CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 SURFACTANT

The term of "surfactant" is a abbreviation of surface active agents; examples of surfactants include soaps and detergents. Surfactants are among the most versatile products of the chemical industry. Surfactants are molecules that consist of hydrophilic and hydrophobic moieties: referred to as heads and tails, respectively (see 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, usually with the carbon numbers greater than eight. Most surfactants have the tail portion consisting of a long 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 amphiphiles. Depending on the nature of the hydrophilic head group, the surfactants can be classified into four main classes (Rosen, 1989): cationic, anionic, nonionic, zwitterionic.

Surfactants do exactly what their name implies; they accumulate
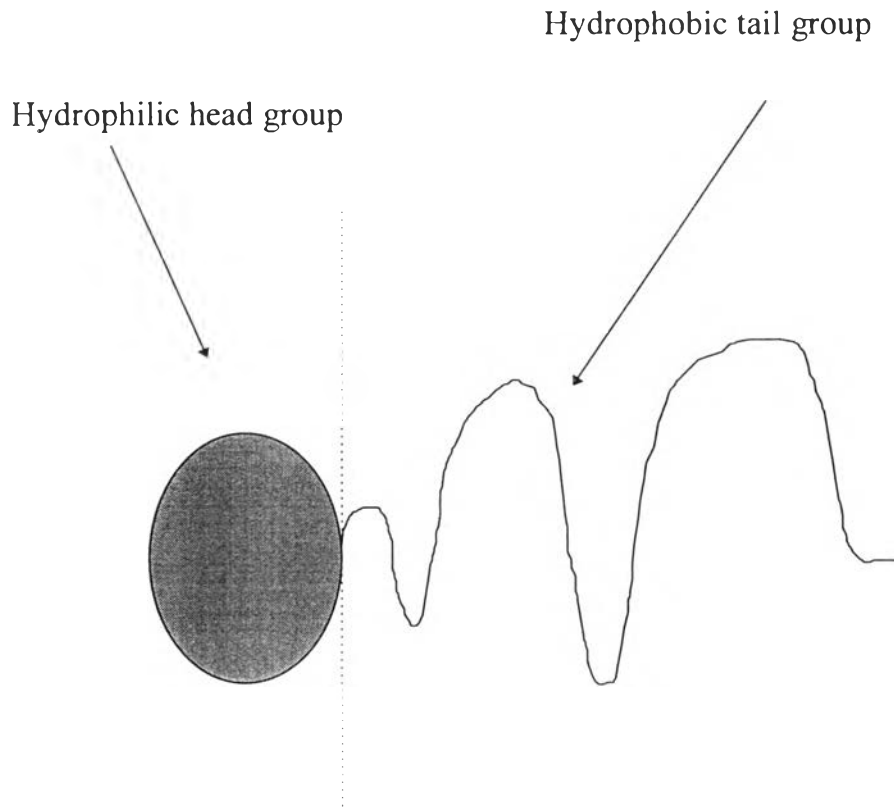
Hydrophobic tail group

Hydrophilic head group

Figure 2.1 Schematic of surfactant molecule (monomer)
(Rosen, 1989).

