Multiple Emulsion Stability: Pressure Balance and Interfacial Film Strength

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1.1   INTRODUCTION

Multiple emulsions, or emulsions having ternary, quaternary, or more complex structures, have been studied since their first description in 1925 (Seifriz, 1925). The simplest multiple emulsions, sometimes called "double emulsions," are in fact ternary systems, having either a water-in-oil–in-water or an oil-in-water–in-oil structure, whereby the dispersed droplets contain smaller droplets of a different phase. Multiple emulsions have a number of potential applications in pharmaceutical, cosmetic, food, and separation sciences. The pharmaceutical applications of multiple emulsions include use as vaccine adjuvants (Gresham et al., 1971), red blood cell substitutes (Zheng et al., 1993), lymphatic drug-targeting vehicles (Yoshioka et al., 1982; Omotosho, 1989), prolonged drug

delivery systems (Elston et al., 1970; Fukushima et al., 1983; Oza and Frank, 1989; Omotosho, 1990; Vaziri and Warburton, 1994), and sorbent reservoirs in drug overdosage treatment (Frankenfeld et al., 1976; Chiang et al., 1978; Moriomoto et al., 1979, 1982).

As is the case for simple emulsions, multiple emulsions are thermodynamically unstable due to the excess free energy associated with the surface of the emulsion droplets. The excess surface free energy arises as a result of the cohesive forces between the molecules of an individual liquid being greater than the adhesive forces between the liquids (Banker and Rhodes, 1979; Martin et al., 1993). On dispersion, the interfacial area of the dispersed phase liquid increases considerably compared to that of the continuous phase liquid. Consider the interfacial free energy (1.1) associated with the interface between two immiscible liquids:

$$\Delta G = \gamma \Delta A, \tag{1.1}$$

where G is the interfacial free energy, γ is the interfacial tension, and A is the total interfacial area of the dispersed phase. The increase in interfacial area results in a thermodynamically unstable system that tends to revert back to the original two-phase system to minimize interfacial area. The dispersed droplets therefore strive to come together to reduce the surface area, which can result in eventual destruction of the emulsion. In order to minimize this effect, a third component, a surfactant, is added to the system to improve its stability.

Multiple emulsions are complex systems where both water-in-oil (W/O) and oil-in-water (O/W) emulsion types exist simultaneously. In the case of water-in-oil-in-water multiple emulsions, the oil droplets have smaller water droplets within them, and the oil droplets themselves are dispersed in a continuous water phase. Oil-in-water-in-oil multiple emulsions, on the other hand, consist of tiny oil droplets entrapped within larger water droplets, which in turn are dispersed in a continuous oil phase. These systems thus differ from the familiar water-in-oil or oil-in-water simple two-phase emulsions in that they have three distinct phases (Pal, 1996). Multiple emulsions typically require two or more emulsifiers, one that is predominately hydrophobic stabilizing the primary W/O emulsion and one that is predominately hydrophilic stabilizing the secondary O/W emulsion. The hydrophobic and hydrophilic emulsifiers are added to the oil and continuous aqueous phases, respectively. The two emulsifiers may interact at the external water/oil interface and interfere with each other's stabilizing performance (Opawale and Burgess, 1998). In addition the osmotic pressure may affect the stability of W/O/W emulsions that is not observed in simple emulsions. If the osmotic pressure is higher in the internal aqueous phase, water will pass into this phase, with the internal droplets swelling until they rupture and release their contents onto the external phase. Transfer of water from the internal to external aqueous phases can cause shrinkage of the internal droplets to occur if a reverse gradient exists; this can also exert a destabilizing influence (Florence and Whitehill, 1985).

It has been demonstrated that the Laplace pressure works against the stability of simple emulsions (Davis, 1981). For water-in-oil emulsions, the addition of a small quantity of electrolyte to the disperse phase was determined to have a stabilizing effect as a consequence of counteracting the Laplace pressure effect. In W/O/W emulsions, the osmotic pressure generated by the presence of electrolytes in the inner dispersed water phase can cause swelling and ultimately bursting of the inner dispersed droplets, so the impact on multiple emulsion stability is negative. In order to balance these two effects, the concentration of electrolytes has to be high enough to counteract the Laplace pressure but sufficiently low to avoid osmotic effects.

The interfaces are the same in multiple emulsion systems as they are in simple emulsions. For example, one liter of a concentrated emulsion can contain up to $5000\,m^2$ of interface (the equivalent to a football pitch). So the interfacial area can be enormous because of the large number of droplets in the system. The large interface presents challenges and requires a quick migration of surfactants in the system to stabilize the dispersed phase(s). The structure and properties of the interface can therefore affect many aspects of the physical properties of emulsion systems. This is the main reason why interfacial characteristics are an important area of study in emulsions and especially multiple-emulsions systems. It has been shown that the stabilities of both multiple and simple emulsions are dependent on emulsifier interfacial film strength, ionic strength, and the presence of various additives. It has been experimentally proven that the interfacial film strength can be used as a means to predict emulsion stability (Burgess, 1997).

In this chapter the effects of pressure balance and interfacial rheological properties on the stability of multiple emulsions are discussed.

