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Demulsifiers in the Oil Industry

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I. INTRODUCTION

According to our traditional understanding of emulsion formation and stabilization, there is a need to introduce mechanical energy and stabilizing agents to a water/oil mixture in order to create stable emulsions. In bench experiments the energy input is typically controlled by means of different kinds of rotors and homogenizers. Under real oil-production conditions, pressure gradients over chokes and valves will guarantee that there will be a sufficiently high mechanical energy input in order to rupture original solution structures and to form new fresh W/O interfaces. Obviously the magnitude of the pressure gradient over the choke/ valve will be decisive for the droplet size distribution in the fresh emulsions. Since the transport over a choke/ valve will mean the creation of a new W/O interface the nature of the emulsion before and after the valve/ choke may differ significantly (1-5).

The lifetime of the emulsion (and the retention time in the full-scale separator) depends on the kind of stability mechanisms involved. There exist several possibilities of finding stabilizing agents (or solid fines) in either the crude oil itself or in added production chemicals. Among the indigenous stabilizers, asphaltenes/resins/ porphyrins are mentioned as possible candidates for the stabilization of W/O emulsions. In most cases it is, however, not possible to pick out one single component responsible for the stability of the dispersed droplets, but several components/fractions in parallel are the source for the stability of the emulsion. The components/fractions in the crude oil show a large range of molecular weights. Lighter components like the resins can act as individual monomers in a similar manner to traditional surfactants. The driving force for their action is the presence of water (and the existence of a W/O interface). Usually the low molecular weight resins have a tendency to be the most interfacially active, i.e., to reach first and cover a fresh W/O interface. However, this is mostly a necessary requirement but not a sufficient one for the formation of stable W/O emulsions. The next step in the stabilization process involves interaction with the heavier crude oil components, i.e., the asphaltenes. Depending on the production history and the fluid properties these molecules can be either in a monomeric or associated state. In the latter case small particles are formed. The formation of these is normally a result of the stacking tendency of the individual asphaltene molecules. These nanosized particles will have a strong tendency to accumulate at the W/O interfaces, if the solution conditions or changes herein so favor. Obviously the final particle size or the flocculation of these nanosized particles is critical with regard to the stabilizing capacity of these entities (6, 7).

It is of crucial importance to understand the stabilizing mechanisms when discussing demulsiflers and the efficiency of these. In this chapter we are going to discuss different types of demulsifiers, i.e., from simple solvents to intriguing macromolecules. It is also our intention to view how new instrumentation can reveal important and to some extent unexpected properties of these chemicals. In this chapter we introduce, in addition to conventional techniques, the use of Langmuir and Langmuir-Blodgett techniques, atomic-force microscopy (AFM) and near-infrared spectroscopy (NIR), when analyzing the effects of the demulsifying chemicals. We can also for the first time report on destabilization experiments (with demulsifiers) at elevated pressures. These experiments have been carried out in a special separation rig constructed for Statoil.

II. EXPERIMENTAL TECHNIQUES

A. The Langmuir Technique

The Langmuir technique is used in order to characterize monolayer properties of surface-active materials. The instrumentation consists of a shallow rectangular container (trough) in which a liquid subphase is added until a meniscus appears above the rim, whereupon the film is spread. The barrier for manipulation of the film rests across the edges of the container. For a more thorough description of the experimental setup, Petty and Barlow (8) are recommended. The surface pressure is measured by means of the Wilhelmy method (8—10). Modification of the trough design has made it possible to carry out the same kind of experiments on a liquid/liquid interface, i.e., the oil/water interface, instead of on the liquid surface. A prototype trough has been designed by KSV Chemicals in collaboration with the University of Compiègne, France (11). The trough, entirely made of Delrin, is a "double" trough (Fig. 1) where the barriers contain holes to allow the flow of the light phase as the compression of the interface proceeds. The Wilhelmy plate is first placed in the aqueous phase, then the oil phase is added until the plate is totally immersed.

The most common and adequate way of presenting the results obtained from the Langmuir technique is a plot of surface pressure as a function of the area of surface available to each molecule, i.e., the mean molecular area. The measurements are carried out at a constant temperature and are known as surface pressure/area isotherms (Fig. 2). The film is compressed at a constant rate by the moving barriers while the surface pressure is continuously monitored. Generally, a number of distinct regions are apparent on examining the isotherm. As the surface area is reduced from its initial high value, there is a gradual onset of surface pressure until an approximately horizontal region is reached. In this region the hydrophobic parts of the molecules, originally distributed near the water surface, are being lifted away. However, this part of the isotherm is often not resolved by the apparatus, because the surface pressure at which this occurs is usually quite small (< 1 mN/m) due to the weakness of interaction between water and the tailgroups. This region is followed by a second abrupt transi-

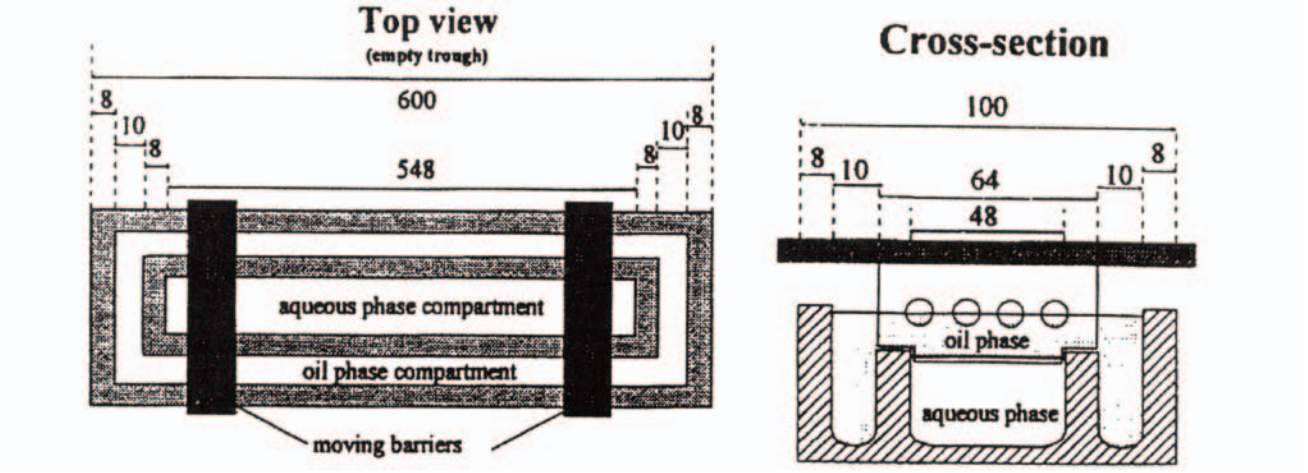


Figure 1 Schematic drawing of the liquid-liquid interfacial trough (size in mm).

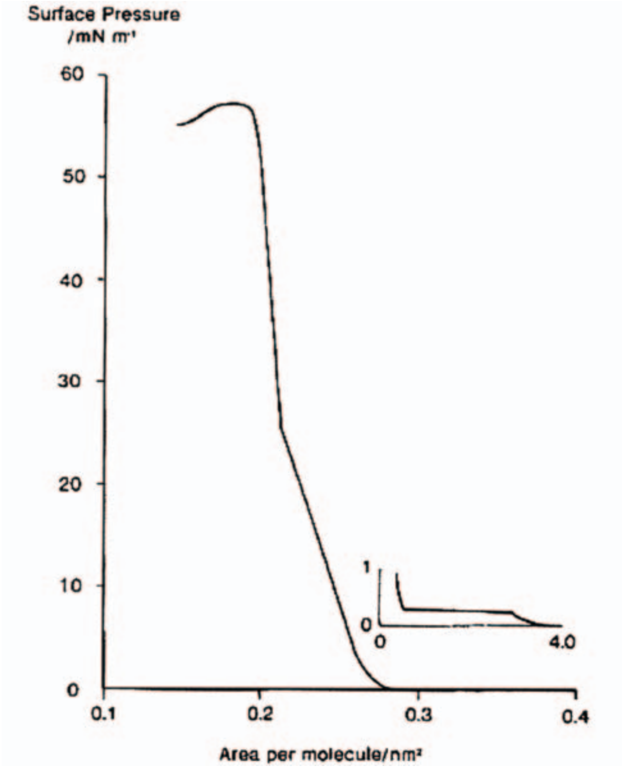


Figure 2 Typical surface pressure/area isotherm of stearic acid on an acidified water subphase.

tion to a steeply linear region, with an approximately constant compressibility.

Further reduction in surface area results in an abrupt increase of slope, and hence reduced compressibility. All these different regions indicate different states of the monolayer, and analogously to bulk matter these are characterized as gas-, liquid- and solid-like (12-14). Additional techniques (15) such as X-ray scattering, electron diffraction, fluorescence, polarized fluorescence, atomic-force microscopy, and Brewster angle microscopy have proved the existence of meso-phases in Langmuir films. The complexity of behavior is a result of the differerent intermolecular interactions in the film (alkyl group/alkyl group and polar group/ polar group interactions) and between the film and the subphase (polar group/subphase interactions). Hence, the interaction forces would undergo certain changes, which would be related to the packing of the molecules in the two-dimensional plane. More details may be found in the books by Gains (9) and Birdi (10).

A sharp break at small areas in the II-A isotherm is attributed to the collapse of the monolayer under the given experimental conditions. In general, the collapse pressure is the highest surface pressure to which a monolayer can be compressed without a detectable movement of the molecules in the film to form a new phase.

In order to investigate the stability of a monolayer, the area loss at constant surface pressure or the decrease in surface pressure at constant area is measured. Different destabilization mechanisms are illustrated by the shape of the relative area relaxation isotherms in Fig. 3. The compression is stopped at a predetermined surface pressure and the relative area loss is plotted as a function of time. Curve (a) in Fig. 3 shows the behavior of a totally stable film, with no area reduction. Isotherm (b) shows an initial area loss, which is attributed to structural rearrangements in the monolayer to form a coherent close-packed film (16—19). This process depends on the rate of compression. Fast barrier movement creates a higher degree of disorder in the monolayer, and the initial area loss is increased. A continuous decrease in area, as illustrated by curve (c), is the result of a slow dissolution of the film-forming material into the subphase or evaporation of the monolayer. This film loss increases with surface pressure, and is a consequence of the huge volume difference between the material in the film and the subphase liquid and gas phase to which the monolayer is exposed. Even a low solubility or vapor pressure may lead to destabilization of the film due to solution or evaporation (20). Isotherm (d) in Fig. 3 is characterized by a relaxation rate that increases with time. This kind of behavior is observed for systems that undergo nucleation and further growth of the film material into bulk fragments (19, 21).

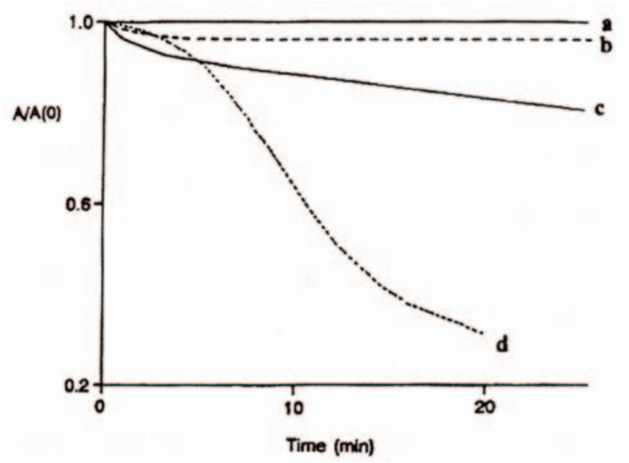


Figure 3 Relative relaxation curves at constant surface pressure for monolayers showing different stabilities: (a) stable monolayer; (b) rearrangements of the film molecules; (c) dissolution of film molecules into the subphase; (d) collapse by nucleation and growth of bulk solid fragments.

B. Langmuir-Blodgett Deposition

The most commonly used process of transferring a floating insoluble monolayer to a solid surface is Langmuir's original method (22). A clean wettable solid is placed in the subphase before a monolayer is spread, and then drawn up through the surface after formation of the film. The transfer process is critically dependent on the surface pressure, so it is desirable to maintain a constant pressure as the film is removed from the surface. Using this kind of deposition technique, both the film and a thin layer of water are transferred to the solid substrate. The water is later removed by drainage or evaporation, leaving a monolayer on the solid surface.

The rate of deposition is an important factor. Optimal values of this parameter depend partly on the rate of drainage of the intervening liquid film from the monolayer/slide interface and partly on the dynamic properties of the monolayer on the liquid surface, i.e., the film viscosity.

When conducting structural studies of Langmuir-Blodgett (LB) films, careful consideration has to be taken of possible effects that might arise during film deposition. Irregularity in the dipping motion may result in formation of striations in the deposited layer. Trapped water droplets between the film and the solid surface is another possible reason for imperfections in the monolayer. Circumstances such as low surface pressure or weak interactions between the film-forming molecules, i.e., the monolayer is not coherent, may result in deposition of irregular films. This is probably a result of expansion, contraction, or flow during the transfer process.

A solid surface, which is not smooth on a molecular scale, may lead to problems when transferring a mono-molecular film on to it. At the moment of deposition the film may bridge over the surface roughness, especially if the film is closely packed and under high surface pressure. This kind of bridging is often supported by the intervening water layer, so when this layer is removed the film may collapse.

C. Atomic-force Microscopy

Atomic-force microscopy (AFM) (23) is a nearly ideal, high-resolution method in providing a molecular-scale topographic view of a variety of solid surfaces, organic, inorganic, or biomolecular. Under optimal conditions this microscopic technique is capable of producing images showing details of molecular resolution in LB films.

The AFM technique exploits the forces that exist between atoms and molecules. The force exerted upon a tip mounted on to a cantilever (with a known spring constant, weaker than the equivalent spring constant between atoms) is monitored as the tip passes over the surface. Measurements of the cantilever deflection, which is proportional to the magnitude of the force, during the scan make it possible to obtain images of the surface topography. All types of materials exert these forces, so there is no restriction regarding composition of the analyzed components. Another important advantage with AFM is that it can operate in a variety of environments. It is especially convenient that the measurements may be performed in air at atmospheric pressure. In addition, AFM may also be operated in liquids.

