

CHAPTER II

HISTORICAL BACKGROUND

2.1 Microemulsion

An emulsion is a mixture of two immiscible liquids, the dispersed phase, existing as discrete droplets dispersed throughout the other, the continuous phase (Rose and Rose, 1961). An emulsion is defined as a substantially permanent heterogeneous liquid mixture of two or more liquids which do not normally dissolve in each other but are held in suspension one in the other. In some systems, the interfacial tension drops to near-zero values, easily on the order of 10^{-3} to 10^{-4} mN/m. The ultralow interfacial tension allows spontaneous or nearly spontaneous emulsification to very small droplet sizes, microemulsion.

Although microemulsions have been produced commercially since the 1930s, significant understanding of their nature has been acquired only during the past decade or so, mainly as a result of the intense interest generated in them. There are many uses of microemulsions, such as displacing of the residual petroleum in the capillaries of the rock, and the exceptionally high solubility of oxygen in fluorocarbons microemulsion as artificial blood (Mathis, 1984). As a result, there have been a number of recent books and review articles devoted to microemulsions (Prince, 1977).

2.1.1 The structure of microemulsion

Microemulsion droplets are on the order of 10-100 nm. Microemulsions are thermodynamically stable. Most microemulsions contain a four or five components namely, water, oil, surfactant, cosurfactant and salt. The most common microstructure is that of spherical droplets dispersed in a continuous phase following the Mitchell and Ninham's assumptions.

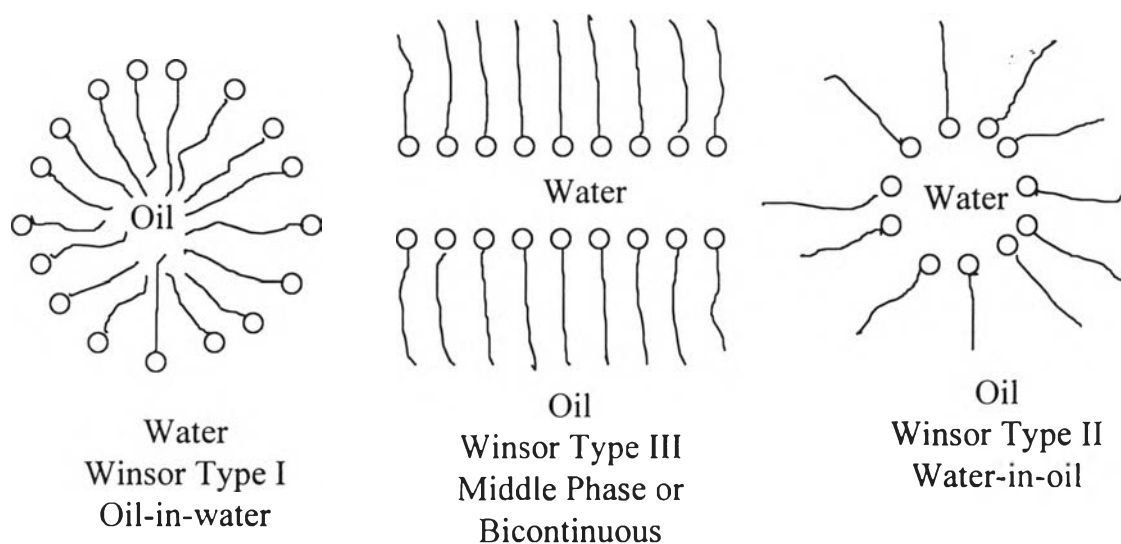


Figure 2.1 Structures of Winsor type I, II, and III microemulsions.

2.1.2 Type of the microemulsion

Winsor had earlier observed that a microemulsion phase can be in equilibrium with either organic or aqueous bulk phase or both. These were latter referred to as Winsor type I, II and III systems. A Winsor type I system is an oil-in-water (o/w) microemulsion with oil droplets dispersed in aqueous media. The Winsor type III system is also known as a bicontinuous or middle phase. Bicontinuous is referred to the system which there is a surfactant-rich microemulsion system in which large sheets of surfactant monolayers are formed with both water and oil in excess. This is observed in going from

Winsor type I to Winsor type II microemulsion system. The Winsor type II system is a water-in-oil (w/o) microemulsion with water droplets dispersed in a continuous organic media.

