.

The recovery of heavy oil requires stimulation for flow. Flow is often achieved by reducing the viscosity of the oil by heating, as in steam-assisted gravity drainage (SAGD) and fire floods, or by the addition of viscosity-reducing agents. The recovery of water-wet bitumen from oil sands begins with a low-energy process of mining followed by conditioning with process water to release the bitumen. After release, the oil is separated in a series of process stages. Flotation of the bitumenous froth from the middlings and tailings is followed by removal of solids and excess water by dilution, demulsification, and centrifugation. The froth invariably contains 30-60% water before dropout. After dropout, the bitumen product contains 2-3% water which must be dehydrated. Bitumen production from a hot- or cold-water extraction process invariably entails a high degree of emulsification of water and air in the oil. The froth (oil-rich phase) must be treated to remove water, solids, and entrapped air.

Generally, in all recovery processes, if saline water is in contact with the oil, then the salts present in the W/O emulsion droplets must be removed. A washing process is used to remove the salts from the oil after pumping from the reservoir and before transportation. In all these processes W/O emulsion formation is prevalent.

Spills of crude oil on the sea quickly form a W/O emulsion known as "chocolate mousse" which contains approximately 80-90% water. Wave action supplies the mixing energy. These must be demulsified (1) as well.

The crude-oil market demands that water in crudes from all these processes must be removed to a level of less than 0.5% **BS&W** (bottoms, solids, and water) (2, 3). In order to remain competitive, emulsions must be resolved economically. The available treatment options are mechanical, thermal, via electrotrea-tors (electrocoalescers), chemical, or a combination of physical and chemical methods. Chemical demulsifica-tion is one of the most economical means of dehydrating oil.

### A. Scope

The following review presents the chemical demulsification of W/O emulsions by first introducing crudes and bitumens in terms of the diagenetic diversity and chemistries of their components. Based on the premise that a full appreciation of demulsification must be preceded by an understanding of the basics of the field and laboratory emulsions, we have reviewed demulsifica-tion and some of the characteristics of light crude, heavy oil, and bitumen emulsions researched globally. Thus, in this work the composition and behavior of the natural emulsifiers present in the crudes and some factors responsible for emulsification in the field and laboratory are addressed first.

The second approach is understanding how the emulsions' natural stabilizers and their environment can be modified to augment destabilization. This is addressed by a description of the interfacial architecture of the emulsions in terms of how the structure may be first understood and then destabilized by probing the pseudostatic film behavior. This is followed by a description of dynamic properties of the interdroplet lamella, and thin-film behavior with and without demulsifiers. In all these systems the modification of the chemistries of the indigenous surfactants at the interfaces together with the dispersed water chemistry are suggested as tools that may be used toward destabilization. The effects of temperature and heat are addressed briefly.

Thirdly, a fourth section discusses chemical demul-sification processes. Flocculation, creaming/sedimentation, and coalescence and the lamella drainage model are covered. The fifth section discusses the expected performance demanded of demulsifiers for various systems and processes.

This is followed by a description of the chemicals used as demulsifiers in practice and in research. The agricultural and petroleum sources of the basic chemical building blocks are indicated. The typical responses for selected types of chemicals are discussed, in terms of published research findings to date.

Lastly, the impact of demulsifier choices and chemistries on petroleum recovery operations are discussed. We conclude with identification of the need for cooperation between research providers, petroleum operations, and chemical suppliers geared towards an effort for full scientific understanding of demulsifica-tion. Examples of crude-oil properties and demulsifica-tion are drawn from over three decades of published results of researchers worldwide. Examples of demul-sification of bitumen W/O emulsions are excerpted from work performed in the author's own laboratory at CANMET.

## II. PROPERTIES OF CRUDES, BITUMEN, AND WATER

### A. General Properties of Crudes and Bitumen

The world's fossil fuel resources consists of natural gas, liquids (oil sand bitumen and petroleum), and solids such as coal and oil shale. Petroleum represents associated gas, crude oil, and heavy oil (4). The appearance of crude oil ranges from watery white to black liquid. The thin nearly colorless liquid is mobile and flows easily, and the almost black liquid is viscous and thick. Light oils have a low boiling point and heavy oils a high boiling point. Petroleums are fairly balanced systems in terms of the interactions of their components in forming a smooth "solution" while occurring "in situ". Crude oil and bitumen are mixtures of organic compounds normally separated by fractionation through boiling-point differences in the components. Bitumens have a higher proportion of higher-boiling-point constituents than conventional crude oil.

Unlike coal, which is solid and whose surface properties and characteristics are reflections of a Cretaceous (5, 6) or Carboniferous (7, 8) geologic period corresponding with depth of burial, etc., crude oil does not bear such a clear correlation. The fluidity of crude oil made it highly mobile during diagenesis and maturation. The crude moved from its source fossil biomass location. In oil sands the heavy bitumens were integrated in loosely held fine rocks consisting of clays and silica. Crude-oil properties are more closely linked to the rocks through which they moved (9, 10). Thus, the composition of the oil varies, depending on the precursors, i.e., the nature of the biomass sediment, the underground environment, the temperatures and pressures experienced under the maturation conditions, and the naturally occurring migrations or separation processes involving inorganic catalysts (11).

Experience has shown that crudes from adjacent wells can be different in composition. The surface, physical, and chemical properties of associated emulsions can be expected to be as diverse and complex as the source crudes and water. The variances in the elemental C, H, and N composition of components such as asphaltenes of crudes from various geologic origins as compiled (10, 12) show no apparent pattern emerging from the data as was the case with coal (5, 7). Sharma et al. (13) have shown the use of bitumen asphaltenes as thermal maturation indicators.

## B. Chemistries of Crude Oils and Bitumen

### 1. Chemical Characteristics

In a series of published works (4, 9), Speight has shown the distribution of various organic structures in conventional crudes relative to heavy oil and bitumen. Heavy oils and bitumens have the largest proportions of polynuclear aromatics and polycycloparaffins, and the lowest proportions of normal and branched-chain paraffins and monocycloparaffins. Heavy oils and bitumens have boiling points higher than those of conventional crudes. The high degree of isomerization in organic chemicals found in all crudes and bitumens accounts for some of the complexity and variability of crudes of similar elemental analytical C, H, N, O, and S composition.

Crude oils have the same elemental make up globally. The carbon content of crude oils is relatively constant, but the varying quantities of hydrogen and heteroatoms are responsible for the major differences between the petroleums. The elemental composition ranges are carbon (83-87%), hydrogen (10-14%), nitrogen (0.1-2%), oxygen (0.05-1.5%), and sulfur (0.05-6.0%). Metals such as vanadium, nickel, and iron occur as metalloporphyrins, which add polar character to the oils. In petroleum refining the metals also poison catalysts. In refining, the nitrogen decreases the yield, and the presence of sulfur not only demands extra processing, but also indicates a lower quality product. These elements constitute a mixture of organic molecules classified as saturates, aromatics, resins, and asphaltenes (**SARA**), and waxes. The classification is empirically based on distillation fractions and solubility in alkanes (9).

Data published on crude-oil composition are often based on **SARA** components. This is illustrated in Table 1. Variations arise from the sources and the methods of extraction. Although the major components of crude oil are the same throughout the geologic origin, the proportions of the

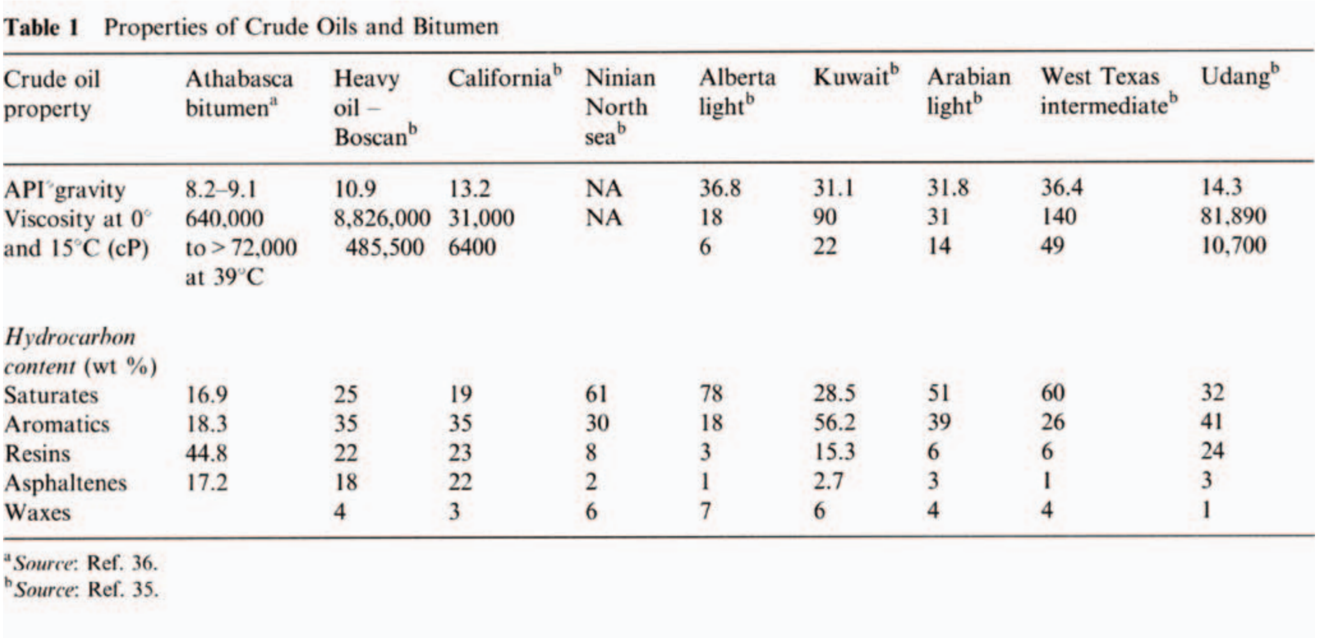


**Table 1** Properties of Crude Oils and Bitumen

| Crude oil property | Athabasca bitumen[a] | Heavy oil – Boscan[b] | California[b] | Ninian North sea[b] | Alberta light[b] | Kuwait[b] | Arabian light[b] | West Texas intermediate[b] | Udang[b] |
|---|---|---|---|---|---|---|---|---|---|
| API° gravity | 8.2–9.1 | 10.9 | 13.2 | NA | 36.8 | 31.1 | 31.8 | 36.4 | 14.3 |
| Viscosity at 0° and 15°C (cP) | 640,000<br>to > 72,000 at 39°C | 8,826,000<br>485,500 | 31,000<br>6400 | NA | 18<br>6 | 90<br>22 | 31<br>14 | 140<br>49 | 81,890<br>10,700 |
| *Hydrocarbon content* (wt %) | | | | | | | | | |
| Saturates | 16.9 | 25 | 19 | 61 | 78 | 28.5 | 51 | 60 | 32 |
| Aromatics | 18.3 | 35 | 35 | 30 | 18 | 56.2 | 39 | 26 | 41 |
| Resins | 44.8 | 22 | 23 | 8 | 3 | 15.3 | 6 | 6 | 24 |
| Asphaltenes | 17.2 | 18 | 22 | 2 | 1 | 2.7 | 3 | 1 | 3 |
| Waxes | | 4 | 3 | 6 | 7 | 6 | 4 | 4 | 1 |

[a] *Source*: Ref. 36.
[b] *Source*: Ref. 35.

**SARA** components and their chemistries differ from source to source. Figure 1 shows a schematic of petroleum as represented by Pfeiffer and Saal (14).

Saturates describe paraffinics and cycloparaffinics or napthenics which are alkyl (methyl, ethyl, isopropyl) substituted cyclopentanes and cyclohexanes. The normal or branched alkanes and cyclic structures consist of one to five rings and various degrees of alkylation. According to Mackay (15), cyclic structures dominate in degraded oils. The saturates are the solvents for the higher-molecular-weight components.

If an oil is described as highly paraffinic and waxes are identified, these are usually "paraffinic waxes" which have basically straight- and branched-chained hydrocarbons ($C_{18}H_{38}$ to $C_{40}H_{82}$). Wax contents up to 50% (Altamount Utah) and as low as 1% in Louisiana can be found (16). Wax solubility in the crude oil is dependent on the chemical composition of the crude, as well as the pressure and the temperature the waxes experience (17, 18). Wax crystallizes out as an equilibrium temperature and pressure is reached around the cloud point of approximately 77°C. Leontaritis (19) describes the wax deposition envelope as the thermodynamic point in the pressure, temperature, phase composition diagram where crystallization occurs. Wax crystals are partially responsible for increased crude-oil viscosity and some of the changes in flow behavior from Newtonian to nonNewtonian. As temperature decreases crude becomes very viscous (pour-point range 16.5°-51.5°C). Thus, the viscosity of the waxy crude will depend on both the oil viscosity and the aggregation of wax crystals, whose sizes depend on the rates of cooling. Methane prevents wax crystal agglomeration, while butane decreases it by dilution (20). Wax is completely hydrophobic and is not surface active. However, the waxes are believed to attach themselves to the nonpolar ends of polar surface-active components of crudes (21). In this form they contribute to emulsion stability by participating in the interfacial film architecture. Their contribution to increased oil phase bulk viscosity assists in preventing coalescence by decreasing the mobility of the droplets (22, 23).

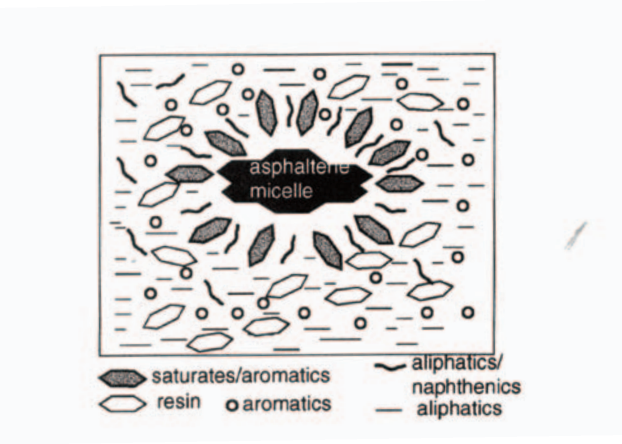


**Figure 1** Schematic of petroleums. (From Ref. 14.)

Aromatics in crude, on the other hand, are similar in structure to saturates, but contain many condensed aromatic rings instead. Low concentrations of oxygen and nitrogen are found in some polycyclic aromatics. Increased amounts of condensed rings of napthenics are attached to the aromatic rings. Molecular weight increases with increased condensation (4).

The polars describe mainly the resins, asphaltenes, and the poryphyrins, as well as the trace nitrogen found in bases, the nonbasic poryphyrins, the oxygen in the phenols, the napthenic acids and esters, and the sulfur in sulfide and disulfide bonds. The polars and the metalloporphyrins are indicated as emulsifier species involved in stabilizing the emulsions (24, 25). Resins, which will be discussed later with asphaltenes, contain O, N, and S in the form of carbazoles, fluor-enones, fluorenols, carboxylic acids, and sulfoxides. These are attracted to water interfaces.

## 2. Crude Oil Acidity

The relative acidity of the crude is an indicator of the presence of polar acidic species such as phenols, napthenics, heterogeneous organic species, and anionic surfactants in the sample (26).

The acid numbers (mg KOH/g crude needed for neutralization) are indicative of the corrosivity of the crude and so suggest a value detrimental to crude (27). Jennings studied 164 crudes from 78 fields to determine an overall view of acidity (28). Worldwide crude oil acid numbers vary from less than 0.01 to as high as 3 (29). Relative to this, values for Canadian heavy oil (0.3-2.8) and bitumen (3.7) appear on the high side, closer to 3 (30, 31). There have been attempts at correlating acid numbers with the stability of emulsions, and using this as an empirical means of selecting demulsifiers for treating Venezuelan crudes (32). However, the correlations have not been tested on other crudes.

A polarity indicator was developed by Bruning, using inverse gas chromatography for 98 Brazilian and 5 foreign (Far East and Russia) crudes (33). The APIO gravities [crude oils are classified by the American Petroleum Index (API°) gravity, which is a number derived empirically (141.5 divided by specific gravity at 15°C minus 131.5)] were correlated with these numbers. Low **API°** corresponded to high polarity. Crudes of extra high polarity (above 500) appeared to be highly degraded or to have high heteroatomic content and a propensity to form very stable emulsions that would require demulsification for more economic processing. However, according to Bruning, high numbers do not necessarily indicate degraded crude (34). Tests must be done to confirm such degradation or oxidation. In most cases the number reflected high asphaltenes and resin contents. Crudes with polarities between 300 and 400 have emulsion separation problems, while low-polarity crudes (from 200 to 300) appear to have no treatment difficulties. These characteristics of crude oils are indicative of the possibility of the formation of tight (very stable) or loose (not very stable) emulsions that require demulsification treatments. Demulsifiers are often selected on this basis as well.

## 3. Physical Characteristics

### *a. Specific Gravities and Viscosities*

The specific gravities of crudes and bitumen vary from 0.75 (57 **API°**) to 0.95 (17 **API°**). **API°** gravity indicates the relative categorization of the crude as light (>30), medium (15-30), and heavy (<15). A high **API°** indicates lighter products that are saleable. Bitumen and heavy oil are of low **API°** with densities closer to water. This presents difficulty in gravity separation techniques. However, viscosity differences are large between crudes and water. Table 1 describes some physical and chemical properties of bitumen and crudes from various sources (35, 36).

The increase in **API°** has been correlated with increased reservoir depth (synonymous with increased temperature), which results in an increased fraction of compounds with less than 12 carbons (more paraffmic) in the crudes (9). High **API°** is normally associated with low asphaltene content and high sulfur content (9). The major physical differences between bitumens, heavy oils, and conventional oils reside in the specific gravity and the viscosity. These are very high in bitumen and heavy oils due to a preponderance of high-molecular-weight aromatic components such as resins and asphaltenes. Bitumen has the highest viscosity, followed by heavy oils, and then conventional crudes, at all temperatures. In a comparison of viscosity with increasing temperature for conventional crudes, heavy oils, and bitumen, there is an almost parallel asymptotic decrease in viscosity as temperature is increased. The highest viscosity values at each temperature were attributed to bitumen, followed by heavy oils and conventional crudes [4] (see Fig. 2).

Waxy crude oils, such as those found in the North Sea (20), would not produce a smooth decline in viscosity with increases in temperature. Wax as fine particles would contribute to a high viscosity and when heated between 50°C and 65°C would melt or solubi-lize in low-molecular-weight components, producing a more homogeneous fluid (17, 18). The properties of crude oils and bitumen are listed in Table 1.

### *b. Molecular Weights and Micellar Sizes*

As determined by vapor-pressure osmometry (**VPO**), the average molecular weights (**MWts**) of Canada's heavy oil from Norman Wells, Countess, and Cold Lake were reported to be 197, 334, and 585 g/mol, respectively (37). Relative to other feedstocks the range appears as given in Table 2.

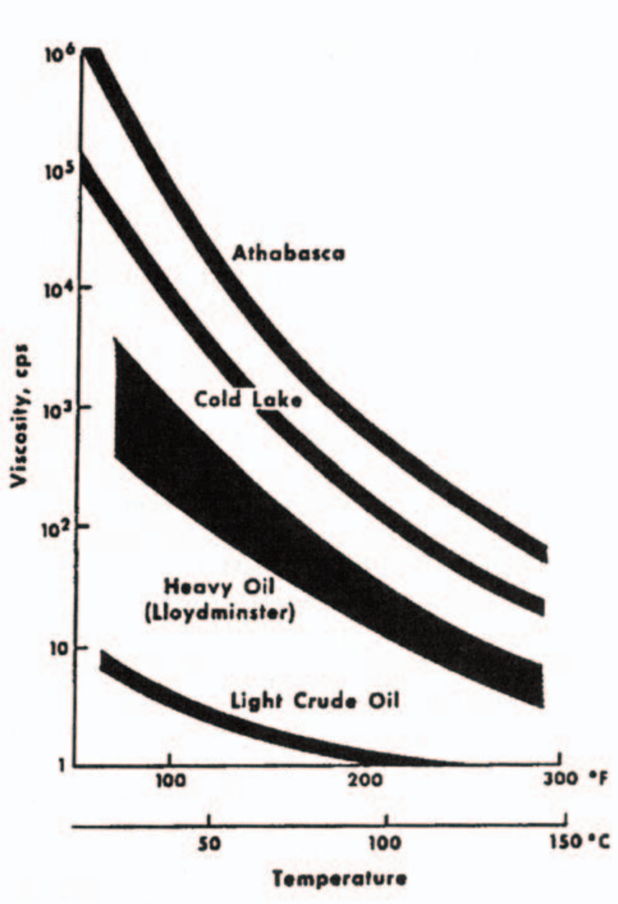


**Figure 2** Viscosity decreases with increasing temperature for conventional crudes compared with heavy oils and bitumens. (From Ref. 4.)

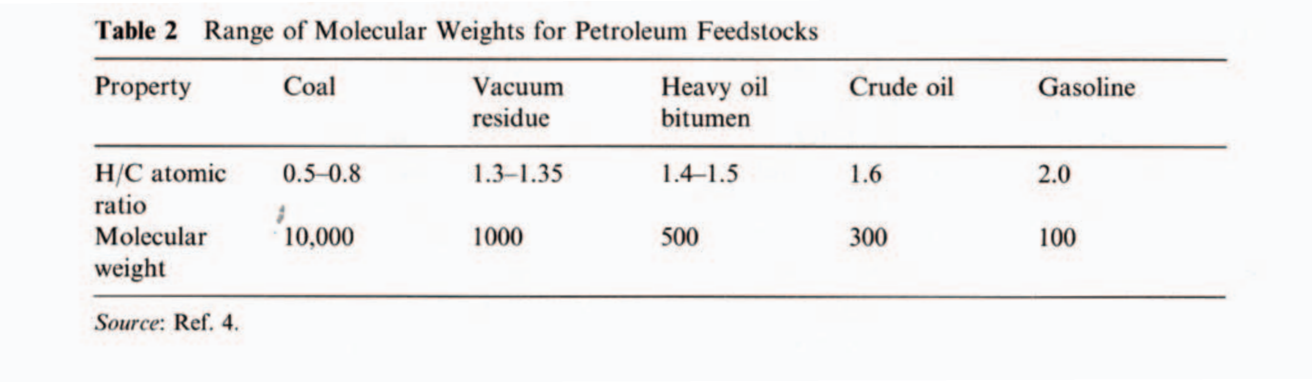


**Table 2** Range of Molecular Weights for Petroleum Feedstocks

| Property | Coal | Vacuum residue | Heavy oil bitumen | Crude oil | Gasoline |
|---|---|---|---|---|---|
| H/C atomic ratio | 0.5–0.8 | 1.3–1.35 | 1.4–1.5 | 1.6 | 2.0 |
| Molecular weight | 10,000 | 1000 | 500 | 300 | 100 |

*Source*: Ref. 4.

For additional data on crude oils with **MWt** around 300 g/mol the reader is referred to Speight (4). High asphaltene content is synonymous with higher **MWt**in oils. In VPO determinations all asphaltenes in heavy oil tend to have higher **MWt**than their resin counterparts (4, 38). The resins are generally of lower **MWt**than the asphaltenes. Ferworn et al. (39) have published data on the average **MWt**(300-500) of some of Alberta's crude oils and their properties and their distributions in various solvents (37). The agglomeration (40) of the asphaltene components and the bitumen behavior with paraffinic solvents are also discussed by Funk (41).

Extensive data on the chemical and physical properties of asphaltenes have been published in several texts. The **MWt**of asphaltenes in various solvents and at various temperatures are reported by Speight (42). The MWts range from 2000 to 7000 g/mol based on geologic period (Cretaceous, Carboniferous, Devonian) and depending on the methods of precipitation. For the pentane-precipitated asphaltenes, when solubi-lized in benzene, the **MWt** reported was 5120 g/mol; when solubilized in pyridine the **MWt** was 13,390 g/ mol. Asphaltenes extracted by 3-pentanone showed higher MWts of 18,000 g/mol. For the heptane-precipitated asphaltenes, when dissolved in benzene, the reported value for **MWt** was 8500 g/mol, and when dissolved in nitrobenzene, the **MWt** was 2880 g/mol. The reported **MWt** of asphaltenes appeared to decrease with polarity of the solvent and increase with concentration in the solvent, suggesting that the association structures or micellar sizes are influenced by thermodynamic solubility-parameter differences between the asphaltenes and the solvent. Resins appear to have a **MWt** close to 700 for pentane solubles and 1050 for heptane solubles. The MWts of resin are less affected by solvents and are generally significantly lower than those of the corresponding asphaltenes (4).

Thus, asphaltenes (43) are high **MWt** pentane- or heptane-insoluble fractions of crudes and are readily peptized by resins which are the alkane-soluble fraction. Figure 3a-c illustrates a few of the various chemical models developed for asphaltenes from structural and chemical analysis. Resins make up the outer protective coating of asphaltene micelles or clusters (43-45). The resins are dissolved in the oil, are also surface active and polydisperse with a range of polarities and aromaticities. Figure 4 illustrates the chemistry for a typical resin molecule (46). Resins sometimes from reversible micelles. The resins are less polar and of lower **MWt** than asphaltenes and appear as dark sticky semisolid liquids in n-alkanes. Manek (23) characterized the asphaltenes and resins of three Canadian heavy oils, one Texas heavy oil, and one California heavy oil to show the relative surfactant-enhanced dispersibility of asphaltenes in resins.

The insolubility of asphaltenes causes deposits in pipes, wells, and valves, and in the formations. Dubbed as the colloids of crudes (47, 48), the asphaltene chemistry has received considerable attention. Asphaltenes are considered as major polar species with high aromaticity and are known as the major building blocks of the mechanical barriers or interfa-cial films formed at the W/O interface. Increased **MWt**s is consistent with high aromaticity and greater numbers of incorporated heterocyclic structures containing the heteroatoms. Their structures have received considerable attention of late.

Even in dilute solutions they associate (49, 50). Published sizes of the micelles vary from 2 to 4 nm. Sophisticated analytical techniques such as small-angle X-ray diffraction (**SAXS**), small-angle neutron scattering (**SANS**), and **NMR** were used to study the asphaltene particle or "micelle" sizes (51). MacKay (15) reported that a **MWt**of 10,000 g/mol would correspond to a 2 to 4-nm cluster. This is very much smaller than a 1-µm water droplet, and considered to be 1/100 to 1/1000 the droplet diameter. This topic is worthy of a review on its own. However, the colloidal properties of asphaltenes, micelles, and

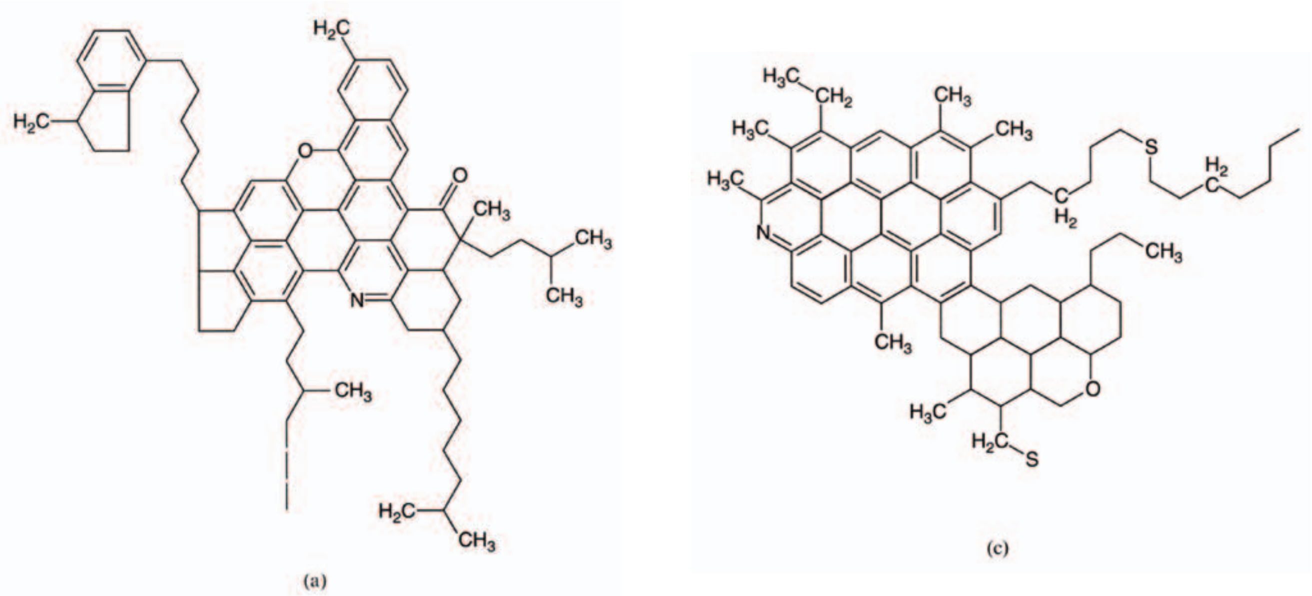
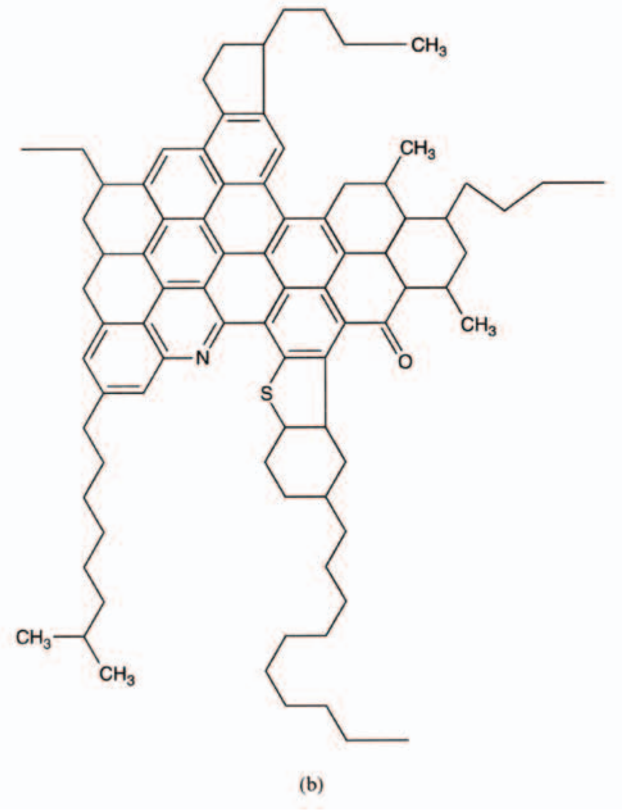


**Figure 3** Models of asphaltene chemical structures: (a) California; (b) Venezuela; (c) Athabasca. (From Refs 4,42, and 43.)



solvent effects are compiled and reported by several authors (52, 53).

From data obtained by **SANS** analysis, Sheu and Storm (48) reported that the sizes of asphaltene micelles in a good solvent such as toluene/pyridine fall in the range 3.0-3.2 nm.

Although asphaltenes have been extensively studied in terms of colloidal (47, 54-56) and fractal properties (37, 57) they are not yet fully understood in terms of their interactions with other components of crudes, solubilities in various solvents and crudes, precipitation, and micellization (58). Asphaltenes appear to be the key component, together with resins, in forming a mechanical skin often described as structurally rigid, viscoelastic, or a deformable interfacial film - and the barrier to coalescence. Much of emulsion stability research which focussed on the film stability described the films in terms of mechanical or rheological behavior with varied characteristics of the system. Figure 5 shows a schematic of these fractions arranged about the interface of a water droplet. The natural surfactants are illustrated with the head group in the water phase and tails in the oil phase. As time progresses the organization of the surface-active species changes in the interfacial region. The changes, which lead to more concentration of species at the interface over time, will be discussed later in this chapter.

