

CHAPTER I

INTRODUCTION

1.1 Background

Emulsions are formed from two immiscible liquids: one constitutes the droplets, which are dispersed in the other liquid which is referred to as the continuous phase. The dispersed phase is sometimes referred to as the internal (disperse) phase, and the continuous phase as the external phase. Two types of emulsion are readily distinguished in principle, depending upon which kind of liquid forms the continuous phase (Figure 1.1): oil-in-water (O/W) for oil droplets dispersed in water and water-in-oil (W/O) for water droplets dispersed in oil (Schramm, 1992).

In some applications, this dispersion must remain perfectly stable and homogeneous over a certain period of time. In many cases, the emulsion may be used as a concentrate and the required period of stability depends to a large extent on the application. However, in many other applications dilution the concentrated emulsion is required. In other words, the concentrated emulsion is dispersed in another liquid and the system may be further homogenized by mechanical means. In some cases, dilution of the concentrated emulsion may be spontaneous. This dilution procedure is used in many medical and pharmaceutical preparations, cosmetics, petroleum products, road construction and maintenance techniques, and agriculture (Chappat, 1994).

The relative volume of the dispersed phase, i.e. the volume fractions and the average size of the droplets, the viscosity of each phase, the nature and the concentration of emulsifier play an important role in emulsion rheological properties and stabilities (Barnes, 1994).

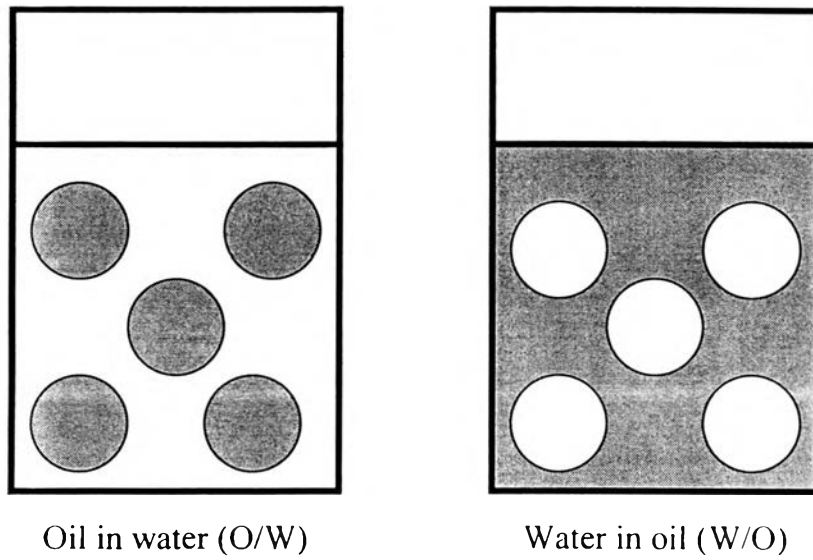


Figure 1.1 Schematic representation of both O/W and W/O emulsions.

1.2 General Aspects

1.2.1 Appearance

Not all emulsions exhibit the classical "milky opaqueness" with which they are usually associated. A tremendous range of appearances is possible, depending upon the droplet sizes and the difference in refractive indices between the phases. A emulsion can be transparent if either the refractive index of each phase is the same, or alternatively if the dispersed phase is made up of droplets that are sufficiently small compared with the wavelength of the illuminating light. Thus an O/W microemulsion of even a crude oil in water may be transparent. If the droplets are of the order of 1- μm diameter, a dilute O/W emulsion will take on a somewhat milky-blue cast: if the droplets are very much larger, the oil phase will become quite distinguishable and apparent. Physically the nature of the simple emulsion types can be determined by methods such as texture, mixing, dyeing, conductance, inversion and fluorescence (Schramm, 1992).

1.2.2 Rheology of Liquid Crystalline Phase

The hexagonal phase is usually a gel which flows uniaxially. Its apparent viscosity is generally about 10 times higher than the lamellar phase, and it shows large time dependent changes (Goldemberg, 1979).

The lamellar phase resembles a viscous liquid. The lipid layers move easily over each other, and this confers lubricant rheology on this phase (Abegg & Boiteux, 1973).