1.2   MULTIPLE EMULSION PRESSURE PROPERTIES

1.2.1   Osmotic Pressure

For W/O/W multiple emulsions the oil phase can be viewed as a membrane separating the inner and outer aqueous phases at the water/oil interface. The thickness of the oil membrane varies with changes in the multiple emulsion composition. Water can pass through the oily membrane from one aqueous phase to the other depending on the osmotic pressure. A higher osmotic pressure in the internal aqueous phase than in the external continuous aqueous phase causes water to pass into the inner water phase, resulting in swelling of the internal droplets before they eventually burst and release their contents. The reserve also applies: if the osmotic pressure is higher in the external aqueous phase than in the inner aqueous phase, water will transfer from the internal phase to the external aqueous phase, causing shrinkage of the internal droplets. If the osmotic difference across the oil layer is extreme, then the passage of water becomes so rapid that almost immediate rupture of the oil droplets occurs with loss of the internal droplets. When the oil layer ruptures,

the inner aqueous phase in the multiple oil droplets disappears instantaneously, mixing with the external aqueous phase and leaving simple emulsions.

The osmotic pressure effect on stability of multiple emulsions has been investigated for almost four decades. W/O/W emulsions, when given in vivo, break down rapidly at the site of injection, with the consequence that no significant delay in response to the entrapped drug is obtained compared to aqueous solutions of the drug (Collings, 1971). It was determined that the premature breakdown of the emulsions in vivo is due to unequal osmotic pressures between the internal and external aqueous phases. The osmotic pressure in the external environment (body fluids) is higher than the internal phase leading to shrinkage of the internal aqueous droplets and/or rupture of the oil layer. Collings (1971) partially solved the problem by incorporating small amounts of sodium chloride in the internal aqueous phase so that this phase was isotonic with the final external phase.

Materials other than electrolytes (e.g., proteins, sugars, and drugs) in the aqueous phase can also exert this effect (Adeyeye and Price, 1990). A variety of materials entrapped in the inner phase of multiple emulsions are found to affect osmotic pressures (Florence and Whitehill, 1982; Cuemen and Zatz, 1988; Garti and Aserin, 1996). The middle phase acts as a semipermeable membrane, and consequently osmotic effects become significant as they control multiple emulsion stability and drug release rates both in vitro and in vivo (Collings, 1971; Davis and Burbage, 1978; Matsumoto and Kohda, 1980; Florence and Whitehill, 1981).

Sodium chloride and other electrolytes added initially in the inner or outer aqueous phase of W/O/W multiple emulsions can migrate across the oil layer and get into the other aqueous phase through molecular migration (Collins, 1971; Chilamkurti and Rhodes, 1980). The migration of the electrolytes induces changes in osmotic pressure over time and consequently alters multiple emulsion stability. It has been observed that multiple emulsions stabilized by Span 83 and Tween 80 are more stable with sodium salicylate incorporated in the inner aqueous phase than with sodium chloride (Jiao et al., 2002). The difference in the stability of the multiple emulsions observed can be attributed to a faster migration of sodium chloride from the inner aqueous phase to the outer aqueous phase and a consequent more significant imbalance in the osmotic pressure compared to that with sodium salicylate.

The transport mechanism of electrolytes through the oily liquid phase has been the subject of many investigations over the past decades. Nevertheless, there remains a lack of a clear understanding as to what and how various formulation parameters of multiple emulsions affect the kinetics and extent of the migration of electrolytes across the middle phase, and thereby influence the osmotic pressure. Partition coefficient, ionization, charge density, molecular weight, and molecular mobility of electrolytes can have some impact on electrolytes' ability to cross the oil phase. The association of electrolytes with the surfactant, which may form inverted micelles in the oil phase, has also been considered (Chilamkurti and Rhodes, 1980).

1.2.2 Laplace Pressure

Laplace pressure arises from the interfacial tension of a mixture of two liquids at a curved interface when one liquid is dispersed as droplets into another liquid. The pressure varies inversely with the radius of curvature and takes the following form:

$$\Delta P = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right), \tag{1.2}$$

where γ is interfacial tension and r is particle radius. For a spherical particle such as a droplet, $r_1 = r_2$, the Laplace equation becomes

$$\Delta P = \frac{2\gamma}{r}. \tag{1.3}$$

Hence a spherical droplet having a radius r in an emulsion will exert greater pressure on the inner concave interface than on the convex side, as expressed in equation (1.3), and the larger surface tension constitutes a larger force pushing inward into the droplet. Because the relationship of ΔP and r is inversed, a smaller radius will result in a larger inward force. Therefore this relationship has important consequences for any curved surface as r becomes very small and γ relatively significant. When this relationship is applied to the context of an emulsion in which two droplets with the same surface tension are connected, the smaller droplet can be expected to experience a greater pressure, driving its collapse and pushing all of its contents into the larger droplet.

When droplet deformation occurs, the Laplace pressure of the deformed droplet will be a function of the radius along the droplet surface. In the extreme cases, as a droplet becomes elongated and cylindrically shaped, the Laplace pressure is reduced to a half that of the original spherical droplet. For multiple emulsions, the Laplace pressure exists in both the inner and multiple droplets. However, because the size of the inner droplets is much smaller, the Laplace pressure on the stability of the inner droplets is much greater than that on the multiple droplets.

The Laplace pressure in the process of emulsification is what causes an emulsion to become thermodynamically inefficient. For an emulsion to form the small, highly curved droplets, extra energy is required to overcome the large pressure that exists in the droplets.

