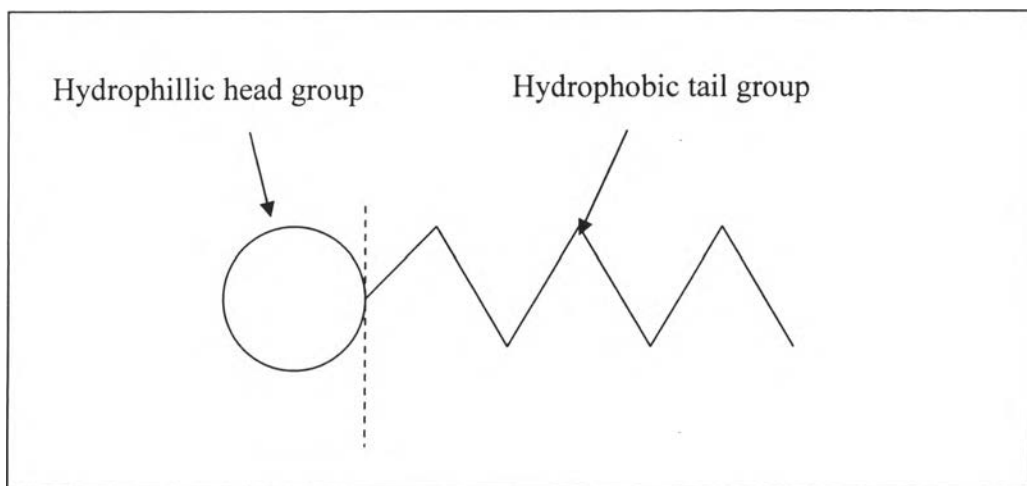


## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Surfactants

The term of “surfactant” is a contraction of surface-active agents. Surfactants are among the most versatile products of the chemical industry such as pharmaceuticals, detergents, drilling muds used in prospecting for petroleum, and flotation agents. A surfactant’s molecule consists of hydrophilic (water-loving) and hydrophobic (water-hating) moieties: referred to as head and tail, respectively (as shown in Figure 2.1). The hydrophilic portion of the surfactant is made of a water soluble species such as ionic or highly polar groups while the hydrophobic portion is made of organic derivative groups. According to the nature of the hydrophilic group, surfactants are classified into four main types: anionic, cationic, zwitterionic, and nonionic (Rosen, 1989).

