1

Petroleum Emulsions

Basic Principles

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This chapter provides an introduction to the occurrence, properties, and importance of petroleum emulsions. From light crude oils to bitumens, spanning a wide array of bulk physical properties and stabilities, a common starting point for understanding emulsions is provided by the fundamental principles of colloid science. These principles may be applied to emulsions in different ways to achieve quite different results. A desirable emulsion that must be carefully stabilized to assist one stage of an oil production process may be undesirable in another stage and necessitate a demulsification strategy. With an emphasis on the definition of important terms, the importance of interfacial properties to emulsion making and stability is demonstrated. Demulsification is more complex than just the reverse of emulsion making, but can still be approached from an understanding of how emulsions can be stabilized.

Importance of Emulsions

If two immiscible liquids are mixed together in a container and then shaken, examination will reveal that one of the two phases has become a collection of droplets that are dispersed in the other phase; an emulsion has been formed (Figure 1). Emulsions have long been of great practical interest because of their widespread occurrence in everyday life. Some important and familiar emulsions include those occurring in foods (milk, mayonnaise, etc.), cosmetics (creams and lotions), pharmaceuticals (soluble vitamin and hormone products), and agricultural products (insecticide and herbicide emulsion formulations). In addition to their wide occurrence, emulsions have impor-

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Figure 1. Photomicrograph of an emulsified droplet of a crude oil, dispersed in the aqueous solution that was used to release it from the mineral matrix in which it was originally held. An interfacial film is obvious at the surface of the droplet.

tant properties that may be desirable, for example, in a natural or formulated product, or undesirable, such as an unwanted emulsion in an industrial process. Petroleum emulsions may not be as familiar but have a similarly widespread, long-standing, and important occurrence in industry. Emulsions may be encountered at all stages in the petroleum recovery and processing industry (drilling fluid, production, process plant, and transportation emulsions). This chapter provides an introduction to the basic principles involved in the occurrence, making, and breaking of petroleum emulsions.

Crude oils consist of, at least, a range of hydrocarbons (alkanes, naphthenes, and aromatic compounds) as well as phenols, carboxylic acids, and metals. A significant fraction of sulfur and nitrogen compounds may be present as well. The carbon numbers of all these components range from 1 (methane) through 50 or more (asphaltenes). Some of these components can form films at oil surfaces, and others are surface active. It is perhaps not surprising, then, that the tendencies to form stable or unstable emulsions of different kinds vary greatly among different oils. Because of the wide range of possible compositions, crude oils can exhibit a wide range of viscosities and densities, so much so that these properties are used to distinguish light, heavy, and bituminous crude oils. One set of definitions can be compiled as follows (*1–3*):

Hydrocarbon	*Viscosity Range (mPa·s), at Reservoir Temperature*	*Density Range (kg/m³), at 15.6 °C*
Light crude oil	<10,000	<934
Heavy crude oil	<10,000	934–1000
Extra heavy crude oil	<10,000	>1000
Bitumen (tar)	>10,000	>1000

Because the viscosities correspond to ambient deposit temperatures, the variation in these properties over different temperatures is even greater than the table suggests. For example, bitumen in the Athabasca deposit of northern Alberta is chemically similar to conventional oil but has a viscosity, at reservoir temperature, of about 10^6 mPa·s (1 million times greater than that of water). During heating, as part of an oil recovery process such as hot-water flotation or in situ steam flooding, emulsions having a wide range of viscosities can be formed, particularly if they are of the water dispersed in oil type. When these different kinds of oils are emulsified, the emulsions may have viscosities that are much greater than, similar to, or much less than the viscosity of the component oil, all depending on the nature of the emulsion formed.

As shown in Table I, petroleum emulsions may be desirable or undesirable. For example, one kind of oil-well drilling fluid (or "mud") is emulsion based. Here a stable emulsion (usually oil dispersed in water) is used to lubricate the cutting bit and to carry cuttings up to the surface. This emulsion is obviously desirable, and great care goes into its proper preparation.

An emulsion may be desirable in one part of the oil production process and undesirable at the next stage. For example, in the oil fields, an in situ

Table I. Examples of Emulsions in the Petroleum Industry

Occurrence	*Usual Type*[a]
Undesirable Emulsions	
Well-head emulsions	W/O
Fuel oil emulsions (marine)	W/O
Oil sand flotation process, froth	W/O or O/W
Oil sand flotation process, diluted froth	O/W/O
Oil spill mousse emulsions	W/O
Tanker bilge emulsions	O/W
Desirable Emulsions	
Heavy oil pipeline emulsion	O/W
Oil sand flotation process slurry	O/W
Emulsion drilling fluid, oil-emulsion mud	O/W
Emulsion drilling fluid, oil-base mud	W/O
Asphalt emulsion	O/W
Enhanced oil recovery in situ emulsions	O/W

[a]W/O means water-in-oil; O/W means oil-in-water. *See* the section "Definition and Classification of Emulsions".

emulsion that is purposely created in a reservoir as part of an oil recovery process may change to a different, undesirable type of emulsion (water dispersed in oil) when produced at the wellhead. This emulsion may have to be broken and reformulated as a new emulsion suitable for transportation by pipeline to a refinery. Here, the new emulsion will have to be broken and water from the emulsion removed; otherwise the water would cause processing problems in the refining process.

Emulsions may contain not just oil and water, but also solid particles and even gas. In the large mining and processing operations applied to Canadian oil sands, bitumen is separated from the sand matrix in large tumblers as an emulsion of oil dispersed in water, and then further separated from the tumbler slurry by a flotation process. The product of the flotation process is bituminous froth, an emulsion that may be either water (and air) dispersed in the oil (primary flotation) or the reverse, oil (and air) dispersed in water (secondary flotation). In either case, the emulsions must be broken and the water removed before the bitumen can be upgraded to synthetic crude oil, but the presence of solid particles and film-forming components from the bitumen can make this removal step very difficult.

Some emulsions are made to reduce viscosity so that an oil can be made to flow. Emulsions of asphalt, a semisolid variety of bitumen dispersed in water, are formulated to be both less viscous than the original asphalt and stable so that they can be transported and handled. In application, the emulsion should shear thin and break to form a suitable water-repelling roadway coating material. Another example of emulsions that are formulated for lower viscosity with good stability are those made from heavy oils and intended for economic pipeline transportation over large distances. Here again the emulsions should be stable for transport but will need to be broken at the end of the pipeline.

Finally, many kinds of emulsions pose difficult problems wherever they may occur. For example, crude oil when spilled on the ocean tends to become emulsified in the form of "chocolate mousse" emulsions, so named for their color and semisolid consistency. These water-in-oil emulsions with high water content tend to be quite stable due to the strong stabilizing films that are present. Mousse emulsions increase the quantity of pollutant and are usually very much more viscous than the oil itself.

All of the petroleum emulsion applications or problems just discussed have in common the same basic principles of colloid science that govern the nature, stability, and properties of emulsions. The widespread importance of emulsions in general and scientific interest in their formation, stability, and properties have precipitated a wealth of published literature on the subject. This chapter provides an introduction and is intended to complement the other chapters in this book on petroleum emulsions. A good starting point for further basic information is one of the classic texts: Becher's *Emulsions: Theory and Practice* (*4*) or Sumner's *Clayton's Theory of Emulsions and*

Their Technical Treatment (*5*) and numerous other books on emulsions (*6–11*). Most good colloid chemistry texts contain introductory chapters on emulsions (*12–14*), and some chapters in specialist monographs (*15, 16*) give much more detailed treatment of advances in specific emulsion areas.

Emulsions as Colloidal Systems

Definition and Classification of Emulsions. Colloidal droplets (or particles or bubbles), as they are usually defined, have at least one dimension between about 1 and 1000 nm. Emulsions are a special kind of colloidal dispersion: one in which a liquid is dispersed in a continuous liquid phase of different composition. The dispersed phase is sometimes referred to as the internal (disperse) phase, and the continuous phase as the external phase. Emulsions also form a rather special kind of colloidal system in that the droplets often exceed the size limit of 1000 nm. In petroleum emulsions one of the liquids is aqueous, and the other is hydrocarbon and referred to as oil. Two types of emulsion are now readily distinguished in principle, depending upon which kind of liquid forms the continuous phase (Figure 2):

1. oil-in-water (O/W) for oil droplets dispersed in water
2. water-in-oil (W/O) for water droplets dispersed in oil

This kind of classification is not always appropriate. For example, O/W/O denotes a multiple emulsion containing oil droplets dispersed in aqueous droplets that are in turn dispersed in a continuous oil phase. The type of emulsion that is formed depends upon a number of factors. If the ratio of phase volumes is very large or very small, then the phase having the smaller volume is frequently the dispersed phase. If the ratio is closer to 1, then

Figure 2. The two simplest kinds of emulsions. The droplet sizes have been greatly exaggerated.

other factors determine the outcome. Table I lists some simple examples of petroleum emulsion types.

Two very different broad types of colloidal dispersions have been distinguished since Graham invented the term "colloid" in 1861. Originally, colloids were subdivided into lyophobic and lyophilic colloids (if the dispersion medium is aqueous then the terms hydrophobic and hydrophilic, respectively, are used). Lyophilic colloids are formed spontaneously when the two phases are brought together, because the dispersion is thermodynamically more stable than the original separated state. The term lyophilic is less frequently used in modern practice because many of the dispersions that were once thought of as lyophilic are now recognized as single-phase systems in which large molecules are dissolved. Lyophobic colloids, which include all petroleum emulsions other than the microemulsions, are not formed spontaneously on contact of the phases because they are thermodynamically unstable compared with the separated states. These dispersions can be formed by other means, however. Most petroleum emulsions that will be encountered in practice contain oil, water, and an emulsifying agent. The emulsifier may comprise one or more of the following: simple inorganic electrolytes, surfactants, macromolecules, or finely divided solids. The emulsifying agent may be needed to reduce interfacial tension and aid in the formation of the increased interfacial area with a minimum of mechanical energy input, or it may be needed to form a protective film at the droplet surfaces that acts to prevent coalescence with other droplets. These aspects will be discussed later; the resulting emulsion may well have considerable stability as a metastable dispersion.

Most kinds of emulsions that will be encountered in practice are lyophobic, metastable emulsions. However, there remain some grey areas in which the distinction between lyophilic and lyophobic dispersions is not completely clear. A special class of aggregated surfactant molecules termed "micelles" and the microemulsions of extremely small droplet size are usually but not always considered to be lyophilic, stable, colloidal dispersions and will be discussed separately.

