

CHAPTER II

HISTORICAL REVIEW

2.1 Nature of Surfactants

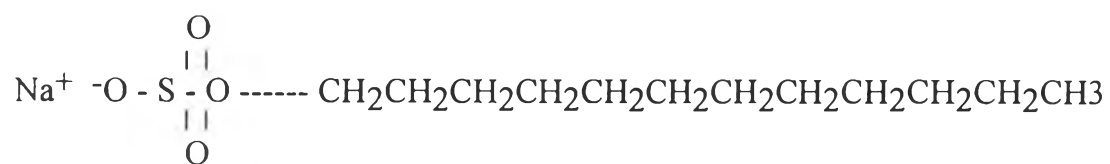
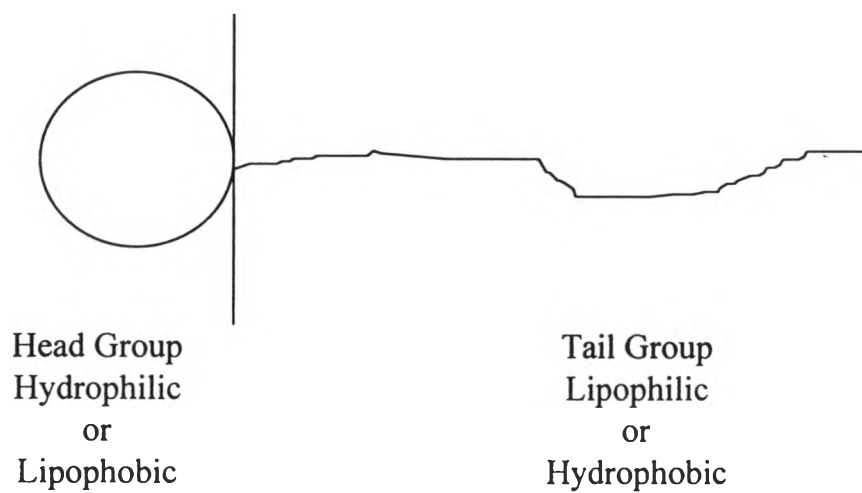
A 'surfactant' is a contraction of the term surface active agent. Surfactant is a substance that has the property of adsorbing onto the surfaces or interface of the system. Surfactants have a characteristic molecular structure consisting of a hydrophilic group and a hydrophobic group as shown in Figure 2.1. 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. Depending on the nature of the hydrophilic head group, the surfactants can be classified into four main classes which are cationic, anionic, nonionic and zwitterionic (Rosen, 1992).

At sufficiently high concentration in solution, surfactant molecules will nucleate to form aggregates called micelles (see in Figure 2.2). The concentration at which this occurs is characteristic of each surfactant and is called critical micelle concentration (CMC).

2.2 Microemulsion

It is well known that two immiscible liquids (e.g., oil and water) can form a macroscopically clear, homogeneous mixture upon addition of a third liquid (dispersing agent) which is miscible with both liquids (Leung, Hou, and Shah, 1988). When surface-active molecules (e.g., surfactants or detergents) are used

as the dispersing agent, the single-phase region may consist of microdomains of dispersed phase and complex association structure



Sodium Dodecyl Sulfate (SDS)

Figure 2.1 Schematic of surfactant molecule (Rosen, 1992).