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 surfactants 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, 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 2.2 shows schematically a surfactant solution containing dissolved monomeric surfactant, a surfactant micelle, and surfactants adsorbed at the air-water interface. Figure 2.3 illustrates the formation of various association structures with increasing surfactant concentration. It is likely that surfactant molecules may form spherical, cylindrical, hexagonal , lamelar and reversed micelle 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
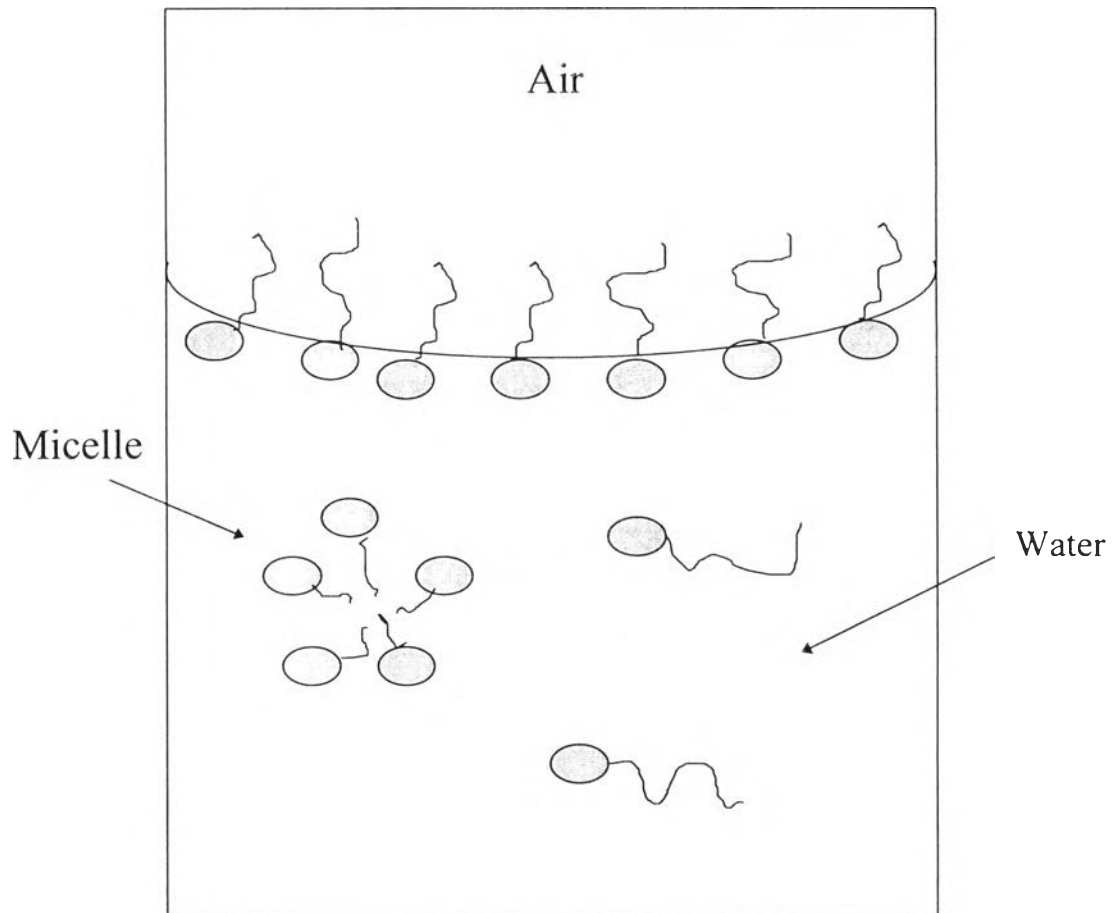
Figure 2.2   Schematic diagram of an ionic surfactant solution showing monomeric surfactant in solution and adsorbed at the air/solution interface and a micellar aggregate (Prud'homme and Khan, 1996).
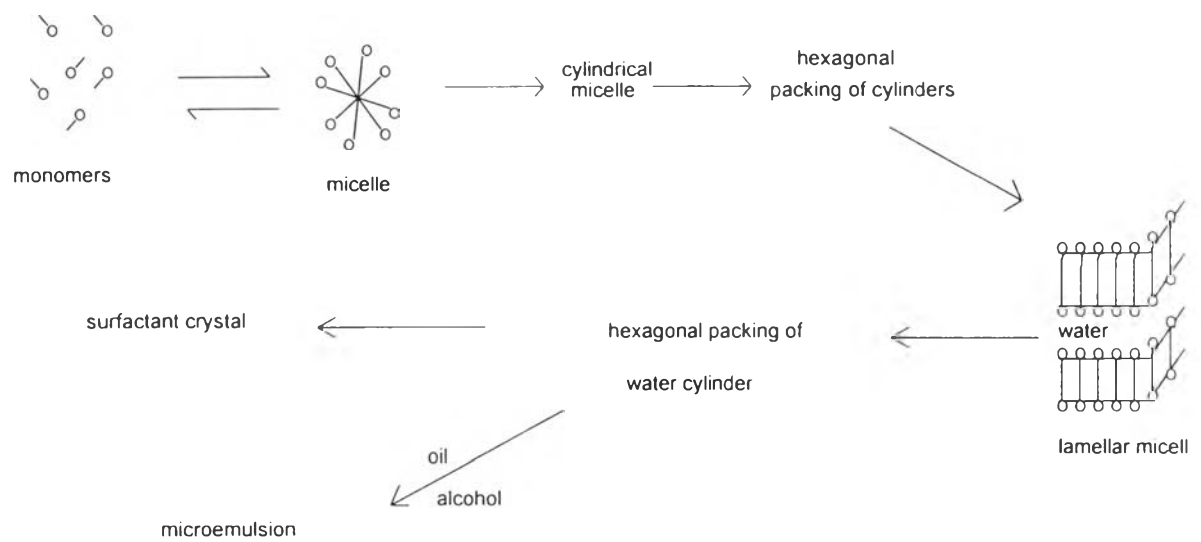
Figure 2.3   A Schematic illustration of surfactant association structures
(Sharma et al., 1991).

in the system (Sharma et al., 1991).