Stability. A consequence of the small droplet size and presence of an interfacial film on the droplets in emulsions is that quite stable dispersions of these species can be made. That is, the suspended droplets do not settle out or float rapidly, and the droplets do not coalesce quickly. Some use of the term stability has already been made without definition.

Colloidal species can come together in very different ways. In the definition of emulsion stability, stability is considered against three different processes: creaming (sedimentation), aggregation, and coalescence. Creaming is the opposite of sedimentation and results from a density difference between the two liquid phases. In aggregation two or more droplets clump together, touching only at certain points, and with virtually no change in

total surface area. Aggregation is sometimes referred to as flocculation or coagulation. In coalescence two or more droplets fuse together to form a single larger unit with a reduced total surface area.

In aggregation the species retain their identity but lose their kinetic independence because the aggregate moves as a single unit. Aggregation of droplets may lead to coalescence and the formation of larger droplets until the phases become separated. In coalescence, on the other hand, the original species lose their identity and become part of a new species. Kinetic stability can thus have different meanings. An emulsion can be kinetically stable with respect to coalescence but unstable with respect to aggregation. Or, a system could be kinetically stable with respect to aggregation but unstable with respect to sedimentation or flotation.

In summary, lyophobic emulsions are thermodynamically unstable but may be relatively stable in a kinetic sense. Stability must be understood in terms of a clearly defined process.

Microemulsions. In some systems the addition of a fourth component, a cosurfactant, to an oil–water–surfactant system can cause the interfacial tension to drop to near-zero values, easily on the order of 10^{-3} to 10^{-4} mN/m; low interfacial tension allows spontaneous or nearly spontaneous emulsification to very small droplet sizes, ca. 10 nm or smaller. The droplets can be so small that they scatter little light; the emulsions appear to be transparent and do not break on standing or centrifuging. Unlike coarse emulsions, these microemulsions are usually thought to be thermodynamically stable. The thermodynamic stability is frequently attributed to transient negative interfacial tensions, but this hypothesis and the question of whether microemulsions are really lyophilic or lyophobic dispersions are areas of some discussion in the literature (*17*). As a practical matter, microemulsions can be formed, have some special qualities, and can have important applications.

Microemulsions can form the basis for an enhanced oil recovery (EOR) process (*18–20*). In an oil-containing reservoir, the relative oil and water saturations depend upon the distribution of pore sizes in the rock as follows. The capillary pressure (P_c), or pressure difference across an oil–water interface spanning a pore, is

$$P_c = 2\gamma \cos \theta / r_p \tag{1}$$

where γ is the oil–water interfacial tension; θ is the contact angle, which is the angle measured through the water phase at the point of oil–water–rock contact; and r_p is the pore radius. The basis for this equation is discussed further in a later section. In an idealized water-wet reservoir, the interfacial tension is fixed at some value, and the contact angle is zero. An analogy can be drawn with the rise of water in capillary tubes of differing radii. In a

reservoir consisting of such capillary tubes that contain water and oil, water will be imbibed most strongly into the smallest radius pores, displacing any oil present in them, until the hydrostatic and capillary pressures in the system balance. The largest pores will retain high oil contents. Now as water is injected during a secondary recovery process, the applied water pressure increases and the larger pores will imbibe more water, displacing oil, which may be recovered at producing wells. There is a practical limit to the extent that the applied pressure can be changed by pumping water into a reservoir, however, so that after water-flooding some residual oil will still be left in the form of oil ganglia trapped in the larger pores where the viscous forces of the driving water-flood could not completely overcome the capillary forces holding the oil in place.

The ratio of viscous forces to capillary forces correlates well with residual oil saturation and is termed the capillary number (N_c). One formulation of the capillary number is

$$N_c = \eta v / \gamma \tag{2}$$

where η and v are the viscosity and velocity, respectively, of the displacing fluid; and γ is the interfacial tension. The functional form of the correlation is illustrated in Figure 3. During water-flooding, N_c is about 10^{-6}, and at the

Figure 3. A generalized capillary number correlation. (Courtesy of K. Taylor, Petroleum Recovery Institute, Calgary.)

end of the water-flood the residual oil saturation is still around 45%. How could a tertiary recovery process be designed so that the remaining oil could be recovered? Lowering the residual oil saturation requires increasing the capillary number. This increase could be done by raising the viscous forces, that is, viscosity and velocity, but in practice the desired orders-of-magnitude increase will not be achieved. But, adding a suitable surfactant and cosurfactant to the water will decrease the interfacial tension from about 30 mN/m by 4 orders of magnitude and thereby increase the capillary number to about 10^{-2}.

The micelles present also help to solubilize the released oil droplets; hence, this process is sometimes referred to as micellar flooding. The emulsions can be formulated to have moderately high viscosities that help to achieve a more uniform displacement front in the reservoir; this uniform front gives improved sweep efficiency. Thus, a number of factors can be adjusted when using a microemulsion system for enhanced oil recovery. These are discussed in detail in Chapter 7.

Making Emulsions. Much of this chapter is concerned with emulsion properties and stability, and as a practical matter chemists frequently have to contend with already-formed emulsions. Nevertheless, a few comments on how emulsions may be made are appropriate. The breaking of emulsions will be discussed later.

Emulsions of any significant stability contain oil, water, and at least one emulsifying agent. The emulsifying agent may lower interfacial tension and thereby make it easier to create small droplets. Another emulsifying agent may be needed to stabilize the small droplets so that they do not coalesce to form larger droplets, or even separate out as a bulk phase. Just a straightforward casual mixing of these components seldom, however, produces an emulsion that persists for any length of time. In the classical method of emulsion preparation, the emulsifying agent is dissolved into the phase in which it is most soluble, after which the second phase is added, and the whole mixture is vigorously agitated. The agitation is crucial to producing sufficiently small droplets, and frequently, after an initial mixing, a second mixing with very high applied mechanical shear forces is required. This latter mixing can be provided by a propeller-style mixer, but more commonly a colloid mill or ultrasound generator is employed.

A method requiring much less mechanical energy uses phase inversion (*see also* the discussion of phase inversion temperature in the section "Emulsifying Agents"). For example, if ultimately a W/O emulsion is desired, then a coarse O/W emulsion is first prepared by the addition of mechanical energy, and the oil content is progressively increased. At some volume fraction above 60–70%, the emulsion will suddenly invert and produce a W/O emulsion of much smaller water droplet sizes than were the oil droplets in the original O/W emulsion.

Physical Characteristics of Emulsions

Appearance. Not all emulsions exhibit the classical "milky" opaqueness with which they are usually associated. A tremendous range of appearances is possible, depending upon the droplet sizes and the difference in refractive indices between the phases. An emulsion can be transparent if either the refractive index of each phase is the same, or alternatively, if the dispersed phase is made up of droplets that are sufficiently small compared with the wavelength of the illuminating light. Thus an O/W microemulsion of even a crude oil in water may be transparent. If the droplets are of the order of 1-μm diameter, a dilute O/W emulsion will take on a somewhat milky-blue cast; if the droplets are very much larger, the oil phase will become quite distinguishable and apparent.

Physically the nature of the simple emulsion types can be determined by methods such as

- ***Texture.*** The texture of an emulsion frequently reflects that of the external phase. Thus O/W emulsions usually feel watery or creamy, and W/O emulsions feel oily or greasy. This distinction becomes less evident as the emulsion viscosity increases, so that a very viscous O/W emulsion may feel oily.
- ***Mixing.*** An emulsion readily mixes with a liquid that is miscible with the continuous phase. Thus, milk (O/W) can be diluted with water, and mayonnaise (W/O) can be diluted with oil. Usually, an emulsion that retains a uniform and milky appearance when greatly diluted is more stable than one that aggregates upon dilution (*15*).
- ***Dyeing.*** Emulsions are most readily and consistently colored by dyes soluble in the continuous phase.
- ***Conductance.*** O/W emulsions usually have a very high specific conductance, like that of the aqueous phase itself, but W/O emulsions have a very low specific conductance. A simple test apparatus is described in reference 15.
- ***Inversion.*** If an emulsion is very concentrated, it will probably invert when diluted with additional internal phase.
- ***Fluorescence.*** If the oil phase fluoresces, then fluorescence microscopy can be used to determine the emulsion type as long as the droplet sizes are larger than the microscope's limit of resolution (>0.5 μm).

Emulsions do not always occur in the idealized form of droplets of one phase dispersed in another. The occurrence of multiple emulsions, of the

types O/W/O and W/O/W, has already been mentioned. Petroleum emulsions may also occur within another type of colloidal dispersion. For example, in a gas-flooding enhanced oil recovery process one of the ways to improve the areal sweep efficiency, that is, to maximize the amount of the reservoir contacted by injected fluids, is to inject the gas as part of a foam. However, most such foams are destabilized by contact with even small amounts of crude oil. The mechanism of destabilization appears (*21*) to involve emulsification of the oil into droplets that are small enough to permit their passage inside the foam's lamellar structure. Such emulsified oil droplets are shown in Figure 4. Once inside the foam lamellae, the oil droplets have a destabilizing effect on the foam by penetrating through and possibly spreading over the aqueous–gas interface. The limiting step, however, is apparently the emulsification and imbibition of oil into the foam.

Droplet Sizes. As stated previously, colloidal droplets are between about 10^{-3} and 1 μm in diameter, and in practice, emulsion droplets are often larger (e.g., the fat droplets in milk). In fact, emulsion droplets usually

Figure 4. Photomicrograph of an enhanced oil recovery process foam containing emulsified crude-oil droplets. The droplets have traveled within the narrow lamellae to accumulate and sometimes coalesce in the plateau borders of the foam, where they are held preferentially. The presence of such emulsified oil droplets in the foam structure has a destabilizing effect on the foam.

have diameters greater than 0.2 μm and may be larger than 50 μm. Emulsion stability is not necessarily a function of droplet size, although there may be an optimum size for an individual emulsion type. Characterizing an emulsion in terms of a given droplet size is very common but generally inappropriate because there is inevitably a size distribution. The size distribution is usually represented by a histogram of sizes, or, if there are sufficient data, a distribution function.

In some emulsions, a droplet size distribution that is heavily weighted toward the smaller sizes will represent the most stable emulsion. In such cases changes in the size distribution curve with time yield a measure of the stability of the emulsions. The droplet size distribution also has an important influence on the viscosity. For electrostatically or sterically interacting droplets, emulsion viscosity will be higher when droplets are smaller. The viscosity will also be higher when the droplet sizes are relatively homogeneous, that is, when the droplet size distribution is narrow rather than wide (*4*).