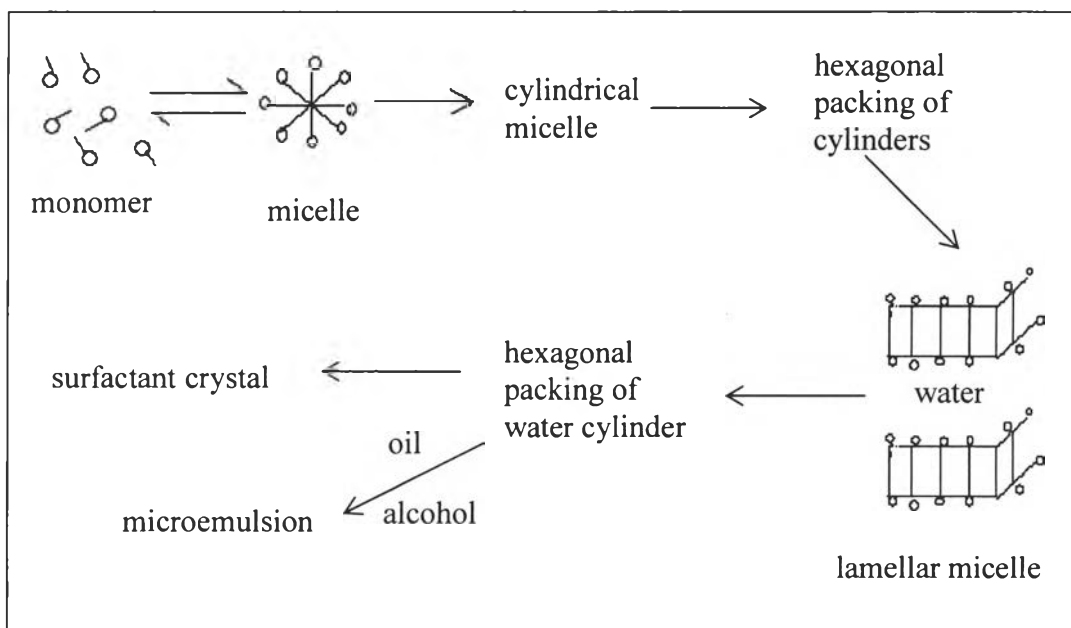


**Figure 2.1** Schematic structure of surfactant molecule monomer (Rosen, 1989).

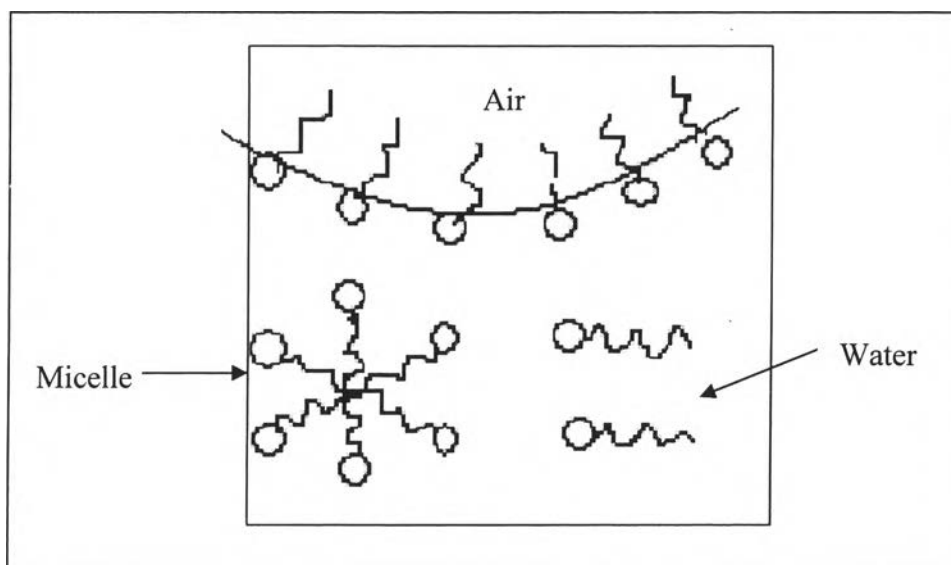
One of important characteristics of surfactants that, when present at low concentrations in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree of the surface or interface free energies of those surfaces (or interfaces). The interface denotes a boundary between any two immiscible phases and the surface indicates an interface where one phase is a gas, usually air and the other is an aqueous phase (Rosen, 1989).

One of significant phenomena associated with surfactant molecules is the formation of micelles. In water or aqueous solutions, normal micelles occur with the hydrophobic groups in the interior and the hydrophilic groups exposed to the external aqueous solvent. These may be spherical, rod-like, disk-like, or lamellar structures depending upon the physicochemical conditions such as pH, temperature and the presence of various electrolytes (Rosen, 1989). The interior of the micelle is often said to act like a very tiny oil droplet (no larger than a few nm in diameter) as shown in Figure 2.2. 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 (Sharma *et al.*, 1991). Furthermore, the solubilization increases as the number of micelles in the solution increases (Clarence and Neogi, 1985). The lowest surfactant concentration at which micelles are present is known as critical micelle concentration (CMC). In a nonpolar solvent, inverse micelles occur with surfactant head groups (often branched or twin-tailed) being on the outside in contact with similar groups of the surrounding solvent. Figure 2.3 shows schematically a surfactant solution containing dissolved monomeric surfactant, a surfactant micelle, and surfactants adsorbed at the air-water interface.

Surfactants play an important role in separation processes including flotation. Flotation involves bubbling an insoluble gas (usually air) into an aqueous stream. Materials to be removed adhere to the bubbles as they rise through the solution and the bubbles are accumulated at the surface as froth or foam which is skimmed off overhead. Surfactant is useful to both facilitate adhesion of target materials to the bubble surface and to act as a froth promoter/stabilizer. Since reduction in interfacial tension at both air/water and oil/water interfaces is probably one of the causes of the surfactant's synergism (Scamehorn, 2000).