1.2.3 Balance between Laplace Pressure and Osmotic Pressure

Consider a water droplet of radius r containing a certain amount of salt in a solvent (oil phase) in equilibrium at the water/oil flat interface. The film around this water droplet can be assumed (for simplicity) to be impermeable

to water and capable of preventing coalescence. The Laplace pressure $2\gamma/r$ of a droplet containing a salt, dispersed in the solvent, will cause shrinkage of the droplet. However, the osmotic pressure will cause swelling of the droplet, leading to a counterbalanced water diffusion. In the ideal case the osmotic pressure is given by

$$\prod_{osm} = mRT = m_o\left(\frac{r_o}{r}\right)^3 RT, \tag{1.4}$$

where m is the molar concentration of salt and m_o refers to the original droplet. The difference between the Laplace pressure and the osmotic pressure can be defined as excess pressure ΔP:

$$\Delta P = \frac{2\gamma}{r} - m_o\left(\frac{r_o}{r}\right)^3 RT. \tag{1.5}$$

The condition that must be fulfilled in order to reach the equilibrium is

$$\frac{d(\Delta P)}{dr} = -\frac{2\gamma}{r^2} + 3m_o\left(\frac{r_o}{r}\right)^3 \frac{1}{r} RT = 0. \tag{1.6}$$

In words, as r decreases, the excess pressure ΔP decreases and equilibrium is reached. Thus

$$2\gamma = 3mRT. \tag{1.7}$$

Equation (1.7) was proposed by Walstra (1996). Walstra's equation shows that an optimal salt concentration in the internal phase exists between the Laplace and osmotic pressures exerted on the inner aqueous droplets.

Stability of W/O/W multiple emulsion containing Span 80 and Tween 80 was evaluated with respect to sodium chloride and sodium salicylate concentrations in the inner water phase (Jiao and Burgess, 2002). In this study we observed that the multiple emulsion droplets deformed and there was coalescence of the inner aqueous droplets as we applied an external force (i.e., a microscopic coverslip) to multiple emulsion samples on a microscope slide. Under certain conditions (e.g., lipophilic surfactant concentration and internal phase osmotic pressure) the destabilized multiple emulsions formed unique metastable structures that had a "dimpled" appearance. The formation of these metastable structures correlated with the real time instability of the W/O/W multiple emulsions investigated. Our study revealed that emulsions with a salt concentrations closer to the optimal value calculated by using (1.7) had maximum stability.

The treatment above is only good for a simplified emulsion system where the osmotic and Laplace pressures are the major forces controlling droplet

stability. There are other factors such as viscosity that influence the dynamics of droplet growth. We take these factors into consideration using the general Navier-Stokes equation to mathematically describe droplet expansion:

$$\rho\left(\frac{\partial v}{\partial t} + (v \bullet \nabla)v\right) - \nabla p(\gamma, t) + \eta\Delta v, \qquad \text{div } v, -0, \qquad (1.8)$$

where $p(\gamma, t)$ is the total pressure at any given point on the droplet surface. The influence of any other factors can be entered into the equation by way of boundary conditions (Mikhin, Stepanow, and Byakov 2003).

1.3 INTERFACIAL RHEOLOGY AND STABILITY

1.3.1 Interfacial Film and Film Strength

Multiple emulsions require surfactants to stabilize both the internal aqueous droplets and the external multiple droplets. The added surfactants adsorb at the water/oil interfaces, reducing interfacial tension and forming an interfacial film that resists droplet coalescence following droplet contact. It has been shown that the stronger this film is, the more stable are the emulsions, and that the interfacial film plays a more crucial role than the reduction of interfacial tension in maintaining long-term emulsion stability to coalescence (Burgess, 1993). The strength of this film, which can be a monolayer, a multilayer, or a collection of small particles adsorbed at the interface, depends on the structure and conformation of surfactant or emulsifier molecules at the interface (Swarbrick, 1997). The structure and conformation can be affected by formulation variables, including surfactant or emulsifier type and concentration, other additives or levels, storage temperature, ionic strength, and pH. For the film to be an effective barrier, it must remain intact when sandwiched between two droplets. If broken, the film has the capacity to reform rapidly. So the film must possess a certain degree of surface elasticity. It has been shown that interfacial elasticity correlates well with interfacial film strength and can be used to predict the stability of multiple emulsions (Opawale and Burgess, 1997). Knowing the relationship between interfacial properties and emulsion stability enables one to rationally approach the research and development of more stable multiple emulsion systems.

The only way significant amounts of immiscible fluids can be mixed together is if the interfacial layer surrounding the dispersed droplets is occupied by an adsorbed layer of molecules that keep the droplets from coalescing. Figure 1.1 shows the importance of the interfacial layer in emulsion systems for the two main classes of surface-active molecules, surfactants and proteins, that stabilize them. Low molecular weight surfactants, lipids, and emulsifiers self-assemble at interfaces with the appropriate part of the molecule associating with the appropriate hydrophilic or hydrophobic phases. Proteins, on the other hand,
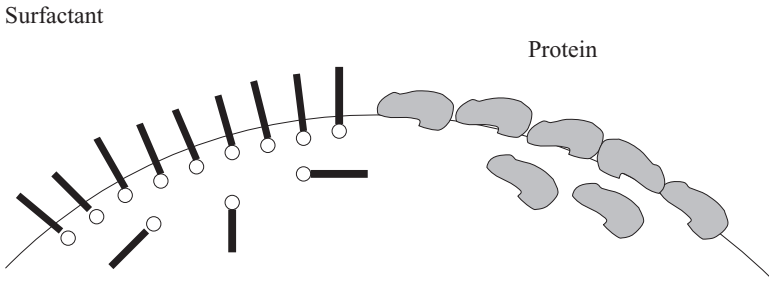
Surfactant

Protein

Figure 1.1 Two classes of surface-active materials in stabilizing emulsions: Surfactant and protein.

