

Stability and Resurfacing of Dispersed Oil

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by

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Abstract

It is well known that chemically dispersed oil destabilizes after the initial dispersion. There is an extensive body of literature on surfactants and interfacial chemistry, which includes an abundance of experimental data on the topic as well as many theoretical approaches to it. This report will summarize both the data and the theory. The phenomenon of resurfacing oil is the result of two separate processes: destabilization of an oil-in-water emulsion and desorption of surfactant from the oil-water interface which leads to further destabilization.

The destabilization of oil-in-water emulsions such as chemical oil dispersions is a consequence of the fact that not all emulsions are thermodynamically stable. Ultimately, natural forces move the emulsions to a stable state, which consists of separated oil and water. What is important is the rate at which this occurs. An emulsion that stays sufficiently stable until long past its practical use consideration may be said to be kinetically stable. Kinetic stability is a consideration when describing an emulsion. An emulsion is said to be kinetically stable when significant separation (usually considered to be half or 50% of the dispersed phase) occurs outside of the usable time.

There are several forces and processes that result in the destabilization and resurfacing of oil-in-water emulsions such as chemically dispersed oils. These include gravitational forces, surfactant interchange with water and subsequent loss of surfactant to the water column, creaming, coalescence, flocculation, Ostwald ripening, and sedimentation.

Gravitational separation is the most important force in the resurfacing of oil droplets from crude oil-in-water emulsions such as dispersions and is therefore the most important destabilization mechanism. Droplets in an emulsion tend to move upwards when their density is lower than that of water. This is true for all crude oil and petroleum dispersions that have droplets with a density lower than that of the surrounding water. More dense oils, which would sink as emulsions, are poorly, if at all, dispersible. The rate at which oil droplets will rise due to gravitational forces is dependent on the difference in density of the oil droplet and the water, the size of the droplets (Stokes' Law), and the rheology of the continuous phase. The rise rate is also influenced by the hydrodynamical and colloidal interactions between droplets, the physical state of the droplets, the rheology of the dispersed phase, the electrical charge on the droplets, and the nature of the interfacial membrane.

Creaming is the destabilization process that is simply described by the appearance of the starting dispersed phase at the surface, without the processes in the intervening spaces being described. In the oil spill world, creaming is the process that might be described as resurfacing.

Coalescence is another important destabilization process, which has been studied extensively in oil-in-water emulsions. Two droplets that interact as a result of close proximity or collision can form a new larger droplet. The end result is to increase the droplet size and thus the rise rate, resulting in accelerated destabilization of the emulsion. Studies show that coalescence increases with increasing turbidity as collisions between particles become significantly more frequent.

Ostwald ripening is another process in the destabilization of oil-in-water emulsions. Ostwald ripening occurs when the larger droplets in an emulsion grow due to absorption of soluble components or very small droplets from the water column. The effect is to remove soluble material from the water column and smaller droplets, resulting in an increased growth of the larger droplets. The phenomenon occurs because the soluble components of the dispersed phase are more soluble in the larger droplets than in the water and the smaller droplets. Although the Ostwald ripening phenomenon has not been investigated with oil-in-water emulsions to the

same extent as other phenomena, it is believed to be important.

Another important phenomenon when considering the stability of dispersed oil is the absorption/desorption of surfactant from the oil/water interface. This process is stated to be the most important process for chemical considerations of surfactants and interfacial chemistry. When surfactants are dissolved in a bulk phase such as water, they start to be absorbed at the oil surface or interface. The system moves toward equilibrium, that is equilibrium amounts of surfactant at the interface and in the bulk phase. Desorption occurs primarily as a result of the lower concentration of surfactants in the bulk phase or water. The surfactants will transfer back and forth from the oil/water interface until an equilibrium of concentration is established in the interface or in the bulk liquid (water). It is well known that in dilute solutions, much of the surfactant in the dispersed droplets ultimately partitions to the water column and thus is lost to the dispersion process. Little, if any, surfactant would partition back into the droplet in a dilute solution, which is the case for oil dispersions at sea. This is one important difference between dilute and concentrated solutions.

This report provides examples of studies and models in all the processes as well as data from experiments and calculations. Data show that for a dilute solution such as a chemically dispersed oil spill, half-lives would vary from 2 to 24 hours, with a typical average value of 12 hours.

Executive Summary

Overall

The destabilization or resurfacing of chemically dispersed oil is reviewed in this report. This phenomena is described as a typical consequence of the formation of oil-in-water emulsions and is due to several well-known destabilization mechanisms. This phenomena results in the rising of oil droplets to the surface where they may or may not form another slick.

Summary

Stability of emulsions usually referred to the resistance of emulsion droplets to coalescence. Several other instability mechanisms have recently been found. Stability therefore refers to resistance to any process that reduces the number of droplets or increases their size. As emulsions are not thermodynamically stable, in the long term they will move back to a more stable position, which is the undispersed state.

One way to view the stability of an emulsion is that, when the dispersed phase is broken into droplets, the surface free energy is increased correspondingly to the size and number of droplets. The increase in interfacial free energy causes the thermodynamic instability of the dispersed phase. Another form of stability is known as kinetic stability, which refers to stability in terms of time. An emulsion is never entirely stable in the kinetic definition, however, it may be considered to be stable if the material is sufficiently stable within the use time of the dispersant. There is no standard convention for considering stability time. Some authors use half-life, which is similar to radiation. This is appropriate because most processes for destabilization of emulsions are exponential or have a similar relationship with respect to process.

The stability of emulsions in an open system such as the ocean is a very different matter than in a closed system such as a jar. The continuous matter in a closed system can be altered to increase stability and surfactant displacement. For example, many food emulsions are rendered stable for months by adding polymers and thickeners to the continuous medium. Other food emulsions are not highly stable.

Destabilization Processes

Gravity separation of emulsions occurs with or without the presence of surfactants. For a given droplet the effect of gravity is simply a function of the difference in density of the oil and the water. The rate at which gravity separation occurs varies as the square of the particle size and inversely as the viscosity of the continuous phase, water in this study (Stokes' equation). This is another of the distinguishing features between oil spill dispersions and closed systems. In closed systems, the gravity separation of the oil droplets can be slowed by controlling the viscosity of the medium or continuous phase. In the food industry for example, this is done in mayonnaise by using viscosity-enhancers for the continuous phase.

Calculations and experimental data show that, for dilute systems such as oil spill dispersions, gravity-induced creaming and coalescence are the primary mechanisms for loss of stability. Creaming is the rising of droplets to the surface and coalescence is the formation of droplets into a liquid at the surface. Both are the result of gravity. As most oils are lighter than water, this is the typical fate of most oil-in-water dispersions. Creaming occurs regardless of surfactant content and a droplet rises at about the same rate whether surfactant is present or not.

Sedimentation is the reverse of creaming and occurs when the oil or dispersed phase is heavier than water. The Stokes' equation is relevant to the rate of either rising or sinking.

When coalescence occurs, two or more droplets join to form one larger droplet. If creaming is not counted as a destabilization mechanism, coalescence is the primary destabilization process for emulsions such as crude oil at-sea dispersions. It is important to understand that much of the coalescence that occurs does so after particles collide. The droplets of a dispersed liquid in an emulsion are in constant motion and therefore they frequently collide. If the interfacial film surrounding the droplets is too weak to withstand the collision, the droplets will coalesce.

Flocculation is the formation of clusters of particles. Typically, the interfacial layer on the droplets involved on the cluster prevents coalescence. Flocculation is caused by attraction between particles such as from van der Waals forces. The fate of flocs, the end product of flocculation, is also creaming, as these clusters have a much greater rise rate than individual droplets. Flocculation has not been studied extensively for crude oil emulsions.

'Depletion flocculation' is another term used to refer to flocculation but, in this case, the process depletes droplets in the emulsion. Either flocculation or coalescence can occur in some emulsions depending on conditions such as the sub-type or concentration of the surfactant. Depletion flocculation is promoted by unadsorbed surfactants in the water, especially if they are in micelles. The presence of micelles, which are thermodynamically stable entities, causes further desorption of surfactants from the emulsion and thus destabilizes it. Depletion flocculation is also enhanced by excessive concentration of surfactant.

Ostwald ripening is the movement of molecules and small particles into larger particles. Ostwald ripening is thermodynamically favoured for this movement. Some studies showed that Ostwald ripening is favoured for oil components such as decane when the water volumes are low, but less favoured when they are high. For oil spills, this would indicate that Ostwald ripening is less of a destabilization mechanism than coalescence.

Phase inversion occurs when the continuous phase of an emulsion inverts to its discontinuous phase. In the context of the type of emulsions discussed here, it is when an oil-in-water emulsion changes to a water-in-oil emulsion. There is little information to indicate that such inversions occur with oil spill dispersions.

A doublet is an intermediate phase between two particles that interact or collide. The outcome of a doublet could be reformation of two individual droplets, coalescence, or flocculation depending on conditions and the strength of the interfacial layer. Fragmentation is the process that describes the formation of the resulting end product. Fragmentation times depend on conditions such as droplet radii, film strength, and phase characteristics.

Processes involving dilute emulsions, such as oil spill dispersions, can be simplified. The energy path leading from a single original particle to a doublet, the intermediate stage upon the collision of two droplets and finally to a coalesced particle, is an important consideration. In the case of dilute emulsions, the stability is most affected by two processes, Ostwald ripening and coalescence. The effect of Ostwald ripening is that sub-microns rapidly disappear, increasing the size of the particles. Coalescence between droplets occurs upon collision.

Processes/Influences Behind Stabilization/Destabilization Processes

The function of any emulsifying agent or surfactant is to stabilize an otherwise unstable system to the degree possible. The emulsifying agent does so by absorbing at the liquid-liquid interface as an oriented interfacial film. The film performs two functions - it reduces the interfacial tension between the two liquids and consequently the thermodynamic instability of the system resulting from the increase in the interfacial area between the two phases and it decreases

the rate of coalescence of the dispersed liquid droplets by forming mechanical, steric, and/or electrical barriers around them. The steric and electrical barriers inhibit the close approach of one droplet to another.

Deformations in the interfacial film can occur as a result of several factors, including collisions and particle-particle interactions. Deformation alone can lead to instabilities in the emulsion. Thin film instabilities arise from heterogeneities in surfactant concentrations.

It has been found that the strength of the film is essential to the stability of the emulsion. The physical strength of the film is important particularly in the event of droplet collisions. It has been noted that, if the film is strong, flocculation is more likely to occur than coalescence and vice versa. For oil spill dispersions, coalescence is the most likely scenario because of the nature of the interfacial films.

Film Buildup and Destabilization Processes

Surfactants readily absorb at the interface between a droplet and the bulk liquid, which is usually water. There are Marangoni fluctuations and instabilities associated with the distribution of surfactant gradients around a droplet. There are several forces that lead to desorption or removal of the surfactant from the interface, particularly to the water from the interface.

Surfactants will distribute between the bulk phase, water, and the interface to achieve equilibrium between the two phases. This equilibrium depends on the water-oil solubility characteristics of the surfactant. In a closed system, this equilibrium is achieved rapidly with little loss of surfactant. In an open system, however, equilibrium is never achieved and the surfactant leaches into the water and, over a period of hours, little surfactant is left in the oil droplets.

The Marangoni effect is an important phenomenon in terms of surfactant stability and dynamics. The Marangoni effect is due to the tendency of surfactant concentrations to quickly distribute over an interface. If there is a deficit in surfactant concentration on one side of a droplet, the surfactant quickly moves to restore the equilibrium concentration over the droplet. The restoration of equilibrium is known as Marangoni stabilization.

Marangoni instability arises as a result of this surfactant flow because the flow continues and results in areas of greater and lesser concentration of surfactant over the droplet interface. Some researchers noted that Marangoni instability was periodic. During a convective stage, fast absorption of surfactant occurs with rapid inflow of surfactant to the interface. During a diffusive stage, desorption occurs and gradients build up until the system becomes unstable again.

Several researchers found that in a flowing field or when droplets are in motion, surfactant thinning occurs on the leading edges and the trailing edges thus has excess surfactant. This condition is known as hydrodynamic destabilization. Experiments show that, at low surfactant concentrations, this occurs at a velocity of 0.0005 m/s and at high surfactant concentrations, the instability will occur at 0.003 m/s. Both these velocities are relevant to larger droplets rising due to Stokes' rising.

Several studies have shown, both experimentally and theoretically, that small surfactants will displace larger surfactants or polymers at the interface. Although studies have shown that as a rule mixed surfactant systems yield more stable emulsions, the difference in size between surfactants is critical to this. A mixed surfactant system with large and small surfactants will essentially be more stable than one stabilized by the small surfactants alone as these small surfactants will displace the larger surfactants at the interface. Some studies showed that adding small surfactants such as Tween and Spans, which are used in oil spill dispersants, actually destabilized emulsions that were stable with larger proteins or polymers as surfactants.

The type of surfactant is also an important factor in emulsion stability. Experiments in which the type of surfactant was varied have shown that the differences can result in vastly different lifetimes of an emulsion. Studies show that the type of surfactant and its chain length are important factors. Several studies have shown that increasing chain length increases stability. It has been shown that the use of polymers to stabilize emulsions has significantly improved stability. An important finding with mixed surfactants, as noted above, is that the smaller surfactants will tend to displace larger surfactants at the interface.

The amount of surfactant is another important factor in emulsion stability. Many researchers have found that there are four conditions that apply for surfactant quantity. The first is a threshold below which the quantity of surfactants is too low to provide any effective stabilization. Between this minimum-effective threshold and another level is the optimal quantity of surfactant to provide good stability. Above this threshold, increasing surfactant often decreases the stability due to surfactant interaction. A fourth condition sometimes identified is surfactant is in such excess that phase inversion or gelation occurs.

Many researchers have found that the presence of sufficient surfactants, i.e., the second factor noted above, is critical for any emulsion stability. Most studies have shown that stability below a critical concentration of surfactant is very low. In fact, low surfactant concentrations have been shown to have the same effect as no surfactant.

Several experiments have shown that excess surfactant will destabilize an otherwise stable emulsion.

Some researchers have found that a mixing time is needed before surfactants can stabilize an emulsion. One researcher defined this as a meso-equilibrium time or the mixing time needed to reach maximum stability.

Researchers have found that the surfaces of emulsion droplets are subject to capillary waves caused by thermal fluxes. It is suggested that there is a film thickness, called the transitional thickness, at which the surface fluctuation becomes unstable and then the fluctuation grows spontaneously. At a given film thickness, the surface corrugations caused by the fluctuations rise to the point at which contact can be made between two adjacent droplets. The thickness at this time is called the critical thickness.

Some researchers identified an oscillatory absorption-desorption behaviour of surfactants and droplets. Droplets rapidly absorbed surfactants and then slowly lost these surfactants. The absorption is accompanied by a small waving motion across the interface. These asymmetrical oscillations can lead to droplet instability.

Changes in temperature cause changes in interfacial tension between the two phases. Temperature can also cause differential changes in other factors such as the relative solubility of the surfactant in the two phases and in diffusion in the system. Surfactants are most effective when close to the point of minimum solubility in the solvent in which they are dissolved. It was found that emulsions were universally more stable at cooler temperatures. This effect, however, runs counter to the trend that more emulsions are formed at higher temperatures. The resulting effect is such that insufficient oil dispersions would be produced at very low sea temperatures to notice the increased stability.

Salinity affects emulsion stability, however, the influence depends on the type of surfactant, temperature, and other conditions. There is no single rule of salinity effect.

Several researchers have found that surfactants in the water bulk phase will precipitate through reactions with ions in the water or through interactions with each other. It is noted that this form of surfactant loss occurs in both closed and open systems.

Some studies noted that energy is important in the early formation of emulsions, with more energy making it more likely that the dispersion phase is moved into the emulsion. One study on crude oils found that there was only about a 10% difference between the stability of a crude oil emulsion whether or not energy was applied continually after formation. Another study that focussed on examining coalescence noted that increasing energy increased the coalescence rate. This effect is understood by the fact that the collision rate is also increased with increasing turbulence or energy input to a system. In an Arabian crude oil emulsion, the half-life was decreased from about 4.5 hours at a low shear rate to about 3.5 hours for a high shear rate.

The viscosity of the continuous phase is an important factor. A viscous continuous phase will form a barrier to surfactant loss from the droplets, a barrier to rapid collisions, and reduce the rise rate of the droplets. Viscosity enhancers and similar additives are used in food and cosmetic preparations to stabilize emulsions. For oil spill dispersions, water is the continuous medium and thus stability becomes an issue.

Interfacial tension is the force exerted between two different liquids. In relation to emulsions, it is more of a concept than a real force as it incorporates many of the forces noted above. The assumption is that the thermodynamic energy of a droplet emulsified in another liquid can be ascribed to this interfacial tension between the two liquids. This is an over-simplification as it combines many of the above-noted forces and considerations into one force.

Other Characteristics

Droplet size is a very important factor in emulsion stability. The smaller the particles and the size range of the particles, the more stable the emulsion. On the other hand, larger particles are more thermodynamically stable and thus size increase is thermodynamically favoured. As noted in many different sources, the forces that relate to stability are very dependent on droplet size. For oil spill dispersions, the wide variety of crude or refined components implies a wide spectrum of particle sizes, which in turn dictates that such emulsions have low stability.

Some studies have shown that changing particle sizes by only a few percent can change emulsion lifetimes very significantly, usually by several factors more than with larger droplets. Calculations show that stability rises as the inverse of the cube of the droplet or particle size. This illustrates the great importance of particle size in determining stability.

Not only is droplet or particle size important, but also the homogeneity of droplet sizes. The more homogeneous the particle size, the more stable the emulsion and vice versa. This is partially explained by the fact that the forces between droplets are more equal when they are similar in size and thus processes such as Ostwald ripening are less prevalent. It should be noted that the sizes of dispersed oil spill droplets are very heterogeneous and thus stability is an issue.

Micelles are clusters of surfactants formed in the water phase. As micelles are even more stable than emulsions, there is a net flow of surfactants from the emulsion through the water phase to form micelles. Micelles do not form until a certain concentration of surfactants is present in the water column. Some researchers have suggested that the presence of free surfactant micelles increases the attraction between droplets because of an osmotic effect.

Forces

The DLVO theory of emulsion stabilization is named after Derjaguin and Landau and a later set of workers, Verwey and Overbeek. This theory proposes a balance between the repulsive and attractive potential energies of interaction between the dispersed particles or droplets.

Repulsive interactions are due to either the similarly charged electrical double layers surrounding the droplets or to solvent-droplet interactions. Attractive forces are largely due to the van der Waals forces between droplets. For a stable dispersion to occur, for whatever length of time, the repulsive forces must be larger than the attractive. The repulsive forces are much greater for a thick interfacial layer and smaller droplets.

Subsequent researchers have shown the limitations of the DLVO theory. One of these is that the effect of the stability of an oil-in-water dispersion is limited to the effect of the surfactant on the surface potential of the dispersed particles and the ionic strength of the dispersing liquid. Several other forces or considerations were not incorporated into the DLVO theory. In addition, the basic DLVO theory is not applicable to nonionic surfactants. Several of these are summarized in this report including concepts such as oscillatory structural forces.

Van der Waals forces refer to intermolecular forces caused by the polarization of molecules that are attractive and present in many fluids. This is one of the prime forces that brings droplets together in a system free of motion or turbulence. Capillary forces arise between two droplets when the distance between them becomes small, such as in a capillary tube, so that there is an attractive force between the two particles. The origin of the forces is the mutual attraction between the two particles.

One of the "new" attractive, and sometimes repulsive, force between particles has been called the oscillatory structural force (OSF). If two large particles or droplets are in a colloidal liquid, i.e., a dispersion of very small particles, and the separation distance between the two particles is smaller than the diameter of the colloidal particles, then there is an attractive force between the two particles because of the osmotic pressure. This force would result in coalescence or flocculation between the two particles, thus depleting the emulsion. Basically, this oscillatory structural force is caused by a great difference in droplet sizes such as in an oil spill dispersion.

In some situations, the oscillatory structural force can be either attractive or repulsive. If small colloidal particles are confined in the gap between two large particles and when the gap between the two larger particles is almost equivalent to several colloidal particle diameters, the colloidal particles in the gap interact with the large droplets as a result of Brownian forces. This long-range structure induces a repulsive structural barrier that helps prevent the large particles from flocculating or coalescing. When the separation distance between two larger particles is smaller than the diameter of the colloidal particles, a net attractive force between the two particles occurs as a result of the difference between the osmotic pressure difference between the bulk and confined regions of the colloidal system. This force tends to oscillate between repulsive and attractive with a frequency equal to the effective size of the colloidal particles. The oscillatory structural force operates over a distance of the diameters of several colloidal particles, which is greater up to 20 times the distance over which the DLVO forces operate.

An important facet of the oscillatory structural force is that a wide poly-dispersibility from colloidal to micron-sized particles is necessary for this to occur. Just a few larger particles will destabilize an emulsion by OSF. Unfortunately, oil spill dispersions such as many oil-in-water emulsions have this poly-dispersibility characteristic and are therefore prone to this instability.

Surfactants, especially ionic surfactants, have an electric charge. Since an emulsion will have similar surfactants distributed throughout, there will be a similar charge on each droplet and thus an electric repulsion between droplets. This is the most significant force that separates droplets and prevents coalescence. While ionic surfactants have the highest charge and form the strongest electrical barriers, they are also the most water-soluble and thus readily partition into

the sea. Nonionic surfactants, which are used extensively in oil spill dispersants, have a lesser charge and pose a weaker electrical barrier to coalescence. Nonionic surfactants, however, do have a lesser tendency than ionic surfactants to partition rapidly to the water phase.

Zeta potential is a measure of the electrophoretic mobility of oil droplets in an applied electric field and is indicative of the droplet-to-droplet charge and thus the emulsion stability. It is not exactly the repulsive electric force discussed above.

Steric forces are interference forces resulting from the presence of large molecules such as polymers or chains. The use of larger polymers as surfactants has been shown to provide stability to emulsions through steric forces.

The mechanical or physical barrier is important to the stability of an emulsion as it increases the resistance of the dispersed particles to mechanical shock and prevents them from coalescing if particles do collide. The mechanical strength of the interfacial layer is strengthened by a tight formation of surfactants at the interface.

Rates of Processes

Stokes' rising rate is given as directly proportional to the square of the particle diameter and the density difference and inversely proportional to the difference in viscosity of the oil and water. This equation is very important in terms of understanding the resurfacing of oil spill dispersions. It shows that for the smallest droplets at 1 m below the slick, the rise rate would be about a year (or forever) and for the largest droplets immediately below the slick, the rise rate is a few seconds. Several researchers have shown that surfactants do not affect the base rise rate. However, many researchers have shown that the rise rate predicted by the Stokes' equation is far too slow compared to experimental measurements. These have been explained by the destabilization processes operating on emulsion droplets, namely coalescence, flocculation, and Ostwald ripening. All of these serve to increase particle diameter and thus significantly increase rise rate. A doubling of a droplet radius results in a quadrupling of the rise rate for that particular droplet.

Coalescence rate is an important factor in the stability of emulsions. This is the time over which two droplets merge and form one droplet. Coalescence times are fairly rapid. Coalescence rates increase with temperature. Collisions will necessarily result in a potential for coalescence. Findings appear to indicate that oblique collisions will result in more coalescence than head-on collisions. More collisions occur in more energetic and turbulent conditions, thus accelerating coalescence.

Ostwald ripening requires a flux of soluble components in the water and a wide distribution of droplet sizes, both of which occur with oil spill dispersions. Among other factors, the rate of Ostwald ripening depends on the square of the inverse of oil viscosity and directly on the diffusion rate of the components. This means that for oil dispersions, Ostwald ripening is most prevalent for light oils.

Brownian motion is random motion of particles in another fluid due to thermal motion and depends on the temperature, among other factors. Brownian motion can be responsible for collisions between particles leading to coalescence.

Bulk mixing is the most common process whereby droplets are transferred around a given area. For open-sea oil dispersions, this is the means by which droplets are moved downward from the surface. Droplet diffusion is another means but this is at least 100 times slower than bulk mixing. A rule of thumb for mixing by waves is that the depth of mixing is about 1.5 times the maximum wave height. Bulk mixing also implies that some droplets that have been mixed

downward are also driven upwards.

Loss of Surfactant to the Water Column

Several measures have shown that most surfactants partition readily into the water column and with increasing dilution, this strongly affects emulsion stability. For dilute situations such as oil spill dispersions, this loss of surfactants is a significant contributor to emulsion stability.

Some Half-lives

The literature as reviewed for this report had several measurements of the half-lives of oil and hydrocarbon emulsions. The half-lives for crude oil emulsions are similar and estimate the average about 12 hours. It should be noted that there are few studies on this, however

Conclusions

There is a vast body of information and experimentation and a broad consensus on the stability of emulsions. Crude oil-in-water dispersions are similar to many other types of emulsions in that they are stable under some conditions for a period of hours. During this time, destabilization processes are underway that result in oil resurfacing.

Crude oil emulsion stability and resurfacing is influenced by the following forces.

1. Natural stabilization/destabilization forces

The most important such force is gravity. As most oils are less dense than water, their emulsion droplets are also less dense than water and will rise. The reappearance of oil on the surface is known as creaming. There are many destabilizing forces applicable to emulsions such as chemically dispersed oil including coalescence, flocculation, Ostwald ripening, and phase inversion. It is known that coalescence of droplets is the most important destabilization process for emulsions similar to dispersed crude oil emulsions.

2. Standard tendency of emulsions to instability

There are many repulsive forces and some attractive forces between droplets. The net result of these forces is to destabilize the droplet after some period of time.

3. Instability of interfacial film with surfactants

The interfacial films stabilized by surfactants undergo a number of destabilization processes. These forces weaken the interfacial film and consequently destabilize the emulsion.

4. Loss of surfactant

In addition to the mechanisms of interfacial stability reduction noted above, there is a net loss of surfactant in dilute emulsions such as oil spill dispersions. This net loss is caused by the tendency of the surfactants to equilibrate between the water bulk phase and the oil droplet interface. As crude oil emulsions are continually being diluted, surfactant movement from the interface to achieve equilibrium constitutes a loss of surfactant to the system. This loss of surfactant accelerates the destabilization of the emulsion.

5. The heterogeneous mixture of compounds in oil

Oil consists of dozens of major constituents, most of which have very different sizes and properties. This results in the formation of droplets of very different sizes.

6. Wide distribution of droplet sizes

There is a wide distribution of droplet sizes in crude oil dispersions, with much of the volume in the micron-sized area. Emulsions of micron-sized droplets are less stable. The presence of even a few larger droplets will destabilize an emulsion as this triggers destabilization

processes such as Ostwald ripening.

7. Low viscosity of water

Because the viscosity of water is low, destabilization processes are more prevalent than in other bulk fluids. The low viscosity of water increases coalescence and the diffusion of surfactants away from oil droplets.

8. Increasing dilution of the emulsion

For dilute emulsions, surfactant desorption becomes surfactant loss. Further surfactant absorption rarely occurs. As crude oil dispersions or emulsions are dilute and become increasingly dilute with time, they destabilize through surfactant loss and many of the other processes noted in this report.

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List of Acronyms

AFM	Atomic force microscopy
ANS	Alaska North Slope - Usually referring to the crude oil mixture at the end of the pipeline
ASMB	Alberta Sweet Mixed Blend - A type of crude oil
CLA	Colloidal liquid aphrons
CMC	Critical micelle concentration
CTAB	Cetyltrimethyl ammonium chloride (a surfactant)
CTAC	Cetyltrimethyl ammonium bromide (a surfactant)
Corexit 9527	Brand name of a dispersant from Exxon
Corexit 9500	Brand name of a dispersant from Exxon
DADMA	Dialkyldimethylammonium bromines
DLVO	Derjaguin Landau Verwey Overbeek - A reference to a theory on surfactant stabilization, with each letter referring to the author of the original theory.
DO	Dispersed oil
ESA	Electrokinetic sonic amplitude
ESS	Emulsion stability simulations
GC	Gas chromatograph - A chemical analytical technique
HLB	Hydrophilic-lipophilic balance
IFT	Interfacial tension
LSW	Lifshitz, Skzov, and Wagner theory
NAPL	Nonaqueous-phase liquid
NMR	Nuclear magnetic resonance
OSF	Oscillatory structural forces

PWSRCA	Prince William Sound Regional Citizens' Advisory Council
RSD	Relative standard deviation
SDS	Sodium dodecyl sulfate • A common ionic surfactant
WAF	Water-accommodated fraction - The sum total of oil in a water sample, including physically dispersed and soluble oil.