**Figure 2.2** Schematic illustration of surfactant association structures (Sharma *et al.*, 1991).



**Figure 2.3** Schematic diagram of an ionic surfactant solution showing monomeric surfactants in solution and adsorbed at the air/solution interface and micelle aggregates (Prud'homme and Khan, 1996).

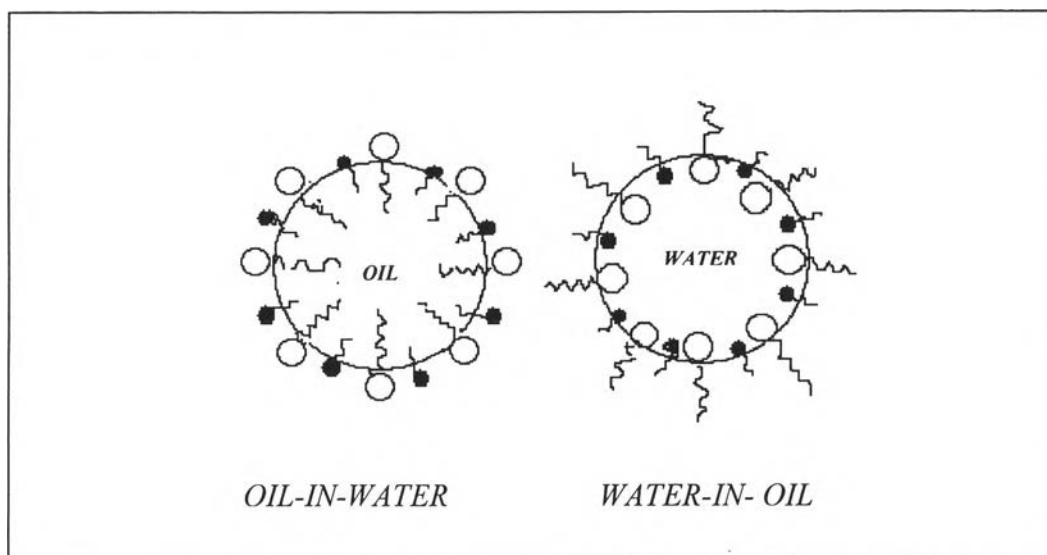
## 2.2 Microemulsion

The term “microemulsions” was introduced by Hoar and Schulman to describe transparent or translucent systems obtained by titration of an ordinary emulsion having a milky appearance to clarity by addition of a medium-chain alcohol such as pentanol or hexanol. These alcohols were later referred to as cosurfactants or cosolvents (Bourrel, 1988). Some preferred the name “swollen micellar solutions” (Prince, 1977) or “solubilized micellar solutions” (Tosch *et al.*, 1959) to describe precisely the same systems as those have called microemulsions by Hoar and Schulman (1943).

Microemulsions are defined to be clear thermodynamically stable dispersions of water, immiscible oil and a surfactant which adsorbs 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; Bourrel, 1988).

The microemulsion system contains transparent dispersion of very small oil-in-water (O/W) or water-in-oil (W/O) droplets with particles of 10-100 nm (0.01-0.1  $\mu\text{m}$ ) diameter that are generally obtained upon mixing the ingredients gently (Rosen, 1989). The oil-in-water type is a dispersion of a water-immiscible liquid or solution, always called the oil (O), in an aqueous phase (W). The oil is in the case, the “discontinuous” (inner phase); the aqueous phase is the “continuous” (outer) phase. The water-in-oil type is a dispersion of water or an aqueous solution (W) in a water-immiscible liquid (O). Figure 2.4 illustrates schematically these two basic microemulsion structures.