Surfactants

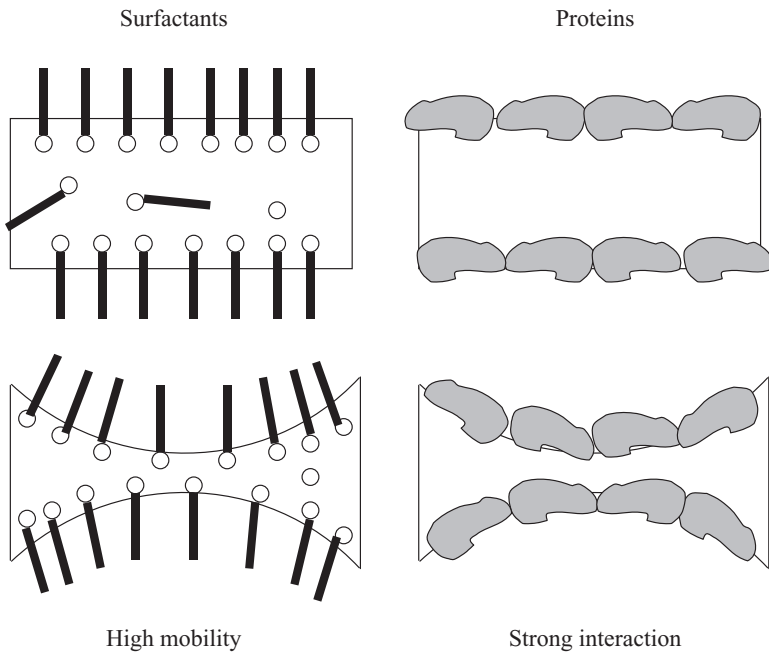Proteins

High mobility

Strong interaction

Figure 1.2 Stability mechanism for surfactants and proteins.

are much larger and more complex macromolecules. Proteins will adsorb at an interface but then proceed to unfold, exposing their hydrophobic groups to the hydrophobic phase.

Figure 1.2 shows how these two very different types of molecules stabilize emulsion systems. Surfactants rely on rapid diffusion to dissipate any disturbances to the interface. This rapid motion will drag fluid along into the inter-lamellar space between droplets, keeping them separated. This activity is known as the Gibbs-Marangoni mechanism. On the other hand, proteins

unfold, develop strong interactions with neighboring protein molecules, and effectively form a gel at the interface. The viscoelastic gel can stretch and deform to absorb deformations in the interface, and hence stabilize against coalescence. The main difference between interfaces stabilized by proteins and surfactants is the viscoelasticity of the interface. Therefore interfacial rheology is a useful probe for comparing these two types of interfaces.

1.3.2   Interfacial Tension and Rheology

The interfacial properties exhibited by emulsifier systems are interfacial rheology, tension, and charge (Burgess and Yoon, 1995; Burgess and Sahin, 1997). Interfacial rheology measures the emulsifier film viscosity and/or elasticity and hence the mechanical barrier to droplet coalescence. Interfacial tension is related to emulsion stability through the Gibbs equation (Eq. 1.1). The interfacial charge on emulsion droplets gives a direct measurement of the electrostatic barrier to coalescence. Interfacial rheology, tension, and charge have been used as predictors of emulsion stability (Burgess and Yoon, 1995; Burgess and Sahin, 1997). Cumper and Alexander (1950), Srivastava (1964), and Burgess (1998) have shown that the interfacial rheology of protein films correlates with O/W emulsion stability.

Interfacial Tension   Lowering of interfacial tension is one way in which the increased surface free energy associated with the formation of droplets can be reduced. Since surfactant molecules continuously adsorb at the interface, interfacial tension will decrease as a function of time until equilibrium is achieved. Reduction of interfacial tension by the addition of a surfactant can serve to preserve the surface area generated during the dispersion process, thus preventing phase separation. Low interfacial tension enhances the formation of smaller emulsion droplets with narrower size distributions and greater kinetic stability (Burgess and Yoon, 1995). The major requirement of a potential surfactant or emulsifier is that it readily form an interfacial film. A rapid decrease in interfacial tension indicates high interfacial activity and a tendency for fast reformation of the surfactant film after rupture. Rapid reformation of a new interfacial film results in increased resistance to droplet coalescence, and hence emulsion stability is improved (Myers, 1988).

The dynamic process of adsorption of emulsifiers and the equilibrium state of the interfacial film can be measured by the change in interfacial tension as a function of time. Dynamic interfacial tension techniques exist that measure without disturbing the interface. Various such techniques to measure interfacial tension have been reported in the literature (Addison and Hutchinson, 1949; Padday and Russel, 1960). The Wilhelmy plate technique is preferred over other techniques because the values obtained are more accurate than those obtained using other techniques such as the capillary rise or du Nouy ring methods (Padday and Russel, 1960). In the latter two methods, the long equilibration time (3–60 hours) and difficulties in accurately positioning the

ring can introduce errors that are not an issue with the Wihelmy plate method.

Interfacial Rheology   It has been reported that for long-term emulsion stability to coalescence and phase separation, the strength of the interfacial film is more important than reduction in interfacial tension (Myers, 1988; Swarbrick, 1990; Martin, 1993). Interfacial rheology is the study of the mechanical and flow properties of adsorbed layers at fluid interfaces, and it has been used to quantify film strength (Murray and Dickinson, 1996; Opawale and Burgess, 1998). Interfacial film strength characteristics can be described in terms of viscous (liquid-like) or elastic (solid-like) properties (Warburton, 1993). In an emulsion stabilized with surfactant-type emulsifiers forming monomolecular films, coalescence is opposed by the elasticity and cohesiveness of the films sandwiched between the two droplets. Multilayers confer high resistance of emulsions to coalescence, as arises from the mechanical strength of layering (Myers, 1988). For films to be efficient barriers, they must not thin out and rupture when sandwiched between the two droplets. The film must therefore possess enough elasticity to assist in preserving its integrity (Myers, 1988).

