EMULSIONS

1. Introduction

An old saying states that “Oil and water do not mix”. Although this is obvious on the macroscopic scale, emulsions are an attempt to accomplish this mixing on a microscopic scale. An emulsion is a dispersion of one liquid in another immiscible liquid, usually in the presence of a third component called an emulsifier. If enough mechanical energy is put into mixing oil and water, droplets of one will form in the other, but this arrangement is usually short lived and they soon separate back into layers when the mixing ceases. The addition of special agents, emulsifiers, into the mixture allows relatively stable droplets of one liquid to form in another, immiscible liquid. Emulsions have been prepared and used for millennia. They have a very broad application and are found in food, coatings, construction products, pharmaceuticals, and cosmetic products. The literature on emulsions is vast, but fortunately there are a few excellent monographs devoted to the subject (1–7). Emulsion droplet diameters are usually in the 0.05–100-μm range. Emulsions comprised of an oil (i.e., organic liquid) dispersed in an aqueous solution are designated by the symbol “o/w” and emulsions comprised of aqueous droplets dispersed in an oil are designated by “w/o”. An emulsion is said to invert when it changes from o/w (oil-in-water) to w/o (water-in-oil), or vice versa (Fig. 1). It is also possible to have more complicated systems such as w/o/w where the droplets themselves are comprised of a w/o emulsion dispersed in an aqueous continuous phase. In principle, it is possible to form o/o emulsions, but in practice the two organic liquids are often too miscible and it is difficult to identify an effective emulsifier (8). However, in special cases block copolymers have been custom designed to stabilize specific o/o and w/w (eg, vesicle systems) emulsions. Complicated systems such as food emulsions can also contain solid particles in addition to the liquid components.

Several different types of emulsions are distinguished in the literature. A (macro)emulsion has a broad distribution of droplet diameters in the 0.05–100-μm range and is turbid and minimally stable. It is the main subject of this discussion of “classical” emulsions. A microemulsion has structural diameters in the 10–50-nm range and is clear, isotropic, and thermodynamically stable. Although microemulsions have superficially similar compositions to macroemulsions, many researchers consider them to be solutions of swollen micelles rather than dispersions of one liquid in another (9). Much theoretical and experimental work has been done on microemulsions, but their practical application has been somewhat limited compared to macroemulsions. Microemulsions generally require much higher levels of emulsifier (10) than macroemulsions (15–30% compared to 1–5% for macroemulsions) and are usually formulated with short chain alcohol stabilizers such as 1-pentanol. The term “miniemulsion” has appeared recently in the literature. A miniemulsion is a subset of macroemulsions in which the particle diameter range of 50–400 nm is achieved by the use of mixed emulsifiers comprised of a surfactant and water-insoluble long-chain alcohol costabilizer such as cetyl alcohol (11). In this discussion, the common term “emulsion” will refer to macroemulsions and “oil” and “water” will refer to the two, immiscible phases.

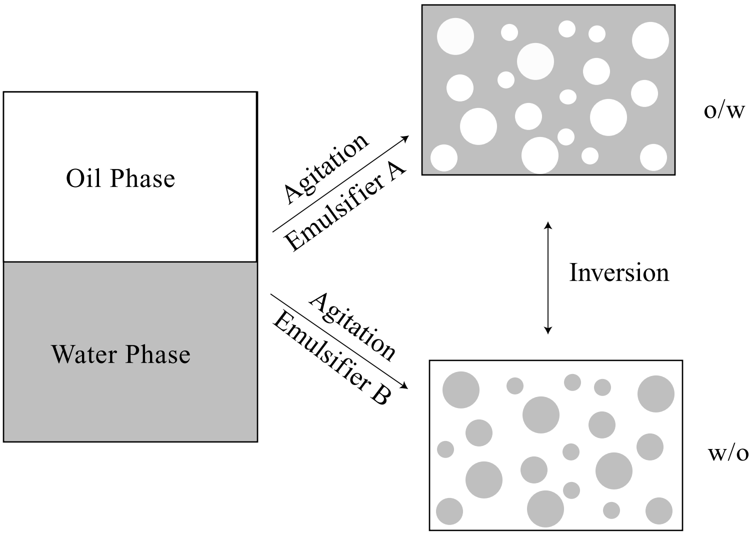

Fig. 1. When water and oil are mixed in the presence of an emulsifier, an emulsion is formed. The type of emulsifier influences the type of emulsion: Emulsifier A (hydrophilic) forms o/w emulsions and Emulsifier B (lipophilic) forms w/o emulsions. Heating an o/w emulsion can convert it to a w/o emulsion (phase inversion).

Emulsifier is a general term that refers to chemical species that occupy the interfacial region between the droplet and the continuous phase. Emulsifiers aid in the formation and stabilization of emulsions. Emulsifiers are amphiphilic molecules, containing both hydrophilic and lipophilic groups, which provide the molecule with some affinity for both the disperse phase and the continuous phase. Emulsion stabilizers are polymeric molecules of higher molecular weight which form a protective steric layer around the dispersed droplets and also have some affinity for both phases. The dispersed, or discontinuous, phase is also referred to as the internal phase, whereas the continuous phase is also referred to as the external phase. Emulsions with an internal phase to total volume ratio of <0.3 are called low internal phase ratio emulsions. The external phase is usually the phase having the higher volume. Emulsions with a ratio between 0.3 and 0.7 are medium internal phase ratio emulsions and those >0.7 are high internal phase ratio emulsions. The maximum packing of spheres is 0.74, so emulsions with internal phase ratios higher than this contain distorted, non-spherical droplets (Fig. 2) or broad particle size distributions. Emulsions have been prepared at >0.95 internal phase ratio and they are, of course, very viscous (12). At internal phase ratios >0.3, whether an emulsion is o/w or w/o depends on the emulsifier selection and method of preparation.