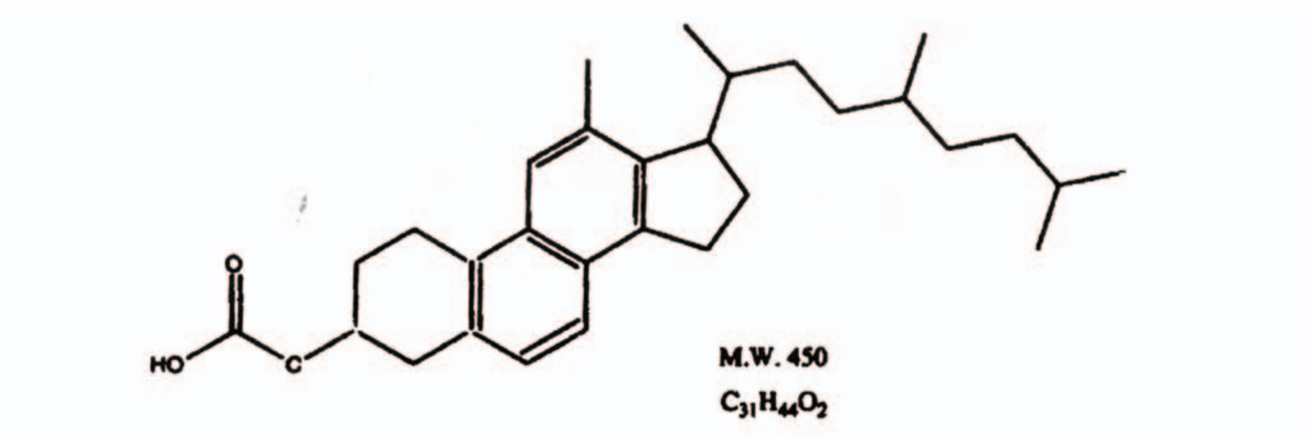


**Figure 4** A model of resin chemical structure. (From Ref. 46.)

Figure 6 describes other components that may be present inside and outside the droplets.

## C. Water

In the petroleum industry, not all W/O emulsions are the same. The nature of emulsions formed in crude oil often depends on many factors: the geologic source and the engineering processes utilized in the crude oil recovery, the chemical and physical characteristics of the crudes and their thermal history, the type of mixing and energy introduced, and, most importantly, the formation and process water chemistry and composition. All these determine the stability and the sizes of the emulsion droplets.

All formation or extraction water differs in ionic composition and pH. Generally, formation water for the North Sea crudes is far more saline than that for the heavy oils and bitumen. Table 3 compares typical water compositions found in emulsions (59-61).

Thus, the W/O emulsions reflect the complexity of the above factors. Since the natural chemistries of crude oils or petroleum contain the stabilizers of the W/O emulsions, the chemical destabilization or demul-sification requires knowledge of not only the emulsion interfaces, but also the physicochemical characteristics of the oil and water.

Parts of this complexity are addressed in published information on chemical destabilization of crude W/O emulsions. Examples include studies on California (62), Salem

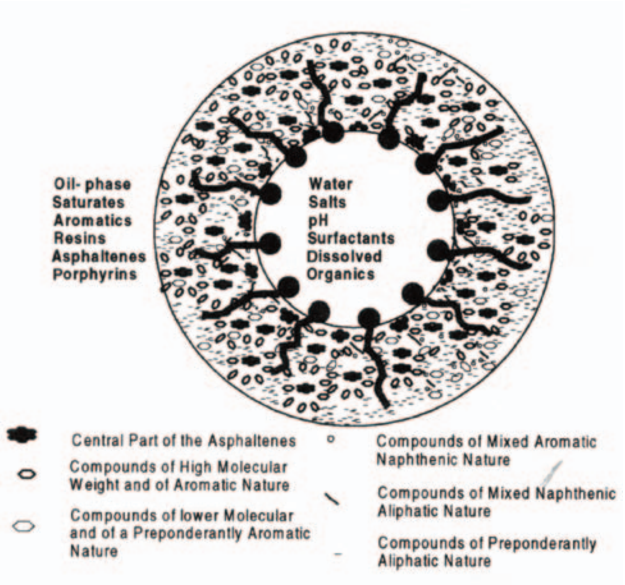


**Figure 5** Schematic of droplet of W/O emulsion with per-troleum fractions arranged in the interfacial layer or skin around the droplet at early stage of formation. Solids and waxes are not indicated.

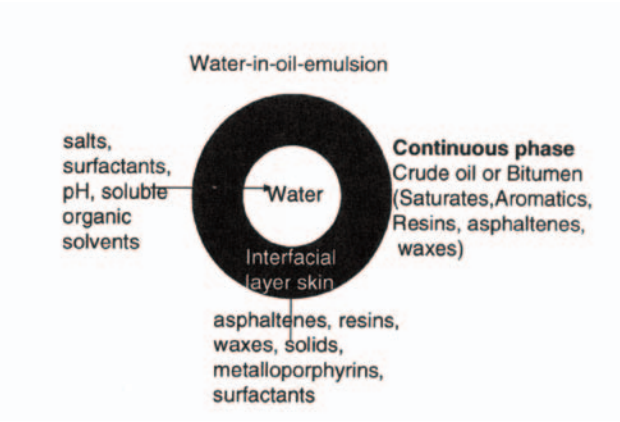


**Figure 6** Schematic of components of crude oils and bitumen to be considered in an emulsion droplet and the interfacial layer.

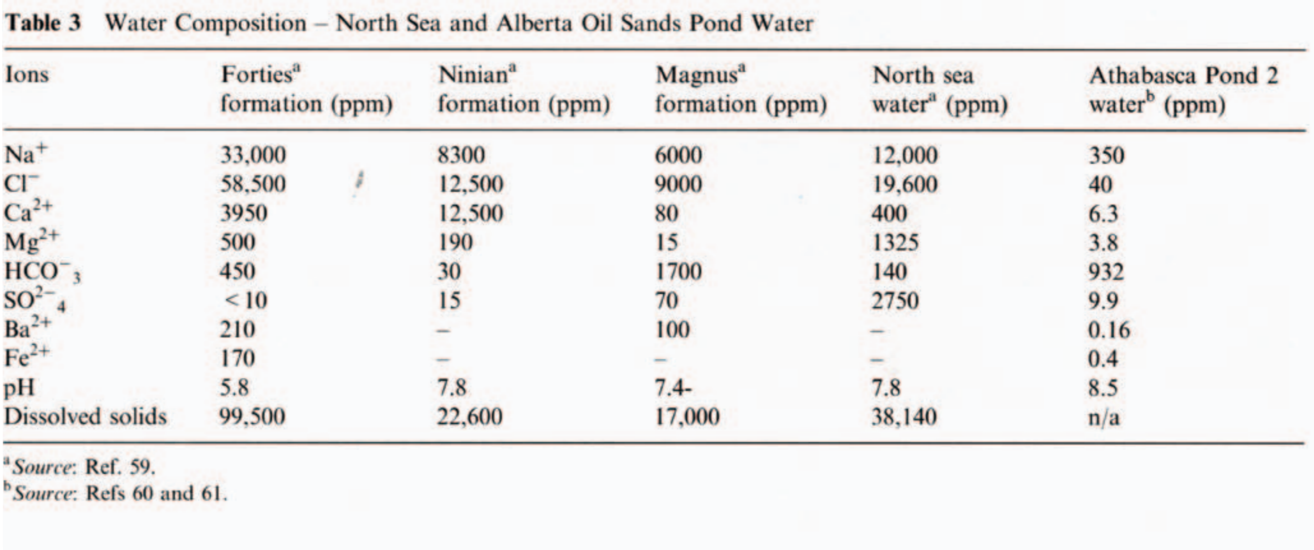


Table 3 Water Composition – North Sea and Alberta Oil Sands Pond Water

| Ions | Forties[a] formation (ppm) | Ninian[a] formation (ppm) | Magnus[a] formation (ppm) | North sea water[a] (ppm) | Athabasca Pond 2 water[b] (ppm) |
|---|---|---|---|---|---|
| $Na^+$ | 33,000 | 8300 | 6000 | 12,000 | 350 |
| $Cl^-$ | 58,500 | 12,500 | 9000 | 19,600 | 40 |
| $Ca^{2+}$ | 3950 | 12,500 | 80 | 400 | 6.3 |
| $Mg^{2+}$ | 500 | 190 | 15 | 1325 | 3.8 |
| $HCO^-{}_3$ | 450 | 30 | 1700 | 140 | 932 |
| $SO^{2-}{}_4$ | < 10 | 15 | 70 | 2750 | 9.9 |
| $Ba^{2+}$ | 210 | – | 100 | – | 0.16 |
| $Fe^{2+}$ | 170 | – | – | – | 0.4 |
| pH | 5.8 | 7.8 | 7.4- | 7.8 | 8.5 |
| Dissolved solids | 99,500 | 22,600 | 17,000 | 38,140 | n/a |

[a] *Source*: Ref. 59.
[b] *Source*: Refs 60 and 61.

(63), Texas (64), Louisiana (65), North Sea (66, 67), Kuwait (68), Assam (69), Indian (70, 71), Boscan and other Venezuelan (72, 73), Velden (74, 75), Bavarian (76), Hungarian (22), Egyptian (77, 78), Norwegian (79-81), and Canadian (82-88) heavy oils and bitumen. The crudes, heavy oils, and bitumens differ geographically, and hence in their diagenetic histories. Their physical and chemical properties reflect their diversity not only in the W/O emulsions formed in them, but also in the response of their emulsions to demulsifiers. Because of the water and electrolytes, petroleum W/O emulsions translate into high processing heat requirements, corrosion problems, and increased transportation costs. Demulsification is a necessity.

## III. FORMATION AND STABILITY OF CRUDE OIL AND BITUMEN EMULSIONS

### A. Production Emulsions and Stability

In the process of crude oil extraction and transportation the formation of emulsions is inevitable. As the immiscible fluid mixtures pass through piping valves, porous rocks, etc., and experience turbulence, especially at high pressure and/or high temperature, breakup and deformation occur. If the ionic composition or pH of the water is favorable, and surface-active agents are present, emulsion formation is enhanced (89-92). The degree of emulsification depends on several factors: the energy of the process, the amounts of surface-active components in the crude oil, the physicochemical properties of crudes, water, and surfactants, and the residence time, as emulsions age. Aged crude-oil interfacial films become more resilient over time (74, 93) and are therefore more difficult to demulsify (94, 95). Finer and more stable emulsions occur with prolonged high-energy input in these systems.

In a destabilization scheme, one first assesses the degree of stability of the emulsion. There is a need to know how much time and energy are crucial for the process, the phase compositions, and the emulsifier(s) chemistry. For the experienced engineer, this information then allows some deductions on the configuration of emulsifiers around the droplets, and the rheological properties of both the interfacial film on the droplet and the interphase lamella between droplets. The viscosities of the emulsions and continuous oil phase are also important for decisions on destabilization (96).

In production the quantities of water in emulsions vary from 30% W/O formed in oil sands extraction processes to 80 or 90% in the form of "chocolate mousse" during an oil spill at sea (97, 98). Real systems are more complex and heterogeneous than the ideal systems. The W/O droplets are fine, well dispersed, and very stable. Asphaltene content is around 17% in bitumenous emulsions and around 2% for North Sea crudes. Figure 7 shows a confocal photomicrograph of a bitumen froth emulsion freshly extracted at **CANMET**. The solids present are shown as white specks; the dark spots are emulsion droplets in a bitumen continuous phase. The composition is 41% bitumen, 44% water, and 15% solids.

Some emulsions exist for a few minutes; others can stay in suspension for years. The life/death cycles are dependent on the stability and the destabilizers. The sizes of the droplets and the rigidity of the surface film barrier determine the lifetime of the emulsion droplets. For convenience in treatment, the terms for definition of stable emulsions

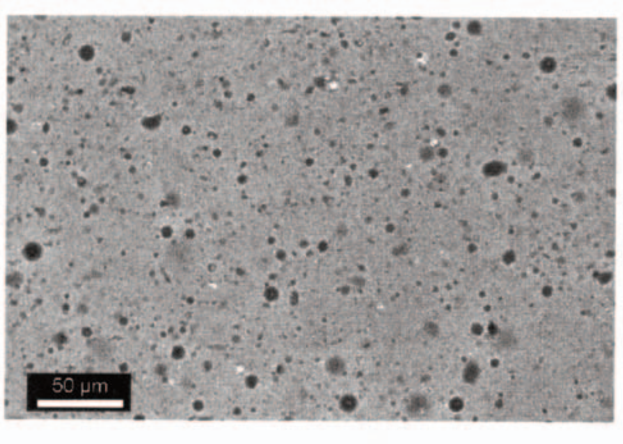


**Figure 7** Confocal photomicrograph of freshly extracted bitumen froth - Dark spots are water droplets, white specks are solids particles. Composition by weight is 41% bitumen, 44% water, 15% solids.

are determined by their persistence in the process time scale, and thus are categorized kinetically only in operational terms. Planned studies on emulsions should consider operational conditions in the experimental design.

It has been found that the finer the emulsions the more stable they are in terms of resistance to coalescence, as the fine emulsions behave as hard nondeform-able spheres (99). The increased ratios of the dispersed water phase to continuous oil phase determine the packing factor. Most often a packing density of 0.74 tends to be critical for destabilization (100) for ideal monodisperse spheres in a hexagonal arrangement in the systems (101). This packing factor increases considerably for polydisperse systems such as crude oil emulsions. With creaming there is increased packing and some deformation occurs in the more elastic systems; the emulsions may appear as foams, with phase ratios between 0.8 and 0.9. Any increase in the critical packing factor can cause instability of the emulsions. Thus, valuable information on stability or instability (102) can also be obtained by varying the volume fraction of the dispersed phase under flow conditions. Here, the emulsion bulk rheological responses are a function of imposed external stresses and constraints and can be signatures to the system stability in a process.

The period of time in which the droplets do not coalesce without mechanical, electrical, or chemical aids has become the kinetic guideline for stable emulsions. In the extraction of oil in the petroleum industry very stable emulsions are undesirable. The exceptions are "orimulsion" fuels (103), made in Venezuela, and/ or emulsions especially tailored in formulation for transportation in pipelines (104, 105). These must be destabilized on delivery (106, 107).

Much of the early literature published on chemical demulsification involved emulsions of crudes from offshore operations and other conventional land-extracted light oils. Thus, much of the knowledge acquired about crude-oil emulsion stability was based on paraffinic crudes of low asphaltene content. It is essential to be aware that results for crudes of the North Sea operations were based on a high wax content, and low asphaltenes and resins content (108) (see Table 1), when compared with results for highly aromatic and asphaltenic heavy oils and bitumen, which are low in wax, and higher in resins. The latter emulsions would be those of Canadian (Alberta) bitumen, heavy oils from Boscan (Venezuela), and Canada and California crudes, which are all highly aromatic and asphaltenic. These W/O emulsions are known to be very stable or "tight" (23).

Generally, oilfield emulsions are most often W/O with the surface-active emulsifiers residing in the crude-oil continuous phase. According to the Bancroft rule (109) the phase for which the emulsifiers are most soluble is the continuous phase. The emulsifiers possess some degree of polarity which attracts them to the water phase. Solid emulsifiers would be very fine particles in a state of incipient flocculation (110). The emulsifiers may be one or more of the following: solids which are partially hydrophobic with contact angle ($\theta \geq 90°$), polar asphaltenes and resins with some partial insolubility induced by solvents which dilute the crude oils, or metalloporphyrins integrated within the asphaltenes (24, 25).

A knowledge of solvents and solubilities is crucial for understanding the (in)stability. The solvent power is a function of the molecular structures. Aromatics have the greater dispersion forces and higher solution energies and thus superior solvent power. For Athabasca bitumen (111) the solvencies are as follows: paraffins < olefins < napthenes < cyclo-olefins < condensed napthenes < aromatics < condensed aromatics. This is also true for other crude and heavy oils (50) to various degrees. Thus, the choice of solvent can determine the degree of emulsion stability.

The structures of asphaltenes, as first deduced by Pfeiffer and Saal (112), showed them as fine aggregated particles solubilized in resins (14). Later, the solvent effects on their colloidal natures and their roles in the resiliency of the interfacial film formed at the boundary between the water droplet and the oil phase became important in the destabilization models (113, 114).

The role of waxes in emulsion stability has been studied in great detail for paraffinic crudes, especially for crudes that were spilt in the sea (115, 116). Waxes are believed to interact hydrophobically with the asphaltene and resin micelles present in the crude oils (18, 20, 21) and become part of the emulsion film. Waxes were hypothesized to adhere to the asphaltenes and resins, since waxes are oil soluble and not srrface active. With such emulsions, the temperature prehistory and cooling rates have a greater impact on the emulsion stability. The rate of cooling influences the wax crystal sizes (17, 18). Thus, the type and history of emulsions must be considered before a demulsification treatment is selected.

Generally, the less soluble, surface-active materials tend to accumulate at the water/oil interface building the film structure. The thickness and concentration of these materials around the droplet periphery build over time until the layer becomes a structural barrier against coalescence with other droplets.

## B. Emulsions on a Bench Scale

Emulsification and demulsification of bench emulsions have been reviewed extensively in the past (89-92). The reader is referred to these publications for a more detailed fundamental background on theories and developments in laboratory measuring techniques for stable emulsions (117). To determine a destabilization program for emulsions it is often advisable to seek to understand first the interfacial properties in the emulsions (118). Most of this understanding is derived from bench studies.

Often, in bench studies aimed at understanding emulsion-stabilization mechanisms, a hypothesis is devised. Most often the components of crudes are first separated, and a model emulsion is prepared from various combinations of the components in a model oil and in water of quality similar to that of formation or process water. The stability or instability is traced either by water resolution or by observing the interfacial film properties under some form of externally applied stress over time. The stress may include temperature increases or solvent changes. The system may then be modified by the demulsifier and the changes in behavior are compared to that without the demulsifier. Deductions are then made about the film mechanics of the system in response to the variables.

When actual crude oil is studied, comparisons of the responses of the components in crude are usually made with those of the whole crude oil under similar conditions.

Often the actual field system is used to test conclusions arrived at on model systems. In many cases the behaviors of several crude oils are compared under similar conditions for rigor. It is therefore important that representative crude oil samples from a process be obtained.

In the following discussions the published experimental findings are presented interrelatedly first in terms of internal oil chemistry at the interface and instabilities based on its composition, secondly in terms of effects of water chemistry, and thirdly in terms of demulsifier interaction. We include the activity of interfacial components involved in the structure of the protective skin, the behavior(s) of this structure with changes to water chemistry or solvency, or the effects of changes in film structure itself due to modification of relative proportions of interfacially active components. In some examples, developments in interfacial rheology, which is both a tool for understanding stable films and a means of rationalizing the effects of demulsifiers in demulsification, are discussed interrelatedly. Films may be sensitive to crude oil type, gas content, aqueous pH, salt content, temperature, age, and the presence of demulsifiers. Demulsifier performance is also influenced by many of these variables.

We distinguish first between the adsorbed skin at the W/O interface and the gap or lamella between approaching drops, which may be described as: W/I-interface/O/I-interface/W. Here, “1” is the boundary layer of the interface on the droplet surface, and O is crude oil or dilute bitumen between two water droplets, interfaces. Figure 8 is a photomicroph of two bitumen-stabilized water/oil droplets showing the interfacial skin and the interdroplet lamella. Figure 9 is a photomicrograph of several water droplets

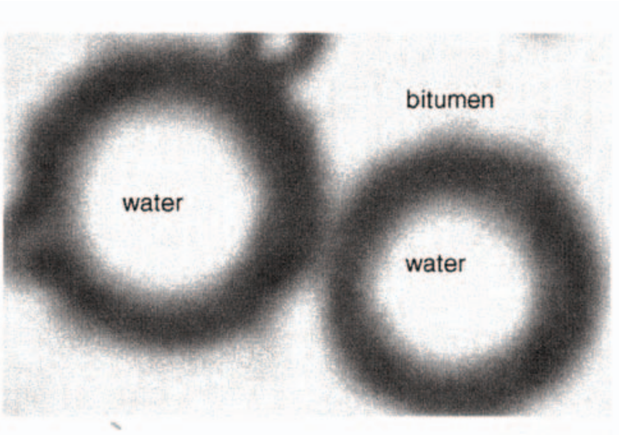


**Figure 8** Photomicrograph of two water droplets showing the interfacial skin and the interdroplet lamella.

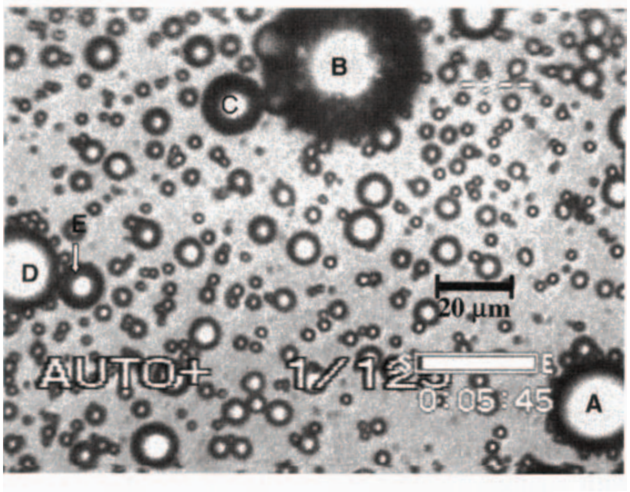


**Figure 9** Photomicrograph of water in bitumen emulsion distribution with interfacial layer shown as the dark ring around the white droplet.

showing thick bitumen interfacial skins as dark circles around the bright water droplet. The continuous phase is the diluted bitumen.

Emulsion formation mechanisms are not the reverse of demulsification mechanisms. Crude-oil emulsion formation may involve one or more mechanisms based on the process of immiscible phases interacting, in time, with energy. To date, the detailed mechanisms are not yet understood completely, especially for petroleum emulsions.

In the laboratory, very reproducible W/O emulsions of monodispersed size distributions can be prepared when all the variables for emulsification are controlled. The variables for a bench laboratory study are: emul-sifier type and concentration, energy of mixing, time of mixing, method of mixing, volume fractions of oil and water phases, type and viscosity of oil, quality of water, and temperature. The mixture is blended in specific vessels, usually with rest intervals to control the rigidity of the film. The conditions are reproduced from batch to batch. In real production this is not often the case. The immiscible phases are subject to variable high shear for 2-8 min in offshore production and 40-50 min in the oil sands extraction process. Emulsion size distributions therefore vary with different systems.

Several bench-scale model emulsions were prepared from bitumen in toluene, by varying only the water quality to observe the basic differences in the emulsions.

Figure 10 (a,c,e) shows a series of photomicrographs of model bitumen emulsions freshly prepared with deionized, 1 mM NaCl and synthetic pond water. Figure 10 (b,d,f) shows that emulsions become larger with age, supporting the kinetic instability. After 24 h there are differences in the final appearance of the emulsion for each sample of water used. The growth of droplets is due to Oswald ripening. It is expected that the interfacial film would differ in strength. Note the increasingly finer emulsions initially formed as the water changed from deionized to NaCl to synthetic pond water under identical experimental conditions. After 24 h the same trend is still observed.

## C. Emulsions' Interfacial Film Structure and Instabilities

Undertaking first to achieve an understanding of the building blocks of the mechanical film could lead to the detection of surface weaknesses at which a demulsifier can be targeted. We illustrate this with examples from the literature.

In a review on formation and stability, Mackay (15) has suggested that the most stable emulsions have water particles in the 1 to 5 λm range, with a film thickness of 1/100 the diameter of the droplet. For bitumen W/O emulsions we have found in our laboratory that these are typical average droplet sizes (see Figs 7, 9 and 10). If we deduce the film structure from the components of crudes, then droplets are much larger than the components in the film. Mackay and Mason (119) have reported that asphal-tene clusters can be about 2-4 nm in diameter and Neumann and Paczynka-Lahme (120) reported that asphaltenes were retained on filters of pores of 35 to 10 nm, while resins were retained on pores of 5 nm. Speight (4) reported that the asphaltene sheets are 10-15 Å by 6-15 Å. Bhardwaj and Hartland (74) reported that on an emulsion droplet the average cross-sectional interfacial area occupied by surface-active species from crude oil was experimentally shown to be 366 Å$^2$, while that for the asphaltenes in toluene was 253 Å$^2$. Larger water droplets (>10 µm), which will cream faster, tend to have a thinner film of between 1/100 and 1/1000 of the droplet diameter, on crude oil emulsions according to MacKay (15).

### 1. Observations of Destabilization of the Pseudostatic Film

The thick protective interfacial skins are considered as largely responsible for the stability of crude oil emulsions.

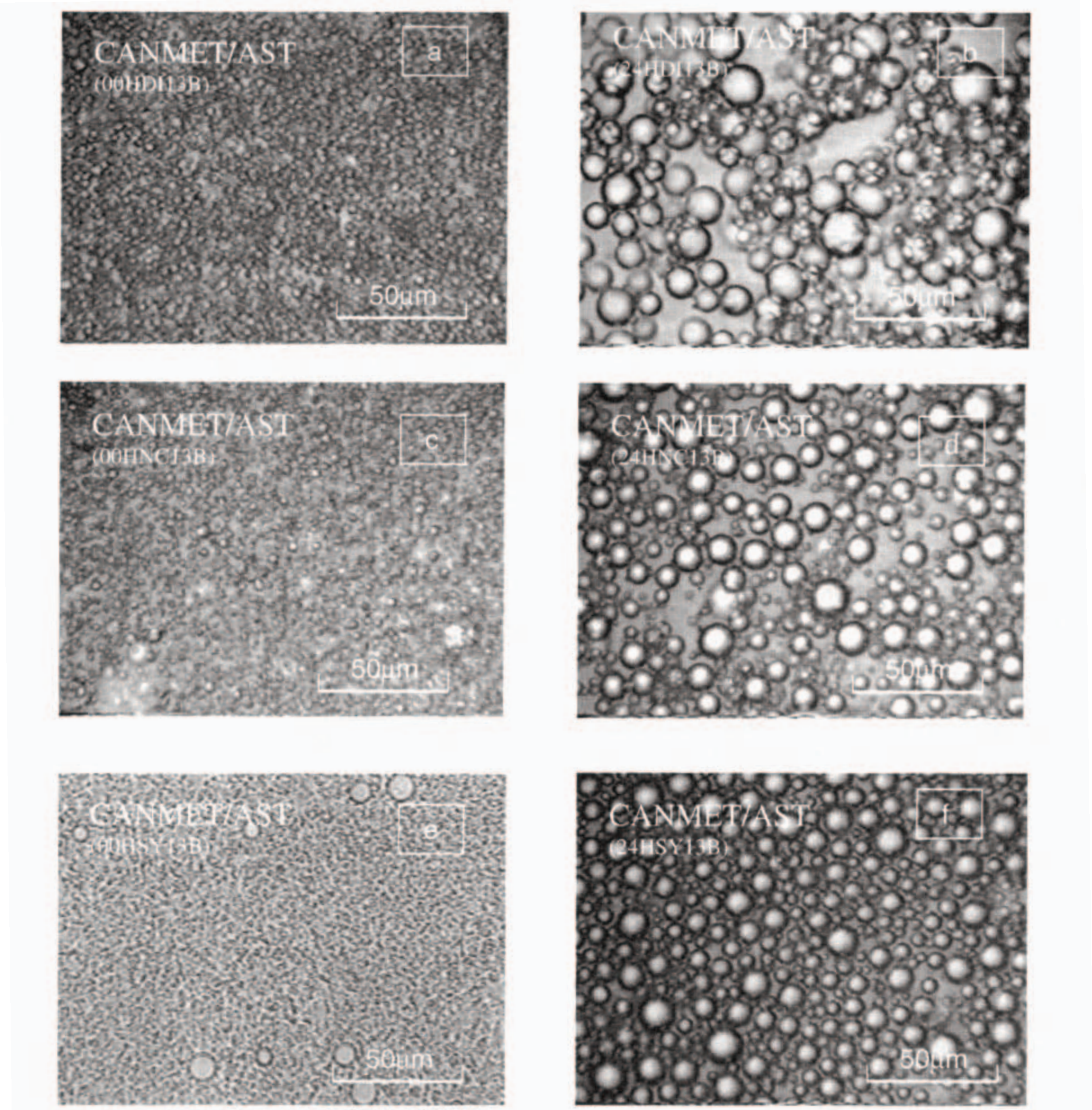


**Figure 10** Photomicrographs of model bitumen W/O emulsion made with 13% synthetic pond water in a 30% bitumen-in-toluene solution. Left - droplets immediately after preparation; right - droplets after 24 h of aging. Deionized water (a,b); 0.001M NaCl (c,d); synthetic water (e,f). (Courtesy of C.W. Angle, in house research, CANMET.)

This has been established in the past half a century in early studies (121). Hunter (122) offered a description of various types of interfaces where he considered two bulk phases separated by a planar phase or skin containing a structure of adsorbed materials and a liquid-like film phase. Based on the complexity of composition and curvatures he categorized them as A,B,C, and D. The differences are based on the mass of adsorbed materials, the sizes of head groups, and the charged ions present. Crude oils mostly match category C which has no coulombic contributions. By using the retraction of sessile drops of water/oil/ water, Roberts, as early as 1932 (123), made the observation of a thick film of oil at the crude oil/ water interface.

In 1948, Lawrence and Kilmer (124) indicated that both good and poor solvents affected the surface viscosity of the film. Poor solvents such as the aliphatics showed higher surface viscosity, while a good solvent such as toluene containing 1% asphaltene in hexane had lower surface viscosity with a plastic film behavior.

In 1954, Blakey and Lawrence indicated that asphaltic components were responsible for the stability of sea water in admiralty fuel oil (125). In 1956, Reisberg and Doscher (126) showed that crude oil films existed at temperatures close to 90°C, indicating the importance of the rigid oil/water interfacial films in stabilizing emulsions.

In 1960, Blair (94) published findings obtained on an elastic membrane, which when compressed, developed wrinkles and thick striations about the point of disturbance for several crude oil/water interfaces. He found that in time the striations disappeared by an annealing process, and the interface then finally assumed a more uniform appearance. After using a surface film balance to measure the spreading forces (from 16 to 31 dyne/cm) for several crude oils on water with and without demulsifiers, he concluded that stability arises from the formation of a condensed and viscous interfacial film of adsorbed soluble material from the petroleum phase. Specific demulsifiers have spreading pressures sufficient to displace the petroleum film, leaving a thin film with little resistance to coalescence.

Since then, many studies were undertaken to understand the nature, strength, and weaknesses of the mechanical barrier or surface film on a droplet relative to emulsion resolution. Often these studies used a combination of microscopic observation of droplets formed and resolved, and interfacial rheological studies.

Thus, the discussions that follow include several important factors. These are that: (1) the activity of interfacial components is involved in the structure of the protective skin; (2) the behavior of this structure changes with water chemistry or solvency due to mass transfer and interfacial dissipation effects; (3) the changes in structure may be due to modification of the relative proportions of components; and (4) for understanding stable films and as a means of measuring demulsification, one may adapt the new developments in interfacial rheology as tools. These are all factors considered in past studies and which are described in the following sections.