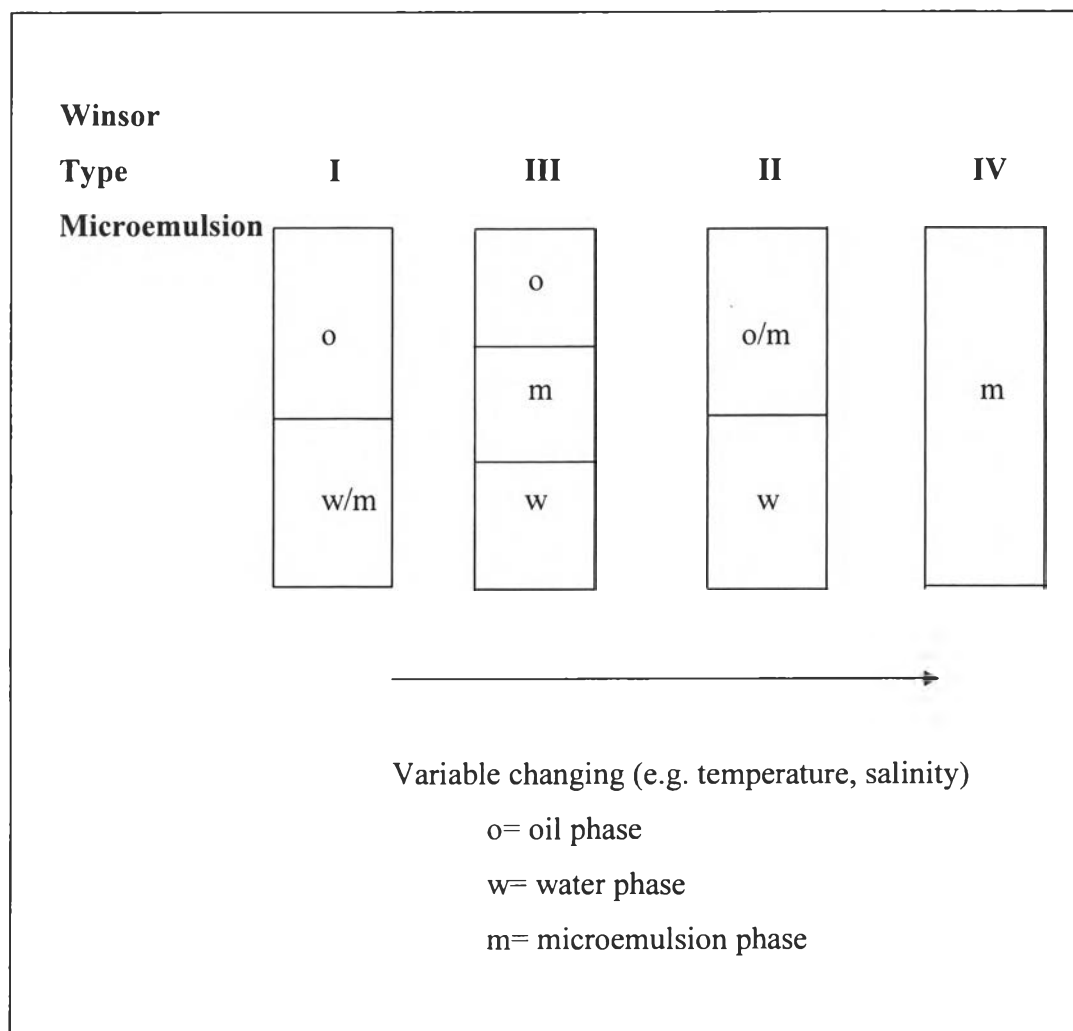
Microemulsion possesses superior characteristics of relatively large interfacial area, ultralow interfacial tension, and large solubilization capacity for both water-soluble and oil-soluble compounds as compared to other colloidal systems (Bourrel and Schechter, 1988).



**Figure 2.4** Schematic diagram for oil-in-water (O/W) and water-in-oil (W/O) microemulsion structures (the smaller molecules represent cosurfactant) (Rosen, 1989).

When a water-soluble surfactant is added to water under the proper conditions and above the CMC, the surfactant forms micelles which dissolve or solubilize oil, resulting in an increase in oil solubility in the aqueous phase. The aqueous phase in equilibrium with an excess oil is known as Winsor Type I microemulsion (Winsor, 1968). Under the proper conditions, as a variable (e.g. salinity, temperature) is changed, this system can transform from the two phase system of the Type I microemulsion and excess oil into a three phase system that consists of an excess oil phase, an excess water phase (both containing little surfactant) and a Winsor Type III microemulsion phase containing high levels of both water and oil and most of the surfactant as shown in Figure 2.5 (Puerto and Reed, 1983). This system attains ultralow interfacial tension (IFT) (e.g.  $< 10^{-4}$  mN/m) between the microemulsion phase and the excess water phase and between the microemulsion phase and the excess oil phase (Barakat *et al.*, 1983). The condition corresponding to equal volumes of oil and water being transferring from the excess phases to form the Winsor Type III microemulsion approximately corresponds to the minimum equal interfacial tensions between the excess phase and the middle phase (Shiau, 1994). As the variable is further changed, the system

becomes two phases again, and now the surfactant predominates in the oil phase in equilibrium with an excess water phase, so called a Winsor Type II microemulsion, as shown in Figure 2.5.