2.2 MICROEMULSION

The term of microemulsion was introduced to the scientific literature by Schulman (1959). It has been described optically isotropic transparent oil and water dispersions containing about equal volumes of oil and water and a combination of surface-active agents. However, 1943 is the year generally given as the "birth date" for microemulsion, since Hoar and Schulman (1943) then identified these transparent water-in-oil dispersions as a new type of colloidal dispersion, which they called the oleopathic hydromicelle. The physical and chemical properties of these systems were studied during the following years. It is interesting that in 1955 the systems were called both micelle-containing solutions (Tosch, Jones, and Adamson, 1959). Meantime, where as Shinoda and Kunieda referred this condition as "swollen micelle" (Prince, 1977). Finally, the term microemulsion became an identifier in the Chemical Abstract data base in 1968.

Microemulsion is defined to be clear thermodynamically stable dispersions of water, immiscible oil and a surfactant which adsorb on a monolayer at the interface between the two solvents. Microemulsion is a stable translucent micelle solution that may contain electrolytes and one or more amphiphilic compounds (Winsor, 1968; Barakat et al., 1983; Puerto and Reed, 1983; Bor-Jier Shiau et al., 1994). The criterion of thermodynamic stability accounts for many of the properties which make microemulsion of practical interest. They are formed spontaneously when the various components are brought together in the proper temperature range, their

infinite stability under shear. However, while the microemulsion is formed spontaneously as they correspond to the state of minimum free energy of a single-phase solution, the emulsions with micro droplets require an energy input (mechanical and /or heat) to form. As Overbeek et al. (1978) described it is composed of small droplets (diameter 5-50 nm) of a liquid dispersed in another liquid by virtue of the presence of a fairly large concentration of suitable surfactants and the microemulsion represents a transition between lyophilic and lyophobic colloids. Ninham (1984) described the most of the microemulsion region is occupied by the bicontinuous phase in which the oil and water apparently interpenetrate in a complicated and highly irregular structure. Figure 2.4 gives an indication of the relative sizes of the surfactant head groups, tails groups, and the oil/water phases of microemulsion. Several systems that show the above three phase behavior with pure single surfactant, either nonionic (Sjoblom et. al.,1987) or ionic (Bink et a.,1989) have been reported. In the case of ionic surfactants, the phase changes are brought about by increasing the electrolyte concentration, whereas the nonionic surfactants, the same sequence of phases is produced by raising temperature (Hunter, 1989). An alternative method for moving a surfactant system through the same sequence of phase is to use a cosurfactant that is often an alcohol.