The structure of various types of microemulsions are illustrated in Figure 2.1. The Winsor type I can be changed into Winsor type II or type III by adding more salt. On the other hand, the Winsor type II also can be shifted to Winsor type III or I by adding water. Figure 2.2 shows the phase transition among three types of microemulsions. Compared to convex film surfactant in an oil-in-water Winsor type I microemulsion, the surfactant film is concave for a water-in-oil Winsor type II microemulsion. For a Winsor type III microemulsion, the average value of the film curvature is around zero (Prince, 1977).

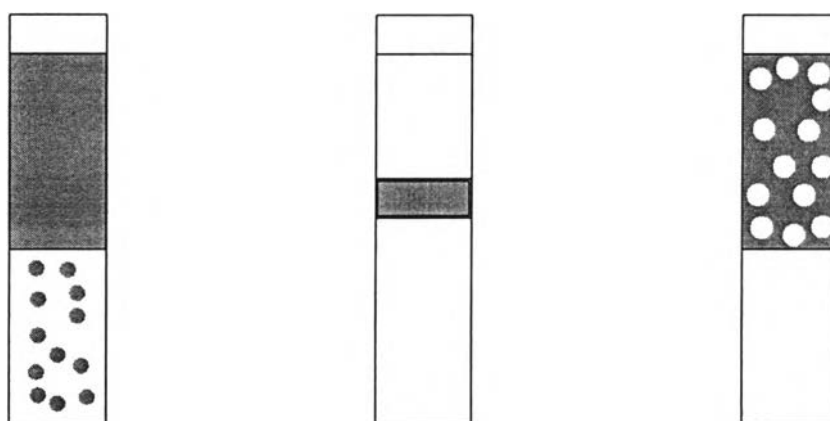


Figure 2.2 Phase behavior among three types of microemulsion.

2.1.3 NaDEHP microemulsion

Di-2-ethylhexyl phosphate (NaDEHP) is an anionic surfactant. NaDEHP has the same carbon tail as that of sodium bis (2-ethylhexyl) sulfosuccinate (AOT), however, the NaDEHP hydrophilic head is smaller than

that of AOT. AOT is widely used in commercial application and theoretical research, and the phase behavior of AOT system has been extensively examined.

The NaDEHP structure is as shown in Figure 2.3. Recently many studies concentrated on the droplet size and the phase transition of NaDEHP microemulsions. The main components of these microemulsions were the NaDEHP, water and a variety of organic compounds.

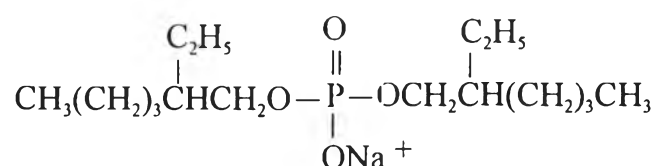


Figure 2.3 Molecular structure of the NaDEHP.

2.2 Emulsion polymerization

In 1932, both Harkins and McBain, (Billmeyer Jr., 1984) independently, observed that polymer particles form monomer of low water solubility in the absence of an emulsifier, and that the formation of particles does not necessarily require the presence of monomer droplets. They observed the size of the polymer particles to be much smaller than that of the droplets and thus concluded that the locus of polymerization must be in the droplets. Fikentscher (1937) noted that even in the presence of micellar emulsifier, the “aqueous phase,” not the monomer droplet, was the probable locus of polymerization. The quantitative work of Heller and Kevens from 1943 to 1945 clearly showed the relationship between the surfactant or the emulsifier concentration and the

number of particles formed both above and below the critical micellization concentration.