There are two main methods for measuring the interfacial rheological properties of adsorbed layers. They can be either dilational or shear methods. Figure 1.3 shows the principle underlying each method, without going into too much practical detail. Interfacial dilational rheology is determined by measuring the change in interfacial tension due to a specific change in interfacial area. This is a measure of the resistance to compression and expansion of the adsorbed layer. Interfacial shear rheology, on the other hand, can be a direct measure of the mechanical strength of the adsorbed layer. Here the interface is subject to a shear stress, and the measured strain is recorded.

When an element of area covered with soluble material is subject to surface contraction, some of the material escapes into the bulk phase and returns when the interface is expanded in interfacial dilational rheology (Murray and
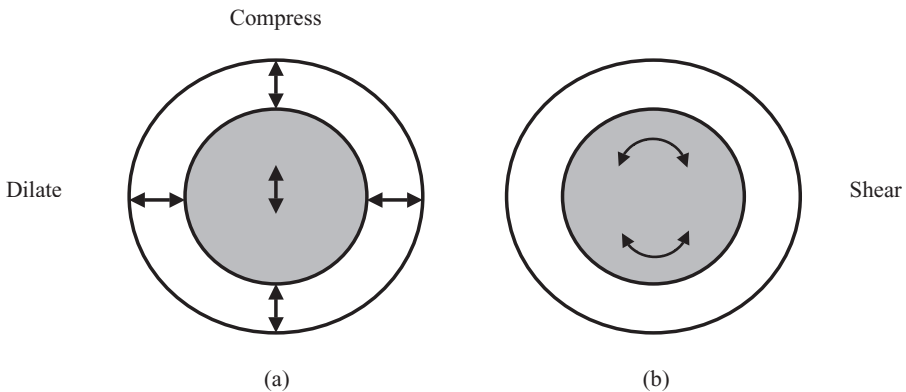

Compress

Dilate

Shear

(a)   (b)

Figure 1.3   Interfacial dilational (*a*) and interfacial shear (*b*) rheology.

Dickinson, 1996). In such experiments the interpretation of interfacial dilational rheology needs to take into account the dilation processes. However, in interfacial shear rheology, a defined interfacial area is sheared to a first-order approximation and is therefore not altered during the shearing process (Sheriff and Warburton, 1975). The interfacial pressure remains constant during the experiment and the material does not diffuse out of or into the interface as a result of rheological measurements. Consequently interfacial shear experiments are less destructive than interfacial dilational experiments, and measurements can provide information on the intramolecular and intermolecular forces acting at the interface (Warburton, 1993). The kinetics of interfacial film formation can also be studied using this technique. Interfacial shear measurements can be performed by several methods: continuous flow, creep compliance, stress relaxation, and oscillation (Warburton, 1993). It is not possible to study film kinetics, and intra- and intermolecular interactions among interfacial molecules, using interfacial dilational techniques, since the interfacial film is continuously destroyed. Using a MK2 surface oscillatory ring rheometer, which operates in the interfacial shear mode, Opawale and Burgess (1998) were able to determine the kinetics of interfacial film formation of Spans (20, 80, 83, and 85) under various conditions (different temperatures, Span concentrations, salts, and macromolecules such as bovine serum albumin and cholesterol).

1.3.3 Multiple Emulsions' Stability and Interfacial Properties

As shown in Figure 1.2, emulsions can be stabilized by surfactants or emulsifiers employing the Gibbs-Marangoni mechanism, which has a very low interfacial viscoelastic modulus, or by protein-like molecules, which employ a viscoelastic mechanism with a naturally high viscoelastic modulus. Both mechanisms result in stable systems individually, but in many commercial emulsions there is often a mixture of these two molecule types.

Figure 1.4 shows an interface stabilized by a mixture of protein and surfactant type of molecules. The surfactants disrupt the strong interactions developed between neighboring protein molecules, effectively weakening the interface. Because the surfactants rely on rapid surface migration, they are constrained by the presence of protein molecules still at the interface. If the protein component is still in the form of a two-dimensional network, effectively caging the surfactant molecules, it can seriously hamper their motion. The net effect is reduced stabilization of each component, and hence the emulsion is reduced in stability.

In principle, it should then be possible to predict the stability of an emulsion system from the interfacial rheology of the continuous phase. Figure 1.5 shows the relative stability to coalescence of an emulsion system stabilized by a protein (beta-lactoglobulin) with increased concentrations of non-ionic surfactant (Tween 20). In this case the presence of surfactants has entirely destabilized the protein emulsion.
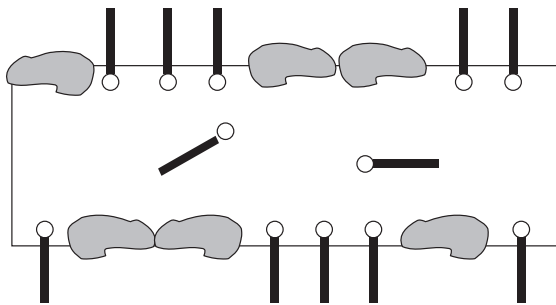
Weak interactions and reduced mobility