**Figure 2.5** Demonstration of microemulsion phase behavior for a model system (Winsor, 1968).

The factors that affect the transition between types of microemulsion are temperature, salinity, oil to water ratio, molecular structure of surfactant and cosurfactant and nature of oil.

In the application of microemulsion for oil recovery, various variables have been investigated to have a significant effect upon recovery including the surfactant concentration, interfacial tension, salinity, oil-to-water ratio, optimal surfactant structure, and cosurfactant concentration.

A research project which investigated the advantages of performing flotation with surfactant amount in the region of microemulsion formation between oil and water phases. Results indicate that if the system forms a Winsor type III microemulsion, flotation efficiency increases (Pondsatabodee *et al.*, 1998). Since this condition corresponds to minimal interfacial tensions between the water and oil phase, the general idea of improving flotation efficiency by choosing conditions where interfacial tensions are substantially reduced appears to be a promising approach (Bourrel, 1988, Scamehorn, 2000).

### **2.3 Froth Flotation**

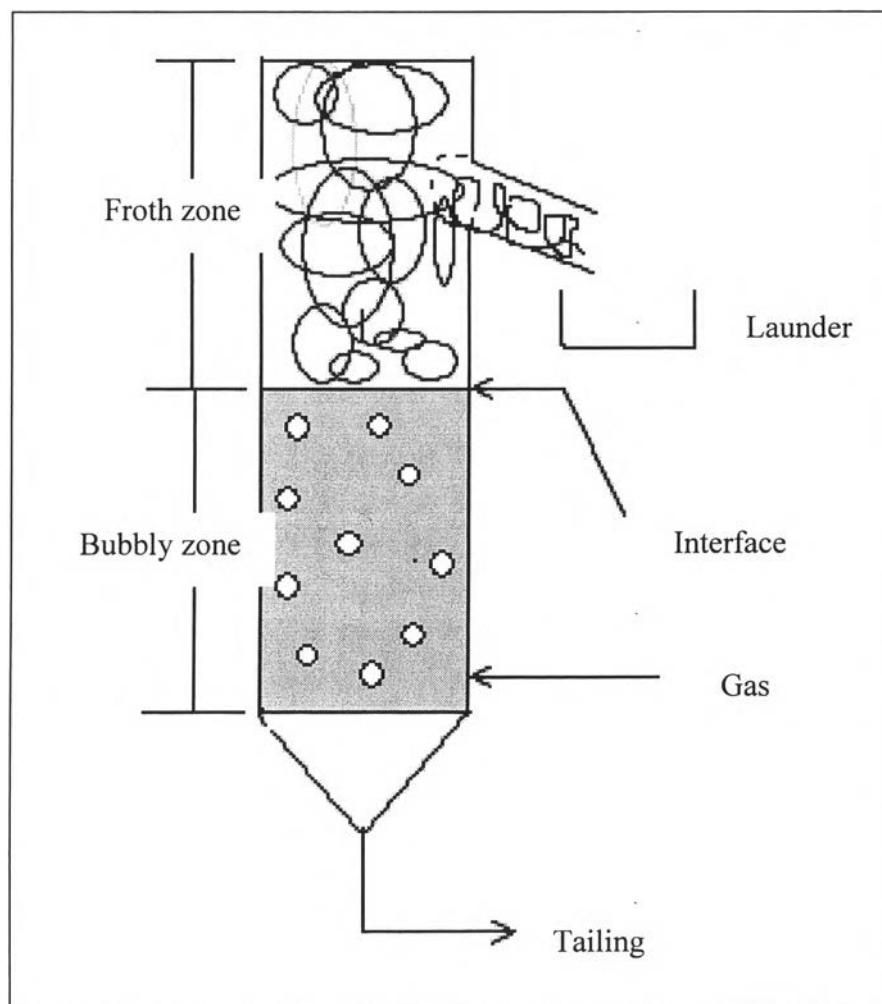
The accumulation of surfactants at the air/water interface, resulting in lowering excess Gibbs free energy of the interface is the principal phenomenon in the formation of stable foams. When a system contains solid particles, surfactants have opposite charge can coadsorb both the surface of the solid and the air/liquid interface leading to accumulate the particulates at the foams. The adhesion of a particulate material to bubbles rising through a liquid is the basis of the froth flotation process (Scamehorn, 2000).