There are three scanning modes for AFM, i.e., contact mode, noncontact mode, and tapping mode (24). In the contact mode the tip is touching the sample surface where the repulsive forces dominate, while the attractive forces dominate in the noncontact mode. The tapping mode represents a compromise between these two, giving better resolution than the noncontact mode and is not as damaging for the sample as the contact mode. A tip in contact with the surface may generate extremely high pressures on the small contact area between the tip and the sample, which may result in indentation of the tip in soft materials. In tapping mode the cantilever is oscillating near its resonance frequency, with a high enough amplitude to allow the tip to dip periodically in the contamination layer. Measuring the change in amplitude or phase for the oscillating cantilever provides images of the surface (Fig. 4).

For more information regarding the use of AFM and related probe techniques for imaging LB films, review articles by Zasadzinski et al. (25) and DeRose and Leblanc (26) are recommended.

D. Test Procedures for Demulsification

It is commonly known that the administration of chemicals is very essential. Depending on the administration procedure one can expect different efficiencies of the demulsifiers. Different administration procedures are reviewed in the following.

The traditional testing of demulsifiers is to undertake bottle-shake tests. In these tests one has a pre-mixed emulsion and the chemical under study is applied. After this the bottle is gently shaken in order to distribute the chemical evenly into the emulsified system. The efficiency of the chemical applied is read from the resolution of the dis-

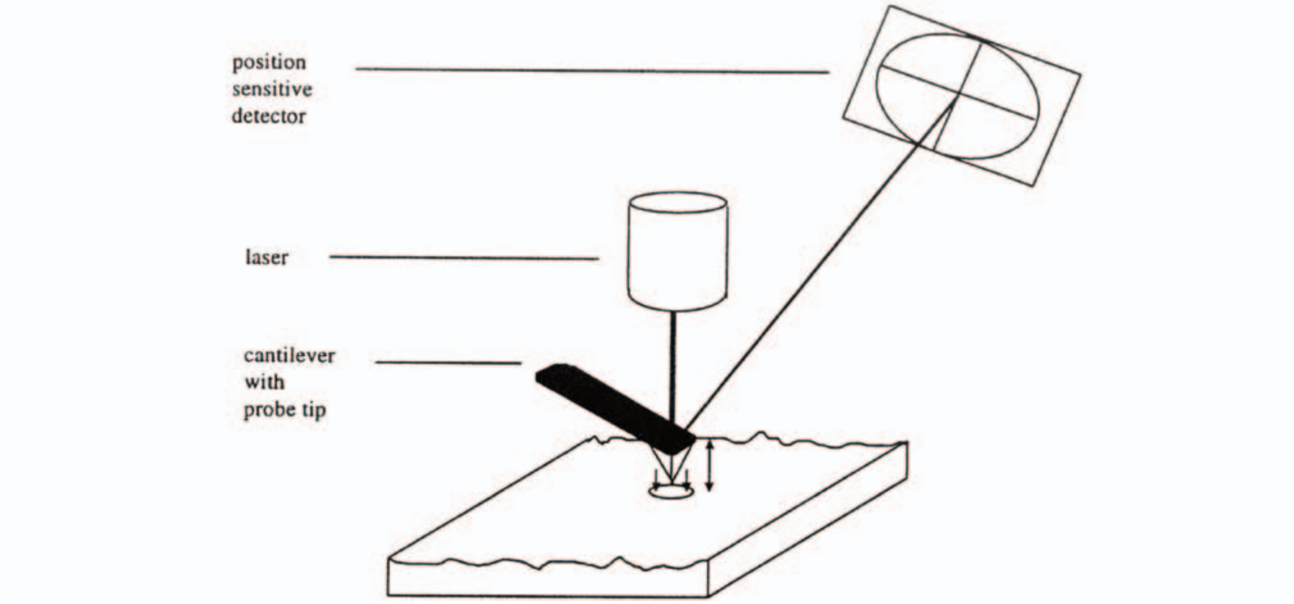


Figure 4 Schematic representation of an atomic-force microscope.

persed phase in volume as a function of time. Normally the size and shape are such that area effects can be neglected. The demulsification normally progresses under stagnant conditions with no mechanical energy input. When the coalescence is in progress there will be a resolution of the dispersed phase as a function of time, i.e., so-called volume-time plots. If the administration of the chemical only results in an accelerated creaming/ sedimentation, there will be an increased concentration of droplets on the top (or the bottom) of the otherwise clear bulk phase. This situation should not be misinterpreted as a breaking of the emulsion, since gentle shaking will redistribute the droplets again.

The weakness of the bottle tests is that a true process is not reproduced. This fact has been accounted for in a variety of test rigs simulating true flow conditions, process kits, and separation conditions. The Statoil R&D Center has recently constructed a special rig for simulation of high-pressure processes. In this rig (Fig. 5) emulsions can be formed at different pressures before being brought into the separation chamber. The final droplet sizes and size distributions are determined by the pressure drop over the chokes and valves. The separation can be performed at elevated pressures if so wanted. The rig is described in detail below.

E. Separation Rig

A separation rig, as illustrated in Fig. 5, is used to prepare W/O emulsions and monitor the separation of them. The principle is that two pressurized fluids meet just before a choke valve (VD1) and flow through the valve into the separation cell. The two fluids can either be oil and water or for instance two premixed oil/water dispersions. Through the choke valve the fluid mixture undergoes a pressure drop. The low-pressure side of the choke valve equals the separator pressure. The pressure drop through the choke leads to the creation of more interface between the oil and water, i.e., water droplets are formed and dispersed into the oil. At the same time the light end of the oil undergoes a phase change from liquid to gas. (The gas evolved may form a foam and may influence the sedimentation and coalescence of the water droplets.) After the cell has been filled, the amount of the different phases (foam, oil, emulsion/ dispersion, and water) is recorded as a function of time. Upstream of the choke valve VD1 there are two other choke valves; one on each line (VD2 and VD3). Through these choke valves the same processes take place as described for VD1. Through VD2 and VD3 dispersions of oil and water can be made. In this way the dispersion which enters

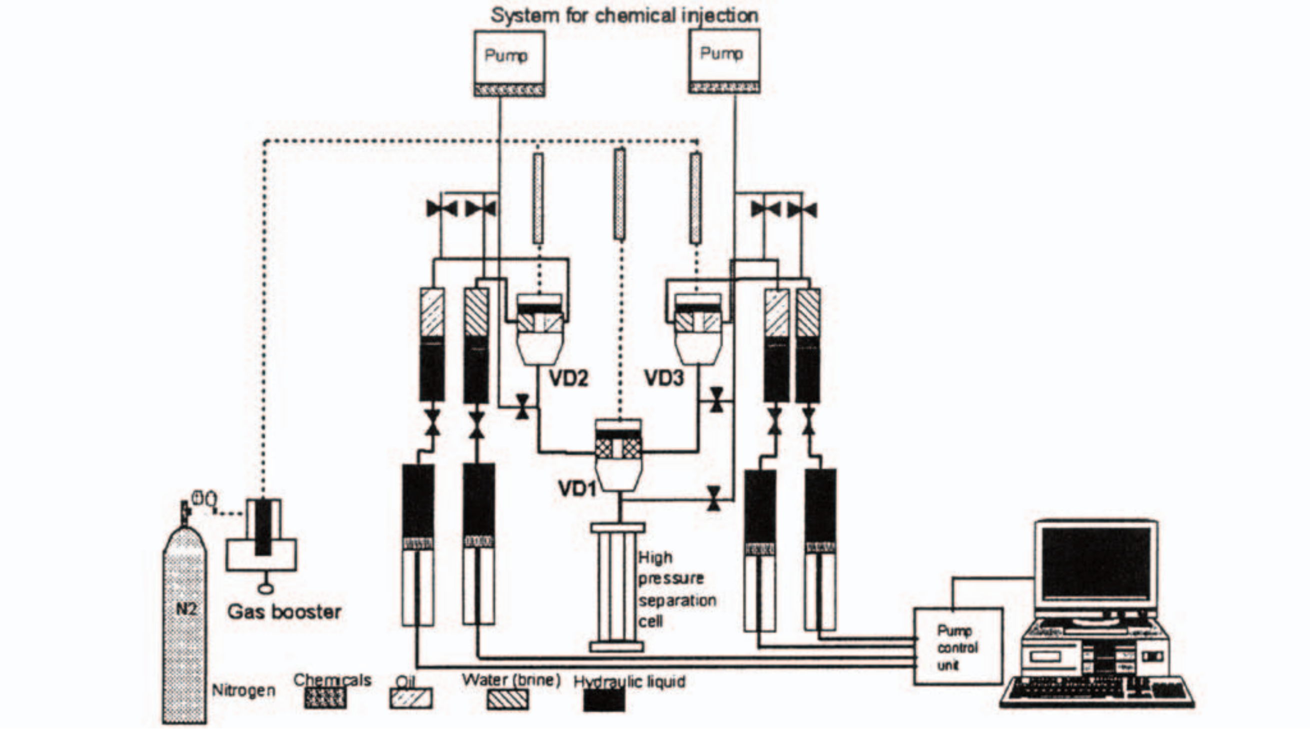


Figure 5 The high-pressure separation rig.

the separation cell can be a mixture of the two dispersions made through VD2 and VD3.

Chemicals can be injected into any of the flow lines; at the high pressure upstream of VD2 and VD3, at the medium pressure upstream of VD1 or at the lowest pressure downstream of VD1 just before the fluid enters the separation cell. Chemicals can also be injected into the bottom of the cell where a stirrer can be used to distribute the chemicals. The injection of for instance demulsifiers takes place through 1/16-inch tubes with very small inner diameters. The chemical injection pumps deliver volumes down to 0.03 ml/h.

The rig consists of four 600-ml high-pressure sample cylinders. Usually, two are filled with water (brine), and two are filled with oil. With the aid of four motor-driven high-capacity piston pumps, water and oil are pumped through the choke valves. The four pumps are independent of each other, but in most of the experimental series the total flow has been kept constant. The pressure drops through the choke valves are back-pressure controlled. The pressure in the separation cell is regulated by a back-pressure controlled valve. The maximum pressure in the cell is 200 bar. The cell is filled with gas, inert or natural gas, to the desired pressure before the filling of water and oil into the separation cell starts. The separation cell (450 ml) is made of sapphire, assuring full visibility of the separation process. Video cameras are installed to follow the separation process.

All parts of the rig are thermostated. Temperature, cell pressures, valves, pumps, and video cameras are computer controlled.

The above-mentioned techniques all have in common that they are of macroscopic scale, often enabling diagrams of separated volume as a function of time to be displayed.

III. STABILITY OF WATER-IN-CRUDE OIL EMULSIONS

It is well recognized that these emulsions are stabilized by means of an interplay between different heavy components, organic and inorganic particles, respectively. Heavy components cover asphaltenes, resins, etc. In a depressurized anhydrous crude oil the asphaltenes are normally in a particulate form. The role of the resins (and lighter polar components) is to stabilize the asphaltene dispersion (suspension) by adsorption mechanisms. Owing to this strong interaction the asphaltene particles are prevented from concomitant coagulation and precipitation. The stability will also put some restriction with regard to particle sizes since the largest particles are supposed to show the highest rate of sedimentation. When water is mixed with the crude oil, the situation will drastically change. The system will reach an energetically higher level, where the energy difference is proportional to the interfacial area created during the mixing process. This fresh interfacial area will attract components in the system. The molecules possessing the highest interfacial activity will try to cover the fresh W/O interface and hence minimize the energy level of the system. This category of indigenous components is normally covered by the lighter polar fraction, i.e., the resins. As a consequence a competition situation between resin molecules at the W/O interface and on the solid asphaltene particles will occur. Decisive factors determining the final position of the resins are the hydrophilic/lipophilic balance of these molecules and the corresponding properties of the solid surface. One could imagine that a very hydro-phobic particle surface and a very polar W/O interface would extract different types of resins for the different activities. However, as pointed out, highly interfacially active resins will show preference for the W/O interface over not only less hydrophobic resin molecules but also over asphaltenes. As a consequence the solubility conditions for the asphaltenes will drastically change and a particulate precipitation will take place. With aqueous droplets coated by an interfacial resin film as closest neighbors the asphaltene particles will precipitate and accumulate at the droplet surface. The resulting interfacial properties will be much more rigidified and the stability of the corresponding emulsions profoundly improved. Central mechanisms involved in the stabilization process will hence be both steric and particle stabilization.

The mechanical properties of the protecting interfacial film are essential for the final stability level of the W/O emulsions. Concentrated polymeric interfacial films may display either elastic or viscous properties that make the destabilization process difficult and time consuming. The aromatic asphaltene molecules will normally undergo a stacking into sandwich-like structures as a consequence of the molecular association. The presence of other nanosized-particles like organic wax particles and inorganic clay particles will further enhance the stability level. However, these compounds are not further dealt with in the present chapter.

The interfacial conditions are reflected in the level of the interfacial pressure (π). Sjöblom et al. (27) showed that there is a correlation between the level of π and the macroscopic emulsion stability. Preferably the interfacial pressure should be above 10-14 mN/m for stable emulsions. Aromatic molecules such as benzene will substantially lower the level of π. With increasing content of aromatic molecules the interfacial activity of the indigenous surfactants will be canceled and hence the emulsion stability will vanish. The dilution with aromatic solvents is in practical use in many places in the world where heavy crude oils create transport and emulsion problems.