## 2. Measuring Instability of the Film by Pendant-drop Retraction

Pendant-drop retraction experiments on 10 crudes were conducted by Strassner (113, 127). A pendant drop is illustrated in the schematic of Fig. 11. Strassner studied asphaltene and resin films as the interfacial area of the drop was varied. He described the films as either mobile and/or as transition films. The mobile film was a semisolid skin which, under compression, momentarily distorted. The transition films showed no distortion under drop contraction. Pendant-drop retraction experiments were conducted on medium to light crude oils of varied asphaltene-to-resin ratios for which he categorized film rigidities. Since heavy Venezuelan crude oil of high viscosity could not be measured by this technique, he extracted the resin and asphaltenes from this crude. He then varied the asphaltene-to-resin ratio in both the emulsions and in the films. He showed that the resins contributed to mobile films and the asphaltenes to more rigid incompressible films. He concluded that asphaltene and resin interactions were mainly responsible for the film properties of crude oil. The rigid films had high interfacial viscosity and the mobile films low interfacial viscosity.

Further examination of the films by changes in pH of the brine phase led to the conclusions that the rigid films formed by asphaltenes were stronger in acidic pH, became intermediate at neutral pH, and were mobile at basic pH. This behavior was characteristic of the asphaltenes' amphotericity. In addition, stronger oil wetting of silica occurred at acidic pH. The mobile resin films were stronger in basic pH, and weaker in acidic pH. This was also an indication of

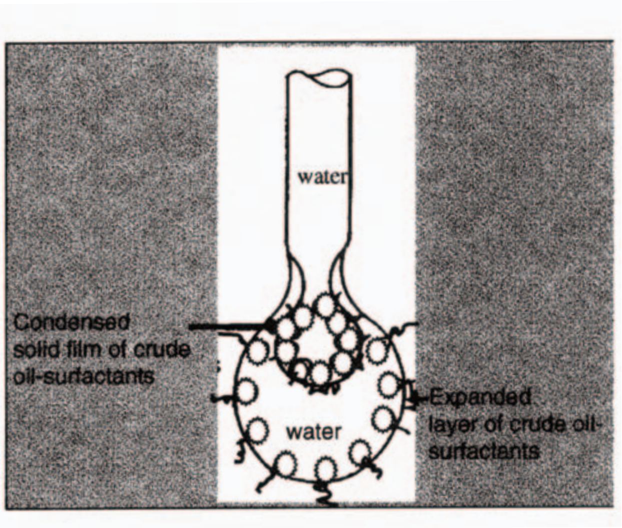


**Figure 11** Schematic of a pendant drop with a condensed film of surface-active material on retraction, and expanded film during expansion. (From Ref. 74.)

the resins weakly acidic nature.

Strassner (127) examined a third component, “waxes”. He showed that resin and waxes do not oil-wet silica. Waxes had no significant effect. He concluded that the waxes only contribute to increased viscosity of the oil phase. At low salt concentrations asphaltenes plus resins will oil-wet silica at acidic pH, but will water-wet silica at basic pH. He examined Venezuelan crude oil and distilled water, and found the most breakout of water occurred at pH 10. In this case there was a transition to a mobile weak film, and interfacial tension was still high. However, when the water was changed to a bicarbonate solution, this transition occurred at pH 6, where maximum water breakout was observed at the high interfacial tension. The role of interfacial tension is discussed later in this text.

MacLean and Kilpatrick (21) recently confirmed that the integrity of the films was sensitive to solvency parameters such as aromaticity and asphaltene-to-resin ratios, as well as polar functional groups. They confirmed Strassner’s findings, using North Sea crudes (113). They suggested that modifying the state of dissolution of asphaltenes should decrease the ability to stabilize the emulsions, and that asphaltenes are solu-bilized with resins and can only stabilize in a state of incipient flocculation. They inferred that as a molecular solution asphaltenes do not stabilize emulsions. The state of dispersion of asphaltenes (molecular versus colloidal) is critical to the strength or rigidity of the interfacial films and hence the stability of petroleum emulsions (48, 52). The balance of acidic to basic groups in its structure, and with that of resins, determines the degree of association for film formation. Earlier, Fordedahl et al. (128) in studies of crude oil emulsions in high electric fields by dielectric spectro-scopy showed the influence of interaction between indigenous surfactants. They claimed that resins alone are not stabilizers, and that asphaltenes are the stabilizers even though resins have high interfacial activity. A mixture of 1% asphaltenes and 1% resins gave the critical ratios required to give the necessary film rigidity for a stable emulsion. However, these emulsions were still less stable than the original crude from which the fractions of asphaltenes and resins were derived (129).

Cottingham et al. (130) destabilized and restabilized shale oil emulsions by adding proportions of pentane solubles (resins) to shale oil emulsions, thus quickly separating the phases. They stabilized the emulsions indefinitely by adding both solubles and insolubles to the emulsions. These factors among others can be considered in demulsincation.

Recently, Puskas et al. (131), using **FTIR**, Raman, **VPO**, **X-Ray**, rheology, **SAXS**, and **UV** techniques, conducted an extensive characterization study of fractions that were deemed to be structural components of Hungarian paraffmic-based crude-oil emulsions. They attributed stability of the interfacial emulsion film to a solid hydrophobic paraffin derivative or organocolloid of lamellar structure containing polar end groups. Together with asphaltenes, resins and oleophilized solids as components of the film structure, they deduced the formation of a cohesive three-dimensional film structure. The interfacial film had mechanical stability and flexibility. The increased viscosity of the crude oil also increased the coherent structure of the paraffin particles or waxes. They found that toluene softened the structure containing the paraffin particles and caused an increase in viscosity.

Mackay and coworkers (15, 132) performed emulsi-fication studies, using wax and asphaltene mixtures as stabilizers. They showed that waxes are not stabilizers on their own but, together with asphaltenes at a high ratio and proper blending, form stable emulsions. They tried to quantify stability by indexing it to the proportion of mass ratios of each crude oil component to total oil mass. The number was indicative of a strong or weak mechanical film barrier. They claimed that asphaltenes alone form a strong interfacial film, resins make the asphaltene barrier less rigid and more easily deformed, and wax aids in film rigidity. All these findings suggest that the internal chemistries of the crude oil components or solvents may be a few of the control parameters useful for selection of demulsifiers.

Bridie et al. (1) found that asphaltenes are two to five times more effective than waxes as stabilizing agents. In a stable emulsion containing 6.6% asphaltenes and 9.8% wax, the emulsion was still stable if 90% of asphaltenes were removed. Waxes as crude oil stabilizers for North Sea crudes have been investigated by Thompson et al. (133, 134) who showed that waxes melt as the temperature increases, and separation efficiency increases at 60°C, which is above the wax melt temperature.

The roles of interfacially active fractions of crude in emulsion stability were confirmed by Felian et al. (135) and Sjöblom et al. (136). According to Sjöblom et al., when discussing the impact of chemical destabilization, there must be a strong basis for understanding the stability mechanism. The interactions between the destabilizer and the active components of crude oil will dictate the sequence for destabilization in the system. They studied 10 Norwegian crudes of various **SARA**and wax contents. Some had high ratios of resins to asphaltenes. They found palmitic acid as an active stabilizer. When compared with heavy oil standards, asphaltene contents in North Sea crudes are extremely low, which suggests that other factors must enter into forming the stable interfacial films. Sjöblom et al. (136) indicated that palmitic acids, which they identified in their crudes, would adsorb very readily at the W/O interface and, because of their nonbulky nature, may tend to pack efficiently depending on the concentration. On the other hand, Acevedo et al. (52) attributed surface activity of the interfacial film partially to carboxylic acids, which they were able to extract from asphaltenes of Venezuelan heavy crudes. They concluded that carboxylic acids were integrated within the asphaltene micelles at the W/O interface. Other studies (137), conducted on Russian crudes, show the influence of the components on emulsion film strength (138, 139).

## 3. Surface Pressures Used as Measure of Film Instabilities with Demulsifiers

A Langmuir balance was adapted for studying the interfacial films of crude oil/water by Kimbler et al. (140). They plotted the surface pressures, ∏, versus area as the film was compressed and observed the normal pattern of phase transitions such as gaseous (flat slightly rising), expanded (rise), and condensed liquid (change in slope of rise) phases. Figure 12 shows a schematic of the typical surface pressure/area isotherm for a simple surfactant, a monolayer of myristic acid measured in a Langmuir apparatus (141). Variations in the shapes of the curve indicate the state of the film. Collapsed films were identified by observation of the changes in the shapes of the isotherm.

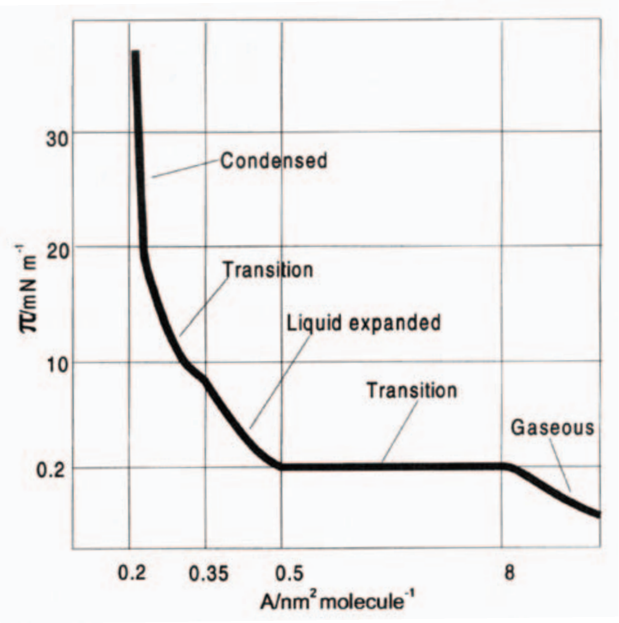


**Figure 12** Schematic showing transitions of a typical surface pressure/area(Π/A) isotherm for a compressed mono-layer of surfactant myristic acid spread on 0.1M HC1 in a Langmuir-trough apparatus. (From Ref. 141.)

Kimbler et al. (140) studied the addition of a desta-bilizer such as Triton X-100, which produced only expanded crude-oil films. It was noted that a drop in film pressure at a constant compressed area might be indicative of film dissolution or reorientation of structural elements. Changes in temperatures may change the adsorption rate and the buildup of interfacial film, and decrease the bulk viscosity. Temperature may change the rate of the relaxation process at constant compressed area (fall in film pressure), or change the rate of buildup of resistance to film compression (142).

Jones et al. (59) used a similar Langmuir-like trough for studying crude oil/water interfaces. They examined crudes such as Kuwait, Iranian, Ninian, Forties, and Magnus. Using the changes in the shapes of the ∏-area curves and the fall in pressures (relaxing), they distinguished three types of film behavior: incompressible nonrelaxing (Iranian heavy and Ninian), incompressible relaxing (Forties and Kuwait), and compressible relaxing (Forties freshly added to water). On heating, the temperature increase caused the incompressible relaxing film to become a compressible relaxing film. The Magnus crude made a weak compressible film which became rigid and nonrelaxing and insensitive to temperature increases even in low bulk phase, when the light ends were evaporated. They suggested that high interfacial viscosities can be obtained by compressing the interfacial film, showing how the rate of thinning of these films can be greatly reduced based on their responses to compression. The kinetics of the relaxation process would determine the extent of the dynamic barrier to coalescence. Demulsifiers would change this.

By observing the responses of the films to two demulsifiers, they found that the ethoxylated phenol was a film displacer and inhibitor for aged films and that the carboxylic acids containing alkoxylated ester were film inhibiting if added to crude oil before contact with the water. They also found that $Ca^{2+}$ ions rendered the film incompressible and this resulted in a more stable emulsion. They also suggested that pendant-drop retraction could not be used to distinguish between relaxing compressible films and incompressible relaxing films. They suggested that viscous buildup should be shown; otherwise, interpretations based on the pendant-drop experiments can be misleading.

The Langmuir-balance technique was adapted for the study of Indian crudes by Singh and Pandey (69). They separated the crudes into anionic, cationic, and nonionic fractions and studied the effects of electrolytes and pH on their film properties. Maximum film pressure was observed for films made with the anionic fraction and minimum film pressure for the cationic fractions. Increased electrolyte concentrations caused increased viscosity and less resolution of emulsions. Film pressures were maximum at pH 12 and more stable emulsions resulted. The electrolyte also had an adverse effect on the demulsifier.

Singh (143) followed up this study to understand the performance of unidentified demulsifiers with a change in solvent properties. By noting the relative decrease in surface pressures resulting from added demulsifiers in various solvents, he found that benzene was the best in that it helped the demulsifier to lower the surface film pressures. The lowering of interfacial tension was measured at the same time and the results suggested that rapid adsorption occurred. It was concluded that structure, orientation, and film pressures were the most important factors in demulsifier performance.

Mohammed et al. (144, 145), in a series of studies, examined several aspects of emulsion films with and without demulsifiers as well as their chemistries. Using the Langmuir balance for studying the air/ crude/water interface, they examined the surface pressure n-area isotherm for monolayers of Buchan crude's asphaltenes and resins and their mixtures, spread on distilled water at pH 6.2 and 25°C. They found that the asphaltenes upon compression formed solid films, that could withstand pressures up to 45 mN $m^{-1}$ in contrast to the resin films at 7 mN $m^{-1}$ which thereafter collapsed. The asphaltenes formed highly stable emulsions in contrast to the resins alone, which formed the least stable emulsions. They found that film compressibility and emulsion stability decreased as resin content increased. Temperature increases caused no significant effects on asphaltene monolayer compressibility as was observed earlier by Reisberg and Doscher (126) for natural crude oil films.

Nordli et al. (146), using the Langmuir-balance technique, studied the monolayer properties of the interfacially active fractions extracted from six North Sea crude oils over a subphase of distilled water and simulated formation water. The pH and salinity were varied. They compared additives such as butanol, benzyl alcohol, and octylamine, added to the subphase, to note changes in film compressibilities. A typical phase-change pattern for Langmuir curves of surface pressure versus area was observed for all cases. The smallest specific area attributed to the liquid expanded states was reached by the lowest-molecular-weight species. Films, in this case, were more condensed as the temperature increased. At constant pressure, the changes in the surface pressure were monitored over time for each film. The time for relaxation was 60 min for the low-molecular-weight fraction, and 320 min for the high-molecular-weight fraction. Distilled water in the subphase showed decreased specific area for the same film, and a pH of 2.6 caused a shift to higher specific area. Salt had no significant effects.

According to Taylor and Mingins (142) a drop in film pressure at constant compressed area may be indicative of film dissolution or reorientation of structural elements. If there is no resistance to compression, an unstable emulsion results. Changes in temperature may change the adsorption rate and the buildup of the interfacial film. A decrease in the bulk viscosity may change the rate of the relaxation process (fall in film pressure) at constant compressed area and change the rate of buildup of resistance to film compression.

## D. Destabilization and Interfacial Film Rheology

Developments in measurement techniques for monitoring interfacial changes occurred for the purpose of understanding emulsion stability. However, the techniques were equally useful in measuring destabilization induced by changes to the internal natural chemistries of the system or with addition of chemical demulsifiers. The adaptation of the Langmuir film balance was only one tool for a pseudo-static system. However, as the fluid dynamics in the films and interphase (or lamella) of two approaching droplets or in a highly concentrated emulsion dispersion was discovered to be more complex and bore similarity to the polyhedral structures of foams, the need to study the emulsion interfacial films under stresses became apparent. Much was learned from foam studies.

A detailed treatise on the fundamentals and applications of thin films, i.e., lamella plus surface film, is found in Ivanov (147). The two major forces involved in the lamella behavior are thermodynamic (disjoining forces) and hydrodynamic. Further in-depth studies on the thermodynamics are presented in de Feijter (148) and Hirasaki (149) and on the hydrodynamics in Maldarelli and Jain (150). Because of the complexity of this topic, which is not within the scope of this chapter, the following discussions will be limited to the understanding that this research brought about concerning the nature of the films and the process of film thinning by chemical demulsification.

The interfacial rheology of films has been extensively discussed by Edwards et al. (151) and briefly by Tadros (152), and reviewed in relation to emulsions and foams by Malhotra and Wasan (153). A two-dimensional fluid interface can only be treated as an independent body when it is highly viscous or highly elastic. It cannot be treated separately from the bulk fluid which may provide viscous drag and influence the direction of flow. Simply, interfacial rheology describes the flow behaviour in the interfacial region between two immiscible fluid phases. The adsorbed surface-active components at the crude oil/water interface alter the hydrodynamic resistance to interfacial flow. As the molecular weight of the adsorbed species increases, the interface exhibits viscoelastic behavior. This is most likely in the case of bitumen W/O emulsions. The chemical demulsifier interaction alters not only the physical/chemical properties but the rheologi-cal behavior. Figure 13 is a schematic of the physico-chemical and dynamic factors involved in droplet interactions.

## 1. Crude Oil Interfacial Rheology - Background

There are four rheological parameters which describe the response to imposed interfacial stresses or deformation. For a Newtonian interface, the significant rheological properties that determine interfacial motion are the interfacial shear viscosity, $\eta_s$, the interfacial dilational viscosity, $\eta_d$, and the interfacial tension gradient. The interfacial shear elasticity, $\varepsilon$ and viscosity, $\eta_s$, describe the resistance of the interface to changes in shape of the interface element. Here, the area is kept constant and the resistance is measured. On the other hand, the interfacial dilational elasticity, $\varepsilon_d$, and viscosity, $\eta_d$, describe surface resistance to changes in interfacial area. The interface is expanded without shear and the resistance is measured. Figure 14 shows schematically the shear and dilational forces on an interface in determining shear and dilational viscosity.

The need for the dilational data arose due to the manifestation of Gibbs-Marangoni effects or surface-tension gradients occurring during film thinning. The surface-tension gradients and hence the elastic behavior are influenced by changes in temperature, concentration of surface-active agents, and/or compression and expansion of the interface. Detailed theoretical treatments of the dilational properties of liquid films can be found in several studies. Kristov et al. (154) performed a parametric study determining the compositional surface elasticity of model systems. Loglio et al. (155) reported on the dilational viscoelasticity of fluid interfaces modeled for transient processes, Edwards and Wasan (156) discussed foam dilational viscosity, and Lucassen-Reynders and Van den Temple (157) reported on the surface dilational modulus caused by variation of surface tension from a small-amplitude sinusoidal area variation. Recently, Yeung et al. (158) modeled the expanding pendant drop in their explanation of interfacial mass-dissipation effects.

## 2. Measuring Destabilization by Dynamic Interfacial Shear Viscometry

Dynamic shear measurements may be conducted by using

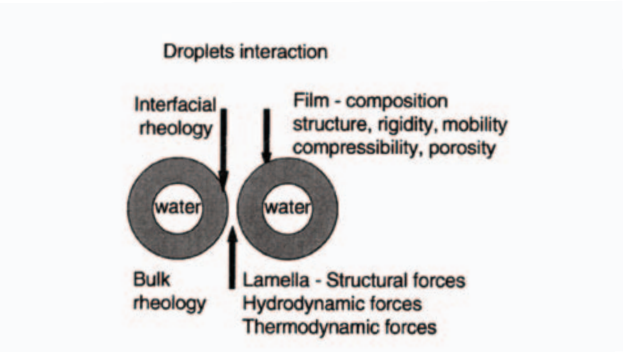


**Figure 13** Schematic on the physicochemical and dynamic factors involved in the droplet interaction.

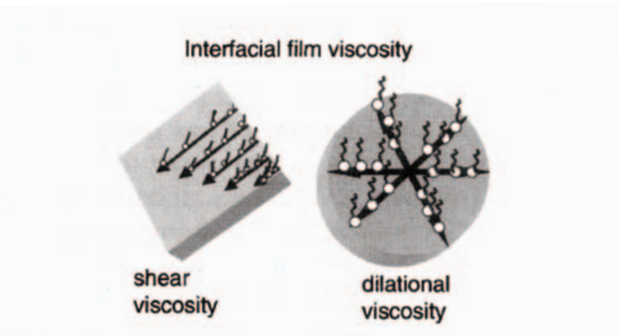


**Figure 14** Schematic of shear and dilational forces involved in measuring the corresponding viscosities at a W/O interface.

several interfacial rheological instruments. A detailed reference list on these is found in a treatise by Malhotra and Wasan (153). Among those specially used for interfacial shear viscometry are a ring visc-ometer, a disk viscometer, a knife-edge viscometer, a deep-channel surface viscometer, and various modifications to these as described by Edwards et al. (151) and Boyd and Sherman (159). The majority of these are for interfacial shear measurements.

Cairns et al. (160) gave a detailed description of interfacial shear viscometry of crude oil/aqueous 1 % **NaCl** systems. Kuwait crude had a low $\eta_S$ and produced unstable emulsions, while Iranian heavy had a high $\eta_S$ and stable emulsions. They showed that $\eta_S$ decreased with increases in **pH** and **NaCl**, and $\eta_S$ increased with aging. The aging effect invariably is a result of interfacial material build up over time, recently described by Neumann and Paczynska-Lahme (120) for crude W/O emulsions. Cairns et al. (160) concluded that the stability of emulsions was favorable when there was a rapid adsorption of surface-active agents (detected by a fall in interfacial tension), followed by a rapid rise in $\eta_S$, and that maximum emulsion stability occurred when **pH** and & #951;$_S$ were highest. When comparing Zakum and Murban (0.08% asphaltenes) with Tia Juana (3.05% asphal-tenes) in the pH range 2-11 a high asphaltene content did not correspond with high $\eta_S$. With $Ca^{2+}$, $\eta_S$ was high and interfacial tension fell rapidly, leading to intermediate emulsion stability; yet with Na, $\eta_S$ was low, interfacial tension fell slowly, and emulsions were unstable.

Grist et al. (161) provided a detailed critique of the biconical bob tension pendulum viscometer in interfacial shear viscosity measurements of Forties water/ crude oil systems. They reported that a highly viscous interface reduces oil film drainage and is responsible for the high water content of "chocolate mousse" in oil spills as well as increased emulsion stability. Graham et al. (162) showed reduced $\eta_S$ with demulsifier and methanol, and that overdosing led to both increased $\eta_S$ and emulsion stability. Wasan et al. (163) in their study of Salem crude/brine, measured the $\eta_S$ responses with a deep-channel interfacial viscometer with and without a petroleum sulfonate demulsifier. The demulsifier activity was enhanced with a cosurfactant such as hexanol. They reported that as $\eta_S$ increased coalescence decreased. Later Pasquarelli and Wasan (164), using a viscous traction shear viscometer, showed that, with Salem crude and demulsifier TRS 10-80, the emulsion became more stable at high $\eta_S$. On examination of the $\eta_S$ of the fractionated crude (one high-asphaltenes fraction and one high-resin fraction) against brine and alkaline water, they found that $\eta_S$ was highest in the high-asphaltene fraction film against first brine and then water, giving 7.1 and 6.7 surface poise, respectively. Under similar conditions, against brine and water phase, respectively, the resins' $\eta_S$ showed 0.004 and 0.00074 surface poise, while the $\eta_S$ of the source crude oil were 0.25 and 0.00043 surface poise, respectively. Taylor (165) also indicated that the aging of the Romashkino, Ninian, and Kuwait crudes with an external added surfactant can retard the buildup of $\eta_S$. Neustadter et al. (166) used the conical bob torsion pendulum rheometer to study the interfacial rheology of Iranian heavy, Kuwait, and Forties crude oil-water films. They showed the same $\eta_S$ for all crudes, and suggested that one cannot use only interfacial shear viscosity to predict emulsion behaviour and that the compressibilities and elasticities are not reflected in this viscosity.

## 3. Destabilization and Dynamic Interfacial Viscoelasticity

To achieve both shear viscous and shear elastic properties, oscillatory measurements can be performed where one movable component of the rheometer is oscillated at given amplitudes and frequencies, and a sinusoidal wave is propagated. The complex modulus, $\varepsilon^*$, is then related to the elastic and viscous vector components, which are the real and imaginary coefficients of the frequency function.

Mukerjee and Kushnick (167) suggested that the interfacial dilational modulus can be obtained by a Fourier-transformed pulsed-drop technique similar to the method used by Clint et al. (168) in which the Langmuir trough was used in studying the interfacial tension ($\gamma$) variation with periodic variation in interfacial area. The frequency-dependent complex modulus, $\varepsilon^*$ (f), is equated to a real elastic modulus, $\varepsilon$(f) (dilational elastic modulus), plus an imaginary modulus $i\varepsilon$ (f) (dilational viscosity modulus), and set equal to ($d\gamma/dA/A$). The dilational elastic modulus is the interfacial tension gradient which is in phase with the area, A, change. The dilational viscosity modulus is 90° out of phase with the area change.

Mukerjee and Kushnick (167) showed that at low frequency the demulsifier behaves as a soluble mono-layer, and at high frequency as an insoluble monolayer. Variation in interfacial tension from a local change in area is virtually instantaneous. This gradient is short circuited when the demulsifier molecule moves to and from the surface to bulk or is sufficiently soluble in the bulk phase.

Mukherjee and Kushnick's definitions were as follows: the interfacial tension increment, dy, per unit fractional area change, dA/A, is equated to the complex modulus, $\varepsilon^*$ (f);

$$\varepsilon^*(f) = \varepsilon'(f) + i\varepsilon''(f) = \mathrm{d}\gamma / \mathrm{d}A/A \qquad (1)$$

$$= \mathrm{d}_\gamma / \mathrm{d}\ln A \qquad (2)$$

Where ε′(f) and ε”(f) are the real and imaginary components at a frequency f.

For an air/liquid system a measure of the surface-tension variation resulting from the imposed periodic area variation in the Langmuir trough is performed. If both dilational viscous $\eta_d = \varepsilon$ (f) and dilational elastic $\varepsilon_d = \varepsilon'$ (f) data are needed, and if a Langmuir-type trough is used, then one barrier can be oscillated and another barrier can be used to adjust the extent of the interfacial area. The calculation of the complex modulus, $\varepsilon^*$, requires complete scans at different frequencies.

There are many difficulties associated with this technique when applied to crude oil systems according to Mukherjee and Kushnick (167). They by-passed these difficulties by using the method developed by Neustadter and coworkers (168, 169) for crude oil systems by following the dynamic interfacial tension with step changes in interfacial area. A complete frequency spectrum is obtained by Fourier transform (FT) of the dynamic interfacial tension data:

$$\varepsilon^*(f) = 2\pi i f / \Delta\ln A \int_0^\infty \Delta\gamma(f) e^{-2\pi i f t}\, \mathrm{d}t \qquad (3)$$

$$\varepsilon'(f) = 2\pi\, i f / \Delta\ln A\, [\text{Real FT } (\Delta\gamma)] \qquad (4)$$

This is the dilational elastic modulus or the interfacial tension gradient which is in phase with the area change.

At low frequency they found that the demulsifier behaved as soluble monolayers and the tension was governed by the bulk concentration and did not change with change in area. At high frequency the demulsifiers behaved as insoluble monolayers and the change in interfacial tension resulting from area change was instantaneous:

$$\varepsilon''(f) = 2\pi\, i f / \Delta\ln A\, [\text{Imaginary FT } (\Delta\gamma)] \qquad (5)$$

This is the dilational viscosity modulus which occurs when the demulsifier is soluble in the bulk liquid. Area compression and expansion produce a tension gradient, which is diminished by the periodic transfer of demulsifier to the bulk from the surface and vice versa. The viscosity component amplitude is 90° out of phase with the area change.

This technique was used to show that demulsifica-tion effectiveness can be correlated with a low dynamic interfacial tension gradient, especially at low interfacial shear viscosity and this is evidenced by a sharp rise in interfacial tension at low frequencies for ineffective demulsifiers.

Alternatively, interfacial tension can also be measured continuously with area changes, with an expanding or contracting pendant-drop instrument adapted to oscillatory measurements as described by Bhardwaj and Hartland (74). Dilational data are obtained without introducing shear as the interface is expanded and contracted. This is also often achieved with an expanding drop volume or bubble-pressure tensiometer (65). Nikolov et al. (170) have recently developed this technique and an instrument to study oil/water systems.

Tambe et al. (171) used model systems of colloidal-laden interfaces of emulsions made up of 2 wt% graphite, 20 ml deionized water, and 30 ml decane. They modeled the system to understand factors that control the colloid-stabilized emulsions as was studied previously by Wasan and Menon (172, 173). They showed that, for viscoelastic films of finite dilational elasticity, interfacial rheology plays a dominant role in film-drainage rates. They suggested that the characteristic relaxation times are related to the ability of a demulsifier molecule to diffuse to the interface in response to a concentration gradient while minimizing the Marangoni flows, which retard film drainage. They suggested that the film-drainage rate is sensitive to the dilational elasticity of the interfaces. For viscous interfaces (zero dilational elasticity) the drainage rate is independent of interfacial dilational viscosity.

Neustadter et al. (166) earlier measured interfacial dilation elasticities, $\varepsilon_d$, and viscosity, $\eta_d$, for Iranian crude oil/water and deduced that the extent of the relaxation process was not a function of time due to the lack of change in viscosity, $\eta_d$, at fixed frequency. However, as frequency changed, $\eta_d$ decreased, indicating that the relaxation involved the interchange of bulk material to and from the interface. The increased elas-ticy, $\varepsilon_d$, with time suggested that there was irreversible adsorption of high-molecular-weight species.

Nordli et al. (146) later found larger relaxation time for the films with the higher-molecular-weight surface-active species derived from North Sea crude. For crude W/O emulsions, Neumann and Paczynska-Lahme (120) concurred that the emulsions are stabilized by thick films with Gibbs elasticity, and the more the interfacial activities of the components differ from each other the higher the elasticity modulus of the multicomponent films.

During compression and expansion, a molecular relaxation process occurs for that time scale. It is expected that there will be characteristic relaxation rates (times). It is expected that the molecular relaxation process will include: (1) increased packing by surface diffusion of low-molecular-weight species; (2) molecular conformational changes of irreversibly adsorbed high-molecular-weight species; (3) deso-rption; and (4) readsorption of low-molecular-weight reversibly adsorbed molecules. These may occur during the compression and expansion stages. The response can also be interpreted as solvent losses from the molecular films.

Neustadter et al. (166) indicated that, if the frequency of the longitudinal wave is varied, the bulk-to-interface interchange occurs during compression/ expansion of the film. There may be a short-circuiting of the interfacial tension gradient, and then information on the relaxation rates and dilational properties may be obtained. In this interchange one may observe a low apparent compression modulus. A phase shift between the imposed strain (change in area) and resultant stress (change in interfacial tension) would occur. Different interfacial tensions with compression/expansion would be produced with molecular reorientation of irreversibly adsorbed species. With the increase in frequency of oscillation there is less bulk to interface interchange. Only for species of greater solubilities and shorter chain length would diffusional interchange be important. For the long-chain irreversibly bound components, which are almost insoluble, slower reorientation will occur. Neustadter et al. (166) emphasized that relaxation plays an important role in the behavior of the crude oil/water interface. With age, low dilation elasticities increase and no change in dilation viscosities occur.

## E. Further Studies on Shear and Dilational Viscosity of Crudes

In 1987, Eley et al. (72) used the pendant-drop retraction method in the study of film compressibilities of crude oil/water interfaces for three crudes. These varied in asphaltene content. Libya (Brega) had 0.46 g/L, Kuwait 3.7 g/L, and Tia Juana (Venezuela) 5.94 g/L. They added a dispersant containing a nonionic oil-soluble surfactant, and observed increased film compressibilities. The concentration of effective dispersant correlated with the asphaltene content. At the same time the decreased interfacial tension corresponded with increased film compressibilities and this was explained as a displacement of asphaltenes from the interface by the dispersant.