2. Formation and Stabilization

There is a very large increase in interfacial surface area when an emulsion is formed from layers of two immiscible liquids. This can be a 7–8 order of magni-

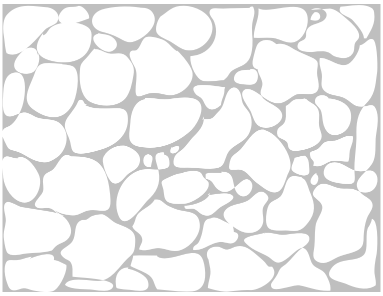

Fig. 2. Because emulsion droplets can distort, emulsions of >0.95 internal phase ratio are possible. Close-packed spheres reach a maximum of only 0.74 internal phase ratio.

tude increase. To accomplish this, work must be done, some of which remains in the system as potential energy and some of which is dissipated as heat. The free energy of formation, ΔG_{form}, is a function of the work done and the increase in configurational entropy:

$$\Delta G_{\mathrm{form}} = \Delta A\gamma - T\ \Delta S_{\mathrm{config}} \tag{1}$$

where ΔA is the increase in interfacial surface area, γ is the interfacial tension, T is the (absolute) temperature, and $\Delta S_{\mathrm{config}}$ is the configurational entropy resulting from creation of a large number of droplets. The work term $\Delta A\gamma$ is much larger than the entropy term, so the ΔG_{form} is a positive quantity. As a consequence of the increased potential energy, emulsions are inherently thermodynamically unstable. Upon formation, the system naturally tries to minimize its energy by minimizing the interfacial surface area, which results in spherical droplets. In most cases, when mechanical energy is used to mix two pure immiscible liquids, the droplets have such high interfacial tension that the system reverts quickly to two layers, the lowest energy configuration. The addition of an emulsifier tends to lower the interfacial tension, thus allowing emulsions to form more easily. Emulsifiers also stabilize the droplets enough to have a finite, useful lifetime by providing a protective barrier against coalescence (ie, recombination).

Because emulsions are metastable, it is a question of when, not if, they will lose stability. Therefore, the preparation of emulsions is the challenge of formulating a system that is at least stable enough to meet the demands of the particular application for the required timescale. In practice, some emulsions can be stable for years, whereas others exist for a very short time. For example, a simple salad dressing of vinegar, vegetable oil, and spices often barely exists as an emulsion for long enough, after shaking, to pour it onto a salad. In contrast, mayonnaise (an o/w emulsion) is stable for months. The stability and physical characteristics of emulsions depend on many variables including the nature of the liquids, temperature, additive types and amounts, order of addition of additives, and the type and amount of mechanical or chemical energy used to form the emulsion. Formulating emulsions can be as much of an art as it is a science.

2.1. Emulsifiers. Emulsifiers are the key to producing stable emulsions. Emulsifiers have two main functions: lowering interfacial tension, which makes

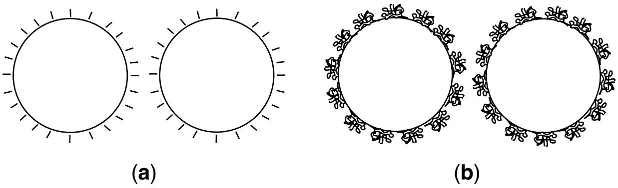

Fig. 3. There are two major mechanisms for achieving colloidal stability of emulsion droplets. The first is electrostatic repulsion accomplished by adsorbing ionic surfactants (**a**). The second is steric stabilization accomplished by adsorbed polymer and nonionic surfactants (**b**). Adsorbed polymer is shown larger than actual scale.

droplet formation less energy intensive, and providing colloidal stability (ie, stability against coalescence) to the droplet by forming an electrically charged (Fig. 3**a**) and/or steric (Fig. 3**b**) layer at its interface with the continuous phase. There are three main types of stabilizers for emulsions:

1. Monomeric surfactants. These are low molecular weight amphiphilic molecules (ionic or nonionic) that can diffuse to the interface quickly to provide stability during emulsion formation. They are mobile and move in and out of the interface in a dynamic way.
2. Polymers. These species are higher molecular weight than surfactants, have some affinity for both phases, are slower to adsorb than surfactants, but provide significant steric stabilization. They have multiple attachment points to the droplet surface, so they tend to adsorb very strongly and remain at the interface.
3. Particles. These are usually much smaller than the droplets and provide a hard, protective coating on the droplet (Fig. 4). One mechanism of attachment is by heterocoagulation of the particles onto the large droplet. Examples include various types of clays and activated carbon as well as solidified fats.

To attain stability, the emulsifiers need to cover the surface of the droplets completely and remain firmly adsorbed. The amount of emulsifier needed for a given emulsion is highly dependent on the droplet size (ie, surface area), the

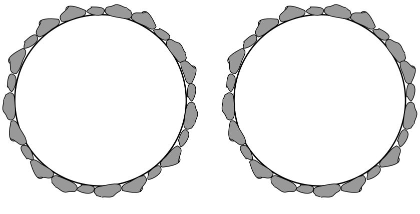

Fig. 4. A third way to achieve colloidal stability is by adsorbed solid particles on the droplet surface, which is less common than electrostatic or steric stabilization. One mechanism for covering the surface with particles is heterocoagulation. Particles are shown larger than actual scale.

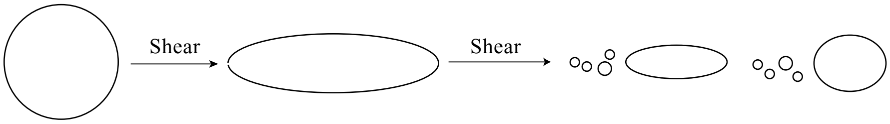

Fig. 5. When a droplet undergoes shear, it distorts and breaks into smaller droplets. Very small droplets are formed by tip-streaming, leading to an overall broad size distribution.

emulsifier efficiency, and the composition of the two phases. Coarse emulsions my require $<1\%$ emulsifier based on the total formulation, whereas $>5\%$ emulsifier may be required for fine emulsions. The typical range is 1–5% for a large number of emulsions. Additional stability can be accomplished by thickening the continuous phase with high molecular weight synthetic polymers and natural gums.

2.2. Formation. The most common method of preparing emulsions employs mechanical shear to achieve droplet breakup (Fig. 5). Droplet size distributions are generally broad and follow a log normal distribution pattern. Unimodal or near-unimodal distributions are uncommon. When the emulsion components are subjected to high mechanical shear and turbulent flow, it is the size distribution of the micro-eddies in the flow pattern that influences the emulsion droplet size distribution (13,14). Clearly, the rheology of both liquids is a critical variable during the emulsification process. The dynamic interfacial tension is also of importance because the droplets need to be stabilized as soon as they are formed or they could recombine. This is why higher molecular stabilizers such as polymers are not effective emulsifying agents during the formation of the emulsion. Increasing the concentration of the emulsifier, usually a surfactant, will decrease droplet size up to the point where the hydrodynamics of the system becomes the limiting factor. The process of emulsification is extremely complex from a modeling perspective due to the hydrodynamics and the multitude of interacting variables. This is why emulsification is mainly an experience-based endeavor.