From Winsor's intermicellar equilibrium concept (see Figure 2.5), spherical micelles having oil cores and dispersed in water are called an S_1-phase, or water-external phase. The inverse of this is the oil-external, or S_2-phase. An intermediate lamellar structure, which may be a gel or liquid crystal, is termed the G-phase. Any of these structures can be equilibrium with the others when they separately constitute immisicible phases. To denote this situation one writes, for example, $(S_2 + G)$, which mean two immiscible phases in equilibrium, on composed of water containing spherical micelles
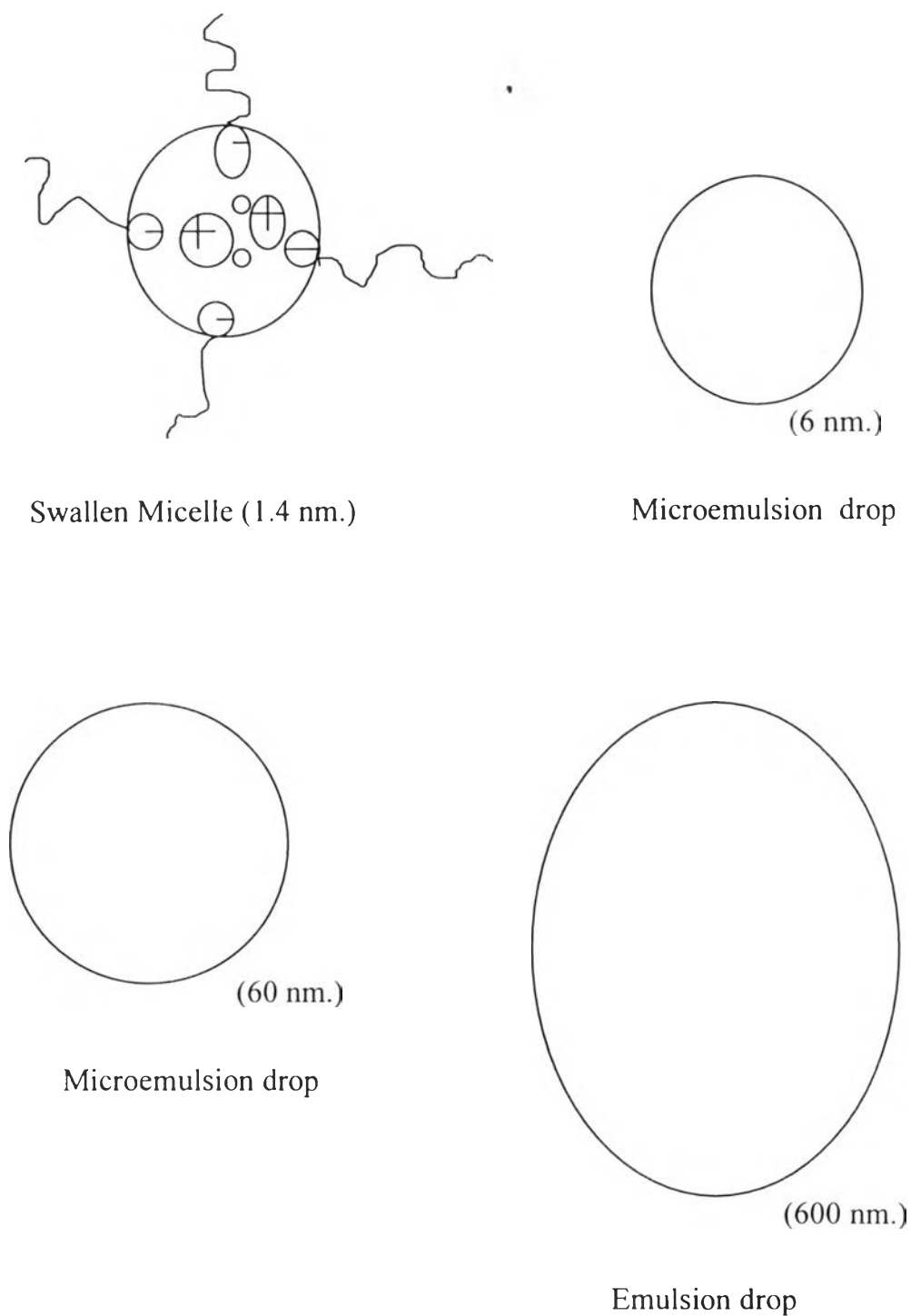
Swallen Micelle (1.4 nm.)

(6 nm.)

Microemulsion drop

(60 nm.)

Microemulsion drop

(600 nm.)