A. Coalescence

Coalescence is defined as the combination of two or more droplets to form a larger drop. When these droplets approach each other, a thin film of the continuous phase will therefore be trapped between the droplets, and it is obvious that the properties of this film will determine the stability of the emulsion (28). The mechanism of coalescence occurs in two stages: film thinning and film rupture. In order to have film thinning there must be a flow of fluid in the film, and a pressure gradient present. It is obvious that the rate of film thinning is affected by the properties of the colloidal system. Some of the most important parameters (29) are defined as viscosity and density of the two phases present, interfacial tension and its gradient, interfacial shear and dilational viscosities and elasticities, drop size, concentration and type of surfactant present at the interface, and forces acting between the interfaces. Considerable effort has been made to develop models for prediction of the rate of film thinning and critical film thickness. Reynolds (30) made the first mathematical analysis of parallel disks. He assumed the bounding interfaces to be solid and the film to be of uniform thickness. Frank and Mysels (31) investigated dimple formation and drainage through the dimple. Later models of film thinning are those of Zapryanov *et al* (32) and Lin and Slattery (33, 34). Zapryanov investigated surfactant partitioning at the interface using the parallel-disk model. This model has later been extended to account for the adsorption/desorption kinetics of surfactants (35). Film rupture is a nonequilibrium process that may occur as a result of flow instabilities, temperature fluctuations, electric fields, or Marangoni effects (36). Investigations by de Vries (37) and Lang (38) showed that there exists a critical film thickness. Above this thickness the probability of rupture is zero, and below it the probability of rupture increases with decreasing film thickness. Scheludko and Manner (39) investigated the rupture of thin liquid films between two droplets in relation to fluctuations at the interface. He also developed an expression for the critical film thickness with only van der Waals forces acting: $d_c = [A\pi/32K^2\gamma_0]^{0.25}$, where A is the Hamaker constant, γ_0 is the interfacial tension between the continuous and dispersed phase, and K is the wavenumber of the surface fluctuations. Vrij (40) has derived an alternative expression for d_c; for larger thicknesses: $d_c = 0.268[A^2R^2/\gamma_0\pi f]^{0.14}$, where R is the droplet radius, and f is dependent on d. For small thicknesses: $d_c = 0.22[AR^2/\gamma_0 f]^{0.25}$. According to the first equation d_c ∞ →when $\gamma \rightarrow 0$, i.e., the film should spontaneously rupture at large d values. However, this is not the case since emulsion droplets become highly stable when $\gamma \rightarrow 0$. Also, the first equation predicts that as $R \rightarrow 0$, $d_c \rightarrow 0$, i.e., small emulsion droplets would never rupture. Sonntag and Strenge (41) showed that d_c will not change when the contact area is varied. This is due to the fact that the lamella formed between two droplets, at nonequilibrium separations, does not have an idealized planar interface between them. Sonntag and Strenge (41) also showed that emulsion films of octane/water droplets stabilized by a nonylphenol ethoxylated surfactant plus an oil-soluble surfactant had a d_c independent of γ_0.

IV. GENERAL THEORY OF DEMULSIFIER ACTION

Commercially available demulsifiers can generally be described as "chemical cocktails." The terminology is introduced in order to describe the fact that one expects to find a synergistic effect of one or two (or more) active components that are dissolved in an active solvent. The solvent should be so hydrophobic that the active components can be readily dissolved in the crude oil. From this one can see that here are some general rules of thumb for the demulsifiers. Below, we summarize some of the most pertinent features. We can briefly classify the demulsifiers according to their molecular weight, as high molecular weight (HMW) and low molecular weight (LMW) demulsifiers and pure solvents.

The HMW molecules include different kinds of polymers and macromolecules (block copolymers, etc.), together with polyelectrolytes. Typical HMWs should be > 5000 g/mol. The LMW demulsifiers are in most cases some types of oil-soluble surfactants with co-operativity between the molecules. The solvents in use can be classified according to the polarity. Simple examples on increasing polarity would be pure paraffinic hydrocarbons < aromatic hydrocarbons < alcohols < diols, etc.

A. Low Molecular Weight (LMW) Demulsifiers

Basically, the functionality of this category of demulsifiers is based on two specific mechanisms, i.e., increased interfacial activity and changed wettability of stabilizing components, respectively. The increased interfacial activity results in a suppression of the inter-facial tension. Hence, these molecules tend to replace other, already existing molecules at the interface. This is a thermodynamical result, but in practice it can be difficult for these surfactant-like molecules to reach the W/O interface. A common retention mechanism is the adsorption on to solid material, primarily asphaltenes, but also inorganic oxides and organic waxes. The adsorption process can change the wettability of the solid particles. In order to complete the adsorption process the LMW adsorbent must complete with naturally occurring dispersants like resins. The final equilibrium conditions on the surface of the solid particles will hence reflect a balance between attraction to the surface, interaction with resin-like molecules on the surface, and retention mechanisms in the bulk phase.

B. High Molecular Weight (HMW) Demulsifiers

These molecules are actually supposed to penetrate the interfacial film surrounding the water droplets and hereby to alter the rheological properties of the film material. From the low dosage levels used, i.e., 5-20 ppm, one can conclude that these molecules are extremely efficient as film modifiers. A critical and decisive step for the HMW demulsifiers to perform optimally is the time requirement for the diffusion to the interfacial membrane and for the reorientation movement inside the film until local equilibrium is attained.

C. Solvents

The action of the solvent can be manifold. However, the commonly used aromatics efficiently dissolve the aromatic particles in a swelling process leaving behind oligomeric and monomeric asphaltenes. As shown before, an increasing aromatic content will gradually decrease and finally eliminate the interfacial activity of the indigenous crude oil components. By experimentally following the interfacial pressure as a function of the aromatic concentration one can conclude qualitatively if the level of emulsion stability is high or low.

Most chemical agents used for demulsification are preferentially oil-soluble blends consisting of HMW polymers. These blends commonly consist of: (1) flocculants (large, slow acting polymers); (2) coalescers (LMW polyethers); (3) wetting agents; and (4) solvents/cosolvents. Some chemical structures of demulsifiers used for breaking crude oil emulsions have been listed by Jones et al. (42). Much work has been carried out in order to identify and understand the mechanisms behind chemical demulsification. Fiocco (43) concluded that the interfacial viscosity was kept at a low level when demulsifiers were present. Later on it was realized that the interfacial shear viscosity of crude oil emulsions does not have to be very low in order to ensure accelerated water separation (44).

Wasan and coworkers (45, 46) investigated the coalescence of systems containing petroleum sulfonates. They concluded that the coalescence rates correlated well with the interfacial shear viscosity, while no correlation was observed with the interfacial tension. Aveyard and coworkers (47, 48) investigated the correlation between surfactant interfacial behavior, surfactant association, and the destabilization efficiency. They observed a clear correlation between the demulsifier concentration at optimal demulsification efficiency and the critical micellization concentration (CMC) of the demulsifier in the crude oil system as long as simple surfactants were used. This means that the monomer activity of the surfactants is crucial the for destabilization of the emulsion system. Wasan and coworkers (49, 50) investigated in detail the processes taking place at the O/W interface during a destabilization process with a LMW amphiphilic compound. From studies of different additives they concluded that oil-soluble destabilizers should be able to partition into the aqueous droplets in order to act as destabilizers. The concentration of the demulsifier inside the droplets should be high enough to ensure a diffusion flux to the O/W interface. In order to be efficient as destabilizers the additives must show a high rate of adsorption to the interface. Wasan and coworkers also emphasized the importance of sufficiently high interfacial activity of the demulsifier to suppress the interfacial tension gradient. In this way the film drainage will be accelerated and droplet coalescence will be promoted. Little (51) suggested that the sequence of steps leading to demulsification of peteroleum emulsions involves the displacement of asphaltic material from the interface by the demulsifier followed by the formation of demulsifier micelles which solubilize and/or stabilize the asphaltene compounds in the oil.

Krawczyk (44) investigated the influence of different demulsifiers on the stability of water-in-crude oil emulsions. He defined a partitioning coefficient, KP = c_a/c_0, where c_a refers to the demulsifier concentration in the aqueous phase, and c_0 to the concentration in the oil phase. He concluded that demulsifiers with K = 1 gives the best results. He also concluded that the interfacial activity and adsorption kinetics of the demulsifier are important parameters. The interfacial region can be expected to be more dynamic, and considerable interfacial fluctuations may occur in the presence of medium-chain alcohols.

The mechanism behind a destabilization with surfactants is probably an interfacial competition. In this situation the indigenous crude oil film will be totally or partially replaced by a surfactant layer which cannot stabilize the crude oil emulsion. When comparing two different hydrophobic surfactants, tetraoxyethylene-nonylphenol ether (Triton N-42) and sodium bis-(2-ethylhexyl)sulfosuccinate (AOT), it was found that the ionic surfactant, AOT, was more efficient than the nonionic analogue. Three different hydrophilic, fluorinated surfactants were also investigated in Ref. 52. They were all very efficient as destabilizers, probably because of their high interfacial activity (53, 54). As mentioned earlier, Wasan and coworkers (49, 50) have analyzed in detail the processes taking place at the O/W interface during destabilization. The results for the hydrophobic surfactants are in direct agreement with their conclusions. Also, in the case of common solvents where we found medium-chain alcohols to be efficient as destabilizers, the results also correspond with their conclusions. The medium-chain alcohols are soluble in all three pseudophases and will therefore partition between these. The hydrophobic surfactant AOT is soluble in water up to a few per cent, and will therefore also be present in the aqueous phase, whereas Triton N-42 is completely water insoluble. This will most likely contribute to the differences between the surfactants.

Aveyard and coworkers (47, 48) have stressed the importance of monomer activity when simple surfactants are used as demulsifiers. For a commercial demulsifier the interfacial tension between oil/water seems to pass through a minimum for NaCl concentrations between zero and 1 M. According to Menon and Wasan (55), AOT has been found to have a cmc at approximately 300 ppm in a water/oil system with asphaltenes present. This means that in our destabilization tests, where the concentration of AOT is up to 100 ppm, the results correspond with the conclusions from Aveyard (47, 48). Fluorinated surfactants have been investigated for systems containing both distilled water and synthetic formation water (52). The results showed that the resolution of water was faster when synthetic formation water was used as the dispersed phase. The explanation of this might be in accordance with Aveyard's conclusions (47, 48). In the case of Triton N-42 the influence of salt is not believed to be significant since this is a nonionic surfactant, and its phase behavior is not so sensitive to the addition of salt.

The mechanism behind destabilization with macromolecules is very dependent on the size of the molecule. Polymers of lower molecular mass can show a strong affinity to the oil/water interface, adsorb irreversibly and destabilize in this way. Another route of destabilization is flocculation. Flocculation is an aggregation process in which droplets form three-dimensional clusters, each droplet retaining its individual identity. In order to model the importance of flocculation in the destabilization of model systems, one can investigate α-alumina dispersions (52).

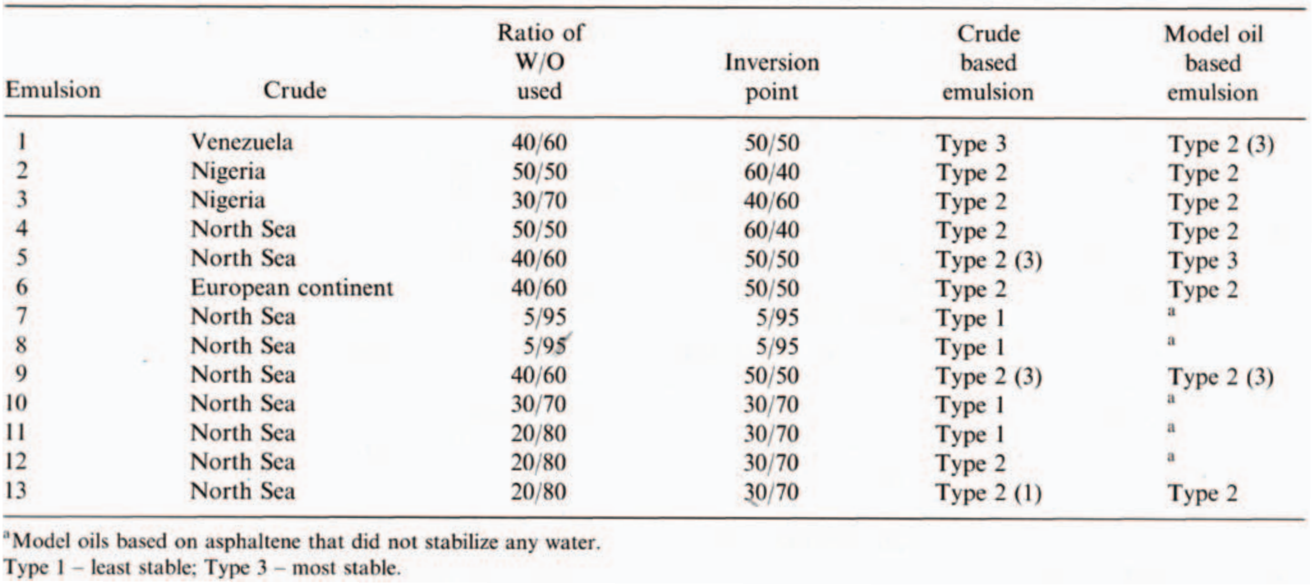
V. EXPERIMENTAL DEMULSIFICATION

In this section we compile information about demulsifiers active in W/O emulsions (or added prior to the emulsification) and their performance in Langmuir and Langmuir-Blodgett films. We have also performed an AFM study on the demulsifiers in order to visualize the interactions taking place between indigenous crude oil surfactants and the LMW/HMW demulsifiers.

A. Crude Oil Matrix

The crudes span geographically over large areas: North Sea, European continent, Africa, Asia, etc. This is a necessity since if the crude oils in the test matrix are interrelated one cannot universalize the results. Table 1 lists the crude oils and their origin. To start with we determined the inversion point (or alternatively, the maximum content of water that can be introduced into the oil without a phase separation). We have chosen to study emulsions that are 10% below the inversion point. Exceptions in this respect are the two European crudes with 5% water stabilized. The crude oils were characterized by means of density, surface tension, and viscosity measurements. The results are summarized in Table 2. All experiments involving emulsions were carried out at 50°C. The reason for working at elevated temperature is to melt the wax in the oils and thereby prevent the influence of the wax on emulsion stability. The elevated temperature is also more closely related to the real working temperature used in the processes in the field.

Table 1 Crude Oils and Their Origin. Types 1–3 Refer to Increasing Emulsion Stability; Model Emulsions are Based on Extracted Asphaltenes



Emulsion	Crude	Ratio of W/O used	Inversion point	Crude based emulsion	Model oil based emulsion
1	Venezuela	40/60	50/50	Type 3	Type 2 (3)
2	Nigeria	50/50	60/40	Type 2	Type 2
3	Nigeria	30/70	40/60	Type 2	Type 2
4	North Sea	50/50	60/40	Type 2	Type 2
5	North Sea	40/60	50/50	Type 2 (3)	Type 3
6	European continent	40/60	50/50	Type 2	Type 2
7	North Sea	5/95	5/95	Type 1	[a]
8	North Sea	5/95	5/95	Type 1	[a]
9	North Sea	40/60	50/50	Type 2 (3)	Type 2 (3)
10	North Sea	30/70	30/70	Type 1	[a]
11	North Sea	20/80	30/70	Type 1	[a]
12	North Sea	20/80	30/70	Type 2	[a]
13	North Sea	20/80	30/70	Type 2 (1)	Type 2

[a] Model oils based on asphaltene that did not stabilize any water.
Type 1 – least stable; Type 3 – most stable.