They adapted an interfacial shear rheometer (plate/ rod) to measure the shear viscoelasticity of the system with and without dispersant. At an applied shear stress, creep curves for the system were monitored. There were no instantaneous elasticity and viscosity for the Kuwait and Tia Juana crudes with and without dispersant. They attributed this to a network structure of flocculated asphaltenes in the films. They found that there was some dilatancy in their crude oil films, described as a “stick/slip” flow in their flow curves. However, this flow was attributed to thick films of asphaltene particles building up at the interface. Using creep measurements, they examined a model system of asphaltenes/n-heptane/toluene. They found a retarded elastic deformation, which was different from the response of the crude oils. This suggested to them that there was a different type of interfacial structure formed with the model oil, and this may be attributed to the solvency of the medium and not to the lower asphaltenes content in the model system.

Further details of interfacial rheology of crude-oil emulsion films are discussed extensively by Menon et al. (174), Neustadter et al. (166), Mohammed et al. (175), Tambe et al. (176), and Mukherjee and Kushnick (167). They discussed the effects of demulsi-fiers on the interfacial properties governing the crude-oil demulsification.

Neustadter et al. (166) first discussed the crude-oil interfacial film in terms of pseudostatic film compressibility when the Langmuir balance was used for studying the liquid/liquid interface. This technique showed less variation in adsorption and showed that all but the most surface-active species were squeezed out during compression. The whole interphase region was then probed using a biconical bob torsion pendulum device suitable for high interfacial shear measurements. It responded to small changes in adsorption in the interphase region.

Highly viscous interfacial films retarded the rate of film drainage during coalescence of water droplets. They found that a highly viscous film at pH 6 led to maximum stability. They also suggested that to increase the interfacial viscosity of a low interfacial viscosity film, one should compress it. Interfacial shear viscosities were investigated with all three crudes, Iranian heavy, Kuwait, and Forties, which had similar interfacial shear viscosities.

Interfacial rheology should be used with care as a predictive tool for emulsion stability/instability. Graham et al. (162) showed that there was reduction in interfacial shear viscosity of Forties crude oil/water interface with demulsifier added in methanol. Cairns et al. (177) revealed for

Zakum, Murban, and Tia Juana crudes/water systems, that interfacial shear viscosity, $\eta_S$, decreased with increased pH, and $\eta_S$ decreased with increase in electrolyte NaCl. Also, $\eta_S$ increased over time. This did not correlate with the asphaltenes content.

Wasan et al. (163) used a deep-channel viscometer in studying the interfacial shear viscosity of Salem crudes/water with and without the addition of petroleum sulfonate and salts, as well as Illinois crude/brine with pentadecyl benzenesulfonate. They showed a decreased coalescence time with decreased shear viscosity. A viscous traction shear viscometer was used for fractionated crude oil/brine by Pasquarelli and Wasan (164), who showed that increased interfacial shear viscosity is correlated with decreased coalescence. Later, Wasan correlated interfacial shear viscosity with film-drainage time to determine effective demulsifiers (178).

Taylor (165) observed that surfactants used as destabilizers retard the build up of material at the oil/water interface for aging Ninian, Romaskino, and Kuwait crudes. Mohammed et al. (144) studied the theological behavior of the North Sea Buchan crude oil/double-distilled water interface by oscillatory interfacial shear rheometry, using the biconical bob the-ometer in the oscillation and creep modes. They used creep measurements to obtain relaxation data. This crude is known to produce very stable emulsions, yet its heptane-precipitated asphaltenes were only 0.058 g/ml. They attributed Newtonian viscosity to the adsorption of low-molecular-weight components of crude, and the build up of the interfacial films to high-molecular-weight components forming a network structure with viscoelastic properties. They investigated the effects of temperature and of demulsifiers Unidem 120 and BJ 18 in xylene on the film viscoelas-ticity. They found that at 45°C the interfacial film vis-coelasticity became more liquid-like. The increased viscosity with increase in temperature was a result of loss of light ends. The Unidem 120 caused a change in the aged film character from solid-like to liquid-like, and BJ 18 prevented the film buildup. They traced these effects through the relaxation time from creep curves with and without demulsifiers, as well as observing a decreased viscous component in the oscillatory measurements.

Chen et al. (179) used optical microscopy to study the same crude-oil emulsions in an electric field. They modeled the system with a computer simulation based on a hard-sphere model describing the droplets as stabilized by a rigid asphaltene film. They identified two different types of coalescence. The mobile interfacial films led to low emulsion conductivities owing to immediate droplet/droplet coalescence, and the incompressible interfacial film led to low emulsion conductivities due to droplet-chain formation and bridging between the electrodes.

Malhotra (180), in a parametric study, showed that interfacial mobility and the rate of film drainage depend on the interfacial shear viscosity when the viscosity is in the range $10^{-5}$ to $10^{-3}$ Pa.ms. Outside this range the interfacial viscosity had no effect. Interfacial viscosity as low as $< 10^{-5}$ Pa.ms can lead to stable emulsions (181).

The reported information on film rigidity, compressibility, and other aspects of interfacial rheology indicates that the highly viscous and elastic films are stable. In most of the compressibility studies on crude oil films, the films were made with the various surface-active components of crude oil and/or the crude oil itself. The drop-retraction, Langmuir-type trough, and pendant drops pulsed at various frequencies of expansions and contractions were tools for studying the mechanics and fluid dynamics of the dilating interfacial films. In addition, sophisticated shear rheometers, including oscillatory and creep measurements, were used to obtain shear viscosity, elasticity, and film relaxation data. Typically, these measurements were made with and without demulsifiers, with changes in water quality, pH, or solvent properties when demulsifiication was investigated.

Wasan and coworkers (63, 65, 174) extended techniques for studying film rheology of the foam lamella to studies of crude-oil emulsion lamella. Using a capillary balance technique and light interferometry, the film thinning of foams was studied with and without chemical demulsifiers, with solvent properties changed, etc. (182). They confirmed that there were two contributions to emulsion stability - a structural component that originates from the nature of the bulk phase, and an adsorbed-layer contribution to film stability (170). This will be covered in another chapter in this series.

## F. Destabilization and Interfacial Tensions

The equilibrium interfacial tension between water and oil is a measure of the adsorption of surface-active components to the interface and can be related to surface excess by the Gibbs equation (183). However, in crude oil systems the activity/concentrations of the surface-active components are not easily determined. Indirect measures are applied. In most process conditions with short resident times, it is the dynamic inter-facial tension gradient that is important. Interfacial tension also tells whether or not the demulsifier is surface active, and as will be shown later, this is important for demulsification. The interfacial tension gradient is the important factor for rendering the interface immobile. The interfacial tension gradient is used in a measure of Gibbs surface elasticity, E, or as an indication of changes in free energy. When the interface is expanded or contracted, then $E = -d\gamma/d\ln\Gamma$, where $\gamma$ is the measured interfacial tension, and $\Gamma$ is the interfacial concentration or Gibbs surface excess. This elasticity is an indication of the ability of the interface to adjust the interfacial tension when stressed.

The interfacial tension, $\gamma$, in the Gibbs adsorption equation is used for equilibrium conditions as bitumen components are adsorbed. Measurement techniques available are extensive. Some of these methods are: duNouy ring, maximum bubble pressure, drop volume, Wilmhelmy plate, sessile drop, spinning drop, pendant drop, capillary rise, oscillating jet, and capillary ripples. These and many others are referenced extensively by Malhotra and Wasan (153). These authors also showed that there is no correlation between emulsion stability and interfacial tension. The nature of the film dominates stability. Some relationships between interfacial tensions and crude oil properties follow.

The interfacial tension values of crude oil/water or asphaltenes-resins/water are strongly dependent on pH and salt content of the aqueous phase. With toluene as the solvent, bell-shaped $\gamma$-pH curves were observed for heavy Venezuelan crude/brine systems (125), distilled-water washings of diluted bitumen/air (11), and light crudes (126). Luthy et al. (184) showed similar results for heavy southern Californian, light Arabian, and waste petroleum oil/brine systems. Figure 15 illustrates the interfacial tension pH effect of crude oil/water systems (184). A bell-shaped $\gamma$-pH curve with a maximum at pH 6 was observed for all crudes. Similar findings were observed for Zakum, Murban, and Tia Juana medium crude oil/water interfaces, with pH changes showing a maximum interfacial tension at pH 6 by Cairns et al. (185). They suggested that increased emulsion stability is expected to occur at very high and low pH only because of adsorption of surface-active components at these pH values. The interfacial tension in these cases reflects only the adsorption of interfacially active components at the interface. Acevedo et al. (186) found similar results for Venezuelan crudes and explained that, at low pH (< 7), the adsorption of basic groups is dominant. At high pH (>8), ionized carboxylic acids integrated in the adsorbed asphaltenes micelles are dominant, and an acid-base pair is adsorbed in the neutral region (pH 6-8). Xu (187) showed that the dynamic interfacial tension of the bitumen/water interface decreased with increased caustic concentrations as the interface aged. Similar decreases were noted as the bitumen concentration increased, indicating that adsorption of natural surfactants after saponification is time dependent. Similar observations were made for Ratawi asphaltenes (188). Through interfacial tension measurements the critical micelle concentrations of light and heavy fractions of Ratawi asphaltenes and desorption kinetics in organic solvents (189) were studied.

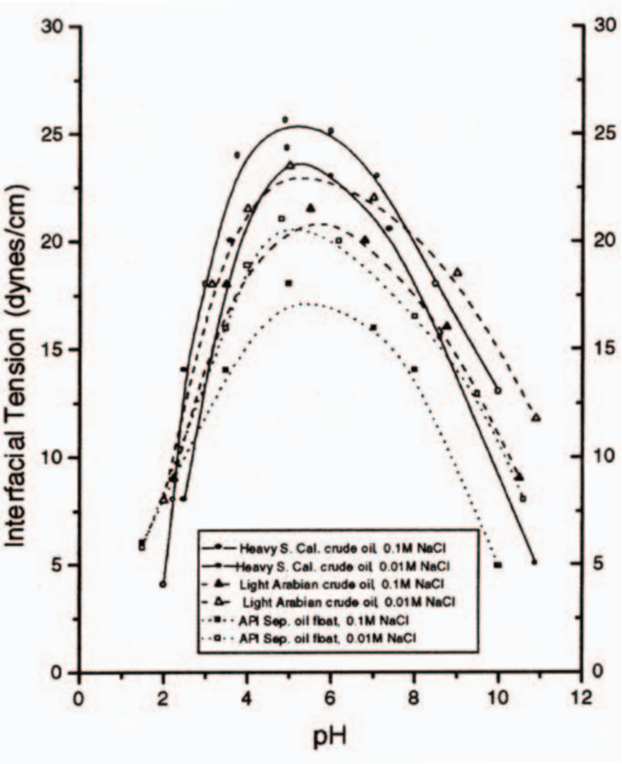


**Figure 15** Interfacial tension changes with pH, showing the maximum for various crudes. (From Ref. 184.)

In all cases adsorption at the W/O interface is very slow and time dependent. The rate is lower for acidic and neutral pH. At basic pH, adsorption is much faster. These are often reported as aging effects, especially as changes at the interfaces go on for days or weeks. Malhotra (180) discussed detailed adsorption models and related this to film-drainage rates.

One can thus offer the conjecture that demulsification may be enhanced when films are weaker, which may or may not correspond with a high interfacial tension, since the film properties/architecture are dependent on many factors that in turn depend on both the crude oil and the water. Eley et al. (72) and others discussed earlier have shown that, at acidic and neutral pH, the films are solid-like and highly viscous. Large increases in interfacial viscosity and elasticity were observed for crude oil/water with a change in pH from neutral to alkaline (73).

The times for development of an adsorbed layer or the conditions by which adsorption is minimized are factors which can be used to improve chemical demul-sification. There is no correlation between decrease in interfacial tension and increased coalescence rates (190), notwithstanding the data showing decreased shear viscosity and increased coalescence rates (163).

Low interfacial tension is important for decreased energy requirements in the emulsion formation stage, but it does not appear to play such a role in demulsi-fication. At an interfacial tension of 5 dyne/cm, in order to overcome LaPlace pressure and break up of a drop of 10 µm, one requires an external pressure gradient of 100 psi/cm, and for a 0.1-µm drop, a gradient of $10^6$ psi/cm. The increase in interfacial energy for changing 10 ml water into droplets of 10 /xm at interfacial tensions of 5 dyne/cm is $3\times10^4$ dyne/cm. If we compare this energy with that required to raise the temperature of the same water by 1°C at an energy cost of $4.2\times10^8$ dyne/cm, then the emulsification process of producing droplets from a bulk uses significantly less energy than the energy needed for temperature change or the energy for breakup of an already formed emulsion droplet. The smaller droplets behave as hard spheres. Thus, an easier means of destabilization would be by chemical demulsification augmented by changes in internal natural surfactant composition.

## G. Effects of Temperature and Heat on Destabilization

Heat has its own advantages and disadvantages in the demulsification process (135, 191). Heat may also contribute to the disruption of emulsion film material by the differential expansion of the water inside the droplets, perhaps creating higher burst pressures. With increasing temperature the viscosity and density differences between water and heavy crude oils begin to diverge. The density of the oil is reduced faster than the density of the water as temperature increases, showing a larger divergence below 150°C. Since heat increases the density differences between bulk oil and water droplets it leaves a greater chance of accelerated settling, between 50°C and 125°C.

Also, as heating reduces the bulk viscosity of the oil, it also reduces the fluid resistance (106). The settling of water droplets is faster in less viscous oils. Because heating puts increased energy into a system there is a higher frequency of droplet collisions.

The increased temperature of the system may lower the interfacial shear viscosity, which may lead to an improved rate of film drainage between adjacent drops. Menon and Wasan (62) demonstrated the decrease in interfacial viscosity of shale oil/water at increased temperatures and showed analogous behavior at increased demulsifier concentration. Thompson et al. (133) reported that, at increased temperatures, some incompressible nonrelaxing films tend to relax and the rate of buildup of the resistance to film compression increases. Demulsifiers then reduce the kinetic barrier to coalescence.

Sometimes heat will deactivate the demulsifier if its solution chemistry is sensitive to heat. The cloud points of the nonionics occur at specific temperatures based on the chemical structure and oil-phase chemistry. In aromatic oils the phase-inversion temperature (PIT) is lower than the cloud point; in n-paraffins and cyclo-paraffms the PIT is higher than the cloud point. Phase inversion may result in some cases (192, 193) as the temperature approaches the cloud point.

Heating may augment destabilization of stable crude emulsions in which waxes play a large role. This is more likely with highly paraffinic crudes found in the North Sea (20) and paraffin wax crystals melted by heat. With asphaltenic or highly aromatic crudes, heating has less effect on the stability of the emulsions unless the viscosity and density of the interfacial barrier and continuous phase are reduced considerably. Stockwell et al. showed that the heating prehistory affected the emulsion stability of North Sea crudes but not the Canadian asphaltenic crudes (17). This was related to the crystallization sizes of the waxes in the North Sea crudes and the absence of wax crystals in the asphaltenic Canadian crudes. Neumann and Paczynka-Lahme (120, 194) held that, at increased temperatures, the interfacial films with asphaltenes remain intact but with the resins, stability increases. At high temperatures, resins form liquid-crystalline lyotropic mesophases for several crudes tested at 90°C. Stable films are suggested to have considerable viscoelasticity (195). Breaking emulsions with high resin contents is not easy because of the formation of either hexagonal or lamella liquid crystals at the interface at high temperatures.

Sometimes heating enhances the transport of the demulsifier chemicals to the interface as well. A combination of heating and demulsifiers was found to be synergistic in breaking stable emulsions formed with Alaskan North Slope, Bonny Light, and BCF-17 crudes in a simulated spills study conducted by Stroem-Kristainsen et al. (196). This synergism with heat was also observed for breaking other North Sea (197) crudes' W/O emulsions (66, 198) and Nigerian (199) crude oil emulsions, when heat alone was ineffective. Nonionic surfactants performed better as demulsifiers at elevated temperatures for Hungarian (135) Algyo crude oil emulsions. If heat solubilizes the stabilizing surfactants into either the oil or water phase, the interfacial film will be weakened, leading to destabilization of the emulsion.

## IV. CHEMICAL DEMULSIFICATION PROCESS

Emulsification and demulsification are both complex processes. However, as noted earlier, demulsification is by no means the opposite of emulsification (200, 201). This is especially the case in the petroleum industry. In order to demulsify a crude W/O emulsion efficiently, it has been emphasized that it is advantageous to understand first the characteristics of the emulsions, the nature of interfacial films, and hence the causes of stability. Accordingly, in choosing a demulsification protocol, one would first identify key factors responsible for the stability, find the target properties to modify toward destabilization, introduce sufficient energy to promote coalescence, and find the best conditions to allow phase separation.

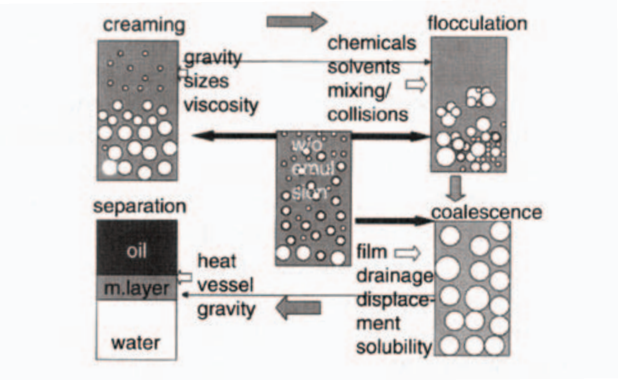


**Figure 16** Schematic illustrating the various stages of demulsification process.

Demulsification of emulsions can be summarized by four phenomena occurring either sequentially or simultaneously. These are flocculation and/or aggregation, creaming or sedimentation, coalescence, and phase separation. The efficiency depends upon the matching of the demulsiner with the process residence time, the concentration and stability of the emulsion, the temperature, the process vessel, and the mixing, all of which affect the aggregates before coalescence occurs. These various stages are illustrated in Figure 16. The figure shows a schematic describing four stages of demulsification. It summarizes the changes as the emulsion is influenced by chemicals, solvents, mixing conditions, size distributions of the droplets, heat, and the vessel used for separation.

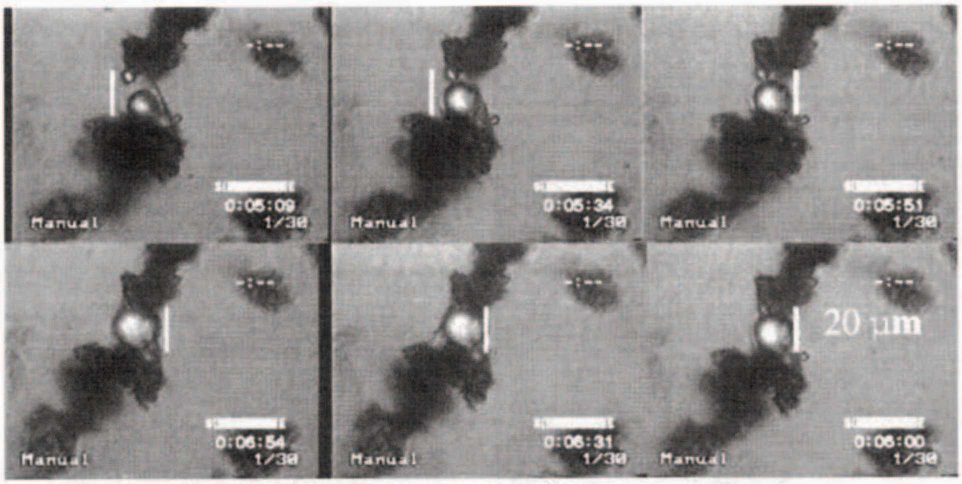


**Figure 17** Photomicrograph of flocculation and coalescence of a bitumen-stabilized W/O emulsion after treatment with an oil-soluble demulsifier. (From Ref. 82.)

Figure 17 is a photomicrograph of flocculation and coalescence of a bitumen-stabilized W/O emulsion after treatment with an oil-soluble demulsifier. The large droplet approaches the smaller droplet and they eventually coalesce. In this case, coalescence is the rate-determining step. Figure 18 shows bitumen W/ O emulsions droplets before and after treatment with a demulsifier in the oil phase. The aggregates of larger droplets, after treatment, indicate that coalescence occurs during or before flocculation. Note the change in the distribution of finer droplets from 10 s to 24 h after treatment.

In industry, if crude oil emulsions do not coalesce and/or phase separate in a given time frame, and persist throughout the process, the emulsion is deemed stable or tight. Demulsification can be monitored by bulk phase separation over time and/or by a more fundamental approach of examining the interfacial dynamics which provides some understanding of the demulsification mechanisms. The first is used in the field and/or as part of a laboratory study. Here, efficiency is defined as the rate of coalescence and water resolution, by tracing the fraction of water resolved over time and using an initial slope of the curve as an efficiency factor (202). The second approach is more complex and is most often used in research. It includes flocculation, coalescence, and film-drainage phenomena. In the second approach, monitoring the growth of droplets over time or the disappearance of droplets into the bulk phase provides data that have been used in the development of many models on coalescence kinetics (203-205). However, obtaining experimental data to test these models relies on techniques such as microscopy and image analysis, light scattering, or turbidimetry (62, 76, 206, 207). Many theories (208, 209) have been developed for the droplet growth or disappearance over time as a measure of emulsion stability (90, 210) and instability (211). Droplet growth through water attraction by holes developed in the interface, or by Oswald

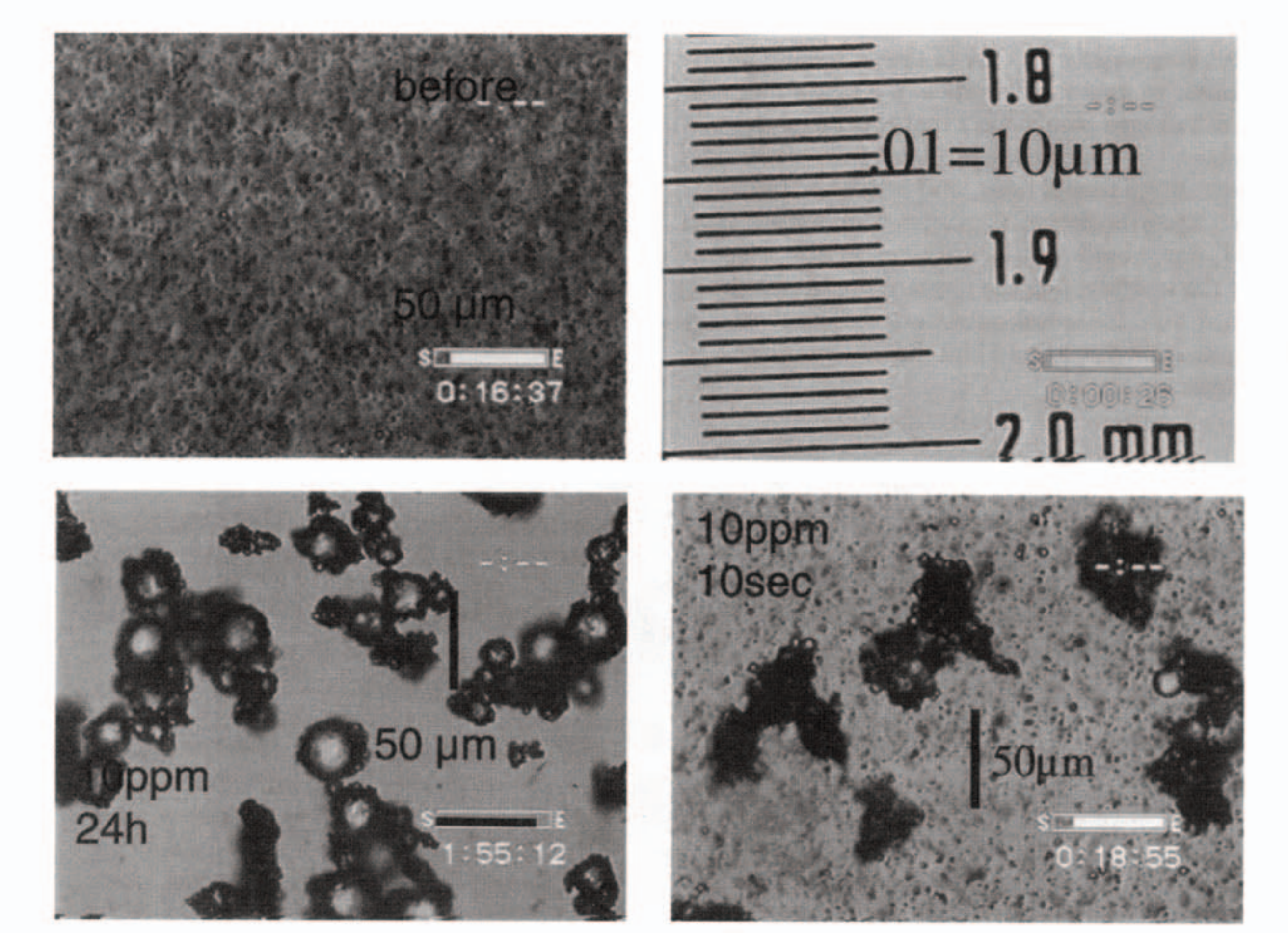


**Figure 18** Photomicrograph of bitumen W/O emulsion before and after treatment (after 10 s and 24 h clockwise) with a demulsifier showing the aggregates of larger droplets with smaller droplets attached. (From Ref. 82.)

ripening mechanisms, are a few of the reasons behind coalescence. The lamella drainage approach involves the interplay of both surface/interfacial forces and hydrodynamic forces (212). Interfacial rheology is important in the latter.

## A. Creaming and Coalescence

For a simple two-phase system consisting of an upper organic phase and a lower oil/water emulsion phase, Ostrovsky and Good (213) distinguished between the kinetic and aggregative instability of macroemulsions. The kinetic instability was identified as sedimentation or creaming, which was distinguished from aggregative instability. They developed a model in which the system coalescence occurred under agitation, and then traced coalescence and sedimentation times. The latter arose out of their studies on drop size versus agitation relationships, the former through low interfacial tension (range 0.024-0.33 dyne/cm) and coalescence-time correlations.

However, according to Vold and Vold (214), creaming is the separation of an emulsion into a concentrated and a dilute fraction through centrifugation or gravitational settling. The concentrated part is rich in the dispersed phase and the remaining dilute phase has finer droplets. The rate of creaming of noninteracting particles depends on density differences and the square of the droplet radius. If particles are interacting and held in a confined space, the rate of creaming involves complex hydrodynamics, wall effects, and hindrances. If the particles are aggregated the creaming rates are higher than the rate with the primary particles owing to the larger aggregate radius and the relative porosity (tightness or loose nature) of the aggregate. Flocculation may help to accelerate creaming, as particle concentration increases. The floc which is sedi-menting more rapidly also sweeps or intercepts smaller droplets during the mass movement. Visually, creaming appears as a moving boundary of highly turbid material away from a lesser turbid material. This boundary is used to trace separation rates.

If coalescence or rupture of the interdroplet films common to two contacting droplets occurs during or before creaming, the destabilization rates are measured by tracing the changes in droplet size distributions with time, or by counting the number of droplets of specific diameters over the same time. In the case where a droplet merges with the bulk, the times of both approach and merge are measured.

One of the first theoretical interpretations of the coagulation process for hydrophobic sols was developed by Smoluchowski (215). This was later extended to flocculation and coalescence kinetics (216). Becher (89, 100, 117, 211) describes these theories in some depth. He stated that demulsifieation is the most important and the most complete example of emulsion stability. There is a distinction between a dilute emulsion system and a concentrated system. In the dilute system it is expected that the rate of flocculation is much lower than the rate of coalescence. As the droplets increase in number (or volume fraction), there is a much faster increase in the rate of flocculation and a slower increase in the rate of coalescence. In highly concentrated emulsions, coalescence can be rate determining. Over a certain range of concentrations the two processes can be the same order of magnitude.

One can thus add chemicals in a dilute system such that the rate of flocculation is unaffected but coalescence is inhibited. In some cases, creaming can be ruled out if the densities of the two phases are adjusted closely as in bitumen emulsions. Becher has noted that tracing the number of particles as a function of time is more sensitive than the specific interface method, as a 10% decrease in interfacial area is accompanied by a 27% decrease in the number of particles for a fixed size distribution.

Smoluchowski (215) modeled the decrease in particle numbers over time. In the model there was no distinction between single droplets, primary particles, and aggregates. The number of particles diffusing through a sphere surrounding a given particle in a unit time is equal to the number of particles adhering to a single particle. Therefore, for fast, irreversible flocculation alone in a dilute dispersion Smoluchowski's expression is:

$$N = N_0/(1 + a N_0 t) \tag{6}$$

where $N_0$ = the number of particles at time zero, N = the number of particles at time t, a = rate-determining constant = 8πDr, D = diffusion coefficient = kT/6πηr, r = droplet diameter, k = Boltzmann constant, $T$ = temperature, η = the viscosity, and the half-life of an emulsion becomes $1/aN_0$. A plot of 1/N versus t gives the rate constant a, which approximates to a = $10^{-11}$ $cm^3s^{-1}$.

In a flocculating concentrated emulsion, $aN_0 \gg K$, and the contribution of unreacted primary particles is negligible. A rapid flocculation rate relative to the rate of coalescence is given by Van den Tempel (216):

$$N = N_0\,[1 - \exp(-Kt)]/KT \tag{7}$$

Here, K = coalescence rate constant, and T= absolute temperature. When the rates are equal for both coalescence and flocculation, a=$10^{-12}$ to $30\times10^{-11}$ $cm^3s^{-1}$. When coalescence is slow the collision frequency and the duration of collisions are more important. In this case, mixing enhances collision frequency.

Smoluchowski's theory assumed that coagulation has been going on for a long time and the system is near steady state. Flocculation is considered irreversible. Van den Tempel (216) assumed that the rate of coalescence is proportional to the number of points of contact between the particles in an aggregate. He considers flocculation and coalescence to occur simultaneously. The number of primary particles not yet combined into aggregates is:

$$N_1 = N_0\,(1 + aN_0t)^{-2} \tag{8}$$

the number of aggregates is $N_V$:

$$N_v = aN_0{}^2\,t\,(1 + aN_0t)^{-2} \tag{9}$$

and the number of primary particles in unit volume associated into all aggregates is:

$$N_0 - N_1 = N_0\,[1 - 1/(1 + aN_0t)^2] \tag{10}$$

The average number of primary particles in an aggregate is:

$$N_a = N_0 - N_1 / N_v = 2 + aN_0\,t \text{ at time } t_1 \tag{11}$$

because coalescence has taken place. If *M* is the average number of separate particles existing in an aggregate at time t, then *M* can be unity if coalescence is fast, and slightly less than $N_a$ if coalescence is slow. The rate of coalescence is then proportional to M—1, i.e., the number of contacts between particles in an aggregate. Van den Tempel claimed that in dilute emulsions a small aggregate consists of one large particle with one or two smaller ones and these build up linearly. *M* increases by adherence of new particles and the rate of increase in *M* is caused by flocculation:

$$\mathrm{d}M/\mathrm{d}t = aN_0 - k(M - 1) = aN_0 - kM + k \tag{12}$$

where *K* is the rate of coalescence. Integrating for *M*=2 when t = 0,

$$M - 1 = aN_0/k + (1 - aN_0/k)\exp(-kt) \tag{13}$$

The number of primary particles, whether flocculated or not, was found by adding the number of unreacted primary particles to the number of particles in an aggregate:

$$N = N_1 + N_vM \tag{14}$$

$$= N_0/(1 + aN_0t) + aN_0^2\,t/(1 + aN_0t)^2 \{aN_0/K + (1 - aN_0/K)\exp(-Kt)\} \tag{15}$$

The first term in Eq. (15) is the number of particles found if each aggregate has been counted as a single particle; the second describes the number of particles that enter the aggregate and is not found in the classical Smoluchowski treatment. Here, the composition of the aggregate is taken into account. When K= oo, coalescence is immediate, and the expression is reduced to the first term. When K= 0 no coalescence occurs, and N= $N_0$ for all times t. For $0 < K < \infty$, the rate of aggregation changes the particle concentration.