Emulsion drop

Figure 2.4   Relative size of the surfactant moiety and its head group and luophilic tail, compared to the size the disperse phase water droplet. The dimensions are diameters (After Overbeek, 1978).
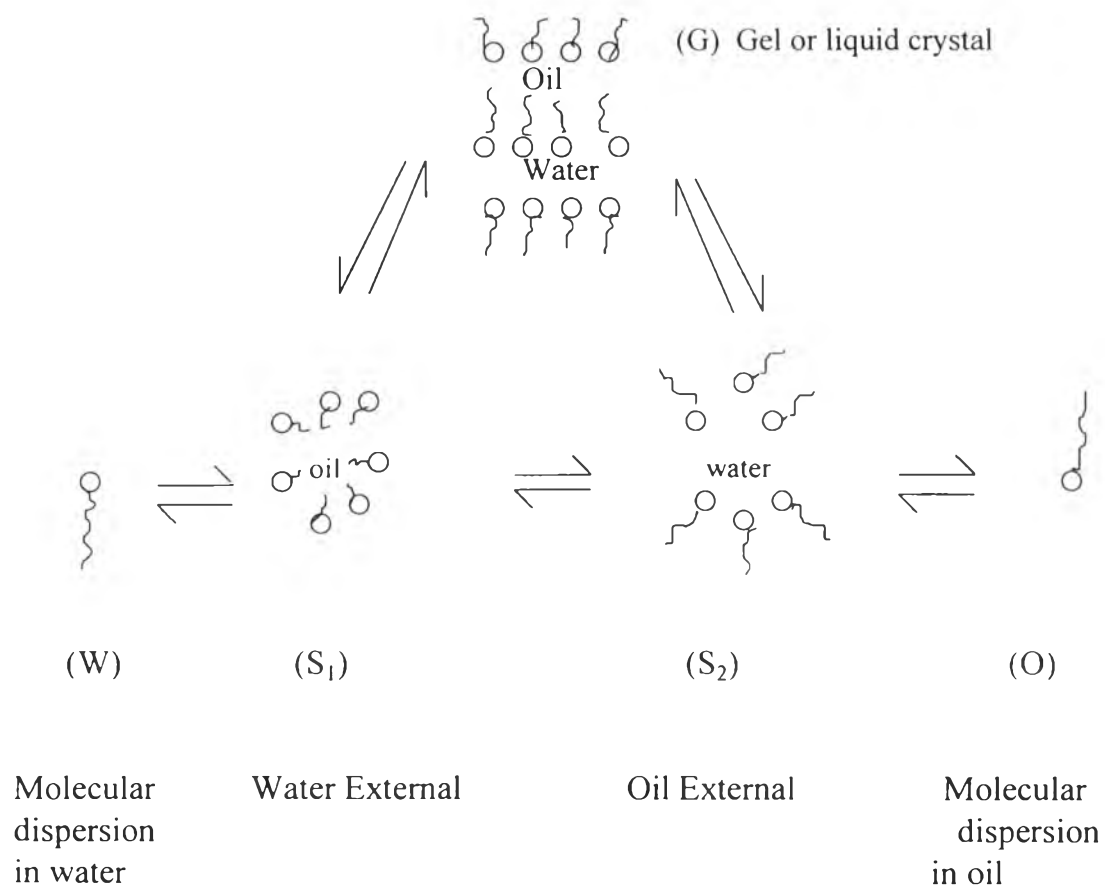
Figure 2.5 Schematic Winsor's concept of intermicellar Equilibrium.
(Healy et al., 1974).

dispersed in oil and the other composed of lamellar micelles with no identifiable external phase. In addition, there arise the situations that within a single phase, S_1 and G or S_2 and G can coexist. There are micelle structures other than those included here. It is immediately evident that a large variety of phases can be expected to exist in equilibrium. For example, $O + S_1$ is Winsor's type I, $S_2 + W$ is type II, and $W + (S_1 + S_2) + O$ is type III (Healy et al., 1974).

In the oil industry, microemulsion was applied in oil recovery to remove the resident oil in a porous medium (Healy et al., 1974; Healy et al., 1975; Healy et al., 1977). 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 FROTH FLOTATION