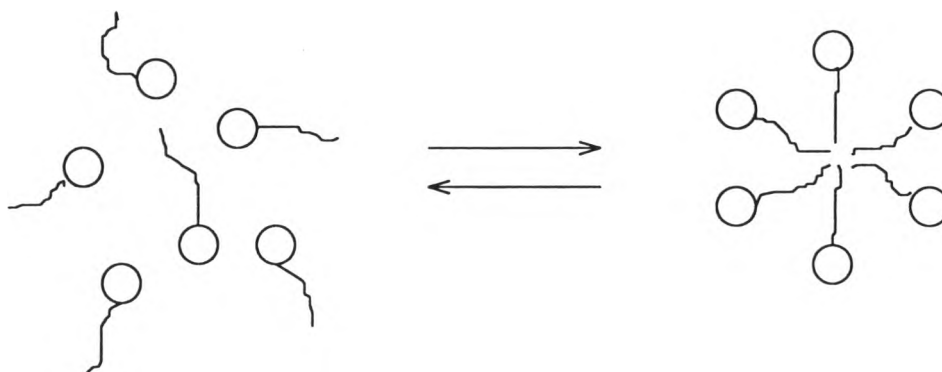


Figure 2.2 Schematic diagram of micellization.

of molecules. Such a single-phase region is often referred to as a ‘microemulsion’. Figure 2.3 represents a schematic ternary-phase diagram for microemulsions composed of microdomain with various possible association structure.

A microemulsion was described as a transparent or translucent system formed spontaneously upon mixing oil and water with a relatively large amount of ionic surfactant together with a cosurfactant (e.g., an alcohol of medium chain length (C₄ to C₇)). The system contained dispersion of very small oil-in-water (O/W) or water-in-oil (W/O) droplets with radii on the order of 100 to 1000 Å. Figure 2.4 represents schematically these two basic microemulsion structure. Microemulsion possesses special characteristics of relatively large interfacial area, ultralow interfacial tension, and large solubilization capacity as compared to many other colloidal systems.