If the droplet size is large enough, then optical microscopy can be used to determine the size and size distribution. Emulsions with somewhat smaller droplet sizes can be characterized by using cryogenic-stage scanning electron microscopy. If the emulsion concentration is not too high, and the droplets are very small, light scattering can yield droplet size information. When a beam of light enters an emulsion, some light is absorbed, some is scattered, and some is transmitted. Many dilute, fine emulsions show a noticeable turbidity given by

$$I_t / I_0 = \exp(-\tau l) \tag{3}$$

where I_t is the intensity of the transmitted beam, I_0 is the intensity of the incident beam, τ is turbidity, and l is the length of the path through the sample. From Rayleigh theory, the intensity of light scattered from each droplet depends largely on its size and shape and on the difference in refractive index between the droplet and the medium. For an emulsion, each spherical droplet scatters light having an intensity I_d at a distance x from the droplet, according to the following relationship:

$$I_d / I_0 \propto r^6 / x^2 \lambda^4 \tag{4}$$

where λ is the wavelength of the light and r is the droplet radius.

The scattering intensity is proportional to $1/\lambda^4$, so blue light (λ = 450 nm) is scattered much more than red light (λ = 650 nm). With incident white light, a dilute emulsion of 0.1–1-μm size droplets will, therefore, tend to appear blue when viewed at right angles to the incident light beam. If the droplets are smaller than 50 nm or so, the emulsion will appear to be transparent.

These approaches to determining droplet size distributions are discussed in detail in Chapter 3.

Conductivity. Conductivity can be used to distinguish O/W from W/O emulsions because the conductivity is very high when the aqueous phase is continuous and conductivity is very low when oil is the continuous phase. Of the numerous equations proposed (*4*) to describe the conductivity of emulsions (κ_E), two are cited here for illustration. If the conductivity of the dispersed phase (κ_D) is much smaller than that of the continuous phase (κ_C), $\kappa_C \gg \kappa_D$,

$$\kappa_E = \frac{8\kappa_C(2-\phi)(1-\phi)}{(4+\phi)(4-\phi)} \tag{5}$$

where ϕ is the dispersed-phase volume fraction. If, on the other hand, the conductivity of the dispersed phase (κ_D) is much greater than that of the continuous phase (κ_C), $\kappa_C \ll \kappa_D$,

$$\kappa_E = \frac{\kappa_C(1+\phi)(2+\phi)}{(1-\phi)(2-\phi)} \tag{6}$$

Further discussion of emulsion conductivity and some practical examples for emulsions flowing in pipelines are given in Chapter 5.

Rheology. ***Bulk Viscosity Properties.*** The rheological properties of an emulsion are very important. High viscosity may be the reason that an emulsion is troublesome, a resistance to flow that must be dealt with, or a desirable property for which an emulsion is formulated. The simplest description applies to Newtonian behavior in laminar flow. The viscosity, η, is given in terms of the shear stress, τ, and shear rate, $\dot{\gamma}$, by:

$$\tau = \eta\dot{\gamma} \tag{7}$$

where η has units of millipascal seconds. Many colloidal dispersions, including the more concentrated emulsions, do not obey the Newtonian equation. For non-Newtonian fluids, the coefficient of viscosity is not a constant, but is itself a function of the shear rate, thus:

$$\tau = \eta(\dot{\gamma})\dot{\gamma} \tag{8}$$

A convenient way to summarize the flow properties of fluids is by plotting flow curves of shear stress versus shear rate (τ versus $\dot{\gamma}$). These

curves can be categorized into several rheological classifications. Emulsions are frequently pseudoplastic: As shear rate increases, viscosity decreases. This kind of flow behavior is also termed shear-thinning. An emulsion may also exhibit a yield stress, that is, the shear rate (flow) remains zero until a threshold shear stress is reached—the yield stress (τ_Y)—then pseudoplastic or Newtonian flow begins. Pseudoplastic flow that is time dependent is termed thixotropic. That is, at constant applied shear rate, viscosity decreases, and in a flow curve hysteresis occurs. Several other rheological classifications are covered in the Glossary: dilatancy, rheopexy, and rheomalaxis. Even viscosity itself is represented in many ways, as shown in Table II.

Some very useful descriptions of experimental techniques have been given by Whorlow (*22*) and others (*23, 24*). Very often measurements are made with an emulsion sample placed in the annulus between two concentric cylinders. The shear stress is calculated from the measured torque required to maintain a given rotational velocity of one cylinder with respect to the other. Knowing the geometry, the effective shear rate can be calculated from the rotational velocity. One reason for the relative lack of rheological data for emulsions, compared with that for other colloidal systems, is the difficulty associated with performing the measurements in these systems. As suggested by Figure 5, for a practical O/W emulsion, the sample may contain suspended particles in addition to the oil droplets. In attempting to conduct a measurement, a number of changes may occur in the sample

Table II. Glossary of Bulk Viscosity Terms

Term	*Symbol*	*Explanation*
Absolute viscosity	η	$\eta = \tau/\dot{\gamma}$ and can be traced to fundamental units independent of the type of instrument
Apparent viscosity	η_{APP}	$\eta_{APP} = \tau/\dot{\gamma}$ but as determined for a non-Newtonian fluid, usually by a method suitable only for Newtonian fluids
Differential viscosity	η_D	$\eta_D = d\tau/d\dot{\gamma}$
Specific increase in viscosity	η_{SP}	$\eta_{SP} = \eta_{Rel} - 1$
Intrinsic viscosity	$[\eta]$	$[\eta] = \lim_{C\to 0} \lim_{\dot{\gamma}\to 0} \eta_{SP}/C$ $[\eta] = \lim_{C\to 0} \lim_{\dot{\gamma}\to 0} (1/C) \ln \eta_{Rel}$
Reduced viscosity	η_{Red}	$\eta_{Red} = \eta_{SP}/C$
Relative viscosity	η_{Rel}	$\eta_{Rel} = \eta/\eta_0$ η_0 = viscosity of the pure solvent or dispersion medium

chamber that make the measurements irreproducible and not representative of the original emulsion (25). These changes may include

- creaming of the droplets, causing a nonuniform distribution within the chamber, or even removal of all droplets into an upper phase away from the region in which measurements are made
- centrifugal separation of oil, water, and solid phases, making the emulsion radially inhomogeneous, and possibly breaking the emulsion
- shear-induced coalescence or finer dispersion of droplets, changing the properties of the sample
- sedimentation of the solids, causing a nonuniform distribution within the chamber, or even removal of all solids from the region in which measurements are made

It is frequently desirable to be able to describe emulsion viscosity in terms of the viscosity of the continuous phase (η_0) and the amount of emulsified material. A very large number of equations have been advanced for estimating suspension (or emulsion, etc.) viscosities. Most of these are empirical extensions of Einstein's equation for a dilute suspension of spheres:

$$\eta = \eta_0 (1 + 2.5\phi) \tag{9}$$

Figure 5. Some rheological measurement problems that may be encountered with practical oil-field emulsions. Initially, the O/W sample contained in the cylinders on the left may be homogeneous, containing oil droplets (•), fine particles (—), and large particles (○). After some time, the sample may become quite stratified, as shown at right.

where η_0 is the medium viscosity and ϕ is the dispersed-phase volume fraction and is <1. For example, the empirical equations typically have the form (*4*):

$$\eta = \eta_0(1 + \alpha_0\phi + \alpha_1\phi^2 + \alpha_2\phi^3 + \cdots) \tag{10}$$

where the αs are empirical constants, and the empirical equations may include other terms, as in the Thomas equation,

$$\eta = \eta_0[1 + 2.5\phi + 10.5\phi^2 + 0.00273 \exp(16.6\phi)] \tag{11}$$

These equations assume Newtonian behavior, or at least apply to the Newtonian region of a flow curve, and they usually apply if the droplets are not too large and if there are no strong electrostatic interactions. A more detailed treatment of these relationships is given in Chapter 4.

Emulsions can show varying rheological, or viscosity, behaviors. Sometimes these properties are due to the emulsifier or other agents in the emulsion. However, if the internal phase has a sufficiently high volume fraction (typically anywhere from 10 to 50%) the emulsion viscosity increases because of droplet "crowding" or structural viscosity and becomes non-Newtonian. The maximum volume fraction possible for an internal phase made up of uniform, incompressible spheres is 74%, although emulsions with an internal volume fraction of 99% have been made (*15*). Figure 6 shows how emulsion viscosity tends to vary with volume fraction; the drop in viscosity at ϕ = 0.74 signifies inversion. At this point the dispersed-phase volume fraction becomes 0.26, in this example, and the lower value of ϕ is reflected by a much lower viscosity. If inversion does not occur, then the viscosity continues to increase. This condition is true for both W/O and O/W types.

A graphic and important example is furnished by the oil spill "chocolate mousse" emulsions formed when crude oil spills into seawater. These water-in-oil emulsions have high water contents that may exceed 74% and reach ϕ = 0.80 or more without inverting. As their common name implies, these mousse emulsions not only have viscosities that are much higher than the original crude oil but can become semisolid. With increasing time after a spill, these emulsions weather (the oil becomes depleted in its lower boiling fractions), and apparently the emulsions become more stable, more solid-like, and considerably more difficult to handle and break.

Interfacial Viscosity. The foregoing discussion of rheology has dealt with the bulk viscosity properties. A closely related and very important property is the interfacial viscosity, which can be thought of as the two-dimensional equivalent of bulk viscosity, operative in the oil–water interfacial region. As droplets in an emulsion approach each other, the thinning of

Figure 6. The influence of volume fraction on the emulsion type and viscosity of a model emulsion. (Reproduced with permission from reference 4. Copyright 1965 Robert E. Krieger, Inc.)

the films between the droplets, and their resistance to rupture, are thought to be of great importance to the ultimate stability of the emulsion. Thus, a high interfacial viscosity can promote emulsion stability by retarding the rate of droplet coalescence, as discussed in later sections. Further details on the principles, measurement, and applications to emulsion stability of interfacial viscosity were reviewed by Malhotra and Wasan (*26*).