Table of Contents

Abstract	iii
Executive Summary	v
Acknowledgements	xiv
List of Acronyms	xv
1. Introduction	1
1.1 Objective	1
1.2 Scope	1
1.3 Organization	1
2. Introduction to Destabilization and Resurfacing	1
3. Review of the Literature on Destabilization of Emulsions	2
3.1 Surfactant-stabilized Emulsions in General	2
3.2 Stabilization by Particles	7
3.3 Studies of Stability of Food Oil Emulsions	11
3.4 Studies of Surfactant-stabilized Oil Emulsions	15
3.5 Studies of Stability of Crude Oil or Petroleum Emulsions	16
3.6 Effects of Salinity, Temperature, and Dilution on Resurfacing	20
3.7 Measurement of Emulsion Destabilization	20
4. Physics of the Destabilization Processes	21
4.1 The Basics	21
4.2 Interfacial Tension Approaches to Stability	26
4.3 Tadros	27
4.4 Wasan's Theory on Oscillatory Structural Forces (OSF)	29
4.5 Applicability of the Stokes' Equation	31
4.6 The Urbina-Villalba Approach to Emulsion Stability Simulations (E-SS)	32
4.7 The Standard Kinetics Approach to Emulsion Stability	32
4.8 The Lifshitz, Slezov, and Wagner Theory of Ostwald Ripening	33
4.9 Kinetic Approach to Brownian and Gravitational Coagulation in Dilute Emulsions	33
4.10 A Model to Describe Emulsion Stability	37
4.11 The Marangoni Effect	38
4.12 Kinetics of Destabilization Processes	38
4.13 Lifetime of Dilute Emulsions with Doublet Formation	41
4.14 Hydrodynamic Instability of Emulsions	42
4.15 Importance of Droplet Deformation on the Stability of Emulsions	43
4.16 Emulsion Stability Viewed as Film Rupture	45
4.17 Calculations of Coalescence Time	46
4.18 Models Focussing on Film Drainage between Two Drops	47
4.19 Nonlinear Rupture Theory to Predict Stability Time	47

5.	Loss of Surfactant to Water Column: Desorption	48
5.1	Studies on Surfactant Absorption and Loss	48
5.2	Theoretical Studies of Surfactant Loss	52
5.2.1	Adsorption Approach Using Langmuir Kinetics	52
5.2.2	An Empirical Approach	52
5.2.3	Application of Several Absorption Models to Absorption/Desorption ..	53
5.2.4	Kinetics of Absorption	55
5.2.5	Absorption of Surfactants Based on Chemical Potential	56
6.	Summary	58
6.1	Stability	58
6.1.1	Thermodynamic	58
6.1.2	Kinetic	58
6.1.3	Closed Versus Open Systems	59
6.2	Destabilization Processes	59
6.2.1	Gravity	59
6.2.2	Creaming	59
6.2.3	Sedimentation	59
6.2.4	Coalescence	59
6.2.5	Flocculation	60
6.2.6	Ostwald Ripening	60
6.2.7	Phase Inversion	60
6.2.8	Doublet Formation and Fragmentation	60
6.2.9	Dilute Emulsions	60
6.3	Processes/Influences Behind Stabilization/Destabilization Processes	61
6.3.1	Film or Interfacial Film	61
6.3.2	Film Strength	61
6.3.3	Film Buildup and Destabilization Processes	61
6.3.4	Other Factors	64
6.3.5	Other Characteristics	64
6.4	Forces	65
6.4.1	DLVO Theory	65
6.4.2	Attractive Forces	65
6.4.3	Repulsive Forces	66
6.5	Rates of Processes	67
6.5.1	Particle or Droplet Rising/Destabilization Rate	67
6.6	Some Half-lives	68
7	Conclusions	69
8	References	73
Tables		
1	Stabilization of Toluene-in-Oil Emulsions by Silica Particles	8
2	Tests of the Resurfacing of Oil	17
3	Emulsion Half-lives from the Literature	69

Figures

1	The Process of Creaming	3
2	The Process of Sedimentation	3
3	The Process of Coalescence	4
4	The Process of Ostwald Ripening	4
5	The Process of Flocculation	9
6	The Stabilization of a Toluene-in-water Emulsion as Stabilized by Silica Particles - Particle Size	9
7	The Stabilization of a Toluene-in-water Emulsion as Stabilized by Silica Particles - Amount of Particles	10
8	The Stabilization of a Toluene-in-water Emulsion as Stabilized by Silica Particles - Particle Lifetime	10
9	Effectiveness with Time - ASMB with Corexit 9500	18
10	Effectiveness with Time - ASMB with Corexit 9527	18
11	Effectiveness with Time - ANS with Corexit 9500	19
12	Effectiveness with Time - ANS with Corexit 9527	19
13	The Forces and Influences on Two Droplets Approaching Each Other	22
14	The Process of Marangoni Stabilization	39
15	The Process of Marangoni Stabilization	39
16	The Process of Surfactant Absorption	49
17	The Process of Surfactant Desorption	49
18	The Process of Surfactant Absorption and Desorption in a Closed System	50
19	The Process of Surfactant Absorption and Desorption in an Open System	50
20	A Chemical Dispersion Scenario showing the Progression of the Slick, Emulsion Fate, and Mass Balance (a)	71
21	A Chemical Dispersion Scenario showing the Progression of the Slick, Emulsion Fate, and Mass Balance (b)	72

1. Introduction

1.1 Objective

The objective of this report is to address the issue of destabilization and resurfacing of dispersed oil.

1.2 Scope

This report covers the literature from the inception of the oil spill concerns to August of 2005 and focuses primarily on issues related to the destabilization of oil-in-water emulsions such as chemically dispersed oil. This report summarizes some of the key papers in the area, about which there exists an extremely vast body of literature. There are many entire books devoted to the topics of emulsion stability and surfactant absorption. Only the most relevant and best examples of the literature were selected for this report.

This report contains some mathematical models. Only the most important models are reported on and their development is summarized briefly. Only about one out of every hundred equations was included in the report. The equations are important as they show the relationship of various stability facets to input factors.

1.3 Organization

The report begins with a summary and outline of the topic in Section 2. A review of emulsion stability studies in the literature is provided in Section 3. Section 4 is a summary of the physics of destabilization processes. Section 5 is a summary of surfactant dynamics as it relates to emulsions. Section 6 is the summary of the report and Section 7 provides the conclusions. The references are listed in Section 8.

2. Introduction to Destabilization and Resurfacing

Almost every paper on the topic of the stability of emulsions notes that emulsions are not stable (Menin and Wasan, 1985; Ivanov et al., 1985; Melik and Fogler, 1988; Shen and Hartland, 1994; Walstra, 1996; Van Oss, 1996; Gurkov et al., 1998; Reiffers-Magnani et al., 2000; Robins, 2000; Shields et al., 2001; Hunter, 2001; and Birdi, 2003). It is typically noted that emulsions are not thermodynamically stable, but may be kinetically stable depending on the time scale considered. In the case of kinetic stability, emulsions are not stable in terms of many years either and the scale of time considered typically relates to consumer products and may be months. In terms of oil spill dispersions, half-life is only a few hours.

There are several forces and processes that result in the destabilization and resurfacing of oil-in-water emulsions such as chemically dispersed oils. These forces include gravitational forces, creaming and sedimentation, coalescence, Ostwald ripening, flocculation, and surfactant interchange with water and subsequent loss of surfactant to the water column.

The most important force in resurfacing of oil droplets from an oil-in-water emulsion is gravitational separation (Basaran et al., 1998). Droplets in an emulsion tend to move upwards when their density is lower than that of water. This is true for almost all crude oil and petroleum dispersions as they usually have droplets with a density lower than that of the surrounding water. More dense oils are poorly, if at all, dispersible (Pingas, 2000). The rate at which oil droplets will rise due to gravitational forces is dependent on the difference in density of the oil droplet and the water, the size of the droplets (Stokes' Law), and the rheology of the continuous phase (Basaran et al., 1998). The rise rate is also influenced by the hydrodynamical and colloidal interactions between droplets, the physical state of the droplets, the rheology of the dispersed phase, the

electrical charge on the droplets, and the nature of the interfacial membrane.

Creaming is a process that is simply described by the appearance of the starting dispersed phase at the surface, without the processes in the intervening spaces being described (Robins, 2000; Robins et al., 2002). Creaming is the process that might be described in the oil spill world as resurfacing. Robins (2000) describes creaming at length, noting that it is a very important phenomena in the food-processing business. As much as 40% of the cost of developing a new food emulsion involves the long-term testing related to creaming. Creaming and sedimentation are illustrated in Figures 1 and 2. Sedimentation is the reverse of creaming and occurs when the dispersed phase is more dense than water.

Coalescence is the joining of two or more droplets to form a larger droplet. Coalescence is an important destabilization process in oil spills. Changes in droplet size resulting in coalescence have been monitored as an emulsion destabilizes. Dukhin and Goetz (2005) monitored the coalescence of water droplets in a water-in-kerosene emulsion using a newly developed acoustic unit. They found that the original droplets, which were about 0.4 μm in size, slowly coalesced into larger droplets. At about 10 hours, the droplets increased to about 5 μm in size. Coalescence is illustrated in Figure 3.

Ostwald ripening may be an understated mechanism in the destabilization of oil-in-water emulsions (Taylor, 1998). Basically, Ostwald ripening is the growth of larger emulsion droplets by absorption of soluble components from the water column. The effect is to remove soluble material from the water column, and smaller droplets, resulting in an increased growth of the larger droplets. The phenomenon occurs because the soluble components of the dispersed phase are more soluble in the larger droplets than in the water and the smaller droplets. Although the Ostwald ripening phenomenon has not been investigated with oil-in-water emulsions to the same extent as other phenomena, it is believed to be quite important (Taylor, 1998). Studies of undecane, hexadecane, benzene, and octane-in-water emulsions have shown that Ostwald ripening is an important factor in destabilization (Taylor, 1998). Ostwald ripening is illustrated in Figure 4.

Flocculation is another process that occurs when two particles interact. In flocculation, two or more particles come together to form an agglomerate of particles, but the particles do not coalesce. Flocculation is illustrated in Figure 5.

It is well known that there is an exchange of surfactants between the target droplet and the surrounding water (Hiemenz and Rajagopalan, 1997). This promotes destabilization of the emulsion. When the water is in a large ratio to the droplet concentration, surfactant is largely lost and destabilization is relatively rapid. In laboratory tests, the ratio of the oil to water then becomes important in simulating the conditions at sea.

There is an increasing amount of analytical power and new experimental methods being applied to dispersions (Dukhin and Goetz, 2001). Many of the references that have a theoretical base as presented here, also have extensive experimental information to compare to the theoretical approaches.

3. Review of the Literature on Destabilization of Emulsions

3.1 Surfactant-stabilized Emulsions in General

Engels et al. (1995) studied the stabilization of a simulated oil consisting of an ether and an ester with ethyoxylated nonionic surfactants. A phase inversion was found to occur on heating and was used to prepare finely dispersed oil-in-water emulsions. Engels et al. found that the formation of a bicontinuous or lamellar structure was necessary for a finely divided oil-in-water

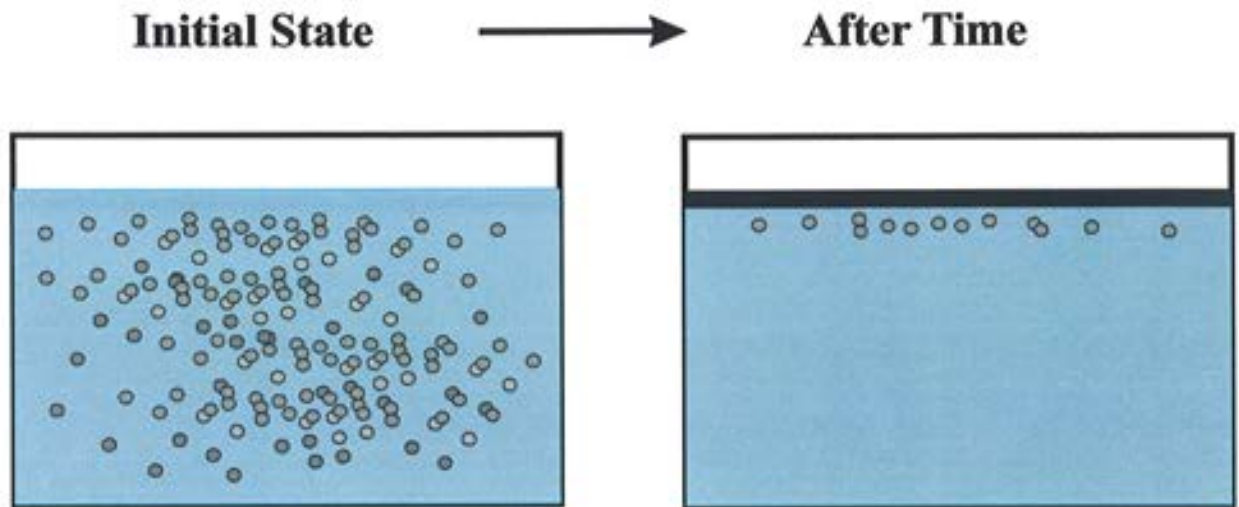


Figure 1 The Process of Creaming Most of the droplets or particles move upwards under the influence of gravity to form an oil layer on the surface. Creaming is the most important phenomenon in resurfacing of oil spill dispersions

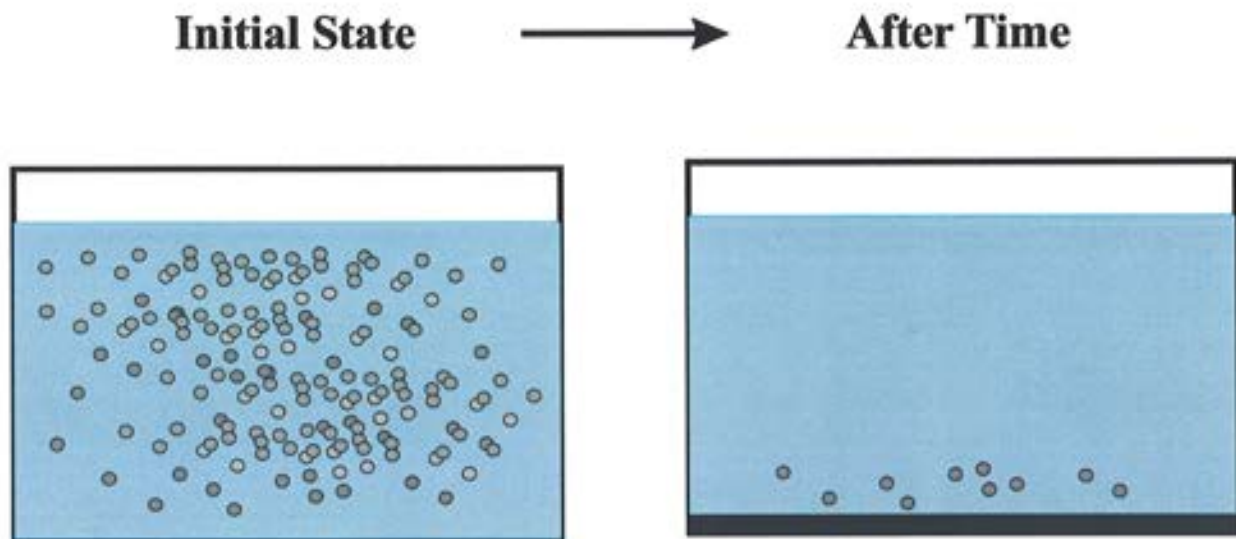


Figure 2 The Process of Sedimentation Most of the droplets or particles move downward under the influence of gravity to form an oil layer on the bottom of the water body or vessel. This process is applicable to dense oils.

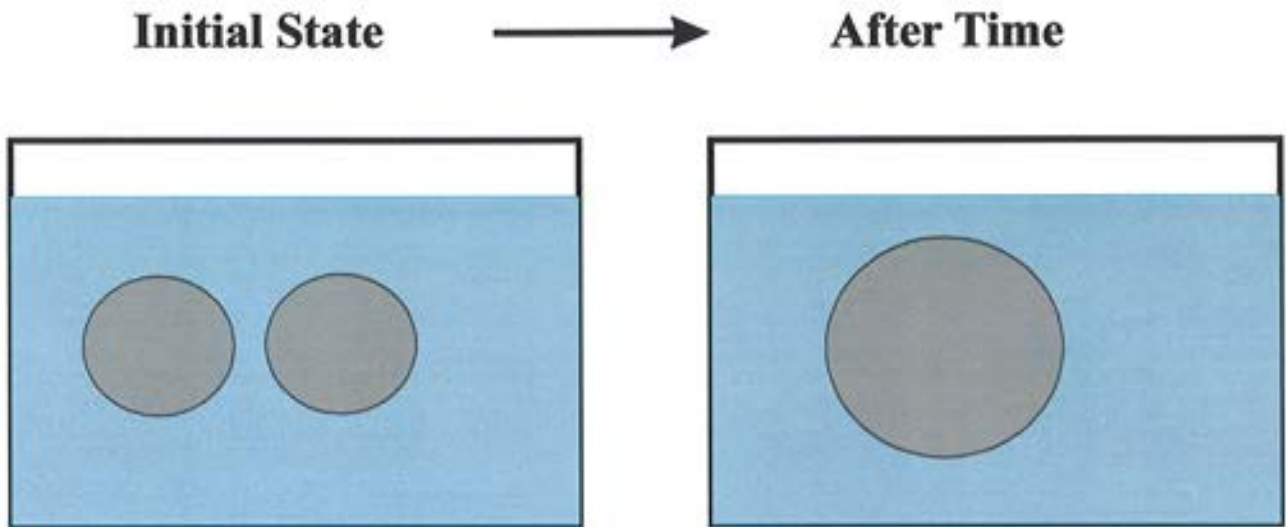


Figure 3 The Process of Coalescence Two or more particles interact to form a single larger particle. Coalescence is an important phenomenon in the resurfacing of oil spill dispersions

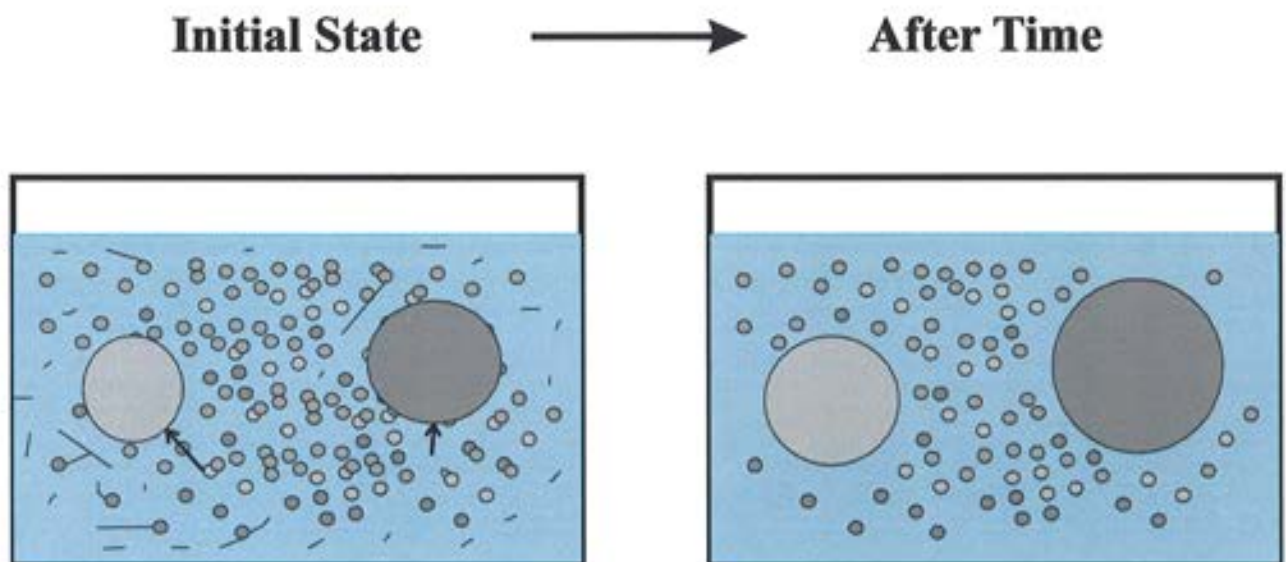


Figure 4 The Process of Ostwald Ripening Soluble components in the water column and very small droplets are more soluble in the larger droplets and diffuse into these larger droplets.

emulsion. It was found that this fine dispersibility was necessary for stability along with the properties of the fluid in which this occurs. In this case, a lamellar gel phase shielded against re-coalescence. This would obviously not be the case with oil spills as the lamellar gel phase does not occur.

Breen et al. (1996) reviewed the topic of emulsions and emulsion stability. They note that the stability of any emulsion is largely due to the nature of the interfacial film that is formed on droplets. The stability of this film is strongly dependent on the surfactant adsorption-desorption kinetics, solubility, and interfacial rheological properties such as elasticity and viscosity. Surface diffusion and surface absorption are two factors that significantly influence the magnitude of interfacial tension gradients in the thin film.

Söderman and Bulinov (1996) summarized the use of nuclear magnetic resonance (NMR) to measure self-diffusion in emulsions. They note that it is difficult to measure an absolute creaming rate for emulsions because of the broad size distribution of emulsion particles. For an isolated droplet in a continuous medium, the creaming is a direct function of the difference in density of the oil and the water and the square of the particle size, and is inversely proportional to the viscosity of the water or the continuous medium. The viscosity gives the usual control mechanism for the destabilization of emulsions, as the viscosity of the continuous phase can be raised to high values to control creaming. The half-lives of a series of emulsions were measured at between 1 hour to 11 days, depending on the amount and type of surfactants as well as the viscosity of the medium.

Sjöblom et al. (1996) studied various types of emulsions using dielectric spectroscopy. The level of breakdown in various emulsions was the target datum point. This technique was applied to a variety of water-in-oil emulsions and unknown emulsions. Separation after one hour was found to vary from 2 to 100%, depending on the type of crude oil and the surfactant.

McClements and Dungan (1997) studied decane-in-water emulsions using nuclear magnetic resonance. The decane was super-cooled and was at 30% in water. Stabilization was by a nonionic surfactant, polyoxyethylene sorbitan monolaurate, Tween 20. It was found that surfactant enhances the induced crystallization by altering colloidal interactions between droplets. Creaming measurements show that flocculation was enhanced in emulsion when the free surfactant concentration was increased. McClements and Dungan proposed that the presence of free surfactant micelles increases the attraction between droplets because of an osmotic effect and this attraction facilitates the ability of solid crystals from one droplet to induce crystallization in an adjacent droplet.

Lye and Stuckey (1998) studied the structure and stability of colloidal liquid aphrons (C.L.A.), which are proposed emulsion structures consisting of an oil droplet surrounded by a 'soapy solution' stabilized by nonionic surfactants and then surrounded by ionic surfactants. The half-lives of the decane and decanol-in-water emulsions, stabilized with sodium dodecyl sulphate and alcohol ethoxylate surfactants, varied from 15 to 35 minutes.

Chen et al. (2000) studied the effect of pH on the stability of n-pentane-in-water emulsions using the surfactants Triton SP-190 and Triton X-100. The stability was measured by the volume of oil phase separated and the size of the dispersed droplets. It was found that the addition of inorganic acids destabilized emulsions made with Triton SP-190. Other testing indicated that acids may interfere with the surfactants at the oil-water interface and thus destabilize the emulsion. This shows the importance of the surfactant and its presence at the oil-water interface.

Langevin (2000) described experiments on the influence of interfacial rheology on emulsion properties. Surface wave devices were used to measure the surface viscoelasticity of the

droplets and this was related to emulsion stability.

Shebukin et al. (2001) studied the stabilizing forces of interfacial adsorbed layers of surfactants on droplet coalescence. The methods used were the compression of two individual droplets up to their coalescence and up to the rupture of the formed single droplet, evaluation of the free energy of interaction by measuring the contact rupture force for smooth spherical particles, rheological study of the interfacial layers by the torque pendulum method, scanning electron microscopy of the interfacial layer morphology, and study of the stability with respect to Ostwald ripening. The studies showed that the mechanical strength of the interfacial layer is critical as well as the nature of the non-polar liquid.

Porras et al. (2004) studied the formation of decane-in-water nano-emulsions stabilized with mixed surfactant systems including Span 20, Span 80, Tween 20, and Tween 80. It was shown that the mixtures of surfactants provide more stable systems than one surfactant alone. The time history of the droplets was monitored along with the droplet sizes. For low water concentrations, the breakdown could be largely attributed to Ostwald ripening. For high water concentrations, the breakdown could be attributed to coalescence.

Saito et al. (2004) studied the stability of benzene-in-water emulsions stabilized with PEG-*block*-P(H)MA-*block*-polystyrene, PS-*block*-P4VP-*graft*-PEG, microspheres_{1,2}, and microspheres_{3,4} emulsifiers. All formed oil-in-water emulsions and the stability was improved by increasing the ratio of arm number of PEG to PS in the polymer and the formation of supermolecules. Half-lives ranged from about 3 to 8 hours.

Surfactant-stabilized emulsions are not thermodynamically stable and droplets will resurface as a result of a number of forces outlined in Section 2 (Aveyard et al., 2003). Under certain conditions, surfactant-stabilized emulsions might be considered kinetically stable, depending of course on the time frame considered. Emulsions may be stable from minutes to hours, but rarely over years. Binks and Whitby (2005) indicated that due to the large interfacial energy of an emulsion, it will never be thermodynamically stable. Ideal conditions, however, may promote some kinetic stability.

Koh and coworkers (2000) studied the stability of poly(dimethylsiloxane) oil-in-water in using a combination of nonionic and cationic surfactants. Phase separation and optical microscopic observations showed that the principal mechanism for emulsion destabilization at high salt concentration was coalescence and this was accelerated at high temperatures. The droplets ranged in size from 0.1 to 20 μm , typical of most emulsions.

Shioi and Kondo (2004) studied coalescence of oil and heptane with the surfactant DEHPA, Di-2-ethylhexyl phosphoric acid. The interface had intrinsic instability which induced the self-pulsing of the dynamic interfacial tension and the macroscopic interfacial flow due to the Marangoni effect. The coalescence time decreased as the aging time increased, during which the oil/water interface was kept intact. The coalescence time varied from 2 to 70 seconds. Coalescence time was found to be completely independent of the interfacial coverage or composition of the surfactants and was only affected by the interfacial flow at the interface. The researchers concluded that the spontaneous interfacial flow retarded coalescence since it interrupted the fusion process.

Tadros et al. (2004) studied the stabilization of Isopar M (isoparaffinic oil) and cyclomethicone using inulin, a polymeric surfactant. Emulsions prepared using the inulin-based surfactant have large droplets but the addition of a co-surfactant, Span 20, significantly reduced the droplet size. The stability of the emulsions was investigated and the more stable ones would last, in part, up to one year. This long-term stability was attributed to the use of the polymeric inulin.

Dagastine et al. (2004) studied the forces between oil micro-droplets in solution by Atomic Force Microscopy (AFM), which measures forces at nanometre scale lengths. While this study did not result in quantitative force measurements, it was the first reported use of AFM to conduct this type of experiment. Filip et al. (2005) also studied emulsions with AFM, however, they used a surfactant-stabilized water-in-oil emulsion. Filip et al. found that the surfactant concentration was critical to stability and were able to define regions of critical stability based on surfactant content.

Neuman et al. (2004) studied the stability of silicone oil-in-water emulsions as a function of surfactant and salt concentrations. They found that emulsions formed from n-hexane and the silicone oil were much more stable if synthesized silicone oil was used rather than the industrial product. This occurred when the volume fraction of the oil was 20 in the solution. There was some indirect evidence that, from 25 to 55% volume fraction, the linear silicone chains may be absorbed close to a monolayer at the oil-water interface. This suggests that, in the case of the synthesized oils, there is a preferential adsorption of linear chains at the interface that reduces coalescence.

Niraula et al. (2004) studied the effect of alkyl chain length and concentration of surfactant on the rheological properties of mineral oil-in-water emulsions. These emulsions were stabilized with various homologues of glucopyranoside. The rheological properties were in turn used to describe emulsion structure and stability. It was found that the average droplet size decreased with both the length of the alkyl tail and the bulk concentration of the surfactant. The stability of the emulsion also increased, as did its storage stability. The authors noted that good quality emulsions can only be produced in the presence of high concentrations of surfactant of between 2 to 7% surfactant by weight.

Batista et al. (2005) studied the kerosene emulsion stabilization of biosurfactants produced by indigenous bacteria from petroleum-contaminated sites. They found that kerosene could be maintained at up to 50% of the original emulsion volume for 48 hours.

Freire et al. (2005) studied the aging mechanisms of perfluorocarbon emulsions using image-analysis techniques. Oil-in-water emulsions of n-perfluorohexane and perfluorodecalin were prepared using the emulsifiers lecithin, Span 20, and Pluronic F-68. The stability of the emulsions depended on temperature and other factors. Two aging mechanisms, coalescence and molecular diffusion, were found to be important. Analysis of mean droplet size during the period of monitoring showed that coalescence is more common than previously reported for these systems. Coalescence increases as the temperature rises.

Acharya et al. (2005) studied the stability of emulsions formed by new gemini-type surfactants and sodium dodecyl sodium sulfate. The half-life of the oil-in-water emulsions was between 50 to 100 seconds.

3.2 Stabilization by Particles

Several studies have been done of oil-in-water emulsions stabilized by particles (Aveyard et al., 2003). These studies have shown that the irreversible adsorption of particles leads to much more stability than for surfactant-stabilized emulsions. Surfactant-stabilized emulsions are less stable because the adsorption of surfactants at the droplet interface is reversible and dynamic (Aveyard et al., 2003). Solid-particle-stabilized emulsions, sometimes known as Pickering emulsions, have many interesting properties. The effectiveness of the solid in stabilizing emulsions depends on the size, shape, concentration, and wettability of the particles and on the interactions between particles (Aveyard et al., 2003). Unlike surfactant-stabilized emulsions, particle-stabilized emulsions can be highly stable and show little creaming within a few days

(Aveyard et al., 2003). For particle-stabilized emulsions, stability to creaming decreases progressively with decreasing particle concentration. There is also a strong relationship between the size and stability of the stabilizing particles. The coalescence, lifetime, and other factors in the formation of an emulsion from toluene and silica particles are shown in Table 1.

Table 1 **Stabilization of Toluene-in-Oil Emulsions by Silica Particles**
(Data after Aveyard et al., 2003)

Percent SiOH	Particle Diameter μm	% Coalescence	Time	Time Units
100	150	90	2	minutes
79	120	5	8	minutes
76	75	0	3	years

Figure 6 shows the stabilization of a toluene-in-water emulsion as stabilized by silica particles from data from Aveyard et al. (2003). This figure shows that the coalescence is strongly dependent on the particle size of the solid stabilizer. Figure 7 shows the same dependency on particle size but taken as the percentage of particles used to stabilize the toluene. This shows that there is also a dependency on the quantity of particles, but it should be noted that particle diameter is decreasing with a decreasing amount of particles. The lifetime of the emulsion is very strongly influenced by particle size as shown in Figure 8. The lifetime of the emulsion is orders-of-magnitude different when particle size changes by only a few percent. This is noted as being quite different from surfactant-stabilized emulsions (Aveyard et al. 2003).

Simovic and Prestidge (2004) studied the stabilization of poly(dimethylsiloxane) emulsion droplets with silica nanoparticles as a stabilization. The coalescence kinetics were measured using optical microscopy. The adsorbed layers of nanoparticles introduced a barrier to coalescence but only reduced the coalescence kinetics somewhat. Formation of more highly and rigid layers did reduce the coalescence kinetics. At the point where a monolayer of particles exists, coalescence is limited. When the nanoparticle coverage is > 0.7 or < 1.0 , structures change and coalescence is more prevalent. Coalescence kinetics of between 50 to 70% took place over a time range of 40 to 80 minutes.

Horezov and Binks (2004) developed an automated analyzer to study emulsion stability. The device uses a light-scattering technique and subsequent computer analysis. Tests on latex particle dispersions showed half-lives varying from 2 to 24 hours.

Binks and Whalley (2005) studied the stability of a non-polar oil stabilized with silica particles. They were able to improve emulsion stability somewhat by adding cationic surfactants and controlling pH. They found that increasing the polarity of the oil phase increased emulsion stability and this was attributed to the adsorption of polar-solvent molecules to the silica surface.

Kraglyakov and Nustayeva (2005) studied the stability of oil-in-water emulsions stabilized by silica particles, focussing on the relationship of capillary pressure to stability. Experiments showed that at high capillary pressure the emulsion stability has a maximum when the contact angles between particles and emulsion are at equilibrium. Explanations of this are given in terms of capillary theory.