Table 2 Physical Characteristics of Crude Oils

Crude nr.	Surface tension, γ_{ao}(mN/m) at 25°C	Density (g/ml), δ 25°C	Interfacial tension with 3.5% NaCl (mN/m)	Viscosity (cP), 25°C	Viscosity (cP), 50°C	Asphaltene content (%)
1	27.0	0.88	23.95	35.7	13.8	7.82
2	26.5	0.84	23.06	8.95	4.34	2.58
3	27.8	0.87	16.20	70.8	20.05	5.16
4	27.6	0.87	27.79	14.3	2.12	3.63
5	25.9	0.86	27.66	15.6	6.97	11.69
6	26.9	0.83	28.00	12.0	5.96	1.86
7	24.8	0.84	19.75	2.93	1.93	Negligible
8	24.7	0.84	21.31	3.05	2.35	Negligible
9	29.9	0.92	25.08	Above critical viscosity	50.95	2.59
10	24.5	0.80	23.5	3.95	2.37	Negligible
11	25.4	0.82	23.86	5.38	2.69	0.5
12	26.8	0.84	31.80	12.7	5.43	1.99
13	24.8	0.81	25.45	3.27	2.09	2.19

Table 3 Interfacial Tensions of Low Molecular Weight Chemical Additives

Nr.	Chemical	Interfacial tension (25 ppm), γ_{wo}(mN/m)	Interfacial tension (50 ppm), γ_{wo}(mN/m)	Interfacial tension (100 ppm), γ_{wo}(mN/m)
1	Fatty alcohol ethoxylate	27.8	25.4	23.6
2	Vinylidene alcohol	40.2	40.0	39.4
3	Sulfosuccinate	12.4	9.3	5.3
4	Linear monoisopropylamine alkylbenzene sulfonate	5.3	2.6	1.3
5	Emulsifier for hydrophobic system	14.9	11.7	7.5
6	Coconut fatty acid diethanolamide	27.5	23.7	19.8
7	Plasticizer	36.5	36.2	36.5
8	Rape oil fatty acid diethanol	26.5	23.2	19.3
9	Anionic/nonionic blend	4.5	2.6	1.6
10	Emulsifier for polymerization processes	39.3	39.4	38.6
11	Fatty alcohol	39.2	38.5	38.4
12	Long-chain fatty alcohol	38.3	35.4	31.5
13	long-chain α-olefin	39.4	38.8	38.6

Oil phase = 30/70 toluene/decane.
Aqueous phase = 3.5% NaCl.

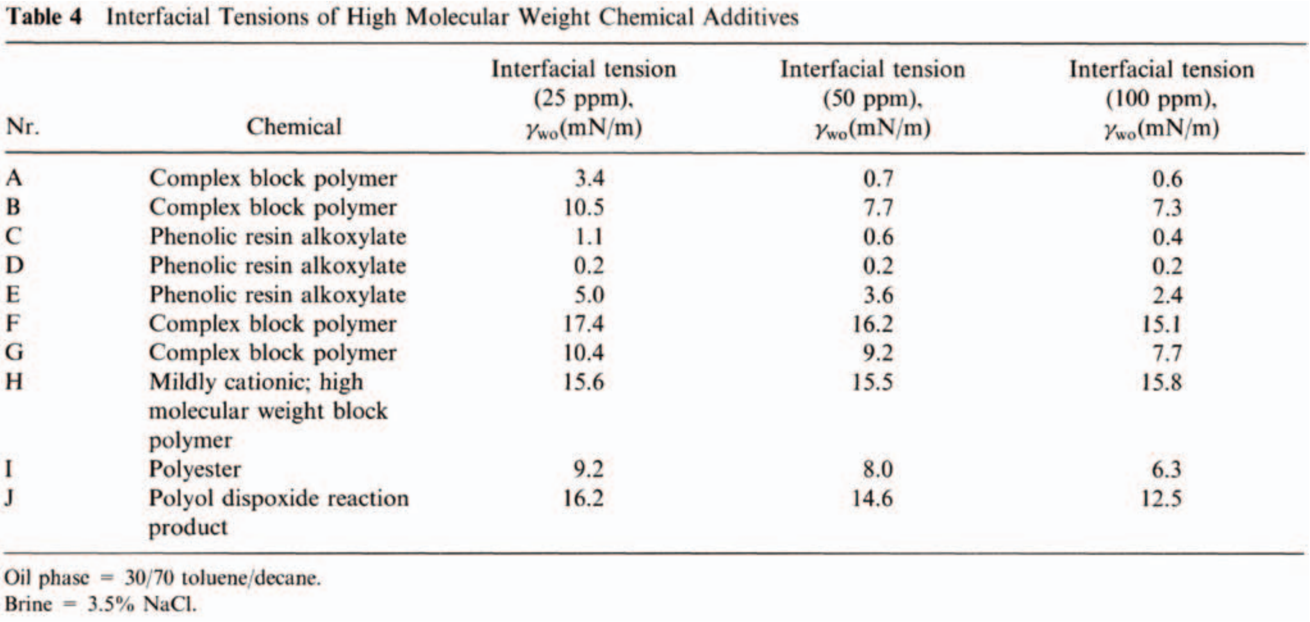


Table 4 Interfacial Tensions of High Molecular Weight Chemical Additives

Nr.	Chemical	Interfacial tension (25 ppm), γ_{wo}(mN/m)	Interfacial tension (50 ppm), γ_{wo}(mN/m)	Interfacial tension (100 ppm), γ_{wo}(mN/m)
A	Complex block polymer	3.4	0.7	0.6
B	Complex block polymer	10.5	7.7	7.3
C	Phenolic resin alkoxylate	1.1	0.6	0.4
D	Phenolic resin alkoxylate	0.2	0.2	0.2
E	Phenolic resin alkoxylate	5.0	3.6	2.4
F	Complex block polymer	17.4	16.2	15.1
G	Complex block polymer	10.4	9.2	7.7
H	Mildly cationic; high molecular weight block polymer	15.6	15.5	15.8
I	Polyester	9.2	8.0	6.3
J	Polyol dispoxide reaction product	16.2	14.6	12.5

Oil phase = 30/70 toluene/decane.
Brine = 3.5% NaCl.

B. Chemical Additives

The chemicals added represent two of the categories mentioned above, i.e., the LMW and HMW demulsifiers. The definition of these additives (see Tables 3 and 4) is very general. However, froma functional point of view their interfacial activity under operational conditions is of interest. The interfacial tension between an organic phase (30/70 toluene/decane) and an aqueous phase (with 3.5% NaCl) was determined upon addition of 25, 50, and 100 ppm of additives; γ_0 without additives is 36.3 mN/m.

C. Destabilization

Experimental conditions are found in the paper by Djuve et al. (56).

The stability of the different crude oil-based emulsions varies a lot. The water cuts range from 5 to 60%. These values can be compared with the stability for the model emulsions containing only dissolved asphaltene residues (see Table 1). This large difference in the water cut dispersed cannot be explained by the differences in asphaltene content alone (Table 2). The large difference in stabilization ability reflects the wide and different distribution in size, state, structure, polarity, and mass that exists between the asphaltenes found in each oil. It is generally believed that it is mostly the state of the asphaltene and not the amount that controls the stability in an W/O emulsion, i.e., whether the asphaltenes are in a particulate form or not.

The effect of adding a demulsifier is presented in Tables 5 and 6. Table 5 contains the test results for LMW additives, and Table 6 gives the test results when the HMW additives have been used. Both tables refer to the percentage of water separated after 30 min. From the tables, some interesting features are revealed.

Naturally, the addition of demulsifiers affect the rate of separation. If we compare the separation rate of water from crude oil emulsions with the addition of chemicals compared with blank samples, it is clear that the addition can enhance separation. This is not true for all chemicals added. Some demulsifiers have no apparent effect on separation and some demulsifiers even make the emulsions more stable. For the last case the separation of water after addition of demulsifier is lower than without demulsifier. The average separation without addition of any chemicals is 21.5% of water after 30 min and particularly for the LMW chemicals a reduced separation is observed. The HMW chemicals on the other hand seem to enhance separation.

The difference found in the performance between the HMW and LMW chemical activites should be traced back to the interfacial film and the added species. It should be noted that the interfacial tension measurements for the demulsifiers refer to a pure W/ O interface, while the demulsifier action actually refers to a W/O interface covered by indigenous components, like asphaltenes, resins, waxes, etc. With a weak reversible adsorption on to the film material, the destabilizing effect of the LMW additives (e.g., oil-soluble surfactants) will be rather limited, if penetration into the film material is obstructed. From Langmuir

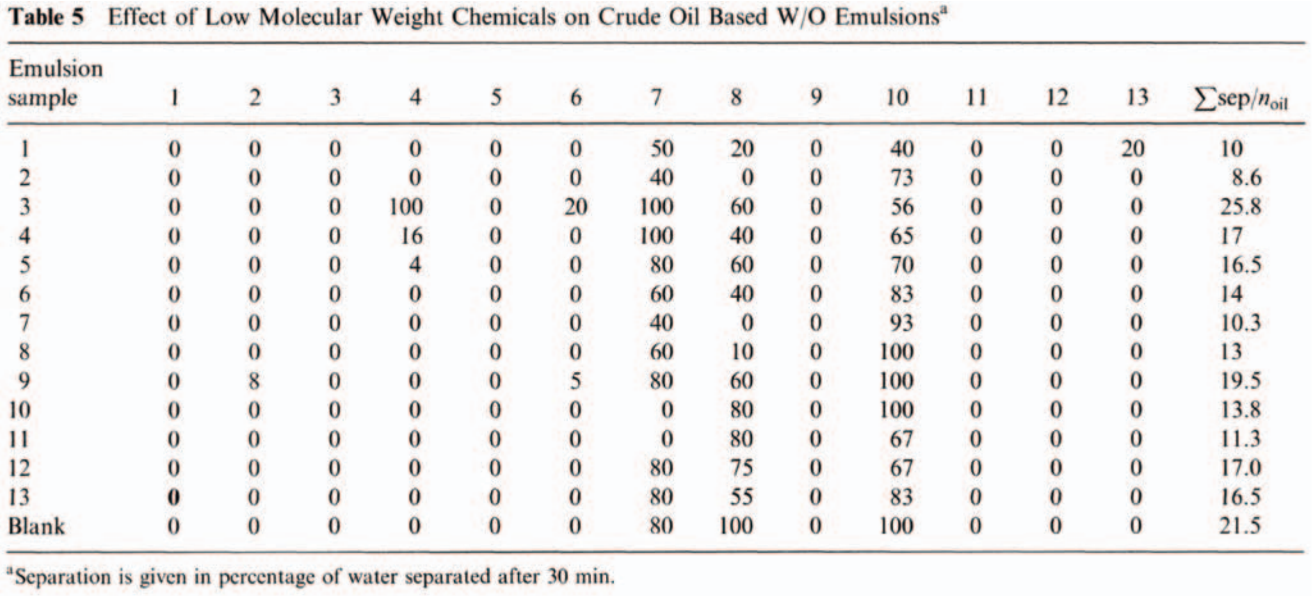


Table 5 Effect of Low Molecular Weight Chemicals on Crude Oil Based W/O Emulsions[a]

Emulsion sample	1	2	3	4	5	6	7	8	9	10	11	12	13	$\sum$sep/n_{oil}
1	0	0	0	0	0	0	50	20	0	40	0	0	20	10
2	0	0	0	0	0	0	40	0	0	73	0	0	0	8.6
3	0	0	0	100	0	20	100	60	0	56	0	0	0	25.8
4	0	0	0	16	0	0	100	40	0	65	0	0	0	17
5	0	0	0	4	0	0	80	60	0	70	0	0	0	16.5
6	0	0	0	0	0	0	60	40	0	83	0	0	0	14
7	0	0	0	0	0	0	40	0	0	93	0	0	0	10.3
8	0	0	0	0	0	0	60	10	0	100	0	0	0	13
9	0	8	0	0	0	5	80	60	0	100	0	0	0	19.5
10	0	0	0	0	0	0	0	80	0	100	0	0	0	13.8
11	0	0	0	0	0	0	0	80	0	67	0	0	0	11.3
12	0	0	0	0	0	0	80	75	0	67	0	0	0	17.0
13	0	0	0	0	0	0	80	55	0	83	0	0	0	16.5
Blank	0	0	0	0	0	0	80	100	0	100	0	0	0	21.5

[a]Separation is given in percentage of water separated after 30 min.

studies of asphaltene films it is known that polymeric demulsifiers can penetrate the films and strongly modify the film properties (57).

Each demulsifier also behaves differently, depending on which oil the emulsion is based on (Tables 5 and 6). That was expected since most of the crude oils are not interrelated.

Based on the results from the bottle tests outlined above a selection of crudes for the next experiments was made, omitting the crude oils that caused either spontaneous separation or a complete separation within 30 min.

D. Model Emulsions Based on Asphaltene

Generally, for water-in-crude oil emulsions the indigenous component thought to have the largest effect on stability is the asphaltenes. Therefore, model systems based on asphaltenes were prepared for selected oils. From Table 1 one can observe that not all precipitated asphaltene fractions could stabilize a model emulsion. However, many model emulsions had a similar stability as the original crude oil-based emulsion, indicating that the fraction extracted from the oil plays a central role in the stabilization.