Figure 1.4   Mixed protein and surfactant interfaces: Weak protein interactions and restricted diffusion of surfactants result in reduced stability and probable film rupture.
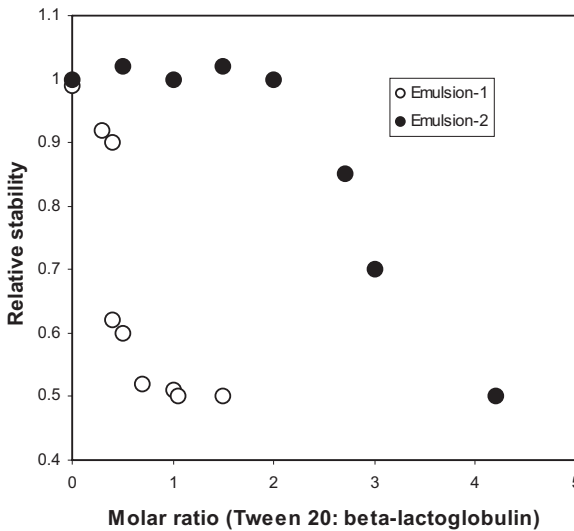

Figure 1.5   Coalescence stability of protein-stabilized emulsions as a function of surfactant (Tween 20) concentration.

1.3.4   Determination of Interfacial Properties

As was mentioned earlier, there are two basic methods of measuring interfacial rheology: dilational and shear (Murray and Dickinson, 1996). The practical and theoretical aspects underlying these measuring methods are briefly discussed here.

Interfacial Dilational Rheology   Dilational rheology, as the name suggests, is a method that deals with the expansion and compression of the interface. Simply put, it is a mechanical system that is constructed to allow the interface to be expanded and contracted, usually in a sinusoidal manner, while the interfacial tension is simultaneously monitored. The first such method used a standard Langmuir trough, as shown in Figure 1.6. Barriers normal to the surface are used to gradually compress or expand the interface to control the surface concentration of insoluble monolayers. A small modification to this method allows the barriers to be oscillated sinusoidally, producing small changes in the surface area.

Assume that there is no exchange of surfactant occurs between the surface and the bulk, the compression/expansion cycle will cause a change in the surface tension. As the surface is compressed, the effective surface concentration increases, and the interfacial tension will go down. Conversely, expanding the surface will result in an increase in the surface tension. The relationship between surface area and surface tension is shown in Figure 1.7.

The surface dilational modulus ($|E|$) is given as

$$|E| = A \cdot \frac{d\gamma}{dA}. \tag{1.9}$$

The surface dilational modulus is then split into the elastic (E') and viscous (E'') components. If the surface is purely elastic, then the phase lag (θ) will be zero; if it is viscous, then $\theta = 90$. In practice, the behavior is usually intermediate between the two extremes, and the two components can be calculated as follows:
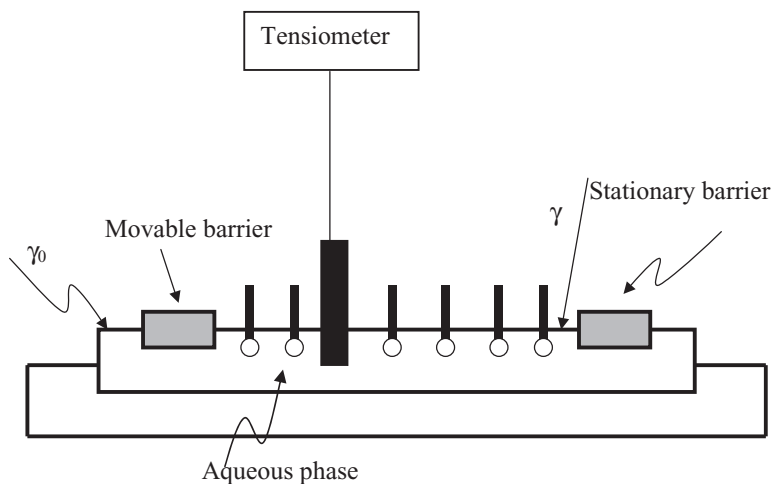

Figure 1.6   Use of a Langmuir trough fitted with oscillating barriers to change the surface area A while simultaneously monitoring surface tension.
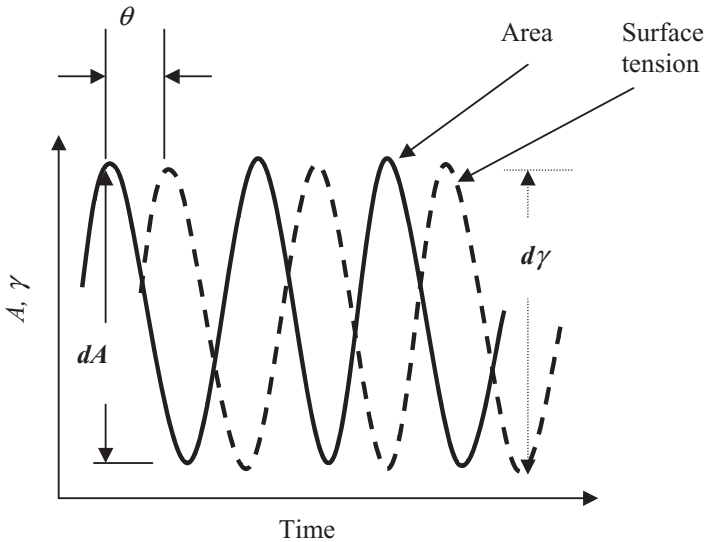
Figure 1.7   Time-dependent relationship between area and surface tension during a typical dilational rheology experiment.
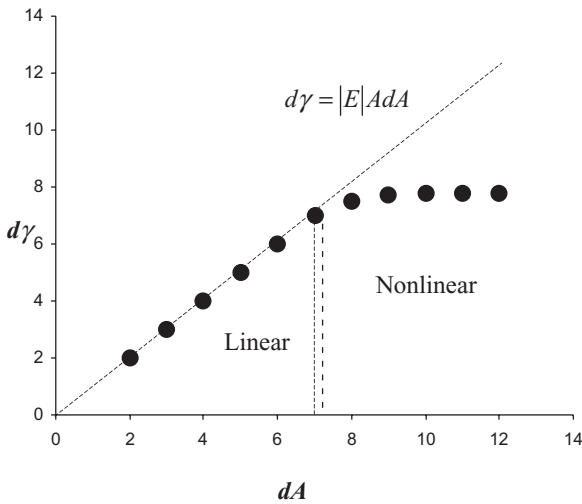