Xu et al. (2005) studied oil-in-water emulsions stabilized by silica nanoparticles using regular blender and microchannel methods. They found that the microchannel method, which provides higher energy and closer contact, resulted in more stable emulsions with a much reduced polydispersity compared to emulsions formed using a homogenizer. In the case of emulsions formed using the microchannel method, it was found that the silica aggregates formed

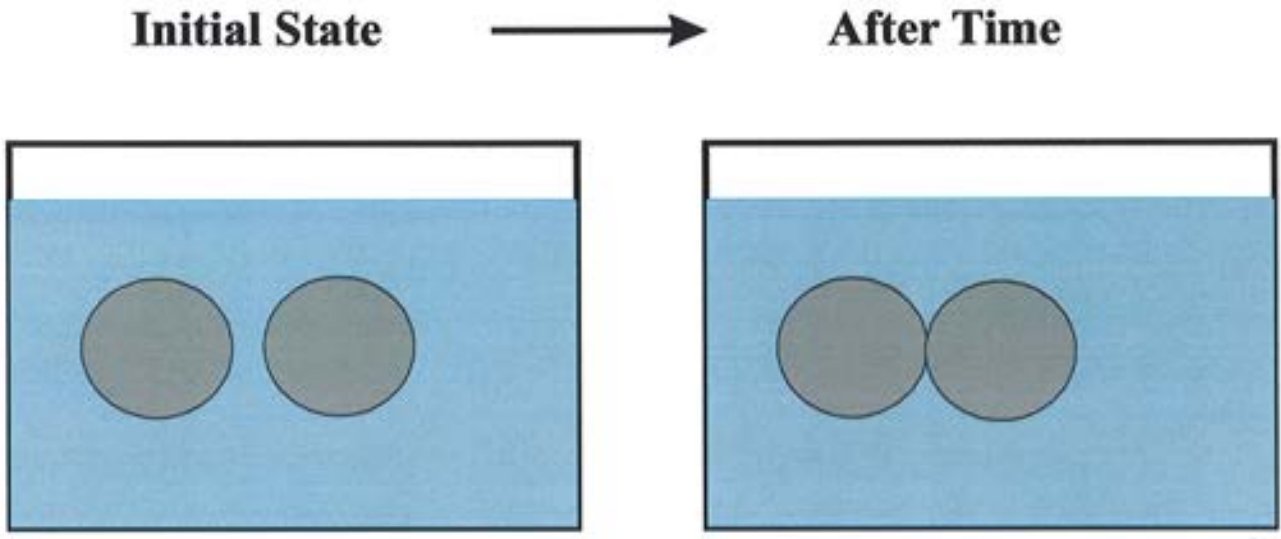


Figure 5 The Process of Flocculation Two or more particles interact to form an agglomerate of separate particles.

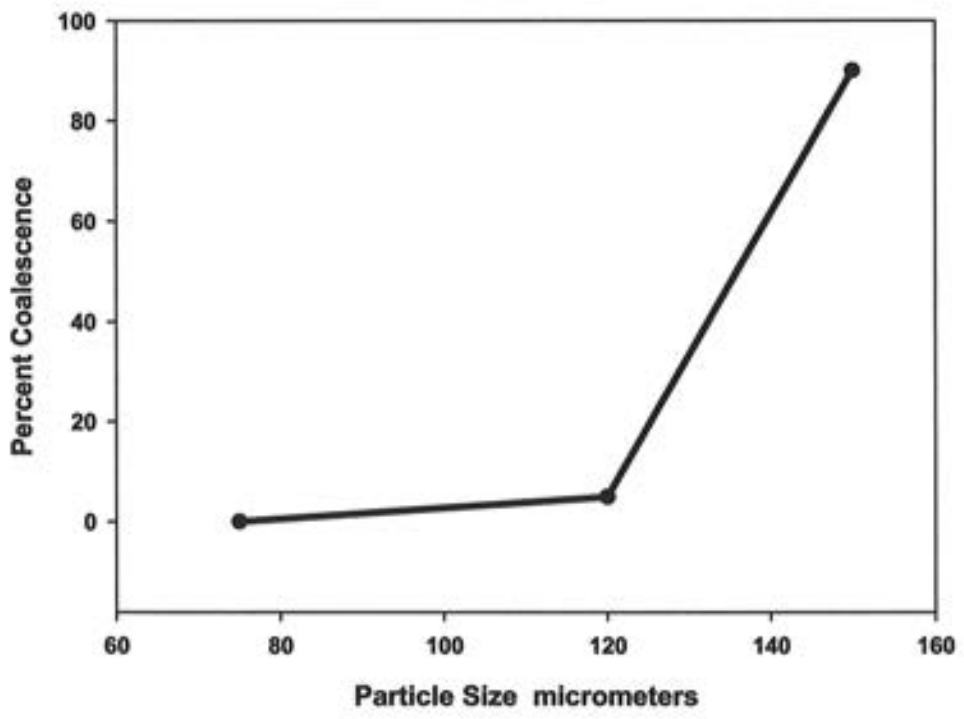


Figure 6 The Stabilization of a Toluene-in-water Emulsion as Stabilized by Silica Particles (Data from Aveyard et al., 2003) This Figure shows that the greater the particle size, the more the coalescence.

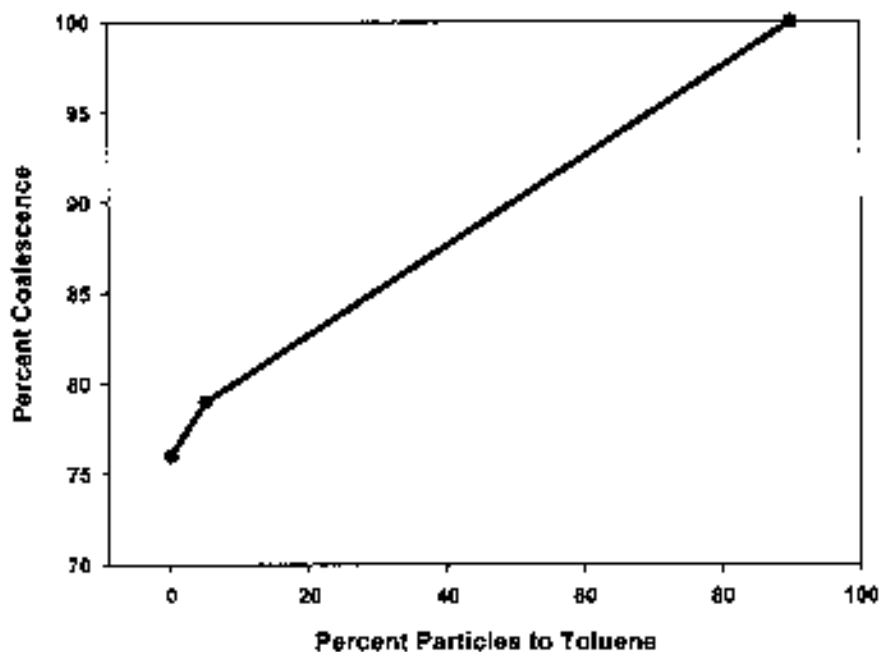


Figure 7 The Stabilization of a Toluene-in-water Emulsion as Stabilized by Silica Particles (Data from Aveyard et al., 2003) This figure shows a dependency on particle quantity, but it should be noted that the particle diameter is decreasing with decreasing amount of particles.

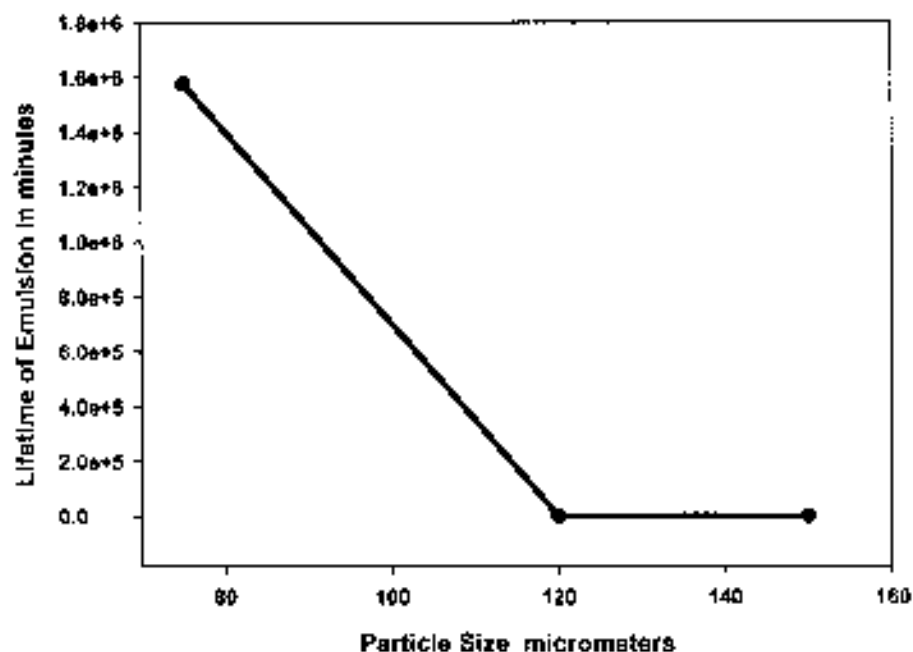


Figure 8 The Stabilization of a Toluene-in-water Emulsion as Stabilized by Silica Particles (Data from Aveyard et al., 2003) This figure shows that the lifetime of the emulsion is very strongly influenced by particle size

shell-like structures or layers around the droplets and probably were a monolayer. In the case of emulsions formed using a homogenizer, the surface layer was thinner and did not constitute a complete monolayer.

Giermanska-Kahn et al. (2005) studied self-stabilized solid particles consisting of paraffin wax crystals. Wax crystals of colloidal size were prepared and were stable for up to months under quiescent conditions. Addition of a surfactant, CTAB, resulted in destabilization after only a few hours. It was postulated that the surfactant deformed the ellipsoidal forms of the wax, resulting in destabilization. Application of shear also resulted in destabilization.

Melle and coworkers (2005) studied solid-stabilized decane-in-water emulsions. The solids were paramagnetic carbonyl iron particles. Because of the magnetic nature of the particles, magnetic fields could be used to manipulate the emulsion.

Kralchevsky and coworkers (2005) studied the thermodynamics of particle-stabilized emulsions (Pickering emulsions) using theoretical approaches. They found that the bending or deformation of the particle layer is a crucial parameter to emulsion stability.

3.3 Studies of Stability of Food Oil Emulsions

Dalgleish (1996) reviewed the stability of food emulsions, noting that stability was the major factor in food preparation and development. Food emulsions are different from oil-in-water emulsions in that they can be made concentrated to control creaming and coagulation by rendering the continuous medium highly viscous. Proteins, casein, etc. may thus be used as agents to prevent droplets from coalescing. Food oil-in-water emulsions are sometimes fluid, although they may have partly crystalline oil phases.

Not all food emulsions are required to have long-term stability. e.g., salad dressings may have very little stability. Italian dressing is an example of an oil-in-water emulsion that has a half-life in minutes. Re-emulsification by shaking is necessary before use. This particular dressing is very relevant to crude oil-in-water emulsions in that its half-life is similar to at-sea emulsions, the vegetable oil is similar to a very light crude oil, and sometimes surfactants are used that are identical to oil spill dispersants.

On the other hand, some food oil-in-water emulsions such as mayonnaise must remain stable for very long periods of time. These are generally kept stable by adding several co-surfactants and using a highly viscous continuous phase to minimize gravitational flow and Brownian diffusion, and thus coalescence and creaming.

Basaran et al. (1994) studied the gravitational separation of corn oil emulsions stabilized by a nonionic surfactant, Tween 20, and xanthum gum. They developed a technique using ultrasonic imaging to visualize the emulsion at 0 and 24 hours and present 2-dimensional images of the emulsion. Creaming of the corn oil was found to be fast at low concentrations (<0.0075 wt%) and at high concentrations (>0.02 wt%) of xanthum gum. At concentrations between the low and high concentrations, creaming was much lower. It was found that the xanthum gum increased the viscosity and lowered the colloidal interactions, two factors that influence the rate of gravitational rise. The presence of the xanthum gum also causes the rising droplets to flocculate to an extent rather than rising due to coalescence.

Gullapalli and Sheth (1999) studied the stability of mineral oil and olive oil emulsions with respect to the nature of the dispersed phase, emulsifier compositions, and processing parameters. The size of the droplets in the mineral oil-in-water emulsions was independent of the hydrophilic-lipophilic balance (HLB) of an optimized emulsifier blend, whereas the droplet size of olive oil-in-water emulsions was the smallest at the optimum HLB of the emulsifier blend. The

nonionic emulsifier reduced the particle size of mineral oil emulsions more efficiently than did that of olive oil emulsions. The nature of the dispersed phase, HLB of the emulsifier blend, or initial droplet size had no influence on the final stability of the emulsions. This difference from typical emulsion findings was attributed to the optimization of the emulsifier blend and other processing parameters.

De Vleeschauwer and Van der Meeren (1999) studied phospholipid-stabilized emulsions which typically have a poor stability, especially when prepared in the presence of electrolytes. These emulsions, made of soybean oil, were produced in a much more stable form using steric stabilizers along with the phospholipids. The steric stabilizers were surfactants from the Bilj series.

Rousseau (2000) describes food emulsions noting that fat is the oil in oil-in-water emulsions. It was observed that fat-in-water emulsions have similar properties and phenomena as oil-in-water emulsions.

Demetriades and McClements (2000) studied the influence of sodium dodecyl sulfate (SDS) on the flocculation of droplets in 20% soybean oil-in-water emulsions stabilized by whey protein by using light scattering, rheology, and creaming measurements. At low concentrations, the SDS concentrations were low enough to prevent depletion flocculation by surfactant micelles. In the absence of SDS, emulsions were prone to droplet flocculation. Flocculation led to an increase in emulsion viscosity, pronounced shear thinning behaviour, and accelerated creaming. When the concentration of surfactant was increased, the emulsion stability range shifted to different pH values.

Reiffers-Magnani et al. (2003) studied soya oil-in-water emulsions stabilized with whey and methylcellulose. It was found that below the phase-separation threshold, the creaming rate was faster than the one predicted by the Stokes' equation due to methyl-cellulose-induced depletion flocculation. Above the phase-separation threshold, the destabilization of the emulsion involved different mechanisms, depending on the type of emulsifier adsorbed at the oil-water interface. In the case of droplets stabilized with Tween 40, depletion flocculation led to a complete creaming of the fat globules. Phase separation led to the formation of two polymer-rich phases.

Palanuwech and Coupland (2003) studied confectionary-coating fat emulsions using Tween 20 and a polymeric emulsifier. Very small particles were generated by high energy input and formed more stable emulsions. The emulsions were subjected to cooling-crystallization cycles to test stability. It was found that the Tween 20 actually destabilized emulsions under some circumstances as this small surfactant interfered with the polymer at the interface.

Thanasukarn et al. (2004) studied palm oil-in-water emulsions with emphasis on stability at freeze-thaw points. The emulsifier type (Tween 20, whey protein isolate or casein) influenced the physical properties of the 20% hydrogenated palm oil-in-water stability. Stability was assessed by differential scanning calorimetry after the cooling-heating cycles and by measuring creaming and separation. Tween 20 emulsions showed the most destabilization with the temperature changes through the fat crystallization point. It should be noted that Tween 20 is a common ingredient in oil spill dispersants.

Klinkesorn et al. (2004) studied corn oil emulsions stabilized with maltodextrin and Tween 80. Stability was determined by measuring the height of the creamed oil in a test tube. Half-lives of the emulsions varied from about 100 to 150 hours and depended primarily on the concentration of the maltodextrin. Very high concentrations of maltodextrin were also detrimental to stability, but low levels increased stability significantly more than when no maltodextrin was added.

Cu and coworkers (2005a, 2005b) studied the influence of temperature, salinity, and pH on the stability of corn oil-in-water emulsions surrounded by one-, two-, or three-layer interfacial membranes. The interfacial membranes were composed of lactoglobulin, I-carrageenan, and phosphate buffers. Tertiary membranes provided better stability than double membranes which were better than single membranes.

3.4 Studies of Surfactant-stabilized Oil Emulsions

McClements (1994) studied n-hexadecane emulsions containing different values of Tween 20 using ultrasonic techniques and creaming measurements. McClements found that rapid creaming occurred at high surfactant concentrations of >7%. This was attributed to depletion flocculation caused by excess surfactant-forming micelles. This was evident in the ultrasonic signal which showed high scattering when this occurred.

Dickson et al. (1995) studied the osmotic pressure, rheology, and creaming of concentrated oil-in-water emulsions made from mineral oil, 1% surfactant, and with the addition of polysaccharide. Two different surfactants were used, Tween 20 and sodium dodecyl sulfate (SDS). The data on the studies show that there is a strong and complex relationship between creaming stability and rheological behaviour. The emulsions had a half-life of only a few hours without the addition of polysaccharide, which served to increase the viscosity of the continuous phase. With adequate polysaccharide, the stability increased greatly with only a few percent creaming in a number of days.

Hou and Papadopoulos (1996) studied the stability of a 3-way water-in-oil-in-water emulsion made from hexadecane as the oil and Tween 80 as the surfactant. The emulsions were formed using micro-pipettes and bringing the components directly into contact. Results were explained using a model for the interaction energy, van der Waals and Coulombic, between a single internal water droplet and the external aqueous phase, as well as between two internal water droplets. A key parameter in the model is the effective thickness of the adsorbed layer of surfactants which determines the net interaction energy.

Holt et al. (1997) studied the coagulation of toluene-in-water emulsions, stabilized by sodium hydroxide, in a glass micro-capillary using video-enhanced microscopy. The observation of doublets, transitory structures when droplets contact, was also performed. The lifetime of the doublets varied from about 1 to 10 seconds. The half-lives of the single droplets varied from about 5 to 15 hours.

Ho (1998) studied model hexane-in-water emulsions with a variety of ionic surfactants. The electrokinetic stability was monitored using ESA or electrokinetic sonic amplitude. It was found that ESA correlated strongly to stability. Surfactant concentration initially gave rise to an increase in the ESA. At higher concentrations, the ESA levelled off or even decreased with further increases in surfactant concentration. The type of surfactant also changed ESA, with ESA increasing with increasing alkyl chain length. More hydrophilic headgroups gave rise to lower ESA than did less hydrophilic ones.

Wiacek et al. (2001) studied emulsions formed from tetradecane and dialkyldimethylammonium bromides (DADMA) as stabilizers. They found that DADMA could act as emulsion stabilizers but that specific factors such as surfactant concentration, pH, temperature, and mixing time are critical to stable lifetime. Wiacek et al. (2002) also studied tetradecane-in-oil emulsions stabilized with the new nonionic surfactants, N-alkyl-[N, N-bis(3-lactobionylamido)propyl] amine, when N-alkyl was dodecane, hexadecane, or octadecane. Some of the emulsions were less stable when these surfactants were added. It was concluded that hydrogen bonding between the surfactant/alcohol and alcohol-water polar groups played an

essential role in emulsion stabilization. Zeta-potential was used as a critical measurement technique.

Dickinson and Ritzoulis (2002) studied the creaming and rheology of five tetradecane oil-in-water emulsions using sodium caseinate and an ionic surfactant, sodium dodecyl sulfate (SDS). They found that the presence of both SDS and sodium caseinate increases the overall stability with respect to creaming. Creaming removed half the oil at times ranging from a few minutes to a few hours, depending on the experiment. Excess SDS promotes fast destabilization through fast creaming as a result of unabsorbed surfactant micelles which promoted flocculation of the oil droplets. This behaviour was quite different from a previous study in which these authors found that a combination of caseinate, SDS, and Tween 20 systems reduced emulsion stability as indicated by fast creaming and shear-thinning rheology. Adding sodium chloride was found to increase the extent of non-Newtonian behaviour and increase the degree of creaming for SDS-containing emulsions. In contrast to this, the current system of SDS and sodium caseinate was relatively insensitive to salt content.

Dickinson and Ritzoulis (2002) note that factors other than interfacial phenomena can also affect the stability of an emulsion. These factors include the viscosity and visco-elasticity of the continuous phase, the volume fraction of the dispersed phase, the average size of the droplets, and the distribution of the droplet sizes. The authors also note that, for every emulsifying substance, three or four broad regimes of concentration can be envisioned. At low concentrations of the emulsifying agent, there is not enough agent to stabilize the emulsion. In this case, the emulsion may degrade through bridging flocculation and coalescence. The second concentration regime is one in which there is sufficient surface-active agent to provide effective steric stabilization. The third concentration regime is when there is enough surface-active material to promote the process known as depletion flocculation, which then destabilizes the emulsion. The fourth concentration regime, envisioned as only theoretical, is one in which the concentration of the emulsifier is so great that a gel formation takes place.

Jiao and coworkers (2002) studied three-way mineral oil-in-water emulsions (W:O:W) stabilized with Span and Tween surfactants. They noted that emulsion instability arises from the immiscibility of the dispersed and continuous phases. When the dispersed phase is broken into droplets, the surface free energy is increased. The increase in interfacial free energy causes thermodynamic instability of the dispersed phase, leading to droplet coalescence. Jiao et al. proposed that the dimpling effect of a microscope cover slide might be used as an accelerated stability test.

Al-Sabagh (2002) studied 13 nonionic surfactants to stabilize asphalt emulsions. The stability of the emulsions was determined by hatch-settling time, particle size analysis, and rheological characterization. The optimum stability of the oil-in-water emulsions was obtained with a surfactant HLB range of 10 to 13 with 70% asphalt as the dispersed phase. Surfactant mixtures were tested and it was found that a narrow range of HLB enhanced the stability of between 95 to 155 days. Tests of the carbon number in the surfactant showed that the increase in carbon number enhances the stability of the emulsions. Measurements show that the longer length of carbon chain increased the viscosity and the stability of the asphalt emulsions by hindering the coalescence rate. It is important to note that this is a closed system with only 30% water.

Horvath-Szabo et al. (2003) studied the emulsion stability of a sodium naphthenate system with toluene and water. It was found that adding heptane greatly reduced the stability of the system and resulted in a much reduced region of stability on a phase diagram.

Dickinson et al. (2003) studied the combination of ionic calcium and nonionic surfactant, Tween 20, on the visual creaming behaviour and rheology of n-tetradecane-in-water emulsions. A stability diagram was drawn based on the phase separation time, typically 48 hours. It was found that depletion flocculation may be induced by excess caseinate, excess surfactant, or a combination of both. The authors conclude that global stability behaviour can be understood in terms of the effect of ionic calcium on the nature of the adsorbed caseinate layer around the droplets and the size and state of aggregation of the non-adsorbed caseinate and on the ability of Tween 20 to displace caseinate from the surface of the emulsion droplets.

Kelley and McClements (2003) studied the stability of hexadecane-in-water emulsions using bovine serum and SDS surfactant, focussing on the thermal stability of these emulsions at elevated temperatures. Extensive droplet flocculation was observed only in emulsions held at 90°C and these emulsions creamed very rapidly. If added before heating, the SDS improved the high temperature stability, but did not do so if added after heating.

Michaut et al. (2004) studied multiple emulsions formed from tetradecane and Span 80 or poly(sodium acrylate) using rheology. The study showed that polymeric surfactant improved stability as it does not migrate to the droplet interfaces through the oil phase.

Kim and coworkers (2004) studied n-hexadecane-in-water emulsions stabilized by β -lactoglobulin at different pH. Droplet sizes doubled within a few hours and emulsions became destabilized after several hours. The effect of pH was measured and found to be critical to stability.

Fernandez et al. (2005) studied the stability of oil-in-water emulsions such as those used for lubrication in the copper-rolling process. Four parameters were measured: droplet size distribution, zeta potential, surface tension, and contact angle. Zeta potential measures the electrophoretic mobility of oil droplets in an applied electric field and indicates the droplet-to-droplet charge and thus emulsion stability. The experimental results show that the zeta potential is a main indicator of emulsion stability. For zeta potential (ζ) greater than -10 V, the emulsion is completely destabilized and is not suitable for reuse in copper-rolling.

Delahery and Rajagopalan (2005) studied the destabilization of metal-working fluids using a wavelength absorption of the fluid. This is basically a turbidimetric result. They compared this to conventional methods and found that the method yielded similar but more conservative results. The differences over 24 hours were about 50% in terms of creaming or oil left in the fluid.

Chen and Tao (2005) studied the stability of coal slurry and oil-in-water emulsions. The emulsion was prepared using sorbitan monooleate with the components in a colloidal mill. It was found that the emulsion stability increased with decreasing oil-to-water ratio, with the optimum at 1:1. Higher stirring intensity increased emulsion stability by up to 15 minutes, after which time it decreased.

Deng et al. (2005) studied the destabilization of oil emulsions from enhanced oil recovery with the intent of improving the separation of the emulsions. They found that the settling times were about a half-life of 40 minutes with a demulsification agent and about 90 minutes without a demulsifier.

Liu and McGrath (2005) studied a toluene-in-water emulsion stabilized with Triton-100. They found that initial energy input into the creation of the emulsions was critical in terms of stability and other factors such as droplet size. Creaming results showed that there were major differences in the stabilities of different types of emulsions formed. The microstructure of the emulsion dictated the stability and this in turn was dictated by a number of formation factors, especially the energy.

3.5 Studies of Stability of Crude Oil or Petroleum Emulsions

Zaki (1997) studied the emulsification of Geisum crude oil using Dodecyl benzene sulfonic acid sodium salt surfactant. The purpose was to find means to transport this crude oil via pipeline at a lower viscosity than the starting oil. The emulsions were relatively stable within 14 days only if the oil content was greater than 80% or conversely the water content was less than 20%. This has implications for oil dispersion at sea because the dispersions are always very dilute and therefore unstable.

Kang et al. (2000) studied the stability of crude oil emulsions with sodium naphthenate surfactants with a view to improving the recovery of secondary oil. Polyacrylamide was added as an additional stabilizer, which had a positive effect only at low surface pressures. The addition of alkali also affected stability. Half-lives of the emulsions varied from 60 to 120 minutes.

Shields et al. (2001) studied the creaming of weakly or depletion-flocculated kerosene-in-water emulsions. Given that the droplet diameter was less than 13 μm , it was found that the Stokes' equation described the emulsions. The emulsions were stabilized with nonionic surfactants of the alkyl and alcohol-ethoxylate types and ionic surfactants including sodium dodecyl sulfate and cetyltrimethylammonium chloride. The results showed that the emulsions were weakly flocculated unless additional surfactant was added, in which case the destabilization of the emulsions by flocculation was accelerated. Theoretical analysis of the emulsions showed that the electrostatic exclusion between micelles and droplets greatly increased the attractive reaction.

Torres and Zamora (2002) studied the emulsification of Pemex crude oil using laboratory systems with various impeller systems. Sixteen commercial surfactants were also used. It was found that the type of surfactant and mixing energy were important in the stability of the emulsions.

Pingus et al. (2002, 2003) studied the resurfacing of crude oil emulsions using a standard flask test method. Dispersant was pre-mixed with oil and placed on water in a test vessel. The test vessel was agitated on a moving table shaker. At the end of the shaking period, a settling period was allowed and then a sample of water taken. The oil in the water column was extracted from the water using a pentane/dichloromethane mixture and analyzed using gas chromatography. Test results are given in Table 2 and illustrated in Figures 9 to 12.

Several repeat runs were conducted enabling the calculation of variance, which ranged from 1 to 5%. The difference between the static and shaken runs was 8%. The difference between shaken and static results would be expected to converge over time as the curves generally appear to converge. The individual differences for each of the four experiments (ASMB and ANS with Corexit 9527 and Corexit 9500) are similar except that the average difference for the ASMB and Corexit 9500 is slightly lower. The data were correlated to provide more universal prediction of this phenomenon. It was found that the simplest equation for the shaken samples was $z = a + b \ln x + c \ln y$ and for the static samples was $z = a + b \ln x - c/y$. Z is the effectiveness at a time t in hours, x is the standard effectiveness value and y is the time in hours. Further generalizations of these equations yielded the following.

The equation for shaken samples is:

$$\text{Effectiveness at time (\%)} = -4 + 12 * \ln(\text{standard value}) - 5 * \ln(\text{time in hours}) \quad (1)$$

and for the static samples is:

$$\text{Effectiveness at time (\%)} = -53 + 13 * \ln(\text{standard value}) + 8 * (\text{time in hours}) \quad (2)$$

Table 2 Tests of the Resurfacing of Oil (Fingas et al., 2003)

ASMB - C9500			ASMB - C9527		
Time	Settling (%)	Mixing (%)	Time	Settling (%)	Mixing (%)
20 min	37.5	61.1	20 min	55.2	44.0
60 min	25.0	44.9	60 min	32.0	47.0
90 min	22.0	45.8	90 min	25.2	40.0
3 h	19.4	45.1	3 h	20.8	39.5
6 h	18.0	35.6	6 h	23.8	41.8
17 h	37.5	54.6	17 h	20.1	40.7
23 h	21.2	18.6	20 h	20.9	43.0
24 h	15.9	25.0	24 h	20.0	31.1
30 h	13.8	27.4	30 h	13.3	54.9
48 h	13.3	17.3	48 h	19.2	28.0
54 h	15.1	25.9	54 h	18.6	20.8
72 h	10.6	21.2	72 h	15.2	23.3
76 h	20.7	13.2	76 h	19.0	25.1
96 h	15.4	13.8	96 h	15.3	31.3

North Slope - C9500			North Slope - C9527		
Time	Settling (%)	Mixing (%)	Time	Settling (%)	Mixing (%)
20 min	49.2	33.1	20 min	34.5	35.5
60 min	28.3	42.4	60 min	26.2	41.4
90 min	25.1	52.8	90 min	20.5	51.1
3 h	16.9	38.9	3 h	19.2	51.6
6 h	14.6	45.8	6 h	13.9	51.4
17 h	9.5	14.5	17 h	17.6	63.2
20 h	10.4	27.2	23 h	15.6	57.3
24 h	10.5	24.8	24 h	18.8	32.5
30 h	10.3	20.5	30 h	17.1	22.5
48 h	7.6	17.7	48 h	10.9	29.1
54 h	5.0	16.7	54 h	17.6	35.5
72 h	9.0	15.4	72 h	18.3	25.3
76 h	9.3	17.2	76 h	18.1	31.3
96 h	7.8	15.5	96 h	18.0	28.3

Legend

- ASMB - Alberta Sweet Mixed Blend
- ASMB - Alberta Sweet Mixed Blend
- North Slope - Alaska North Slope crude
- Settling - measured after 10 min
- Mixing - measured after 10 min
- C9500 - Corexit 9500
- C9527 - Corexit 9527

The half-lives for the emulsions were: for Alberta Sweet Mixed Blend oil and Corexit 9500 and Corexit 9527 static conditions about 10 hours, and for shaken samples about 30 hours. For Alaska North Slope oil and the same dispersants, the half-lives were similar but appeared to vary more.