Flotation is one of adsorptive bubble separations which is a process where a species is adsorbed at an interfacial between a dispersed phase (bubbles) and a continuous phase. Flotation involves the removal of particulate by frothing, whereas foam fractionation involves the separation of soluble species by foams (Scamehorn and Harwell, 1989).

Flotation involves bubble and soluble gas (usually air) into an aqueous stream. Materials to be removed adhere to the bubbles as they rise through the

process unit and are concentrated in the foam (called a froth in this case), which is skimmed off overhead. Surfactant is useful to both facilitate adhesion of target material to the bubble surface and to acts as a froth promoter/stabilizer. (Feng and Aldrich, 2000).

Figure 2.6 represents a basic unit of froth flotation process to remove oil from wastewater. In froth flotation, there is a driving force that causes oil droplets from the solution to attach to the surface of the air bubbles rising through the froth flotation column. Air is introduced at the bottom of the froth flotation 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 and it is collected in a launder. Hence, there are two distinct zones in the flotation column that consists of a



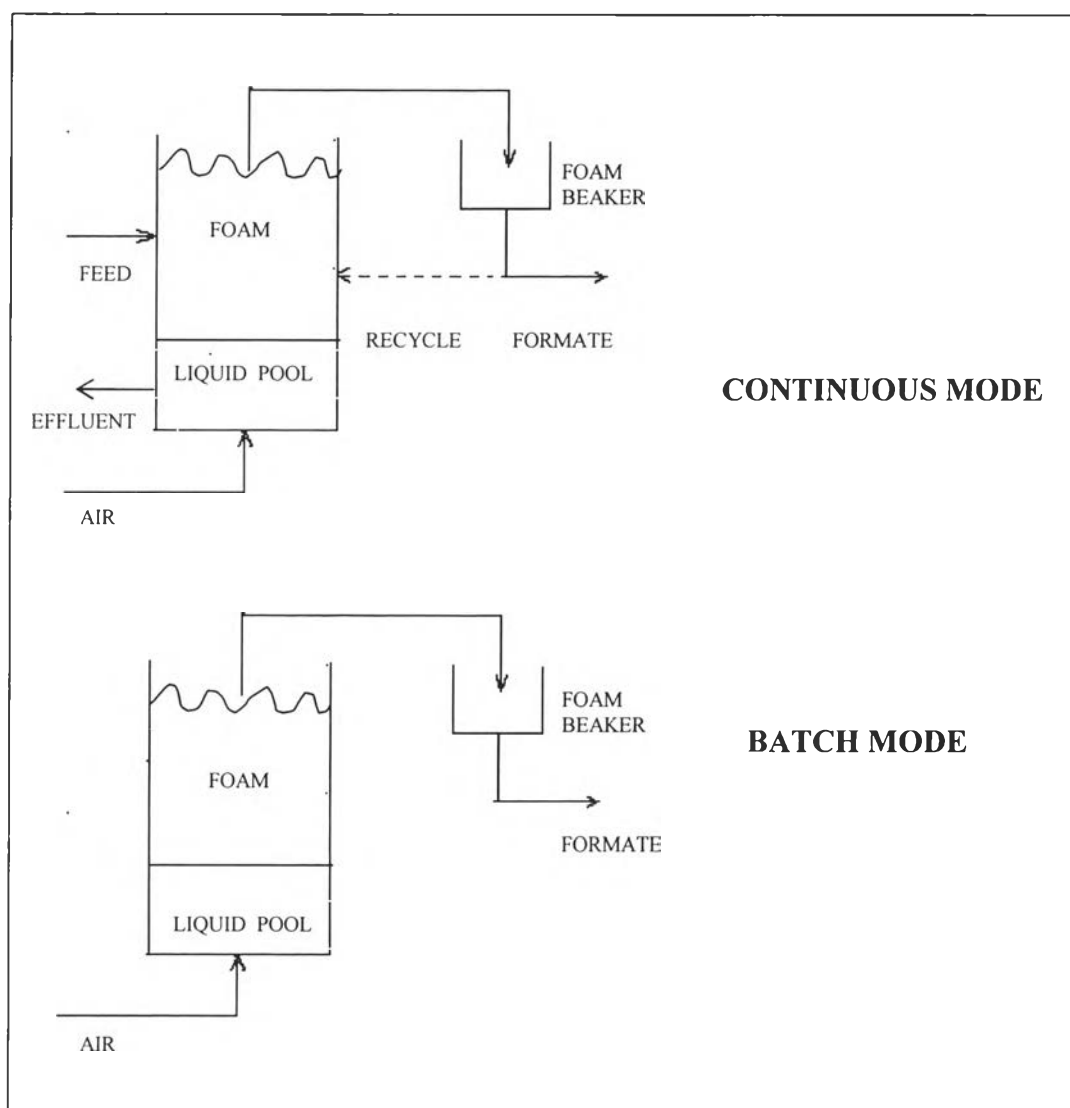
**Figure 2.6** Schematic diagram of a froth flotation column (Pal and Masliyah, 1989).