Properties of the Interfaces

In simple two-phase colloidal systems, a thin intermediate region or boundary, known as the interface, lies between the dispersed and dispersing phases. Interfacial properties are very important because emulsified droplets have a large interfacial area, and even a modest interfacial energy per unit area can become a considerable total interfacial energy to be accommodated. For example, suppose we wish to emulsify one barrel (159 L) of oil into water. For this illustration consider the oil to be in 1 large drop that we repeatedly subdivide into drops of half the previous radius. Thus, the initial drop of r = 33.6 cm becomes eight drops of r = 16.8 cm, and so on. Figure 7 shows that the total surface or interfacial area produced increases by a factor of 2 with each cut. The initial interfacial area of 1.42 m^2 increases to 7.4×10^5

Figure 7. Total area and energy changes involved in emulsifying 1 barrel of oil into water by dispersing into progressively finer droplets.

m^2 by the time droplets of 0.64-μm radius have been produced. This increase is greater than 5 orders of magnitude! The larger interfacial area will have a significant total free energy as shown in Figure 7. If the interfacial tension is 35 mN/m, then by the time the droplet size is $r = 0.64$ μm, the total energy will have increased from 0.05×10^4 to 2.6×10^4 J. This 2.6×10^4 J of energy had to be added to the system to achieve the emulsification. If this amount of energy cannot be provided, for example, by mechanical shear, then another alternative is to use surfactant chemistry to lower the interfacial free energy, or interfacial tension.

The energy plotted in Figure 7 was obtained by multiplying the total area by the interfacial tension. Now if a small quantity of a surfactant was added to the water, possibly a few tenths of a percent, that lowered the interfacial tension to 0.35 mN/m, it would lower the amount of mechanical energy needed in the example by a factor of 100. From the area per molecule that the adsorbed emulsifying agent occupies, the minimum amount of emulsifier needed for the emulsion can also be estimated. In practice, lowering interfacial tension alone may not be sufficient to stabilize an emulsion, in which case other interfacial properties must be adjusted as well. These simple calculations do, however, show how important the interfacial properties can become when colloidal-sized species are involved, as in emulsions.

Surface and Interfacial Tensions. Regarding the molecules in a liquid, the attractive van der Waals forces between molecules are felt equally by all molecules except those in the interfacial region. This inequality in the van der Waals forces pulls the interfacial molecules toward the interior of the liquid. The interface thus has a tendency to contract spontaneously. For this reason, droplets of liquid and bubbles of gas tend to adopt a spherical shape, because this shape reduces the surface free energy. For two immiscible liquids, a similar situation applies, except that it may not be so immediately obvious how the interface will tend to curve. There will still be an imbalance of intermolecular forces and a configuration that minimizes the interfacial free energy.

The surface free energy has units of millijoules per square meter (1 mJ/m^2 = 1 erg/cm^2), reflecting the fact that area expansion requires energy. Surface free energies are usually described in terms of contracting forces acting parallel to the surface or interface. Surface tension (γ°), or interfacial tension (γ), is the force per unit length around a surface, or the free energy required to create new surface area. Thus, the units of surface and interfacial tension are millinewtons per meter (1 mN/m = 1 dyne/cm). These units for surface and interfacial tension are numerically equal to the surface free energy. Interfacial tensions are frequently intermediate between the values of the surface tensions of the liquids involved and are smallest when the liquids are the most chemically similar (for pure liquids).

Many methods for the measurement of surface and interfacial tensions, details of the experimental techniques, and their limitations are described in several good reviews (*27–29*). Some methods that are used most in emulsion work are the du Nouy ring, drop weight or volume, pendant drop, and the spinning drop. The spinning drop technique is applicable to the very low interfacial tensions encountered in the enhanced oil recovery and microemulsion fields (*30*). In all cases, when solutions rather than pure liquids are involved, appreciable changes can take place with time at the surfaces and interfaces.

Young–Laplace Equation. Interfacial tension causes a pressure difference to exist across a curved surface, the pressure being greater on the concave side (i.e., on the inside of a droplet). In an interface between phase A in a droplet and phase B surrounding the droplet, the phases will have pressures p_A and p_B. If the principal radii of curvature are R_1 and R_2, then

$$\Delta p = p_A - p_B = \gamma(1/R_1 + 1/R_2) \tag{12}$$

Equation 12 is the Young–Laplace equation (*31*). It shows that $p_A > p_B$; the pressure inside a droplet exceeds that outside. For spherical droplets in an emulsion,

$$\Delta p = p_A - p_B = 2\gamma / R \tag{13}$$

so that Δp varies with the radius, R. (More details are given in refs. 13 and 31.) The Young–Laplace equation forms the basis for some important methods for measuring surface and interfacial tensions, such as the pendant, sessile, and spinning drop methods and the maximum bubble pressure method (*27–30*). In primary oil recovery from underground reservoirs, the capillary forces described by this equation are responsible for holding back much of the oil (residual oil) in parts of the pore structure in the rock or sand. Any secondary or enhanced (tertiary) oil recovery process strategies are intended to overcome these same forces (*32*). In the example involving microemulsions in enhanced oil recovery (discussed under the heading "Microemulsions"), the Young–Laplace equation was used, without introduction, to demonstrate how lowering interfacial tension can facilitate emulsification and incremental oil recovery. In that example r, the pore radius, was used in place of R in the Young–Laplace equation, and the contact angle was included.

Contact Angles and Wetting. When a droplet of oil in water comes into contact with a solid surface, the oil may form a bead on the surface, or it may spread and form a film. A liquid having a strong affinity for the solid will seek to maximize its contact (interfacial area) and form a film. A liquid with much weaker affinity may form into a bead. The affinity is termed the wettability. Because there can be degrees of spreading, another quantity is needed. The contact angle, θ, in an oil–water–solid system is defined as the angle, measured through the aqueous phase, that is formed at the junction of the three phases. Whereas interfacial tension is defined for the boundary between two phases, the contact angle is defined for a three-phase junction.

If the interfacial forces acting along the perimeter of the droplet are represented by the interfacial tensions, then an equilibrium force balance can be written as

$$\gamma_{W/O} \cos \theta = \gamma_{S/O} - \gamma_{S/W} \tag{14}$$

where the subscripts refer to water (W), oil (O), and solid (S). Equation 14 is Young's equation. The solid is completely water-wetted if $\theta = 0$ and only partially wetted otherwise. Equation 14 is frequently used to describe wetting phenomena, so two practical points are important. In theory complete nonwetting by water would mean that $\theta = 180°$, but this contact angle is not seen in practice. Also, values of $\theta < 90°$ are often considered to represent "water-wetting", and values of $\theta > 90°$ are considered to represent "non-water-wetting". This assignment is rather arbitrary because it is based on correlation with visual appearance of droplets on surfaces.

These considerations come into play in oil recovery schemes applied to reservoirs of mixed wettability or where the rock is predominantly oil-wetting. Another example is the case of the so-called Pickering emulsions,

emulsions stabilized by fine particles. A film of close-packed particles has considerable mechanical strength, which contributes to the stability of an emulsion. The most stable emulsions occur when the contact angle is close to 90°, so that the particles will collect at the interface. Combining Young's equation with the oriented wedge theory (*see later,* "Emulsifying Agents") allows some predictions to be made. If the contact angle for a fine particle at the O/W interface is $\theta < 90°$, then most of the particle will reside in the aqueous phase. In this case an O/W emulsion is indicated. Conversely, if $\theta > 90°$, then the particle will be mostly in the oil phase, and W/O is predicted.

Adsorption at Interfaces: Surface Activity. ***Surfactants.*** Some compounds, like short-chain fatty acids, can be partly soluble in both water and oil. This dual solubility is because such molecules are amphiphilic or amphipathic; that is, they have one part that has an affinity for the oil (the nonpolar hydrocarbon chain), and one part that has an affinity for the water (the polar group). The energetically most favorable orientation for these molecules is at the oil–water interface, so that each part of the molecule can reside in the solvent for which it has the greatest affinity (*see* Figure 8).

Figure 8. Surfactant associations in an O/W emulsion. The size of the surfactant molecules compared to the oil droplets has been exaggerated for the purposes of illustration.

These molecules that form oriented monolayers at interfaces show surface activity and are termed surfactants. As there will be a balance between adsorption and desorption (due to thermal motions), the interfacial condition requires some time to establish. Because of this time required, surface activity should be considered a dynamic phenomenon. This fact can be seen by measuring surface tension versus time for a freshly formed surface.

A consequence of surfactant adsorption at an interface is that it provides an expanding force acting against the normal interfacial tension. If π is this expanding pressure (surface pressure), then $\gamma = \gamma_{\text{initial}} - \pi$. Thus, surfactants tend to lower interfacial tension; if a low enough value of γ is reached, emulsification can take place because only a small increase in surface free energy is required, for example, when $\pi \sim \gamma_{\text{initial}}$. If solute–solvent forces are greater than solvent–solvent forces on the other hand, then molecular migration away from the interface can occur and cause increased surface tension (e.g., NaCl [aq]).

Gibbs has thermodynamically described the lowering of surface free energy that results from surfactant adsorption. The general Gibbs adsorption equation for a binary, isothermal system containing excess electrolyte is

$$\Gamma_s = -(1/RT)(d\gamma/d\ln C_s) \tag{15}$$

where Γ_s is the surface excess of surfactant (mol/cm^2), C_s is the solution concentration of the surfactant (M), and γ may be either surface or interfacial tension (mN/m). This equation can be applied to dilute surfactant solutions in which the surface curvature is not great and where the adsorbed film can be considered a monolayer. The packing density of surfactant in a monolayer at the interface can be calculated as follows. The surface excess in a tightly packed monolayer can be calculated from the slope of the linear portion of a plot of surface tension versus the logarithm of solution concentration (*see* Figure 9). From this slope, the area per adsorbed molecule (a_s) can be calculated from

$$a_s = 1/(N_A\Gamma_s) \tag{16}$$

where N_A is Avogadro's number. Numerous examples are given by Rosen (*33*).

Surface Films. Insoluble polar molecules (e.g., long-chain fatty acids) exhibit an extreme kind of adsorption at liquid surfaces. That is, they can be made to concentrate in one molecular layer at the surface. These interfacial films often provide the stabilizing influence in emulsions because they can both lower interfacial tension and increase the interfacial viscosity. Increasing interfacial viscosity provides a mechanical resistance to coalescence. Such systems also lend themselves to the study of size, shape, and

Figure 9. The association behavior of surfactants in solution, showing the critical micelle concentration (CMC).

orientation of molecules at an interface. Having an adsorbed layer lowers the surface tension (to γ) by the surface pressure $\pi = \gamma_{initial} - \gamma$, as already noted. In a surface balance (pioneered by Langmuir and others) π versus the available area of surface (A) can be determined directly. Another approach is to measure the lowered surface tension (Wilhelmy plate) and calculate π. For very low film pressures, an ideal gas law analogy,

$$\pi A = nRT = nN_A kT \tag{17}$$

allows calculation of the effective area per molecule (A/nN_A) in the monolayer; here n is the number of moles, R is the gas constant, T is absolute temperature, and k is the Boltzmann constant.