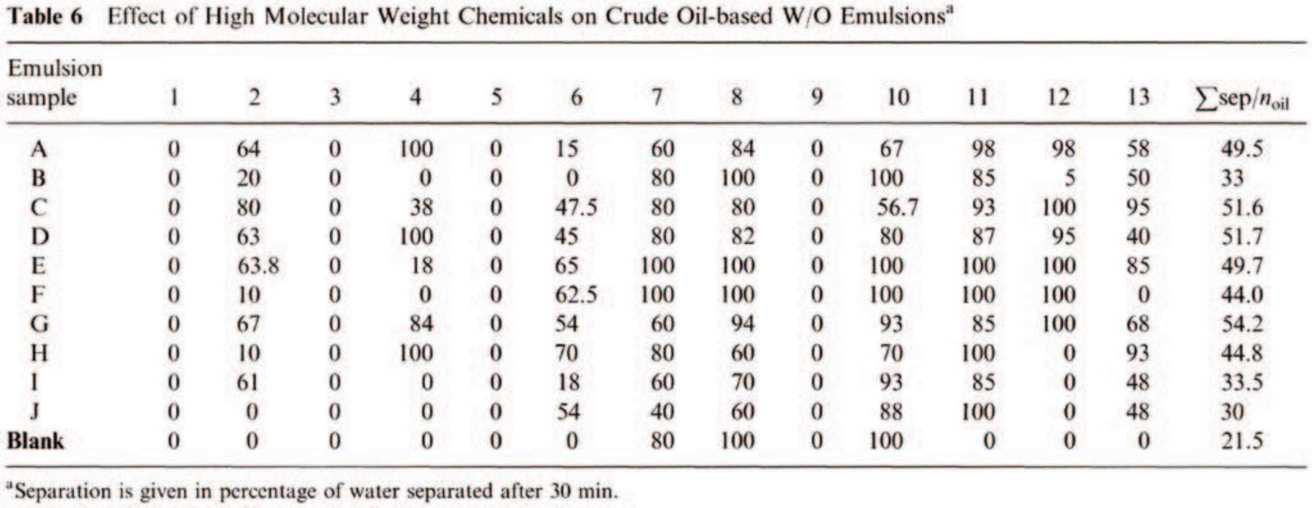


Table 6 Effect of High Molecular Weight Chemicals on Crude Oil-based W/O Emulsions[a]

Emulsion sample	1	2	3	4	5	6	7	8	9	10	11	12	13	$\sum$sep/n_{oil}
A	0	64	0	100	0	15	60	84	0	67	98	98	58	49.5
B	0	20	0	0	0	0	80	100	0	100	85	5	50	33
C	0	80	0	38	0	47.5	80	80	0	56.7	93	100	95	51.6
D	0	63	0	100	0	45	80	82	0	80	87	95	40	51.7
E	0	63.8	0	18	0	65	100	100	0	100	100	100	85	49.7
F	0	10	0	0	0	62.5	100	100	0	100	100	100	0	44.0
G	0	67	0	84	0	54	60	94	0	93	85	100	68	54.2
H	0	10	0	100	0	70	80	60	0	70	100	0	93	44.8
I	0	61	0	0	0	18	60	70	0	93	85	0	48	33.5
J	0	0	0	0	0	54	40	60	0	88	100	0	48	30
Blank	0	0	0	0	0	0	80	100	0	100	0	0	0	21.5

[a]Separation is given in percentage of water separated after 30 min.

The representability of such a “model emulsion” vis-à-vis the original emulsions has been debated. This brings forward the question of stabilization mechanisms and the state of asphaltenes. Basically we try to mimick interfacial conditions from true crude oil-based emulsions to model emulsions. In order to do so it is essential that the model oil used (heptol) can promote particle formation in the asphaltenes. In this way there should be a similarity in asphaltene-based nanoparticles located at the W/O interface in both types of emulsions under study. Since the asphaltene particles will hinder an efficient coalescence of the aqueous droplets, one can expect approximately the same level of stability against coalescence and similar actions of the demulsifiers. Addition of demulsifiers to the asphaltene-stabilized model emulsions accelerated in some cases the resolution of water. In particular three demulsifiers seemed to be most efficient, i.e., A, C, and G. It is obvious when comparing Tables 6 and 7 that the same demulsifiers are effective in both model emulsion systems and true crude oil-based W/O emulsions. This means that we can trace back the destabilization effect to an interaction between the demulsifying agent and the asphaltene fraction in the crude, and that this interaction is the most significant one. Other possibilities for interactions leading to destabilization would be demulsifier/ wax particles, demulsifier/resins, demulsirier/solid inorganic particles, etc. An investigation of asphaltene-stabilized W/O emulsions has obviously shed light on fundamental destabilization mechanisms in the crude oil-based emulsions.

Table 4 shows that the demulsifiers A and C exhibit a low interfacial tension, i.e., of the order of a couple of units. In the case of G, $\gamma_{W/O}$ is about 10 times higher and reaches a value of $\simeq$ 10 mN m^{-1}. Obviously, pure displacement processes, where demulsifiers A and C (owing to a lower interfacial tension toward water) can create a new interface and in this way destabilize an emulsion, play a role in the destabilization process. Also, G has a $\gamma_{W/O}$ value lower than that of pure asphaltenes at the interface. In the latter case $\gamma_{W/O}$ is around 20—25 mN/m.

E. Demulsifiers Used as Inhibitors

We have also added the destabilizing agents directly to the oil *before* the emulsification. The result as revealed from Tables 8 and 9 is very encouraging. In most cases there is a substantial enhancement in the efficiency of the action of the added chemicals, also for the low molecular species. The reason for this can be two-fold, i.e., either an interfacial competition or a strong bulk interacation between the demulsifier added and the stabilizing crude oil species. The interfacial competition can be traced back to the $\gamma_{W/O}$ values. Although the concentrations of the demulsifier added are small (≈ 50 ppm) and there is most likely not enough molecules to create a stable emulsion with all the water molecules dispersed, some molecules of A, B, and G present at the interface can cancel the stabilizing properties of asphaltene particles at the W/O interface. A strong bulk interaction between the demulsifiers and the asphaltenes must change the state of the asphaltene particles in order to cancel their stabilizing effects. Obviously, one should anticipate the demulsifying agents dissolving the asphaltene particles to substantially smaller units *not* possessing stabi-

Table 7 Effect of High Molecular Weight Chemicals on Asphaltene-based Model Emulsions[a]

Emulsion chemical	1	2	3	4	5	6	9	13	$\sum$ sep/n_{oil}
A	0	92.5	0	80	0	92.5	0	0	33.1
B	0	0	3	43	0	43	0	0	11
C	58	88	77	46	0	75	0	0	43
D	0	0	0	0	0	62.5	0	0	7.8
E	15	87.5	6.6	5	0	40	0	0	19.3
F	0	0	0	0	0	27.5	0	0	3.4
G	90	90	3.3	12.5	0	90	0	75	45.1
H	0	0	3	0	0	10	0	0	2
I	0	0	0	0	0	80	0	0	10
J	0	0	3	0	0	18	0	0	3
Blank	0	0	0	0	0	0	0	0	0

[a] Separation is given in percentage water separated after 30 min.

Table 8 Effect of High Molecular Weight Chemicals as Inhibitors on Crude Oil Emulsions[a,b]

Emulsion chemical	1	2	3	4	5	6	9	13	$\sum$sep/n_{oil}
A	75	92	7	100	55	80	100	35	68.0
B	40	44	77	80	85	78	85	25	64.3
C	0	94	53	78	65	93	63	100	68.3
D	35	94	0	100	60	83	45	65	60.3
E	43	76	67	78	0	60	88	85	62.9
F	50	84	0	80	63	73	53	5	51.0
G	0	98	73	100	75	83	75	95	74.9
H	65	98	70	100	78	93	83	100	85.9
I	100	92	0	76	60	88	80	100	74.5
J	78	92	47	82	83	80	70	100	79.0
Blank	0	0	0	0	0	0	0	0	0

[a] Chemicals added before emulsification.

[b] Separation in percentage water separated after 30 min.

lizing effects. There are some indications that this might be the case (58).

VI. DEMULSIFICATION UNDER LABORATORY AND FIELD CONDITIONS

Normally, the bottle-shake tests with depressurized crude oils are upscaled to real separation conditions topside. However, it has been constantly pointed out that the samples in use at the laboratory are not representative of the samples from the same field. The main reason for this is that the laboratory samples have undergone oxidation upon storage.

Another essential deviation in sample representability is due to the time delay in sampling of the crude oil samples to be compared. It is well known that the crude oil characteristic from a field consisting of several wells (up to 30—40) wells) will change over time. The best way to overcome the classical difficulties with representative samples is to work with pressurized samples. The separation rig presented in Fig. 5 has the great advantage of permitting this and preventing the crude oils under study to contact air. In addition to this the mixing conditions (the magnitude of ΔP over the chokes) can be adjusted to real process conditions.

Table 9 Effect of Low Molecular Weight Chemicals as Inhibitors on Crude Oil Emulsions[a] (Chemicals added before emulsification)

Emulsion chemical	1	2	3	4	5	6	9	13	$\sum$ sep/n_{oil}
1	1	46	0	44	0	25	0	0	13
2	0	72	0	0	0	0	0	0	8
3	0	0	0	100	73	73	0	0	27
4	0	52	0	70	40	80	0	0	27
5	0	80	0	90	53	70	23	45	40
6	65	7	0	0	4	0	0	10	22
7	0	80	0	0	0	0	0	0	9
8	0	70	0	0	83	0	3	5	21
9	0	72	0	0	0	48	58	20	22
10	0	66	0	0	0	0	0	10	8
11	0	40	0	0	0	38	0	8	10
12	0	0	0	0	0	0	0	0	0
13	0	4	0	0	0	0	0	0	5
Blank	0	0	0	0	0	0	0	0	0

[a] Separation in percent water separated after 30 min.

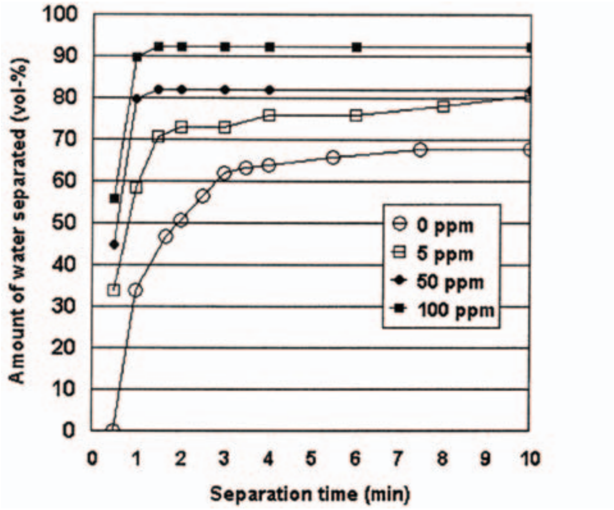


Figure 6 Examples of separation as function of time. Oil 1 with 20% water cut; Demulsifier B.

A. Tests of Demulsifiers —- Comparison with Field Tests

The laboratory tests were conducted to qualify the separation rig by performing tests as tsimilar as possible to the field tests done previously. An important difference between the tests performed offshore and in the laboratory is the type of separator. The field tests were performed in a horizontal continuous gravity separator whereas the separation in the laboratory rig took place in a vertical batch separator. The oils and brine used in the laboratory were sampled offshore and kept under pressure until the tests were performed.

In the laboratory tests only one module of the separation rig was used. Only one oil was tested at a time, and there was a pressure drop through only one of the choke valves (VD1 in Figure 5). Oil and water were mixed upstream of VD2. There was no pressure drop through VD2. The demulsifier was mixed into the flow line just downstream of VD2. The pressure drop in the system was through VD1 just ahead of the separation cell. The oils tested were at their bubble points at 11 bar and 60°C. The experiments

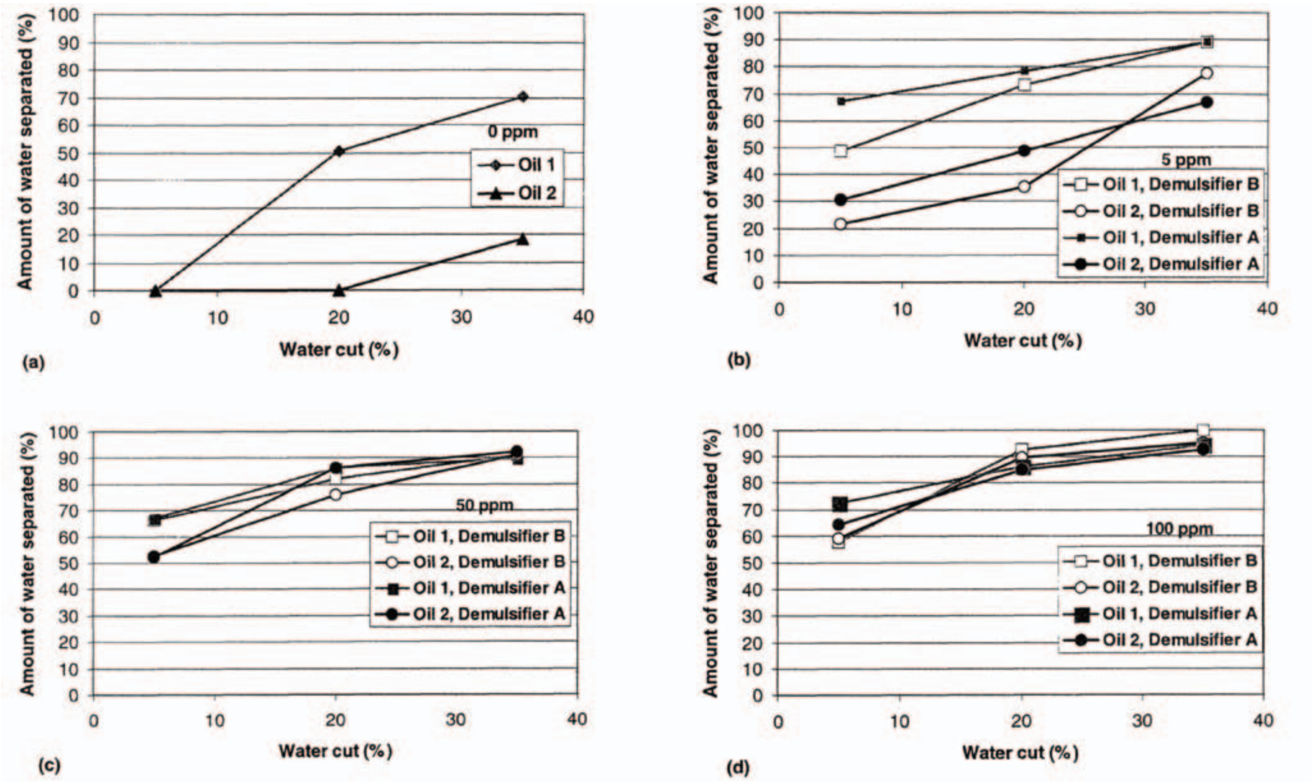


Figure 7 Amount of water separated after 1.5 min for the two oils 1 and 2 at various water cuts and for the two demulsifiers A and B at various concentrations (1.5 min separation time corresponds to 2 min separation time in Fig. 6. In Fig. 6 the filling time of 30 s is included in the separation time).

were performed at 60°C and with a pressure drop through VD1 from 11 to 7 bar. The separation took place under 7 bar pressure. They were typical North Sea crude oils with density and viscosity values for stabilized oils at 60°C at ≃ 0.8 g/ml and ≃ 3.5 mPa. There were small differences in the characteristics of the oils. The more dense oil was also the more viscous oil. The compositions of the two tested demulsifiers were totally different from each other. Three concentrations of the demulsifiers were tested: 5, 50, and 100 ppm. In addition, tests without demulsifier were performed. The water cut values were 5, 20, and 35 vol. %.