Further reviews of coalescence and flocculation kinetics were reported by Becher (211), Tadros and Vincent (90), and Hartland (217). For all practical purposes the above treatments usually suffice in crude-oil studies. Extensive treatments of coalescence and flocculation kinetics were modeled as required for various other emulsion applications. Borwanker et al. (218) developed a mathematical model to account for flocculation and coalescence kinetics occurring simultaneously. They modified Van den Tempel's treatment for coalescence to include coalescence occurring in small flocs. They showed how the rate-controlling mechanism could change from coalescence-rate controlling to flocculation-rate controlling during an emulsion lifetime. They further extended the model for concentrated emulsions.

The disappearance of droplets by counting numbers of particles in a given field of view is modeled kineti-cally for most experimental data. Bhardwaj and Hartland (206) have shown that, with their demulsifier and crude oil emulsions, coalescence occurred in the first few seconds by a binary coalescence mechanism, then, after a lag of 7 min, the coalescence time was several minutes. The coalescence was enhanced by gentle mixing to improve collision frequency (with solids this is called orthokinetic coagulation), in contrast to the quiescent approach which relies on Brownian motion or thermal convection currents for collisions. Menon and Wasan (62) traced the number of droplets per unit volume as a function of time for water-in-shale oil emulsions. They fitted their data to

$$N = N_o\exp(-Kt) \tag{16}$$

where *N* is the number of droplets per unit volume of aqueous phase, $N_0$ is the number of droplets per unit volume at initial time, *K* is the coalescence rate constant, and t is the time in seconds. After the addition of demulsifier, the plot of number of droplets versus time was not linear and could not be represented by a first-order rate equation. They used a rate expression containing both coalescence and flocculation rate constants (211) for the system treated with demulsifier. Here, a is the flocculation rate constant:

$$N = N_o/(1+aN_o t) + aN_o^2 t/(1+aN_o t)^2 \, [aN_o/K + (1-aN_o/K)\mathrm{e}^{-kt}] \quad (17)$$

They showed that the coalescence rate constant, *K*, increases while the flocculation rate constant decreases with increased demulsifier concentration. Flocculation is high at low demulsifier concentration. At increased concentration it breaks the interfacial film and promotes coalescence. A plot of initial coalescence rate constant versus dosage indicates that the demulsification of this system was in a flocculation-rate controlling state, within its environment. Aggregation is reversible and the drop identity is not lost.

Mixing or agitation has been shown to augment coalescence by enhancing the rates of collisions. Menon and Wasan (62) have shown that the flocculation rate constant increases to a maximum with increasing speed of mixing. In order to promote coalescence there is an optimum mixing speed for every system. Redispersion occurs with excessive mixing or high rates of mixing.

Mason et al. (219) concurred on system specificity for mixing, when they showed that aged crude emulsions had less droplet growth during mixing and that separation was slow. However, the aged emulsion required increased demulsifier concentrations and a longer mixing time after demulsifier addition. This led to larger droplet size and faster separation. An emulsion mixed for 45 min had a mean size of 61 μm in contrast with 28 μm for 15 min of mixing at the same speed. Larger droplet size could promote boundary coalescence instead of binary coalescence. They used the half-lives of oil and water (i.e., time required to generate a clear layer containing one half of the oil or water initially present in the emulsion) for slowly separating systems as a measure. They also showed that for the size range between 25 and 30 μm, separation was a function of age, demulsifier concentration, and mixing time, and that mixing time could be optimized with lower demulsifier concentration, or could provide a measure of demulsifier efficiency.

Bhardwaj and Hartland (206) showed that binary coalescence improved with demulsifier and with mixing. Increasing temperature from 20° to 40°C was significant in producing increased droplet sizes over time with 100 mg/L demulsifier. The higher dosages reduced the coalescence time from 5.2 s (50 mg/L) to 4.2 s (100 mg/L). They found that initial rapid coalescence was followed by slow coalescence. They traced coalescence rates by plotting the natural logarithm of interfacial area per gram of dispersed phase against time, using the slope as a measure of coalescence rate (fractional decrease of surface area per minute). As a measure of binary coalescence rate, the droplet diameter growth was traced with time. Fast coalescence corresponds to a few seconds of binary coalescence time. Sjöblom et al. (136) showed that increased speed of mixing over time for North Sea crude oil emulsion produced decreased droplet sizes. Thus, the experimenter should be aware that if the objective of the work is emulsifica-tion, high speeds are desirable; if demulsification is the objective, then mixing must be done gently and with great care.

Tracing the resolved volume fraction of the collected bulk free-water layer over time is also a common means of measuring destabilization (220). Centrifugal forces cause the droplets to flocculate and cream faster, facilitating the drainage of thin liquid films formed between them (221-230). Void and Maletic (231) indicated an Arrhenius type of relationship between centrifugal forces and dosage of demulsifiers for demulsification of an ideal O/W emulsion.

Before coalescence occurs between the primary drop and the bulk separated phase, or between two or three interacting droplets, increased hydrostatic pressures are developed in the creamed layer, regardless of whether the creaming is achieved by gravity or centri-fugation. These pressures are the driving forces for drainage. Not every collision results in coalescence. This is because coalescence time depends on the rate of film drainage between the droplets. Allan and Mason (232) and Hartland (233) predicted that the film thinning was inversely proportional to the droplet diameter.

In another view, Vold and Vold (214) suggest that holes are formed in the interfacial film and this allows the droplets to merge. Ivanov and Dimitrov (234) indicated that holes are due to surfactant depletion at the interface. However, extensive studies conducted to understand the mechanism of destabilization of the thin/thick films formed between two droplets, or between droplet and bulk phase, indicate that the process is much more complex and may involve more than one mechanism. These are not all fully understood as yet for crude oil and bitumen systems.

## B. Film (Lamella) Drainage - Model of Coalescence

A model of coalescence via film-drainage phenomena and flow dynamics has been discussed theoretically and exper-

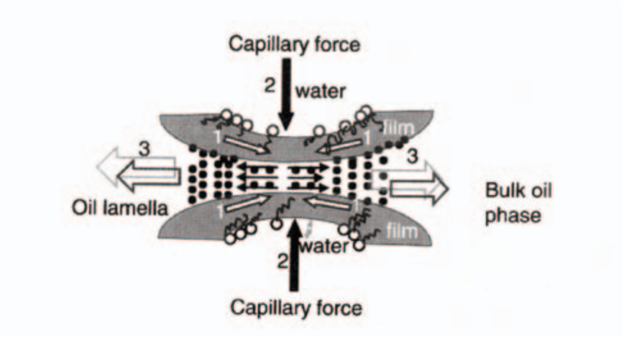


**Figure 19** Schematic of a dynamic bitumen film lamella between two approaching water droplets which are stabilized by an interfacial skin.

imentally by several investigators over the past decades (235). From this body of work the belief is that the coalescence process of two or more droplets, drop/drop, drop/bulk, can be divided into three steps: approach, film drainage, and rupture. Film drainage is a function of bulk and interfacial fluid rheology in a balance of hydrodynamic and thermodynamic (sum of all surface forces) interactions. The hydrodynamic interactions increase rapidly as the gap width between the droplets decreases. The flow results from hydrostatic pressures normal to the surface due to the nature of the interfacial fluid in a given space. The interfacial fluid is affected by the tangential mobility and deformation of the droplets' interfaces. Figure 19 is a schematic which shows the lamella of two approaching water droplets stabilized by a bitumen film. Some of the forces for the draining process are illustrated.

Surface forces include both long and short range. The long-range forces are van der Waals attraction, steric, and, lately, structural forces (151, 236). The short-range forces include the chemical bonding to surface groups, dipole interaction, hydrophobic bonding, and Born repulsion. The short-range forces determine the interfacial structure, and the long-range forces determine whether the emulsion droplets are aggregated/flocculated. The surface forces are lumped together and are also called disjoining pressures/forces - a term coined by Derjaguin (237). These are important in very thin films of thicknesses less than 100 nm. A positive disjoining pressure gradient is required to impart resistance to film thinning, and a negative disjoining pressure has the opposite effect and increases in magnitude as the film thins. However, in simpler systems such as soap-film experiments, Scheludko and Exerowa (238, 239) showed that the negative disjoining pressure depends on the inverse third power of film thickness.

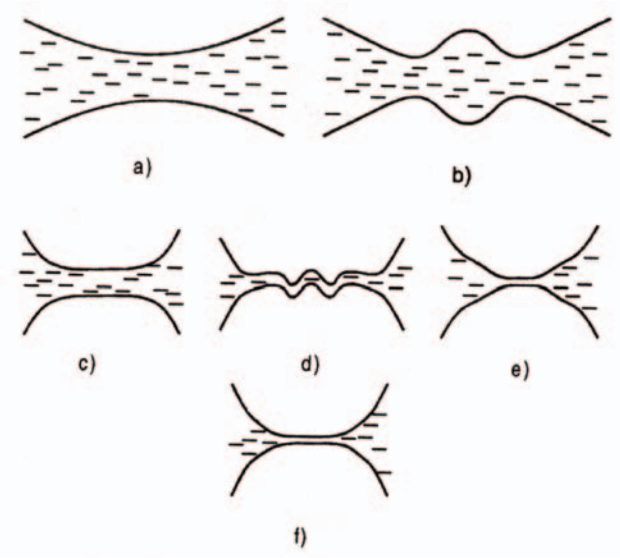


**Figure 20** Schematic of the evolution of a thin liquid lamella between two approaching droplets (147,151): (a) droplets' mutual approach with slight deformation of interfaces; (b) dimple formation on surfaces; (c) near plane-parallel film; (d) thermal or mechanical fluctuations at interface; (e) black (common) film formation; (f) growth of black film or Newton film to equilibrium radius.

The stages of thinning for a simple emulsion system can be described as follows (see Fig. 20 for a schematic example of an ideal foam system for comparison):

1. When two droplets are approaching, the thickness, <5, decreases rapidly with time, and dimpling (also corrugations or oscillations) precedes the formation of a plane parallel film.
2. As the viscous and interfacial resistance forces in the film increase the film is slowly thinned to a critical thickness, $\delta_{cr}$, for rupture.
3. Rupture occurs when a hole is formed.

Step 2 has the slowest rate of thinning and is thus a rate-limiting step that determines the film lifetime. The thinning rates of steps 1 and 3 are fast. If we examine this in terms of flow we can explain the simple drainage process by what has been observed under a microscope.

Increased capillary forces at the Plateau borders allow film drainage to occur until the films have thinned to an upper limit of about 100 nm. The film reaches a metastable state and may rupture suddenly due to dust particles, thermal or mechanical shocks, or may just reach a critical thickness that it can no longer sustain. A hole in the film may form as a result of thermal fluctuations of the two expanding droplet surfaces, and at the same time there are forces working to maintain an equilibrium film thickness. These forces originate from the surfactant monolayer which is undergoing dilating and shearing deformations, causing stresses and opposing flow. The tangential bulk stress from the film liquid causes surface-layer flow. The droplets are pushed together by external pressures such as buoyant forces, or other applied forces such as dynamic pressure gradients in the continuous medium.

Thick films (≈500 nm) before drainage appear as colorful interference fringes created by passing a monochromatic light beam through the film, and this can be measured from interferometric patterns (240). The thicknesses would correspond to the wavelength of the color. As the film thins down to thicknesses below the wavelength of visible light (10-100 nm), the film appears to be black. During thinning, liquid flows out in a radial flow pattern to the Plateau borders pulled by osmotic or capillary pressures. Very thin films with negative disjoining pressures, and with low viscosity will follow Reynold's law for radial flow, where the change in thickness, D, in time, t, is $d(l/D^2)/dt = aP$, where P is the hydrostatic pressure, a is a constant ( $= 4/3\eta r^2$), r is the radius of the film, and η is the viscosity of the fluid. Reynold's flow expresses the motion of a fluid being squeezed between two approaching solid surfaces with fixed interfaces. Detailed treatments of Reynold's flow are given by Hunter (122). Emulsion films approximate to type C in the Hunter categorization of film types.

Film lifetime is taken as the time taken to reach a given thickness plus the breaking time at that thickness. When this critical thickness, $\delta_{cr}$, is reached, and if there is an equilibrium black film, it only persists at an equilibrium or stable state provided that the barrier of potential energy is high enough. In foams the first black films, known as the common films (10-100 nm thickness, and gray or silvery), precede the second black films known as Newton black films (5 nm thickness, black). The Newton films are seen to appear after the colors of the interferometric pattern (created by the film's dispersion of the monochromatic light beam) change into gray, silver, or black. The Newton films may form spots or holes.

Drainage rates are low for rigid films and high for mobile films. The stability of the films is dependent on the rheological properties of the interfacial layer, the adsorbed layer of surface-active materials, the temperature, and the composition of the fluid and its dynamics inside the droplets. Most theoretical analyses of film drainage describe the relationship between the coalescing forces (which are suction forces at the Plateau borders and which promote drainage), the bulk phase, and the interfacial effects that resist drainage. Since the film-drainage step is rate determining, investigations have been focussed on the kinetics through the many drainage models, the important effects being the critical collapse thickness and time, bulk viscous effects, and the interfacial viscosity and elasticity. Various hydrodynamic models of the film-drainage process have been developed (241—248).

Several generalized models that account for mobility of the surface, kinetics of adsorption - desorption of surfactants, surface and bulk diffusion, surface rheological properties, and flow in both film and bulk phases were developed by Wasan (236) and Nikolov et al. (249). They introduced the concept of structural forces resulting from the narrow size distribution of micelles or colloids forced into the restricted volume of the film. The thinning process for these films becomes stepwise through various stratification stages as each micellar layer flows out. The approximate sizes of micelles has been be determined from these steps as a photocurrent detects the change in the light transmitted (240). There were correlations found between the number of film-thickness transitions and the increased chain length of simple surfactants such as N-alkyl sulfates. Stepwise thinning depends on effective micellar volume, polydispersity, film size, and film thickness. The driving force for this drainage is the gradient of the chemical potential of the micelles at the film's periphery.

Nikolov et al. (250) derived an expression for multi-layering of the micelles, relating them to the interaction free energy. They also integrated disjoining pressures with respect to film thickness in their theoretical model. The reader is referred to the references for more detail. According to Nikolov et al., an increase in surface viscosity means a decrease in mobility and a longer drainage time. A low surface viscosity means that the Gibbs-Marangoni effect has more impact on drainage time and coalescence rate. They reported that the estimated drainage time for a mobile surface with no surfactant is small in comparison with an immobile surface having large surface rheological stresses. Thin-film drainage times of foams were shown to increase with the increased dilatational modulus and with increased surfactant carbon chain length (248, 251, 252). According to these authors, drainage is very important in preceding coalescence, and is affected by film viscosity, film thickness, surface diffusion, surfactant adsorption, both surface shear and dilational viscous properties, surface shear, and dilational elastic properties, as discussed earlier.

Thus, a demulsifier that would enhance drainage rates and film thinning may also counteract Marangoni flows through the demulsifier's competitive adsorption. Drainage time is long when the interfacial tension gradient is high, shear elasticity is high, and both bulk and surface diffusion of demulsifier cannot counteract the tension gradient. Demulsifiers can reduce the drainage time by inducing decreased interfacial viscosity and lower interfacial film elasticity while promoting high interfacial mobility.

When the interfacial shear elasticity is moderate, at moderate surface viscosity, the thinning velocity will be greater than the Reynolds velocity. An increased surface viscosity means decreased surface mobility and a longer drainage time. These are all factors to be considered in decisions toward positive steps of destabili-zation.

Although stable diluted bitumen films are more complex than soap films, they appear to follow a classical film-drainage pattern without demulsifier as shown in a study by Angle et al. (82) and reproduced in Fig 21, 22.

Figure 21 shows actual droplets of water surrounded by a film of bitumen. The fine particles forming the structural barrier component of the bitumen film can be seen around the bright water droplet. Other stabilizers preventing coalescence are in the film lamella. The drainage of an actual film of bitumen between two water droplets is depicted in Fig. 22 in frames 1-5. It was observed by Angle et al. that, generally, for a stable bitumen film, a typical drainage time to a common film was 25 min and to arrive at a Newton film was approximately 30 min in a 300-µm film diameter. Film thicknesses were measured by interferometry, using a capillary balance technique for plane parallel films (A.D. Nikolov and D.T. Wasan, personal communication, 1998) (253).

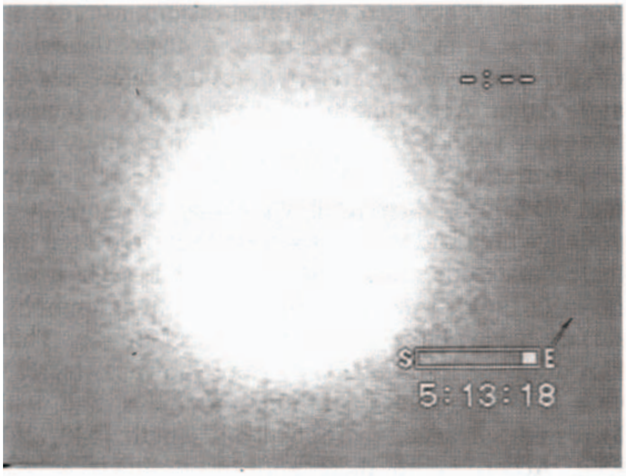


**Figure 21** Photomicrograph of stabilizing asphaltenes particles in a 300-µm diameter bitumen film structure between two bitumen-stabilized water droplets.

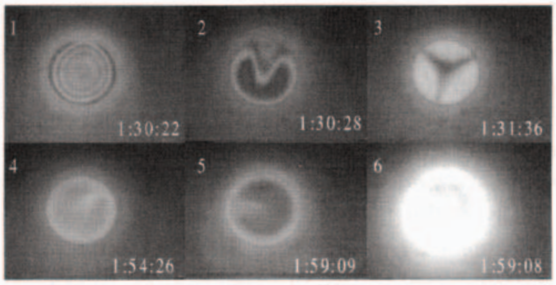


**Figure 22** 2 Photomicrograph of film drainage and thinning of a 300-µm diameter bitumen film (lamella) over time, as measured by videomicrography, capillary balance techniques, and interferometry. (From Ref 82.)

In Fig. 22, the multiple colors (frame 1 - dark gray) depict a thick film before drainage. The plane white/gray depicts a drained stable bitumen film closely resembling a common film (frame 4) or stable Newton black film (frame 5). A close-up photomicrograph shows the uniformly sized and distributed particles of asphaltenes and resins at the interface of the water droplet, but held in the confined space within the lamella (frame 6). These uniformly sized aggregates are responsible for providing a structural component of disjoining pressure in a coherent stable bitumen film according to Wasan's structural stabilization model. Angle et al. (82) showed that an oil-soluble demulsifier increased film-thinning rates up to a critical film radius and for an optimum concentration of demulsifier. Not all emulsion systems would follow this drainage process before coalescence. Although stepwise thinning may occur, the diluted bitumen and crude oil/water interfaces are more networked and require chemicals to achieve demulsifica-tion. Other effects of demulsifier blends on crude-oil film properties, rheology, drainage, and, lately, film thickness stability for Louisiana crudes are reported by Kim et al. (65).

The choice of demulsifiers is not an easy process as there are thousands of patents published on various formulations.

## V. PERFORMANCE DEMANDS ON DEMULSIFIERS

### A. Basic Behaviors Expected of Demulsifiers

From this review, it would appear that the basic demands on demulsifiers are the abilities to have one or more of the following behaviors: (1) strong attraction to the oil/water interface with the ability to destabilize the protective film around the droplet and/or to change the contact angle of the solids which may be part of the interfacial film; (2) ability to flocculate the droplets; (3) ability to promote coalescence by opening pathways for water's natural attraction to water; and (4) promotion of film drainage and thinning of the interdroplet lamella by inducing changes to the interfacial rheology such as decreased interfacial viscosity and increased compressibility.

It has been shown by Berger et al. (64) and confirmd by Kim et al. (63) that equal partitioning of demulsifier from the oil into the water phase appears to be important for an effective demulsifier. The change in Gibbs free energy for transfer of surfactant from oil to water is related to the relative equilibrium solubilities or partitioning coefficient of the demulsifier in either phase. It would suffice to infer that partitioning would occur only if the interface barrier's pores are opened by adsorption of surfactant. Transfer would also entail diffusion through the film based on a strong attraction to the water phase. However, partitioning would not be a dominant factor when the other effects such as dissolution of the interfacial material or their flocculation by the demulsifier (82) occur. The demulsifier's relative solubility in oil is important for mass transport to the interface, and where this is inadequate, carrier solvents have been used. Demulsification mechanisms include displacement, disruption by adsorption, solubilization, and competition with the emulsifier for interfacial sites. The work of desorption of the emulsifier from the interface would be important for the process.

Strong attraction to the oil/water interface is often dependent on diffusibility and interfacial activity of the demulsifier. This also involves speed of migration to the interface and the ability to compete or interact with the emulsifier by one or more mechanisms. The demulsifier must be relatively soluble in the continuous phase yet not completely soluble, and able to transport itself to the interface. In some cases, if the interface is stretched, the demulsifier must get there before the emulsifier can readsorb. The presence of demulsifier in the dispersed water phase has been shown to increase the rate of film drainage (254). According to Mukerjee and Kushnick (167, 255, 256) an effective demulsifier lowers the interfacial tension gradient and enhances the coalescence rates by rapidly diffusing to the interface. For fast diffusion, the molecular weight of the demulsifier becomes important. It may also dampen the growth of surface waves which alternatively stretch and compress the film. Thus, as the gradient in the film is created, the demulsifier may counter the inward flows. If it counters the inward flows it may enhance drainage, depending on the flexibility of the film. If it makes the surface more rigid, the liquid in a film does not drain as rapidly, but drains more slowly than would a film with a flexible surface. This leads to both reduced thinning and rates of coalescence.

When the continuous phase is not compatible with the demulsifier, carrier solvents are used. Most carrier solvents are alcohols or benzene derivatives such as glycols and xylene. Carrier-solvent effects were emphasized by Neustadter et al. (166) with xylene being a good carrier for the demulsifier. Wasan and coworkers (63, 164, 182) showed that alcohol not only acted as a cosurfactant but was also a good carrier solvent. The relative solubility of the demulsifier is thus related to the organic groups, the polar groups, the configuration of the demulsifier, and the molecular weight. Most successful demulsifiers are of intermediate molecular weight as is shown in the next section. Temperature and solvent effects on the demulsification of North Sea crude oil emulsions were investigated in some detail by Sjöblom and coworkers (81, 136). Of the large number of solvents investigated only three were considered to be effective destabilizers.

A demulsifier with the ability to destabilize the protective film around the droplet can create changes to the film as well as to the natural stabilizers. The demulsifier may influence the droplet interfacial film material by displacement (98, 115, 257), complexation, changing the solubility in the continuous phase, changing the viscosity of the interfacial film, or through quick diffusivity (65, 258) and adsorption, thus inhibiting the Gibbs-Marangoni effect, which counteracts film drainage.

An example of film dissolution and displacement is shown in Fig. 23, which shows the effects of a fast-acting demulsifier on a diluted bitumen W/O emulsion. The action is traced clockwise as the demulsifier solution flows in a capillary in which the stable bitumen emulsion is held within the confined space but not deformed. At time 5 min:45 sec the system is untreated. At time 6 min:00 sec, the movement of the demulsifier solution into the emulsion is initiated as a destabiliza-tion front. The demulsifier contact front causes the interface of the droplets to be broken

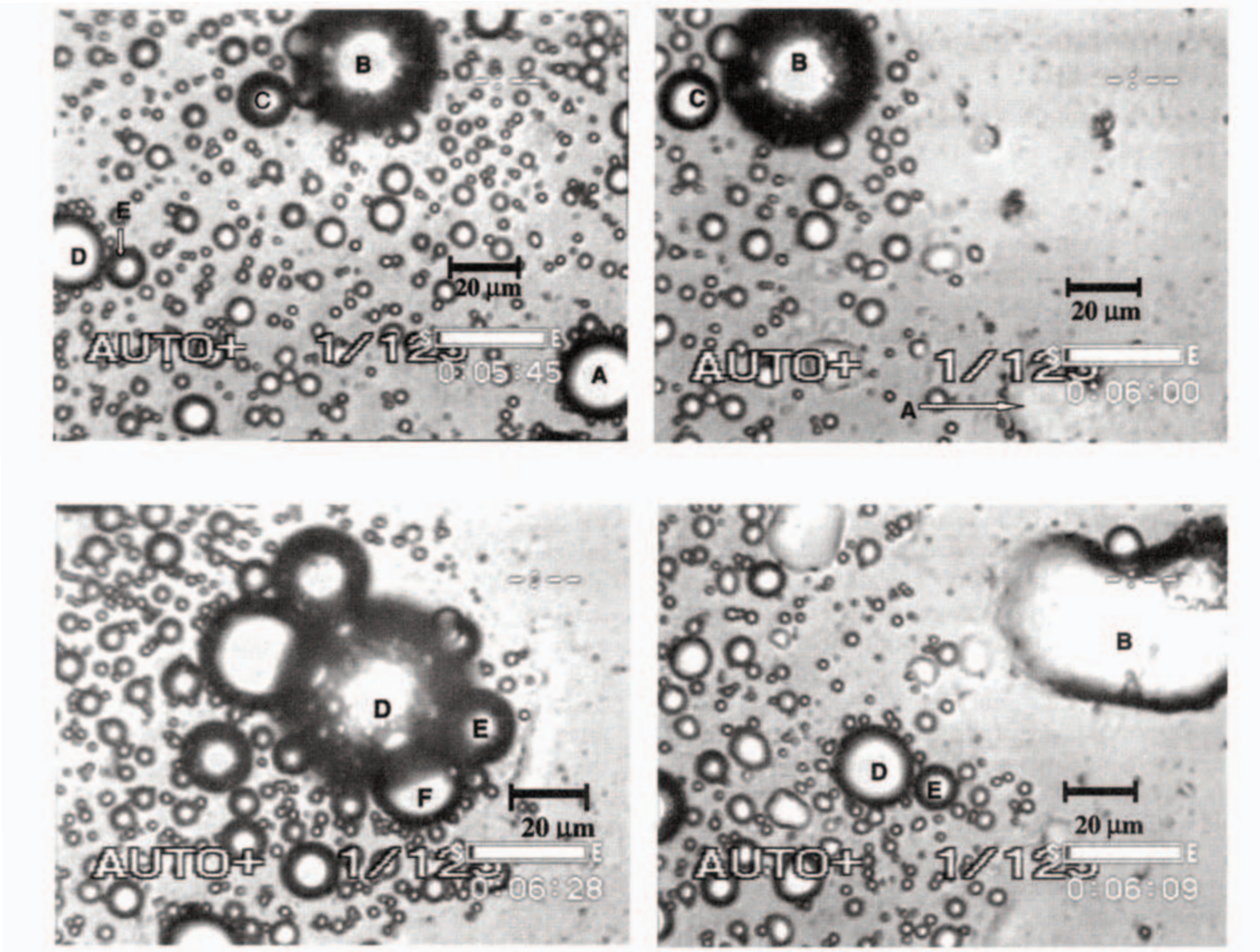


**Figure 23** Photomicrograph of a moving front of solvent plus a fast-acting demulsifier dissolving/disrupting the interfacial material on contact, causing instant demulsification. Measurements were in real time.

by disruption or dissolution. There is also growth of the droplets with diffusion of the demulsifier solution into the sample, as seen in D (time 6 min:09 sec to time 6 min:28 sec). The large droplets are broken, leaving the smaller more rigid droplets in the solution. It appears that the interfacial material is being disrupted by the demulsifier. Note the relatively large droplet, B, with its attached colony of fine droplets.

## B. Demulsifier with Ability to Flocculate Droplets

Based on the interparticle distance or tightness of packing of droplets, the ability to flocculate may not be a necessary criterion for demulsifiers. When there is a high volume fraction of water droplets in the oil, as shown in Fig. 10, the emulsions are already in close contact and in a state of readiness for demulsification. In this case the added demulsifier must have mass-transport power to be integrated into the gaps between the droplets. High diffusibility helps with demulsification and heating may improve the transport. If the residual emulsions left in the oil are around 3% water and the droplets are very finely dispersed and widely distributed, the flocculating ability of the demulsifier is required to gather up the droplets. This happens more often in oily effluent treatment and in very dilute systems where droplet collisions are not frequent. Then, indeed, the high-molecular-weight and highly branched demulsifier molecules with an affinity for the water droplet provide some advantage. Here, gentle mixing will provide an additive effect.

### C. Demulsifier Creating Surface Changes to Solid Stabilizers

Lucassen-Reynder and Van den Tempel (259) emphasized that, in order to develop a strong interfacial film, solids as emulsifiers require a certain tightness of packing but this needs material and time to be built. The solids, which are W/O stabilizers (62, 260), have the correct wettability (261) or three-phase contact angle at the interface (174, 262-264). The role of solids as stabilizers is complex (174, 208, 265). The nature of the solids can be changed by a demulsifier. The demulsifier may adsorb on to the solids causing them to be more oil or water wettable. Often wetting agents of low molecular weights achieve this function. Thus, solids become more compatible with either the hydrophobic or hydrophilic phase, and are easily transported into the continuous phase away from the interface.

The nature of the solids may be variable, and may be one or more of the following species of minerals encountered in the petroleum production process: aluminum sulfates, calcium carbonates, iron sulfides, clays, drilling muds, crystallized paraffins, and asphal-tenes. Most often after association with petroleum, inorganic solids adsorb the organics and form complexes with improved surface activity and thus influence the bulk rheology (266). It is thus desirable for a demulsifier to remove minerals to the water phase and the paraffins and organics to the oil phase (which can be treated easily by the refiners), while leaving a clean, sharp mirror-like interface of oil and water. Asphaltenes as partially solubilized solids are best recommended to be solubilized into demulsifier micelles in the oil phase. In fact, Little (267) has suggested that the demulsifiers must be such that they form micelles in the oil phase and do not themselves become stabilizers to the droplets by creating a more rigid interface stronger than the original natural emulsifiers.

### D. Demulsifier Inhibition of Film Forming Before Emulsification

In some situations demulsifiers have been used to inhibit emulsification (97). Demulsifiers used as inhibitors (1) in emulsification was considered in the prevention of “chocolate mousse” formation for oil spills (1, 268, 269). This topic has received considerable attention as increased environmental concerns demanded clean up of oil spills. Consequently, technology and chemical demulsifiers have been developed to address sea spills. However, discussion of this topic warrants a separate section, as a large part of the understanding of paraf-finic W/O emulsions and demulsifier chemistry was stimulated by North Sea operations and oil spills at sea.

In downhole applications where mixing is very thorough and the temperature is high, reduced viscosity of the oil decreases the high lift pressure requirements. The use of demulsifiers as emulsion inhibitors has been indicated as an advantage. Sometimes a high concentration of fine micrometer-sized droplets would produce higher viscosity in some cases than the oil alone. The fine emulsions produced would consequently counteract the decrease in oil viscosity caused by temperature increases, and thus inhibition of emulsification with chemicals is advantageous.

### E. Demulsifier Working Together with Process Equipment

One or more of the above demulsification mechanisms may be required for fast or slow resolution, depending on the production process. Generally high-throughput processes demand more complete chemical treatment and fast resolution. In contrast, low-volume throughput such as vertical treaters, or systems where the residence time is longer as the material travels through pipes in a turbulent environment and mixing is continuous, demands a slower-acting demulsifier. If heat is encountered the demulsifier must be capable of performing at the higher temperature. Synergy is often desirable to reduce costs of chemicals or heat.