2.3. Stabilization. In order for an emulsion to be stable, the droplets need to exist as discrete entities uniformly dispersed in the continuous phase. If the droplets are not sufficiently stabilized, they will coagulate when they collide during mixing or through Brownian motion. This process is called coalescence and it leads to gross separation of the two liquid phases or "breaking" of the emulsion (Fig. 6). Simple mixing usually cannot reestablish the emulsion. It is also possible for droplets to maintain their integrity, but rise to the top due to gravity if the droplets are less dense than the continuous phase. This is called creaming (Fig. 7) and can usually be reversed, at least temporarily, by simple mixing. The creaming, or sedimentation, velocity, v, is related to the droplet radius, r, the difference between the densities of the internal and external phase, $\Delta\rho$, and the external phase viscosity, η, by the following equation, as derived from Stokes law:

$$V = 2r^2\Delta\rho/9\eta \tag{2}$$

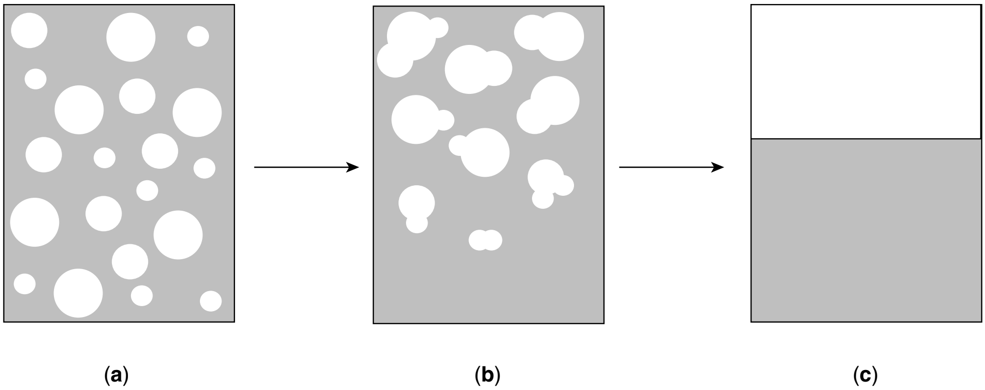

Fig. 6. If droplets (**a**) are not sufficiently stabilized to maintain their structural integrity under stress (eg, high electrolyte concentration), they begin to coalesce (**b**) and eventually lose their identity as the system phase separates (**c**) or "breaks". This process is irreversible.

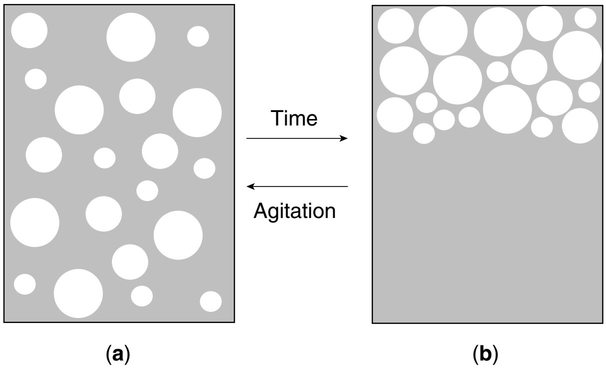

Fig. 7. Unless the external phase is thickened or the density of the internal and external phases is matched, the effect of gravity over time causes a well dispersed emulsion (**a**) to cream (**b**). Note that the individual emulsion droplets maintain their integrity and can be redispersed. In a w/o emulsion, the internal phase would sediment.

Raising the viscosity of the continuous phase will slow the creaming process, as will reducing the droplet size or adjusting the density of the droplet to match closely the density of the external phase. Droplets may also retain their identity, but form multidroplet aggregates. This is known as flocculation (Fig. 8) and can usually be reversed, at least temporarily, by simple mixing. Flocculated droplets are not actually in physical contact with each other, but are held in close proximity in a shallow potential energy minimum.

Potential Energy Diagrams. Stability and instability are best explained by using potential energy diagrams. Potential energy diagrams are derived from the total attractive and repulsive energies, ΔG_{tot}, acting between two droplets as they approach one another:

$$\Delta G_{\text{tot}} = \Delta G_{\text{elec}} + \Delta G_{\text{steric}} - \Delta G_{\text{vdw}} - \Delta G_{\text{depl}} \tag{3}$$

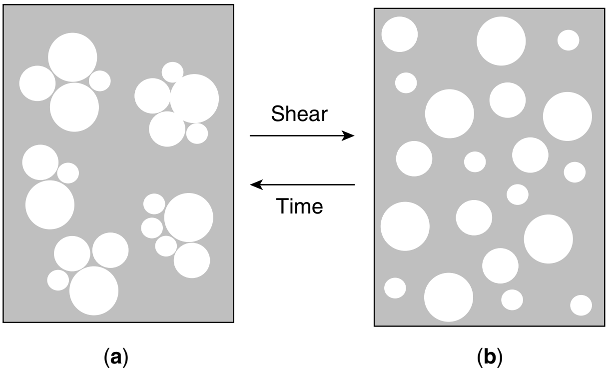

Fig. 8. A flocculated emulsion (**a**) contains aggregates of droplets held in a shallow secondary minimum of potential energy. The droplets are not actually touching each other, so they can be redispersed by shear (**b**). At rest, they return to the flocculated state (**a**).

where ΔG_{elec} is the electrostatic repulsion energy, $\Delta G_{\mathrm{steric}}$ is the steric repulsion energy, ΔG_{vdw} is the van der Waals attraction energy, and ΔG_{depl} is the depletion attraction energy. The significance of these types of interparticle potential energy will be explained in the following discussion.

Emulsion droplets can possess kinetic energy from several sources including mechanical mixing, gravity, and thermal (Brownian) motion. When two droplets collide, they will coalesce unless there is a sufficiently high potential energy barrier to keep them apart. This is the key to emulsion stability. When no emulsifier is present, the main force acting between the two droplets in close proximity is van der Waals attraction, which is basically the universal phenomenon that “all matter attracts matter”. The attractive force pulls the droplets together into the primary energy minimum resulting in coalescence. Figure 9 shows the potential energy curve for the two droplets approaching one another. Potential energy is plotted on the vertical axis and interdroplet separation is plotted on the horizontal axis. The strength of the van der Waals attraction is a function of the material composition (ie, as expressed by its Hamaker constant) and varies as the inverse of the droplet separation distance (12). The ΔG_{vdw} for organic liquid droplets is only ~15–50 % of the ΔG_{vdw} for pigments and metal oxide particles. Consequently, the van der Waals attraction of droplets for each other is significant over the fairly short distance of ~5–10-nm droplet separation.