If sufficient oil phase is added or if the surfactant concentration is sufficiently high, a reverse hexagonal phase will form. In a reverse hexagonal phase, water forms a discontinuous layer and oil forms a continuous phase and the water cylinders are packed in a hexagonal array. The reversed

hexagonal phase is usually a gel with a similar viscosity to the regular hexagonal phase (Jones, 1987).

In between each of the liquid crystalline phases one usually encounters cubic phases, or viscous isotropic phases. The structure of these phases is not unequivocal. There are at least two types of cubic phase structures: a normal water continuous phase and a reversed phase in which the alkyl chains are continuous. Viscous isotropic phases show an extremely rigid gel rheology in which there is no easy flow in any direction because the aggregates repel each other in a three-dimensional network (Francois, 1985).

The effect of head group size and phase volume of oil on the structure of micellar and liquid crystal aggregates can be seen very clearly by looking at the temperature dependence of nonionic surfactant emulsions. As temperature is increased, the head group hydration decreases and consequently the head groups are able to approach each other more closely and the spherical aggregates eventually become lamellar aggregates at the cloud point of the surfactant. Above the cloud point of the surfactant, inverse phases are formed, and they separate from the water phase (Lochhead, 1985).

The viscosities of these liquid crystalline compositions are extremely high, and the lamellar phase has pseudoplastic rheology. This phase is the most important of all liquid crystalline phases for stability of dispersed systems in conditioners. Liquid crystal structures can be identified by examination in a polarizing microscope. One structure, the cubic phase, is isotropic and therefore non-birefringent. This phase cannot be seen in a polarizing microscope, but evidence of its existence can be assumed from its rubbery-gel rheology (Rober, 1992).

1.2.3 Stability

Stable emulsions are often required during industrial processing. On the microscopic scale, the reasons that the droplets remain dispersed fall into two broad categories: (1) physical barriers to coalescence and (2) electrical repulsion between droplets. An example of a physical barrier is the presence of finely divided solids at the oil-water interface. Of primary concern, however, is the consideration of the electrical force because its influence is significant at relatively longer distances. Electrical repulsive forces arise when the double layers surrounding charged droplets overlap, and thus the "thickness" of the double layer in relation to the size of the particle is an important parameter (Isaacs & Chow, 1990).

A consequence of a small droplet size and presence of an interfacial film on the droplets in emulsions is that quite stable dispersions of these species can be made. That is, the suspended droplets do not settle out or float rapidly, and the droplets do not coalesce quickly. Some use of the term stability has already been made without definition (Shaw, 1985).

Colloidal species can come together in very different ways. In the definition of emulsion stability, stability is considered against three different processes; creaming (sedimentation), aggregation, and coalescence. Creaming is the opposite of sedimentation and results from a density difference between the two liquid phases. In aggregation, two or more droplets clump together, touching only at certain points, and with virtually no change in total surface area. Aggregation is sometimes referred to as flocculation or coagulation. In coalescence, two or more droplets fuse together to form a single larger unit with a reduced total surface area (James, 1979).

In aggregation the species retain their identity but lose their kinetic independence because the aggregate moves as a single unit. Aggregation of droplets may lead to coalescence and the formation of larger

droplets until the phases become separated. In coalescence, on the other hand, the original species lose their identity and become part of a new species. Kinetic stability can thus have different meanings. An emulsion can be kinetically stable with respect to coalescence but unstable with respect to aggregation. Alternatively, a system could be kinetically stable with respect to aggregation but unstable with respect to sedimentation or flotation (Schramm, 1992).

Once aggregation has taken place in an emulsion, there remains the question of stability to coalescence. Usually emulsion made by mixing together two pure liquids are not very stable to increase the stability, an additional component is usually needed, and it forms a film around the dispersed droplets to provide a barrier to both aggregation and coalescence. Although numerous agents and mechanisms are effective, the additional component is frequently a surfactant. Stability to coalescence involves the mechanical properties of the interfacial films (Miller, 1985).