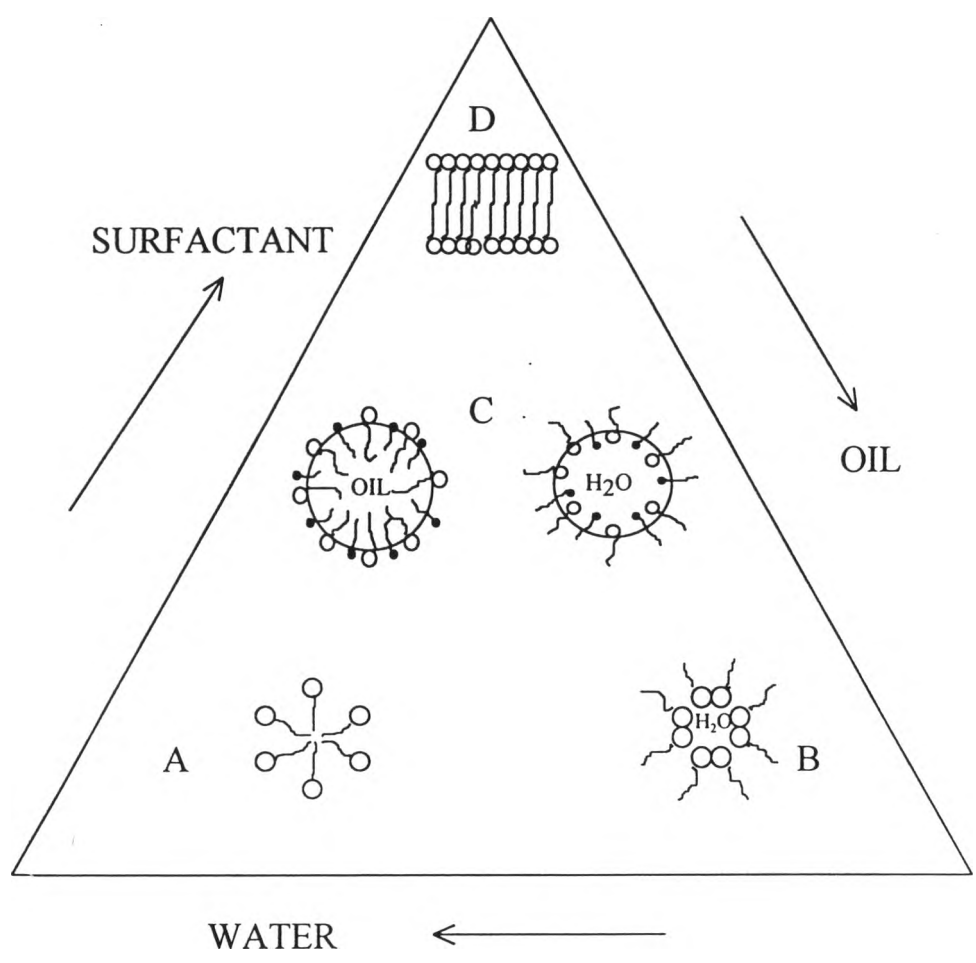


Figure 2.3 Schematic ternary-phase diagram of an oil-water-surfactant microemulsion system consisting of various associated microstructures. A, Normal micelles or O/W microemulsions; B, reverse micelles or W/O microemulsions; C, concentrated microemulsion domain; D, liquid-crystal or gel phase (Leung, et al., 1988).

In general, the formation of microemulsions involves a combination of three to five components: oil, water, surfactant, cosurfactant, and salt. The chemical structure of surfactant, cosurfactant, and oil strongly influences a microemulsion phase diagram (Malcolmson, Lawrence, 1995).

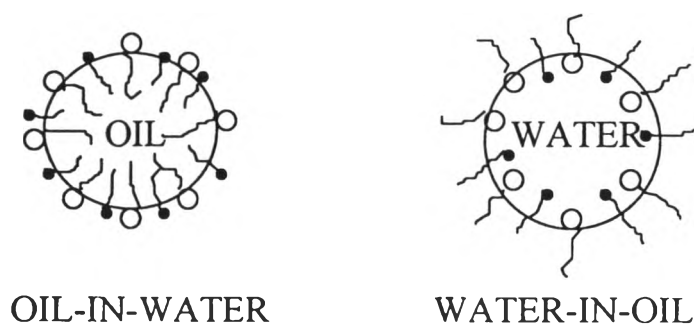


Figure 2.4 Schematic diagram for oil-in-water (o/w) and water-in-oil (w/o) microemulsion structures (the smaller molecules represent cosurfactant).

The most studied phase equilibria of microemulsions are probably known as the Winsor-type microemulsion (Winsor, 1954). The study is normally carried out by using a salinity scan, as shown in Figure 2.5. One can prepare such a system by mixing equal volumes of brine and oil with a proper surfactant and cosurfactant. By increasing the salinity, one can simply visualize a progressive change in the phase diagram and behavior.

In a low-salinity region, the Winsor's type I system represents a lower-phase O/W microemulsions in equilibrium with excess oil. In a high-salinity

region, the Winsor's type II system consists of an upper-phase W/O microemulsion in equilibrium with excess brine. It is clear that both Winsor's type I and Winsor's type II phase equilibria are driven by the bending stress of interfacial film.