bubbly zone and a froth zone. At the bottom of the column, the tailing stream withdrawn at the bottom of the column. In the bubbly zone, the rising air bubbles in this zone collect oil or hydrophobic particles and bring them to the froth zone. The air bubbles can also pick-up some of the undesirable hydrophilic particles. In a froth zone, oil is removed in form of froth by rising through the top of the column and then froth is skimmed off and broken as liquid (Pal and Masliyah, 1990).

Froth flotation technique can be operated in both batch and continuous modes as illustrated in Figure 2.7. In a batch operation solution is transferred to the column at the outset. After that air is introduced through the column until no further foaming occurs or a separation has been achieved. Some of the coalesced foam may be returned to the foam column similar to that in a batch distillation column. The concentration of solution within the column and foam are continuously changing during the operation as well as the concentration of surfactant. In a continuous operation, the entering liquid may be introduced into the liquid pool or into the foam section of the column. Overhead product is drawn off at the top of the column and underflow from the liquid pool. Some of the overhead may be recycled analogous to a distillation column (Carleson, 1989). Because the solution is fed continuously into the column at a specific rate as well as froth and liquid are removed continuously during the operation leading to the generation of a steady state, the concentrations of surfactant and oil in the liquid column are maintained at constant levels as same as the concentrations of them that extracted into the froth.

Wungrattanasopon *et al.* (1996) studied the effect of two types of surfactants, cetyl pyridinium (CPC) and sodium dodecyl sulfate (SDS), and NaCl on the removal efficiency of tert-butylphenol (TBP) by using foam flotation process. This process was operated in the batch mode. It was found that the TBP removal was maximum when the surfactant concentration approached the CMC. Without the addition of NaCl, CPC gave higher TBP removal than SDS did. Nevertheless, the addition of NaCl resulted in a significant reduction of the ability of CPC to remove TBP while it improved the ability of SDS to remove TBP.



**Figure 2.7** Configurations for froth flotation operation (Carleson, 1989).

Pondsatabodee *et al.* (1998) investigated the removal of ortho-dichlorobenzene (ODCB) from water by batch froth flotation under the Windsor Type III microemulsion. The cationic surfactant studied was more effective than either monosulfate or the disulfate anionic surfactants. The oil flotation efficiency increased as the initial surfactant concentration increased, the salinity increased, and the oil/water ratio decreased.

Ratanarojanatum (1995) studied the effect of mixed surfactants, sodium dodecyl sulfate (SDS) and nonylphenol polyethoxylate (NP(EO)<sub>10</sub>) on the removal of ODCB. The Winsor Type III system gave a higher percentage of ODCB removal than the Type II or Type I system. For the system containing a surfactant concentration of 7% and a weight fraction of SDS of 0.8, the highest ODCB removal of 91% was obtained corresponding to the surfactant removal of 65%.