Yeung et al. (2003) studied the shear-induced coalescence of emulsified crude-oil droplets using a micro-pipette technique. They noted that crude oil droplets suspended in water possess negative surface charges which give rise to double-layer repulsive forces between the drops. According to conventional DLVO theory, the magnitude of this repulsion is more than enough to prevent coalescence of the droplets. Tests of this using the micro-pipette technique showed that this theory is correct when the droplets are brought together directly or head-on

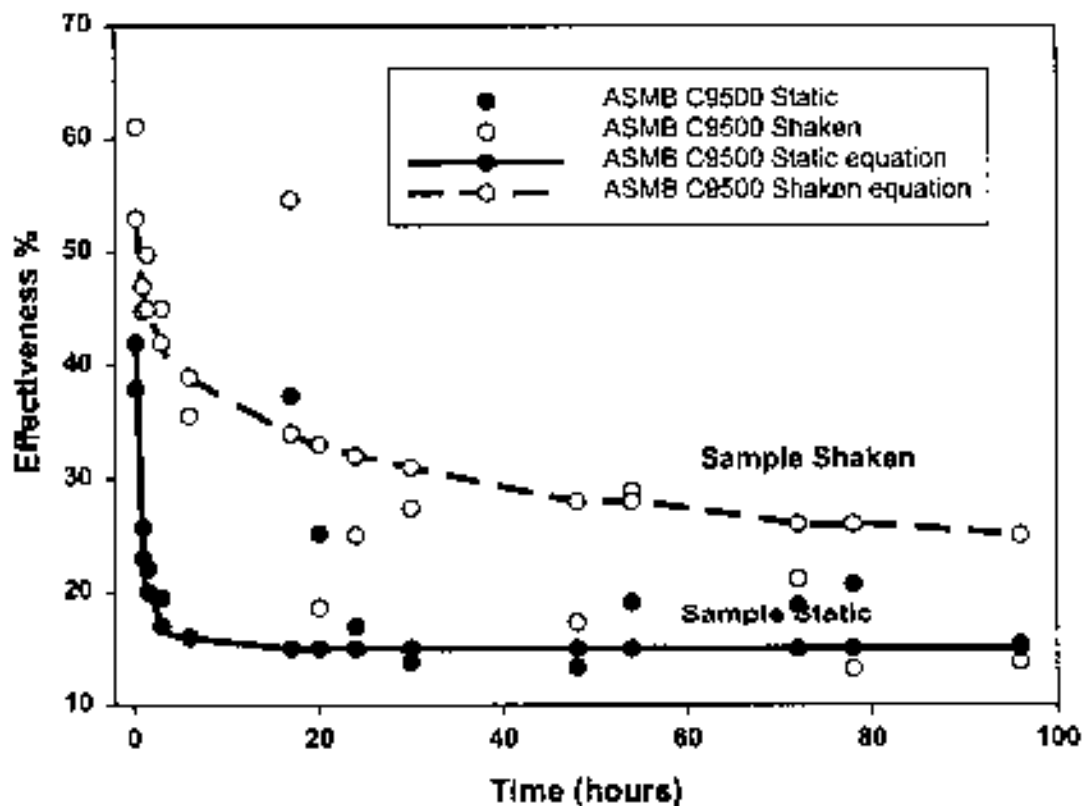


Figure 9 Effectiveness With Time - ASMB with Corexit 9500

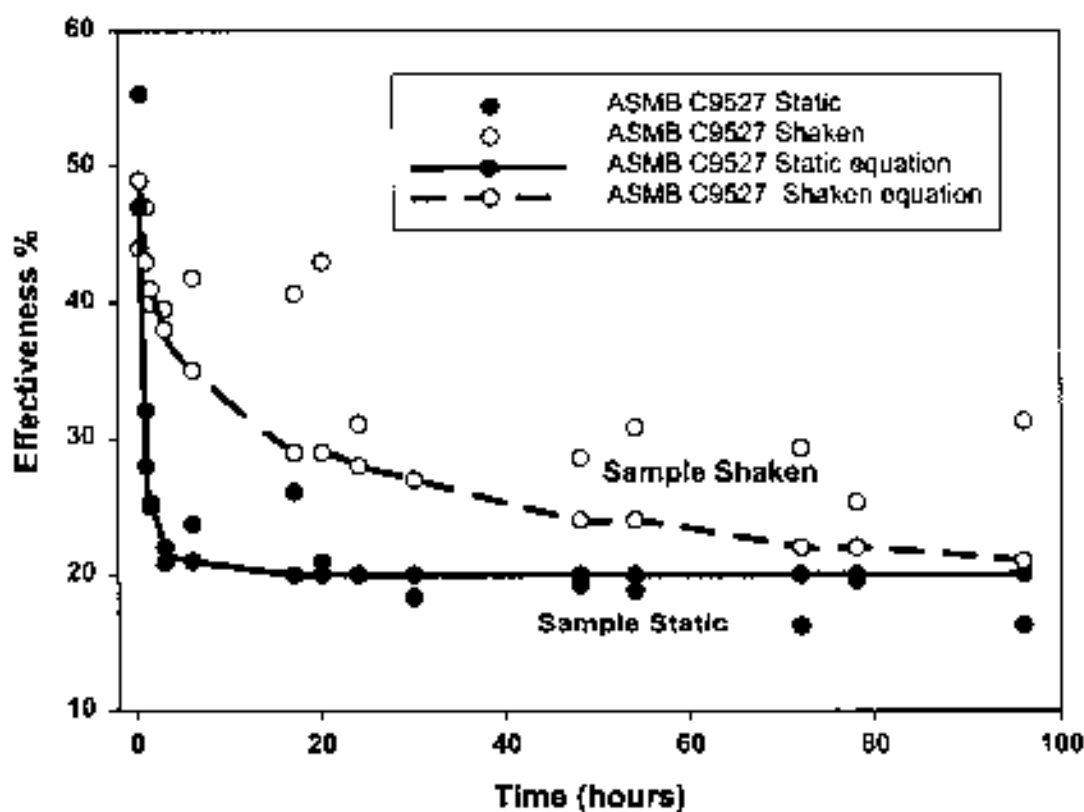


Figure 10 Effectiveness With Time - ASMB with Corexit 9527

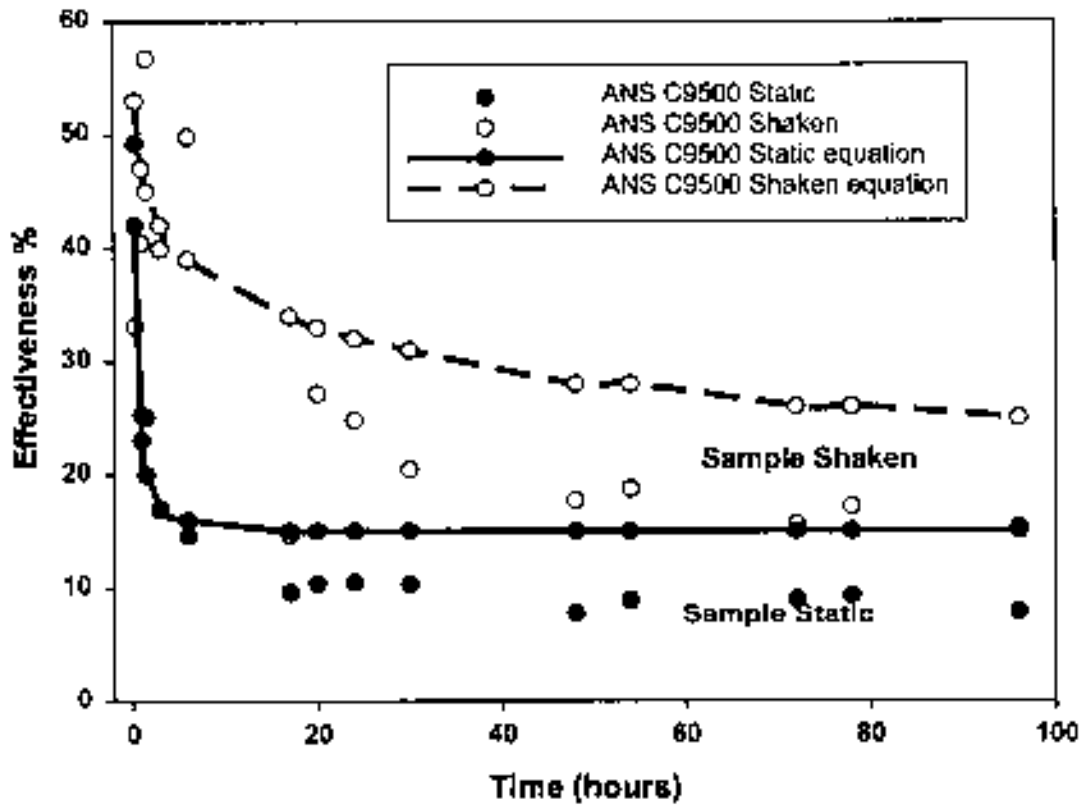


Figure 11 Effectiveness With Time - ANS with Corexit 9500

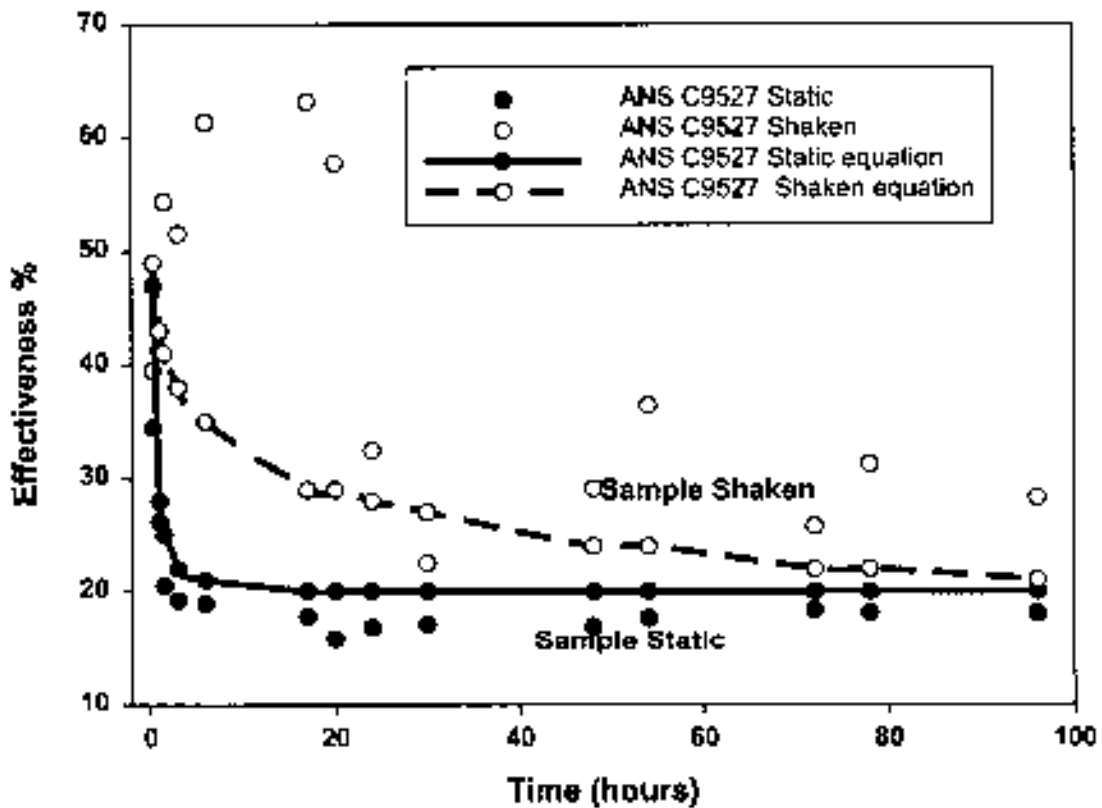


Figure 12 Effectiveness With Time - ANS with Corexit 9527

(Yeung et al., 2000). When two droplets are brought together indirectly or in an oblique fashion, however, the droplets will readily coalesce. The authors note that an oblique encounter must necessarily give rise to lateral relative motion or shearing between the droplet surfaces. They suggest that the charge distributions at the surface must be heterogeneous and thus, when droplets approach obliquely, the charges may be lower, allowing coalescence. Or stated another way, if repulsion across any given area between the two droplets was weak enough to allow an oil bridge to form across the water film, coalescence of the droplets would inevitably follow. This hypothesis of surface heterogeneity explains coalescence without invoking any additional colloidal interactions such as hydrophobic forces.

Xu et al. (2003) studied the stability of crude oil emulsions stabilized by interfacially active material also derived from the crude oils. Lifetimes varied from less than 10 seconds to over 1800 seconds. It was found that the aliphatic acids in particular decreased the stability of the emulsions.

Sterling et al. (2002, 2004) studied the coalescence of Arabian crude oil emulsions with the dispersant Corexit 9500. For the range of pH from 4 to 10 and salinity, 10 ‰, 30 ‰, and 40 ‰, the ζ potentials range from -3 to -10 mV. This potential would not be sufficient to produce significant resistance to coalescence. Coalescence kinetics of the premixed crude oil and dispersant were determined with a range of shear rates and salinity. It was found that increasing shear rate increases coalescence. Sterling and coworkers found that the dispersed oil fraction decreased with increasing coalescence and especially with time. The half-life extrapolated from the data implies that the half-life of the Arabian crude oil emulsion with Corexit 9500 dispersant was about 5 hours for a shear rate of 5 s^{-1} , about 4.5 hours for 10 s^{-1} , about 4 hours for 15 s^{-1} , and about 3.5 hours for a shear rate of 20 s^{-1} .

Schulz et al. (2004) studied water-diesel emulsions and used a procedure called INSEDEF to evaluate these emulsions. This procedure was deemed to be applicable to water/diesel emulsions although it was developed to characterize solid-liquid emulsions. The stability of the water-diesel emulsions was tested through programmed cooling and using the thermobalance component of the process.

Pang et al. (2004) studied the emulsification of petroleum waxes in a closed system. They found that optimal conditions were: amount of emulsifier 6 to 8%, temperature 85 to 95°C, high stirring velocity, and emulsifying time of 20 to 30 minutes.

3.6 Effects of Salinity, Temperature, and Dilution on Resurfacing

Menin and Wasan (1985) noted that almost all emulsions are more stable at lower temperatures, to a limit, and less stable at higher temperatures.

Clausse et al. (1999) studied the stability of water-in-oil and three-way emulsions noting that rapid changes in temperature have a strong destabilizing effect. Lower temperatures may in fact also destabilize emulsions by increasing water transport across the oil phase.

Sterling et al. (2002, 2004) studied the effects of salinity on chemically dispersed oil and found that there was little effect. Salinity had a limited influence on coalescence, but it was suggested that it had a greater influence on initial droplet formation than on subsequent droplet entrainment.

3.7 Measurement of Emulsion Destabilization

Several techniques are used to measure emulsion stability (Somasundaran et al., 2003). The most common is simply sample resolution or measuring the amount creamed or sedimented by volumetric techniques. Rheological methods have been used, particularly for concentrated

systems. There is a strong correlation between rheological properties such as viscosity and elasticity and stability in concentrated systems.

4. Physics of the Destabilization Processes

The overall forces and physics of the destabilization processes are illustrated in Figure 13.

4.1 The Basics

The basis for much of the physics and chemistry surrounding emulsion stability is that emulsions are not thermodynamically stable (Rosen, 1989; Walstra, 1996). One view of this is that two immiscible liquids are combined or one immiscible liquid is dispersed into another immiscible liquid. Since the interfacial tension between these two liquids will always be greater than zero despite the amount or type of surfactants, there is a force or energy leading toward destabilization. Furthermore, the interfacial energy is vastly increased by increasing the area between the two liquids through the process of increasing the number of droplets. This results in an energy imbalance that will tend to force the two media to separate.

Kinetic stability is another consideration when describing an emulsion. An emulsion is said to be kinetically stable when significant separation, usually considered to be half or 50% of the dispersed phase, occurs outside of the usable time. Therefore, if the time of use is one day, an emulsion with a half-life of more than one day may be considered to be usable. In food emulsions, this stability should be well past the stated shelf life. It should be noted, however, that food emulsions are poor examples for crude oil-in-water emulsions because their stability can be controlled in closed systems by adding enough surfactants and gelling the water media, thereby negating coalescence and suppressing surfactant loss.

The function of any emulsifying agent or surfactant is to stabilize (somewhat) an otherwise unstable system. The emulsifying agent does so by absorption at the liquid-liquid interface as an oriented interfacial film. This oriented film performs two functions: a) it reduces the interfacial tension between the two liquids and consequently the thermodynamic instability of the system resulting from the increase in the interfacial area between the two phases, and b) it decreases the rate of coalescence of the dispersed liquid droplets by forming mechanical, steric, and/or electrical barriers around them. The steric and electrical barriers inhibit the close approach of one droplet to another. The mechanical barrier increases the resistance of the dispersed particles to mechanical shock and inhibits them from coalescing when they do collide. When emulsions form, the emulsifying agents or surfactants reduce the amount of work required for formation.

Stability usually refers to the resistance of the droplets to coalescence (Rosen, 1989). Creaming, or standard gravity separation, was not considered to be destabilization in classical terms because it occurs with or without emulsifier stabilization. The classic destabilization processes were considered to be coalescence, flocculation, and phase inversion. The rate of coalescence was stated to be the only quantitative measure of emulsion stability. These factors have now changed to encompass broader areas as shown in the present review.

It has been found that the rate at which the droplets of a macroemulsion coalesce from larger droplets depends on a number of factors: the physical nature of the interfacial film, the existence of an electrical or steric barrier on the droplets, the viscosity of the continuous phase, the size distribution of the droplets, the phase volume ratio, and the temperature. These factors are dealt with in greater detail in this section.

The physical nature of the interfacial film is important. The droplets of dispersed liquid in an emulsion are in constant motion and frequently collide. If the interfacial film surrounding the two colliding droplets in an emulsion ruptures, the droplets will coalesce to form a larger droplet

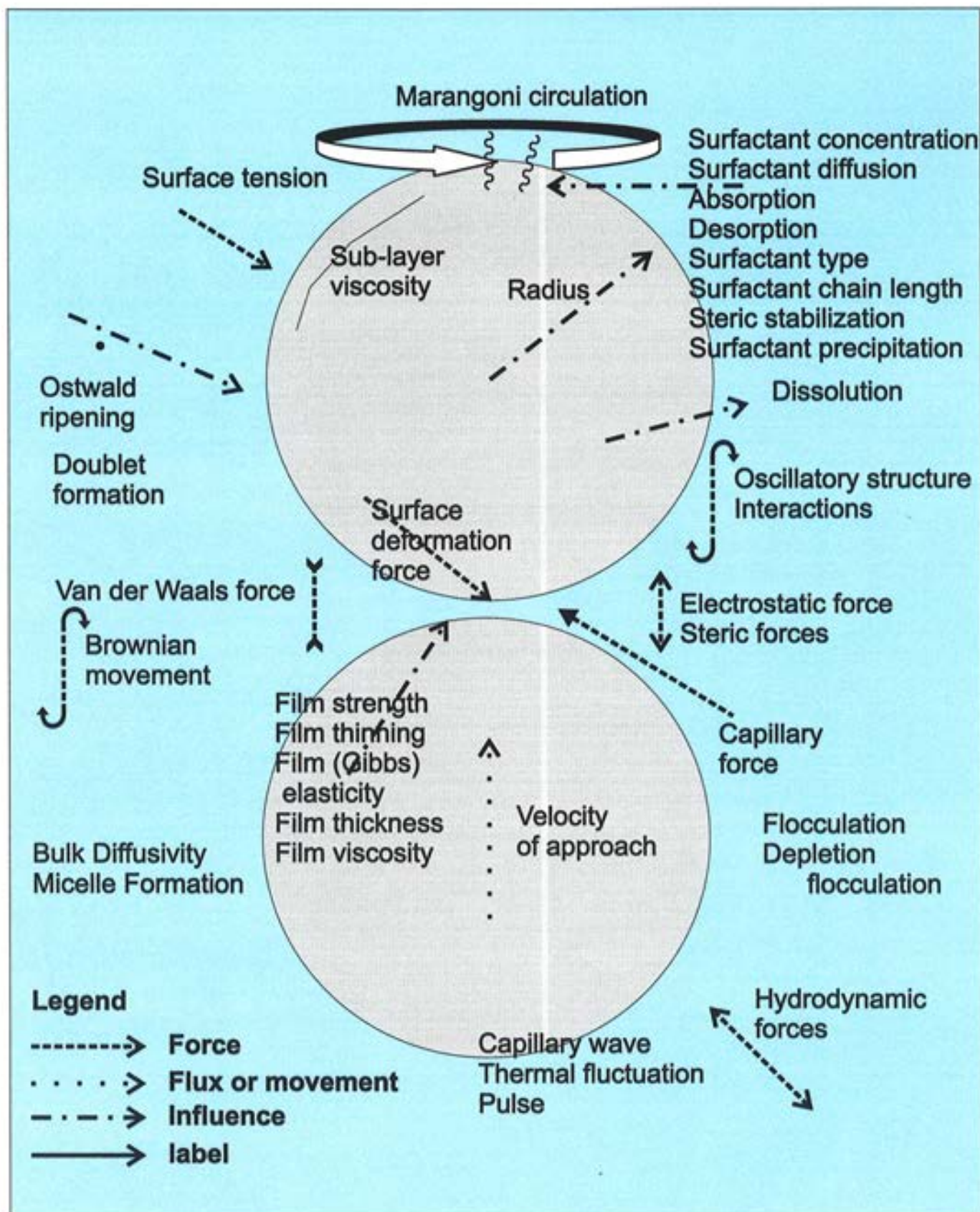


Figure 13 The Forces and Influences on Two Droplets Approaching Each Other.

and eventually the emulsion will separate and break. The strength of the film then becomes an important factor in emulsion stability. Highly purified surfactants tend to form weak interfacial films, whereas mixtures of different types of surfactants tend to form stronger films, although there is evidence that smaller surfactants displace larger ones at the interface. For this reason, mixtures of a water-soluble and an oil-soluble surfactant are often used in oil spill dispersants, e.g., a mixture of Span and Tween surfactants.

The presence of an electrical charge on the dispersed droplets can create an electrical barrier preventing two particles from closely approaching each other. While ionic surfactants are sometimes used in oil spill dispersants for this purpose, these surfactants will rapidly partition to the water phase in dilute systems such as at sea. Nonionic surfactants, such as those that typically constitute the bulk of oil spill dispersants, have a lesser charge and would pose a weak electrical barrier to coalescence.

The viscosity of the continuous phase is an important factor in dispersion stability. An increase in the viscosity of the continuous phase reduces the diffusion of the droplets and thus the frequency of collisions. This is given by the classic equation:

$$D = \frac{kT}{6\pi\eta r} \quad (3)$$

where D is the diffusion rate,

k is the Boltzmann constant,

T is the absolute temperature,

η is the viscosity of the liquid continuous phase, and

r is the radius of the droplets.

It is obvious from this equation that the diffusion occurs inversely to the viscosity of the continuous phase. This is very important for oil spill dispersion as the viscosity of the continuous phase is that of water and is in fact very low. Therefore, there is a high diffusion rate, high collision rate, and potential for coalescence. This contrasts with many food emulsions in which the continuous phase is deliberately rendered viscous to reduce coalescence and thus increase stability.

Another factor influencing the rate of coalescence of the droplets is the size distribution of the droplets. The smaller the range of sizes, the more stable the emulsion. The larger particles have less surface area for the volume and thus are more thermodynamically stable and tend to grow at the expense of the smaller droplets. As this process continues, the emulsion destabilizes. An emulsion with a fairly uniform size distribution is more stable than one with a wide distribution of particle sizes. This factor is also significant when discussing oil spill dispersants. Oil spill dispersants have wide distribution of droplet sizes because of the nature of crude oil and the wide distribution of compounds in it (NAS, 2005). Oil spill dispersants are therefore less stable by nature than some other types of emulsions.

The phase-volume ratio of the dispersed phase is important in closed systems in which the amount of the dispersed phase rises to the volume of the continuous phase. In such cases, phase inversions could take place and an oil-in-water emulsion could invert to a water-in-oil emulsion. This is not significant in the case of oil spill dispersants at sea.

Temperature is an important factor in emulsion stability as a change in temperature causes changes in interfacial tension between the two phases. Temperature can also cause differential changes in other factors such as the relative solubility of the surfactant in the two phases and in the diffusion in the system. Emulsifying agents are usually most effective when near the point of

minimum solubility in the solvent in which they are dissolved because at this point they are most surface-active. Since the solubility of the emulsifying agent usually changes with temperature, the stability of the emulsion also changes with temperature. The classic equation to describe this is by Smoluchowski (Rosen, 1989):

$$\frac{dn}{dt} = 4\pi D r n^2 \quad (4)$$

where $\frac{dn}{dt}$ is the rate of diffusion-controlled coalescence,

D is the diffusion,

r is the collision radius (distance between centres when coalescence begins), and

n is the number of particles per cm^3 .

Combining this equation with diffusion equations yields an expression for the rate of coalescence of particles and thus for the stability of the emulsion:

$$\frac{d\bar{V}}{dt} = \frac{4}{3} \frac{V k T}{\eta} e^{-E/kT} = A e^{-E/kT} \quad (5)$$

where $\frac{d\bar{V}}{dt}$ is the rate of the coalescence of droplets or the stability of the emulsion,

V is the volume of the dispersed phase, e.g., volume per unit volume,

k is Boltzmann constant,

T is the absolute temperature,

E is the energy barrier to coalescence,

η is the viscosity of the liquid continuous phase, and

A is the collision factor as defined by the left portion of the equation.

The forces between particles or droplets are an important physical consideration in describing stability (Rosen, 1989). The stronger the force between particles, if opposite sign, the greater the stability of an emulsion. These forces might be considered to be of four types: soft or electrostatic forces, hard sphere, van der Waals, and steric forces.

The soft or electrostatic forces and van der Waals interparticle forces are described in the well established theory of the stability of dispersions by Derjaguin and Landau (in 1941) and Verwey and Overbeek (in 1948) and this theory is thus now called the DLVO theory. The theory presumes a balance between the repulsive and attractive potential energies of interaction between the dispersed particles or droplets. Repulsive interactions are due to either the similarly charged electrical double layers surrounding the particles or to solvent-particle interactions. Attractive interactions are believed to be mainly due to the van der Waals forces between particles. For dispersion to occur, the repulsive forces must be larger than the attractive forces.

The potential energy of attraction (in a vacuum) was given by Hamaker (developed in 1937) as:

$$V_a = \frac{-Aa^2}{12H} \quad (6)$$

where V_a is the energy of attraction,

A is the Hamaker constant,

a is the radius of the particle or droplet being considered, and

H is the distance between the surface of the particles.

For liquids, the A is replaced by A_{eff} or the effective Hamaker constant is an average of the constant for the particles and the dispersion medium.

The repulsion energy for a relatively thick double layer can be given by (Rosen, 1989):

$$V_r = \frac{\epsilon_r a^2 \Psi_0^2}{2} (1 + e^{-\kappa H}) \quad (7)$$

where V_r is the potential energy of repulsion,

ϵ_r is the dielectric charge of the dispersing liquid,

a is radius of the droplets or particles,

Ψ_0 is the surface potential of the droplets,

k is Boltzmann constant,

H is the distance between the two particle surfaces, and

R is the separation distance between the two particles to their centres.

This changes for thin electric layers and large particles as (Rosen, 1989):

$$V_r = \frac{\epsilon_r a^2 \Psi_0^2}{R} e^{-\kappa R} \quad (8)$$

where factors are identical to equation (7).

This shows that the repulsion force is much greater for a thick layer and smaller droplets.

These relationships can also show that, for certain situations when the layer is strong but repulsive forces are not overwhelming, coalescence will not occur, but flocculation is a highly likely scenario.

Energy considerations can be used to calculate stabilities for coalescence and flocculation. A simple comparison of rate constants can be used to describe stability (Rosen, 1989):

$$W_{st} = \frac{K_a}{K} \times e^{V_{bar}/kT} \quad (9)$$

where W_{st} is the stability of the emulsion,

K_a is the rate for diffusion-controlled coalescence,

K is the rate of slow coalescence due to an energy barrier,

and the remainder of the terms represent the energy barrier

where V_{bar} is the energy barrier to coalescence,

k is Boltzmann constant, and

T is the absolute temperature.

The terms in equation (9) can be described by plotting the stability (W_{st}) against the

concentration of the added surfactant to show the energy barrier to coalescence. Alternatively, the rate constant (K) can be determined from the slope of the plot of the log of change in diffusion in time versus the log of the concentration of added surfactants.

Rosen (1989) notes that the DLVO theory has limitations. The effect of the stability of an oil-in-water dispersion is limited to the effect of the surfactant on the surface potential of the dispersed particles, the effective Hamaker constant, the ionic strength of the dispersing liquid, plus many other factors. Since surfactants are used at low concentrations, the main effect of ionic surfactants would be expected to be on the surface potential of the dispersed droplets. While this is observed to a certain extent experimentally, Rosen notes that the situation is in fact much more complicated than this. Furthermore, the DLVO theory does not cover nonionic surfactants.

Rosen notes that, while the DLVO theory may be considered useful in predicting the effect of ionic surfactants to aggregation, it does not lead to a full understanding of the effects of surfactants on the stability of dispersions. The following other factors must also be considered. Absorption of surfactants to larger than colloidal sizes, which is the case with oil dispersions, may change the contact angle that these make with the continuous phase liquid, e.g., the water. Secondly, surfactants that have long chains or are polymeric may form non-electrical steric barriers to coalescence or flocculation. Thirdly, in liquids of lower dielectric constants, the electrical barriers may indeed be absent. A fourth item noted is that there is no current means of measuring the electrical barrier posed by a dispersed droplet with surfactants, which is called the Stern layer. Zeta potential, which can be readily measured, is often represented as an estimate of the potential of the Stern layer. The Zeta potential, however, is actually the potential at the plane of the shear or the distance from the charged surface (Stern layer) where the solvated droplet and solvent move with respect to each other.

An important source of stability for emulsions is the steric barriers produced when portions of the surfactant absorbed at the droplet interface extend into the liquid phase and then interact with each other. These interactions result in greater emulsion stability than with smaller surfactants, but smaller dispersants may displace larger ones.

4.2 Interfacial Tension Approaches to Stability

Another classical engineering approach to studying emulsion stability has been to use concepts relating to interfacial tension (Friberg and Yang, 1996). This begins with the assumption that the thermodynamic energy of a droplet emulsified in another fluid can be ascribed to the interfacial energy or tension between the two liquids. This is an over-simplification as shown in Section 4.1 where several other considerations are summarized. If it assumed, however, that all the forces reside in the concept of interfacial surface tension, then it can be assumed that the effect of the surfactant is to lower the interfacial tension to the point at which the energy difference of the interfacial tension is very low. If the interfacial tension of the droplet is close to that of the continuous phase or dispersing liquid, then an emulsion is possible. Stability is achieved if the interfacial tension of the droplet to the dispersing phase is less than zero, although this never occurs.

The condition for emulsion formation then becomes:

$$\gamma_{o,w} \leq 0 \quad (10)$$

where $\gamma_{o,w}$ is the interfacial tension of the oil droplet and water.