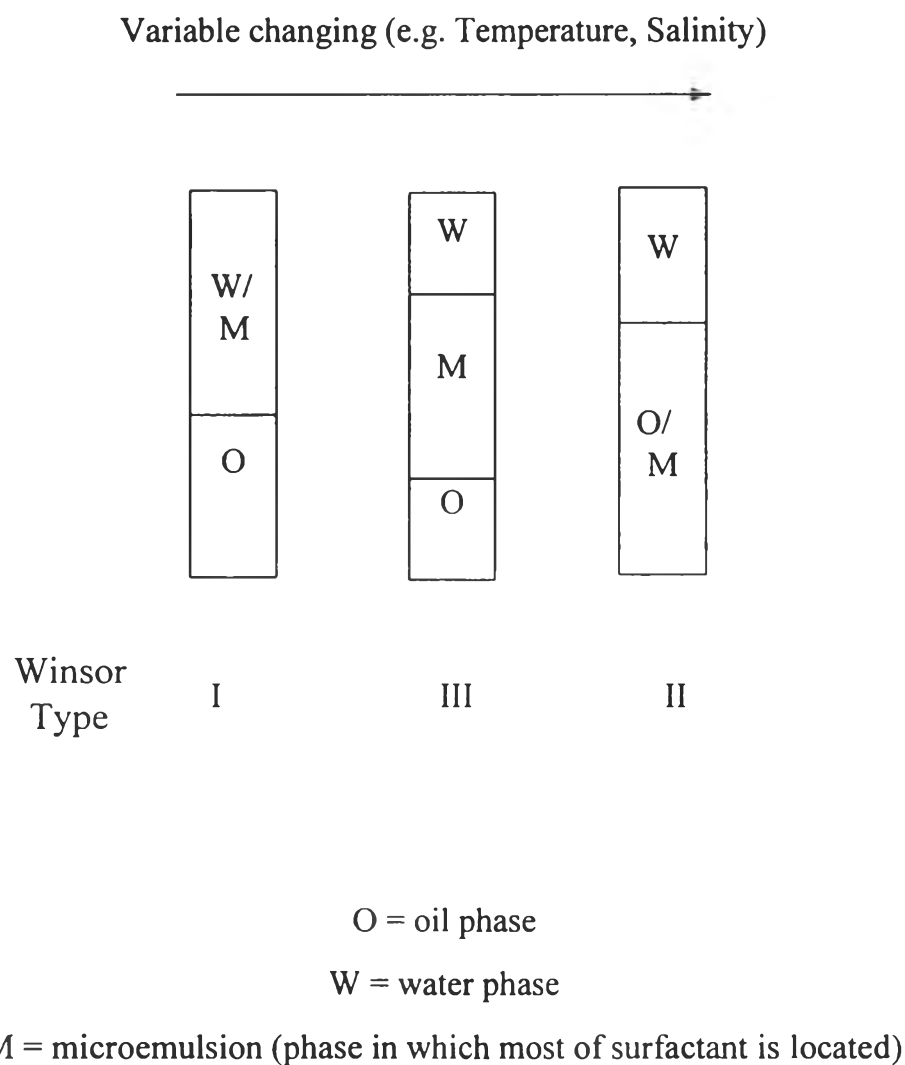


Figure 2.5 Effect of relevant variable on phase behavior of microemulsion.

In an intermediate-salinity region, the Winsor's type III system is composed of a middle-phase microemulsion in equilibrium with both excess oil and brine. The optimal salinity is defined as the salinity at which equal volumes of brine and oil are solubilized in the middle-phase microemulsion. The structure of this middle-phase microemulsion has not been determined conclusively. Based on the data of ultracentrifugation, there are proposed that the middle phase is a O/W microemulsion near the boundary close to the low-salinity region, and a W/O microemulsion near the boundary close to the high-salinity region. Thus, a middle-phase microemulsion at the optimal salinity would represent a continuous phase inversion from O/W to W/O structure. A bicontinuous structure has been widely examined both experimentally and theoretically. It is the attractive force between microemulsion droplets that leads to a transition of both Winsor's type I and Winsor's type II to Winsor's type III microemulsions. The transition from Winsor's type I to Winsor's type III microemulsions has been attributed to the coacervation of normal micelles (Shah, 1981), while the transition from Winsor's type II to Winsor's type III microemulsion is associated with the percolation phenomena of W/O droplets. Both these transitions have also been associated with critical phenomena. Thus the phase equilibria of Winsor's type III systems are governed by both attractive force between droplets and interfacial bending stress.

A part from the conventional salinity scan, the transition of a Winsor-type system from O/W to W/O structure can also be produced by changing any of the following variables in a systematic way:

1. Increasing alkyl chain length or molecular weight of surfactant.
2. Increasing surfactant concentration.
3. Increasing aromaticity of oil.
4. Decreasing the chain length of oil.
5. Increasing alcohol chain length (more oil soluble) or concentration.