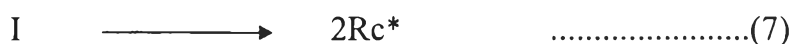
Harkins (1947) published a series of quantitative studies on both styrene and isoprene, both in the presence and absence of micelles. As noted above, the early work was limited to monomers of very low water solubility. Work in the mid-1940s on monomers, such as methyl methacrylate, which were more water soluble, raised doubts about assumptions that micelles were the exclusive initial locus of polymerization. Baxendale and co-workers (1946) published a definitive study showing that methyl methacrylate (MMA) polymerized, in the presence or absence of soap, via a homogeneous nucleation process in which soap micelles played no role (Rose and Rose, 1961).

Because of the importance of synthetic rubber to economy and way of life, the bulk of the work reported in the early years was in terms of highly water insoluble monomers, such as styrene and butadiene, and therefore work, and theories on heterogeneous or micellar polymerization prevailed in the literature. Following the initial period, reports about homogeneous nucleation began to appear in much greater number. However, the complexities of the chemistry and exceptions to the rule of theory also increased.

Emulsion polymerization is a major factor in the manufacture and formation of products used in many raw material and application areas. Among of the major examples are such diverse products as paints, coatings, floor polishes, adhesives, textile finishes, carpet and textile backings, rubber goods, automotive and aircraft tires, and others. An understanding of emulsion polymerization and the subsequent behavior of the dispersion that results is necessary in order to design processes. In many ways the most critical

ingredient, in the emulsion polymerization process, is the surfactant, or soap, both in the polymer initiation and growth steps and in the subsequent stabilization of the emulsion and properties throughout storage, and formulation.

The initiation step in emulsion polymerization is generally believed to occur in the aqueous phase; the initiator decomposes, either thermally or via a redox process (an one-electron transfer reaction), to a free radical.



The following step has been proposed to occur in either of two general ways; (a) The radicals enter a monomer-swollen emulsifier micelle where polymerization of monomer takes place, to form a monomer-swollen polymer particle. (b) The radicals initiate monomer polymerization in the aqueous phase, forming an oligomeric radical. The oligomeric radical precipitates when it grows long enough to exceed its solubility in the aqueous phase, thus forming a stable primary particle or coagulating with a previously formed latex particle.

In the first instance, the surfactant supplies a micelle in which monomer dissolves, and to which the initiator radical migrates to start the actual polymerization. The second mechanism represents another role that the surfactant plays, that of stabilizing the growing oligomer via adsorption. In either case, that first polymer molecule results in the formation of a polymer particle, which then continues to absorb monomer and to serve as a locus for further polymerization.

Ingredients for emulsion polymerization

The traditional emulsion polymerization system initially consists of four components: water, monomer, surfactant and initiator.

1) Water: Water is normally used as the dispersing medium in emulsion polymerization. The aqueous phase provides an excellent heat sink for the exothermic polymerization reaction, while it provides a low-viscosity product even at high conversion of monomer to polymer. Water acts as the solvent for the stabilizing surfactant and initiator.

2) Monomer: Emulsion or microemulsion polymerization is an example of a free radical mechanism. In order of polymerization to occur, the monomer involved require a degree of unsaturation. There are a large number of possible monomer structures. The most common structure is of the form $\text{CH}_2=\text{CX}_1\text{X}_2$, where X_1 and X_2 may be of a variety of substituents. Such species are called vinyl monomers, for example;

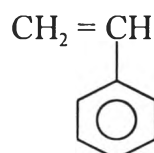


Figure 2.4 Molecular structure of vinyl monomer (styrene).

3) Surfactant: Formation of stable monomer emulsion or microemulsion in water can be difficult in the absence of any surface active agent. High-speed dispersions can produce an emulsion, but often this is unstable and two distinct layers eventuate. The large interfacial area between the liquids (monomer and water) implies that the emulsion has a high free energy compared with the separated phases. The addition of a soap, or surface active agent (surfactant), can lower the interfacial tension, thus forming a more stable emulsion.

4) Initiator: The initiator system in emulsion polymerization must generate a free radical to commence the polymerization process. The initiator is usually water-soluble, although monomer-soluble initiators can be used for specific purposes. There are a variety of initiator types which decompose either by a thermal and/or a redox mechanism. The most common types are those containing peroxy linkages, such as hydrogen peroxide or potassium persulfate. However, some monomers can become initiators when excited to a high energy state either photochemically or thermally.