But since this rarely or never occurs, the condition is typically set to a value such as 10^{-2} to 1, varying with the author's opinion (Friberg and Yang, 1996). It should be noted that the

interfacial tension for most crude oils to sea water is about 25 to 30 mN/m.

An important part of the interfacial concept is that the contact angle a droplet of liquid a makes with liquid b can be described as a function of the interfacial tension.

The condition for equilibrium (stability) can be given by (Friberg and Yang, 1996):

$$\gamma_{a/d} = \gamma_{w/d} + \gamma_{a/w} \cos\theta \quad (11)$$

where $\gamma_{a/d}$ is the interfacial tension between air, the droplet, or oil-air.

$\gamma_{w/d}$ is the interfacial tension between water and the droplet or oil-water,

$\gamma_{a/w}$ is the interfacial tension between air and water or water-water, and

θ is the contact angle between the oil and water.

Substituting the typical values for crude oil (40 for oil-air, 30 for oil-water) and for water-air (70) interfacial tensions, we see that the cos of θ should be close to 0 to have a stable emulsion

4.3 Tadros

Tadros (1983, 2004) reviewed the long-term stability of emulsions, particularly the application of rheology to studying stability. Tadros reviews the procedures for studying stability of emulsions in the long term but performing the evaluations on an accelerated basis, which are:

1. subjecting the emulsion to temperature cycling;
2. applying centrifugal forces to detect the separation; and
3. subjecting the emulsion to vibration and investigation by microscopy.

Rather than these methods, Tadros suggests the use of rheological methods, which can include:

1. steady-state shear stress rate measurements;
2. constant stress (creep) measurements using a constant stress instrument; and
3. dynamic (oscillatory) measurements carried out on a constant strain instrument.

Tadros describes several breakdown mechanisms:

1. creaming or sedimentation, both by gravity forces;
2. flocculation caused by van der Waals attraction when there is not enough repulsion between the droplets;
3. Ostwald ripening caused by the difference in solubility between the small and large droplets;
4. coalescence induced by thinning and disruption of the liquid film between droplets; and
5. phase inversion whereby the disperse phase and medium interchange.

Creaming or sedimentation is simply caused by gravity. If the density of the oil is lighter than that of water, it will rise and if the density of the oil is greater than that of water, it will sink. This occurs regardless of surfactant stabilization, which simply changes the rate at which it occurs, depending on the many factors described in this report.

Flocculation of emulsions may occur when the van der Waals attractive energy exceeds the repulsive energy. Flocculation could be considered to be 'weak' or 'strong'.

Ostwald ripening or disproportionation may occur when the solubility of the oil is significant. The small droplets with higher solubility than the larger ones tend to dissolve on storage and become deposited on the larger ones.

Two distinct instability processes may be distinguished for emulsion systems: coalescence and phase inversion. Coalescence results from the thinning and disruption of the liquid film between the droplets with the ultimate joining of these droplets. Finally, some oil separation can

be observed. Phase inversion involves the changing of the disperse and medium phase. The disperse medium forms the droplets and the dispersed droplets form the continuous phase. In other words, the oil-in-water emulsion becomes a water-in-oil emulsion.

Tadros assesses creaming or sedimentation mathematically. Creaming or sedimentation occur primarily when the particle size is above 100 nm and the difference in density of the oil and water is greater than about 0.1 g/ml. At this point, the particles will exceed the Brownian diffusion physics and thus will cream or sediment. It should be noted that Brownian motion is important in determining the fate of emulsions. Pagnaroni et al. (2005) studied the Brownian dynamics of systems and conducted simulations of the compression and expansion of monolayers adsorbed at a planar interface. They found that the preference of one type of surfactant depends on the dynamics of the system.

The rate of creaming or sedimentation of very dilute solutions follows Stokes law (Tadros, 2004):

$$v_s = \frac{2}{9} \frac{R^2 \Delta\rho g}{\eta_w} \quad (12)$$

- where v_s is the rising or sedimentation velocity of the oil droplet,
- R is the particle radius,
- $\Delta\rho$ is the difference in density between the oil droplet and water,
- g is the gravitational constant, and
- η_w is the viscosity of the medium or water in this case.

For more concentrated solutions in which the volume fraction is between about 0.1 and 0.2, the rate of creaming or sedimentation is reduced below Stokes rate:

$$v = v_s (1 - 6.55\phi) \quad (13)$$

- where v is the adjusted oil rising/sedimentation velocity,
- v_s is the rising or sedimentation velocity of the oil droplet calculated using the Stokes' equation above, and
- ϕ is the volume fraction that the oil is of the total volume.

If the volume fraction is 0.1, then the rise rate is reduced by approximately 65%.

Several methods can be applied to assess the creaming or sedimentation of emulsions. One common method is to use graduated cylinders and observe the creaming fraction directly. The turbidity of the emulsion can be measured by optical methods. The density of the emulsion has been measured using ultrasonics or in some cases information on droplet size and distribution have been used.

Emulsion flocculation in dilute solutions can be measured by measuring the turbidity as a function of time:

$$\tau = A n_0 (V_0 + 2n_0 k t) \quad (14)$$

- where τ is the rate of flocculation,
- A is an optical constant,
- n_0 is the number of droplets at the start of the experiment,

V_d is the volume of the droplets,
 k is the rate constant of flocculation, and
 t is the time.

Ostwald ripening can be assessed by:

$$\omega = \frac{d}{dt} (r_c^3) = \frac{8}{9} \frac{DS_{c,m}V_m}{RT} \quad (15)$$

where ω is the Ostwald ripening rate,
 r_c is the critical radius of a droplet,
 D is the diffusion coefficient of the disperse phase in the continuous phase,
 $S_{c,m}$ is the particle size with the largest radius,
 V_m is the molar volume of the dispersed phase,
 R is the gas constant, and
 T is the temperature.

This equation can be used simply to evaluate Ostwald ripening by plotting r^3 versus t to give a straight line from which the rate of Ostwald ripening can be calculated.

The rate of coalescence can be measured by following the droplet number (n) or average droplet size (d) as a function of time. Since the driving force for coalescence is the thinning and disruption of the liquid film between the droplets, the rate follows a first order kinetics which can be given by:

$$n = \left(\frac{n_0}{K_c}\right) (1 - \exp(-K_c t)) \quad (16)$$

where n is the droplet number or average droplet size,
 n_0 is the initial droplet number, and
 K_c is the rate constant of coalescence.

Phase inversion is the fourth mechanism by which Tadros describes destabilization processes. This has not been noted in open systems such as would be the case for oil spill dispersions. Tadros distinguishes between the following two processes: catastrophic phase inversion induced by the volume increase in the disperse phase and transition produced by changing temperature and/or adding electrolyte.

4.4 Wasan's Theory on Oscillatory Structural Forces (OSF)

Wasan et al. (2004) discuss the stability of macro-dispersions such as emulsions and summarize an additional force that stabilizes or destabilizes emulsions, that of micelles and particle structuring and layering in the confined space between two larger droplets.

Wasan et al. point out that, although the classical DLVO approach is useful, additional forces are needed to explain interactions. In the classical DLVO approach, the properties of the dispersion medium can be characterized by such parameters as dielectric permittivity or shear viscosity coefficient, both conveniently described macroscopic parameters. The DLVO approach on the microscopic level is to describe the reaction between droplet pairs using two forces: the van der Waals forces, as described by the Hamaker theory (Coons et al., 2005), and the electrostatic force as described by the Debye-Hueckel theory.

Several authors have noted that some other interactions may be overlooked by the DLVO theory. One of these is the mean force due to the volume exclusion effect in a many-body system.

In a many-body system, the interactions between two particles or droplets are different from the interactions of two particles/droplets alone in a free space. This difference is due to the indirect interactions through the many other particles or bodies in the system. Thus in a many-body system, the apparent interaction between two droplets is affected by the many other droplets or the collective behavior of the system. The basic feature of such a force or system is that the force is concentration-dependent and diminishes as the concentration decreases.

Wasan et al. (2004) called this new force the volume exclusion effect. This effect brings an extra attractive force to the interaction of particles or an overall emulsion depletion effect. It can be viewed on the physical basis of a case where there is a polydisperse system, or one that has a wide variety of droplet sizes, such as is true in the case of crude oil-in-water systems. If two large droplets or particles are in a colloidal liquid (colloidal implies small droplets or particles), and the separation distance between the two large particles is smaller than the diameter of the colloidal particles, then there is an attractive force between the two particles because of the osmotic pressure. This would result in coalescence or flocculation, thus depleting the emulsion. Some researchers have, in fact, estimated the potential of this depletion force when the size ratio between particles is large and the suspension is dilute.

Wasan et al. (2004) noted that some researchers suggested that this depletion force would cause phase separation in a mixture of colloidal particles. In fact, such separation has been noted in several different types of systems in several experiments. It is now considered a well-documented phenomenon. A force estimation equation has been developed for the potential of the mean force between two hard-sphere particles immersed in a fluid of small particles:

$$U_i = -kT \ln g' \quad (17)$$

- where U_i is the force potential,
- k is the universal gas constant,
- T is the temperature, and
- g' is the radial distribution function.

The oscillatory structural force (both attractive and repulsive) becomes apparent when small colloidal particles are confined in the gap between two large particles. When the gap between two suspended larger particles is of the order of several colloidal particle diameters, the colloidal particles in the gap interact with the large droplets as a result of Brownian forces. The forces induce ordering among the particles and this order propagates over several particle diameters. In the case of a film, the structured regions near the two opposing surfaces overlap, giving rise to the oscillatory structural force. This long-range structure induces a repulsive structural barrier that helps prevent the large particles from flocculating or coalescing. When the separation distance between two larger particles is smaller than the diameter of the colloidal particles, a net attractive force occurs between the two large particles as a result of the difference in osmotic pressure between the bulk and confined regions of the colloidal system. Wasan et al. (2004) point out that the effective interaction between two large particles is found to be oscillatory with a period of oscillation equal to the effective size of the colloidal particles.

The structural stabilization barrier is high when the concentration of the small or colloidal particles is high and the particle layer forms between the larger particles. The emulsion is considered to be stable. When the concentration of colloidal particles is low, the stabilization barrier is much less and flocculation or coalescence occur. The range of the structural and depletion forces is of the order of several diameters of colloidal particles (5 to 100 nm) and operates over scale lengths far greater than DLVO scale lengths which are less than 5 nm. These forces have therefore greatly influenced emulsion stability.

Particle size is an important factor in the oscillatory structural force. If polydispersity exists, as it does in a crude oil-in-water emulsion, then the emulsion may not be very stable. Theoretical study shows that a 30% polydispersity decreases the structural barrier of the oscillatory structural force by a factor of 3. Wasan et al. (2004) suggest that a simple way to destabilize an emulsion is to add a small amount (for example only about 1% would work) of larger particles. It is significant to note that crude oil-in-water emulsions would have such large size distributions.

Wasan et al. (2004) studied the phenomenon using latex particles of small and large sizes. A further study was performed using food emulsions. Another study using dodecane and an ionic solvent showed that the emulsion was more stable at a concentration of 4% of surfactant than at 8 % and at 1% surfactant. These emulsions had a mean droplet size of 1.2 μ with a polydispersity of 35%. It is important to note that in this dodecane-in-water emulsion the surfactant was in the water. The authors noted that the addition of more surfactant increased the micellar concentration of surfactant and this increased the polydispersity of the emulsion. According to the oscillatory structural force theory, this in turn decreased the stability of the emulsion and the emulsion also began to flocculate because of the higher micelle content.

4.5 Applicability of the Stokes' Equation

The Stokes' equation describes the rising of droplets as a function of particle size:

$$s = \frac{2\Delta\rho g a^2 F(\Phi_v)}{9\eta} \quad (18)$$

where s is the rise rate,

$\Delta\rho$ is the difference in density between the disperse and droplet phases,

g is the gravitational constant,

a is the droplet radius,

$F(\Phi_v)$ is a volume-dependent correction factor and is 1 for dilute solutions, and

η is the difference between the viscosity of the disperse and droplet phases.

The equation is often simplified to (Friberg and Yang, 1996; Walstra, 1996):

$$s = \frac{2\Delta\rho g a^2}{9\eta} \quad (19)$$

where the substituents are the same as above.

Tadros (1983) noted that the Stokes' equation may not be as useful as calculating the centre of mass of an emulsion, or mass rate of creaming, which he gives as:

$$v = \sum_i \frac{8\pi g n_i a_i^3 \Delta\rho}{27\eta_0 V} \quad (20)$$

where v is the velocity of the centre of mass of the emulsion,

g is the gravitational constant,

n_i is a particle of a given size,

a_i is the particle radius,

$\Delta\rho$ is the difference in density between the disperse and droplet phases,

η is the oil viscosity, and

V is the volume of the dispersed phase.

Reiffers-Magnani et al. (2000) found that the Stokes' equation did not accurately predict the creaming of a soybean oil emulsion due to depletion flocculation.

Shields et al. (2001) studied diesel-in-water emulsions stabilized with ionic and nonionic surfactants and found that the Stokes' equation was applicable to droplets less than 15 μm in size.

4.6 The Urbina-Villalba Approach to Emulsion Stability Simulations (ESS)

Urbina-Villalba (2004) and Urbina-Villalba et al. (2005) developed a simulation procedure for emulsion stability. The simulation takes into account the forces and interactions of particles. The ESS displacement of a given particle during a period of time is the result of two contributions, the thermal interaction of the suspended particle with the solvent and the average diffusion of the particle. The thermal interaction of the particle with the solvent is modelled using a random walk with a Gaussian distribution with zero mean. The particles may aggregate and also coalesce as a result of Brownian motion and their own interaction forces. In the case of oil-in-water emulsions stabilized with ionic surfactants, the repulsive barriers between drops are the results of electrostatic repulsion.

Equations founded on Hamaker (Coons et al., 2005) and Sader are used to develop a model of the charge interaction between particles (droplets). The equations are used in a computer program to simulate emulsion stability. Flocculation and stability simulations are performed and presented in the paper and compared to empirical results. It is claimed that the ESS model provides an insight into the stability of emulsions by allowing the effects of drop size, different surfactants, etc. to be examined.

Urbina-Villalba and Garcia-Suere (2001) also used a modified Brownian dynamic to simulate the evolution of oil/water emulsions. The emphasis is on the competition between stabilization by surfactants and coalescence. The study shows that, if the surfactant concentration is low, droplets will have insufficient surfactant to prevent coalescence. Mixing time is important to allow surfactant distribution over the droplets formed. The meso-equilibrium time is defined as the time to achieve minimum stability. It was found that the log of the meso-equilibrium time is directly proportional to the log of surfactant concentration. Several surfactants show meso-equilibrium times of 182, 54, and 0.1 seconds with hexane in water. Higher times might be shown in different systems. Because of these factors, calculations show that the number of droplets in a system declines at an exponential rate with time.

4.7 The Standard Kinetics Approach to Emulsion Stability

Standard kinetics can be used to describe emulsion stability (Lye and Stuckey, 1998). If the stability of a given emulsion can be described as being first-order, that is by the concentration of the starting product alone, then the reaction can be described by:

$$\frac{V_c(t)}{V_c(0)} = \exp(-kt) \quad (21)$$

where $V_c(t)$ is the volume of the dispersed phase at time t .

$V_c(0)$ is the concentration of the dispersed phase at time 0, or starting concentration,

k is the first order rate constant, and

and t is the time elapsed.

The half-life of the emulsion can be given by:

$$t_{1/2} = \frac{\ln 2}{k} \quad (22)$$

where $t_{1/2}$ is the half-life of the emulsion.

4.8 The Lifshitz, Slezov, and Wagner Theory of Ostwald Ripening

The Lifshitz, Slezov, and Wagner (LSW) theory of Ostwald ripening has been tested against several model systems (Taylor, 1998). It is generally conceded that this is the best available model to describe Ostwald ripening, although it may result in differences up to a factor or 2 to 3 from observed values (Taylor, 1998). The development of the LSW value is complicated, however, one end result is a description of the aging rate:

$$\omega = \frac{dr_c^3}{dt} = \frac{4}{9} \alpha = \frac{8Dc_s \gamma M}{9\rho^2 RT} \quad (23)$$

where ω is the aging rate, the rate of increase of the cube of the critical radius.

r_c is the critical radius at which the rate of change of droplet radius is zero, that is the droplet is in equilibrium with the bulk phase - at this point all droplets below this radius will decrease in size and above this size, will grow as a result of Ostwald ripening.

t is the time at the point of consideration, and

$$\alpha \text{ is rate fraction or: } \alpha = K \frac{Dc_s}{\rho} \quad (24)$$

where K is the rate constant of an Ostwald ripening situation.

D is the diffusional flux of the soluble components.

c_s is the bulk solubility of the oil, and

ρ is the viscosity of the oil.

γ is the interfacial tension between the oil and the water.

M is molar mass of the oil.

R is the universal gas constant, and

T is the temperature in Kelvin.

4.9 Kinetic Approach to Brownian and Gravitational Coagulation in Dilute Emulsions

Dukhin and Sjöblom (1996) studied the kinetics of Brownian and gravitational coagulation in dilute emulsions. They note that past work was focussed on concentrated systems, whereas kinetics predominate in dilute systems. It is noted that creaming, Brownian, gravitational, and orthokinetic (shear) flocculations control the evolution of the droplet size distribution. Four components are necessary to quantify the emulsion kinetics: forces dictating droplet movement and interaction, droplet loss mechanisms and their rate, population balance equation, and floe structure theory such as fractal theory.

The most general and exact approach in emulsion kinetics is achieved by using droplet size distribution. The time and space dependence of droplet size distribution can be established by the solution of the population balance equation. Dukhin and Sjöblom (1996) suggest that the droplet size balance achieved in aerosol systems should be applied to dilute aqueous emulsions. The main task in elaborating mathematical modeling of the dilute emulsion kinetics is the derivation of the kernels of the particle distribution equations. Later it is shown that reliable kernels for particle balance equations are available for rapid flocculation but not for slow flocculation.

Kukhin and Sjöblom (1996) show that the collision efficiency between droplets can be shown to be:

$$E_{12} = \left(2 \int_2^{\infty} \frac{\exp(U_{12} / kT)}{s^2 G} ds \right)^{-1} \quad (25)$$

where E_{12} is the collision efficiency between a particle designated as 1 and another particle designated as particle 2. (It is important to note that the inverse of E_{12} is the stability ratio.)

U_{12} is the velocity between droplets,

k is Boltzmann constant,

T is the absolute temperature,

s is the interparticle distance, and

G is the hydrodynamic interaction parameter. For many systems it could be taken as 1.

In an earlier work, Shulepov et al. (1995) proposed to separate the collision efficiency and the interparticle attraction as a function of the degree of electrical charge. They then proceeded to develop models for low electrical charge and high electrical charge situations. They noted that this resulted in quite different results than when using static models only, such as the base DLVO theory.

There is a lack of experimental data for the rate of droplet loss in emulsions, particularly as it relates to rapid flocculation. Dukhin and Sjöblom (1996) used rapid coagulation theory to focus on rapid Brownian flocculation in monodisperse suspensions. The collision process is similar to that of emulsions. The rate of loss of droplets of intermediate dimensions is determined by simultaneous action of Brownian movement and gravitation. This regime corresponds to a Peclet number on the order of 1. A comprehensive theoretical description of the interaction and description of interaction in this regime is lacking. A quantification of the flocculation rate in the secondary minimum is achieved only by looking at van der Waal's forces at large distances. The approach to deal with this is to define collision efficiencies of flocculation in the primary and secondary minimum as being the same.

Dukhin and Sjöblom (1996) note that for very small particles (not relevant to oil-in-water emulsions), the creaming velocity is much less than the velocity by Brownian motion. Calculation shows that in this case creaming velocity might be less than 1 mm/day. Calculations of particle interactions show that for systems such as crude-oil-in-water emulsions, gravity-induced flocculation and creaming form the primary mechanism of particle loss.

Systematic experimental investigations of slow flocculation in emulsions are not available in the literature and there is disagreement between theory and the limited experiments performed. Gravitational flocculation in the primary minimum has been insufficiently studied as well. The

reliable mathematical kernel for the population balance equation is absent in the case of slow flocculation.

Flocculation rate has been studied as a function of droplet deformation resulting from a variety of forces. Dukhin and Sjöblom (1996) noted that there are differing theories between droplet deformation and thin film instabilities. Droplet deformations result from collisions, whereas thin-film stabilities arise from inhomogeneities in surfactant distribution on the droplet surface or to other forces such as interactions that result in an instability on the droplet face. Brownian motion in the liquid introduces a drag force between droplets. When this is taken into account, a model for the stability of these emulsions can be developed. A set of equations describing thin-film changes during curing and showing Brownian coagulation is derived by forming a set of equations of droplet deformation within gravitational coagulation. This set of equations can then accurately predict droplet deformation during slow Brownian coagulation.

Dukhin and Sjöblom (1996) develop an equation that can be used to estimate stability on the basis of these deformation reactions:

$$W = \left(\frac{2D}{a^3} \int_0^t F(t)E(t)dt \right)^{1/3} \quad (26)$$

where W is a generalized stability function,

D is the diffusion of the droplets,

a is the particle size of the droplets,

$F(t)$ is a function of the inter-droplet forces and is another expanded model, and

$E(t)$ is a function of the strength of the droplet film and is also another expanded model.

It should be noted that stability rises as a cube of the particle size, showing the importance of particle size to stability.

Verbeek et al. (1997) studied the stability of emulsions. These authors used the works of Dukhin and Sjöblom (1996) to further develop stability relations. It should be noted that both Dukhin and Sjöblom were also authors of the Verbeek paper.

Verbeek et al. (1997) noted that the time of rapid coagulation, using the Smoluchowski relationship, can be described as:

$$\tau_{sm} = \frac{1}{8\pi a^3 D_0 n} \quad (27)$$

where τ_{sm} is the time of rapid coagulation,

a is the droplet radius,

D_0 is the diffusion coefficient, and

n is the number of particles in the unit volume.

Assuming that D_0 and n can be calculated using standard relationships, the time to rapid coalescence can be given as:

$$\tau_{sm} = \frac{\pi a^3 \eta}{kT\phi} \quad (28)$$

where τ_{co} is the time of rapid coagulation,
 a is the droplet radius,
 η is the oil viscosity,
 k is the Boltzmann constant,
 T is the temperature, and
 ϕ is the volume proportion of oil in the emulsion.

When a repulsive force between the droplets exists due to double-layer interaction, the rate of coagulation decreases and the following equation can be used as an approximation of coalescence time:

$$\tau = W'_{\infty} \tau_{co} \quad (29)$$

where τ is the time of rapid coagulation, and
 W'_{∞} is the stability ratio.

W , the stability ratio can be approximated by (Verbeek et al., 1997):

$$W = \frac{\text{integral of repulsive forces}}{\text{integral of attractive forces}} \quad (30)$$

where W is the stability ratio,
 integral of forces is:

$$\text{integral} = \int_0^{\infty} \frac{\beta(h)}{(2+h)^2} \exp\left(\frac{V(h)}{kT}\right) dh \quad (31)$$

where $\beta(h)$ is the rationalized distance or h/a which is the distance between droplet surfaces divided by the droplet radius,
 h is the distance between droplet surfaces,
 $V(h)$ is the repulsive or the attractive force,
 k is Boltzmann constant, and
 T is the temperature.

Performing the integration in equation (31) and simplifying, one can write the stability ratio as:

$$W \approx \left[\frac{2}{\pi} \frac{\delta^2 V_{max}}{\delta r^2 kT} \right]^{1/2} \exp\left(-\frac{V_{max}}{kT}\right) \quad (32)$$

where W is the stability ratio of any droplet,
 $\delta^2/\delta r^2$ is the second derivative of the remaining function with respect to the repulsion,
 V_{max} is the maximum repulsion between droplets,
 k is Boltzmann constant,
 T is the temperature, and
 h_{max} is the maximum distance between droplets.

Dukhin et al. (2001) also developed a generalized model for the electrokinetic stability of emulsions. This is based on recent progress in the measurement and interpretation of ion accumulation and motion in the stagnant part of the electrical double layer caused by surfactant stabilization. Unlike earlier models, this new model assumes conductivity in the stagnant layer. The model describes the conductivity in terms of two parameters, ζ (the zeta potential) and K'' (the electrokinetic charge). Since both of these can be measured, Dukhin et al. describe a means to use this to further delineate the distribution of absorbed ions between the diffuse layer and the Stern layer.

4.10 A Model to Describe Emulsion Stability

Civan et al. (2004) developed a new stabilization model and demonstrated this model on a variety of literature data covering both oil-in-water and water-in-oil emulsions. They begin the model formation study by describing the emulsion decomposition as an irreversible reaction as:



where R_1 is the stable emulsion,
 P_1 is the dispersed phase, and
 P_2 is the continuous phase.

Civan et al. (2004) then considered this breakdown to be a power-law function of the instantaneous emulsion fraction available for decomposition according to:

$$dX/dt = k_d (X_c - X)^n \quad (34)$$

where X is the instantaneous decomposed fraction of the emulsion,
 X_c is the maximum achievable fraction of emulsion decomposition or limiting emulsion fraction,
 n is the order of reaction,
 t is time, and
 k_d is the decomposition rate constant.

The authors considered that the decomposition may be delayed by a certain time and thus the initial conditions can be defined by:

$$X = 0, t = t_d \quad (35)$$

where t_d is the time delay until decomposition begins.
 Combining this with the previous equations, the solution to the decomposition equation is:

$$(X_c - X)^{1-n} = X_c^{1-n} - (1-n)k_d(t-t_d) \quad (36)$$

Thus a plot of $[(X_c - X)^{1-n} - (X_c - X_c)^{1-n}]$ vs time relative to the initiation of decay or the decay delay time should yield a linear correlation. Civan and coworkers suggested that a linear regression be used to determine the best estimates of the parameters for the decay. The slope, m , of the line is equal to $(1-n)k_d$. The rate parameter is obtained by:

$$k_d = m/(1-n) \quad (37)$$

Civan et al. (2004) suggest that $n = 0.4$ from a variety of experimental data fits. However,

the order, n , varied from 0.18 to 1.73 in a variety of tests of experimental data

The half-life of the emulsion can be determined by substituting $X = 0.5X_0$ and thus:

$$(1 - 1_0)^{1/2} = 0.567 k_f^{-1} \quad (38)$$

4.11 The Marangoni Effect

An important phenomenon in surfactant stabilization of oil-in-water emulsions is the effect known as Marangoni stabilization and destabilization. Marangoni effects arise from the tendency of surfactant concentrations to quickly distribute over an interface. If there is less surfactant concentration on one side of a droplet than on the other side, surfactant quickly moves to restore the surfactant equilibrium over the droplet. This surfactant flow is called Marangoni stabilization (Shioi et al., 2000; Velarde et al., 1996). Marangoni instability arises as a result of this surfactant flow as the flow continues and results in areas of greater and lesser surfactant concentration over the droplet interface. Marangoni stabilization and destabilization are illustrated in Figures 14 and 15.

Agble and Mendes-Tatsis (2001) developed a series of equations to predict Marangoni circulation. The theoretically predicted stability of various binary liquid-liquid interfaces with several surfactants was predicted. These were also compared to experimental observations. A Marangoni coefficient was developed that assists in predicting stability with the inclusions of the Marangoni effect. Predicted and experimental results show that the stability of emulsion systems varies significantly with different surfactants.

Lavabre et al. (2005) studied Marangoni instability in the surfactant CTAB (cetyltrimethylammonium bromide) and found it was periodic. This periodicity was measured and was about 1000 seconds for this particular system. It was noted that the convective instability appears on a transient basis and the systems periodically switched between a slow and a more rapid transport regime. A correlation was clearly established between surfactant movement, surface tension, and electrical potential oscillations. During the convective stage, surface tension data showed fast adsorption due to the fast inflow of surfactant at the interface. During the diffusive stage, desorption occurred and gradients built up until the system became unstable again.

4.12 Kinetics of Destabilization Processes

Kralchevsky et al. (2003) describe the kinetics of emulsion stabilization. They propose that Ostwald ripening could be predicted as:

$$\frac{4\pi}{3} \frac{d}{dt} R^3(t) = 4\pi D R V_1 [c_\infty(t) - c_{eq}(R)] \quad (39)$$

where R is the droplet radius under consideration,

t is the time,

D is the diffusivity of the component in the continuous phase,

V is the volume of the molecule under consideration,

c_∞ is the number volume concentration of the component in the continuous medium, and

c_{eq} is the equilibrium concentration of the component for the droplet.

Subsequently, Kralchevsky et al. (2003) show that the flux contributing to Ostwald ripening, or the flux to the large droplets, is:

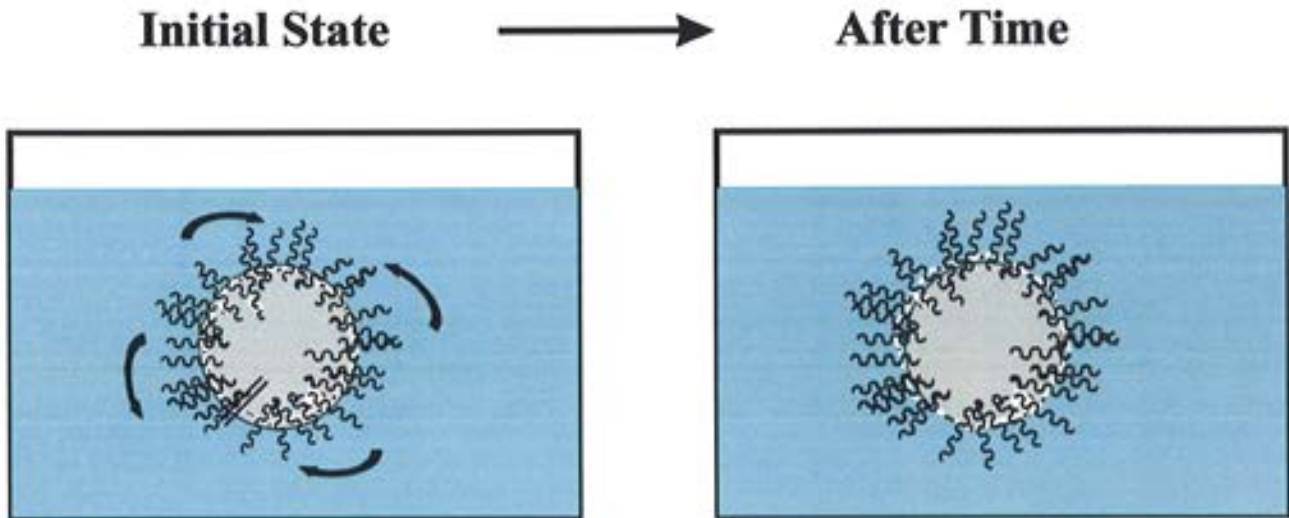


Figure 14 The Process of Marangoni Stabilization The surfactants are distributed around the droplet to equalize distribution.