Classification of Surfactants. Surfactants are classified according to the nature of the polar (hydrophilic) part of the molecule, as illustrated in Table III. In-depth discussions of surfactant structure and chemistry can be found in references 33–35.

In aqueous solution, dilute concentrations of surfactant act much as normal electrolytes, but at higher concentrations very different behavior results. This behavior (illustrated in Figures 8 and 9) was explained by McBain in terms of organized aggregates called micelles in which the lipophilic parts of the surfactants associate in the interior of the aggregate and leave hydrophilic parts to face the aqueous medium. (Details are given in refs. 16 and 31.) The concentration at which micelle formation becomes

Table III. Surfactant Classifications

Class	*Examples*	*Structures*
Anionic	Na stearate	$CH_3(CH_2)_{16}COO^-Na^+$
	Na dodecyl sulfate	$CH_3(CH_2)_{11}SO_4^-Na^+$
	Na dodecyl benzene sulfonate	$CH_3(CH_2)_{11}C_6H_4SO_3^-Na^+$
Cationic	Laurylamine hydrochloride	$CH_3(CH_2)_{11}NH_3^+Cl^-$
	Cetyl trimethylammonium bromide	$CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$
Nonionic	Polyoxyethylene alcohol	$C_nH_{2n+1}(OCH_2CH_2)_mOH$
	Alkylphenol ethoxylate	$C_9H_{19}–C_6H_4–(OCH_2CH_2)_nOH$
Zwitterionic	Lauramidopropyl betaine	$C_{11}H_{23}CONH(CH_2)_3N^+(CH_3)2CH_2COO^-$
	Cocoamido-2-hydroxypropyl sulfobetaine	$C_nH_{2n+1}CONH(CH_2)_3N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$

significant is called the critical micelle concentration (CMC). The CMC is a property of the surfactant and several other factors, because micellization is opposed by thermal and electrostatic forces. A low CMC is favored by increasing the molecular mass of the lipophilic part of the molecule, lowering the temperature (usually), and adding electrolyte. Surfactant molecular weights range from a few hundred up to several thousand.

Some typical CMC values for low electrolyte concentrations at room temperature are

Surfactant Class	*CMC (M)*
Nonionic	10^{-5}–10^{-4}
Anionic	10^{-3}–10^{-2}
Amphoteric	10^{-3}–10^{-1}

The solubilities of micelle-forming surfactants show a strong increase above a certain temperature, termed the Krafft point (T_K). This increase in solubility is explained by the fact that the single surfactant molecules have limited solubility, whereas the micelles are very soluble. Referring to Figure 10, below the Krafft point the solubility of the surfactant is too low for micellization, and solubility alone determines the surfactant monomer concentration. As temperature increases, the solubility increases until at T_K the CMC is reached. At this temperature a relatively large amount of surfactant can be dispersed in micelles, and solubility increases greatly. Above the

Figure 10. The solubility–micellization behavior of surfactants in solution, showing the Krafft point.

Krafft point, maximum reduction in surface or interfacial tension occurs at the CMC because now the CMC determines the surfactant monomer concentration.

Cohesion, Adhesion, and Spreading. Two phases A and B may have an interface between them, AB. Cohesion, adhesion, and spreading can be defined for the changes shown in Figure 11 (involving always unit surface area). The work of cohesion represents the energy required to increase interfacial area by two square units. Thus the energy required to disperse oil into finer and finer droplets, to make an emulsion, increases as the interfa-

Figure 11. Cohesion, adhesion, and spreading. All indicated changes are per unit area, ΔG is the Gibbs free energy change, and the subscripts denote oil (O), water (W) and air (A).

cial tension between the droplets increases. The work of adhesion is the energy involved when two surfaces, initially in contact with each other, are separated to each contact a third phase. The work of adhesion relates to, for example, surface energy changes involved when an oil droplet initially in contact with a solid particle becomes released into water. Spreading occurs when, for example, emulsified oil droplets reach the air–water interface and spread over the surface. This spreading is a mechanism for demulsification; a negative spreading coefficient should thus tend to contribute to emulsion stability. Spreading is also a mechanism for defoaming by emulsions (*36*). Petroleum emulsions have been used to prevent the formation of foams, or destroy foams already generated, in various industrial processes (*37*).

Stability of Emulsions

Meaning of Stability. Most emulsions are not thermodynamically stable. Rather they possess some degree of kinetic stability, and it is important to distinguish the degree of change and the time scale. As mentioned previously, coalescence and aggregation are processes in which particles, droplets, or bubbles are brought together with (coalescence) or without (aggregation) large changes in surface area. Thus, there can be different kinds of kinetic stability. This discussion of colloid stability will explore the reasons why colloidal dispersions can have different degrees of kinetic stability and how these are influenced, and can therefore be modified, by solution and surface properties. The discussion is carried further, and in more detail, in Chapter 2.

Encounters between particles in a dispersion can occur frequently because of Brownian motion, sedimentation, or stirring. The stability of the dispersion depends upon how the particles interact when these encounters happen. The main cause of repulsive forces is the electrostatic repulsion between like-charged objects. The main attractive forces are the van der Waals forces between objects.

Electrostatic Forces. ***Charged Interfaces.*** Most substances acquire a surface electric charge when brought into contact with a polar medium such as water. For emulsions, the origin of the charge can be ionization, as when surface acid functionalities ionize when oil droplets are dispersed into an aqueous solution, or the origin can be adsorption, as when surfactant ions or charged particles adsorb onto an oil droplet surface. Solid particles can have additional mechanisms of charging. One is the unequal dissolution of cations and anions that make up the crystal structure (in the salt type minerals, for example). Another is the diffusion of counterions away from the surface of a solid whose internal crystal structure carries an opposite charge because of isomorphic substitution (in clays, for example). The

surface charge influences the distribution of nearby ions in the polar medium. Ions of opposite charge (counterions) are attracted to the surface, but those of like charge (co-ions) are repelled. An electric double layer, which is diffuse because of mixing caused by thermal motion, is thus formed.

In a practical petroleum emulsion situation, the degree of surface charging is more complicated. An example is the bitumen–water interface, which becomes negatively charged in alkaline aqueous solutions as a result of the ionization of surface carboxylic acid groups belonging to natural surfactants present in the bitumen. The degree of negative charging is very important to the success of bitumen recovery processes from in situ oil sands and also separation processes from surface oil sands, such as the hot-water flotation process (*38–42*). The degree of negative charge at the interface depends on the pH and ionic strength of the solution (*38, 39*) and also on the concentration of natural surfactant monomers present in the aqueous phase (*40, 41*). With bitumen, as with other heavy crude oils, more than one kind of surfactant may be produced (*42*), and the solution concentrations of the surfactants depend also on reaction conditions (temperature, etc.) and on the extent of competing reactions such as the adsorption of the surfactants onto solid (clay) particles that are present (*43, 44*).

Electric Double Layer. The electric double layer (EDL) consists of the charged surface and a neutralizing excess of counterions over co-ions, distributed near the surface (*see* Figure 12). The EDL can be viewed as being composed of two layers:

- an inner layer that may include adsorbed ions
- a diffuse layer in which ions are distributed according to the influence of electrical forces and thermal motion

Gouy and Chapman proposed a simple quantitative model for the diffuse double layer, assuming, among other things, an infinite, flat, uniformly charged surface and point-charge ions. (Further details are given in refs. 14, 31, and 45.) Taking the surface potential to be ψ°, the potential ψ at a distance x from the surface is approximately

$$\psi = \psi^\circ \exp(-\kappa x) \tag{18}$$

The surface charge density is given as $\sigma^\circ = \epsilon\kappa\psi^\circ$, where ϵ is the permittivity and κ is not conductivity but a special variable defined in equation 19; thus, ψ° depends on surface charge density and the solution ionic composition (through κ). The variable $1/\kappa$ is called the double-layer thickness, and for water at 25 °C it is given by

$$\kappa = 3.288\sqrt{I} \qquad (\mathrm{nm}^{-1}) \tag{19}$$

Figure 12. Simplified illustrations of the electrical double layer around a negatively charged colloidal emulsion droplet. The left view shows the change in charge density around the droplet. The right view shows the distribution of ions around the charged droplet. (Courtesy of L. A. Ravina, Zeta-Meter, Inc., Long Island City, NY.)

where I is the ionic strength, given by $I = (1/2)\ \Sigma_i c_i z_i^2$, in which c_i are the individual ion concentrations and z_i are the respective ion-charge numbers. For a 1–1 electrolyte,

$$1/\kappa = 1 \text{ nm for } I = 10^{-1} \text{ M}$$
$$1/\kappa = 10 \text{ nm for } I = 10^{-3} \text{ M} \qquad (20)$$

In fact an inner layer exists because ions are not really point charges and an ion can approach a surface only to the extent allowed by its hydration sphere. The Stern model specifically incorporates a layer of specifically adsorbed ions bounded by a plane, the Stern plane (*see* Figure 13 and refs. 14, 31, and 45). In this case the potential changes from ψ° at the surface, to $\psi(\delta)$ at the Stern plane, to $\psi = 0$ in bulk solution.

Electrokinetic Phenomena. Electrokinetic motion occurs when the mobile part of the electric double layer is sheared away from the inner layer

Figure 13. Simplified illustration of the surface and zeta potentials for a charged emulsion droplet dispersed in high and low electrolyte concentration aqueous solutions. (Courtesy of L. A. Ravina, Zeta-Meter, Inc., Long Island City, NY.)

(charged surface). The four types of electrokinetic measurements are electrophoresis, electro-osmosis, streaming potential, and sedimentation potential, of which electrophoresis finds the most use in industrial practice. Good descriptions of practical experimental techniques in electrophoresis and their limitations can be found in references 46–48.