Electrostatic Stabilization. If the emulsion is electrostatically stabilized by ionic surfactants, then the potential energy curve can be calculated using the measured quantities of droplet size and zeta potential (15), from which the droplet surface potential is derived. Zeta potential, expressed in millivolts (mV), is frequently used as an approximation of the electric double layer potential surrounding the particle. The well-known DLVO (Derjaguin and Landau and Verwey and Overbeek) theory (16,17) describes the ΔG_{elec} and ΔG_{vdw} terms quite well. The potential energy curve has a maximum that acts as a barrier to coalescence (Fig. 10). A zeta potential of 30–40 mV (negative or positive) is usually sufficient for good stability. This creates a maximum in the repulsive energy curve of ~20 kT, depending on droplet size. This maximum in the potential energy can

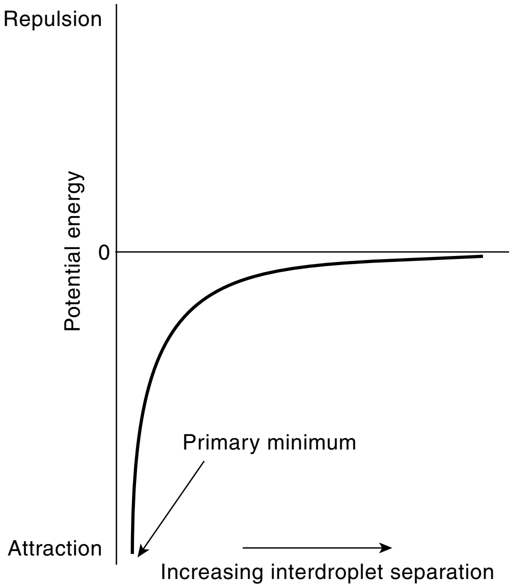

Fig. 9. When two bare (ie, no adsorbed emulsifier) droplets approach each other, they are strongly affected by van der Waals attractive forces. With no repulsive force to keep them apart, they coalesce onto the deep primary minimum of potential energy.

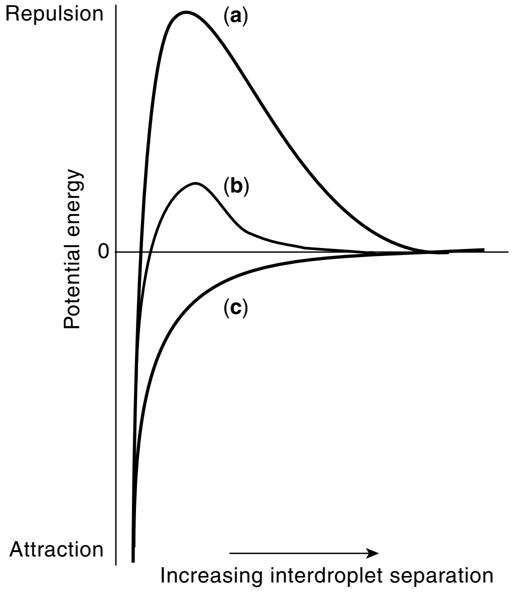

Fig. 10. If the emulsion droplets are stabilized by adsorbed ionic surfactant, then the sum of the electrostatic repulsion and van der Waals attraction results in a net repulsive energy barrier. At low electrolyte concentration (eg, 0.001 *M*), the barrier is sufficiently high to prevent coalescence (**a**). Medium electrolyte concentration reduces the barrier height significantly (**b**). At high electrolyte concentration (eg, 1.0 *M*) only the van der Waals attraction remains and the droplets coalesce into the primary minimum (**c**).

be used to calculate the coagulation rate of the droplets, thus getting an estimate of the length of time the emulsion will remain stable from coalescence. When the kinetic energy of the droplets exceeds the potential energy maximum, the droplets fall into the primary minimum and coalesce. For reference, the thermal (kinetic) energy of the droplets is 1.5 kT. The potential energy maximum is lowered significantly by adding electrolyte to the emulsion (Fig. 10). This is the basis for breaking an emulsion using salt. According to the Schulze-Hardy rule, divalent and especially trivalent ions are much more effective at causing coagulation (ie, coalescence) than monovalent ions.

Steric Stabilization. Droplets can also be stabilized sterically by using nonionic oligomeric surfactants or polymers at the interface to form a physical rather than a charge repulsive barrier (18). This involves the $\Delta G_{\mathrm{steric}}$ term. The droplets cannot get close enough to each other to fall into the primary minimum and coalesce if the polymer surface layer exceeds the 5–10-nm van der Waals interaction distance. The potential energy curve for this system is shown in Figure 11 for two different continuous phases. If the continuous phase is a good solvent for the steric stabilizer, then no energy minimum will be present and the emulsion will be stable. But if the continuous phase is a poor solvent for the steric stabilizer, then a secondary energy minimum can occur, leading to flocculation. If this energy minimum is deep, then it will be difficult to deflocculate the emulsion even for a short period of time. When the temperature of a nonionically stabilized emulsion is increased, the continuous phase can become a poor solvent for the stabilizer molecules. This leads to destabilization and possibly phase inversion.

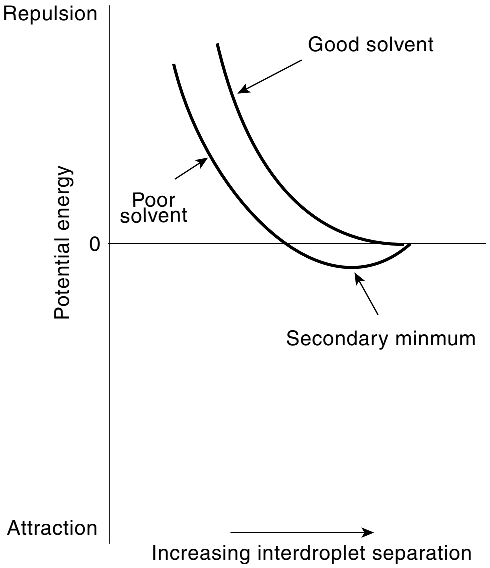

Fig. 11. If the emulsion droplets are stabilized by adsorbed polymer for which the continuous phase is a good solvent, then a steric barrier exists to keep the droplets apart and stable. If the continuous phase is a poor solvent for the polymer, then a secondary minimum forms resulting in droplet flocculation. Flocculation is reversed by continuously supplying energy equivalent to the secondary minimum depth.

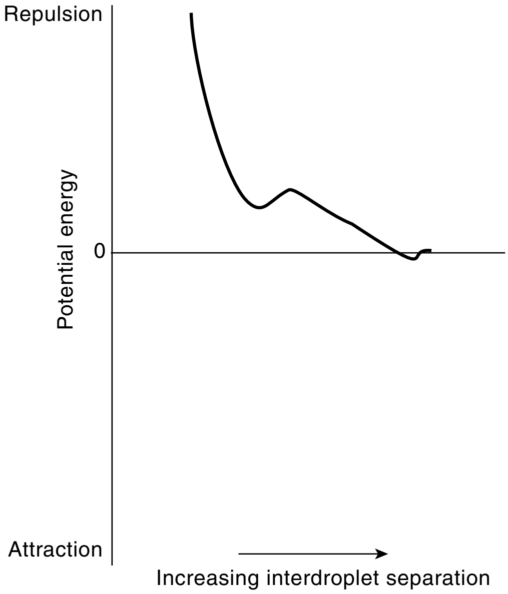

Fig. 12. If the emulsion droplets are stabilized by both electrostatic and steric mechanisms, then a compound potential energy curve results. Electrosteric stabilization takes advantage of both mechanisms at the same time.