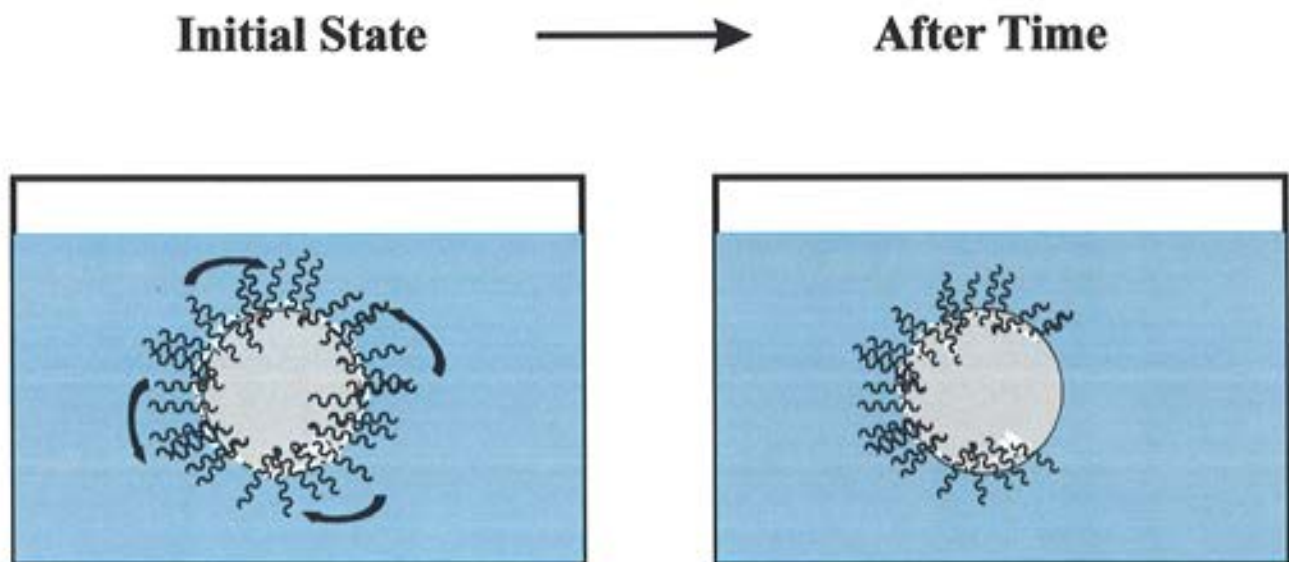


Figure 15 The Process of Marangoni Destabilization The surfactants are distributed around the droplet to equalize distribution and movement continues leaving an imbalance of surfactant concentration.

$$j(R, t) = Q \left(-\frac{1}{RR_p} - \frac{1}{R^2} \right) f(R, t) \quad (40)$$

where j is the flux for a given radius, R , at time, t ,
 Q is the total concentration of the component of interest,
 R is the radius of the particles under consideration,
 R_p is the median radius, and
 $f(R, t)$ is the distribution of the particle sizes of radius R , at time, t .

$$Q \equiv D b c_s V_1 \quad (41)$$

where Q is the total concentration of the component of interest,
 D is the diffusivity of the component in the continuous phase,
 b is an empirical constant,
 c_s is the total concentration of the component, and
 V_1 is the volume of the component of interest.

Kralchevsky et al. (2003) provide a criterion for the threshold of rapid coagulation of identical particles as:

$$n_c^{critical} \propto \frac{1}{Z^6} \tanh^{-1} \left(\frac{Ze\psi_s}{4kt} \right) \quad (42)$$

where n_c is the critical number at which coalescence occurs rapidly,
 Z is the particle charge,
 b is the height of the energy barrier to coalescence,
 ψ is surface potential,
 k is Boltzmann constant, and
 t is the time.

Kralchevsky et al. (2003) also derived a droplet lifetime as:

$$\tau_{in} = \frac{6\pi\eta R_d^2}{F_z} \ln \left(\frac{h_m}{h_f} \right) = \frac{9\eta}{2g R_d \Delta\rho} \ln \left(\frac{h_m}{h_f} \right) \quad (43)$$

where τ_{in} is the droplet lifetime,
 η is the viscosity of the interface,
 R_d is the droplet radius,
 F_z is the electric force,
 h_m is the initial film thickness,
 h_f is the final film thickness,
 g is the gravitational constant, and
 $\Delta\rho$ is the difference in density between the droplet and medium.

Kralchevsky et al. (2003) show experimental data of droplet radii versus droplet lifetimes.

The lifetime for about 10 μm droplets is about 2 seconds and for 3 μm droplets is about 40 seconds for a system of oil droplets in a small system.

Kralchevsky and coworkers also describe three scenarios for two-particle collisions depending on the type of particle-particle interactions: a) if the repulsive forces are predominant, the two colliding particles will rebound and the colloidal dispersion will be stable; b) when, at a given separation distance, the attractive and repulsive forces counterbalance each other, aggregates or flocs of attached particles can appear; and c) when the particles are fluid and the attractive interaction across the film is predominant, the film will be unstable and will rupture, which leads to the coalescence of the droplets. In emulsions such as oil spill dispersions, the latter is more likely.

Kralchevsky et al. (2003) showed that the stability of emulsions, using the Derjaguin approximation, could be described as:

$$W_p = \frac{1}{E_c} = \left[\frac{8\pi kT}{-U_p(S_m)} \right]^{1/2} \frac{\beta(S_m)}{(S_m + 2)^2} \exp \left[\frac{U_p(S_m)}{kT} \right] \quad (44)$$

where W_p is the stability of the emulsion,

E_c is the collision efficiency of two particles,

k is Boltzmann constant,

T is the temperature,

U_p is the energy of interaction between particles at maximum interaction energy,

S_m is the separation at maximum interaction energy,

β is the hydrodynamic factor, and

U_p is the energy of interaction between particles.

4.13 Lifetime of Dilute Emulsions with Doublet Formation

Dukhin et al. (2003) proposed that dilute emulsions could lead to simplifications of lifetime considerations for an emulsion. The energy path leading from a single original particle to a doublet, which could either lead to coalescence, a floc, or fractionation into two single particles, could be used to describe lifetimes of emulsions containing small particles or mini-emulsions. Dukhin et al. note that emulsion stabilization is strongly affected by two specific emulsion processes, Ostwald ripening and coalescence. The result of Ostwald ripening is that the sub-micron droplets rapidly disappear, increasing the size of the larger particles. Considering energy, a mini-emulsion is not stable against secondary aggregation, flocculation, or coalescence due to the potential energy barriers. Flocculation may be reversible, but destabilization gradually occurs due to coalescence. The mechanism of kinetic stabilization due to aggregate fragmentation is less efficient for emulsions than for suspensions because of coalescence in aggregates.

Two types of aggregation in the form of coalescence are defined: rapid coagulation and slow coagulation. Rapid coagulation is defined as a process in which all collisions are effective. Slow coagulation can be explained by partial efficiency of collisions because of the existence of an energy barrier. In the case of application to oil dispersions, slow coalescence is initially presumed to occur due to the energy barrier of the presence of surfactants. As the surfactants partition into the water, however, this energy barrier minimizes and the system is prone to rapid coalescence.

Dukhin et al. (2003) conclude that coalescence and fragmentation time are the two main characteristics of a mini-emulsion that determine its stability. Fragmentation time is the time of existence of doublets or other aggregates that form in the emulsion. Both coalescence and fragmentation time are functions of droplet radius and both increase rapidly with increasing radius.

It is noted that some information, such as experimental data and the theory of the retardation of van der Waals forces, is not sufficiently known to provide accurate prediction equations.

As coalescence is possible only during the fragmentation time, the determination of coalescence and fragmentation times under real conditions remains a challenge. Dukhin et al. note that there are now some data for doublet formation times and coalescence times under relatively real conditions.

Dukhin et al. proposed the following relation for emulsion stability times:

$$t = t_{sm} \frac{t_{sp} + t_d}{t_d} \quad (45)$$

where t is the emulsion lifetime,
 t_{sm} is Smoluchowski particle lifetime,
 t_{sp} is the single particle lifetime, and
 t_d is the double lifetime.

Measurements in systems have shown t_d and t_{sm} ranging from 0 to 10 minutes and in one case from 0 to 100 minutes. This would yield overall emulsion lifetimes ranging from minutes to a few hours, depending on doublet lifetimes.

4.14 Hydrodynamic Instability of Emulsions

Danov et al. (2003) studied emulsion droplets in a capillary to examine the effect of droplet movement. They found that surfactant thinning occurred on the leading edge of the droplet due to hydrodynamic forces and that the trailing edge has excess surfactant. This has consequences on emulsion stability when there are droplets rising through the water column, such as is the case with oil spills. A further phenomenon observed is that surfactant molecules desorb from the trailing edge of the droplet and absorb to other droplets in the area, particularly at the surfactant-depleted leading edge.

Triton 100 was used as a prototype model for both the theoretical and experimental portions. Starting with conventional theory, the stability-instability transition of the droplets subjected to hydrodynamic forces can be described by a system of two differential equations:

$$p + Ah + \frac{1}{x} \frac{d}{dx} \left(x \frac{dh}{dx} \right) = 0 \quad (46)$$

$$\frac{d}{dx} \left[x \frac{d}{dx} \left(\frac{1}{x} \frac{dp}{dx} \right) + N_1 x^2 h - N_2 x^2 p \right] = (qR)^2 \frac{dp}{dx} - \left(\frac{4}{(qR)^2} + x^2 \right) N_2 x h \quad (47)$$

where p is a dimensionless pressure parameter,
 A is a dimensionless Hamaker constant,
 x is a dimensionless droplet radius,
 h is the dimensionless interdroplet spacing,
 N_1, N_2 are dimensionless groupings of the absorption isotherms,
 q is the diffusion across the droplets, and
 R is film radius.

These equations were solved and, with the addition of experimental data, stability-instability curves were drawn. These curves considered the velocity of the emulsion droplet, the film thickness, and the separation between droplets. When applied to a firm division, this shows that at low surfactant concentrations, a velocity of 0.0005 m/s resulted in instability and at high surfactant concentrations, a velocity of 0.003 m/s resulted in instability. As these conditions appear to be well within those expected for oil spill dispersions, this may be a serious form of instability of emulsion droplets.

Danov et al. (1999) had earlier developed a theoretical model for calculating the influence of surfactants on the approaching velocity of two non-deformed bubbles. This model took into account the influence of Gibbs elasticity, bulk and surface diffusivities, and surface viscosity. The governing equation for the surface velocity was calculated numerically to find the velocity of approach relative to the generalized Taylor velocity. The calculations show that the interfaces become immobile with an increase in the surface viscosity. The same behaviour is observed with an increase in the Gibbs elasticity. An increase in the bulk diffusion coefficient leads to fast saturation of the interfaces, which counter-balances the surface gradient of the surfactant, suppresses the Marangoni effect, and makes the interfaces mobile. Valkovska and Danov (2000) had also studied diffusion coefficients for thin film liquid drainage. They concluded that the effect of surface diffusion on film drainage is stronger than that predicted in earlier theoretical studies. This was confirmed by studies of the drainage of nitrobenzene films stabilized with dodecanol.

Danov et al. (2003) conclude that movement of an emulsion droplet results in an instability in the surfactant concentration. The concentration decreases at the front end of the droplet and increases at the trailing edge of the droplet. Surfactant transfer between two droplets can occur if they are close enough. The diffusion of surfactant between two droplets may also result in destabilization and coalescence of the two droplets. Experiments and calculations show that increasing velocities and the film radius have destabilizing effects on the emulsions.

Lee and Pozrikidis (2006) also studied the deformation of droplets in a Navier-Stokes flow. They noted similar effects as those noted by Danov et al. (1999) and (2003).

4.15 Importance of Droplet Deformation on the Stability of Emulsions

Ivanov et al. (1999) analyzed the relative importance of droplet deformation, surfactant transfer, and interfacial rheology on the properties and stability of emulsions. The appearance of deformation in the zone of contact between two interacting droplets has a number of consequences. This deformation increases the importance of the intermolecular origin and gives rise to contributions from the interfacial dilation and the bending energy. The flattening increases the viscous dissipation in the gap between the two colliding drops and thus prolongs the lifetime of the doublet of two such drops. The critical thickness of the gap between the two droplets also depends on whether or not the drops are deformed. The factors that facilitate the flattening in the zone of contact between the two emulsion drops are the increase in droplet size, the decrease in interfacial tension, the bending energy for water-in-oil emulsions, the increase in droplet-droplet attraction, and the suppression of droplet-droplet repulsion. The presence of surfactant strongly affects the interfacial tension, the bending moment, and all kinds of DLVO and non-DLVO surface forces operative in the gap between two droplets.

The rheological and dynamic properties of the surfactant adsorption monolayers (Gibbs elasticity, surface diffusivity, surface viscosity, and adsorption relaxation time) are major factors in the stability of emulsions under dynamic conditions. The solubility of the surfactant in one of the two phases can determine whether oil-in-water or water-in-oil emulsions will be formed. A criterion is developed for emulsion stability accounting for the interplay of all thermodynamic and factors noted.

Ivanov et al. (1999) develop the terms for the energy of interaction between two deformable emulsion droplets as the sum of the forces including: dilation, bending, van der Waals, electric, ionic correlation surface force, hydration, protrusion and steric interaction, oscillatory structure force, and some other smaller contributions.

The buoyancy force on a droplet is calculated as:

$$F = \frac{4}{3} \pi a^3 g \Delta \rho \quad (48)$$

where F is the buoyancy force,

a is the droplet radius,

g is the gravitational constant, and

$\Delta \rho$ is the difference in density between the oil and the water

It should be noted that, while this equation is similar to that of the Stokes' equation, the force is related by the cube of the droplet radius rather than the rising rate as in Stokes' equation to the square of the droplet radius.

Ivanov et al. (1999) note that the surface of an emulsion droplet is corrugated by capillary waves caused by thermal fluctuations or other perturbations. There is a film thickness, called the transitional thickness, at which the respective surface fluctuation becomes unstable and this surface corrugation begins to grow spontaneously. At a given film thickness, called the critical thickness, the unstable maximum surface corrugations on the two opposite droplet surfaces can touch each other. Using the calculations developed, the droplet lifetime as a function of droplet radius is calculated and compared to experimental data. Droplet lifetimes vary from 0.2 to 160 seconds. The droplet lifetime for a 15 μm particle is about 200 seconds; for a 20 μm particle, about 100 seconds; and for a 50 μm particle, about 10 seconds. It should be noted that in oil spill dispersions most particles are under 20 μm and the volume mean diameter particle size is about 12 to 15 μm . Less than half the volume is under this value. Thus, only about half the particles in concentrated situations, such as directly under the slick, have lifetimes greater than about 100 seconds.

Ivanov et al. (1999) conclude that the occurrence of flocculation in an emulsion is significantly affected by the appearance of deformation in the zone of contact of two interacting droplets. The appearance of such a deformation has the following consequences.

- i) It enhances the importance of the surface forces of intermolecular origin and gives rise to contributions from the interfacial dilation and the bending energy.
- ii) The velocity of approach is different for two deformed and non-deformed drops.
- iii) The flattening increases the viscous dissipation in the gap between two colliding drops and thus prolongs the lifetime of the doublet of two such drops.
- iv) The critical thickness of the gap between two droplets also depends on whether or not the drops are deformed.

Equations relating to each effect had been developed.

Ivanov et al. (1999) note that the following factors facilitate the flattening in the zone of contact between two emulsion droplets:

- i) the increase of droplet size (this becomes crucial above about 20 μm);
- ii) the decrease of the interfacial tension;
- iii) the increase of droplet-droplet attraction and suppression of the droplet-droplet repulsion;
- iv) the decrease of the tangential mobility of the interfaces;
- v) the high droplet volume fraction forces the emulsion drops to deform because of the

restricted volume; and

vi) the larger the external force, F , exerted on the droplets, the larger the deformation upon collision.

Ivanov et al. (1999) conclude that the major effect of the presence and transport of surfactant in emulsions is to affect:

i) the interfacial tension and the bending moment;

ii) the presence of surfactant adsorption monolayers and surfactant micelles in the films influencing the DLVO forces;

iii) the rheological and dynamic properties of the surfactant adsorption monolayers determine the stability of emulsions under dynamic conditions; and

iv) in the case of emulsions from non-pre-equilibrated oil and water phases, the process of transfer of surfactant from the continuous phase toward the droplets (or vice versa) is found to have a destabilizing effect.

4.16 Emulsion Stability Viewed as Film Rupture

Chesters and Bazhlekov (2000) studied emulsion stability from the point of view of the deformation, drainage, and rupture of the film between colliding droplets in the presence of insoluble surfactants under the influence of van der Waals forces. Equations were developed based on the lubrication equations in the gap between the drops and the creeping flow approximation of Navier-Stokes' equations, coupled with velocity and stress-boundary conditions at the interfaces. A non-uniform surfactant concentration at the interfaces, governed by a convection-diffusion equation, leads to a gradient of the interfacial tension, which in turn leads to additional tangential stress on the interfaces or Marangoni effects.

The equations are solved to yield boundary-integral methods. The range of dispersed to continuous-phase viscosity ratios is investigated for a range of values for dimensionless inputs, including surfactant concentrations. It was found that a fair approximation to these results can be provided by a simple expression for critical surfactant concentration and critical thicknesses of the interfaces. Numerical simulation shows that the minimal film thickness that would occur before rupture varies little with surfactant concentrations up to a certain point, after which such surfactant concentration reduces the probability of rupture.

Chesters and Bazhlekov (2000) noted that a very simple relationship could predict the critical film rupture thickness:

$$h_c = (A/2)^{1/3} \quad (49)$$

where h_c is the critical thickness before film rupture leading to coalescence occurs, and A is the dimensionless Hamaker constant.

Further development leads to the equation for minimum thickness at conditions when the viscosity ratio (oil-to-water) is very low:

$$h_{min} = \frac{0.18}{(\tau)^{2/3}} \quad (50)$$

and when the viscosity ratio of oil-to-water is high,

$$h_{min} = \frac{0.6}{(\lambda^* \tau^*)^{1/2}} \quad (51)$$

where h_{min} is the minimum film thickness before rupture,
 τ^* is the dimensionless stress applied to the system, and
 λ^* is the dimensionless viscosity ratio, oil-to-water.

Chesters and Bazhlekoy (2000) summarize their results as being the influence of surfactants, viscosity ratio, and other parameters on the critical or minimum thickness of the film. For droplets in the millimeter size, the influence of diffusion is negligible, while the influence of van der Waals forces can be described by an approximate relation for the critical film rupture thickness. Drainage is then virtually unaffected by the presence of surfactants down to some film thickness - a transition thickness at which a transition to immobile interfaces sets in. In other words, low concentrations of surfactant have little effect on the emulsion stability as the critical film thickness does not change that much with the addition of a surfactant compared to having no surfactant.

For smaller droplets, the influence of diffusion becomes more significant, alleviating gradients in surfactant concentration, thereby reducing the effect of surfactants on drainage. At small Peclet numbers, the effect of surfactants is virtually eliminated and the system behaves as a surfactant-free one with a slightly reduced interfacial tension.

4.17 Calculations of Coalescence Time

Li (1996) developed a model for predicting coalescence time. The model is based on the dynamics of the thinning film with mobile interfaces. The effects of surface tension gradient and surface viscosity upon the surface mobility, drainage, and rupture of a dimpled liquid film are included. The model was compared to actual systems of glycerol in water stabilized by Tween 20. The time prediction model developed is:

$$t_c = 0.23 f \frac{\pi^{4.0} \mu F^{0.030-0.01} R^{1.54-0.01}}{\gamma_{\infty}^{1.035-0.01} B^{1.46-0.01}} \quad (52)$$

where t_c is the coalescence time,
 f is a dimensionless radius parameter,
 μ is a dimensionless potential term,
 F is the force exerted on the droplet,
 ω is the dimensionless area occupied by the surfactant,
 R is the radius of the droplet when the droplet ruptures,
 γ is the dimensionless interfacial tension difference, and
 B is the dimensionless Boussinesq surface force.

This equation was used to calculate the coalescence times from various systems of glycerol in water stabilized with Tween 20. The agreement was generally within an order-of-magnitude. The experimental values of times ranged from 15 to 360 seconds and the calculated ones ranged from 6 to 60 seconds.

4.18 Models Focussing on Film Drainage between Two Drops

Yeo et al. (2001, 2002, 2003) and Yeo and Matar (2005) developed a series of models for emulsion stability based on film drainage between two drops. Their studies focussed on Marangoni-driven local continuous film drainage between two drops induced by an initially nonuniform interfacial distribution of insoluble surfactant. Using the lubrication approximation, a coupled system of fourth-order nonlinear partial differential equations was derived to describe the spatial and temporal distributions of the surface film. Numerical solutions of the governing equations were obtained using the numerical method of lines and placement of appropriate boundary conditions. The effect of variables such as the viscosity ratio, background surfactant concentration, Peclet number, and van der Waals interaction forms on the dynamics of the draining film were studied. Marangoni stresses were found to cause large deformations in the liquid film. Thickening of the film at the leading edge of the surfactant was accompanied by rapid and severe thinning far upstream. Under certain conditions, the severe thinning leads directly to film rupture due to the influence of van der Waals forces. Time scales for rupture, promoted by Marangoni-driven local film drainage, were compared with those associated with the dimpling effect that accompanies the approach of two droplets.

The surfactant diffusive time scale was found to be:

$$T_d = \frac{R_d^2}{D} \quad (53)$$

where T_d is the time scale for surfactant diffusion,

R_d is the droplet radius, and

D is the surfactant diffusion rate.

The time scale for Marangoni-driven spreading is:

$$T_c = \frac{\mu R_d}{\varepsilon S} \quad (54)$$

where T_c is the time scale for Marangoni-driven spreading,

μ is the ratio of viscosity between the two phases,

R_d is the droplet radius,

ε is the ratio between the axial and radial dimensions, and

S is the difference in surfactant concentration of the concentrated portion and the depleted portion of the droplet.

4.19 Nonlinear Rupture Theory to Predict Stability Time

Lin et al. (2000) investigated the effects of a soluble surfactant on the dynamic rupture of thin liquid films. A nonlinear coupling evolution equation was used to simulate the motion of thin liquid films on free surfaces. A generalized Frumkin model was adopted to simulate the absorption/desorption kinetics of the soluble surfactant between the surface and the bulk phases. Numerical simulation results showed that the liquid film system with soluble surfactant is more unstable than that with insoluble surfactant. A generalized Frumkin model was substituted for the Langmuir model to predict the instability of liquid film with soluble surfactant.

Extensive model development was conducted and using these models, a simple qualitative expression of the linear rupture time was developed:

$$T_r = - \frac{1}{\omega_m} \ln(H_r) \quad (55)$$

where T_r is the rupture time for the film,
 ω_m is the maximum disturbance growth rate, and
 H_r is the initial film thickness.

Numerical calculation using the generalized Frankin model shows that the surfactant solubility increases as the values of the absorption/desorption rate constant increase, as the bulk diffusion constant increases, and the film system subsequently becomes unstable. The surfactant solubility decreases as the rate of equilibrium and interaction among molecules increases, which increases the film stability. An increase of relative surface concentration will initially result in a decrease of corresponding shear drag force, increasing the Marangoni effect. Lin et al. (2009) noted that the effect of van der Waals forces is the most powerful factor that causes the rupture of the film.

5. Loss of Surfactant to Water Column: Desorption

It is well known that in dilute solutions much of the surfactant in the dispersed droplets ultimately partitions to the water column and is lost to the oil dispersion process. Little if any surfactant would partition back into the droplet in a dilute solution. This is one important difference between dilute and concentrated solutions. Figures 16 and 17 show the absorption and desorption processes. Figures 18 and 19 show the difference between dilute and concentrated situations.

This loss of surfactant is related to the absorption of surfactant at the oil/water interface or the reverse of this, the desorption of the surfactant at the oil/water interface. It is stated that this is the most important process for the chemical consideration of surfactants and interfacial chemistry (Shioi et al., 2000; Dukhin et al., 1995). When surfactants are dissolved in a bulk phase such as water, they start to be absorbed at the oil surface or interface. The interfacial tension may decrease until equilibrium is reached. The kinetics of this interfacial decrease with surfactant absorption are well known, but the desorption kinetics are less well studied (Shioi et al., 2000; Dukhin et al., 1995). Desorption occurs primarily as a result of the lower concentration of surfactants in the bulk phase or water. The surfactants will transfer back and forth from the oil/water interface until an equilibrium of concentration is established in the interface or in the bulk liquid (water).

In the case of oil-in-water emulsions such as crude oil dispersions, such equilibrium is never established as the dilution of the oil droplets into the water phase is constantly decreasing. Thus there is a net movement of surfactant molecules from the oil droplet interface into the water column. This results in continuous destabilization of the droplets until there is little surfactant left (Shioi et al., 2000). The major question is the length of time until significant destabilization takes place.

5.1 Studies on Surfactant Absorption and Loss

Shioi et al. (2000) studied surfactant absorption/desorption using sodium dodecyl sulfate and n-heptane as oil. They found that the interfacial tension between the oil and water decreased to about half in 30 seconds indicating desorption of the surfactant from the oil droplet interface into the bulk water phase. A kinetic prediction system was developed, which is detailed in Section 5.2.1.

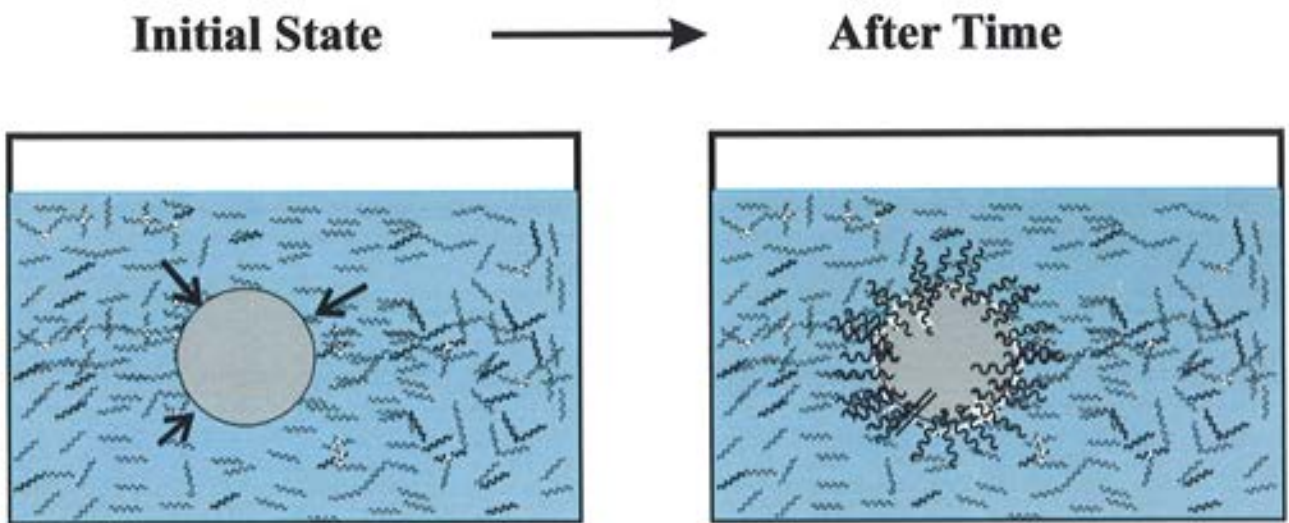


Figure 16 The Process of Surfactant Absorption The surfactants absorb to the oil droplet interface.

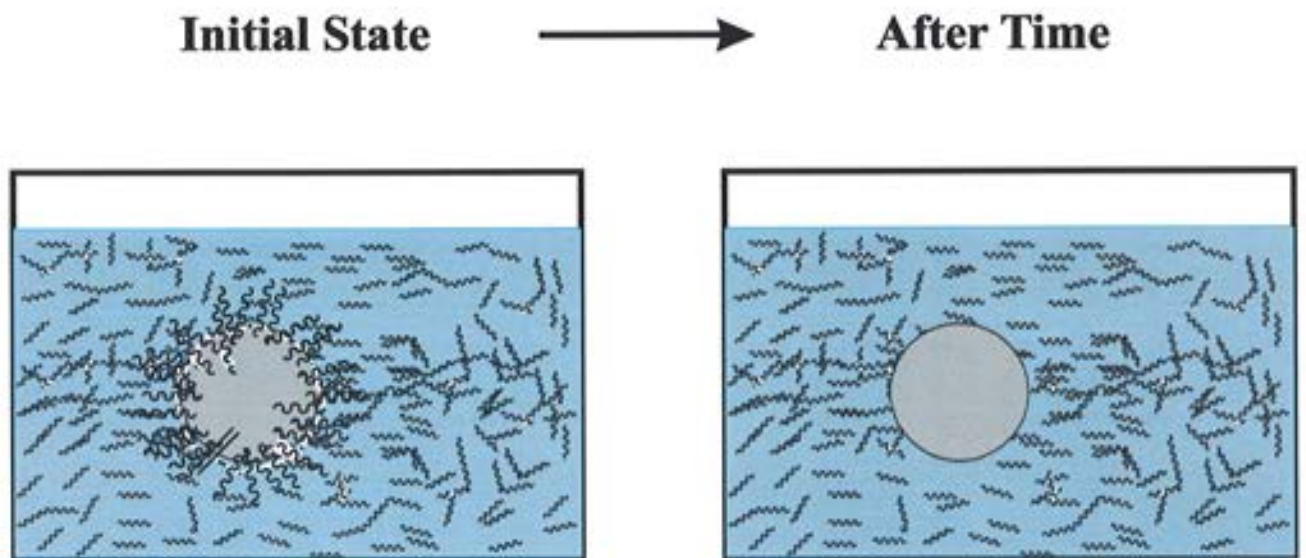


Figure 17 The Process of Surfactant Desorption. The surfactants desorb from the Oil Droplet interface to the bulk water. The concentration of surfactants moves to achieve equilibrium between the water and the interface.