In electrophoresis an electric field is applied to a sample and causes charged droplets or particles and any attached material or liquid to move toward the oppositely charged electrode. Thus the results can be interpreted only in terms of charge density (σ) or potential (ψ) at the plane of shear. The latter is also known as the zeta potential. Because the exact location of the shear plane is generally not known, the zeta potential is usually taken to be approximately equal to the potential at the Stern plane (Figure 13):

$$\zeta = \psi(\delta) \tag{21}$$

where δ is the distance from the droplet surface to the Stern plane. In microelectrophoresis the dispersed droplets are viewed under a microscope, and their electrophoretic velocity is measured at a location in the sample cell where the electric field gradient is known. This measurement must be done at carefully selected planes within the cell because the cell walls become charged as well and cause electro-osmotic flow of the bulk liquid inside the cell.

The electrophoretic mobility, μ_E, is defined as the electrophoretic velocity divided by the electric field gradient at the location where the velocity

was measured. It remains then to relate the electrophoretic mobility to the zeta potential (ζ). Two simple relations can be used to calculate zeta potentials in limiting cases:

- Hückel theory. For droplets of small radius (r) with "thick" electric double layers, meaning that $\kappa r < 1$, it is assumed that Stokes' law applies and the electrical force is equated to the frictional resistance of the droplet, $\mu_E = \zeta\epsilon/(1.5\eta)$.
- Smoluchowski theory. For large droplets with "thin" electric double layers, meaning droplets for which $\kappa r > 100$, $\mu_E = \zeta\epsilon/\eta$.

These theories are discussed in more detail in references 14 and 50.

With these relations zeta potentials can be calculated for many practical systems. Within each set of limiting conditions the electrophoretic mobility is independent of particle size and shape as long as the ζ potential is constant. For intermediate values of κr, the Henry equation and many other equations apply (*46, 47, 49*).

Repulsive Forces. In the simplest example of colloid stability, emulsion droplets would be stabilized entirely by the repulsive forces created when two charged surfaces approach each other and their electric double layers overlap. The repulsive energy, V_R, for spherical droplets is given approximately as

$$V_R = \frac{B\epsilon k^2 T^2 r \gamma^2}{z^2} \exp(-\kappa H) \tag{22}$$

where the spheres have radius r and are separated by distance H, B is a constant ($3.93 \times 10^{39}\ A^{-2}s^{-2}$), z is the counterion charge number, and

$$\gamma = \frac{\exp[ze\psi(\delta)/2kT] - 1}{\exp[ze\psi(\delta)/2kT] + 1} \tag{23}$$

Dispersion Forces. van der Waals postulated that neutral molecules exert forces of attraction on each other that are caused by electrical interactions between three types of dipolar configurations. The attraction results from the orientation of dipoles that may be (1) two permanent dipoles, (2) dipole–induced dipole, or (3) induced dipole–induced dipole. Induced dipole–induced dipole forces between nonpolar molecules are also called London dispersion forces. Except for quite polar materials, the London dispersion forces are the more significant of the three. For molecules the force varies inversely with the sixth power of the intermolecular distance.

For dispersed droplets (or particles, etc.) the dispersion forces can be approximated by adding the attractions between all interdroplet pairs of

molecules. When added this way, the dispersion force between two droplets decays less rapidly as a function of separation distance than is the case for individual molecules. For two spheres of radius r in a vacuum, separated by distance H, the attractive energy V_A can be approximated by

$$V_A = -\frac{Ar}{12H} \tag{24}$$

for $H < 10$–20 nm and $H \ll r$. The constant A is known as the Hamaker constant and depends on the density and polarizability of atoms in the particles. Typically 10^{-20} J $< A < 10^{-19}$ J. When the particles are in a medium other than vacuum, the attraction is reduced. This reduced attraction can be accounted for by using an effective Hamaker constant

$$A = \left(\sqrt{A_2} - \sqrt{A_1} \right)^2 \tag{25}$$

where the subscripts denote the medium (1) and particles (2).

The effective Hamaker constant equation shows that the attraction between particles is weakest when the particles and medium are most chemically similar ($A_1 \sim A_2$). The Hamaker constants are usually not well known and must be approximated.

DLVO Theory. Derjaguin and Landau, and independently Verwey and Overbeek (*45*), developed a quantitative theory for the stability of lyophobic colloids, now known as the DLVO theory. It was developed in an attempt to account for the observation that colloids coagulate quickly at high electrolyte concentrations, slowly at low concentrations, and with a very narrow electrolyte concentration range over which the transition from one to the other occurs. This narrow electrolyte concentration range defines the critical coagulation concentration (CCC). The DLVO theory accounts for the energy changes that take place when two droplets (or particles) approach each other, and involves estimating the energy of attraction (London–van der Waals) versus interparticle distance and the energy of repulsion (electrostatic) versus distance. These, V_A and V_R, respectively, are then added together to yield the total interaction energy V. A third important force occurs at very small separation distances where the atomic electron clouds overlap and causes a strong repulsion, called Born repulsion. The theory has been developed for several special cases, including the interaction between two spheres, and refinements are constantly being made.

The value of V_R decreases exponentially with increasing separation distance and has a range about equal to κ^{-1}, and V_A decreases inversely with increasing separation distance. Figure 14 shows a single attractive energy curve and two different repulsive energy curves, representing two very different levels of electrolyte concentration. The figure shows the total interaction energy curves that result in each case. Either the attractive van

der Waals forces or the repulsive electric double-layer forces can predominate at different interdroplet distances.

With a positive potential energy maximum, a dispersion should be stable if $V \gg kT$, that is, if the energy is large compared to the thermal energy of the particles ($15kT$ is considered insurmountable). In this case colliding droplets should rebound without contact, and the emulsion should be stable to aggregation. If, on the other hand, the potential energy maximum is not very great, $V \sim kT$, then slow aggregation should occur. The height of the energy barrier depends on the surface potential, $\psi(\delta)$ and on the range of the repulsive forces, κ^{-1}. Figure 14 shows that an energy minimum can occur at larger interparticle distances. If this energy minimum is reasonably deep compared to kT, then a loose, easily reversible aggregation should occur.

Practical Guidelines. The DLVO calculations can become quite involved, requiring considerable knowledge about the systems of interest. Also, they present some problems. For example, some distortion of the spherical emulsion droplets will occur as they approach each other and begin to seriously interact; these interactions cause a flattening. Also, our view of

Figure 14. The effect of different repulsive potential energy curves (1 and 2) on the total interaction energy for a given attractive energy curve. (Reproduced with permission from reference 16. Copyright 1981 Butterworth Heinemann Ltd.)

the validity of the theory is changing as more becomes known about the influence of additional forces such as those due to surface hydration. The DLVO theory nevertheless forms a very useful starting point in attempting to understand complex colloidal systems such as petroleum emulsions. Empirical "rules of thumb" can be used to give a first estimate of the degree of colloidal stability that a system is likely to have if the zeta potentials of the droplets are known.

Zeta Potential Criteria. Many types of colloids tend to adopt a negative surface charge when dispersed in aqueous solutions having ionic concentrations and pH typical of natural waters. For such systems one rule of thumb stems from observations that the colloidal particles are quite stable when the zeta potential is about –30 mV or more negative, and quite unstable because of agglomeration when the zeta potential is between +5 and –5 mV. An expanded set of guidelines, developed for particle suspensions, is given in reference 48. Such criteria are frequently used to determine optimal dosages of polyvalent metal electrolytes, such as alum, used to effect coagulation in treatment plants.

For example, as stated earlier, in order to separate bitumen from oil sands, a significant negative charge must be present at the oil–water interface. This negative charge is needed to aid in the release of the bitumen from the sand matrix, and is also needed to prevent attachment of the released and emulsified droplets to codispersed solid particles such as clays. In fact, in the flotation recovery process for bitumen the optimal processing condition correlates with maximizing the negative charge, or zeta potential, on the droplets (*41*). On-line measurements of the emulsified bitumen droplet zeta potentials can be used to monitor and control the continuous oil recovery process, as indicated in Figure 15 (*50*). In the Figure 15 example, the maximum (negative) emulsion droplet zeta potential achieved was about –35 mV, which is consistent with the "good stability" guideline just described.

Schulze–Hardy Rule. The transition from stable dispersion to aggregation usually occurs over a fairly small range of electrolyte concentration. This condition makes it possible to determine aggregation concentrations, often referred to as critical coagulation concentrations (CCC). The Schulze–Hardy rule summarizes the general tendency of the CCC to vary inversely with the sixth power of the counterion charge number (for indifferent electrolyte). Further details and original references are given in references 13 and 51.

A prediction from DLVO theory can be made by deriving the conditions under which $V = 0$ and $dV/dH = 0$. The result is

$$\mathrm{CCC} = \frac{9.75B^2\epsilon^3k^5T^5\gamma^4}{e^2N_\mathrm{A}A^2z^6} \tag{26}$$

Figure 15. Plot of oil recoveries versus process aid addition level from the hot water flotation processing of an oil sand in a continuous pilot plant. Also shown is the correspondence with the zeta potentials, measured on-line, of emulsified bitumen droplets in the extraction solution. (Plotted from data in reference 50.)

showing that for high potentials ($\gamma \rightarrow 1$), the CCC varies inversely with z^6. As an illustration, for a hypothetical emulsion, equation 26 predicts a CCC of 1.18 M in solutions of sodium chloride. The critical coagulation concentrations in polyvalent metal chlorides would then decrease as follows:

Dissolved Salt	*z*	*CCC (mol/L)*
NaCl	1	1.18
$CaCl_2$	2	0.018
$AlCl_3$	3	0.0016

Broad Influence on Stability. In general, when electrical surface charge is an important determinant of stability, it is easier to formulate a very stable O/W emulsion than a W/O emulsion because the electric double-layer thickness is much greater in water than in oil. (This condition is sometimes incorrectly stated in terms of greater charge being present on droplets in an O/W emulsion). This is not to say that W/O emulsions cannot be stabilized, however. Many reasonably stable oil-field W/O emulsions are stabilized by another mechanism: the protective action of viscoelastic, possibly rigid, films formed on the droplets by macromolecules or solid particles.

Kinetics. Thus far this chapter has mostly been concerned with an understanding of the direction in which reactions will proceed. However, from an engineering point of view, it is just as important to know the rates at which such reactions will proceed. Two principal factors determine the rate of aggregation of droplets in an emulsion: the frequency of droplet encounters and the probability that the thermal energy of the droplets is sufficient to overcome the potential energy barrier to aggregation. The rate of aggregation can be given as $-(dn/dt) = k_2n^2$ where k_2 is the rate constant and n is the number of droplets per unit volume at time t. For $n = n_0$ at $t = 0$,

$$1/n = k_2t + 1/n_0 \tag{27}$$

During the process of aggregation, k_2 may not remain constant.