Some of the results are shown in Figs 6 and 7. The main results in the laboratory tests were:

1. Oil 1 had better separation characteristics than Oil 2. (Oil 1 was the lighter of the two oils.)
2. Demulsifier A performed better than Demulsifier B at concentrations of 5 and 50 ppm (for water cuts of 20 and 35%).
3. Demulsifier B performed better than Demulsifier A at 100 ppm (for water cuts of 20 and 35%).
4. No increase in separation efficiency was observed when the concentration of Demulsifier A was increased from 50 to 100 ppm.
5. Demulsifier B increased the separation efficiency with increasing concentrations up to 100 ppm.
6. Foam was never any problem (stable for a maximum of 30 s).

All these results confirmed the offshore field-test results. In addition, one could observe visually in the laboratory tests how the demulsifiers affected the system. Without demulsifier in the system an emulsion layer always formed between the oil and the water phase. When the demulsifier was added, no such separate emulsion layer was observed (except for 5 ppm demulsifier in the system with 5% water cut in the more viscous oil).

Results from the laboratory separation rig have also been verified with results from other field tests.

As a conclusion to this section one can say that a laboratory test kit has been constructed which can be used to test oils and chemicals in pressurized systems. The results are consistent with results achieved under offshore field conditions. The results obtained in the laboratory are based on correct sampling and handling of the fluids. The oil samples are kept under pressure and are never exposed to air during storing. Further, the results show that we can dose with chemicals down to concentrations as low as 5 ppm. The advantages of laboratory studies are smaller volumes, cheaper tests, more parameter variations can be performed

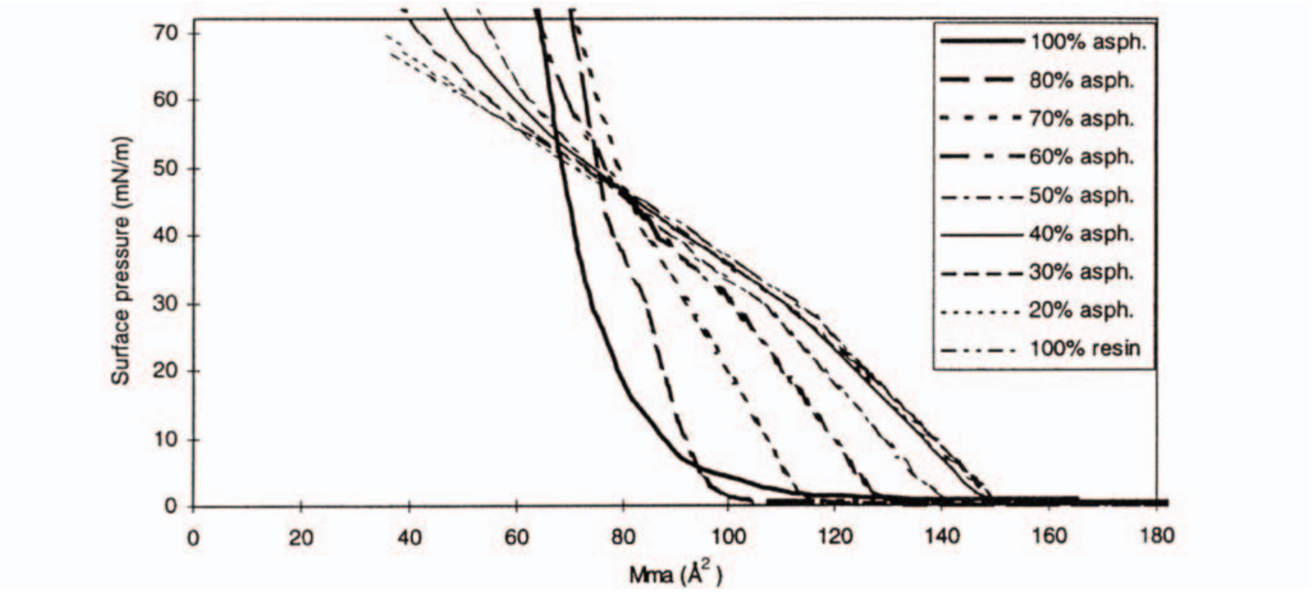


Figure 8 II-A is isotherms of asphaltene/resin mixtures spread from pure toluene on pure water (bulk concentration = 4 mg/ml).

within short time limits, and access to more advanced characterization systems (e.g., drop size measurements) is available.

The separation rig has also been used to show the influence of an internal separator pressure up to 180 bar on the separation characteristics and efficiency.

B. Langmuir Films

In order to obtain a better understanding of the mechanisms behind the effect of asphaltenes and resins on emulsion stability, we chose to investigate the film properties of these components. Such studies provide information on the rigidity and stability of films consisting of indigenous surface-active material. The rigidity of the interfacial film is important for the stability of emulsions, in as much as a rigid film on the emulsion droplets prevents coalescence, while a highly compressible film is more easily ruptured, leaving the droplets free to coalesce.

By means of the Langmuir technique, asphaltenes are found to build up close-packed rigid films, which give rise to quite high surface pressures. Resin films, on the other hand, are considerably more compressible (Fig. 8). This may explain the experimental observations showing that asphaltenes are able to stabilize crude oil-based emulsions, while resins alone fail to do so. Singh and Pandey (59) also concluded that a high interfacial pressure correlated with high W/O emulsion stability. On adding asphaltenes and resins together to a mixed film, the properties gradually change from a rigid to a compressible structure as the resin content is increased. The resins start to dominate the film properties when the amount of this lighter fraction exceeds 40 wt% (Fig. 8). The more hydrophilic resin fraction starts to dominate the film properties owing to the higher affinity towards the surface.

The influence of chemical additives on asphaltene films on the water surface and at the oil/water interface have also been studied by means of the Langmuir technique. This was done in order to view the interaction between demulsifiers added and asphaltenes, and to show the importance of this on emulsion stability.

The film properties of pure demulsifiers of high molecular weight are shown by the isotherms in Fig. 9. The shape of some of these isotherms, especially that of Demulsifier G and to some extent those of H and I, resembles pure resin films. The others, especially Compound A, give more rigid films, characteristic of the pure asphaltene film.

Compressible resin films will not alone stabilize a crude oil emulsion. Related to this, demulsifiers, which form films of low rigidity and high compressibility, should be the most efficient. When used as demulsifiers, the efficiency depends on the ability of the chemicals to interact with and modify the film built up by asphaltene particles.

Addition of demulsifiers of high molecular weight to the asphaltene film gave the isotherms in Fig. 10. The influence of the chemicals G, H, and I is most pronounced with respect to an increased compressibility, together with a reduced rigidity. The effect of this kind of manipulation of the asphaltene film is similar to the effects observed when

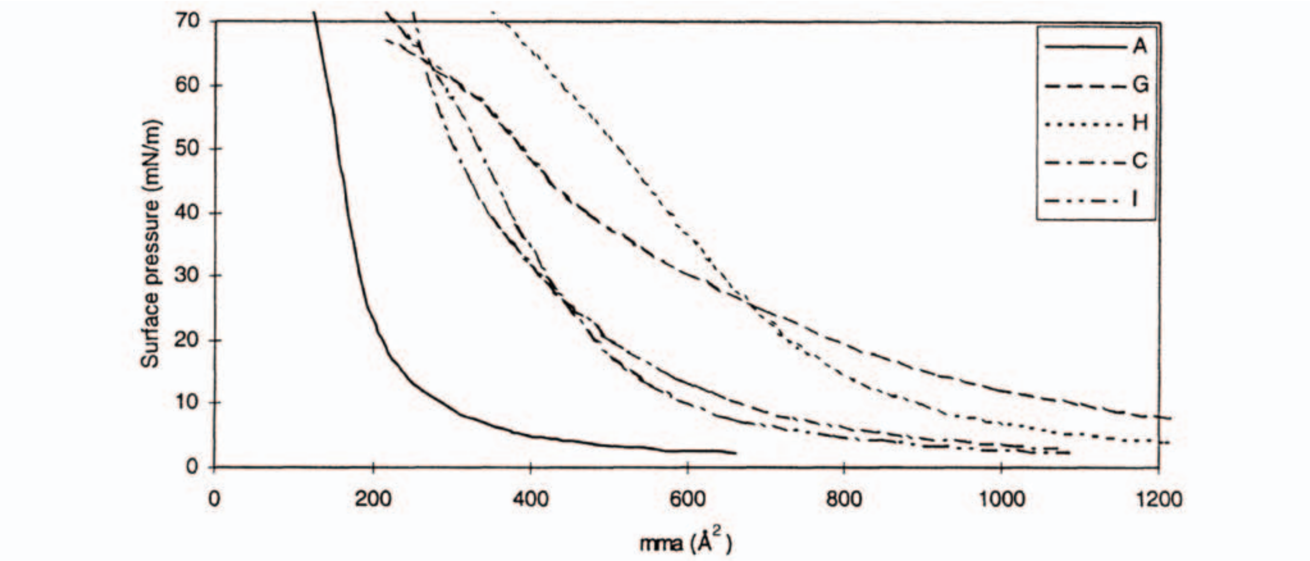


Figure 9 Π-A isotherms of high molecular weight demulsifiers on pure water.

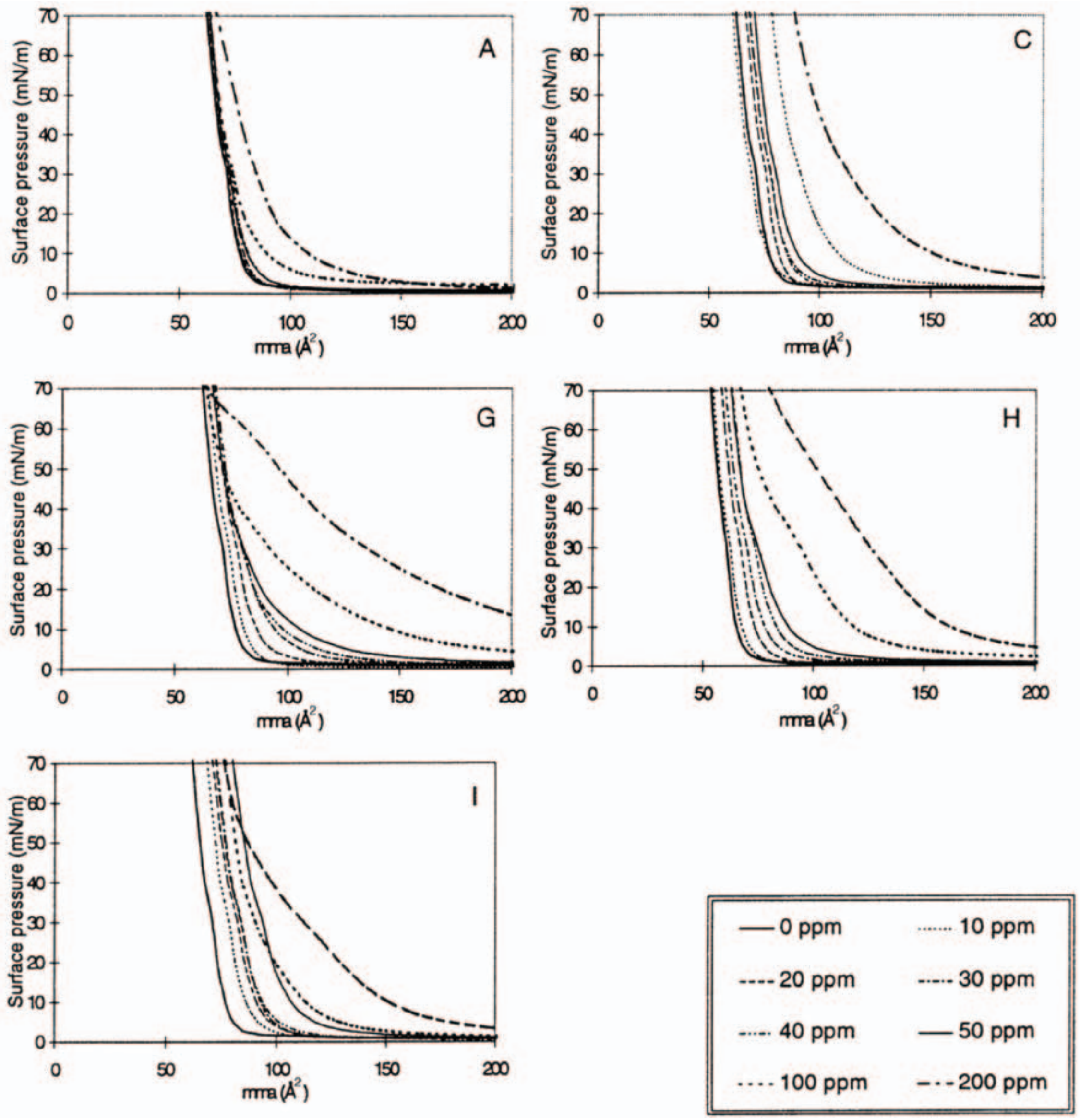


Figure 10 Π-A isotherms of mixed monolayers of asphaltenes and varying concentrations of different demulsifiers on pure water.

resins are mixed together with asphaltenes (Fig. 8). However, the concentration needed to achieve the same effects is considerably lower when demulsifiers are used instead of resins. Demulsifier A has a quite small influence on a film of asphaltenes. A comparison with Fig. 9 shows that chemical A is the component with the most rigid and asphaltene-like film behavior of all the tested HMW demulsifiers.

From the film studies outlined above one can conclude that the best candidates for emulsion breaking should be G, H, and I. However, the efficiency depends not only on the direct influence of chemical additives within the film, but also on the ability of demulsifiers to reach the W/O interface in an emulsion (diffusion through the fluid). This is a critical step regarding the effective concentration of demulsifiers at the interface. These aspects make it difficult to undertake a direct comparison between the influence of demulsifier on Langmuir surface films, where all demulsifier molecules are implanted in the film, and on real emulsions.