If both electrostatic and steric stabilizers are used, then a compound curve results (Fig. 12). Electrosteric stabilization is often the most robust type of stabilization because it takes advantage of both mechanisms in case the emulsion is subjected to multiple instability stresses such as high electrolyte and temperature fluctuations.

Depletion Flocculation. High molecular weight nonadsorbing polymer thickeners are often dissolved in the continuous phase to retard creaming and to adjust the rheological properties of emulsions. These polymers can cause another type of instability called depletion flocculation. The polymers set up an osmotic force between the bulk continuous phase where they reside and the interdroplet space from which they are excluded (Fig. 13). This attractive energy ΔG_{depl} is added to the omnipresent ΔG_{vdw} energy term. The result is a secondary minimum in the potential energy curve (Fig. 14) that can lead to flocculation of the droplets (19,20). As with other forms of flocculation, mixing can redisperse the droplets, but they soon return to the flocculated state. Note that flocculation is not necessarily bad, as long as it does not lead to creaming or coalescence. In fact, an extensive flocculation network can prevent creaming in some circumstances. If the polymers contain multiple groups that can adsorb onto the droplets, then this can lead to bridging flocculation at low polymer concentrations and a uniform bridged network structure at high concentrations.

Interfacial Structure. It should be clear at this point that emulsions are stabilized by establishing electrostatic and/or steric barriers at the droplet surface. Both types of barriers are effective for o/w emulsions, but only steric barriers are effective in w/o emulsions due to the low dielectric constant of the continuous phase. The structure of the interfacial region is quite complex. By

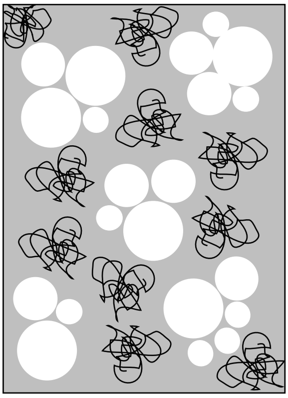

Fig. 13. Depletion flocculation occurs when nonadsorbing polymer dissolved in the continuous phase is excluded from regions between the droplets. This sets up an osmotic pressure difference that causes flocculation in a secondary minimum of the potential energy. Depletion flocculation is reversible with shear, but it reforms quickly when the shear is removed. Polymer molecules are shown much larger than actual scale.

judiciously choosing emulsifier systems, tightly packed films or structures such as liquid crystals can be formed at the droplet surface (21). For example, this happens in high internal phase ratio emulsions where there is so little continuous phase that the concentration of the emulsifiers in that phase is quite high. These tightly packed structures provide a significant protective barrier and structure properties to stabilize the emulsion. The packing properties of the

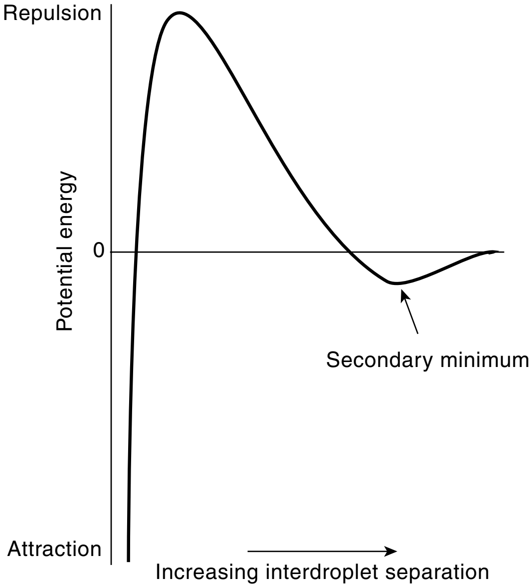

Fig. 14. The potential energy curve for a depletion flocculated ionically stabilized emulsion shows that the sum of the van der Waals attraction and the osmotic attraction cause a secondary minimum (eg, Fig. 10).

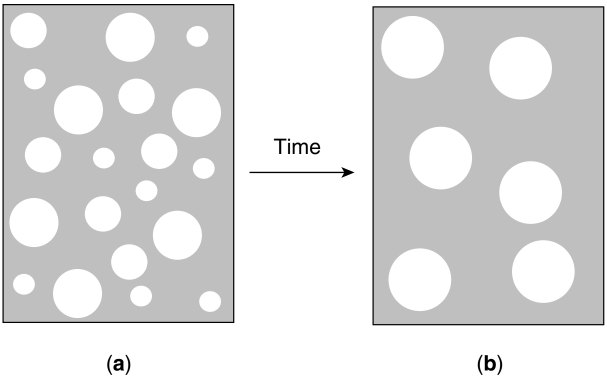

Fig. 15. If the internal phase of an emulsion (**a**) has even a slight solubility in the external phase, then molecules of the internal phase may diffuse from the small droplets to the large droplets. This coarsening of the emulsion (**b**) is called Ostwald ripening and is a serious formulation problem.

different chemical species at the interface is very important but not well understood. Therefore, the choice of optimal emulsifiers and stabilizers is still somewhat of an empirical and experience-based task.

2.4. Ostwald Ripening. Another phenomenon that could be considered a form of instability is Ostwald ripening. Emulsions are never perfectly unimodal, so there are both larger and smaller droplets in a given sample. There is a driving force for the migration of the internal phase from the smaller to the larger droplets. The pressure (or chemical potential) of molecules inside a droplet is inversely proportional to the radius of the droplet. The result is a coarsening of the emulsion as it minimizes interfacial surface area (Fig. 15). It is surprising that this can happen even when the solubility of the internal phase is as low as a few ppm in the external phase. The growth of the large droplets at the expense of the small droplets can lead to changes in rheology, efficacy, and physical appearance (eg, creaming). Ostwald ripening is often accelerated by elevated temperatures. One way to slow Ostwald ripening is to slow down the diffusion of the internal phase molecules through the interfacial region. This can sometimes be accomplished by judicious choice of low molecular weight costabilizers that are very insoluble in the continuous phase (1) or by creating a more impervious barrier using liquid crystalline structures at the interface. Ostwald ripening is a serious problem for the formulator and can be a very difficult eliminate.