Considering the stabilities of both aggregation and coalescence, the factors favoring emulsion stability can be summarized as follows. The low interfacial free energy makes it easier to maintain large interfacial area and mechanically strong film acts as a barrier to coalescence and may be enhanced by adsorption of fine solids or of close-packed surfactant molecules. Electric double-layer repulsion acts to prevent collision and aggregation. Small volume of dispersed phase reduces the frequency of collisions and aggregation. Higher volumes are possible (for close-packed spheres the dispersed-phase volume fraction would be 0.74), but in practice the fraction can even be higher. If the droplets are electrostatically or sterically interacting, the droplet size become small. High viscosity slows the rates of creaming and coalescence (Cavallo, 1990).

1.3 Surfactant and Surfactant Mixtures

The term "surfactant" is abbreviation of surface active agent; examples of surfactant include soaps and detergents. Surfactants are among the most versatile products in the chemical industry. Surfactants are molecules that consist of hydrophilic and hydrophobic moieties: referred to as heads and tails, respectively (Fig. 1.2). The hydrophilic portion of the surfactant is made of a water soluble species as well as the hydrophobic portion of the surfactant is made of organic derivative groups, usually with the carbon numbers greater than eight. Most surfactants have the tail portion consisting of a nonpolar chain (which can be classified into three major groups: hydrocarbons, fluorocarbons and silicone based polymers). This structure is known as amphiphilic and surfactants are considered to be amphiphilic. Depending on the nature of the hydrophilic head group, the surfactant can be classified into four main classes: cationic, anionic, nonionic and zwitterionic (Rosen, 1989).

Surfactants do exactly what their name implies; they accumulate at surfaces, thereby altering the properties of solutions and interfaces which they contact. In fact, the surfactant monomers adsorb at the gas-liquid interface so that the hydrophilic portion of the molecules extend into the liquid phase and hydrophobic tails extend into the gaseous phase. As can be expected, the adsorption of surfactant at the gas-liquid interface significantly affects the physical properties of the aqueous interface. Surfactant is capable of decreasing the surface energy of a liquid at relatively low concentration (Adamson, 1990).

Another significant phenomena evidenced by surfactant molecules (in this case in aqueous solution) is the formation of micelles. The hydrophobic portion of the surfactant is repelled by water while the hydrophilic portion of the molecule attracts to water. The result is that singular surfactant molecules align together in globular, quite often form spherical, and colloids with the

hydrophilic portion on the exterior and the hydrophobic portion on the interior. The resulting formation is called a micelle. The center core of the micelle has properties of a pseudo-oil phase; micelles are thus referred to as dispersed oil drops. Figure 1.3 shows schematically a surfactant association structures. It is likely that surfactant molecules may form spherical, cylindrical, hexagonal, lamellar and reversed micelles structures in solution by adjusting the proper physicochemical conditions such as pH, temperature and the presence of various electrolytes. If oil is present in the system, these association structures can solubilize the oil, and can produce a clear, thermodynamically stable system. Depending on the nature of the oil phase and the oil-to-water ratio, the oil can be a continuous or disperse phase in the system (Prud'homme & Khan, 1996).

The adsorption behavior of mixtures of soluble surfactant at interfaces and their consequent effect on interfacial properties vary significantly over a wide range of relative concentrations. At surfactant concentration below the mixed cmc, the interface is only sparsely converted by surfactant molecules and a significant amount of "bulk-like" water remains at the interface. As the concentration increases, surface tension decreases substantially and a "saturated" interfacial monolayer of adsorbed mixed surfactant molecules forms. Here, the average area per molecule at the interface becomes constant. (Sharma *et al.* 1991).