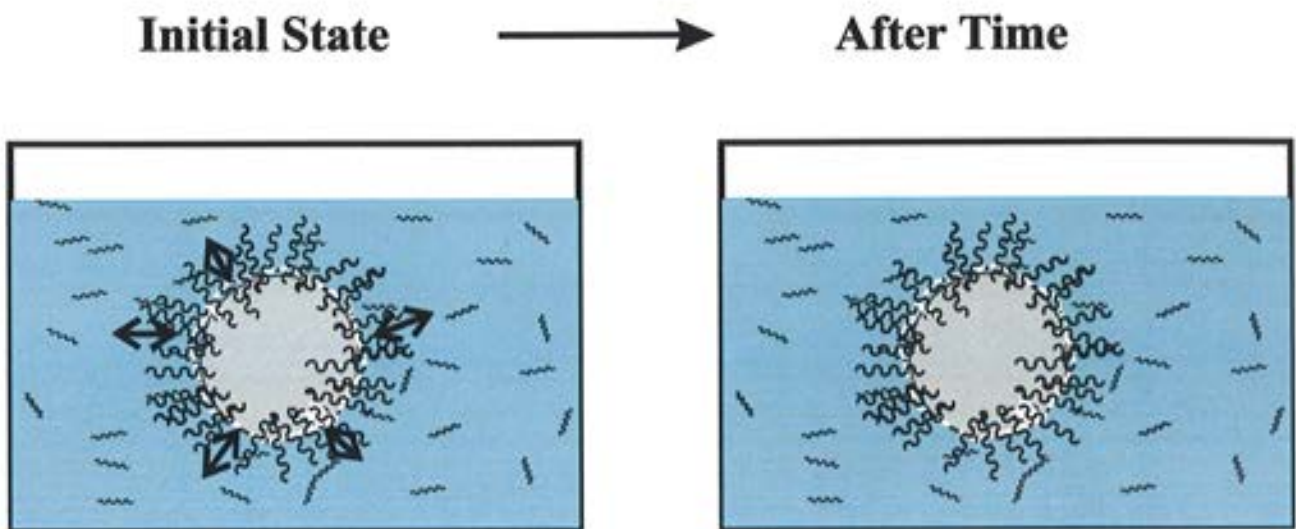


Figure 18 The Process of Surfactant Absorption and Desorption in a Closed System The surfactant concentration in the bulk water and on the interface remain about the same.

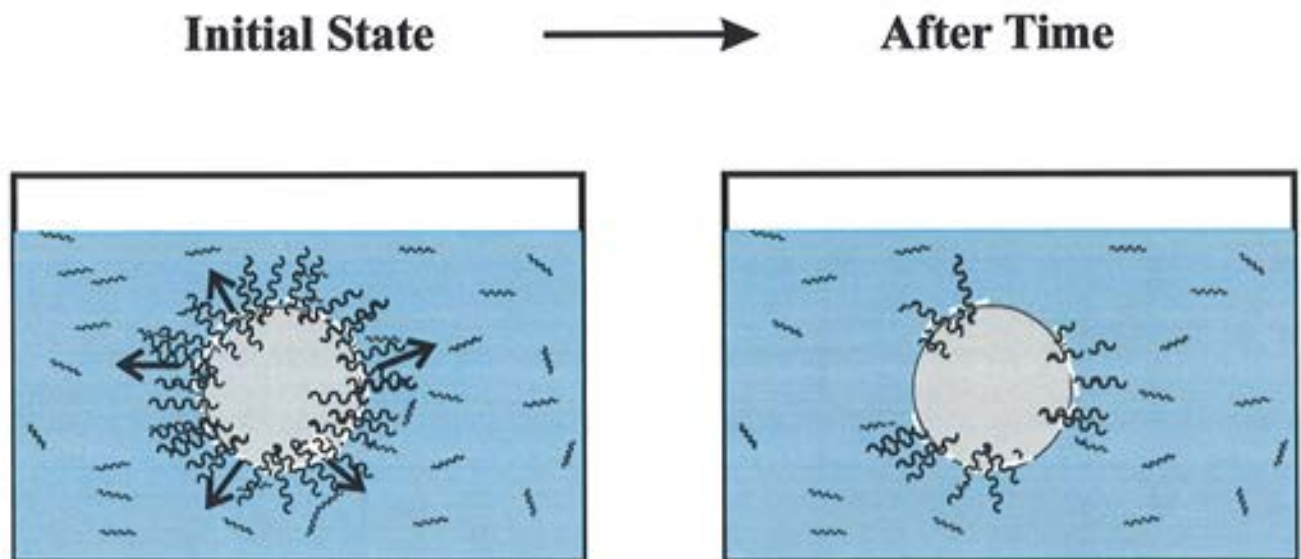


Figure 19 The Process of Surfactant Absorption and Desorption in an Open System The surfactant concentration on the interface continually decreases as the surfactants in the bulk system dilute.

Fan et al. (2003) studied surfactant drainage from an oil droplet using imaging ellipsometry/reflectometry. The oil was squalene, C_{30} , and the nonionic surfactant $C_{12}E_6$ was the test liquid. At low surfactant concentrations, $< 10\%$ of CMC, they observed film recovery due to the Marangoni effect. At high surfactant concentrations, there were minimal interfacial tension gradients. As more surfactant was added, the equilibrium thickness of the interface decreased as a result of partitioning of surfactant at the oil-water interface.

Casford et al. (2003) studied the competitive adsorption of sodium dodecyl sulfate with polyethylene oxide surfactants. Sum frequency vibrational spectroscopy was used to study the interfaces. They found that competitive adsorption occurred, leading to rapid desorption of the surfactants. Desorbed surfactants formed complexes or diluted in the bulk phase.

Liu et al. (2004) studied the surfactant loss involved in secondary oil recovery processes. They noted that surfactant loss is the major concern in chemical oil recovery processes. Although loss to the reservoir walls by adsorption is a problem, loss to the water column also weakens the effectiveness. Studies of alkaline-surfactant slug injection, which results in loss of surfactant to the water column, show that such loss could be minimized by choosing a different surfactant. Surfactants that had synergism with the alkaline flood could also result in additional oil recovery even if lost in the water column.

Ikezoe et al. (2004) studied the adsorption and desorption of an alkyl sulfate type of surfactant from a water/nitrobenzene interface. A quasi-elastic laser-scattering technique was used to measure the interfacial electric potential. They found that there were chemical oscillations with periodic adsorption and desorption of alkyl sulfate ions. In addition, there was a rapid or abrupt adsorption of the surfactant molecules at the surface with a slow desorption of the ions from the interface. From the analysis of the video, the workers concluded that each abrupt adsorption was accompanied by a small wavy motion across the interface. This motion travelled slower than the convective mass transfer. The abrupt adsorption is caused by non-linear amplification of the mass transfer of ions from the bulk phase to the liquid interface by a type of Marangoni convection, which was generated by the local adsorption of the surfactant ions at the liquid interface resulting in the heterogeneity of the interfacial tension. The process appeared to follow an oscillatory format.

Kovalchuk and Volhardt (2004) studied oscillations at the interface. Oscillations of the electrical potential through the interface and of interfacial tension were observed by transfer of ionic species through an oil/water interface and a liquid oil membrane interposed between two aqueous solutions. It was found that auto-oscillations of the surface tension occur at the air/water interface with the dissolution of a surfactant droplet in the bulk water. These oscillations are asymmetrical and are believed to be associated with in-equilibria in the systems associated with surfactant-transfer mechanisms.

Fukuda (2005) proposed that lipophobicity, repulsion to oil, was an important characteristic in improving surfactant performance for certain surfactants and that this improved adsorption characteristics.

Seamhorn and Harwell (2005) studied the precipitation of mixed surfactants from solution. They note that the precipitation of surfactants is of considerable importance in petroleum applications. Anionic surfactants react with divalent cations and precipitate readily, as would be expected from ionic reactions. However, Seamhorn and Harwell also point out that many mixed surfactant systems also precipitate due to interactions between different types of surfactants.

Zhao et al. (2005) conducted studies of the interfacial tensions of crude oil from a Chinese field and a octylmethylnaphthalene surfactant. They found that in high salinity waters, the surfactant reacted with the sodium ions to produce soap, which partitioned very much into the water phase.

5.2 Theoretical Studies of Surfactant Loss

5.2.1 Adsorption Approach Using Langmuir Kinetics

An approach to adsorption and desorption of surfactants at the interface is to begin with Langmuir kinetics (Shioi et al., 2000, Dukhin et al., 1995). The Langmuir kinetic is:

$$\frac{d\theta}{dt} = -\theta + Kc(1 - \theta) \quad (56)$$

where θ is the fraction of interfacial area covered by the surfactant,
 t is the time, here dimensionless as scaled by the rate constant,
 K is the equilibrium constant, and
 c is the concentration of the surfactant in the bulk phase next to the oil.

The next relationship to predict the absorption and desorption of surfactants at the interface is Frankin's equation of state (Shioi et al., 2000):

$$\Pi^* = -\ln(1 - \theta) - a\theta^2 \quad (57)$$

where Π^* is a dimensionless interfacial pressure,
 θ is the fraction of interfacial area covered by the surfactant, and
 a is a parameter for attractive interactions between surfactants at the interface.
The interfacial pressure may be approximated by using the interfacial tension such as:

$$\Pi = \gamma_0 - \gamma \quad (58)$$

where Π is a dimensionless interfacial pressure,
 γ_0 is the interfacial tension without surfactant, and
 γ is interfacial tension with surfactant.

Combining the above equations, one can obtain the following (Shioi et al., 2000):

$$\frac{d\gamma}{dt} = \frac{-1}{1 - \theta} - 2a\theta^2 \quad (59)$$

where γ is interfacial tension with surfactant,
 θ is the fraction of interfacial area covered by the surfactant,
 a is a parameter for attractive interactions between surfactants at the interface. Shioi et al. (2000) found this to vary from 0.05 to 1.4 and was typically around 1.3 with normal oil.

5.2.2 An Empirical Approach

Cowell et al. (2000) conducted a series of studies on the surfactant remediation of nonaqueous-phase liquids (NAPL). They measured the partitioning of an ethoxylate nonionic surfactant. The empirical equation obtained was:

$$C_p = \frac{k}{cmc^{\alpha} H T^{\beta}} \quad (60)$$

where C_p is the maximum concentration of the surfactant in the non-aqueous phase, NAPL or oil.

k is the partitioning constant, 5.3×10^5 , as found in this study.

cmc is the critical micelle concentration, which ranged from 100 to 700 in this study.

H is the interfacial tension between the oil and water, which ranged from 28 to 40 in this study.

α is an empirical constant, found to be 0.4 in this study, and

β is an empirical constant, found to be 6.2 in this study.

The empirical results in the study showed that 26 to 406 g/l. of surfactant resided in the oil phase of the system at the time measured. This would correspond to 2.6 to 40.6% of the surfactant as the test systems were dosed to 1000 g/l..

5.2.3 Application of Several Absorption Models to Absorption/Desorption

Ravera et al. (2000) describe the use of multiple models to apply to modelling the absorption/desorption of surfactants at the interface. The transfer of surfactants is noted as also affecting the stability of the emulsion itself as the interface stability is changed by surfactant transfer. The authors note that the problem of liquid-liquid surfactant has been ignored compared to that of liquid-vapour transfer.

Absorption of surfactants at the interface involves different time-dependent mechanisms, resulting in the transfer of molecules from/to the interface to restore the equilibrium state. There is also an exchange of surfactant below the interface, in an area called the sub-layer. Diffusion is the controlling mechanism for absorption dynamics in most cases.

The basic absorption kinetics can be described by (Ravera et al., 2000):

$$\frac{d\Gamma}{dt} = \Phi_a - \Phi_d - \Phi_{in} \quad (61)$$

where Γ is the overall absorption of surfactant,

Φ_a is the flux of surfactant to the interface from the bulk solution or absorption,

Φ_d is the flux of surfactant to the bulk solution from the interface or desorption, and

Φ_{in} is the flux of surfactant to the interface from the sub-layer.

A variety of basic absorption/desorption models are available to use and each has some assumptions with it (Ravera et al., 2000):

Henry Model

$$\frac{d\Gamma}{dt} = k_a - k_d \Gamma \quad (62)$$

where Γ is the overall absorption of surfactant,

k_a is the rate of surfactant absorption to the interface from the bulk solution,
 k_d is the rate of surfactant desorption from the interface,
 Γ_0 is the flux of surfactant to the bulk solution from the interface or desorption, and
 the flux of surfactant to the interface from the sub-layer is not included.

Freundlich Model

$$\frac{d\Gamma}{dt} = k_a - K\Gamma^m \quad (63)$$

where Γ is the overall absorption of surfactant,
 k_a is the rate of surfactant absorption to the interface from the bulk solution,
 K is the rate of desorption,
 Γ^m is the flux of surfactant to the bulk solution from the interface or desorption,
 m is the order of the absorption or number of layers, and the flux of surfactant to the
 interface from the sub-layer is not included.

Van der Waals Model

$$\frac{d\Gamma}{dt} = k_a - k_d \frac{\Gamma_\infty}{1 - b\Gamma_\infty} \exp\left\{ \frac{b\Gamma_\infty}{1 - b\Gamma_\infty} - \frac{2H\Gamma_\infty}{kT} \right\} \quad (64)$$

where Γ is the overall absorption of surfactant,
 k_a is the rate of surfactant absorption to the interface from the bulk solution,
 k_d is the rate of surfactant desorption from the interface,
 Γ_∞ is the flux of surfactant to the bulk solution from the interface or desorption,
 b is an empirical constant,
 H is the repulsion term,
 k is Boltzmann constant,
 T is the temperature, and
 the flux of surfactant to the interface from the sub-layer is not included.

Langmuir Model

$$\frac{d\Gamma}{dt} = k_a \left(1 - \frac{\Gamma}{\Gamma_\infty} \right) - k_d \Gamma \quad (65)$$

where Γ is the overall absorption of surfactant,
 k_a is the rate of surfactant absorption to the interface from the bulk solution,
 k_d is the rate of surfactant desorption from the interface,
 Γ_∞ is the flux of surfactant to the bulk solution from the interface or desorption,
 Γ_∞ is the saturated concentration of the surfactant on the interface, and
 the flux of surfactant to the interface from the sub-layer is not included.

Franklin Model

$$\frac{d\Gamma}{dt} = k_a \left(1 - \frac{\Gamma}{\Gamma_s} \right) - k_d \Gamma - \exp\left(\frac{2H\Gamma}{kT}\right) \quad (66)$$

- where Γ is the overall absorption of surfactant,
 k_a is the rate of surfactant absorption to the interface from the bulk solution,
 k_d is the rate of surfactant desorption from the interface,
 Γ_s is the flux of surfactant to the bulk solution from the interface or desorption,
 Γ is the saturated concentration of the surfactant on the interface,
 H is the repulsion term,
 k is Boltzmann constant,
 T is the temperature, and
the flux of surfactant to the interface from the sub-layer is not included.

2-States Model

$$\frac{d\Gamma}{dt} = k_a \left(1 - \omega_1 \Gamma_1 \right) - k_d \Gamma_1 + k_{a2} \left[\frac{\omega_1 \omega_2}{\omega_2} \right] (1 - \omega_2 \Gamma_1) - \frac{\omega_1 - \omega_2}{\omega_2} \Gamma_2 - \Gamma_2 \quad (67)$$

- where Γ is the overall absorption of surfactant,
 k_a is the rate of surfactant absorption to the interface from the bulk solution,
 ω_1 is the surface area of the interface,
 Γ_1 is the flux of surfactant to the bulk solution from the interface or desorption,
 k_d is the rate of surfactant desorption from the interface,
 k_{a2} is the rate of surfactant transfer to the interface from the sub-layer,
 ω_2 is the surface area of the sub-layer,
 ω_1 is the surface area of the interface,
 α is an empirical constant,
 ω_2 is the average area of the two layers,
 Γ_1 is the absorption of the surfactant on the interface, and
 Γ_2 is the absorption of the surfactant at the sub-layer.

Kavera et al. (2000) also describe techniques to measure the partition coefficient of surfactants between oil and water. They note that the partition coefficients of several surfactants have been measured and they provide these values. For example, Triton 100, a surfactant similar to that of oil spill dispersants, has a partition coefficient of 0.82 between n-hexane and water, 0.71 between n-heptane and water, and 0.26 between iso-octane and water. These partition coefficients indicate that, at equilibrium, most of this particular surfactant will reside in the water. In open systems, this equilibrium will not be reached and most of the surfactant will move to the water.

5.2.4 Kinetics of Absorption

Noskov (1996) studied the absorption of surfactants with short chains at the liquid-gas interface. A theoretical approach was combined with experiments to yield the kinetics of the interchange as being in the millisecond time frame.

The basic absorption time can be described as:

$$t = \Gamma^2 c^{-3} D^{-1} \quad (68)$$

where t is the time of absorption,
 Γ is the absorption of the surfactant,
 c is the surfactant bulk concentration, and
 D is the diffusion coefficient.

This is combined with several other developments and experimental data to yield two solutions, a jet solution:

$$\Gamma = \left(\frac{dT}{dc} \right) FI_n \left((-ikv_0 / D)^{1/2} a_0 \right) \quad (69)$$

where Γ is the absorption of the surfactant,
 T is the temperature,
 c is the concentration of the surfactant in the bulk solution,
 F is a constant,
 I_n is a Bessel function of n^{th} order,
 ikv_0 is the initial surfactant velocity,
 D is the diffusion coefficient, and
 a_0 is the mean radius of the jet.

And a complex solution:

$$\frac{\sigma - \sigma_0}{\sigma} = - \frac{2E(\pi v_0 \mu q / \lambda - E)}{q(E^2 + (\pi v_0 \mu q / \lambda - E)^2)} \quad (70)$$

where σ is the interfacial tension of the system,
 σ_0 is the oil-air interfacial tension,
 E is the change in interfacial tension with the change in absorption,
 v_0 the oil density,
 μ is the viscosity of the oil,
 q is the density of the surfactant flux,
 λ is the distance from the jet source to the nose of consideration, and
 a_0 is the jet radius at the exit.

Noskov (1996) also describes experiments that lead to the measurement of absorption times on the order of milliseconds. Emphasis is placed on the fact that much experimental data is still missing to describe the absorption more exactly.

5.2.5 Absorption of Surfactants Based on Chemical Potential

Fainerman et al. (1998) developed a series of prediction algorithms starting from chemical potentials. These algorithms describe mixed monolayers of surfactants with different molar area values, monolayers with both surfactants and proteins or polymers that are capable of re-orientation at the interface. The models consider the effect of self-regulation of the surface layer composition as caused by surface pressure. It is noted that this modelling approach allows for the consideration of surfactant interaction and the occupancy of different areas by surfactants.

Beginning from chemical potential, the surface pressure exerted by surfactants develops into the von Szyszkowski equation:

$$\Pi = \gamma_0 - \gamma = \frac{RT}{\omega} \ln(1 + K_1 x_1) = \frac{RT}{\omega} \ln(1 + b_1 c_1) \quad (71)$$

and the Langmuir equation:

$$\Gamma^* = \frac{1}{\omega} \frac{b_1 c_1}{1 + b_1 c_1} \quad (72)$$

where Π is the surface pressure,

γ_0 is the initial interfacial tension,

γ is the established interfacial tension,

R is gas constant,

T is the temperature,

ω is the molar surface area occupied by the surfactant,

K is the distribution coefficient of the surfactant - between the interface and bulk,

x_1 is the fraction of the surfactant at the interface,

b is the surface-bulk distribution coefficient, and

c_1 is the concentration of the surfactant.

Further development leads to the relation of the interfacial pressure to surface area coverage, which is also the Frumkin equation:

$$\Pi = - \frac{RT}{\omega} [\ln(1 - \theta) + a\theta^2] \quad (73)$$

where Π is the surface pressure,

R is gas constant,

T is the temperature,

ω is the molar surface area occupied by the surfactant,

a is the interaction parameter for species at the interface, and

θ is the surface coverage of the surfactant.

Further development and a comparison of the absorption of two surfactants at the interface yield:

$$\frac{\Gamma_1^*}{\Gamma_2^*} = \frac{b_1 c_1}{b_2 c_2} \exp\left(\frac{\Pi(\omega_2 - \omega_1)}{RT}\right) \quad (74)$$

where the subscripts 1 and 2 refer to different surfactants, 1 and 2.

Γ is the absorption coefficient of the surfactant at the interface,

b is the surface-bulk distribution coefficient,

c is the concentration of the surfactant,

Π is the surface pressure.

a is the molar surface area occupied by the surfactant,
 R is gas constant, and
 T is the temperature.

This is an important result as it implies that a smaller surfactant will expel a larger one from the interface given that their concentrations are about equal. Indeed, other studies in this report confirm that this is the case.

Continuing development of the models also results in the prediction of the change in desorption of proteins or surfactants from the interface with time, also the MacRitchie equation:

$$\frac{d\Pi}{dt} = k \exp\left(-\frac{\Pi a\omega}{RT}\right) \quad (75)$$

where Π is the surface pressure,
 t is the time,
 k is a constant,
 a is the molar surface area occupied by the surfactant,
 R is gas constant, and
 T is the temperature.

This equation shows that the change in the interfacial pressure is exponential with time, depending on the surface area occupied by the surfactant. This would imply that larger surfactants would yield emulsions with longer stability.

Fainerman et al. (1998) note that these equations and findings can be derived by a two-dimensional solution applying Butler's equations for the chemical potentials in a Gibbs dividing surface. The new equations developed here described mixed monolayers of surfactants with different molar area values as well as proteins capable of re-orienting at the surface. An important finding is that smaller surfactants will push off larger surfactants, proteins, or polymers from the interface. The surface pressure also influences the thickness of the interfacial layer.

6. Summary

6.1 Stability

6.1.1 Thermodynamic

Stability usually refers to the resistance of emulsion droplets to coalescence. As several other instability mechanisms have recently been found, stability now refers to resistance to any process that either reduces the number of droplets or increases their size. As emulsions are not thermodynamically stable, in the long term they will move back to a more stable position, which is the undispersed state.

One way to view the stability of an emulsion is that when the dispersed phase is broken into droplets, the surface free energy is increased in a way that corresponds to the size and number of droplets. The increase in interfacial free energy causes the thermodynamic instability of the dispersed phase.

6.1.2 Kinetic

Kinetic stability refers to stability in terms of time. While an emulsion is never entirely stable according to the kinetic definition, it may be considered to be stable if the material is sufficiently stable within the use time. There is no standard convention for considering stability time. Some authors use half-life, similar to radiation, which is appropriate because most processes that destabilize emulsions are exponential, or analogous functions, with respect to process.

6.1.3 Closed Versus Open Systems

The stability of emulsions in an open system such as the ocean is a very different matter than in a closed system such as a jar. The continuous matter in a closed system can be altered to increase stability and surfactant displacement. For example, many food emulsions are rendered stable for months by adding polymers and thickeners to the continuous medium. Other food emulsions are not highly stable. Italian salad dressing is an example of interest as both the oil and the surfactants bear relationship to oil dispersions in open water. This salad dressing must be re-emulsified by shaking before each use and stays in useable form for only minutes. In a study noted in this report, an emulsion formed from a crude oil using an ionic surfactant changed from stable in 14 days only if the water content was less than 20%. At higher water contents, the same emulsion was stable for only a few minutes.

6.2 Destabilization Processes

6.2.1 Gravity

Gravity separation of emulsions occurs with or without the presence of surfactants. For a given droplet, the effect of gravity is simply a function of the difference in density of the oil and the water. The rate at which gravity separation occurs varies as the square of the particle size and inversely as the viscosity of the continuous phase, which is water in this study. This is one of the distinguishing features between oil spill dispersions and closed systems. In closed systems, the gravity separation of the oil droplets can be slowed by controlling the viscosity of the medium or continuous phase. This is carried out in mayonnaise for example by using viscosity enhancers for the continuous phase. For dilute systems such as oil spill dispersions, calculations and experimental data show that gravity-induced creaming and coalescence are the primary loss mechanisms.

6.2.2 Creaming

Creaming is the rising of droplets to the surface as a result of gravity. As most oils are lighter than water, this is the typical fate of most oil-in-water dispersions. Creaming occurs regardless of surfactant content and a droplet rises at about the same rate with or without surfactant. Sometimes the term creaming is used to collectively describe all processes involved in emulsion destabilization, while other times, it refers to gravitational rise only. Throughout this report, creaming refers to gravitational rise only.

6.2.3 Sedimentation

Sedimentation is the reverse of creaming and occurs when the oil or dispersed phase is heavier than water. The Stokes' equation is relevant to the rate of either rising or sinking.

6.2.4 Coalescence

Coalescence is the formation of droplets into a liquid at the surface. It occurs when two or more droplets join to form one larger droplet. Classically, gravity separation was not counted as a mechanism of destabilization. If creaming is not counted as a destabilization mechanism, coalescence is the primary destabilization process for emulsions such as crude oil-at-sea dispersions.

It is important to understand that much of the coalescence that occurs does so after particles have collided. The droplets of a dispersed liquid in an emulsion are in constant motion and therefore collide frequently. If the interfacial film surrounding the droplets is too weak to withstand the collision, the droplets will coalesce.

As a side note, emulsions stabilized with solid particles tend to be much more stable than those stabilized with surfactants. It is suggested that this is a result of the more rigid film formed by solid particles. Some researchers noted that coalescence is more prevalent in salt water than in fresh water.

6.2.5 Flocculation

Flocculation refers to the formation of clusters of particles. Typically, the interfacial layer on the droplets involved in the cluster prevents coalescence. Flocculation is caused by attraction between particles such as from van der Waals forces. The fate of flocs, the end product of flocculation, is also creaming, as the clusters have a much greater rise rate than individual droplets. Flocculation has not been studied extensively for crude oil emulsions. One study on kerosene emulsions showed that flocculation does occur with these emulsions, especially with excess surfactant.

'Depletion flocculation' is another term used to refer to flocculation, but this occurs when the process is depleting droplets in the emulsion. In some emulsions, either flocculation or coalescence can occur depending on conditions such as subtype or concentration of the surfactant. Depletion flocculation is promoted by the presence of unadsorbed surfactants in the water, especially if they are in micelles. The presence of micelles, which are thermodynamically stable entities, causes further desorption of surfactants from the emulsion, thus destabilizing it. Depletion flocculation is also enhanced by excessive concentration of surfactant, which also leads to micelle formation, which in turn leads to depletion flocculation.

6.2.6 Ostwald Ripening

Ostwald ripening is the movement of molecules and small particles into larger particles. Ostwald ripening is thermodynamically favoured for this movement. Some studies showed that Ostwald ripening is favoured for oil components such as decane when the water volumes are low, but less favoured when they are high. For oil spills, this would indicate that Ostwald ripening is less of a destabilization mechanism than coalescence.

6.2.7 Phase Inversion

Phase inversion is the change in an emulsion when the continuous phase is inverted to the discontinuous phase. In the context of the type of emulsions discussed here, it is the change of an oil-in-water emulsion to a water-in-oil emulsion. There is little information to indicate that such inversions occur with oil spill dispersions. There are not enough extensive studies of the long-term stability under a wide variety of conditions to state whether such a process has ever occurred.

6.2.8 Doublet Formation and Fragmentation

A doublet is an intermediate phase between two particles interacting or colliding. The outcome of a doublet could be reformation of two individual droplets, resulting in coalescence or flocculation, depending on conditions and the strength of the interfacial layer. Fragmentation describes the formation of the resulting end-product. Fragmentation times depend on conditions such as droplet radii, film strength, and phase characteristics. Fragmentation times of a few to 100 minutes would yield overall emulsion half-lives from minutes to a few hours.

6.2.9 Dilute Emulsions

Processes involving dilute emulsions, such as oil spill dispersions, can be simplified. The energy path leading from a single original particle to a doublet, the intermediate stage upon the collision of two droplets and finally to a coalesced particle, is an important consideration. In the

case of dilute emulsions, the stability is most affected by two processes, Ostwald ripening and coalescence. The effect of Ostwald ripening is that sub-microns rapidly disappear, increasing the size of the particles. Coalescence between droplets occurs upon collision. Two types of coalescence are defined, rapid and slow coagulation. Rapid coagulation is when all collisions result in coalescence. Slow coagulation is when many collisions do not result in coalescence to the presence of a large energy barrier. In the case of oil spill dispersions, initially slow coalescence occurs because of the energy barrier, then as surfactant is lost, this changes to a rapid coagulation process.

6.3 Processes/Influences Behind Stabilization/Destabilization Processes

6.3.1 Film or Interfacial Film

The function of any emulsifying agent or surfactant is to stabilize, to the degree possible, an otherwise unstable system. The emulsifying agent does so by absorbing at the liquid-liquid interface as an oriented interfacial film. The film performs two functions. It reduces the interfacial tension between the two liquids and consequently the thermodynamic instability of the system resulting from the increase in the interfacial area between the two phases and it decreases the rate of coalescence of the dispersed liquid droplets by forming mechanical, steric, and/or electrical barriers around them. The steric and electrical barriers inhibit the close approach of one droplet to another.

Deformations in the film can occur as a result of several factors, including collisions and particle-particle interactions. Deformation alone can lead to instabilities in the emulsion.

Film film instabilities arise from heterogeneities in surfactant concentrations and other similar factors. The appearance of a zone of deformation on a droplet can influence later interaction behaviour. Researchers have flagged deformation as a sign of unstable droplets, noting that the coalescence rate and other similar factors are much higher for droplets that show signs of deformation.

6.3.2 Film Strength

It has been found that the strength of the film is essential to the stability of the emulsion. The physical strength of the film is important, particularly if droplets collide. It has been noted that, if the film is strong, flocculation is more likely to occur than coalescence and vice versa. For oil spill dispersions, coalescence is the most likely scenario because of the nature of the interfacial film.

6.3.3 Film Buildup and Destabilization Processes

Absorption and Desorption - Surfactants readily absorb at the interface between a droplet and the bulk liquid, usually water. Marangoni fluctuations and instabilities are associated with the distribution of surfactant gradients around a droplet. There are also several forces that lead to desorption or removal of the surfactant from the interface, particularly to the water from the interface.

Movement toward Equilibrium - Open/closed Systems - Surfactants will distribute between the bulk phase, water, and the interface to achieve equilibrium between the two phases. This equilibrium depends on the water-oil solubility characteristics of the surfactant. In a closed system, this equilibrium is achieved rapidly with little loss of surfactant. In an open system, however, equilibrium is never achieved, the surfactant leaches into the water, and over a period of hours, little surfactant is left in the oil droplets.

Marangoni Stabilization/Destabilization - The Marangoni effect is an important phenomenon in terms of surfactant stability and dynamics. The Marangoni effect is due to the tendency of surfactant concentrations to quickly distribute over an interface. If there is a deficit in surfactant concentration on one side of a droplet, the surfactant quickly moves to restore the equilibrium concentration over the droplet. The restoration of equilibrium is known as Marangoni stabilization.

Marangoni instability arises as a result of this surfactant flow because the flow continues and results in areas of greater and lesser surfactant concentration over the droplet interface. Some researchers have noted that Marangoni instability was periodic and was about on the order of 1000 seconds for one particular system. It was noted that convective instability periodically switched between a slow and a more rapid transport regime. During a convective stage, fast absorption of surfactant occurred with rapid inflow of surfactant to the interface. During a diffusive stage, desorption occurred and gradients built up until the system became unstable again.

Hydrodynamic Destabilization - Several researchers found that in a flowing field or when droplets are in motion, surfactant thinning occurs on the leading edge and there is excessive surfactant on the trailing edge. This condition is known as hydrodynamic destabilization. Experiments show that at low surfactant concentrations, this occurs at a velocity of 0.0005 m/s and at high surfactant concentrations, the instability will occur at 0.003 m/s. Both these velocities would apply to larger droplets due to Stokes rising.