## VI. CHEMICAL NATURE OF DEMULSIFIERS

### A. The Users’ Dilemma with Available Information

No single chemical by itself has been found to perform every destabilization and resolution function required in a process. This is the main reason why blends of chemicals are formulated. Each component in the blend addresses the change of a specific emulsion characteristic.

The most common problems encountered in any application of macromolecular surfactants are the matching of the commercially available products to a required end effect, according to Hancock (270). Manufacturers have assembled product combinations and provided end-use categories such as desalting chemicals, oil-slick dispersants, oil-well water-flooding viscosity improver, oil-well wettability improver, demulsifiers for W/O emulsions stabilized by heavy, light or high-acid-number oils, etc. Most chemical suppliers, based upon their experience, have put together application kits consisting of possible combinations of products that may work. Demulsifiers are labeled fast droppers, desalters, dehydrators, etc. A guide for selection is usually the relative solubility number (RSN), defined as the amount of water in milliliters required to reach cloud point at 25°C for 1 g of demulsifler dissolved in 30 mL of a solvent system containing 4% xylene in dioxane. The RSN is normally provided with the product specifications. It is rare that all basic systematic knowledge of the manufacture, composition, and performance trends are disclosed to the user.

Faced with this applications knowledge gap, the practitioner would first perform conventional bottle tests (271) to decide which are the most effective "chemical" products for the application in mind, working with samples that represent field samples as closely as possible. The screening is usually done on the spot and its success is aimed at convincing the engineers in the production application. Past experience then becomes an asset to the chemical-service representative. Although bottle tests are used for estimating the ranges of treating temperature, retention times, and settling times, it must be borne in mind that it is only a guide. It is estimated that 6-8 h of separation time in a bottle test is equivalent to 24 h in a process (272).

However, to date, it is generally agreed, by both researchers and practitioners that bottle testing is still a good guide (257). The bottle test is static and does not model closely the dynamic effects of water droplets dispersed or coalescing in the actual equipment such as control valves, pipes, inlet delivery, baffles, water wash, etc. If the point of injection of chemicals is upstream of the settler, then the test approximates the situation better. It is, however, still crucial that the characteristics of the emulsion be understood before the treatment system is selected (273, 274).

A typical laboratory bottle test is indicated in Fig 24 and 25, which illustrate the separations of a model 30% W/O bitumen (Athabasca, Alberta) emulsion at 50°C with two demulsifiers, A and B. In Fig. 24 (top photograph) the emulsion was allowed to resolve over 24 h by gravity. This is compared with the bottom photograph which shows the same treated emulsion assisted in separation by centrifugation immediately after demulsifier addition. The difference illustrates that enhancement of separation with a process aid such as centrifugation is useful for this system if time is a factor. The demulsifiers are considered to be effectively

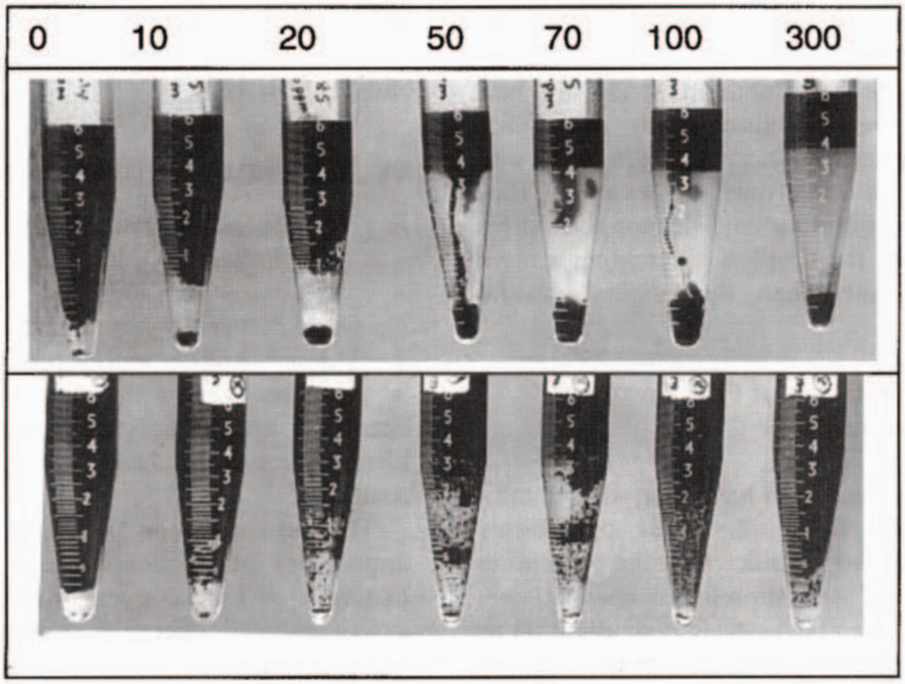


**Figure 24** Separation of bitumen W/O emulsion in tubes after demulsifier A was added: (top) by centrifugation; (bottom) by gravity separation. Dosages are indicated at the top.

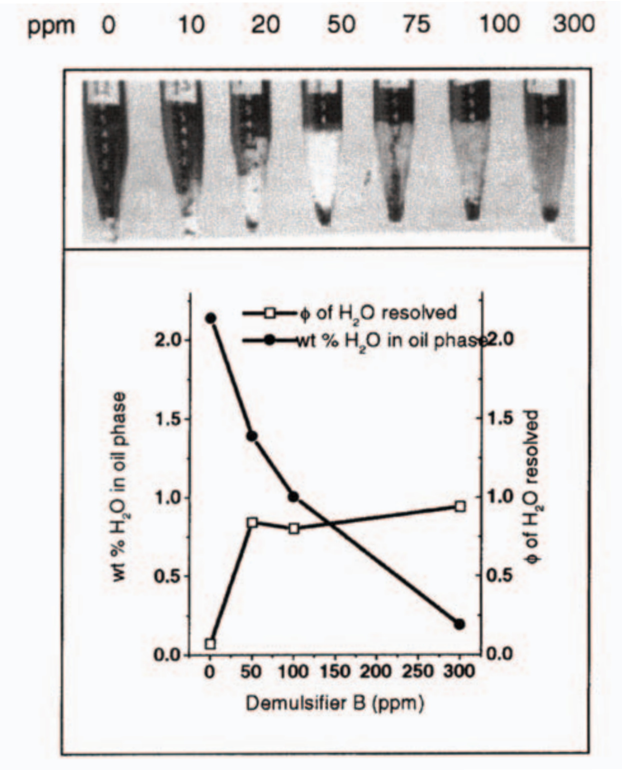


**Figure 25** Resolution of water and decrease in oil-phase moisture traced by changes in each phase of a bitumen W/ O emulsion after demulsifier B was added at 50°C; middle phase is not visible. Top-photograph of its separation, showing clarity and optimum dosage.

fast droppers. The dosages are indicated at the top. A dosage dependence is shown as separation has an optimum dosage at 70 ppm in Fig. 24. Figure 25 illustrates an improvement in emulsion resolution at 50 ppm, showing water clarity. Overdosing is observed between 70 and 300 ppm, indicated by a turbid water phase, which suggests inversion to an O/W emulsion. The resolution is represented graphically by a plot of volume fraction of water resolved, on the right Y axis and the moisture reduction of the oil phase on the left Y axis against dosage showing effectiveness. The interface pad or middle phase is not represented (275) as it was not apparent.

Researchers first used the bottle tests preliminarily to select effective potential chemical demulsifiers, then would carry out further investigative studies on mechanisms for understanding demulsification phenomena for the crude at hand. Some studies are not concerned with the chemical identity of demulsifiers, but only with the effects or the demonstration of phenomena for developing the theory. It is important to demonstrate demulsifier relative effectiveness for these studies.

## B. Choosing Demulsifiers

Most of the research laboratories (IIT, University of Bergen/**NTU**, Energy Technology of **CANMET**, Environment Canada, British Petroleum, and Indian, Egyptian, Petroleum Institutes, among others) characterize and classify both the emulsions and the demulsifiers to determine some common factors that may be used in the extraction process. The test results would act as a prescreening step to the refiners when evaluating the crudes, or as a means of preparing to deal with specific demulsification problems.

Recently, there have been many studies to explore the selection of demulsifiers by more scientific and/or empirical means for matching the emulsion or oil with the demulsifier properties. Some advances as to what is useful and what is not have been made. Demulsifiers are required to have intermediate solubility in the crude oil or bitumen and not to form strong associations with other components of the crude. Sometimes the matching of RSN and equivalent alkane carbon numbers (**EACNs**) with **BS&W** are used as selection tools.

The determination of **EACN** is based on the minimum interfacial tension derived from a test surfactant in a series of hydrocarbon solvents, and then in the crude oil. The alkane carbon numbers are assigned to the solvent. In its determination for the crude oil/component, the minimum interfacial tension (**IFT**) against the reference surfactant may match one of the reference hydrocarbon solvent. The n-alkane with this minimum would be the **EACN** for the crude. The demulsifiers are tested in a similar way to the surfactants and are assigned preferred alkane carbon numbers (**PACN**) in the crude. This appeared to be a way of predicting their behavior in crude oils from their behavior in the n-alkanes. However, this process is long and labor intensive.

Cash et al. (276) and Cayais et al. (277) used **EACNs** of crudes and matched the numbers with **PACNs** of demulsifiers.

De Silva et al. (278) correlated the **RSN** with performance information and crude-oil properties to arrive at a predictive tool for choosing demulsifiers. They attempted to derive an alternative to the bottle test by considering the oil, its acidity, associated water, salinity, and demulsifier **RSN** and **EACN** relating the demulsifier affinity for oil and water. An unstable system was defined as having equal affinities for oil and water. This surfactant affinity difference was empirically related to solubility, **EACN**, and **RSN**. Their conclusion was that a less polar demulsifier of **RSN**= 8 would be suitable for a more polar crude oil. A nonpolar paraffinic oil required a polar demulsifier of **RSN**= 12. However, most often these empirical correlations become specific to the laboratory samples, and cannot be universally applied unless the models are tested globally.

Berger et al. (64) used 2400 field samples in bottle tests to correlate **RSN**with **BS&W** (water drop). From their studies they claimed no correlations between hydrophilic/lyophilic balance (**HLB**), RSN, and demulsifier performance for crude oil emulsions. They suggest that in the choice of demulsifiers the demulsifiers can be first characterized by their **PACN** and paired with the **EACN**of crude. In bitumen or crude oil systems the matching of **EACN**of the crude to the actual carbon numbers of the demulsifiers may be important for compatibility. To date, extensive studies have not been conducted to validate this.

In the earlier studies, a method of demulsification which was believed to be reliable was the reversal or inversion of the emulsion types. High concentrations of hydrophilic soaps accomplished this. The anionics were among the first to be used for this purpose. The nonionics were an improvement over the years. Later, a guide to the selection of demulsifiers was also sought in the **HLB** originally established for emulsifiers.

**HLB** is a number assigned originally to nonionic surfactants based on the hydrophilic head groups and hydrocarbon tails on an empirical scale, developed as a method for selecting simple emulsifiers for O/W or W/ O systems. This was based on the surfactant dispersi-bility in water at ambient temperature. For demulsification, the **HLB**scale suggested that demulsifiers should possess **HLBs** in the intermediate range (8-11), which is neither oil soluble (O<**HLB**<6), nor water soluble (**HLB** > 12) (68). Emulsifiers for O/W systems have high **HLB**numbers, wetting agents have intermediate **HLB**numbers, and emulsifiers of W/O emulsions have low **HLB**numbers. The **HLB**scale was originated by Griffin (279) and was later modified to include linear ethoxylated polymeric surfactants (280). Both solubility and **HLB**changed with changes in the hydrophilic portion in a series of ethoxylated and propoxylated compounds such as nonyl phenol formaldehyde resins. However, predicting an emulsifier type from molecular structure alone was not possible.

Shinoda's **HLB**temperature or phase-inversion temperature (PIT) became an important property of the surfactant-oil-water system (281). For nonionics, the **PIT** occurs below the temperature at which the surfactant preferentially partitions into the water phases as oil-soluble micelles and above the temperature at which it partitions preferentially into the oil phase as water-swollen inverted micelles. The **PITs** are affected by salinity, alcohol, temperature, and type of oil. The **PIT** indicated the point of emulsion inversion from oil/water to water/oil type. This was especially true for nonionic ethoxylated hydrocarbon surfactants, which obeyed Bancroft's rule for water solubility at low temperature and oil solubility at high temperature. This behaviour was illustrated in a linear relationship between **HLB**and **PIT** for ethoxylated hydrocarbon surfactants in cyclohexane and water. A lower **HLB**of 10 corresponded to a low PIT of 30°C (282) and a high **HLB**corresponded to higher **PITs**. Thus, an **HLB**balance in the molecules may be important where solubilities are concerned, but this property still has conflicting connotations in demulsification, especially for polymeric surfactants where branched configuration and molecular weight of the chemicals are more important in the changing interfacial environment. Crude oil and bitumen complexity would present new difficulties for using this parameter as the sole criterion for selection of demulsifiers.

Hayes et al. (283) related the $\mathbf{EACN}_{\min}$ with the **HLB**of ethoxylated alcohols (dinonyl phenols, tridecanols), in which **HLB**is the ethylene oxide percentage divided by 5. They found a simple linear relationship between **HLB**and $\mathbf{EACN}_{\min}$. The **EACN**values of 5-20 were in the range corresponding to **HLBs** of 11-12, for which the emulsion inverts or there is a transition region between oil and water solubility. However, **HLB**is still not simple to apply to demulsification especially with highly branched hydrophobes in complex systems such as crudes and anionic surfactants. Walker et al. (284) emphasized that **HLBs** of 7-9 are effective for demulsifiers of crude oil emulsions, as they represent emulsifiers of neither emulsion type, but are effective wetting agents. However, Cooper et al. (285) suggest that **HLB**is important in demulsifier efficiency, showing that heavy oil emulsions have optimum demulsification at **HLBs** 4-6. On the other hand, Berger et al. (64) found no correlations.

Aveyard et al. systematically studied phase behavior of the specific nonionics with varied **HLBs** to illustrate demulsification (202). They emphasized that changing the **HLB**of the system and not the **HLB**number of the surfactant can promote the demulsification of crude or model emulsions. The **HLB**of the system of Forties crude oil emulsion with ethoxylated phenol-formaldehyde resins was changed by increasing salt concentrations in the water phase. Inversion occurred close to the critical aggregation concentration. Anionic **AOT** in water/nonane emulsion showed a similar response, but at lower salt concentrations in the water. They indicated that the preferred curvature of the surfactant at the interface is modified by the **HLB**of the system.

Israelachvili (286) presented an overview on the phase inversion of emulsions based on the geometry of adsorbed surfactants, the sizes of the heads and tails, and the volume of the surfactants at the interface. W/O emulsions were favored by smaller less hydrated headgroups, higher ionic strength, smaller interfacial space occupied by heads, higher pH for cationics, lower pH for anionics, and higher temperatures for nonionics. W/O emulsions are favored also by a shorter length, *L*, of tails with surfactants occupying a larger volume, v, into the interface. The tail group would be either branched unsaturated chains or double chains. Nonionics at higher temperatures have greater oil penetration, and often are aided by cosurfactant addition. On the other hand, O/W emulsions were favored by large, more hydrated headgroups, lower ionic strength, larger head diameter/chain length ratio, lower pH for cationics, higher pH for anionics, and lower temperatures for nonionics, the single saturated chains, shorter chains, less oil penetration, and higher-molecular-weight oils. Intermediate to this measure is the bicontinous lamella phase where the surfactant's volume/area × length = 1 (V/A×L), the occupied space is square in geometry at the interface and it corresponds to an **HLB**of 10.

Sharma et al. (71) used a concept of deformation of closely clustered W/O crude oil emulsions to explain demulsification by inversion. This explanation bore some similarity to the wedge concept used for changes in head and tail geometry of surface-active agents that adsorb on the interface of the droplet while promoting demulsification.

Marshall (287) investigated the emulsion inversion point (**EIP**) as a function of **HLB**for simple nonylphe-nol ethoxylates (**NPE**$_x$) where × ranged from 3 to 25, in a paraffin-oil base W/O emulsion. The state of orientation of the **NPE**$_X$ was modeled to show the change in configuration of the polyethylene oxide chains, from zigzag or fully extended to meandering in the water phase with changes in × between 9 and 12. The EIP occurred with eight ethylene oxide (**EO**) units at **HLB**= 12.3. The HLBs in these systems were also related to the curvature at the interface. A W/O interface was convex toward oil and concave toward water. This curvature changed with the stabilizer. This suggested that a change in the stabilizer property can induce demulsification.

Some of these studies indicate that **HLB**is not the only property of the chemical which determines the demulsifier power. Cooper et al. (285) indicated that water reduction was dependent on the chemical structure of the surfactant when two surfactants with similar **HLBs** gave opposite results. The effects of the interaction of the chemical structure with emulsion interfaces are the more important factors in demulsification, as these influence the film rheology of the system.

## C. Types of Chemicals

Chemicals used as demulsifiers may be simple surfactants. These may be cationic such as quaternary amines $(NR_1R_2R_3R_4)^+$, where R can be any alkyl or aryl group; anionic such as sodium dodecybenzenesul-fonates ($R\text{-}PhSO_3Na$), petroleum sulfonates ($RSO_3^-M^+$) and sodium di-iso-octylsulfonosuccinates [$ROOCC(CH_2COOR)H\ SO_{3-}Na^+$, trade name Aerosol OT]; nonionic such as fatty alcohol ethers [$CH_3(CH_2)_{10}CH_2O(C_2H_4O)_nH$], fatty esters [$(CH_3(CH_2)_{10}COO\ (C_2H_4O)_nH$], alkyl phenol ethers [$R\text{-}Ph\text{-}O\text{-}(C_2H_4O)_nH$], polyoxypropylene glycol ethers, and fatty amides; and zwitterionic such as alkylbetaine derivatives [$RCH_2COO^-N^+(CH_3)_2$], which are pH dependent. Simple copolymers of EO and propylene oxide (**PO**) may be used alone or in combination with a surfactant.

Staiss et al. (288) have summarized the developments in chemical demulsifiers and their effective dosages used until 1991. They indicated then that the most recent developments in poly(ester amines) at very low dosages were most efficacious for crude oils (Table 4). Table 5 extends this development to encompass some of the demulsifiers used by research groups globally to date. Table 5 summarizes some of the chosen chemistries or products used in published studies on demulsification of a variety of crude W/O emulsions world wide. Aerosol OT is still used today in formulations and is one of the few demulsifiers approved by the Norwegian environmental authorities (284). Aerosol OT still appears to be successful in demulsify-ing conventional crude emulsions. However, it easily partitions into the water phase and cannot be available for a long time.

However, there are many more combinations of chemicals synthesized to reduce the effective dosages (77, 89).

**Table 4** Chemicals Used as Demulsifiers of Crude Oil Emulsions

| Up to year | Dosage (ppm) | Chemicals as demulsifiers |
|---|---|---|
| 1920 | 1000 | Soaps, salts of naphthenic acids, aromatic and alkylaromatic sulfonates Turkish red oil, and sulfated castor |
| 1930s | 1000 | Petroleum sulfonates, "mahogany soaps," oxidized castor oil, and sulfosuccinic acids (Aerosol OT) |
| 1935 | 500–100 | Ethoxylates of fatty acids, fatty alcohols, and alkylphenols |
| 1950 | 100 | EO/PO copolymers, *p*-alkylphenol – formaldyhyde resins + EO/PO and modifications |
| 1965 | 30–50 | Amine alkoxylates |
| 1986 | 5–20 | Polyesteramines and blends |

*Source*: Ref. 288.

The patent literature covers thousands of chemicals. A few examples for bitumen and heavy oils are indicated in Refs 83-88. Other simpler compounds have also been used and some of these appear in the footnote.

Most of the bases or intermediates used in the synthesis of demulsifiers are derived from either agricultural or petroleum sources. Table 6shows examples of the bases as published by Hancock's schematic (270). All large-scale production of EOs and POs are synthesized from naphtha (a crude-oil distillate feed-stock) or natural gas. Benzene is obtained from naphtha and, from benzene, phenol is obtained.

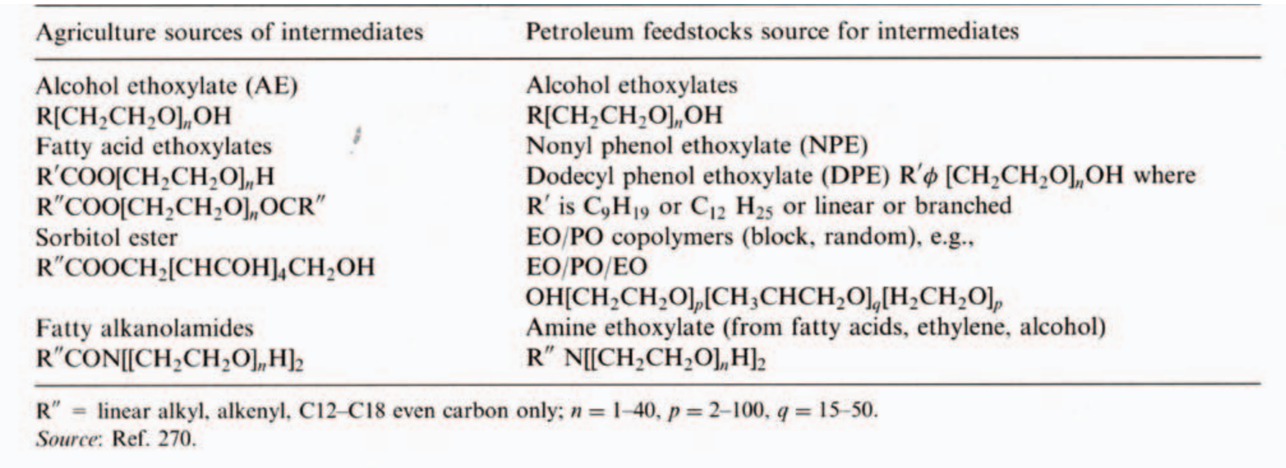
**Table 5** Chemicals Used as Demulsifiers for W/O Emulsions in Crude Oils from Literature Survey to Date

| Year | Dosage (ppm) | Molecular weight | Successful demulsifier chemicals published |
|---|---|---|---|
| 1948 | Varied | Very high | Polyoxethylene |
| 1974 to 1980 | | Low | Aerosol OT, alkoxylated phenol + alkoxylated ester + soap of carboxylic acids<br>Petroleum sulfonate and n-hexanol, pentadecyl benzenesulfonate |
| 1981–1990 | Varied | Varied | Nonylphenol ethoxylate (NPE), Octylphenol ethoxylates (OPE), and formaldehyde resins; polyethers, polyols, blends; Oxyalkylated phenol resins where alkyl = amyl, butyl, nonyl oxyalkylated polyols with EO varied Aerosol OT and Triton X – R EO (9–30); straight chain and branched chain; butanols, hexyl to decylamines, NPE (4–20) |
| 1991–1999 | 25 | 3500–4500 | Varied molecular weights of EO/PO; phenol – formaldehyde glycidyl ether<br>Bisphenol A glycidyl ether with EO/PO |
| | 20–40 | | Iminobis (polyoxyalkylene) polyester |
| | 32 | 2500 | EO/PO copolymer hexanetriol ether blend with poly(thioalkylene oxide) of polyethers |
| | 100–1000 | 25,000, 4000 | Alkoxylated polyol |
| 1991–1999 | 20–300 | 7500,3700 | EO/PO block copolymers; straight chains and cross-linked, branched |
| | | 8400 | complexes of EO/PO with polyfunctional amine |
| | | 13,500 | Sorbitan – monolaurate, mono-oleate |
| | | 400,000 | Polyoxyphenol (NP, DP 1–9), polyalkylenepolyamine formaldehyde ethoxylate (11–25) |
| | | | Trade names, such as Dissolvan 4455<br>Corexit 95000, Breaxit 126,<br>Novolak resols, polarchem, tetronics |

---

* Chemicals: Selection is of extreme importance in tailoring to the crudes as well as operating conditions. Examples are: polyoxyalkylene (ethylene, propylene) substituted phenols, alcohols, esters, ketones, aldehydes, amines, nitrocom-pounds, organometallic salts, solvents.
Physicochemical: combinations of chemical and physical, e.g., demulsifier, mixing and heating to high P or Temp, increasing dispersed phase by 10-20% by adding very dilute demulsifier.

**Table 6**Intermediates for Demulsifiers and Their Feedstocks



| Agriculture sources of intermediates | Petroleum feedstocks source for intermediates |
|---|---|
| Alcohol ethoxylate (AE) | Alcohol ethoxylates |
| $R[CH_2CH_2O]_nOH$ | $R[CH_2CH_2O]_nOH$ |
| Fatty acid ethoxylates | Nonyl phenol ethoxylate (NPE) |
| $R'COO[CH_2CH_2O]_nH$ | Dodecyl phenol ethoxylate (DPE) $R'\phi\ [CH_2CH_2O]_nOH$ where |
| $R''COO[CH_2CH_2O]_nOCR''$ | $R'$ is $C_9H_{19}$ or $C_{12}\ H_{25}$ or linear or branched |
| Sorbitol ester | EO/PO copolymers (block, random), e.g., |
| $R''COOCH_2[CHCOH]_4CH_2OH$ | EO/PO/EO |
| | $OH[CH_2CH_2O]_p[CH_3CHCH_2O]_q[H_2CH_2O]_p$ |
| Fatty alkanolamides | Amine ethoxylate (from fatty acids, ethylene, alcohol) |
| $R''CON[[CH_2CH_2O]_nH]_2$ | $R''\ N[[CH_2CH_2O]_nH]_2$ |

$R''$ = linear alkyl, alkenyl, C12–C18 even carbon only; $n = 1$–$40$, $p = 2$–$100$, $q = 15$–$50$.

*Source*: Ref. 270.

Any product that includes EO and PO as copolymers are generally highly surface active. Their oil solubilities are determined by, not only the molecular weight, but also the EO (hydrophilic) content as well as the PO (hydrophobic) components. Generally, experience has shown that for the solution behavior of nonyphenol ethoxylates, the lower the EO content the lower the cmc in an aqueous phase, and the lower the surface tension (290).

Recently, demulsifier chemicals supplied have been polymerized surfactants containing EO and PO as linear blocks or random copolymer chains ($EO_X/PO_y$;/ $EO_Z$; $PO_y/EO_X/PO_y$), added to various polyglycols (289) whose molecular weight may be varied. Starting with poly(propylene glycols) of selected molecular weight, the EO is polymerized sequentially or randomly. Compounds with more EO groups are more water soluble, and with more PO groups are more oil soluble. The lower molecular weights are more water soluble than the high molecular weights, which are more oil soluble. The solution phase behavior of these compounds is affected by salt content, increased temperatures, and solvent type at these temperatures. For example poly(ethythylene oxide) (**PEO**) is more readily soluble in toluene at high temperatures than at room temperatures (291). Lower consolute temperatures depend on the molecular weights and polymer concentrations.

For demulsifiers of crude W/O emulsions, a low **EO** content is preferred, at low molecular weights of 1500-3500. The random copolymers are usually of lower molecular weights. However, factors such as the concentration, solvent, and temperature affect the phase behaviors of these demulsifiers. Because of the wide applications and versatility of these compounds there have been extensive studies on their chemistries (291). Their properties are as diverse as the many core molecules with which they can be copolymerized.

Table 6 illustrates some of the simple intermediates for demulsifiers derived from either agriculture or petroleum feedstocks. In some respects all of the above may be used as demulsifiers. In addition to these are the final reaction products of block copolymers of **EO**/ **PO** polymerized with initiators such as glycerol, phenol-formaldehyde resins, melamine-formaldehyde resins, polyamines, siloxanes, and polyols. The flexibilities of the backbone structures are designed for function as emulsifying agents, and the molecular weights range from 3000 to 100,000, and in some cases higher. Demulsifiers for O/W emulsions will have typically 80% **PEO**, while for W/O emulsions 20-50% PEO. The limited W/O solubility is the driving force for attraction to the interface. These are commonly formulated into multicomponent solutions in aromatic solvents and used at levels from 5 to 100 ppm. These, however, are inferior as wetting agents or for deter-gency. The simpler linear surfactants are more suitable.

To date there are thousands of products appearing in directories and patent literature. Generally, the compounds with EO/PO copolymers are exceptionally surface active and they migrate and spread readily at the interface. The fatty amines and quaternary cationics adhere to all surfaces including asphaltenes, resins, naphthenic acids, paraffin waxes, inorganic clays, carbons, and silica (288).

As the chemistries improved and became more complex over the years, there was also a decrease in active concentrations of demulsifiers required to demulsify crude W/O emulsions. The efficacious demulsifiers such as the poly(ester amines) or combinations of bases with **EO** and poly(propylene oxide) copolymers (289) fit into this category as is shown in Table 4. Some published cases of successful outcomes for the various demulsifiers follow in Table 5.

Taylor (68) reported success in the demulsification of Kuwait crude oil emulsion with ethoxylated nonyl-phenol-formaldehyde (**NPE**) resins in which the EO content varied from 0 to 20 mol. They found optimum demulsification with n = 5 mol of **EO** per phenol group and strong evidence of **NPE** interacting with the asphaltenes of the bulk. Here, water solubility was changed with change in the length of the hydrophobic portion of the **NPE** resins.

Aveyard et al. (257) studied the demulsification rates of North Sea Forties crude oil emulsions using a homologous series of octyl phenol polyethoxylates [Triton X series - $C_8H_{17}ø(EO)_n$], where n varied from 3, 5, 9-10, 16, to 30. Crude oil was solubilized in the water phase for n = 12 and greater. Maximum water resolution was obtained for compounds with n = 9-10 at 500 and 2000 ppm. The compounds with lower n values partitioned in the oil phase as monomers at dosages below the critical aggregation concentration (cac). Maximum resolution rates were found to coincide with the cac of each demulsifier in the homologous series. Of course, in most homologous series of this type it is expected that not only temperature, but also alkane chain length, cosurfactant, and molecular structure would change the solubility.

The demulsification of the crude oil emulsions with Aerosol **OT**, an anionic surfactant, was also studied with change in **HLB**of the system via increasing the salt concentrations. Similarly, the cac coincided with maximum rate of resolution at different salt concentrations. At low salt concentrations AOT is water soluble, stabilizing O/W emulsions, which invert to W/O emulsions with increased salt concentration. At high salt concentrations (0.7-1 M) 10 molecules of AOT solubilized one molecule of water in crude oil. Salt has a drastic effect on the distribution of aggregated AOT, especially at concentrations greater than the cac.

Sharma et al. (71) chose polyoxyethylene alkylphe-nols, their sulfonates, and sodium sulfonates in various combinations as demulsifiers for W/O emulsions from the Assam fields of India. They found xylene to be a better solvent than water for the effective demulsifiers. Successful demulsifiers were those of the non-ylphenol type with 30 molecules of EO per mole, and the octylphenols with 40 molecules of EO per mole, followed by treatment with polyvalent cations. All demulsifiers studied were of **HLB-**between 13 and 18 in various combinations. The W/O emulsions were from crudes of relatively low asphaltene (0.27, 0.35, and 0.25%) and resin (0.1, 0.15, and 0.1%) and high wax (11, 5, and 15%) contents. The emulsions were between 15 and 25% water content and of high salt content. They introduced a new concept to select the demulsifier by using the ratio of the number of **EO** units in the surfactant over the number of carbon atoms in the surfactant, instead of the **HLB**for demulsifier selection. They found no interaction between the demulsifier and natural emulsifiers from the crude oil emulsions.