Phoochinda (1999) focused on the effect of NaCl added to mixed surfactants of SDS and NP(EO)<sub>10</sub> on microemulsion formation and efficiency of flotation for removing ODCB from water. It was found that a small amount of NaCl added to mixed surfactants could improve microemulsion formation. At high concentrations of NaCl, precipitation and liquid crystal limited the solubilization capacity of solution. The mixed surfactants of 3 and 5 wt% of SDS and NP(EO)<sub>10</sub> were selected for froth flotation experiments. The prepared solution, i.e. water excess and middle phases (w-m), water excess and oil excess phase (w-o) and water excess phases, middle phases and oil excess phases (w-m-o) were transferred to the flotation column to determine oil removal efficiency. The results showed that the ODCB removal in the w-m-o system was much higher than the w-o and w-m systems. The effect of NaCl in the w-m-o system was studied and the study showed that the addition of 0.5 wt% of NaCl increased the ODCB removal. The effect of each phase was also studied. The results showed that when the volume of the oil phase decreased and volume of the water phase increased in the w-o system, the ODCB removal decreased. When the volume of the middle phase increased and volume of the water phase decreased in the w-m system, the ODCB removal increased.

Feng and Aldrich (2000) investigated the removal of diesel from aqueous emulsions by using batch flotation. The stability of these emulsions was characterized and factors such as pH and salinity affecting the stability of the emulsion were investigated. In addition, the effects of anionic and cationic surfactants, original diesel content, air-flow rate, surfactant dosage, and the air distributor sinter were investigated. In terms of the effect of pH on the diesel removal, it was concluded that when pH increased, the diesel-water emulsion stability constant ( $K_s$ ) increased as a result of the unstable leading to rapid destruction of the emulsion, and enhancing the diesel removal efficiency. For the

effect of NaCl concentration, it was found that the emulsion was gradually destabilized by the increase in the amount of NaCl. It was found that, the oil could be removed effectively with the cationic surfactants, which were octadecyl amine chloride (ODAC) and cetyl trimethyl ammonium chloride (CTMAC), but less so with the anionic surfactant, which was SDS. Under the optimal condition, up to 99% of the diesel could be removed. This amounted to a residual diesel concentration of less than 10 ppm.

Samuthjarindr (2001) reported the relationship between foam stability and froth flotation efficiency in oily wastewater treatment. Sodium dodecyl benzenesulfonate (SDBS) and the Novous CE 2680 was used as the surfactant and flocculant, respectively. The first part of this work was to investigate the operational parameters affecting foam stability by using batch flotation columns. The experimental results showed that the foam height was significantly affected by the air flux. The concentration of the surfactant added also affected positively the foam height. The column diameter in the studied range did not affect the foam height. The second part was to determine froth flotation efficiency in treating the oily wastewater treatment using a continuous froth flotation unit. From the experimental result, it was found that the oil removal reached 90% efficiency at the CMC of the surfactant and 250 mg/l of the cationic polyelectrolyte . The addition of the polyelectrolyte gave much higher efficiency of the oil removal than using only the surfactant. Furthermore, when only 0.5CMC of the surfactant was used, the oil removal efficiency decreased to 77.5%.

In the year 2003, Withayapanyanon correlated the oil removal by froth flotation to the ultra-low interfacial tension. Ethylbenzene was selected as a model oil contaminant for studying the removal efficiency by the batch mode. A single surfactant (sodium di-1,3-dimethylbutyl sulfosuccinate, AMA) and mixed surfactants (sodium bis-2-ethylhexylsulfosuccinate, AOT, and mono- and dihexadecyl diphenyloxide disulfonate sodium salt, Dowfax 8390) were selected to form microemulsion with ethylbenzene. Results showed that at 3% NaCl, 0.3% AMA, the system provided the maximum oil removal (99.55%) but did not correspond to the minimum interfacial tension found in Winsor's Type III microemulsion. In addition, flotation using the mixed surfactants was not achieved due to the low stability of the

froth. It was concluded that the ultra-low interfacial tension of the middle-phase microemulsion is not the sole factor affecting the flotation process. Foam ability and stability are other parameters involving oil removal efficiency in the froth flotation process.