Surfactant Displacement - Mixed Surfactants - Several studies have shown, both experimentally and theoretically, that small surfactants will displace larger surfactants or polymers at the interface. Although studies have shown that mixed surfactant systems yield more stable emulsions as a rule, the size difference between surfactants is critical to this. A mixed surfactant system with large and small surfactants will essentially be more stable than one stabilized by the small surfactants alone, as these small surfactants will displace the larger surfactants at the interface. This condition is predicated on the fact that the concentration of surfactants at the interface is great and there actually is interference between surfactants.

Some studies showed that adding small surfactants, such as Tween and Spans as used in oil spill dispersants, actually destabilized emulsions that were stable with larger proteins or polymers as surfactants. Similar results were found with a common ionic surfactant, SDS, which destabilizes surfactants compared to polymers. This may not be entirely relevant to oil spill dispersions, but indicates that dispersions might be made more stable with polymers if all other conditions were met.

Surfactant Type and Chain Length - The type of surfactant used is important. Experiments in which the surfactant was varied have shown that the differences in type can result in vastly different lifetimes of an emulsion. It is beyond the scope of this report to discuss surfactants, however, suffice it to say that the choice of surfactant can greatly affect emulsion lifetimes and is therefore an important consideration.

Studies show that the type of surfactant and the chain length are important factors. Several studies have shown that increasing chain length increases stability. The use of polymers to stabilize emulsions has significantly improved stability. One study showed that linear chains offered an improved stability over branched chains. Another study showed that, not only was the stability increased with increased alkyl chain length on the surfactant, but also that the droplet size was smaller. An important finding with mixed surfactants, as noted above, is that the smaller surfactants tend to displace larger surfactants at the interface. Several researchers noted that

stability increased with increasing alkyl chain length on the surfactant.

Researchers who used alcohols as co-surfactants to stabilize emulsions found hydrogen bonding of the alcohols between surfactant and alcohol and also between the alcohol and water. Use of alcohols as co-surfactants for oil spill dispersants has been tried but was found to not very effective because of loss of the alcohol due to the high dilution rates.

Surfactant Quantity - The amount of surfactant used is an important factor in emulsion stability. Many researchers have found that there are four conditions that apply for surfactant quantity. The first is a threshold below which the quantity of surfactant is too low to provide any effective stabilization. Between this minimum-effective threshold and another level is the optimal quantity of surfactant to provide good stability. Above this threshold, increasing surfactant often decreases the stability due to surfactant interaction. A fourth condition is sometimes identified in which surfactant is in such excess that phase inversion or gelation occurs.

Many researchers have found that the presence of sufficient surfactants, i.e., the second level noted above, is critical for any emulsion stability. Most studies have shown that stability below the critical surfactant concentration is very low. In fact, it has been shown that low surfactant concentrations have the same effect as no surfactant. Several experiments have shown that excess surfactant will destabilize an otherwise stable emulsion. One researcher found that concentrations of greater than 7% would result in rapid destabilization and creaming.

Mixing Time - Some researchers have found that a mixing time is needed before surfactants can stabilize an emulsion. This refers to the mixing of the surfactant with the oil to achieve a relatively good distribution. One researcher defined this as a meso-equilibrium time, or the mixing time needed to reach maximum stability. For a hexane-in-water emulsion, various surfactants required from 0.1 to 183 seconds of mixing before reaching maximum stability. Obviously, this mixing would be difficult to achieve in oil spill dispersions as dispersant must be applied from above and mixing occurs only through random processes.

Thermal Fluxes - Researchers have found that the surfaces of emulsion droplets are subject to capillary waves caused by thermal fluxes. It is suggested that there is a film thickness, called the transitional thickness, at which the surface fluctuation becomes unstable and then the fluctuation grows spontaneously. At a given film thickness, the surface corrugations caused by the fluctuations rise to the point where contact is made between two adjacent droplets. The thickness at this time is called the critical thickness. This information was used to calculate droplet lifetimes. It was found that a 15- μm droplet had a lifetime of 200 seconds, a 20- μm droplet, 100 seconds, and a 50- μm droplet, 10 seconds. This applies to oil spill dispersions as these droplet sizes represent the top end of the dispersions that are present.

Pulses - Some researchers found that there was an oscillatory absorption-desorption behaviour of surfactants and droplets. Droplets rapidly absorbed surfactants and then slowly lost these surfactants. The absorption is accompanied by a small waving motion across the interface. The wave motion travels slower than the convective mass transfer of surfactants. The abrupt absorption is caused by amplification of the mass transfer of ionic surfactants from the bulk phase by a type of Marangoni convection, which in turn is caused by a heterogeneous concentration of surfactants at the interface. These asymmetrical oscillations can lead to droplet instability.

Temperature Fluctuations - Changes in temperature cause changes in the interfacial tension between the two phases. Fluctuations in temperature can also cause differential changes in other factors such as the relative solubility of the surfactant in the two phases and diffusion in the system. Surfactants are most effective when near the point of minimum solubility in the solvent in which they are dissolved. It was found that emulsions were universally more stable at cooler temperatures. This runs counter, however, to the trend that more or better emulsions are formed at higher temperatures. The resulting effect is such that not enough oil dispersions would be produced at very low sea temperatures to notice the increased stability.

6.3.4 Other Factors

Salinity - Salinity affects emulsion stability, but the degree of effect depends on the type of surfactant, temperature, and other conditions. There is not a simple rule of salinity effect.

Surfactant Precipitation - Several researchers have found that surfactants in the water bulk phase will precipitate through reactions with ions in the water or interactions with each other. It is noted that this is a form of surfactant loss in both closed and open systems.

Energy - Studies in the field had noted that energy is important in the early creation of emulsions. The more energy, the greater the dispersion phase is moved into the emulsion. One study on crude oil emulsions found only about a 16% difference between the stability of a crude oil emulsion, whether energy was applied continually after formation or not applied. Another study that focussed on examining coalescence noted that increasing energy increased the coalescence rate. This effect is understood by the fact that the collision rate is also increased with increasing turbulence or energy input into a system. The half-life of an Arabian crude oil emulsion was decreased from about 4.5 hours at a low shear rate to about 3.5 hours for a high shear rate. Surfactants reduce the amount of energy required to produce emulsions in the first place and reduce the thermodynamic instability to a small degree.

Viscosity of the Continuous Phase - The viscosity of the continuous phase of an emulsion is an important factor. A viscous continuous phase will form a barrier to surfactant loss from the droplets, a barrier to rapid collisions, and reduce the rise rate of the droplets. Viscosity enhancers and similar additives are used in food and cosmetic preparations to stabilize emulsions. For oil spill dispersions, water is the continuous medium and stability is therefore an issue.

Interfacial Tension - Interfacial tension is the force exerted between two different liquids. In relation to emulsions, it is more of a concept than a real force as it incorporates many of the forces noted above. The assumption is that the thermodynamic energy of a droplet emulsified in another liquid can be ascribed to this interfacial tension between the two liquids. This is an oversimplification as it combines many of the above-noted forces and considerations into one force.

6.3.5 Other Characteristics

Droplet Size - Droplet size is a very important factor in emulsion stability. The smaller the particles and the size range of the particles, the more stable the emulsions. On the other hand, the larger particles are more thermodynamically stable and thus size increase is thermodynamically favoured. As noted in many different sources, the forces that relate to stability are very dependent on droplet size. For oil spill dispersions, the wide variety of crude or refined components implies a wide spectrum of particle sizes. This in turn dictates that such emulsions have low stability.

Some studies have shown that changing particle sizes by only a few percent can change emulsion lifetimes very significantly, usually several factors more than with larger droplets. Calculations show that stability rises as the inverse of the cube of the droplet or particle size. This illustrates the extreme importance of particle size in determining stability.

Not only is droplet or particle size important, but also the homogeneity of droplet sizes. The more homogeneous the particle size, the more stable the emulsion and vice versa. This is partially explained by the fact that the forces between droplets are more equal when they are similar in size and thus destabilization processes such as Ostwald ripening are less prevalent. It should be noted that the droplet sizes of dispersed oil spills are very heterogeneous and stability is therefore an issue.

One approach to stability and droplet size was to determine the lifetime of different droplet sizes. It was found that a droplet of 10 μm has a lifetime of about 2 seconds and a droplet of 3 μm has a lifetime of about 40 seconds, showing the importance of droplet size in determining lifetime.

Miscelle Formation - Micelles are clusters of surfactants formed in the water phase. Because micelles are even more stable than emulsions, there is a net flow of surfactants from the emulsion, through the water phase to form micelles. Micelles do not form until a certain concentration of surfactants is present in the water column. Some researchers have suggested that the presence of free surfactant micelles increases the attraction between droplets because of an osmotic effect.

6.4 Forces

6.4.1 DLVO Theory

The DLVO theory of emulsion stabilization is named after Derjaguin and Landau and a later set of workers, Verwey and Overbeck. This theory proposes that there is a balance between the repulsive and attractive potential energies of interaction between the dispersed particles or droplets. Repulsive interactions are due to either the similarly charged electrical double layers surrounding the droplets or to solvent-droplet interactions. Attractive forces are largely due to the van der Waals forces between droplets. For a stable dispersion to occur (for whatever time), the repulsive forces must be greater than the attractive forces. The repulsive forces are much greater for a thick layer and smaller droplets.

Subsequent researchers have shown the limitations of the DLVO theory. One of these is that the effect of the stability of an oil-in-water dispersion is limited to the effect of the surfactant on the surface potential of the dispersed particles, the effective Hamaker constant, and the ionic strength of the dispersing liquid. Several other forces or considerations were not incorporated into the DLVO theory. In addition, the basic DLVO theory is not applicable to nonionic surfactants. Several of these are summarized in this report including concepts such as oscillatory structure forces. Rosen (1989) notes that some of the other factors that might be considered are absorption of surfactants to larger particles, as is the case with oil spill dispersions, may change the contact angle that the droplets make with the continuous liquid phase. Also under consideration is that surfactants that have long chains may form non-electrical steric barriers to coalescence or flocculation. Another consideration suggested is that there is no means to measure the electric barrier of the Stern layer, the interfacial layer, and the charged layer surrounding the droplet. The Zeta potential, which is described later, is not a direct measure of the Stern layer.

6.4.2 Attractive Forces

van der Waals - Van der Waals forces refer to intermolecular forces due to the polarization of molecules. These forces are prevalent throughout chemistry and are known to influence many reactions and systems. They are attractive and present in many fluids and are one of the prime

forces that bring droplets together in a system free of motion or turbulence..

Capillary - Capillary forces arise between two droplets when the distance between them becomes small so that there is an attractive force between the two particles such as in a capillary tube. The origin of the forces is the mutual attraction between the two particles.

Oscillatory Structure Force - One of the 'new' attractive, and sometimes repulsive, forces between particles has been called the Oscillatory Structure force (OSF). If two large particles or droplets are in a colloidal liquid, i.e., a dispersion of very small particles, and the separation distance between the two particles is smaller than the diameter of the colloidal particles, then there is an attractive force between the two particles because of the osmotic pressure. This force would result in coalescence or flocculation between the two particles, thus depleting the emulsion.

Basically, OSF is caused by a wide difference in droplet sizes, such as would be present in an oil spill dispersion.

In some situations, the oscillatory structure force can be either attractive or repulsive. If small colloidal particles are confined in the gap between two large particles and when the gap between the two larger particles is about equivalent to several colloidal particle diameters, the colloidal particles in the gap interact with the large droplets as a result of Brownian forces. The Brownian forces induce an ordering among the particles and this ordering propagates over several particle diameters. The structured regions near the two opposing surfaces overlap, giving rise to the oscillatory structural force. This long-range structure induces a repulsive structural barrier that helps prevent the large particles from flocculating or coalescing. When the separation distance between two larger particles is smaller than the diameter of the colloidal particles, a net attractive force between the two particles occurs as a result of the difference between the osmotic pressure difference between the bulk and confined regions of the colloidal system. This force has a tendency to oscillate between repulsive and attractive, with a frequency equal to the effective size of the colloidal particles (wavelength of the distance). The oscillatory structure force operates over a distance of the diameters of several colloidal particles which is greater by up to 20 times the distance that the DLVO forces operate.

An important facet of the oscillatory structure force is that a wide poly-dispersibility from colloidal to micron-sized particles is necessary for this to occur. Just a few larger particles will destabilize an emulsion by OSF. Oil spill dispersions have this characteristic and therefore are prone to instability.

6.4.3 Repulsive Forces

Electrical Forces - Surfactants, especially ionic surfactants, have an electric charge. Since similar surfactants will be distributed throughout an emulsion, there will be a similar charge on each droplet and thus an electric repulsion between droplets. This is the most significant force separating droplets and preventing coalescence. While ionic surfactants have the greatest amount of charge and form the strongest electrical barriers, they are also the most water-soluble and thus readily partition into the sea. Nonionic surfactants, which are used extensively in oil spill dispersants, have a lesser charge and pose a weaker electrical barrier to coalescence. Nonionic surfactants, however, have a lesser tendency than ionic surfactants to partition rapidly to the water phase.

Zeta potential is a measure of the electrophoretic mobility of oil droplets in an applied electric field and is indicative of the droplet-to-droplet charge and thus the emulsion stability. It is not exactly the repulsive electric force discussed above. Measures of crude oil emulsions showed

Zeta potentials varying from -3 to -10 mV. This was judged to be insufficient to prevent coalescence.

Steric Forces - Steric forces are interference forces resulting from the presence of large molecules such as polymers or chains. The use of larger polymers as surfactants has been shown to provide stability to emulsions through steric forces. Steric forces might be viewed as interference to movement or penetration by a combination of simple presence and a hindrance to external molecules.

Mechanical Forces or Barriers - The mechanical or physical barrier is important to the stability of an emulsion as it increases the resistance of the dispersed particles to mechanical shock and inhibits them from coalescing if particles collide.

6.5 Rates of Processes

6.5.1 Particle or Droplet Rising/Destabilization Rate

Stokes' Rising Rate - The classic Stokes' equation is:

$$s = \frac{2\Delta\rho ga^2}{9\eta} \quad (76)$$

where s is the rise rate.

$\Delta\rho$ is the density difference between the disperse and droplet phases.

g is the gravitational constant.

a is the droplet radius.

$F(\Phi_p)$ is a volume dependent correction factor and is 1 for dilute solutions, and

$\Delta\eta$ is the difference between the viscosity of the disperse and droplet phases.

This equation is very important in terms of understanding the resurfacing of oil spill dispersions. It shows that for the smallest droplets at 1 m below the slick, the rise rate would be about a year (or forever) and for the largest droplets immediately below the slick, rise rate is a few seconds. Several researchers have shown that surfactants do not affect the base rise rate, but others question whether the Stokes' rate is far too slow.

Many researchers have shown that the rise rate predicted by the Stokes' equation is far too slow compared to experimental measurements. These might be explained by the destabilization processes described in this report, namely coalescence, flocculation, and Ostwald ripening. All of these serve to increase particle diameter and thus significantly increase rise rate. A doubling of a droplet radius results in a quadrupling of the rise rate for that particular droplet.

Coalescence Rate - Coalescence rate is an important factor in the stability of emulsions. This is the time it takes for two droplets to merge and form one droplet. Coalescence rate should not be confused with overall emulsion lifetimes, as coalescence rate is just one part of the process. The Stokes' rising time is usually the governing factor for overall emulsion stability time. Coalescence rates are fairly rapid and increase with temperature. For heptane-in-water emulsions, measured times of coalescence were from 2 to 70 seconds. For a particle-stabilized emulsion, which is generally very much more stable, coalescence times ranged from about 40 to 80 minutes. One study showed surfactant-stabilized oil emulsions with coalescence times ranging from 15 to 260 seconds.

Collisions will necessarily result in a potential for coalescence. Findings appear to indicate that oblique collisions will result in more coalescence than head-on collisions. As more collisions occur in more energetic and turbulent conditions, coalescence is accelerated in those situations.

Flocculation Rate - Flocculation rate is analogous to coalescence rate except that the droplets form flocs rather than coalesce.

Ostwald Ripening - Ostwald ripening requires a flux of soluble components in the water and a wide distribution of droplet sizes, both of which occur in oil spill dispersions. The rate of Ostwald ripening depends on, among other factors, the square of the inverse of oil viscosity and directly on the diffusion rate of the components. This means that for oil dispersions, Ostwald ripening is most prevalent for light oils.

Brownian Motion - Brownian motion is the random motion of particles in another fluid due to thermal motion and is one of the simplest stochastic processes. Brownian motion depends on temperature, among other factors. Brownian motion can be responsible for collisions between particles leading to coalescence.

Mixing in Bulk - Bulk mixing is the most common process that transfers droplets around a given area. For open sea oil dispersions, this is the means by which droplets are moved downward from the surface. Another means is droplet diffusion, but this is at least 100 times slower than bulk mixing. A rule of thumb for mixing by waves is that the depth of mixing is about 1.5 times the maximum wave height. It should be noted that not all emulsion movement by mixing is necessarily downward as some upward transport of particles or droplets also occurs.

Loss of Surfactant to the Water Column - One study using n-heptane and SDS found that the interfacial tension was reduced by half in 30 seconds. This would indicate that over half of the surfactant had transferred to the water in that time. Another study showed that after about 30 minutes, 3 to 40% of the surfactant resided in the oil. Partition coefficients between water and oil droplets have been measured for several surfactants. For those similar to ones used in oil spill dispersants, the partition coefficient (oil-to-water) varied from 0.82 for hexane, 0.71 for heptane, and 0.26 for iso-octane. For larger components such as dicosane, this coefficient would be very low and much of the surfactant would therefore move to the water phase.

6.6. Some Half-lives

The literature reviewed for this report had several measurements of the half-lives of oil and hydrocarbon emulsions. Some of these papers had graphs from which the half-life of the particular emulsion could be inferred. This is shown in Table 3. The half-life data for crude oil emulsions are all very similar with an average half-life of about 12 hours.

Table 3 Emulsion Half-lives from the Literature

Oil Type	Dispersant/ Surfactant	Summary Average Half- life (hours)	Literature Data			Units	Other Factors
			Nominal	Lower Range	Upper Range		
Arabian Crude	Corexit 9500	4.5	4.5			Hours	Shear rate 5 s ⁻¹
Arabian Crude	Corexit 9500	4	4			Hours	Shear rate 10 s ⁻¹
Arabian Crude	Corexit 9500	7.5	7.5			Hours	Shear rate 20 s ⁻¹
Alaska North Slope	Corexit 9500	15		10	20	Hours	
Alaska North Slope	Corexit 9527	15		10	20	Hours	
Alberta Sweet Mixed Blend	Corexit 9500	18		10	25	Hours	
Alberta Sweet Mixed Blend	Corexit 9527	18		10	25	Hours	
Yuking lubricant	Surfact mix	24	24			Hours	
Kerosene	Various	3		0.5	5	Hours	
Gesium crude	Various	40		0.5	36	Hours	Closed system
Crude oil	Surfact & co-polyamide	1.5		1	2	Hours	
Crude oil	Natural surfactants	0.2		0.01	0.5	Hours	
Hydrocarbons	Average	12					
Decane and Decanol	SDS	0.4		0.25	0.5	Hours	
Toluene	Ionic	10		5	15	Hours	
Tetradecane	SDS	3		0.1	6	Hours	
Tetradecane	Tween 20	24	24			Hours	

7. Conclusions

Crude oil-in-water dispersions are similar to many other types of emulsions in that they are stable under some conditions for a period of hours. During this time, destabilization processes are underway that result in oil resurfacing. Because of movement of the slick, from which the dispersion occurred and because the water column may have differential movement from the slick, resurfacing oil will likely appear in areas outside the slick. As resurfacing is a slow process and goes on for days, most of the oil will not be visible on the surface unless processes such as Langmuir cells were to re-concentrate the oil into slicks or unless there was no relative movement between the surface slick and the water column.

There is a vast body of information and experimentation and a broad consensus on the stability of such emulsions.

The stability and resurfacing of crude oil emulsions are influenced by the following forces.

1. Natural stabilization/destabilization forces

The most important such force is gravity. As most oils are less dense than water, their emulsion droplets are also less dense than water and will rise. The reappearance of oil on the surface is known as creaming.

There are many destabilizing forces to emulsions such as chemically dispersed oil including, coalescence, flocculation, Ostwald ripening, and phase inversion. It is known that coalescence of droplets is the most important destabilization process for emulsions similar to dispersed crude oil emulsions.

2. Standard tendency of emulsions to instability

This report describes the extensive literature on emulsion stability noting that there are many repulsive forces and some attractive forces between droplets. The net result of these forces is to destabilize the droplet after some period of time.

3. Instability of interfacial film with surfactants

The interfacial films stabilized by surfactants are subject to a number of destabilization processes including Marangoni circulation, hydrodynamic destabilization, oscillatory forces,

pulsing, thermal instabilities, surfactant desorption, and others. These forces weaken the interfacial film and consequently destabilize the emulsion.

4. Loss of surfactant

In addition to the mechanisms of interfacial stability reduction noted in point 3, there is a net loss of surfactant in dilute emulsions such as oil spill dispersions. This net loss is caused by the tendency of the surfactants to equilibrate between the water bulk phase and the oil droplet interface. As crude oil emulsions are continually being diluted, surfactant movement from the interface to achieve equilibrium constitutes a loss of surfactant to the system. This loss of surfactant accelerates the destabilization of the emulsion.

5. The heterogeneous mixture of compounds in oil

Oil consists of dozens of major constituents, most of which are very different in size and properties. This results in the formation of very different droplet sizes. In addition, the effect of surfactant is quite different on the various fractions of the oil.

6. Wide distribution of droplet sizes

Because crude oil dispersions have a wide distribution of droplet sizes with much of the volume in the micron-sized area, the emulsions have a lower stability. It has been demonstrated throughout this report that emulsions of micron-sized droplets are less stable. It has also been shown that the presence of even a few larger droplets will destabilize an emulsion as this triggers destabilization processes such as Ostwald ripening.

7. Low viscosity of water

Because the viscosity of water is low, destabilization processes are more prevalent in water than in other bulk fluids. The low viscosity of water increases coalescence and the diffusion of surfactants away from oil droplets in oil-in-water emulsions.

8. Increasing dilution of the emulsion

For dilute emulsions, surfactant desorption is surfactant loss. Further surfactant absorption rarely occurs. As crude oil dispersions or emulsions are dilute and become increasingly dilute with time, they destabilize through surfactant loss and through many of the other processes noted in this report. Crude oil dispersions would be considered less stable than most other emulsions typically considered.

The results of this body of knowledge are illustrated in Figures 20 and 21, which is a hypothetical scenario of an oil spill dispersion. The percent remaining at a given point in time is calculated using a first-order decay with a half-life of 12 hours, the average of half-lives found in this study. The visibility of the oil was estimated from approximate thickness calculations. It was assumed that 30% of the oil was initially dispersed. This shows that some oil, about 5%, would remain in the water column after 30 hours. As the rise time of the very small drop for a very long time. The fact that oil resurfaces over a long period of time and because the remaining droplets would be long, this 5% may indeed remain in the water column slick is moving and spreading, results in the effect that much of the oil is not visible on the surface. It should be re-emphasized that Figures 20 and 21 are only illustrations of the results of the processes described in this study and are not an the results of an exact model.

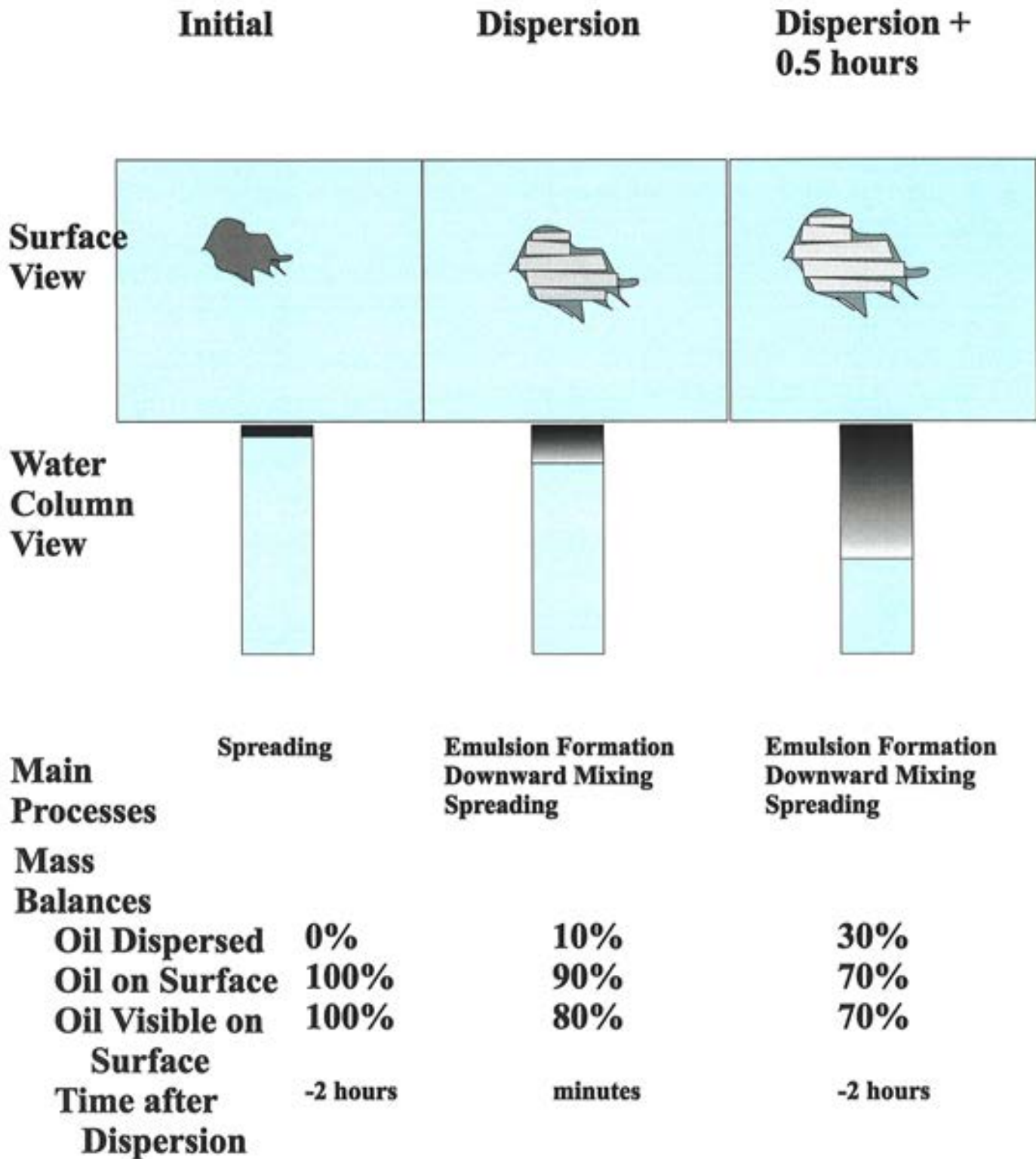


Figure 20 A Chemical Dispersion Scenario Showing the Progression of the Slick, Emulsion Fate, and Mass Balance

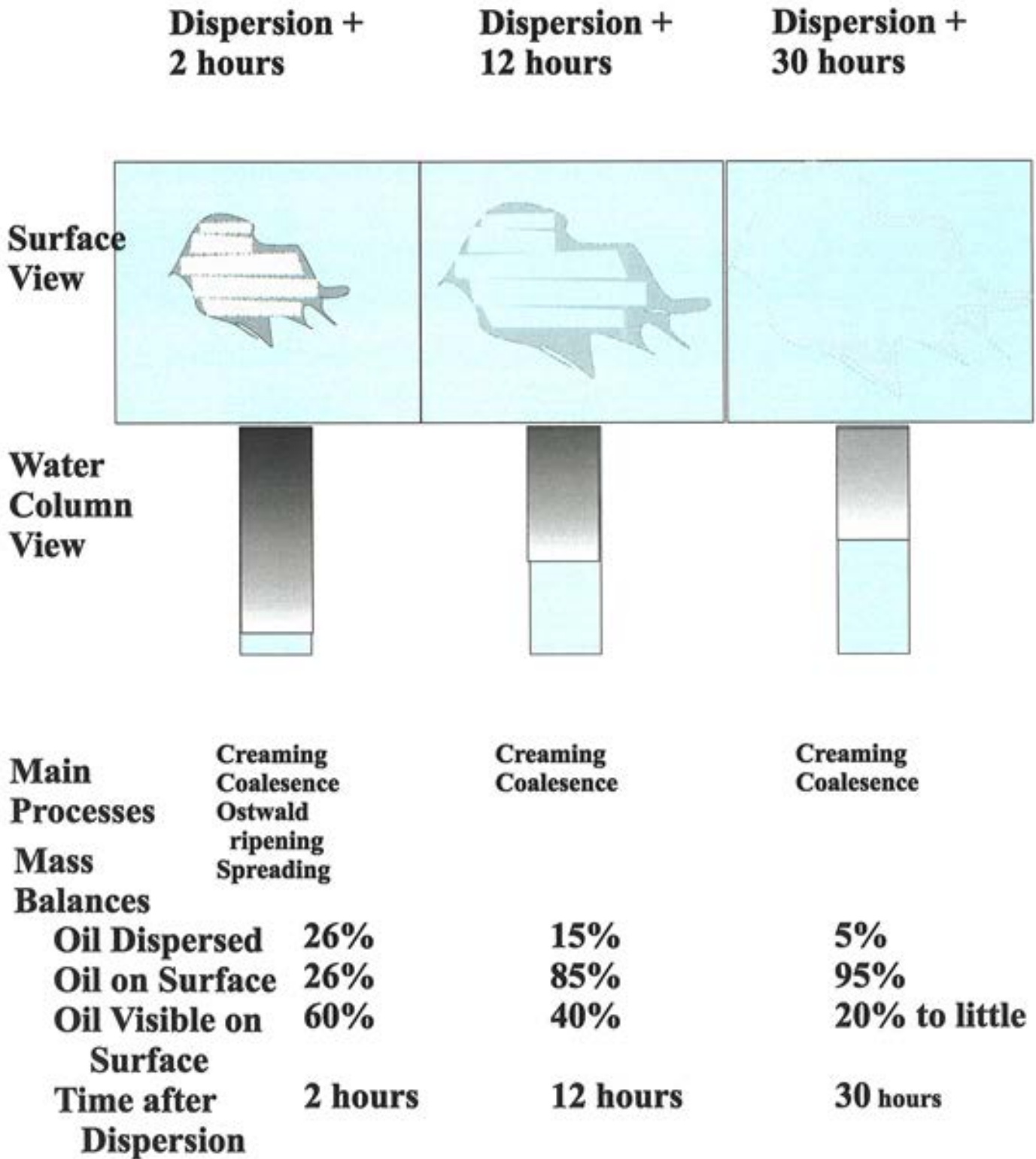


Figure 21 A Chemical Dispersion Scenario Showing the Progression of the Slick, Emulsion Fate, and Mass Balance

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