In order to represent more realistic emulsion conditions, Langmuir interfacial films adsorbed at the O/W interface were analyzed. The isotherms depicted in Fig. 11 illustrate some of the film properties of naturally occurring crude oil

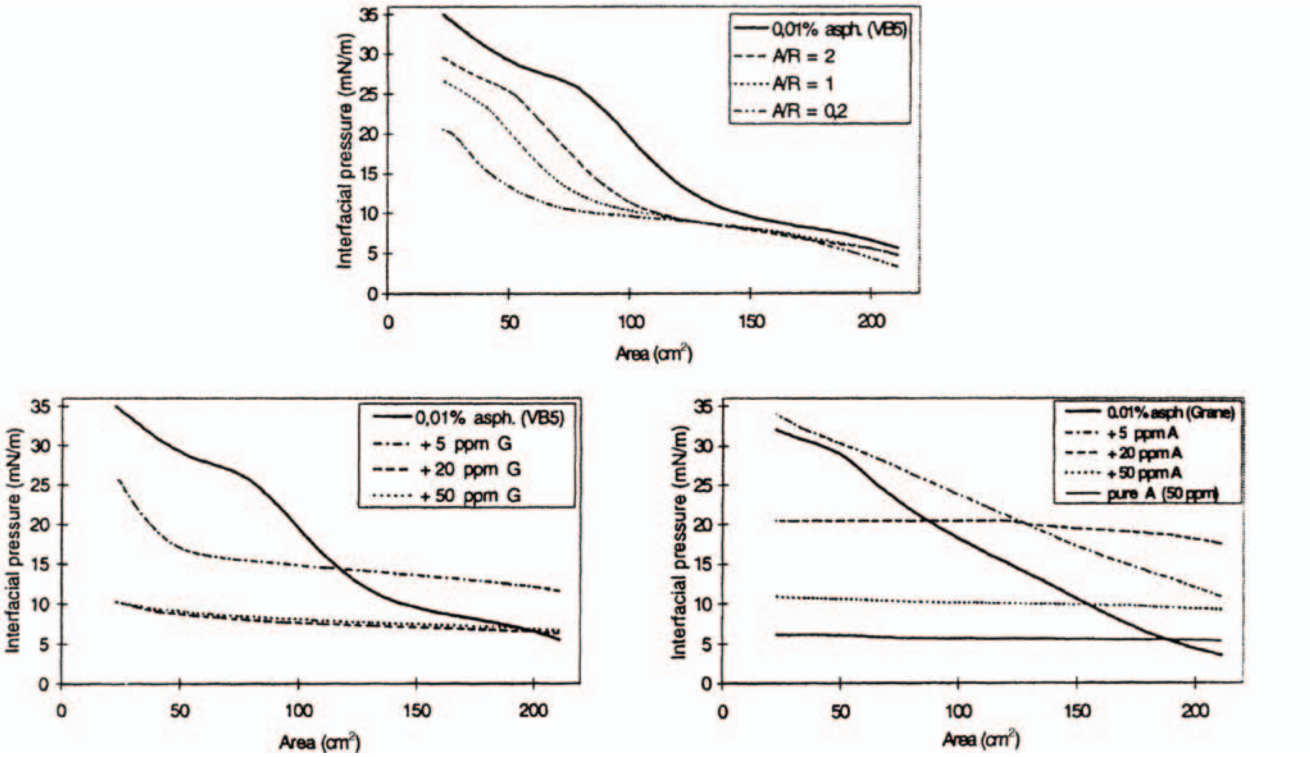


Figure 11 Interfacial pressure isotherms of films formed between water and oil containing different ratios of asphaltenes and resins or different amounts of added chemicals.

components adsorbed at the W/O interface.

The oil phase containing only 0.01 wt % asphaltene gives rise to a less rigid interfacial film than observed at the water surface (Fig. 8). This is most likely due to the possibility of the hydrocarbon tails of the asphaltenes to orient toward the highly aliphatic oil phase, making the interactions between the film material and, hence, the pressure increase during film compression, less extensive. In general, interactions between the bulk phase and interfacial components are different from the water/air case.

Addition of resins to 0.01 wt % asphaltene solutions further reduces the adsorption of interfacially active components on to the O/W interface, even if the total amount of naturally occurring surfactants is considerably higher in these oil phases. The reduction is seen as reduced pressure at constant interfacial area. These changes may be attributed to the ability of resins to disperse asphaltenes in the bulk oil phase, and thus prevent this heavy fraction from building up a stabilizing film between oil and water.

Introducing chemical additives together with asphaltenes into the oil phase may highlight the ability of these chemicals to prevent formation of relatively rigid asphaltene films at the O/W interface. For concentrations higher than 20 ppm of chemical A there is no pressure increase during the compression. Hence, the film that is formed at the interface is highly compressible. So instead of increasing the pressure, the components will build up a multilayer, or the film may dissolve under the influence of compression. An increased inhibitor concentration reduces the interfacial pressure, but has no influence on the film behavior. The reduced pressure is probably as a result of a more complete cover of inhibitor at the interface. That is, fewer components from the asphaltene fraction are adsorbed together with the chemical additive when the inhibitor concentration becomes high enough.

The results obtained upon addition of Demulsifier G are similar to those of A. However, G clearly increases the compressibility of the film even at low concentration. The difference between 20 and 50 ppm is quite small, so it is reasonable to believe that maximum efficiency, resulting from the competing adsorption in a system like this, is already reached at a concentration of 20 ppm in the oil phase.

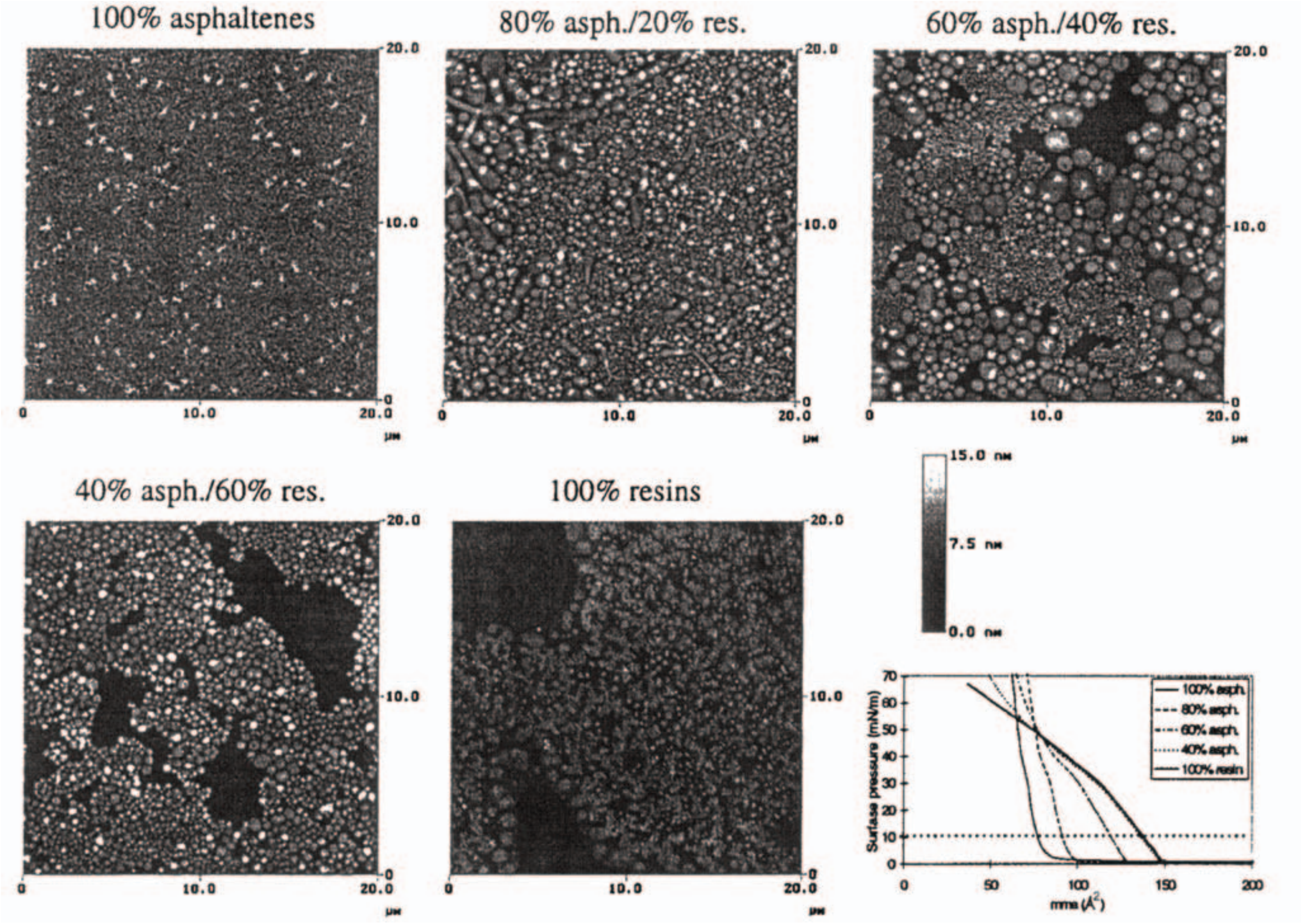


Figure 12 AFM images (20 × 20 μm) of monolayers with increasing resin-to-asphaltene (R/A) ratio; LB film deposited onto mica substrates. The fractions are extracted from a crude from a production field in France (crude F).

With 20 ppm or more of G present, only small amounts of asphaltene will reach the interface.

The results obtained from the Langmuir interfacial film studies are important in explaining why certain chemicals are more effective as inhibitors than as demulsifiers. Obviously, the inhibitor/asphaltene interaction is so strong in the bulk oil phase that the interfacial structures being gradually built up will no longer possess properties required to stabilize W/O emulsions.

C. Langmuir-Blodgett Films Studied by Means of AFM

Monolayers of asphaltenes and resins on the water surface were transferred at a surface pressure of 10 mN/m on to mica substrates by using the Langmuir—-Blodgett technique. In order to visualize the earlier investigated film properties, AFM was used to examine the topography of these deposited layers.

The images shown in Figs 12 and 13 show the structural change in the monolayer at a surface pressure of 10 mN/m, when the composition of the film was gradually changed from pure asphaltenes to pure resins. Images of pure asphaltene show a closed-packed structure of nanosized particles. Addition of resins modifies this rigid structure toward an open structure with regions completely uncovered by film material. Pure resins build up a layer with an open fractal network.

The individual film units increase in size upon addition of resins. This indicates interactions between asphaltenes and resins, providing aggregates of larger dimensions than observed for the pure fractions. Small and moderate amounts of resins give rise to a more polydisperse distribution of the film material, while a further increase in the resin content (i.e., 60 wt % resins) reduces the polydispersity, i.e., the monolayer becomes more uniform in component

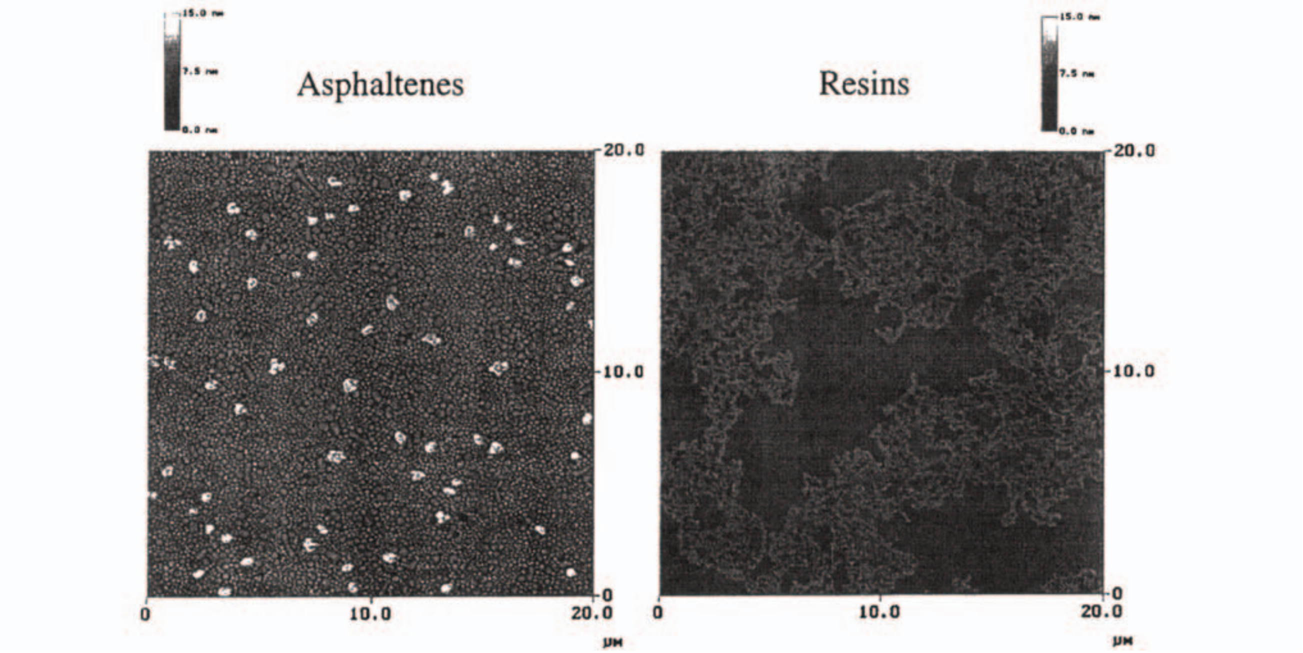


Figure 13 AFM images (20 × 20 μm) of monolayers of pure components from a crude from a production field in the North Sea; LB film deposited on to mica substrates.