If the energy barrier to aggregation is removed (e.g., by adding excess electrolyte) then aggregation is diffusion controlled; only Brownian motion of independent droplets or particles is present. For a monodisperse suspension of spheres, Smoluchowski developed an equation for this "rapid coagulation"

$$n = \frac{n_0}{1 + 8\pi Drn_0t} \tag{28}$$

where r is the radius, and the diffusion coefficient $D = kT/(6\pi\eta r)$. Now $k_2^0 = 4kT/(3\eta)$, where k_2^0 is the rate constant for diffusion-controlled aggregation.

When there is an energy barrier to aggregation, only a fraction $1/W$ of encounters lead to attachment. The variable W is the stability ratio, $W = k_2^0/k_2$. Using W gives "slow coagulation" (hindered) times. In this case, the interaction energy and hydrodynamic viscous drag forces must be considered (*16*).

Finally, particles can also be brought into interaction distances by stirring or sedimentation so that the relative motions of two adjacent regions of fluid, each carrying particles, can cause particle encounters. Coagulation due to such influence is called "orthokinetic coagulation" as distinguished from the Brownian induced "perikinetic coagulation". The theory for orthokinetic coagulation is much more complicated than that for perikinetic and is not discussed here. However, shear can also cause dispersion if the energy introduced allows the interaction energy barrier to be overcome.

Stability to Coalescence. Up to this point, stability to aggregation has been considered. However, once aggregation has taken place in an emulsion, there remains the question of stability to coalescence. Usually emulsions made by mixing together two pure liquids are not very stable. To increase the stability, an additional component is usually needed, and it forms a film around the dispersed droplets to provide a barrier to both

aggregation and coalescence. Although numerous agents and mechanisms are effective, the additional component is frequently a surfactant. Stability to coalescence involves the mechanical properties of the interfacial films. Mechanical properties will be considered further in the next section.

Considering stability to both aggregation and coalescence, the factors favoring emulsion stability can be summarized as follows:

- Low interfacial tension—low interfacial free energy makes it easier to maintain large interfacial area.
- Mechanically strong film—this acts as a barrier to coalescence and may be enhanced by adsorption of fine solids or of close-packed surfactant molecules.
- Electric double-layer repulsion—this repulsion acts to prevent collisions and aggregation.
- Small volume of dispersed phase—this reduces the frequency of collisions and aggregation. Higher volumes are possible (for close-packed spheres the dispersed-phase volume fraction would be 0.74), but in practice the fraction can even be higher.
- Small droplet size, if the droplets are electrostatically or sterically interacting.
- High viscosity—this slows the rates of creaming and coalescence.

An assessment of emulsion stability involves the determination of the time variation of some emulsion property such as those described in the earlier section "Physical Characteristics of Emulsions". The classical methods are well described in reference 9. Some newer approaches include the use of pulse nuclear magnetic resonance spectroscopy or differential scanning calorimetry (52).

Emulsifying Agents. One general theory of emulsion type states that if an emulsifying agent is preferentially wetted by one of the phases, then more of the agent can be accommodated at the interface if that interface is convex toward that phase; that is, if that phase is the continuous phase. This theory works for both solids and soaps as emulsifying agents. For surfactant molecules it is referred to as Bancroft's rule; the liquid in which the surfactant is most soluble becomes the continuous phase. Very often, mixtures of emulsifying agents are more effective than single components. Some mixed emulsifiers may form a complex at the interface and thus yield low interfacial tension and a strong interfacial film.

A second general rule specifies that soaps of monovalent metal cations tend to produce O/W emulsions, but those of polyvalent metal cations will

tend to produce W/O emulsions. Figure 16 illustrates the concept. In the example shown, the calcium ions each coordinate to two surfactant molecules that are aligned with their polar groups near the metal ion. This coordination forces the hydrocarbon tails into a wedgelike orientation. The hydrocarbon tails in a close-packed interfacial layer are most easily accommodated if the oil phase is the continuous phase. Thus, the oriented-wedge theory predicts that the calcium soap will produce a W/O emulsion. For the sodium soap, the charged polar groups of the surfactant tend to repel each other more strongly. This fact, together with the single cation–surfactant coordination, makes it most favorable for the polar groups to be in the continuous phase, and an O/W emulsion results.

An analogous rule to the oriented-wedge and Bancroft theories states that the liquid that preferentially wets the solid particles will tend to form the continuous phase. Thus if there is a low contact angle (measured through the water phase), then an O/W emulsion should form. Exceptions occur for each of these rules, and sometimes one will work where the others do not. They do remain useful for making initial predictions.

An empirical scale developed for categorizing single-component or mixed (usually nonionic) emulsifying agents, using this principle, is the hydrophile–lipophile balance or HLB scale. This dimensionless scale ranges from 0 to 20; a low HLB (<9) refers to a lipophilic surfactant (oil-soluble) and a high HLB (>11) to a hydrophilic (water-soluble) surfactant. In gen-

Figure 16. The oriented-wedge theory of emulsion type.

eral, W/O emulsifiers exhibit HLB values in the range of 3–8, and O/W emulsifiers have HLB values of about 8–18. Empirical tables of HLB values required to make emulsions out of various materials have been published (*53*). If the value is not known, then laboratory emulsification tests are required, using a series of emulsifying agents of known HLB values.

For example, to make a 15% O/W emulsion of a paraffinic mineral oil, a set of emulsion tests is performed with a series of blends of emulsifiers A (HLB 4.7) and B (HLB 14.9):

Emulsifier Blend	*HLB*	*Emulsion Test*
100% A	4.7	no emulsion
87% A + 13% B	6	no emulsion
68% A + 32% B	8	moderate emulsion
48% A + 52% B	10	stable emulsion
28% A + 72% B	12	moderate emulsion
6% A + 94% B	14	no emulsion
100% B	14.9	no emulsion

In this case an HLB of 10 is required to make the O/W mineral oil emulsion.

Various compilations and equations for determining emulsifier HLB values have been published (*15, 53, 54*). For example, in polyoxyethylene alcohols, $C_nH_{2n+1}(OCH_2CH_2)_mOH$, a class of nonionic surfactants, the HLB can be calculated from HLB = $E/5$, where E is the percentage by mass of ethylene oxide in the molecule. Experimentally, the unknown HLB of an emulsifier can be determined by mixing it with an emulsifier of known HLB and an oil for which the HLB required for emulsification is known. A series of tests such as just illustrated in the example can be used to determine the unknown HLB. From the previous definition of spreading it might seem that if an oil does not spread on water, then it should be emulsified in it, and vice versa. Ross et al. (*55*) did, in fact, find a correlation between HLB and the spreading coefficients of oil and water. They found that for a given type of emulsion, both low interfacial tension and a negative value of the appropriate spreading coefficient are necessary.

A limitation of the HLB system is that other factors are important as well. Also, the HLB is an indicator of the emulsifying characteristics of an emulsifier but not the efficiency of an emulsifier. Thus, although all emulsifiers having a high HLB will tend to promote O/W emulsions, the efficiency with which those emulsifiers act will vary considerably for any given system. For example, usually mixtures of surfactants work better than pure compounds of the same HLB.

Just as solubilities of emulsifying agents vary with temperature, so does the HLB, especially for the nonionic surfactants. A surfactant may thus stabilize O/W emulsions at low temperature but W/O emulsions at some higher temperature. The transition temperature, that at which the surfactant

changes from stabilizing O/W to W/O emulsions, is known as the phase inversion temperature (PIT). At the PIT, the hydrophilic and oleophilic natures of the surfactant are essentially the same (another term for this is the HLB temperature). As a practical matter, emulsifying agents are chosen so that their PIT is far from the expected storage and use temperatures of the desired emulsions. In one method (*56*) an emulsifier with a PIT of about 50 °C higher than the storage–use temperature is selected. The emulsion is then prepared at the PIT where very small droplet sizes are most easily created. Next, the emulsion is rapidly cooled to the desired use temperature, at which now the coalescence rate will be slow, and a stable emulsion results.

Protective Agents and Sensitization. The stability of a dispersion can be enhanced (protection) or reduced (sensitization) by the addition of material that adsorbs onto particle surfaces. Protective agents can act in several ways. They can increase double-layer repulsion if they have ionizable groups. The adsorbed layers can lower the effective Hamaker constant. An adsorbed film may necessitate desorption before particles can approach closely enough for van der Waals forces to cause attraction. If the adsorbed material extends out significantly from the particle surface, then an entropy decrease can accompany particle approach (steric stabilization). Finally, the adsorbed material may form such a rigid film that it poses a mechanical barrier to droplet coalescence.

Oil-field W/O emulsions may be stabilized by the presence of a protective film around the water droplets. Such a film can be formed from the asphaltene and resin fractions of the crude oil. When droplets approach each other during the process of aggregation, the rate of oil film drainage will be determined initially by the bulk oil viscosity, but within a certain distance of approach the interfacial viscosity becomes important. A high interfacial viscosity will significantly retard the final stage of film drainage and promote kinetic emulsion stability. If the films are viscoelastic, then a mechanical barrier to coalescence will be provided, yielding a high degree of emulsion stability. More detailed descriptions are given in references 26, 57, and 58.

Sensitizing agents can be protective agents that are added in smaller amounts than would be used normally. Sensitizing agents have several possible mechanisms of action. If the additive is oppositely charged to the dispersed particles, then decreased double-layer repulsion will result. In some kinds of protecting adsorption, a bilayer is formed with the outer layer having lyophilic groups exposed outwards. Addition of enough additive to form only the single layer will have lyophobic groups oriented outward with a sensitizing effect. If the additive is of long chain length, sometimes a bridging between particles occurs and induces aggregation (at higher concentrations protective action takes over because the potential bridging sites become covered).

Creaming, Inversion, and Demulsification

Creaming. Droplets in an emulsion will have some tendency to rise or settle according to Stokes' law. An uncharged spherical droplet in a fluid will sediment if its density is greater than that of the fluid. The driving force is that of gravity; the resisting force is viscous and is approximately proportional to the droplet velocity. After a short period of time the particle reaches terminal (constant) velocity, dx/dt, when the two forces are matched. Thus

$$\frac{dx}{dt} = \frac{2r^2(\rho_2 - \rho_1)g}{9\eta} \tag{29}$$

where r is the particle radius, ρ_2 is the droplet density, ρ_1 is the external fluid density, g is the gravitational constant, and η is the bulk viscosity. If the droplet has a lower density than the external phase, then it rises instead (negative sedimentation). Emulsion droplets are not rigid spheres, so they may deform in shear flow. Also, with the presence of emulsifying agents at the interface, the droplets will not be noninteracting, as is assumed in the theory. Thus, Stokes' law will not strictly apply and may underestimate or even overestimate the real terminal velocity.