6. Increasing temperature of nonionic surfactant system or decreasing temperature of ionic surfactant system.
7. Decreasing the number of hydrophilic group (e.g., ethylene oxide) of nonionic surfactants.

In the oil industry, microemulsion was applied in oil recovery to remove the resident oil in a porous medium. Many variables were considered to have a significant effect upon recovery. These include the surfactant concentration, interfacial tension, salinity, oil-to-water ratio, optimal surfactant structure, and cosurfactant concentration.

2.3 Principle of Froth Flotation

Froth flotation is widely used in several separation processes, including selective separation of minerals, removing ink from paper fibers in paper recycling, and removal of emulsified oil from water. In flotation, air is sparged into the solution and the particles or droplets to be removed adhere to the rising air bubbles and are concentrated in the foam or froth at the top of the flotation cell. The skimmed foam contain the removed phase in high concentration (after the foam is broken) compared to the feed solution. Adding such as surfactants are used to affect the surface properties of the dispersed phase in solution to promote attachment to the air bubbles. Surfactants also promote foaming or act as froth stabilizers. The use of froth flotation for the removal of insoluble organic contaminants from water is illustrated in Figure 2.6. The organic-containing solution is introduced together with surfactant into the flotation column batchwise or continuously and air is sparged into the solution. The surfactant tends to strongly adsorb at the air/water interface with the hydrophobic or tail groups in the air and the hydrophilic or head groups in the

water. A close-packed monolayer of surfactant is formed at the bubble surface under conditions normally employed. The hydrophobic region formed by the tail groups of the surfactant is compatible for dissolved organic solutes which tend to co-adsorb at the bubble surface. Polar regions of the solute molecule can interact with the surfactant head group, affecting solute adsorption at the air-water interface. For example, we have shown that dissolved tert-butyl phenol can be effectively removed from water by either anionic or cationic surfactants (Wumgrattanasopon, Scamehorn, Chavadej, Saiwan, and Harwell, 1996).

The experimental of flotation of dispersed or emulsified oil droplet is complete with surfactant adsorption at the oil-water and at the air-water interface affecting interfacial tensions, droplet and bubble size contact angles, interfacial viscosity, and many other properties which affect flotation, and of course foam stability.

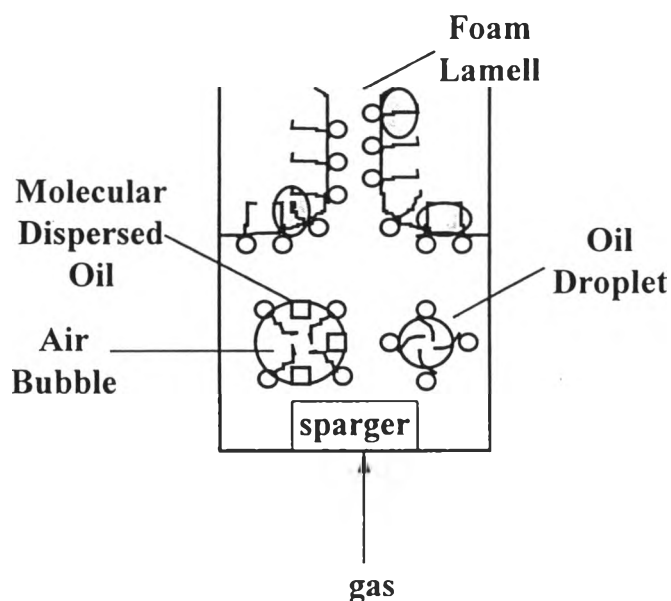


Figure 2.6 Schematic of the foam flotation process.

2.4 Chlorobenzene as a Hazardous Substance

Chlorobenzene and its derivatives are halogen substituted aromatics. Although they are classified as hazardous substances, they are widely used in several industry. They can damage the tissue of human lunge and life. They have more opportunity to contaminate in the waste water. Therefore, they should be removed from the wastes before the wastes were discharged to the environment or reused in the process.