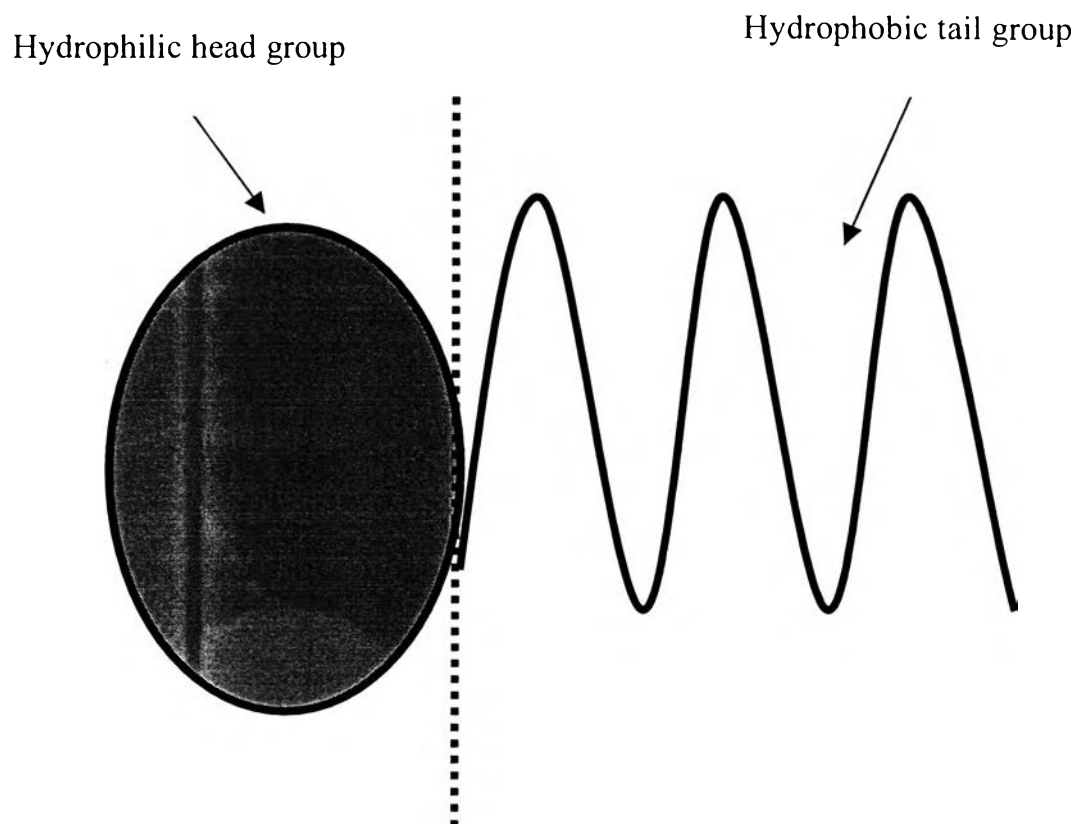


Figure 1.2 Schematic of surfactant molecule (monomer) (Rosen, 1989).