2.5. Biodegradation. Emulsions often contain additives that are subject to biodegradation. The destruction of biodegradable stabilizers and rheology modifiers will lead to degradation of performance properties at best and complete destabilization of the emulsion at worst. Sometimes emulsifiers with biocidal properties such those based on quaternary ammonium salts can be used in the formulations. If that is not possible, then a small amount of biocide may be required to preserve the integrity of the emulsion. When oxidative degradation is an issue, then antioxidants will also have to be part of the formulation.

2.6. Microemulsion Stability. The previous stability discussion does not apply to microemulsions because they are thermodynamically stable isotropic solutions. Microemulsions differ from macroemulsions in that their oil—surfactant components can exist as cylindrical or bicontinuous structures in addition to spheroids (9). The stability and structure of nonionic microemulsions is governed by temperature. As the temperature is increased to the phase inversion temperature (PIT), the structure converts to bicontinuous and then it inverts as the PIT is exceeded. Similar effects can be accomplished for ionic microemulsions by adding electrolyte and certain cosurfactants. Microemulsions may also lose stability when diluted.

2.7. Destabilization. In certain instances, destabilizing an emulsion (ie, demulsification) is desirable. For example, in tertiary oil recovery the w/o emulsion needs to be broken to recover the crude oil. Also, unwanted emulsions may form during a process and they will need to be eliminated. For ionic emulsions, electrolyte can be added to induce coagulation by decreasing the interparticle potential energy barrier. For nonionic emulsions, raising the temperature can bring about flocculation. Purely mechanical means of destabilization include centrifugation, filtration, freezing, and application of mechanical shear. Addition of a surfactant that will disrupt the balance of the system and the interfacial structure can also lead to destabilization.

3. Preparation

The formulation of emulsions is a blend of art and science and is still largely empirical because it is so dependent on the chemical and physical characteristics of the particular materials being emulsified, the order in which they are blended, and the equipment used for the process. Nevertheless, some guidelines can be given that will make the job easier and less time consuming. First, the formulator must know the purpose of the emulsion formulation and how it will be used. Some important considerations are stability requirements (ie, shelf-life), cost, rheology, ease of preparation, environmental conditions for use and storage (eg, temperature extremes), regulatory restrictions, and safety. This section will present some guidelines on how to formulate and produce a robust emulsion once the purpose of the emulsion has been established.

3.1. Formulation. There are literally thousands of emulsifiers available commercially (22,23), so choosing the right ones for a particular system can be a daunting task. Bancroft's rule has been known for almost a century: surfactants that partition preferentially into the water phase tend to form o/w emulsions and surfactants that partition preferentially into the oil phase tend to form w/o emulsions. This is a rule of thumb, but a useful one (24). In addition, experience has shown that two or more emulsifiers are usually needed to attain the most robust stability and this often includes both ionic and nonionic emulsifiers. Given this situation, how does one go about formulating an emulsion? One approach is to search the literature for a system of similar composition and use that emulsion formulation as a starting point for the formulation process. Although this is commonly done, there are also some more systematic ways to formulate an emulsion. The most useful system for choosing emulsifiers is the

HLB system (25,26), where HLB stands for hydrophile–lipophile balance and is a way to match the characteristics of the liquid to be emulsified with the most effective emulsifiers. Unfortunately, just getting an HLB match is often not sufficient to produce an acceptable emulsion formulation. The chemical compositions of the emulsifiers and the liquid to be emulsified also need to be matched to gain the compatibility needed for stability. One problem with the HLB system is that it is temperature sensitive (24), so the PIT of the emulsion system should be measured. This allows the formulator to know the stable temperature range of the emulsion.

The traditional HLB scale ranges from 0 to 20, with lipophilic (literally "oil loving") emulsifiers <9 and hydrophilic emulsifiers >11. Emulsifiers in the 4–6 range are considered w/o emulsifiers and those in the 8–18 range are considered o/w emulsifiers. For comparison, wetting agents occupy the 7–9 range and detergents occupy the 13–15 range. These range designations are based on an extensive experience base of nonionic surfactants. Some ionic surfactants have been assigned HLB values, which had to be determined experimentally in comparison with nonionics. Due to their ionic nature, their HLB values can sometimes be outside of the traditional range. For example, the HLB is ~ 40 for the common surfactant sodium lauryl sulfate. A systematic way of determining the HLB of a liquid is to prepare a series of blends of a lipophilic and a hydrophilic emulsifier such as Span 60 ($\text{HLB} = 4.7$) and Tween 60 ($\text{HLB} = 14.9$) and use them to emulsify the liquid. It is best to start at a high concentration of emulsifier such as 10–15% based on the liquid being emulsified.

Once relatively stable emulsions are identified, the loading of emulsifier can be reduced to fine tune the system. One needs to decide whether an o/w or a w/o emulsion is better for their particular application. As an example, if a 50:50 Span/Tween mixture was the best, then the required HLB would be 9.8 for this particular system. Having the HLB of the liquid then allows the formulator to search publications (22,23) for emulsifiers or mixtures of emulsifiers that have chemical compositions compatible with the liquid in addition to having the appropriate HLB. The required HLB values of common organic liquids, oils, and waxes are also available in the literature.

Considerably more work is then generally needed to compose a formulation that meets all of the applications criteria required by the manufacturer and the end user. This includes choosing appropriate polymeric stabilizers and thickeners, neither of which are part of the HLB scheme. In addition, there may be fragrances, biocides, pigments, and other additives to satisfy the market needs. Once the general emulsion formulation is established, it must be tested and refined to ensure that it will remain stable under the full range of environmental conditions it will be subjected to during transportation, storage and use.

3.2. Equipment and Methods. Mechanical energy is needed to turn the components of a formulation into an actual emulsion. The process is called emulsification and the energy requirements can cover a wide range depending on the application. For example, a farmer needs only minimal mixing in his spray tank to produce a sprayable pesticide emulsion from an emulsifiable concentrate, whereas very high pressures are needed in a homogenizer to produce homogenized milk. The most common mechanical emulsification equipment (4) includes colloid mills, high pressure homogenizers, and jet impact devices

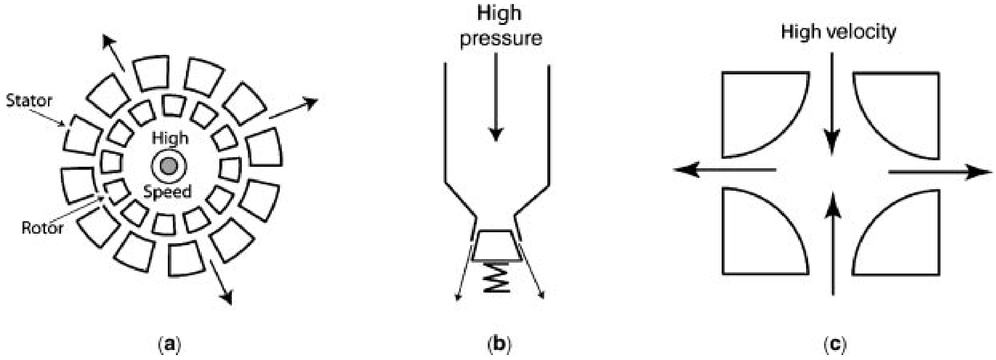

Fig. 16. Most equipment used to make emulsions requires significant energy input. Rotor-stator devices (**a**) utilize high speed shearing action. Homogenizers (**b**) force the emulsion components through a small, spring-loaded gap. Jet impact devices (**c**) force jets of the emulsion components together at very high velocity.