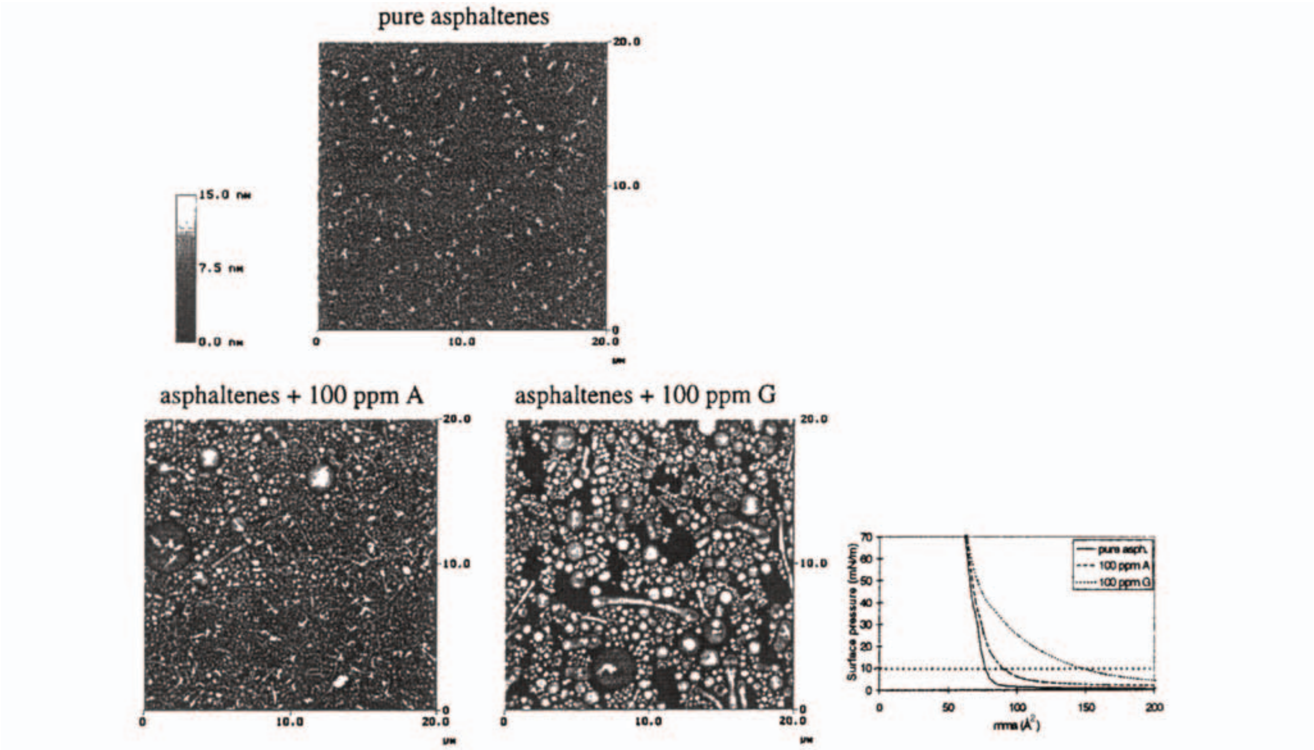


Figure 14 AFM images (20 ° 20 μm) of monolayers consisting of asphaltenes from crude F and 100 ppm high molecular weight demulsifiers/inhibitors; LB film deposited on to mica substrates.

size when one of the pure fractions dominates the film properties.

The AFM images visualize why asphaltenes alone can stabilize emulsions while films dominated by the resin fraction do not. Hence, when the amount of resins present in the film is so large that the structure in the film changes toward a more open fractal network, the efficiency of film components as emulsifier is reduced.

The AFM images of asphaltene films containing 100 ppm of different HMW demulsifiers/inhibitors (Fig. 14) show that the effect of these components on the film is quite similar to the effect on structural changes brought about by the resins. These results indicate that the observed structural changes in the film are qualitatively essential in order to reduce the emulsion stability.

It is important to keep in mind that the AFM images visualize conditions in Langmuir films at the aqueous surface. Once again all interactions between an oil phase and interfacial components are lacking. In a real W/O emulsion there are no guaranteees that all these components will be present at the W/O interface due to solubility in the oil phase. Hence, results from an AFM study of LB films

Table 10 Composition of the Samples

Sample name	Inhibitor concentration (ppm)	Toluene concentration (%)
Crude	0	0
Crude + Toluene	0	1.25
Inhibitor G (300 ppm)	300	0.75
Inhibitor A (300 ppm)	300	0.75

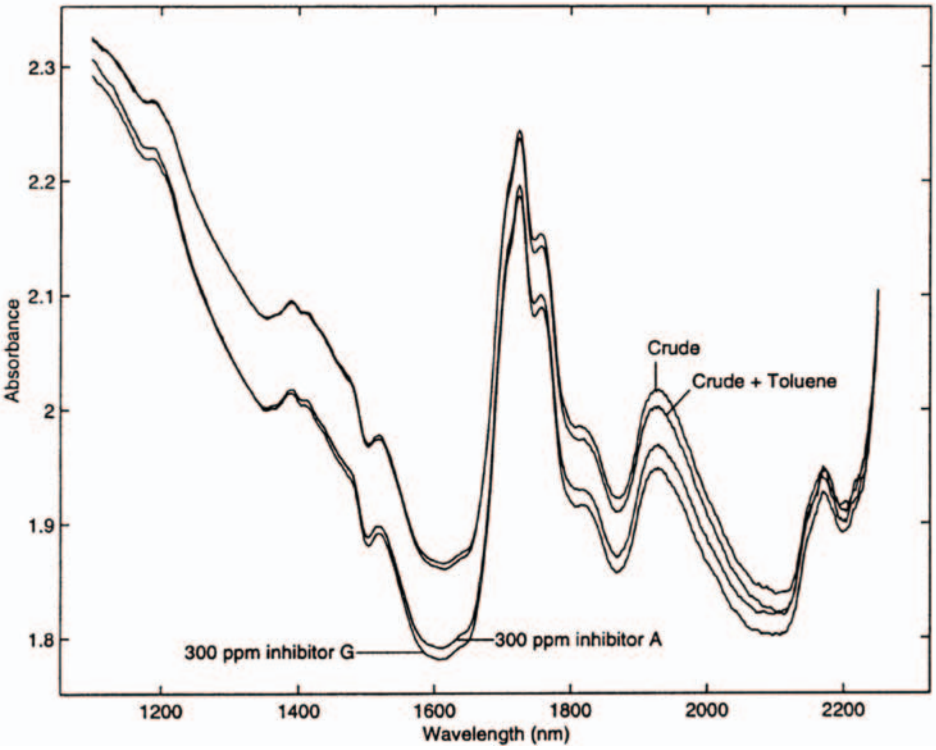


Figure 15 Near infrared spectra of the Grane crude oil with no additives, and with the addition of 500 ppm toluene, 300 ppm inhibitor G, and 300 ppm inhibitor A.

should not be too far-reaching when considering real conditions in W/O emulsions. However, the effect of demulsifiers on the film material remains indisputable.

D. Near-infrared (NIR) Characterization of the Effect of Emulsion Inhibitors

Aggregates of colloidal size scatter near-infrared radiation (γ = 700—2500 nm) in accordance with Rayleigh theory (60). This is observed in the spectrum as a rise of the spectral baseline. The extinction of radiation increases with increasing radius of the scattering particles, and thus the spectrum yields information about the size of the aggregates. The effect of adding two different emulsion inhibitors to a crude oil was determined by means of near-infrared spectroscopy. In previous work (57) by our group it was stated that these inhibitors have a resin-like influence on the aggregation of asphaltenes, i.e., a solvating effect. Near-infrared spectroscopy should thus be able to detect the changes in the aggregation state by direct measurements on the crude oil. The near-infrared sampling of the crude oil was performed on a NirSystems 6500 spectrophotometer, equipped with a fiber-optic sampling probe for transflectance sampling. The wavelength region was set to 1100—2250 nm. The total pathlength was 2.5 mm. The total number of scans per spectra was set to 32 and the sampling was carried out at 25°C. The compositions of the four samples investigated are listed in Table 10.

The inhibitors were diluted in toluene because of their high viscosity. The effect of toluene alone was tested on one of the samples. Figure 15 shows the near-infrared spectra of the four samples.

The interpretation of Fig. 15 is that inhibitors have a solvating effect on the asphaltene aggregates. The reduction in aggregation size is observed as a decrease in the extinction of radiation due to scattering. It is shown that the effect of the inhibitors is more prominent than the effect of toluene alone. The findings suggest that near-infrared spectroscopy could be used for characterization of the effects of inhibitors on crude oils.

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REFERENCES

1. P Becher, ed. Encyclopedia of Emulsion Technology. New York: Marcel Dekker, 1983.
2. K Larsson, S Friberg, Food Emulsions. New York: Marcel Dekker, 1990.
3. J Sjöblom, ed. Emulsions —- A Fundamental and Practical Approach. NATO ASI Series, Vol 363. Dordrecht: Kluwer, 1991.
4. J Sjöblom, ed. Emulsions and Emulsion Stability. New York: Marcel Dekker, 1996.
5. OC Mullins, E Sheu, eds. Structures and Dynamics of Asphaltenes. New York: Plenum Press, 1998.
6. J Sjöblom, Ø Sæther, Ø Midttun, M-H Ese, O Urdahl, H Førdedal. In: OC Mullins, EY Sheu, eds. Structures and Dynamics of Asphaltenes. New York: Plenum Press. 1998, p 337.
7. JD McLean, PM Spiecker, AP Sullivan, PK Kilpatrick. In: OC Mullins, EY Sheu, eds. Structures and Dynamics of Asphaltenes. New York: Plenum Press, 1998, p 377.
8. MC Petty, WA Barlow. In: G Roberts, ed. Langmuir—-Blodgett Films. New York: Plenum Press, 1990.
9. GL Gaines, Jr. Insoluble Monolayers at Liquid—-Gas Interfaces. New York: John Wiley, 1966.
10. KS Birdi. Lipid and Biopolymer Monolayers at Liquid Interfaces. New York: Plenum Press, 1989.
11. L Galet, I Pezron, W Kunz, C Larpent J Zhu, C Lheveder. Colloids Surfaces 151: 85, 1999.
12. DG Dervichian. J Chem Phys 7: 931, 1939.
13. WD Harkins, D Boyd. J Phys Chem 45: 20, 1941.
14. NK Adam. Physics and Chemistry of Surfaces. 3rd ed. London: Oxford University Press, 1941.
15. GA Overbeck, D Möbius. J Phys Chem 97: 7999, 1993.
16. RD Smith, JC Berg. J Colloid Interface Sci 74: 273, 1980.
17. E Pezron, PM Claesson, D Vollard. J Colloid Interface Sci. 138: 245, 1990.
18. M Tomoaia-Cotisel, J Zsako, E Chifu, DA Cadenhead. Langmuir 6:191, 1990.
19. EP Honig, JHT Hengst, D den Engelsen. J Colloid Interface Sci 45: 92, 1973.
20. JH Brooks, AE Alexander. Proceedings of the Third International Congress of Surface Activity, Vol II, p 196.
21. ES Nikomaro. Langmuir 6: 410, 1990.
22. I Langmuir. Trans Faraday Soc 15:62, 1920.
23. G Binnig, CF Quate, C Gerber. Phys Rev Lett. 56: 930, 1986.
24. D Parrat, F Sommer, JM Solleti, Trans Minh Duc. J Trace Microprobe Tech 13: 343, 1995.
25. JA Zasadzinski, R Viswanathan, DK Schwartz, J Garnaes, L Madsen, S Chiruvolu. JT Woodward, ML Longo. Colloids Surfaces 93: 305, 1994.
26. JA DeRose, RM Leblanc. Surfactant Sci Rep 22: 73, 1995.
27. J Sjöblom, L Mingyuan, T Gu, AA Christy. Colloids Surfaces 66: 55, 1992.

28. AH Brown. Chem Ind 30:990, 1968.
29. AJS Liem, DR Woods. Review of Coalescence Phenomena. AIChE Symp Ser 70, 8, 1974.
30. O Reynolds. Phil Trans R Soc (London) A177:157, 1886.
31. SP Frank, KJ Mysels. J Phys Chem 66: 190, 1960.
32. Z Zapryanov, AK Malhorta, N Aderangi, DT Wasan. Int J Multiphase Flow 9: 105, 1983.
33. CY Lin, JC Slatter. AIChEJ 28: 147, 1987.
34. CY Lin, JC Slatter. AIChEJ 28: 786, 1982.
35. AK Malhorta. PhD thesis, Illinois Institute of Technology, Chicago, 1984.
36. CV Sternling, LE Scriven. AIChE J 5: 514, 1959.
37. AJ de Vries, Recl Trav Chim 77: 383, 441, 1958.
38. SS Lang. PhD thesis, University of California, 1962.
39. A Scheludko, E Manner. Trans Faraday Soc 64: 1123, 1968.
40. A Vrij. Disc Faraday Soc 42:23, 1966.
41. H Sonntag, K Strenge. Coagulation and Stability of Disperse Systems. New York: Halsteady-Wiley, 1969.
42. TJ Jones, EL Neustadter, KP Whittingham. J Can Petrol Technol 17: 100, 1978.
43. R Fiocco. US Patent 3 536 529, 1970.
44. MA Krawczyk. PhD thesis, Illinois Institute of Technology, Chicago, 1990.
45. DT Wasan, K Sampath, N Aderangi. AIChE Symp Ser 76: 93, 1980.
46. DT Wasan, NF Djabbarah, MK Vora, ST Shah. Lect Notes Phys 105: 205, 1979.
47. R Aveyard, PB Binks, PDI Fletscher, JR Lu. J Colloid Interface Sci 139: 128, 1990.
48. R Aveyard, PB Binks, PDI Fletscher, RYe, JR Lu. In: J Sjöblom, ed. Emulsions —- A Fundamental and Practical Approach. NATO ASI Series, Dordrecht: Kluwer Academic 1992, p 97.
49. MA Krawczyk, DT Wasan, SS Chandrashekar. Ind Eng Chem Res 30: 367, 1991.
50. DT Wasan. In: J Sjöblom, ed. Emulsions —- A Fundamental and Practical Approach. NATO ASI Series, Dordrecht: Kluwer Academic 1992, p 283.
51. RC Little. Environ Sci Technol 15: 1184, 1981.
52. O Urdahl, AE Møvik, J Sjöblom. Colloid Surface A 74: 293, 1993.
53. HB Clark, MT Pike, GL Rengel. Petrol Technol 7: 1565, 1982.
54. HB Clark, MT Pike, GL Rengel. Proceedings of the AIME International Symposium on Oilfield and Geothermal Chemistry, Houston, TX, 1979, SPE Paper 7894.
55. VB Menon, DT Wasan. Colloids Surfaces 19: 89, 1986.
56. J Djuve, X Yang, U Fjellanger, J Sjöblom, E Pelizzetti. Colloid Polym Sci. In press, 2000.
57. M-H Ese. Langmuir film properties of indigenous crude oil components: influence of demulsifiers, PhD thesis, University of Bergen, 1999.
58. H Kallevik. Characterisation of crude oil and model oil emulsions by means of near infrared spectroscopy and multivariate analysis. PhD thesis, University of Bergen, 1999.
59. BP Singh, BP Pandey. Indian J Technol 29: 443, 1991.
60. 'OC Mullins. Analyy Chem 62: 508—514, 1990.