Adsorptive bubble separation is a process where a species is adsorbed at an interface between a dispersed phase (bubbles) and continuous phase. The dispersed phase with the adsorbed substance is subsequently collected. This definition encompasses two main processes. One of these is foam separation, which includes foam fractionation and flotation (ore flotation, precipitate flotation, ion flotation, molecular flotation, and adsorbing colloid flotation). Flotation involves the removal of particulates by frothing, whereas foam fractionation involves the separation of soluble species by foams (Scamehorn and Harwell, 1989).
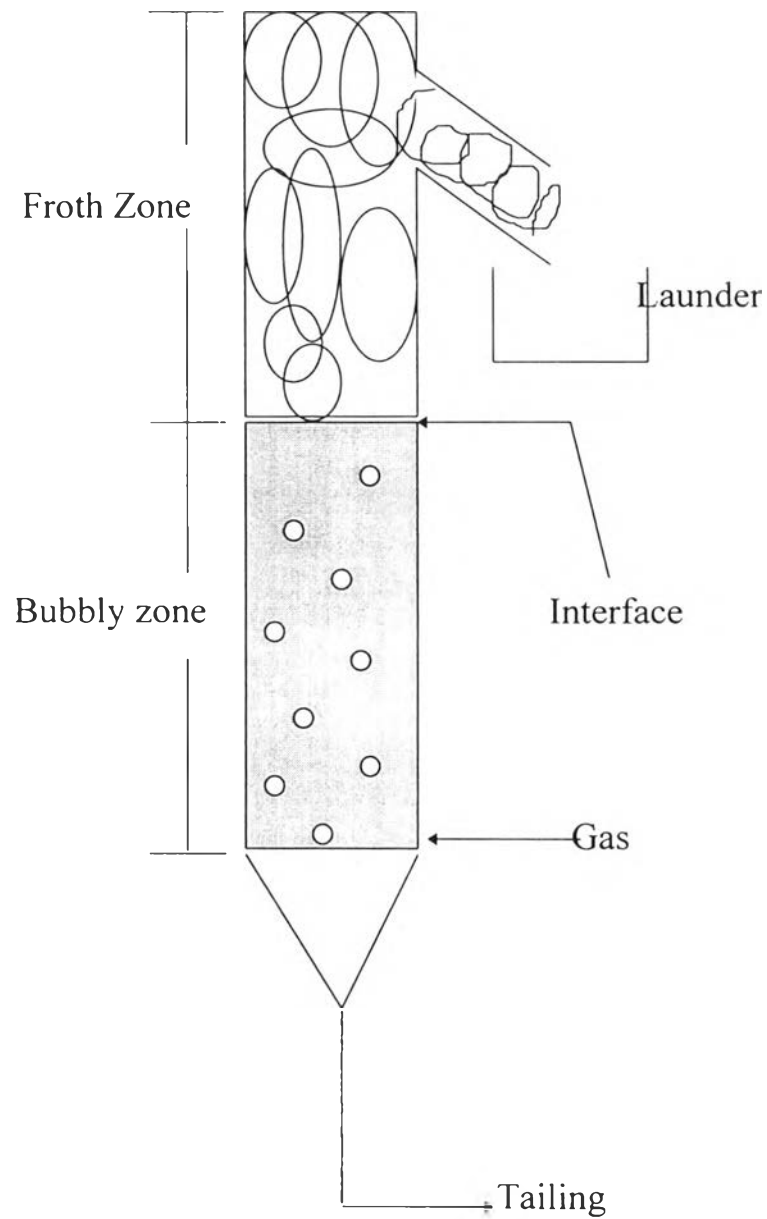
Figure 2.6   Schematic diagram of froth flotation column.
(Pal and Masliyah, 1990).

The basic unit of froth flotation to remove oil from waste water is illustrated in Figure 2.6. Air is introduced at the bottom of the column through a porous sparger. The generated air bubbles rise through a pool of aqueous oil slurry. At the top of the pool, air bubbles form froth. The froth rises to the top of the column and is collected in a launder. Consequently, a flotation column consists of two distinct zones, viz. a bubbly zone and a froth zone. The tailing stream is withdrawn at the bottom of the column. In the bubbly zone, there is a counter-current gas/liquid flow. The rising air bubbles in this zone collect hydrophobic particles and carry them to the froth zone. The air bubbles can also picked-up some of the undesirable hydrophilic particles. These particles are usually entrained in the water being carried up in bubble wakes (Pal and Masliyah, 1990).

Strickland (1980) studied the effect of oil density, collision and attachment efficiencies, crude type, pH, and gas/liquid contact time on cleaning water by gas flotation. It was learned that oil removal was increased by increasing collision and attachment efficiencies and gas/liquid time. Collision efficiency is increased by increasing oil-drop size and gas concentration. An increase of gas concentration is acheived by decreasing gas-bubble size. Sylvester et al. (1980) investigated the effect of inlet oil concentration, air flow rate, bubbles and oil droplets diameters, polyelectrolyte concentration, and temperature on oil removal. The oil drop and air bubble diameters had the most significant effects on the removal rate constants due to bubble/drop interaction. Varying the feed temperature did not have a significant effect on the rate constants. Van Ham et al. (1983) studied the effect of air distribution on the induced air flotation of fine oil in water emulsions. Results were successfully analyzed in terms of a first order kinetic rate model which yielded a value of the removal rate constant. Okada

et al. (1988) studied the effect of zeta potential of oil droplets and bubbles on flotation of oil-in-water mixture. It was found that the separation efficiency, η, for the flotation was strongly dependent on the zeta potentials of both the oil droplets and the bubbles.

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.