The process in which emulsion droplets rise or settle without significant coalescence is called creaming (Figure 17). This process is not emulsion breaking, but produces two separate layers of emulsion that have different droplet concentrations and are usually distinguishable from each other by color or opacity. The term comes from the familiar separation of cream from raw milk. According to Stokes' law, creaming will occur faster when there is a larger density difference and when the droplets are larger. The rate of separation can be enhanced by replacing the gravitational driving force by a centrifugal field. Centrifugal force, like gravity, is proportional to the mass, but the proportionality constant is not g but $\omega^2 x$, where ω is the angular velocity (equal to $2\pi \times$ revolutions per second) and x is the distance of the particle from the axis of rotation. The driving force for sedimentation becomes $(\rho_2 - \rho_1)\omega^2 x$. Because $\omega^2 x$ is substituted for g, one speaks of multiples of g, or "gs", in a centrifuge. The centrifugal acceleration in a centrifuge is not really a constant throughout the system but varies with x. The actual distance from top to bottom of a sedimenting column is usually small compared to the distance from the center of revolution, so the average acceleration is used. The terminal velocity then becomes

$$\frac{dx}{dt} = \frac{2r^2(\rho_2 - \rho_1)\,\omega^2 x}{9\eta} \tag{30}$$

The problem of deaerated bituminous froth produced from the hot-water flotation of bitumen from oil sands can serve as an illustration. This

Figure 17. Creaming, aggregation, and coalescence in an O/W emulsion.

froth is a W/O emulsion from which the water must be removed prior to upgrading and refining. At process temperature (80 °C) the emulsion viscosity is similar to that of the bitumen, but the density, because of entrained solids, is higher. Taking η = 500 mPa·s (59) and ρ_1 = 1.04 g/mL, the rate of rise of 20-μm diameter water droplets under gravitational force will be very slow. According to equation 29:

$$\frac{dx}{dt} = -3.05 \times 10^{-6} \text{ cm/s}$$

$$\frac{dx}{dt} = 96 \text{ cm/year upward}$$

In a commercial oil sands plant, a centrifuge process is used to speed up the separation. The continuous centrifuges can operate at 2500 × *g*, the

droplets having to travel 9 cm to reach the product stream. With the centrifugal force added, according to equation 30, the droplet velocity would become

$$\left(\frac{dx}{dt}\right)' = 2500\left(\frac{dx}{dt}\right)$$

$$\left(\frac{dx}{dt}\right)' = 7.63 \times 10^{-3} \text{ cm/s outward}$$

This result is 2500 × faster than with gravity alone, but the residence time in the centrifuge would have to be about 20 min, and this length of time is not practical. To speed up the separation, naphtha is added to the level of 25%. The naphtha lowers the viscosity to about 4.5 mPa·s (*59*) and lowers the density of the continuous phase to 0.88 g/mL. Now the water droplets would sediment rather than rise under gravitational force, and although the emulsion density is much reduced, the absolute value of the density difference changes very little: $\Delta\rho = -0.07$ g/mL originally, and becomes $\Delta\rho = +0.09$ g/mL! The overall effect is to lower the viscosity by about 2 orders of magnitude. The droplet velocity now becomes $(dx/dt)'' = 1.1$ cm/s, which yields a satisfactory residence time of about 8 s.

In general, for given liquid densities, creaming will occur more slowly the greater the electrical charge on the droplets and the higher the emulsion viscosity. Although a distinct process, creaming does promote coalescence by increasing the droplet crowding and hence the probability of droplet–droplet collisions.

Inversion. Inversion refers to the process in which an emulsion suddenly changes form, from O/W to W/O, or vice versa. This process was encountered in the example of changing emulsion viscosity given in the earlier section, "Physical Characteristics of Emulsions", subsection "Bulk Viscosity Properties" (Figure 6). The maximum volume fraction possible for an internal phase made up of uniform, incompressible spheres is 74%. Although emulsions with a higher internal volume fraction do occur, usually inversion occurs when the internal volume fraction exceeds some value reasonably close to $\phi = 0.74$. Other factors have a bearing as well, of course, including the nature and concentration of emulsifiers and physical influences such as temperature or the application of mechanical shear.

The exact mechanism of inversion remains unclear, although obviously some processes of coalescence and dispersion are involved. In the region of the inversion point multiple emulsions may be encountered. The process is also not always exactly reversible. That is, hysteresis may occur if the inversion point is approached from different sides of the composition scale. Figure 18 shows the irreversible inversion of a diluted bitumen-in-water emulsion brought about by the application of shear (*60*).

Figure 18. Example of the shear-induced inversion of an emulsion of diluted bitumen in water. (Reproduced with permission from Syncrude Canada Limited.

Demulsification (Emulsion Breaking). The stability of an emulsion is often a problem. Demulsification involves two steps. First, agglomeration or coagulation of droplets must occur. Then, the agglomerated droplets must coalesce. Only after these two steps can complete phase separation occur. Either step can be rate determining for the demulsification process. A typical W/O petroleum emulsion from a production well might contain 60–70% water. Some of this (free water) will readily settle out. The rest (bottom settlings*) requires some kind of specific emulsion treatment.

The first step in systematic emulsion breaking is to characterize the emulsion to be broken in terms of its nature (O/W or W/O), the nature of the two phases, and the sensitivity of the emulsifiers. On the basis of such an evaluation, a chemical addition could be made to neutralize the effect of the emulsifier, followed by mechanical means to complete the phase separation. For example, butter results from the creaming, breaking, and inversion of emulsified droplets in milk.

It follows directly from the previous considerations of emulsion stability that if an emulsion is stabilized by electrical repulsive forces, then demulsifi-

*Hence the field term "bottom settlings and water", or BS&W, used to characterize petroleum samples. (*See also* the Glossary.)

cation could be brought about by overcoming or reducing these forces. In this context the addition of electrolyte to an O/W emulsion could be used to achieve the critical coagulation concentration, in accord with the Schulze–Hardy rule. Similarly, demulsifying agents, designed to reduce emulsion stability by displacing or destroying the effectiveness of protective agents, can be applied. An example is antagonistic action, that is, addition of an O/W promoter to break a W/O emulsion (*see* the earlier section "Protective Agents and Sensitization"). These considerations are discussed in further detail in Chapter 9.

Apart from the aforementioned chemical treatments, a variety of physical methods are used in emulsion breaking. These physical methods are all designed to accelerate coagulation and coalescence. For example, oil-field W/O emulsions may be treated by some or all of settling, heating, electrical dehydration, chemical treatment, centrifugation, and filtration. The mechanical methods, such as centrifuging or filtering, rely on increasing the collision rate of droplets and applying an additional force that drives coalescence. An increase in temperature will increase thermal motions to enhance the collision rate, and also reduce viscosities (including interfacial viscosity), and thus increase the likelihood of coalescence. In the extremes, very high temperatures will cause dehydration due to evaporation, and freeze–thaw cycles will break some emulsions. Electrical methods may involve electrophoresis of oil droplets, causing them to collide, to break O/W emulsions. With W/O emulsions, the mechanism involves deformation of water droplets, because W/O emulsions are essentially nonconducting emulsions. Here the electric field causes an increase in the droplet area and disrupts the interfacial film. Increased droplet contacts increase the coalescence rate and thereby break the emulsion. More details on the application of these methods in large-scale continuous processes are given in Chapter 10.

List of Symbols

a_s	area per adsorbed molecule
A	available area of surface .sp 0.2 Hamaker constant
B	a constant ($3.93 \times 10^{39}\ A^{-2}s^{-2}$)
C_s	solution concentration of the surfactant (M)
c_i	individual ion concentrations
D	diffusion coefficient
dx/dt	terminal (constant) velocity (in creaming)
e	elementary electronic charge
g	gravitational constant
H	distance separating spherical emulsion droplets
I	ionic strength

I_0	intensity of incident light beam (in light-scattering experiments)
I_d	intensity of light scattered (in light-scattering experiments)
I_t	intensity of transmitted beam of light (in light-scattering experiments)
k	Boltzmann constant
k_2	rate constant
k_2^0	rate constant for diffusion-controlled aggregation
l	length of path through sample (in light-scattering experiments)
n	number of moles; number of droplets per unit volume at time t
n_0	number of droplets per unit volume at time $t = 0$
N_A	Avogadro's number
N_c	capillary number
p, p_A, p_B	pressure, pressure in phase A, pressure in phase B
P_c	capillary pressure
r	radius of small droplets
r_p	pore radius
R	radius of spherical droplets also used as the gas constant
R_1 R_2	principal radii of curvature
t	time
T	absolute temperature
T_K	temperature, termed the Krafft point, at which solubilities of surfactants show a strong increase due to micelle formation
v	velocity of displacing fluid
V	total interaction energy
V_A	attractive energy for spherical droplets
V_R	repulsive energy for spherical droplets
W	stability ratio
x	distance from droplet at which intensity of scattered light is taken (in light-scattering experiment)
z	counterion charge number
z_i	individual ion-charge numbers

Greek

α_0, α_1, α_2	empirical constants in equations describing emulsion viscosity
γ	oil–water interfacial tension also used as a term in the repulsive energy expression for spherical droplets
$\dot{\gamma}$	shear rate
γ°	surface tension
Γ_s	surface excess of surfactant
δ	distance from droplet surface to Stern plane
ϵ	permittivity
ζ	zeta potential
η	viscosity

$[\eta]$	intrinsic viscosity
η_0	viscosity of continuous phase
η_{APP}	apparent viscosity
η_D	differential viscosity
η_{Red}	reduced viscosity
η_{Rel}	relative viscosity
η_{SP}	specific increase in viscosity
θ	contact angle of an oil–water interface in contact with a solid surface
$1/\kappa$	double-layer thickness
κ_C	conductivity of continuous phase
κ_D	conductivity of dispersed phase
κ_E	conductivity of emulsions
λ	wavelength of light (in light-scattering experiment)
μ_E	electrophoretic mobility
π	expanding pressure (surface pressure)
ρ_1	external fluid density
ρ_2	droplet density
σ	charge density
σ°	surface charge density
τ	turbidity
	shear stress
τ_Y	yield stress
ϕ	dispersed-phase volume fraction
ψ	potential
ψ°	surface potential
ω	angular velocity

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