Figure 1.8   Relationship between $d\gamma$ and dA, showing how $d\gamma$ becomes nonlinear as dA is increased and the surface is stretched beyond its elastic limit.

$$E' = |E|\cos\theta, \quad E'' = |E|\sin\theta. \tag{1.10}$$

Care must be taken to ensure that the surface is not overcompressed, or the interfacial layer may collapse. Figure 1.8 shows the relationship between $d\gamma$ and dA in a typical experiment. The experiments should ideally be conducted
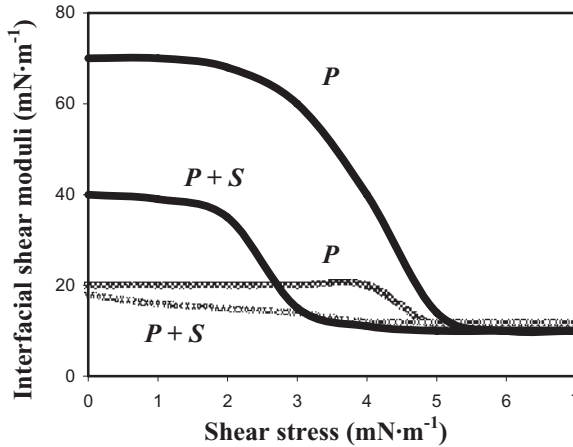
Figure 1.9   Interfacial shear moduli (elastic = solid lines; viscous = dotted lines) for protein alone (*P*) and protein + surfactant (*P* + *S*) at the oil/water interface.

in the linear region, but the length of the linear region does give information about the resistance of the surface to compression and collapse, the same as the stress dependent data shown in Figure 1.9.

A dilational method that has attracted much attention over recent years is the pendant drop method. This method has proved useful for oil/water interfacial rheology. The principle is exactly the same as for standard surface dilational rheology. The interfacial tension is calculated by measuring the size and shape of a liquid drop suspended from a capillary in a less dense fluid. The interfacial area is changed by increasing or decreasing the size of the drop by controlling the liquid flow through the capillary. Changes in the interfacial area and interfacial dilational modules can be calculated. This technique is useful for small sample volumes, for it avoids the hydrodynamic problems encountered when trying to expand/compress the oil/water interface.

A limitation of the dilational method is that it is an indirect method of measurement. The rheological information is inferred from interfacial tension values. The interfacial tension can change through adsorption and desorption effects that are stimulated by the expansion and compression of the interface. For example, for a freely soluble surfactant at high concentrations, there will be a rapid rate of exchange between the surface and the bulk, so at low dilation frequencies, lower than the exchange rate, no changes in surface tension will be detected. At lower concentration, with a much lower exchange rate, changes in surface tension will be measured, but these will be dependent on the exchange rate of the surfactant, not the surface rheological properties: The way to solve this problem is to measure at high frequencies using the surface capillary wave technique. Figure 1.10 shows a schematic of the experimental setup. Capillary waves on the surface of a solution can be induced by thermal or mechanical agitation at high frequencies. The presence of a wave on a surface corresponds to an increase in surface area, the shape of the wave is
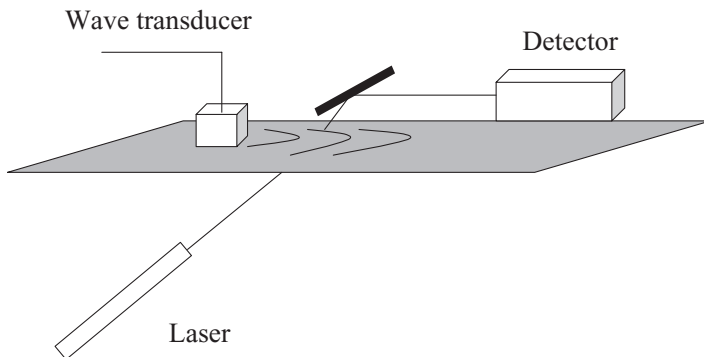
Figure 1.10   Schematic setup for capillary wave-type experiment. The wave transducer excites surface waves. The laser diffraction and detector measure damping of the waves.
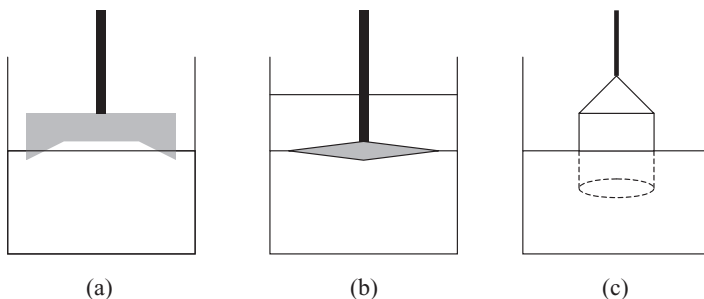

Figure 1.11   Typical geometries for measuring interfacial shear rheology: (*a*) Knife edge for air/water interface; (*b*) bicone for oil/water interface; (*c*) Du Nouy ring for sensitive measurements.

monitored by laser diffraction, and the amplitude/damping of the wave as it propagates along the surface is determined by the elastic and viscous moduli of the surface of the solution. The measurement is difficult to do, and the errors are quite large. Nevertheless, the high-frequency regime required for surfactant systems can in this way be accessed.