(Fig. 16). Colloid mills are rotor-stator devices that rely on very high shear rates (speeds up to 20,000 rpm) to accomplish droplet breakup. These are high energy devices because the actual energy needed to form an emulsion is far greater than the work function described in equation 1. A lot of energy is needed to form the highly curved interface of small droplets. This results in an internal pressure, Δp, called the Laplace pressure:

$$\Delta p = 2\gamma / r \tag{4}$$

The smaller the droplet, the higher the internal pressure (ie, energy). Lowering the surface tension, γ, with surfactants obviously lowers energy requirements somewhat. One of the keys to getting small droplet size is the input of high energy over a very short time. This is accomplished in homogenizers and jet impact systems where residence time is very short.

Traditional colloid mills utilize a cone-shaped rotor, whereas more recent designs can have concentric cylinders with complicated tooling to aid in droplet breakup and turbulent flow (eg,Ultra-Turrax). In high pressure homogenizers, the emulsion components are forced through a small orifice at between 1000 and 5000 psi. Both rotor-stator devices and homogenizers can have single or multiple stages. In the jet impact system (eg, Microfluidics) two liquid jets collide at high velocity thus forming small droplets. The resulting emulsion can be recycled through the unit to attain further droplet size reduction. Other emulsification methods include using ultrasonics, electrostatics, electrocapillarity, and aerosols. Sometimes chemical energy is sufficient to produce an emulsion. This is referred to as “spontaneous emulsification”. Heat of solvation or neutralization can cause localized flow and mixing (Marangoni effect) at the interface leading to emulsification. But use of mechanical energy is still the usual method for achieving emulsification.

3.3. Characterization.

There are many methods for characterizing emulsions and a combination of them is usually needed to construct a complete picture. One of the most common measurements is particle sizing, which can be done by a number of techniques including light scattering, sedimentation, and microscopy. Acoustic methods of characterization have recently been explored (27) for analyzing the droplet size distribution and internal phase volume of complicated systems such as food emulsions. These ultrasonic techniques are nondestructive and noninvasive in addition to being fast. The ultrasonic velocity and attenuation are measured versus frequency, and multiple scattering theory is used to calculate droplet size and phase volume. Electroacoustic methods can be used to measure the zeta potential of emulsion droplets in the concentrated emulsion. These data are useful for calculating interparticle potential energies and the colloidal stability of ionic emulsion droplets. Water content of w/o emulsions is determined by dielectric measurements. Rheological testing of emulsions can be very important to emulsion performance and very challenging to perform. Sophisticated rheometers are now available for assessing the flow characteristics of emulsions in terms of elastic and viscous properties. This is of particular interest in the cosmetics, oil recovery, and food fields. Finally, some characterization of emulsion storage stability should always be done to ensure proper shelf-life. Storage stability should be assessed based on the application requirements and market needs. Possible performance tests include the resistance of the emulsion to freeze–thaw cycling, high temperature swings, vibration during shipment, pH drift, electrolytes, mechanical shear, and biodegradation.

4. Health and Safety and Environmental Issues

Current themes in industrial technology include the improvement of health and safety of workers and consumers, and the cleanup of the environment. There is a trend toward reducing the volatile organic content (VOC) of products and intermediates. Emulsions can help reduce VOCs by replacing organic solvents with water. A good example of this is the use of latex paints in place of solvent-based paints for many coatings applications from house paint to automotive coatings. Latex-based adhesives is another example. As technologists continue to improve the chemistry, more emulsion-based systems will be introduced, thus improving the quality of our work and living environment. A serious environmental issue is the cleanup of oil spills. Oil tends to form relatively stable w/o emulsions with sea water. Cleanup and demulsification of this viscous, persistent pollutant is a challenge because emulsion compositions vary with type of crude oil and conditions of formation. Demulsifiers in the HLB range of 8–11 have been found to have some utility in this application.

5. Uses

Emulsions are encountered in a very wide range of applications in our daily lives. Some emulsions such as milk and latex from the rubber tree have been around for millions of years, whereas many emulsions were developed during the technology revolution of the nineteenth and twentieth centuries. The major areas where emulsions find use will be discussed here.

5.1. Food. A number of common food products are emulsions (28–30). In fact, the word emulsion itself is derived from the Latin *emulgére*, which means "to milk out". The most familiar food emulsions are dairy products. These include the o/w emulsions milk and cream and the w/o emulsions butter and margarine. When milk is homogenized, usually in a two-stage process involving a high pressure homogenizer, the fat droplets are reduced to a very small size and stabilized by natural milk proteins. The internal phase ratio is low (<0.3) for milk and butter, and medium (0.3–0.7) for cream. An example of a food emulsion with a high internal phase ratio (>0.7) is mayonnaise. Mayonnaise is an o/w emulsion prepared in a colloid mill wherein the oil is stabilized by egg yolk and mustard. The egg yolk provides the emulsifiers lecithin and cholesterol and the mustard serves as a particle-type stabilizer. Creamy salad dressings are w/o emulsions thickened with xanthan gum. Other relatively simple food emulsions include creamy soups and sauces, both of which are also thickened to provide better stability. Typical thickeners found in food emulsions are gums such as xanthans, carageenans, pectinates, and alginates. The type of stabilizers that are most often used include proteins, lecithin, cellulosics, starches, and gelatin. Some food products start as emulsions, but end up as a more complex system. Examples include whipped cream, ice cream, and baked goods. One final food example is the so-called "meat emulsion". Although this is not a traditional emulsion, it does consist of fat globules dispersed in a liquid continuous phase stabilized by meat proteins. Clearly the range of emulsions in the food product area is quite broad.