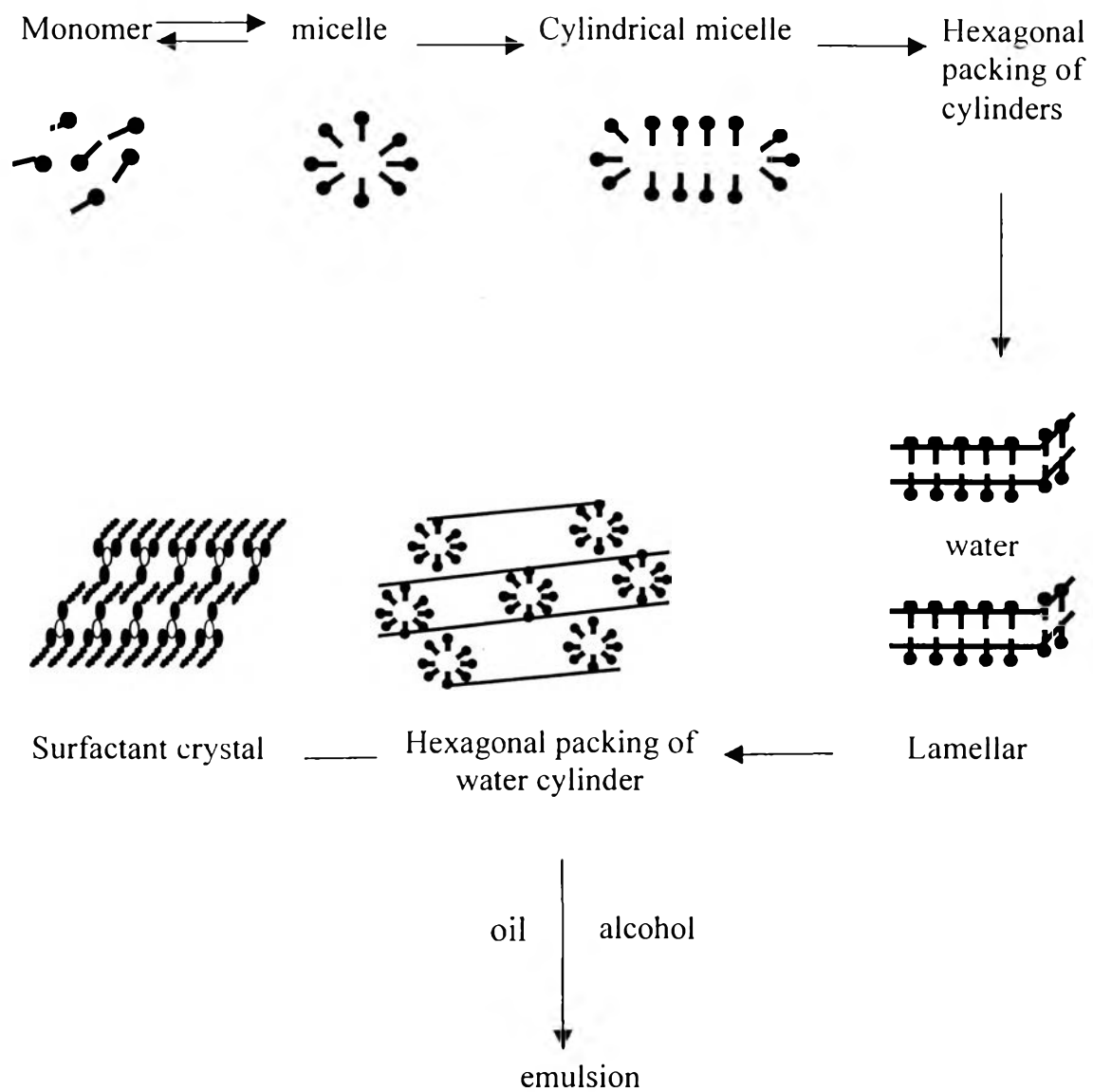


Figure 1.3 A schematic illustration of surfactant association structures (Scharma *et al.* 1991).

1.4 Fatty Alcohol and Fatty Acid

Fatty alcohols are important raw materials for surfactants, emollients (special refatting agents) and emulsifier. Pure fatty alcohols, mainly cetyl alcohol ($C_{16}H_{33}OH$) and stearyl alcohol ($C_{18}H_{35}OH$), are also used as consistency regulators and co-emulsifiers in, for examples, creams lotions and hair rinses. The so-called natural fatty alcohols are obtained by hydration of fatty acid methyl esters. Similarly, linear primary alcohol can be obtained from the Ziegler process. The branched types obtained from oxo-synthesis are important as raw material feedstock, but are not used as alcohols per se. Mixtures of cetyl and stearyl alcohols combined with hydrophilic emulsifiers are known as the 'emulsifying waxes'. In such combinations the fatty alcohols are self-emulsifying. Common combinations are cetearyl alcohol plus sodium cetearyl sulfate, cetearyl alcohol plus PEG-1000 monocetyl ether, cetearyl alcohol plus alkyl trimethyl ammonium bromide. The fatty alcohol gives texture and body to the formulation and acts as consistency regulator (William, 1995).

Fatty acids, like the fatty alcohols, are important raw materials for cosmetic ingredients such as surfactants, emulsifiers and emollients. Fatty acids are obtained by saponification of naturally derived triglycerides. As such, they are seldom used in emulsions. They act as consistency regulators but tend to crystallize in the formulation. Fatty acids especially steric acids, are mainly used in the form of soaps. As pH increases, they become truly anionic and act as oil-in-water (O/W) emulsifiers, forming a group of so-called stearate creams. Commercially available steric acids are often mixtures of C_{16} and C_{18} fatty acids, mainly 1:1. A special application of the fatty acids is their use in alcohol stick formulations, where stearic acid is dissolved in ethanol and then neutralized with sodium hydroxide (William, 1995).