Amarvathi and Pandey (289) synthesized and tested several demulsifying agents of increasing chemical complexity starting from the alkoxylated alkyl phenol-formaldehyde resins. The other compounds were bis(glycidyl ether) **EO/PO** copolymers, **EO/PO** copolymers of amino compounds, and **EO/PO** copolymers of sulfur compounds. In using the **EO/PO** block copolymers for dewatering W/O emulsions of 34% water in Ramashkino naphtha, they found that the copolymers of **MWt** 3500-4500 were best. These polymeric surfactants were made with 60% **EO** condensed with poly(-propylene glycol) of **MWt** 1400-1800. If the **EO** content was above 60% the product showed decreased demulsifying power. For the copolymers of phenolic resin group, the **EO/PO** block copolymer of phenol-formaldehyde resin glycidyl ether was best at removing 100% water and salt from the crude oil emulsions at dosages as low as 25 ppm. A slightly modified bisphe-nol A - bis(glycidyl ether) **EO/PO** copolymer at 20-40 ppm was effective for 42-63% water removal at 30-45°C. The Saudi Arabian crude-oil emulsions containing 36% water and 9% salt was dewatered by 94% and desalted to 0.9% within 30 min by 32 ppm of imino-bis(polyalkylene)polyalkylene polyester. At an even lower dosage of 20 ppm, the **EO/PO** copolymers of hexanetriol ether and the poly(thioalkylene oxides) of polyethers were effective as demulsifiers. For the aromatic amine derivatives of **EO/PO** copolymers, the effectiveness of the diamines were not only dependent on the ratios of **EO/PO** but also on the isomer. The para-substituted diamine having 28 units of **EO** to 80 units of **PO** was best. The *ortho*- and *meta*-substituted diamines did not perform as well. The esters of PPO glycols and **PE** glycols were effective for not only the Indian crude oil emulsions but also West African and North Sea emulsions at 20 ppm. Thus, it appears that greater effectiveness can be achieved by improved design of demulsifiers.

Formulation can be specific to the crude oil emulsions such as was shown for Buchan crude by Mohammed et al. (67). They used nonionic surfactants from the Pluronic (**PE**) and Tetronic series, which differed basically in the degree of **EO/PO**copolymers added to straight chains or branches. In combination with wetting agents and octy- or nonyl-phenol formaldehyde condensates containing **EO/PO**copolymers, they formulated effective demulsifler blends. They indicated that there is some degree of functional specificity in the demulsifier molecules in the interaction with the interfacial films.

Cooper et al. (285) demulsified Alberta's Cold Lake heavy oil emulsions with PEs (block copolymers of **EO/PO**) of **HLBs** of 4-6 or 14. While Tweens (esters of sorbitan and fatty acids of various lengths) and Brij (polymers of EO with terminal fatty alcohols of various lengths) were poor as demulsifiers. Kim and Wasan (63) used demulsifier blends of **EO/PO**as copolymers. They used **EO/PO**diepoxides and **EO/PO**with phenolic resins of varying **MWts** from 3700 to 8000 in their partitioning studies of destabilized emulsion films. They also tested polyamine glycols, alkyl aryl sulfonates, phenolic resins, and polyamines. These showed different performances, with blends having the same partition coefficients between water and oil phases. Sjöblom and Coworkers (81, 136, 292-294) varied the **EO** content from 4, 10, 20, to 30 molecules per unit of nonylphenol ethoxylate; together with solvents, the demulsification of Norwegian crude oil emulsions was thereby optimized. The medium-chain alcohols and amines speeded up the separation. They concluded that amines showed a strong specific interaction with the emulsion film which rendered the film more hydrophilic.

In a series of studies, Zaki (106) treated Geisum crude oil emulsions which was additionally stabilized by the anionic surfactant dodecylbenzenesulfonic acid. They found that 60 ppm of **EO/PO**alkylated alkylphe-nol formaldehyde resins at 50°C was successful. Zaki et al. (78) then used **EO/PO**block copolymers of MWt 5000 and 7000 to destabilize model asphaltene-stabi-lized water-in-benzene emulsions. They found that the efficiency increased for the higher-molecular-weight (7000) polymer. Temperatures in the range 50°-70°C caused increased efficiency. They also synthesized more complex demulsifiers by making further changes to the basic alkylphenol-formaldehyde resins. Zaki and Al-Sabagh (77) recently published some successes with polyalkylphenols-polyalkylenepolyammes formaldehyde ethoxylate in which the molecular weights of the polyethylene glycol used in the synthesis were varied. The alkyl groups in the phenols were either nonyl or dodecyl, and amines were varied from tria-mine to pentamine. The **HLBs** consequently were varied between 10 and 15. They found **HLBs** of 12-13.5 to be optimum for demulsification. Increasing the temperature from 50°C to 70°C enhanced resolution. They demulsified the W/O emulsions of the two crude oils, **MB** and **LB**, which were of high (8.8%) and low asphaltene (1.4%) contents, respectively. The salt content of the water was varied. The higher-asphaltenes, **MB** crude oil emulsions demulsified with an efficiency greater than that of the low-asphaltenes crude oil, **LB**. The nonylphenols were the best in all cases. The demulsifiers with the shorter alkyl groups were better than those with the longer alkyl groups, and efficiency increased with increasing number of amino groups. Molecular weights were within a narrow range for all the synthesized demulsifiers tested. They also showed a variation of demulsifier performance with water quality and temperature.

It would appear that, from fundamental tenets of physical chemistry, the demulsifier structure and chemistry determine the degree of interfacial activity and the **HLB**. In addition, its molecular weight governs viscosity and diffusivity as well as its solubility. The overall structural configuration determines the elasticity and viscosity at an interface or in solution. However, carrier solvents play a major role in the demulsifier configuration as well as in compatibility with the continuous oil phase and at the oil/water interface. These factors all apply in the demulsification of crude oils and bitumen emulsions.

## D. Solvent Effects

Solvents and cosolvents as demulsifiers or as carriers influence demulsification. The solvent not only influences the natural emulsifier components as was shown earlier, but also affects the micellization of the surfactant. Good solvents are those in which the demulsifier can dissolve but remains surface active. Poor solvents do not allow demulsifier dissolution or transport to the interface. For emulsions from North Sea crudes, Graham and coworkers (295, 296) showed that xylene was the best carrier and did not cause aggregation, while 1-propanol and 2-propanol were poor solvents. Sjöblom et al. (294) conducted an extensive survey of solvent effects as carriers and demulsifiers. They found that t-butanols and hexylamine were good solvents. Walker et al. (284) used glycol ethers as good solvents for coupling liquids of different polarity to provide a stable demulsifier mixture. Aerosol OT functions better in alcohol/water or propylene glycol ethers. Sometimes when solvency is reduced there is precipitation of components of crudes.

According to Zaki et al. (78) not only does a good solvent assist in solubility of the demulsifiers, but it also assists in depressing the pour point of the crude to effect demulsification at low temperatures. Water; water-miscible hydroxy compounds such as n-buta-nols, isopropanol, and monoethylene glycols; and aromatic hydrocarbons such as benzene, toluene, and xylene are commonly used solvents. They found that the efficiency of **EO/PO**block copolymers as demulsifiers decreased as the number of methyl groups increased in the aromatic hydrocarbon solvents. The efficiencies were related to the solvation power. However, they concluded that, for breaking W/O emulsions, the solvents for **EO/PO**block copolymers should be preferentially compatible with the dispersed water phase rather than with the oil phase. Oil-soluble demulsifiers may be better at demulsification, depending on the mechanism, as was illustrated earlier. However, demulsifier action can be augmented by the pH of the water around 7.0, low salinity, and increased temperature, as these factors affect the interface surface properties as well as the solution behavior of the demulsifier. The solution properties of the surfactants play a large role in the efficiency of demulsification.

Since the early 1980s, it was believed that demulsifiers had to be high-molecular-weight polymers. These include polymerized alkoxylated polyglycols, polygly-col esters, polymerized oils, alkanolamine condensates such as oxyalkoxylated phenols, and polyamides. Today, the increasing trends are toward lower dosages and more highly surface-active products which are more often polymeric surfactants.

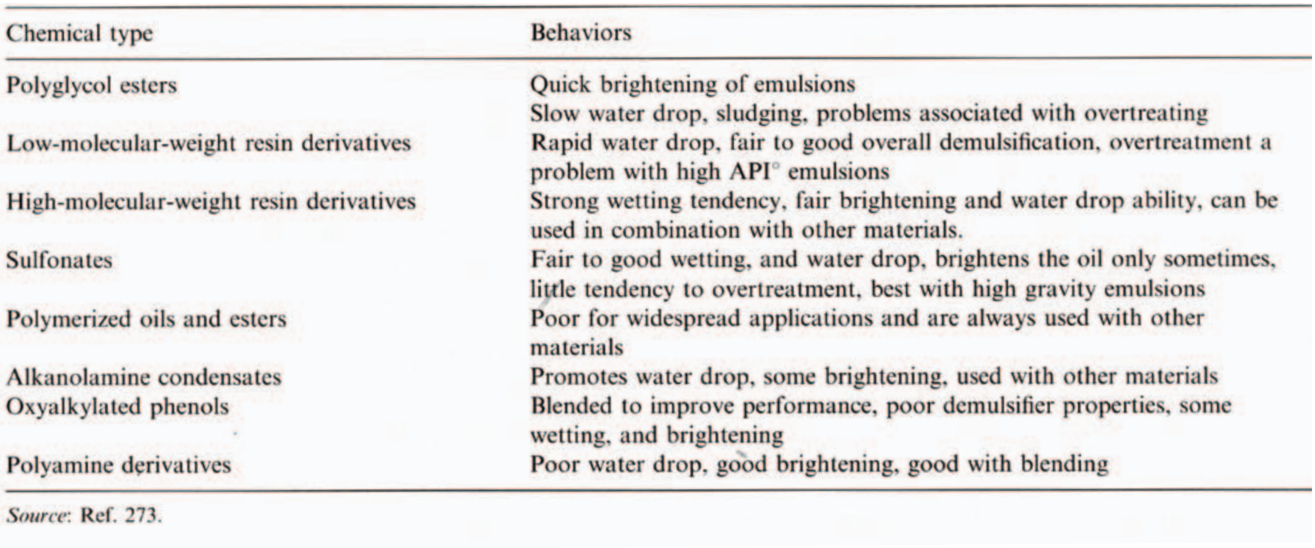
However, it is understood that the selection of a group of chemicals for a specific application takes a great deal of skill and knowledge to arrive at a solution. There are high costs and hence profits associated with a successful formulation, because of high-volume throughput. This market becomes competitive. There are thousands of patents on product formulations for these applications. These are the main reasons behind the lack of detail in formulation and nondisclosure to researchers.

For these reasons the basic understanding of crude oil and bitumen emulsions and demulsification has received considerable attention. Advances in the knowledge of the physicochemical-mechanical structure of the stable emulsions and their films are being made in our laboratory and elsewhere. The films' response to demulsifiers are studied in order to understand the detailed mechanisms of demulsification. This knowledge will provide a more scientific basis for formulating products. The knowledge of surfactant chemistry, the behavior in solutions, the behavior at interfaces, and interactions with the crude-oil solvent base involve a wide interplay of complex processes in designing formulations.

## E. Demulsifier Selection and Petroleum Recovery

Field experience with use of specific chemical groups of

**Table 7**Field Observations of Behaviors of Chemical Types of Demulsifiers



| Chemical type | Behaviors |
|---|---|
| Polyglycol esters | Quick brightening of emulsions<br>Slow water drop, sludging, problems associated with overtreating |
| Low-molecular-weight resin derivatives | Rapid water drop, fair to good overall demulsification, overtreatment a problem with high API° emulsions |
| High-molecular-weight resin derivatives | Strong wetting tendency, fair brightening and water drop ability, can be used in combination with other materials. |
| Sulfonates | Fair to good wetting, and water drop, brightens the oil only sometimes, little tendency to overtreatment, best with high gravity emulsions |
| Polymerized oils and esters | Poor for widespread applications and are always used with other materials |
| Alkanolamine condensates | Promotes water drop, some brightening, used with other materials |
| Oxyalkylated phenols | Blended to improve performance, poor demulsifier properties, some wetting, and brightening |
| Polyamine derivatives | Poor water drop, good brightening, good with blending |

*Source*: Ref. 273.

demulsifiers on conventional crudes is indicated in Table 7 (274). A demulsifier with a low-molecularweight resin base which would perform on a 35 API° oil emulsion with a rapid water drop would be ineffective for heavy oil. Generally, it is easier to treat high API° crude oil emulsions than heavy oils and bitumen because of the many differences in physical/ chemical properties. Thus, in the study of emulsions for demulsification purposes and for the selection and design of demulsifiers it is imperative to know the production operations and the chemical prehistory of the emulsions to be treated. Chemical demulsification is the most economical and commonly used method of dehydration of crudes.

In the first stages of crude oil production, after crude is extracted or drilled, the fluids are under high pressures and temperatures. It is essential to recognize that the first-stage treatment involves the removal of excess of free water and gas. If there are high salt concentrations in the water, a fresh-water wash is conducted. This wash is then followed by addition of demulsifiers and defoamers. The chemical demulsifiers assist in the dropout of the major amounts of water. Further dehydration is achieved by use of hydrotreaters or electrostatic coalescers. This latter cannot tolerate greater than 6% water or solids.

The final criteria for dry oils rest in the treatment process in the plant and the changes in fluid quality that chemical demulsification would require. These factors would influence the chemical selection. The selected treating vessels are also crucial in chemical choices. For instance, if a large settling vessel is used it is desirable to employ a longer-acting demul-sifier for slower adsorption. Gun barrels, although they have a high throughput, have a longer time available for chemicals to perform and fast resolution is not required. The need for augmentation by elec-trocoalescers, which speed resolution, dehydrating filters, and a variety of other physical methods* are indicated by production demands. The mixing requirements and the operations temperature would all be included in the design and would determine the choice of demulsifier.

The mixing, which is crucial for adsorption, may occur in static mixers or during flow conditions in the piping. The major limitations to the equipment and methods used for demulsification would be the small platform space for offshore operations, and the short residence time. For heavy oil or bitumen, or drilling on land, it is easier to use large settling tanks, heater treaters, and dispose of free-water. Retention times may be longer, up to 40 min, and are taken into account in the choice of slower-adsorbing demulsifiers.

After treatment, it is also desirable to have no accumulations at the layer between the oil and the water which forms a middle phase or interface pad. A large middle phase (interface pad) would have to undergo treatment separately as it tends to collect solids, emulsifiers, asphaltenes, and other assorted surface-active impurities. On the one hand, an interface pad presents no problem as the resolved water is drawn out from the bottom of a setting tank, or the pad may act as a filter for the mass transfer of solids into the oil phase. This interface can be removed and treated separately, after oil dehydration. On the other hand, a large pad creates slop oil and presents its own separation and disposal problems. For this reason the user is cautioned against overdosing in treatment. The choice of chemicals used is thus crucial to avoid overdosing or incompatibilities.

These all suggest that a demulsification program must be streamlined to the process in the majority of cases. A very good general review of this streamlining is discussed by Svetgoff (191), in which the economics and retention times are emphasized along with equipment choices (297). Most processes use a combination of chemical addition, heat, electrical methods (electrotreaters, dual-polarity dehydrators), and settling (272). The final results thus depend on the choices of injection points, mixing, temperature, process equipment, demulsifiers, and the characteristics of the crude emulsions. In the majority of cases many combinations of methods are used for complete dehydration. Each type of equipment comes with performance limitations. Economics determines the path in the end.

---

* Physical methods of treatment include the following: heating; centrifuging (used in oil sand extraction): washing through a water column; filtering through porous media passing through high pressure jets, which involves shaving off the interfacial layer as found to be successful on emulsions from Indian crudes; and the application of a sudden pressure drop. The increase of dispersed phase volume by dilution with water only works when soluble inorganics are the stabilizers. Other sophisticated methods are: application of high magnetic fields; application of high electrical fields - the most widely used 6-36 kV-induced polarity on the dispersed phase causes the water droplets to form pearlized strings of oppositely charged ends; application of ultrasonic waves. It is not unusual to use combinations of heat and high pressure.

### F. Other Chemicals for Consideration

If the crude is to be transported either by pipeline or tanker, chemicals such as wax inhibitors for highly paraffinic crudes, corrosion inhibitors, and lubricants are added. The excess of fluids produced in extraction of crude oils are also transported for further treatment to remove solids, water, and impurities before disposal. Demulsification treatment can also be complicated by crudes that have already been subjected to many other chemicals.

In typical offshore production the fluids produced are gathered into a collection line or common manifold. All the lines that feed into this manifold have been subjected to chemicals such as corrosion inhibitors, scale inhibitors, wax inhibitors, and hydrate inhibitors. In enhanced oil recovery of conventional crudes, surfactant micellar floods have been used in the past to promote recovery. For heavy oil, fluid flow is enhanced by viscosity-reducing agents and or diluents. The reality is a more complex system for upgrading or refining.

## VII. RECOMMENDATIONS

Oil clean-up is a necessary requirement to meet environmental specifications before water is discharged into disposal streams or natural lakes or oceans. The producer considering a separation strategy must consider what will be done with what is left behind. It is generally agreed that the job of demulsification is not complete until one has found a place for each fraction of the emulsion system. After the oil is separated from the water, and is recovered, what happens to water-soluble oils, water, solids, and surfactants? The choice of demulsifers can address these problems. If the mineral solids are transported to the water, and the asphaltenes, waxes, and resins are transported into the oil phase, clean-up can be better dealt with. The "reverse" emulsion, which is the O/W emulsion, is mostly found in waste effluent streams and may be a result of overdosing. The demulsification of the latter involves different demulsifier chemistries that are compatible with the continuous water phase. These systems are often very dilute, and flocculants, together with coalescing filter beds or membranes, are chosen for clean-up.

The published literature on demulsification of crude oil emulsions is often based on studies of samples derived from the author's main research sponsors and so the sources of samples are often from the closest geographical location of a production facility. Thus, some collaborative effort between the producer and the researcher is required to ensure that samples are representative for study and actually simulate the real situations. These studies are often only undertaken when expertise is sought by the producer or is identified and offered by the performer after considerable discussions/negotiations.

It is not very often that service companies, which supply technology to the producers, seek external support for the fundamental research to be performed. The chemical service companies have their core competencies based on their knowledge of chemistry and some knowledge of oil production technology. Dessemination of their knowledge does not serve their interest. Therefore, most chemical products supplied by service companies are protected formulations which are coded. These are not identified, chemically, to the producers. Demulsifier formulations and demulsification even to this day still appear to be an art more than a science. However, there are some new developments in the understanding of demulsification. In this paper some of these developments have been highlighted.

### A. Research Needs in This Industry

Research on petroleum emulsion formation, stabilization, and destabilization, and especially interactions with chemical demulsifiers is very necessary for optimizing production. However, this is expensive in comparison with other industries' requirements for emulsion studies. The field of emulsion technology would not have arrived at the present knowledge base had it not been for the initiative of the petroleum industry in finding answers. However, to date there are only a handful of research facilities worldwide that are involved in this type of combined fundamental and applied investigation aimed at understanding crude oil emulsions. In addition to this, few research facilities involved in crude oil emulsions publish their findings. The oil producers keep process and emulsions research results in-house to ensure their competitive edge, and if specialized facilities are engaged, information becomes classified. There is a need for a consistent reporting of the properties of crude oils studied in addition to the chemical identification of surfactants in order to contribute more to the science, as well as compare notes across the broad scientific community.

Thus, the number of articles published on the topic does not reflect the degree of research effort in this field. Crude

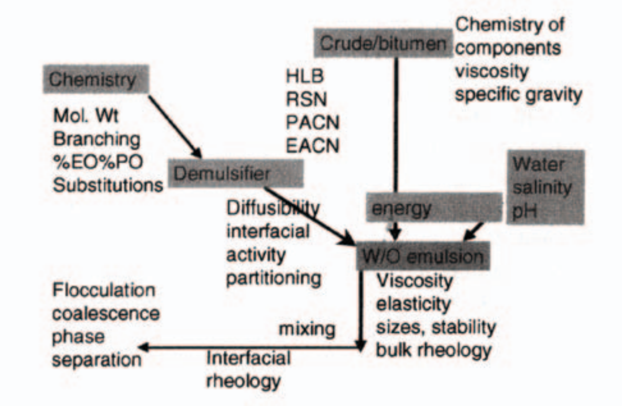


**Figure 26** Schematic summarizing factors that affect demulsification of crude oil and bitumen emulsions as discussed in this chapter

oil prices often dictate the incentives for funding research.

## VIII. CONCLUSIONS

We have discussed the nature and origins of crude oils and bitumens and compared field and bench emulsions first for developing the theme of demulsification. The nature of the crude oil and bitumen emulsions, film architecture, and the developments in their understanding for destabilization have been presented. The influence of the crude oil components on the interfacial skin strength and stability/instability was discussed. Demulsification was discussed in terms of film drainage, compression, coalescence, and water resolution. The demulsification process, chemical choices, and chemistry of the demulsifiers involved in this process were also discussed. Figure 26 provides a summary flow diagram of the factors impacting demulsification, which have been touched upon in this review.

## ACKNOWLEDGMENTS

Support in funding and time was provided partially by **CANMET**, Natural Resources Canada, and the Federal Panel on Energy Research and Development - the energy sector of Natural Resources Canada.

## REFERENCES

1. AL Bridie, TH Wanders, W Zegveld, HB Van Der Heijde. Mar Pollut Bull **11**: 343—348, 1980.
2. **ASTM** Designations **D-96**, 1983; **DA-96**, 1983.
3. S Mitchell, DM Smith. Aquametry, Part III. 2nd ed. New York: John Wiley, 1980.
4. JG Speight. The Chemistry and Technology of Petroleums. New York: Marcel Dekker, 1991, Ch 11, p 14.
5. CW Angle, N Berkowitz. Fuel **70**: 891—896, 1991.
6. CW Angle. MSc thesis, University of Alberta, Edmonton, 1989.
7. L Blom, L Edelhausen, DW Van Krevelen. Fuel **36**: 135—322, 1957.
8. DW Van Krevelen. Coal: Functional Group analysis, Typology Chemistry, Physics, Constitution. Amsterdam: Elsevier, 1961, pp 160—176.
9. RB Long, JG Speight. In: JG Speight, ed. Petroleum Chemistry and Refining. Washington, DC: Taylor & Francis, 1998, Ch 1.
10. JW Bunger, NC Li, eds. Chemistry of Asphaltenes. Advances in Chemistry Series 195. Washington, DC: American Chemical Society, 1981.
11. CW Bowman. Molecular and interfacial properties of Athabasca tar sands. Proceedings of Seventh World Petroleum Congress, Houston, TX. Vol 3, 1967, p 583.
12. JA Koots, JC Speight. Fuel **54**: 179—184, 1975.
13. MM Sharma, GV Chilingarian, TF Yen. In: TF Yen, GV Chillingarian, eds. Asphaltenes and Asphalts. Developments in Petroleum Science Series 40A. New York: Elsevier, 1994, Ch 12.
14. JP Pfeiffer, RNJ Saal. J Phys Chem, 44, 139, 1940.
15. D MacKay. Formation and stability of water-in-crude oil emulsions. Report TU-EE93, **MICROLOG-88**—02079, 1987 (Abstr no. 157, 257, Vol 110, no. 18).
16. RN Turtle. J Petrol Technol (June): 1192—1196, 1983.
17. A Stockwell, AS Taylor, DG Thompson. The rheolo-gical properties of water-in-crude oil emulsions. Presented at Fifth International Symposium: Surfactants in Solution, Bordeaux, France, 1984.
18. AJ McMahon. In: J Sjöblom, ed. Emulsions - A Fundamental and Practical Approach. NATO AST Series 363. Dordrecht: Kluwer Academic, 1992, pp 135—136.
19. KJ Leontaritis. Fuel Sci Technol Int **14**: 13—39, 1996.
20. PA Wheeler. The significance of wax crystal formation in water-in-crude oil emulsion stability. Proceedings of Second Norwegian Institute of Technology Lerkendal Petroleum Engineering Workshop, Trondheim, Norway, 1992, pp 183—192.
21. JD McLean, PK Kilpatrick. J Colloid Interface Sci **189**: 242—253, 1997.
22. S Puskas, J Balazs, T Haraszti, L Turi, I Dekany. The influence of paraffinic deposits and their fractions on the stability of crude oil emulsions. Petroleum abstracts: 1st SPE Brazil Sect et al., Colloid Chemistry in Oil Production, Asphaltenes & Wax Deposition International Symposium, Proceedings 230—235, Abstract no. 627, 639, Vol 36, no. 28, 1996.

23. MB Manek. Interface control for heavy crude oils. Petroluem Abstracts: 1st SPE Brazil sect et al., Colloid Chemistry in Oil Production, Ashphaltenes & Wax Deposition International Symposium, Proceedings 136—141, Abstract no. 627, 638, Vol 36, no. 28, 1996.

24. HN Dunning, JW Moore, MO Denekas. Ind Eng Chem 45: 1759, 1952.

25. CG Dodd, JW Moore, MO Denekas. Ind Eng Chem 44: 2285, 1952.

26. V Hornoff, JK Liu. Dynamic interfacial tension effects of oil sands processing. Proceedings of Fourth World Congress, Chemical Engineering, Karlsruhe, 1991.

27. RL Piehl. Mater Perform 27: 1: 37, 1988.

28. HY Jennings. Soc Petrol Eng J (June) 1975.

29. RJ Parker, ESN Chung. J Can Pet Technol (July-August): 72, 1986.

30. EE Isaacs, KF Smolek. Can J Chem Eng 61: 233, 1983.

31. ST Dubey, PH Doe. Base numbers and wetting properties of crude oil. Proceedings of 66th Annual Technical Conference Exhibition, SPE, Dallas, TX 1991.

32. RL Marquez-Silva, S Key, J Marino, C Guzman, S Buitriago. Chemical dehydration: correlations between crude oil, associated water and demulsifier characteristics in real systems. Proceedings of SPE Oilfield Chemical International Symposium, Houston, TX, 1997, pp 601—607.

33. IMRA Bruning. Oil Gas J 9: 31: 38, 1991.

34. IMRA Bruning. Fuel 69: 646f, 1990.

35. Data from Environment Canada —- Environmental Technology Centre — www.etcentre.org.

36. Syncrude Analytical Methods for Oil Sands and Bitumen Processing. Edmonton: Syncrude Research, 1979, p 123.

37. KA Ferworn. Thermodynamic and Kinetic Modelling of Asphaltene Precipitation from Heavy Oils and Bitumens. PhD thesis, University of Calgary, Alberta, 1995.

38. KA Ferworn. Asphaltene Flocculation and Precipitation. MSc thesis, University of Calgary, Alberta, 1992.

39. KA Ferworn, WY Svrcek, AK Mehrotra. Ind Eng Chem Res 32: 955, 1993.

40. KA Ferworn, AK Mehrotra, WY Svrcek. Can J Chem Eng 71: 699, 1993.

41. EW Funk, Can J Chem Eng 57: 333, 1979.

42. JG Speight. In: TF Yen, GV Chilingarian, eds. Asphaltenes and Asphalts. Developments in Petroleum Science Series 40A. New York: Elsevier, 1994, Ch 2.

43. RB Long. The Concept of Asphaltenes. Advances in Chemistry Series 195, Washington, DC: American Chemical Society, 1981, p 17.

44. TF Yen, GV Chilingarian. In: TF Yen, GV Chilingarian, eds. Asphaltenes and Asphalts. Developments in Petroleum Science Series 40A. New York: Elsevier, 1994, Ch 1.

45. TF Yen. In: TF Yen, GV Chilingarian, eds. Asphaltenes and Asphalts. Developments in Petroleum Science Series, 40A. New York: Elsevier, 1994, Ch 5.

46. NF Carnahan, L Quintero. In: RF Meyer, ed. Fueling for a Clear and Safe Environment, World Petroleum Congress, Houston, TX, 1995, pp 237—250.

47. FJ Nellensteyn. The Colloidal Structure of Bitumens. The Science of Petroleum. Vol 4. London: Oxford University Press, 1938, p 2760.

48. EY Sheu, DA Storm. In: EY Sheu, OC Mullins, eds. Asphaltenes —- Fundamentals and Applications, New York: Plenum Press, 1995, Ch 1.

49. SE Moschopedis, JF Freyer, JG Speight. Fuel 55: 227, 1976.

50. JG Speight, SC Moschopedis. In: JW Bunger, NC Li, eds. Chemistry of Asphaltenes. Washington, DC: American Chemical Society, 1981.

51. CH Bardon, L Barrie, D Espinat, V Guille, Min Hui Li, J Lambard, JC Ravey, E Rosenberg, T Zemb. Fuel Sci Technol Int 14: 203—242, 1996.

52. S Acevedo, MA Ranaudo, G Escobar, LB Gutierrez, X Gutierrez. In: EY Sheu, OC Mullins, eds. Asphaltenes —- Fundamentals and Applications. New York: Plenum Press, 1995, Ch 4.

53. R Cimino, C Correra, A Del Bianco. In: EY Sheu, OC Mullins, eds. Asphaltenes —- Fundamentals and Applications. New York: Plenum Press, 1995, Ch 3.

54. DA Storm, EY Sheu. In: TF Yen, GV Chilingarian, eds. Colloidal Nature of Petroleum Asphaltenes, Asphaltenes and Asphalts 1. Developments in Petroleum Science Series 40A. New York: Elsevier, 1994, Ch 6.

55. CW Wiggins. J Phys Chem 69: 3500, 1965.

56. DA Storm, EY Sheu. Fuel 74: 1140, 1995.

57. SJ Park, GJ Mansoori. Organic deposition of heavy petroleum crudes. Proceedings Fourth International Symposium on Heavy Crudes and Tar Sands, Edmonton, Alberta, 1988, Preprint paper 225.

58. H Pan, A Firoozabadi. SPE production and facilities, AI CHE J 46: 416—26, 2000.

59. TJ Jones, EL Neustadter, KP Whittingham, JCPT (April-June): 100—108, 1978.

60. CW Angle. CANMET Division Report WRC 93—21 (CF). Natural Resources Canada, 1993.

61. Fine Tails Fundamentals Consortium. Advances in Oil Sands Tailings Research, Vol 2, Ch 11. Alberta Department of Energy, Oil Sands and Research Division, 1995.

62. VB Menon, DT Wasan. Sep Sci Technol 19: 555—574, 1984.

63. YH Kim, DT Wasan. Ind Eng Chem Res 35: 4: 1141—1149, 1996.

64. PD Berger, C Hsu, JP Arendell. Designing and selecting demulsifiers for optimum field performance based on the production fluid characteristics. SPE publication of AIME. Proceedings of International Symposium on Oilfield Chemistry, San Antonio, TX, 1987, Paper SPE 16285, pp 457—164.

65. Y Kim, AD Nikolov, DT Wasan, H Diaz-Arauzo, CS Shetty. J Dispers Sci Technol 17: 33—53, 1996.

66. T Stroem-Kristiansen, PS Daling, AB Nordvik. Demulsification of Water-in-Oil (W/O) Emulsions resulting from Offshore Crude Oil Spills by use of Heat and Emulsion Breaker. Phase 1. Marine Spill Response Corporation Technical Report Series 93—026, 1993, pp. 51.

67. RA Mohammed, AI Bailey, PF Luckham, SE Taylor. Colloids Surfaces A: Physiochem Eng Aspects 83: 261—271, 1994.

68. SE Taylor. Chem Ind 20: 770—773, 1992.

69. BP Singh, BP Pandey. Indian J Technol 29: 443—447, 1991.

70. 1C Sharma, I Haque, SN Srivastava. Indian J Technol 20: 175—178, 1982.