5.2. Personal Care and Household Products. Emulsions are very common in personal care products (31). Cold cream, vanishing cream, hand lotion, and deodorant cream are among the emulsions found in the cosmetic and personal care product line. Some of the advantages of emulsions include efficient cleansing action, ease of application, and the ability to apply both water- and oil-soluble ingredients at the same time. Cosmetic emulsions tend to have many ingredients such as fragrances, humectants, pigments, moisturizers, thickeners, preservatives, and pH adjusters, in addition to the usual oils, waxes, emulsifiers, and water. Sensory properties such as coolness, softness, spreadability, and creaminess are important to the success of personal care products. The control of the rheology of cosmetics and personal care emulsions is a critical aspect of the formulation design. Emulsions can also be found in the area of household cleaning and maintenance products. Many furniture, floor, and automobile polishes are oil or wax emulsions in water. Although the wax droplets in these products are often solidified at room temperature, they were liquid at the processing temperatures used to manufacture them. This process is called melt emulsification and it can be used to emulsify many types of low melting solids. If a perfectly clear polish is desired, it is possible to formulate it as a microemulsion.

5.3. Emulsion (Latex) Polymers. Emulsion polymers or latexes are utilized as intermediates for many construction products. Latex polymers are used as binders in latex paint, in adhesives, and in paper coatings. Although the final latex product may actually be a solid dispersed in water, emulsion polymers are produced by emulsifying liquid monomers in water, then carrying out polymerization as the monomers diffuse from the droplets to growing polymer chains in the latex particles. At the end of the polymerization the dispersion is cooled and the resulting polymer particles can be anywhere from very soft and deformable to very hard depending on the particle composition. Particle diameters range from ~50 to ~5000 nm. Emulsion polymerization allows the polymer chemist to achieve much higher molecular weight and much more complicated structure than is achievable in solution polymerization in a solvent. For example, particles having unique morphologies such as core-shell (32), hollow core, and nonspherical geometry can be produced. Emulsion polymerization is an example of a situation where the initial monomer emulsion stability does not have to be very good, but the final emulsion polymer stability has to be excellent. The initial monomer emulsion has to be stable for only a few minutes to a few hours until the polymerization is complete. The final latex polymer often needs to be stable at mechanical shear extremes produced by various coating processes such as blade coating and brushing. The most common application of miniemulsions is in emulsion polymerization. Recently, researchers have substituted supercritical carbon dioxide for the water in emulsion polymerization (33). Special fluorinated and siloxane-based emulsifiers had to be designed to stabilize these systems. At the end of the polymerization, the carbon dioxide is easily removed leaving a finely powdered polymer with no aqueous or solvent residues.

5.4. Pharmaceuticals. Emulsions are being used increasingly as delivery systems for pharmaceutical treatments. The emulsion allows intravenous administration of hydrophobic active ingredients, which are then absorbed more readily due to the small droplet size. Slow release can also be built into the emulsion formulation to prolong the effect of the drug or to reduce its toxicity. Oil and water soluble components can be mixed and delivered in the same formulation. Lipid emulsions have been used to treat malnutrition by intravenous injection (34). These o/w emulsions consist of a vegetable oil emulsified with the naturally occurring emulsifier lecithin. Emulsified fluorocarbons can be used as artificial blood substitutes due to their ability to carry significant amounts of dissolved oxygen and carbon dioxide. Of course lotions, creams, and ointments similar to cosmetic formulations are being used to deliver active pharmaceutical ingredients. Additives for pharmaceutical formulations are highly regulated, so it can be very challenging to formulate a system which has both efficacy and stability while staying within the guidelines of safety and regulatory requirements.

5.5. Agricultural Chemicals. A common type of agricultural formulation is known as an emulsifiable concentrate (EC). The ECs are nonaqueous formulations comprised of a pesticide active ingredient, a solvent, and an emulsifier mixture (35). They are not emulsions as supplied, but easily and quickly form emulsions when added to water with a minimum amount of agitation. The ECs are sold to both farmers and homeowners as a convenient way to deliver pesticide to the target crop. The ECs are most often needed for low melting point active ingredients which are difficult to formulate by other means. The emulsions formed by ECs need to have stability in high salt environments such as fertilizer solutions and hard water. There is a trend away from ECs because of their volatile solvent content, but they will still be used for difficult to formulate active ingredients. Invert or w/o emulsions have also been used as agricultural sprays.

These are usually high viscosity systems that reduce pesticide drift due to larger particle size of the spray droplets and increase retention on the leaf due to the high oil content. Another type of pesticide formulation is a suspoemulsion (36), in which one active ingredient is emulsified and another active ingredient is included in the continuous phase as a finely divided dispersion of solid particles. Although some work has also been done on microemulsion formulations of pesticides, they tend to be too expensive and have some stability problems with temperature changes and upon dilution. Their main advantage is the enhancement of efficacy by improved transport into the target organism.

5.6. Oil Recovery. When oil is recovered from sedimentary formations by conventional means, more than one-half of it can be left behind in the rock (37). This oil is very difficult to remove because it is coating the rock surfaces and not free-flowing. Surfactant-based systems have been developed to enhance the recovery of the trapped oil. When these surfactant solutions are pumped underground, they appear to form microemulsions, bicontinuous structures, and possibly very fine macroemulsions, with the oil. The flow properties of these emulsions through porous media are quite important, therefore much effort has been invested in rheological studies (38). Once the emulsified oil is removed from the ground, the emulsion needs to be broken in order for the oil to be recovered from the process stream. Another application of emulsions in the petroleum industry is to produce relatively low viscosity emulsions of viscous crude oil to make pipeline transport much easier.

5.7. Asphalt Emulsions. Asphaltic bitumen emulsions are used for a number of applications where water repellency is important (1). This is interesting because the emulsions themselves have water as the continuous phase, yet the final asphaltic surface formed during application needs to become hydrophobic. The most familiar use is for road surfacing, where the relatively low viscosity of the $\sim$50% internal phase emulsion allows for easy application of the very viscous asphalt. Final properties depend on the emulsion breaking so that a durable highway surface is formed. Other uses for asphalt emulsions include roof coatings, insulating coatings, and as a water resistant treatment for paper and fabric.

6. Future Trends

Emulsion formulation and application is still a very active technology, with literally thousands of journal articles and patents being written each year, and new applications being developed continually. Work will no doubt continue on lowering VOCs, thus reducing our dependence on organic solvents. One challenge is to increase use of water-based systems in applications where water has traditionally caused corrosion problems such as with lubricants and coatings for metals, especially steel and iron. Another, more exotic, area would be the development of "smart" emulsions that could react or adjust to their environment (39). Applications for smart emulsions could be in materials science, biomedical engineering, or drug delivery systems. Self-assembly of colloidal systems is also an area of intense activity. Clearly, there is a multitude of opportunities available for emulsion technology to grow in the future.

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