Interfacial Shear Rheology   In contrast to the dilational technique, the surface shear methods are direct determinations of the mechanical properties of an interface. The simplest approach is a two-dimensional adaptation of standard three-dimensional viscoelastic measurements performed on a standard rheometer. The only difference is the sensitivity and the geometry. Figure 1.11 shows the geometries commonly used for oil-water interfaces.

In interfacial shear rheology, shear stress is applied as a tangential force (F) acting along the interface. Shear stress can be calculated using the equation below,

$$p_{xy} = Ge_{xy}, \tag{1.11}$$

where p_{xy} is the interfacial shear stress. The Du Nouy ring, commonly used for measuring interfacial tension, can be specifically designed to measure the surface shear viscoelasticity through a method developed by Sherriff and Warburton. The light construction of this geometry makes it particulary sensitive to interfaces with very low rheological properties.

The simplest approach is to apply a standard shear rate, that is, to rotate the geometry at constant speed and measure the induced stress. The geometry is normally held by a torsion wire of known torsion strength, and the rotation between the top and the bottom of the wire allows the stress to be calculated. An variation on this approach is to use the canal viscometer approach. An interface is held between two concentrically circular, rigid walls, and the floor of the vessel is rotated to impart motion of the fluid below the interface. The transmission of motion to the interface from the bulk is measured by following the motion of small Teflon particles at the interface. Although this is a time-consuming measurement, the rheological properties of the bulk fluid can easily be accounted for.

However sensitive the technique, continuous rotation will result in disruption of structures created at the interface. A better approach is to use an oscillatory motion, which, if small enough, should not break down any structures formed at the interface. An oscillating stress with known amplitude is applied, and the resultant strain is measured. The stress and strain relationships are shown in Figure 1.12.

The total viscoelastic modulus G^* is given as

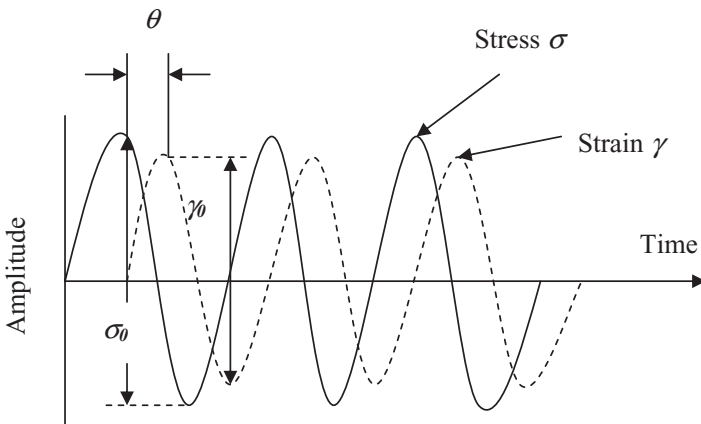$$G^* = \frac{\sigma_0}{\gamma_0}, \tag{1.12}$$

Figure 1.12 Stress–strain relationship for a typical oscillatory surface shear viscoelasticity measurement.

where σ and γ are the amplitudes of the stress and the strain, respectively (γ should not be confused with the surface tension). The stresses and strains are the effective two-dimensional equivalents of the three-dimensional standard viscosity measurements. So the stress here is the applied force per unit distance, and the strain is the distance moved relative to the gap between the geometry and the outer vessel. Similar to the dilational method, if the phase lag is 0 and 90°, the $G*$ is either totally elastic or viscous, respectively. The elastic (G') and viscous (G'') moduli can be calculated as follows:

$$G' = G* \cos\theta, \quad G'' = G* \sin\theta \tag{1.13}$$

The Sherriff and Warburton is a little more complex. A schematic diagram of the apparatus simplifies the complex electronics involved. Basically a galvanometer is fed with a sinusoidal input voltage to oscillate the ring, imparting a known stress to the interface; then a proximity probe is used to measure the strain. The electronics exploit mechanical resonance so that the sensitivity of the interface can be maximized. The mechanical or rheological properties of the interface affect the resonance of the ring as the electronic feedback system keeps the whole system in resonance. The values of the feedback signals are used to calculate the viscous and elastic components of the interfacial viscoelasticity. The light weight nature of this setup allows assessment of very fragile interfaces. The frequency is also not just limited to the resonant frequency; the feedback loops can be used to shift the measurement frequency over a wide range of values.

In summary, measurement of interfacial rheology can take one of two approaches, either dilational or shear. The choice of approach will depend on its suitability to particular applications. The most accurate and reproducible results tend to come from methods that utilize small, reversible applied stresses and strains, thus minimizing any disruption or damage to the interfacial layer.

1.4 CONCLUSIONS

Numerous applications of multiple emulsions in various fields have been reported. More applications need to be realized if multiple emulsions stability is to be fully understood and approaches to stabilize multiple emulsions fully rationalized. The stability of multiple emulsions is influenced by numerous formulation and process variables. As demonstrated in this chapter, long-term multiple emulsion stability is dependent on the osmotic and Laplace pressures of the inner droplets as well as on the pressure balance between them described by the Walstra equation. Stability also equally, in some cases even more, depends on the strength of the interfacial film formed on the interface of droplets of multiple emulsions. This property can be characterized by interfacial rheology.

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