71. 1C Sharma, I Haque, SN Srivastava. J Colloid Polym Sci 260: 616—622, 1982.

72. DD Eley, MJ Hey, MA Lee. Colloids Surfaces 24: 173—182, 1987.

73. S Acevedo, G Escobar, LB Gutierrez, H Rivas, X Gutierrez. Colloids Surfaces A: 71: 65, 1993.

74. A Bhardwaj, S Hartland. Ind Eng Chem Res 33: 1271—1279, 1994.

75. A Bhardwaj, S Hartland. J Dispers Sci Technol 14: 5: 541—557, 1993 (Abstr. no. 229604, Vol 119, no. 22).

76. DJ Miller, R Bohm. J Petrol Sci Eng 9: 1—8, 1993.

77. NN Zaki, AM Al-Sabagh. Tenside Surfactants Deterg 24: 12—14, 16—17, 1997.

78. NN Zaki, ME Abdel-Raouf, AAA Abdel-Azim. Monatsh Chem 127: 1239—1245, 1996.

79. J Sjöblom, L Mingyuan, H Hoiland, E Johnsen. Colloids Surfaces 46: 127—139, 1990.

80. E Johnsen, M Skjarvo, T Lund, J Sjöblom, H Soderlund, G Bostrom. Colloids Surfaces 34: 353—370, 1989.

81. J Sjöblom, H Soederlund, S Lindblad, EJ Johansen, IM Skaervoe. Colloid Polym Sci 268: 389—398, 1990.

82. CW Angle, AD Nikolov, DT Wasan, HA Hamza. Demulsification of water-in-bitumen emulsions: Role of emulsion film thickness stability. Twelth International Symposium on Surfactant in Solution Conference, Stockholm, 1998, Paper B05.

83. DR McCoy, EE McEntire, RM Gipson. Method for Demulsification of Bitumen Emulsions. US Patent 4: 457 371, 1984.

84. DR McCoy, RM Gipson, KB Young. Demulsification of Bitumen Emulsions with a High Molecular Weight Mixed Alkylene Oxide Polyol. Can Patent 1 160 172, 1984.

85. DR McCoy. Method for Demulsification of Bitumen Emulsions using Polyalkylene Polyamine Salts. US Patent 4 439 450, 1984.

86. RB Duke. Demulsification of a Crude Oil Middle Phase Emulsion. US Patent 4 439 450, 1984.

87. DR McCoy, CL Laberge. Demulsification of Bitumen Emulsions with a High Molecular Weight Polyol Containing Discrete Blocks of Ethylene and Propylene Oxide. Can Patent 1 153 717, 1983.

88. EE McEntire, DR McCoy. Demulsification of Bitumen Emulsions using Polymers of Diquaternary Ammonium Monomers Containing Hydroxyl Groups. US Patent 4 387 017, 1983.

89. P Becher. Theory of Emulsions: Creaming, Inversion, and Demulsification. 2nd ed. ACS no. 62, New York: Krieger, 1977, pp 1—149.

90. TF Tadros, B Vincent. In: P Becher, ed. Encyclopedia of Emulsion Technology. Vol 1. New York: Marcel Dekker, 1983, pp 1—102.

91. ESR Gopal. In: P Sherman, ed. Emulsion Science. New York: Academic Press, 1968, pp 1—72.

92. J Sjöblom, ed. Emulsions —- A Fundamental and Practical Approach. NATO AST Series 363. Dordrecht: Kluwer, 1992.

93. SL Mason, K May, S Hartland. Colloids Surfaces A, 96: 85—92, 1995.

94. CM Blair. Chem Ind 20: 538—544, 1960.

95. HP Ronningsen, J Sjöblom, L Mingyuan. Colloids Surfaces A: Physiochem Eng Aspects 97: 119—128, 1995.

96. A Barnes. Colloids Surfaces A: Physicochem Eng Aspects 91: 89—95, 1994.

97. GP Canevari. Mar Pollut Bull 13: 49—54, 1982.

98. A Hayward-Walker, DL Ducey, JR Gould, AB Nordvik. Formation and Breaking of Water-in-Oil Emulsions: Workshop Proceedings. Marine Spill Response Corp. (Kananaskis AB 06/14—15/93), Tech. Rep. Series 93—018.

99. TF Tadros. In: J Sjöblom, ed. Emulsions —- A Fundamental and Practical Approach, NATO AST Series 363. Dordrecht: Kluwer Academic, 1992, pp 173—188.

100. P Becher. Emulsions Theory and Practice. 2nd ed. ACS no. 62, New York: Krieger, 1977, pp 111—116.

101. KJ Lissant. Demulsification —- Industrial Application. Surfactant Science Series 13, New York: Marcel Dekker, 1983.

102. TH Plegue, SF Fruman, JL Zakin. J Colloid Interface Sci 114: 88, 1983.

103. JR Brenan. Pipelining Oil Emulsion. Company Rep., IMO Industries Inc., NC, USA.

104. LA Burkholder, JM Rashan, MH Auerbach, RP Gill. Production and pipeline transportation of heavy crude oils by use of specially formulated emulsions. Third Zulia University et al. Enhanced Oil Recovery International Symposium, Maracaibo, Venezuela, Proceedings 2, 1989, pp 765, 767—777. (Abst. no. 469, 279, Vol 29, 1989).

105. L Berero, A DiLullo, A Lentini, L Terzi. A (Patented) innovative way to produce and transport heavy (and very viscous) oil through dispersion in water (using sodium naphthalene sulfonate condensed with formaldehyde): Laboratory study and field test results. Proceedings of SPE Annual Technical Conference/ Production Operations and Engineering. Vol 2, New Orleans, 1994, pp 283—295.

106. NN Zaki. Colloids Surfaces Chem Abstr 125: 19—25, 1997.

107. VA Adewusi, AO Ogunsola. Chem Eng Res Design 71(A1): 62—68, 1993.

108. KS Pedersen, P Skovborg, HP Ronningsen. Energy Fuels 5: 924f, 1991.

109. WD Bancroft. J Phys Chem. 17: 501, 1913.

110. M Van der Waarden. Kolloid Z 156: 116, 1958.

111. JA Bichard. Oilsands Composition and Behaviour Research. AOSTRA Technical Publication Series 44, 1987, Ch 2, p 27.

112. JP Pfeiffer, RNJ Saal. Asphaltic bitumen as a colloidal system. Proceedings of 16th Colloid Symposium, Stanford University, CA, 1939, p139.

113. JE Strassner. Effect of pH on interfacial films and stability of crude oil—-water emulsions. Proceedings of 42nd Annual Spec of AIME Fall Meeting, 1969, Preprint no. SPE-1969.

114. JE Strassner, J Petrol Technol 243: 303, 1968.

115. A Lewis, M Walker. Formation and Breaking of Water-in-Oil Emulsions Workshop (Kananaskis, Alberta 6/14—15/93). Marine Spill Response Corp. Tech. Rep. Series N 93—018, 1993, pp 223—238.

116. A Lewis, M Walker, K Colcomb-Heiliger. Formation and Breaking of Water-in-Oil Emulsions Workshop (Kananaskis, Alberta 6/14—15/93). Marine Spill Response Corp. Tech. Rep. Series N.93—018, 1993, pp 203—220.

117. P Becher. Emulsions: Theory and Practice. 2nd ed. ACS no. 62, New York: Krieger, 1977, Ch 5.

118. P Sherman, ed. Emulsion Science. New York: Academic Press, 1969, pp 131—216.

119. GD MacKay, SG Mason. Can J Chem Eng 41: 203, 1963.

120. HJ Neumann, B Paczynska-Lahme. Progr Colloid Polym-Sci 101: 101—104, 1996.

121. FF Bartell, DO Niederhauser. Film forming constituents of petroleum oils. API Research Project 27. Fundamental Research on the Occurrence and Recovery of Petroleum, API 1964—47, 1949, p 45.

122. RJ Hunter. Foundations of Colloid Science. Oxford Science Publication Series, Vol II, 1989, Ch 15.

123. CHM Roberts. J Phys Chem 36: 3102, 1932.

124. ASC Lawrence, WJ Killner, J Inst Petrol 34: 821, 1948.

125. C Blakey, ASC Lawrence. J Inst Petrol 40: 203, 1954.

126. J Reisberg, TM Doscher. Prod Mon 21: 43, 1956.

127. JE Strassner. J Petrol Technol 20: 203f, 1968.

128. H Foerdedal, Y Schildberg, J Sjöblom, JL Volle. Colloids Surfaces 124:14: 106: 33—47, 1996.

129. H Foerdedal, J Sjöblom. J Colloid Interface Sci 181: 589—594, 1996.

130. PL Cottingham, FA Birkholz, LG Nickerson. Am Chem Soc Div Fuel Chem 23: 4, 1978, preprint.

131. S Puskas, J Balazs, A Farkas, I Regdon, O Berkesi, I Dekany. Colloids Surfaces A: Physicochem Eng Aspects 113: 279—293, 1996.

132. J Oren, GDM MacKay. Fuel 56: 382—384, 1977.

133. DG Thompson, AS Taylor, DE Graham. Colloids Surfaces 15: 175f, 1985.

134. DG Thompson, AS Taylor, DE Graham. Emulsification and demulsification related to crude oil production. Proceedings of SCI/Institute of Chemical Engineering Symposium, London, 1984.

135. B Felian, J Balazs, J Lakatos-Szabo, I Lakatos. Acta Phys Chem 30: 183—192, 1984.

136. J Sjöblom, O Urdahl, H Holland, AA Christy, EJ Johansen. Progr Colloid Polym Sci 82: 131—139, 1990.

137. RM Murzakov, SA Sabanenkov, AA Gureev. Chem Technol Fuels Oils 16: 69—71, 1980.

138. RZ Syunyaeva. Chem Technol Fuels Oils 16: 407—09, 1980.

139. R Murzakov, SA Sabanenkov, ZI Syunyaev. Chem Technol Fuels Oils 16: 674—677, 1980.

140. OK Kimbler, RL Reed, IH Silberberg. Soc Petrol Eng J 6: 153, 1966.

141. DJ Shaw. Introduction to Colloid and Surface Chemistry. 2nd ed. New York: Butterworth, 1970, p 91.

142. AG Taylor, J Mingins. J Chem Soc Faraday Trans I 5: 1161, 1975.

143. BP Singh. Energy Sources 16: 377—385, 1994.

144. RA Mohammed, AI Bailey, PF Luckham, SE Taylor. Colloids Surfaces A: Physicochem Eng Aspects 80: 237—242, 1993.

145. RA Mohammed, AI Bailey, PF Luckham, SE Taylor. Colloids Surfaces 80: 223—235, 1993.

146. KG Nordli, J Sjöblom, J Kizling, P Stenius. Colloids Surfaces 57: 83—98, 1991.

147. IB Ivanov, ed. Thin Liquid Films —- Fundamentals and Applications. Surfactant Science Series, Vol 29. New York: Marcel Dekker, 1988.

148. JA de Feijter. In: IB Ivanov, ed. Thin Liquid Films —- Fundamentals and Applications. Surfactant Science Series, Vol 29. New York: Marcel Dekker, 1988, Ch 7.

149. GJ Hirasaki. In: NR Morrow, ed. Interfacial Phenomena in Petroleum Recovery. New York: Marcel Dekker, 1991, Ch 2.

150. C Maldarelli, RK Jain. In: IB Ivanov, ed. Thin Liquid Films ——- Fundamentals and Applications. Surfactant Science Series, Vol 29. New York: Marcel Dekker, 1988, Ch 8.

151. DA Edwards, H Brenner, DT Wasan. Interfacial Transport Processes and Rheology. Boston: Butterworth—Heinmann, 1991.

152. TF Tadros. Colloids Surfaces: Physicochem Eng Aspects 91: 39—55, 1991.

153. AK Malhotra, DT Wasan. In: IB Ivanov, ed. Thin Liquid Films —- Fundamentals and Applications. Surfactant Science Series v29. New York: Marcel Dekker, 1988, Ch 12.

154. CI Kristov, L Ting, DT Wasan. J Colloid Interface Sci 85: 362—373, 1982.

155. G Loglio, U Tesser, R Miller, R Cini. Colloids Surfaces 61: 219—226, 1991.

156. DA Edwards, DT Wasan. J Colloid Interface Sci 139: 479—486, 1990.

157. J Lucassen-Reynders, M Van den Temple. Chem Eng Sci 27: 1283—1291, 1972.

158. A Yeung, T Dabros, J Masliyah. Langmuir 13: 6597—6606, 1998.

159. J Boyd, P Sherman. J Colloid Interface Sci 34: 76f, 1970.

160. RJR Cairns, DM Grist, EL Neudstadter. In: AL Smith, ed. Theory and Practice of Emulsion Technology. New York: Academic Press, 1976, pp 135—151.

161. DM Grist, EL Neustadter, KP Whittingham. J Can Petrol Technol (June): 74—78, 1981.

162. DE Graham, EL Neudstadter, A Stockwell, KP Whittingham, RJR Cairns. Symposium on Surface Active Agents. Society of Chemical Industries Colloids Surfaces Chemistry Group, London, 1979, pp 127.

163. DT Wasan, JJ McNamara, SM Sampath, S Aderangi. J Rheol 23: 181f, 1979.

164. CH Pasquarelli, DT Wasan. In DO Shah, ed. Surface Phenomena in Enhanced Oil Recovery. New York: Plenum Press, 1979, p 237f.

165. SE Taylor. Colloids Surfaces 29: 29f, 1988.

166. EL Neustadter, KP Whittingham, DE Graham. In: DO Shah, ed. Surface phenomena in Enhanced Oil Recovery. New York: Plenum Press, 1981, pp 307—326.

167. Mukherjee, AP Kushnick. Effect of demulsifiers on interfacial properties governing crude oil demulsification. Proceedings of 195th ACS National Meeting, Toronto, 1988, ACS Div Petrol Chem Preprint 33; pp 205—210.

168. JH Clint, EL Neustadter, TJ Jones. Proceedings of the Third European Symposium on Enhanced Oil Recovery, Bournemouth, UK, 1981.

169.1C Callaghan, EL Neustadter. Chem Ind 17: 53—57, 1981.

170. AD Nikolov, DT Wasan, M Randie, CS Shetty. Chem Eng Commun 152/153: 337—350, 1996.

171. D Tambe, J Paulis, MM Sharma. J Colloid Interface Sci 171: 163—469, 1995; 147: 137f, 1991.

172. DT Wasan. SPE J 409—117, 1978.

173. VB Menon, DT Wasan, Colloids Surfaces 19: 7—27, 1988.

174. VB Menon, AD Nikolov, DT Wasan. J Dispers Sci Technol 9: 575—593, 1988—89.

175. RA Mohammed, AI Bailey, PF Luckman, SE Taylor. Colloids Surfaces A 91: 129—139, 1994.

176. D Tambe, J Paulis, MM Sharma. J Colloid Interface Sci 171: 463—469, 1995.

177. RJR Cairns, DM Grist, EL Neustadter. In: DO Shah, ed. Theory and Practice of Emulsion Technology. New York: Academic Press, 1976, p 135.

178. DT Wasan. In: J Sjöblom, ed. Emulsions —- A Fundamental and Practical Approach. Dordrecht: Kluwer, 1991, pp 283—295.

179. TY Chen, RA Mohammed, AI Bailey, PF Luckham, SE Taylor. Colloids Surfaces A: Physiochem Engin Aspects 83: 273—284, 1994.

180. AK Malhotra. PhD thesis, Illinois Institute of Technology, Chicago, 1984.

181. DT Wasan, AK Malhotra, N Aderangi. Int J Multiphase Flow 9: 105, 1983.

182. PJ Breen, DT Wasan, YH Kim, AD Nikolov. In: J Sjöblom, ed. Emulsions and Emulsion Stability. Surfactant Science Series, Vol 61. New York: Marcel Dekker, 1996, pp 237—285.

183. SR Ross, ID Morrison. Colloidal Systems and Interfaces. New York: John Wiley, 1988, pp 180—189.

184. R Luthy, R Selleck, T Galloway. Environ Sci Technol 11: 1211—1217, 1977.

185. RJR Cairns, DM Grist, EL Neustadter. Effects of crude oil —- water interfacial properties on water —-crude oil emulsion stability. Proceedings of SCI Symposium Theory and Practice of Emulsion Technology, Brunei University, London, 1974, Ch 8.

186. S Acevedo, G Escobar, LB Gutierrez, H Rivas. Fuel 71: 619, 1992.

187. Y Xu. Energy Fuels 9: 148—154, 1995.

188. EY Sheu, MM De Tar, DA Storm. Fuel 71: 1277—1280, 1992.

189. EY Sheu, MM De Tar, DA Storm, SJ DeCanio. Fuel 71: 299—302, 1992.

190. DT Wasan, K Sampath, N Aderangi. AIChE Symp Ser 76: 93, 1980.

191. J Svetgoff. Petrol Eng Int 61: 48—50, 1989.

192. K Shinoda, H Arai. J Phys Chem 68: 3485, 1964.

193. K Shinoda, H Sagitani. J Colloid Interface Sci 255: 172, 1977.

194. B Paczynska—Lahme. Progr Colloid Polym Sci 83: 196f, 1990.

195. S Friberg. J Colloid Interface Sci 40: 291—295, 1971; 37: 291, 1971.

196. T Stroem—Kristainsen, AB Nordvik, A Lewis, PS Daling. Demulsification by Use of Heat and Emulsion Breaker. Phase 2. Marine Spill Response Corp. Tech. Rep. Series, N94—012, 1994.

197. RJ Fiocco, MA Walsh, JN Hokstad, PS Daling, A Lewis, KW Becker. Improved laboratory demulsifica-tion tests for oil spill response. API-EPA-USCG et al. Proceedings of International Oil Spill Achieving and Maintaining Preparedness Conference, Long Beach, CA, API Publication no. 4620, 1995, pp 165—170.

198. T Stroem-Kristiansen, A Lewis, PS Daling, JN Hokstad, I Singsaas. Weathering and dispersion of naphthenic, ashphaltenic, waxy crude oils. Proceedings of International Oil Spill Conference, Fort Lauderdale, FL, 1997, pp 631—636.

199. B Obah. Nigeria Fed Univ Technol Erdoel Kohle-Erdgas-Petrochem 41: 71—74, 1988.

200. BJ Carroll. In: E Matijevic, ed. Surface and Colloid Science. Vol 9. New York: John Wiley, 1976, pp 1—66.

201. KJ Lissant. Demulsification. New York: Marcel Dekker, 1982.

202. R Aveyard, BP Binks, PD Fletcher, X Ye, JR Lu. In: J Sjöblom, ed. Emulsions —- A Fundamental and Practical Approach. Dondrecht: Kluwer, 1992.

203. SR Reddy, HS Fogler. J Colloid Interface Sci 82: 128—135, 1981.

204. SR Reddy, S Fogler. J Colloid Interface Sci 79: 101—104, 1981.

205. SR Reddy, HS Fogler. J Colloid Interface Sci 79: 98—104, 1981.

206. A Bhardwaj, S Hartland. J Dispers Sci Technol 15: 133—146, 1994.

207. SL Mason, K May, S Hartland. Colloids Surfaces 96: 85—92, 1996.

208. VB Menon, DT Wasan. In: P Becher, ed. Encyclopedia of Emulsion Technology. Vol 2. New York: Marcel Dekker, 1985, pp 1—76.

209. S Hartland. In IB Ivanov, ed. Thin Liquid Films —- Fundamentals and Applications. Surfactant Science Series, Vol 29. New York: Marcel Dekker, 1988, Ch 10.

210. E Nakache, P-Y Longaive, S Aeillo. Colloids Surfaces A: Physicochem Eng Aspects 96: 69—76, 1995.

211. P Becher. Emulsions: Theory and Practice. 2nd ed. ACS No. 62, New York: Krieger, 1977, pp 367—380.

212. DA Edwards, H Brenner, DT Wasan. Interfacial Transport Processes and Rheology. Boston, MA: Butterworth-Heinmann, 1991, Ch 11.

213. MV Ostrovsky, RJ Good. J Disper Sci Technol 7: 95—125, 1986.

214. RD Vold, MJ Vold. Colloid Interface Chemistry. Boston, MA: Addison Wesley, 1983, pp 415—39.

215. M von Smoluchowski. Z Phys Chem 92: 129, 1917.

216. M Van den Temple. Rec Trav Chim 72: 433,442, 1953.

217. S Hartland. In: IB Ivanov, ed. Thin Liquid Films —- Fundamentals and Applications. Surfactant Science Series, Vol 29. New York: Marcel Dekker, 1988, Ch 10.

218. RP Borwanker, LA Lobo, DT Wasan. Colloids Surfaces 69: 135—146, 1992.

219. SL Mason, K May, S Hartland. Colloids Surfaces A: 96: 85—92, 1994.

220. CW Angle, HA Hamza. Evaluation of some biological surfactants as emulsion destabilizers. Proceedings of 59th International Surface and Colloid and 5th International Colloid Science Conference, Clarkson University, Potsdam, NY, 1985; CANMET Div. Rep. ERP/ERL 81—99(CF), 1981.

221. R Vold, K Mittal, A. Hahn. Surface Colloid Science 10. New York: Plenum Press, 1978, pp 45—97.

222. MJ Void. Langmuir 1: 74—78, 1985.

223. AU Hahn, RD Vold. J Colloid Interface Sci 51: 133—142, 1975.

224. CW Angle, JL Picard, HA Hamza. The effects of ultracentrifugal stress on the stability of crude oil/ water emulsions. Proceedings of 38th Canadian Chemical Engineering Conference, Edmonton, Alberta, 1988.

225. RD Vold, KL Mittal. J Soc Cosmet Chem 23: 171—188, 1972.

226. AU Hahn, KL Mittal. Colloid Polym Sci 9: 959—967, 1979.

227. MK Sharma. Curr Sci 46: 131—132, 1977.

228. MK Sharma. Acta Cienca Indica 3: 139—141, 1977.

229. MK Sharma. Progr Colloid Polym Sci 63: 75—77, 1978.

230. AU Hahn, KL Mittal. Colloid Poly Sci 257: 959—967, 1979.

231. RD Vold, M Maletic. J Colloid Interface Sci 65: 390—393, 1978.

232. RS Allan, SG Mason. J Colloid Sci 17: 383, 1962.

233. S Hartland. Chem Eng Sci 22: 1675, 1967.

234. IB Ivanov, DS Dimitrov. Thin Film Drainage. In: IB Ivanov, ed. Thin Liquid Films —- Fundamentals and Applications. Surfactant Science Series, Vol 29. New York: Marcel Dekker, 1988, pp 379—85.

235. JA Kitchener, PR Musselwhite. In: P Sherman, ed. Emulsion Science. New York: Academic Press, 1968, Ch2.

236. DT Wasan. Interfacial transport processes and rheology —- structure and dynamics of thin liquid films. ASEE Chemical Engineering Education, 1992, pp 104—112.

237. BV Derjaguin. Theory of Stability of Colloids and Thin Films. New York: Consultants Bureau, 1989.

238. A Scheludko, D Exerowa. Kolloid Z 165: 148—51, 1960; 168: 24—8, 1959. (Taken from RJ Hunter. Foundations in Colloid Science. Vol IL Oxford: Oxford Science Publications; Clarendon Press, 1989, Chs 15 and 16.)

239. A Scheludko. Colloid Chemistry. Amsterdam: Elsevier, 1966, p 277.

240. AD Nikolov, DT Wasan, SE Friberg. Colloids Surfaces A: 118: 221—243, 1996.

241. RW Flummerfelt, AB Catalano, CH Tong. Proceedings: Surface Phenomena in Enhanced Oil Recovery, 1981, pp 571—594.

242. XB Reed, E Riolo Jr, S Hartland. Int J Multiphase Flow 3: 485, 1977.

243. IB Ivanov, TT Traykov. Int J Multiphase Flow 2: 397, 1976.

244. TT Traykov, ED Manev, IB Ivanov. Int J Multiphase Flow 3: 485, 1977.

245. AD Barber, S Hartland. Can J Chem Eng 54: 279, 1976.

246. AF Jones, SDR Wilson. J Fluid Mech 87: 263, 1978.

247. DT Wasan, SM Shah, M Chan, JJ McNamara. Soc Petrol Eng J 18: 409, 1978.

248. DT Wasan, ME Ginn, DO Shah, eds. Surfactants in Chemical and Process Engineering, Surfactant Science Series 28, 1988.

249. AD Nikolov, DT Wasan, PA Kralchevsky, IB Ivanov. In: N Ike, I Sogami, eds. Proceedings of Yamada Conference XIX. Singapore: World Scientific Publications, 1988.

250. AD Nikolov, PA Kralchevsky, IB Ivanov, DT Wasan. J Colloid Interface Sci 133: 1, 1989; J Colloid Interface Sci 133: 13, 1989.

251. AD Nikolov, DT Wasan, ND Denkov, PA Kralchevsky, IB Ivanov. Progr Colloid Polym Sci 82: 1, 1990.

252. DT Wasan, AD Nikolov, L Lobo, K Koczo, DA Edwards. Progr Surface Sci 39: 2, 1992.

253. AD Nikolov, DT Wasan. Langmuir 8: 2985—2994, 1992.

254. MA Krawczyk, DT Wasan, CS Shetty. Ind Eng Chem Res. 30: 367—375, 1991.

255. S Mukherjee, AP Kushnick. Effect of demulsifiers on interfacial properties governing crude oil demulsification. Proceedings of 195th ACS National Meeting, Toronto, 1988, ACS Div. Petrol. Chem. Preprint, Vol. 33, No. l,pp 205—210.

256. S Mukherjee, AP Kushnick. In: JK Borchardt, TF Yen, eds. Oil Field Chemistry —- Enhanced Recovery and Production Stimulation. Washington, DC: American Chemical Society, 1989, pp 364—374.

257. R Aveyard, BP Binks, PDI Fletcher, JR Lu. J Colloid Interface Sci 139: 128—138, 1990.

258. YH Kim, DT Wasan, PJ Breen. Colloids Surfaces A: Physicochem Eng Aspects 95: 235—247, 1995.

259. J Lucassen-Reynders, M Van den Temple. J Phys 67: 731, 1963.

260. VB Menon, DT Wasan. Colloids Surfaces 29: 7—27, 1988.

261. VB Menon. Characterization of dispersed three-phase systems with applications to solids-stabilized emulsions. Dissertation Abstracts International: Section B Science & Engineering, Vol 47, No. 5 2077-B, 1986.

262. A Gelot, W Friesen, HA Hamza. Colloids Surfaces 12: 27If, 1984.

263. AB Taubman, AF Koretskii. Colloid J Wash 20: 631, 1958.

264. VB Menon, DT Wasan. Colloids Surfaces 29: 7—27, 1988.

265. VB Menon, AD Nikolov, DT Wasan. J Colloid Interface Sci 124: 317—327, 1988.

266. CW Angle, R Zrobok, HA Hamza. J Appl Clay Sci 7: 455—470, 1993.

267. RC Little. Environ Sci Technol 15: 1184—1190, 1981.

268. IA Buist, SL Ross. Emulsion inhibitors: a new concept in oil spill treatment. Proceedings of Oil Spill Conference. American Petroleum Institute, Washington, DC, 1987, p 217.

269. SL Ross. An experimental study of oil spill treating agents that inhibit emulsification and promote dispersion. Report EE87. Ottawa: Environment Canada, 1986.

270. RI Hancock. In: TF Tadros, ed. Surfactants. New York: Academic Press, 1983, pp 287—321.

271. G Leopold. In: LL Schramm, ed. Emulsions Fundamentals and Applications in the Petroleum Industry. Advances in Chemistry Series 231, Washington, DC: American Chemical Society, 1992, Ch 10.

272. R Grace. In: LL Schramm, ed. Emulsions Fundamentals and Applications in the Petroleum Industry. Advances in Chemistry Series 231, Washington, DC: American Chemical Society, 1992, Ch9.

273. VH Smith, KE Arnold. In: HB Bradley, ed. Petroleum Engineering Handbook. SPE, 1992, Ch 19.

274. B Rowan. The Use of Chemicals in Oil Field Demulsification. Spec Publ Royal Soc Chem 107 (Ind Appl Surfactants III), 1992, pp 242—251.

275. CW Angle, T Dabrus, H Hamza. Mechanism of destabilization of water-in-bitumen emulsions by polymeric surfactants. Paper presented at 13th International Symposium on Surfactants in Solution, SIS-2000, Gainesville, FL, June 11—16, 2000, p 25.

276. L Cash, JL Cayais, RS Schechter, G Fournier, D Macallister, T Schares, RS Schechter, WH Wade. J Colloid Interface Sci 59: 39—44, 1977.

277. JL Cayais, RS Schechter, WH Wade. Soc Petrol Eng J (Dec.): 351: 357, 1976.

278. RL De Silva, S Key, J Marino, C Guzman, S Buitriago. Chemical dehydration: correlations between crude oil, associated water and demulsifier characteristics in real systems. Proceedings of SPE Oilfield Chemical International

Symposium, Houston, TX 1997, pp 601—607.

279. WC Griffin. J Soc Cosmet Chem 1: 311, 1949; 5: 249, 1954.
280. HT Davis. Colloids Surfaces A: 9: 9—34, 1994.
281. K Shinoda, H Saito. J Colloid Interface Sci 26: 70, 1968.
282. K Shinoda, H Kuneida. In: P Becher, ed. Encyclopedia of Emulsion Technology. Vol 1. New York: Marcel Dekker, 1983.
283. ME Hayes, M El-Emary, RS Schechter, WH Wade. J Colloid Interface Sci 68: 591—592, 1979.
284. AH Walker, DL Ducey, JR Gould, AB Nordvik. Proceedings of Formation of Water-in-Oil Emulsions. Marine Spill Corp. Tech. Rep. Series 93—018, Kananaskis, Alberta, 1993. 285. DG Cooper, JE Zajic, EJ Cannel, JW Wood. Can J Chem Eng 58: 576—579, 1980.
286. J Israelachvili. Colloids Surfaces A: 91: 1—8, 1994.
287. L Marshall. Cosmet Perfum 90: 37, 1975.
288. F Staiss, R Bohm, R Kupfer. Improved demulsifier chemistry: A novel approach in dehydration of crude oil. SPE Production Engineering, 1991, pp 334—338.
289. M Amarvathi, BP Pandey. Res Ind 36: 198—202, 1991.
290. K Shinoda. J Colloid Interface Sci 24: 4—9, 1967.
291. FE Bailey Jr, JV Koleske, eds. Alkylene Oxides and their Polymers. Surfactant Science Series, Vol 35. New York: Marcel Dekker, 1990, Ch 6.
292. O Urdahl, J Sjöblom. J Dispers Sci Technol 16: 557—574, 1995 (Abstr. no. 37002, Vol 124, No 4)
293. O Urdahl, AE Moevik, J Sjöblom. Colloids Surfaces 74: 293—302, 1993.
294. J Sjöblom, O Urdahl, H Hoeiland, AA Christy, EJ Johansen. Progr Colloid Polymer Sci 82: 131—139, 1990.
295. DE Graham, A Stockwell, DG Thompson. Chemical Demulsification of Produced Crude Oil Emulsions. Spec Publ Royal Soc Chem 45: 73--91, 1983 (Abstract no. 70810).
296. DE Graham, A Stockwell. Selection of demulsifiers for produced crude oil emulsions. Proceedings of Europe Offshore Petroleum Conference, London, 1980, Vol 1, pp 453—58. 297. J Svetgoff. Petrol Eng Int 62(1): 1990 (Abstract no. 476 918, Vol 30, No. 7).