CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Surfactants

Surfactants are among the most versatile products of the chemical industry, appearing in a variety of products such as motor oils pharmaceuticals detergents drilling muds, and flotation agents. For the last decades, the extension of surfactant applications has shown in to such high-technology areas such as electronics printing, magnetic recording, biotechnology, micro-electronics, and vial research.

A surfactant (a contraction of the term surface active agent) is a substance that, when presents 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 interfacial free energies of those surfaces (or interface). The term interface indicates a boundary between any two immiscible phases; the term surface denotes an interface where one phase is a gas, usually air (Rosen, 2004).

A surfactant's molecule consists of hydrophillic (water-loving) and hydrophobic (water-hating) moieties: referred to as head and tail, respectively (as shown in Figure 1).
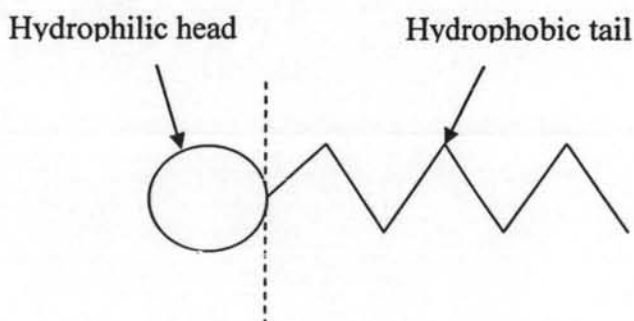

Figure 2.1 Schematic structure of surfactant molecule monomer (Withayapanyanon, 2003).

The hydrophillic 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.

Depending on the nature on the hydrophilic group , surfactants are classified as anionic, cationic, zwitterionic and nonionic surfactants (Rosen, 2004).

1. Anionic surfactants will adsorb onto a positively hydrophilic surface because the surface-active portion of anionic surfactants bears a negative charge, for example, $RCOO^-Na^+$ (soap), $RC_6H_4SO_3^-Na^+$ (alkylbenzene sulfonate).

2. Cationic surfactants will adsorb onto a negatively hydrophilic surface because the surface-active portion bears a positive charge, for example, $RNH_3^+Cl^-$ (salt of a long-chain amine), $RN(CH_3)_3^+Cl^-$ (quaternary ammonium chloride).

3. Zwitterionic surfactants, since they carry both positive and negative charges, they can adsorb onto both negatively and positively charged surfaces without changing the charge of the surface significantly, for example, $RN^+H_2CH_2COO^-$ (long-chain amino acid), $RN^+(CH_3)_2CH_2CH_2SO_3^-$ (sulfobetaine).

4. Nonionic surfactants adsorb onto surfaces with either the hydrophilic or the hydrophobic group oriented toward the surface, depending upon the nature of surface, for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long-chain fatty acid), $RC_6H_4(OC_2H_4)_xOH$ (polyoxyethylenated alkylphenol), $R(OC_2H_4)_xOH$ (polyoxyethylenated alcohol).

A single molecule of surfactant is called monomer and at sufficiently concentration in solution, monomer or surfactant molecules will nucleate to form aggregates called micelles. This process is called micellization that is illustrated in Figure 2.2 and the lowest total surfactant concentration at which micelles are present is critical micelle concentration (CMC).
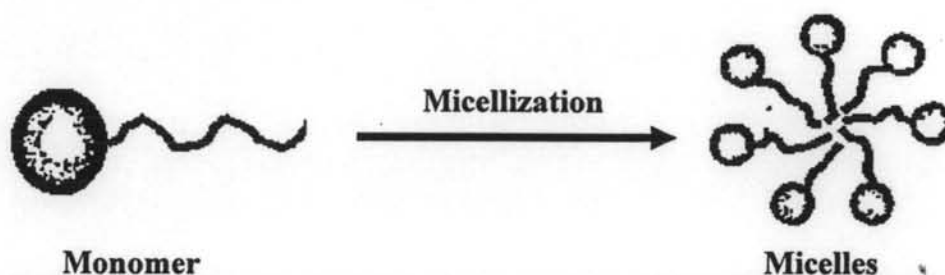
Figure 2.2 Schematic diagram of monomer, micelles and micellization.

Surfactant solutions with concentrations above the CMC can dissolve considerably large quantities of organic materials than surfactant solutions with concentrations below the CMC. Since at the CMC, surfactant molecules form spherical micelles with the hydrophobic or hydrocarbon group on the interior and the hydrophilic group on the exterior. Therefore, oil or organic contaminants that are generally hydrocarbons can solubilize at the center core of micelles. Furthermore, the solubilization increases as the number of micelles in the solution increases (Clarence and Neogi, 1985).

Normal micelles which have hydrophobic part in the interior and the hydrophilic part in the external solvent are form in aqueous solutions or water. Inverse micelles which have hydrophilic part in the interior and hydrophobic part on the outside are formed in nonpolar solvent. Figure 2.3 illustrates the picture of normal and reverse micelles (Rosen, 2004). Figure 2.4 shows the formation of various association structures which increasing surfactant concentration. It is likely that surfactant molecules may form spherical, cylindrical, hexagonal, lamellar with increasing surfactant concentration and reverse 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 in the system (Sharma et al., 1991).
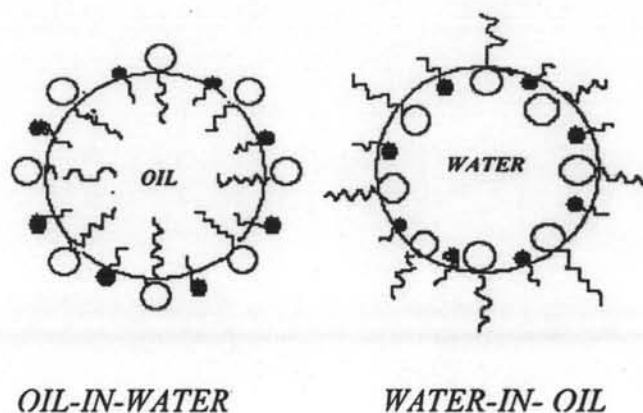
OIL-IN-WATER   WATER-IN- OIL

Figure 2.3 Schematic diagram of normal micelles and inverse micelles.
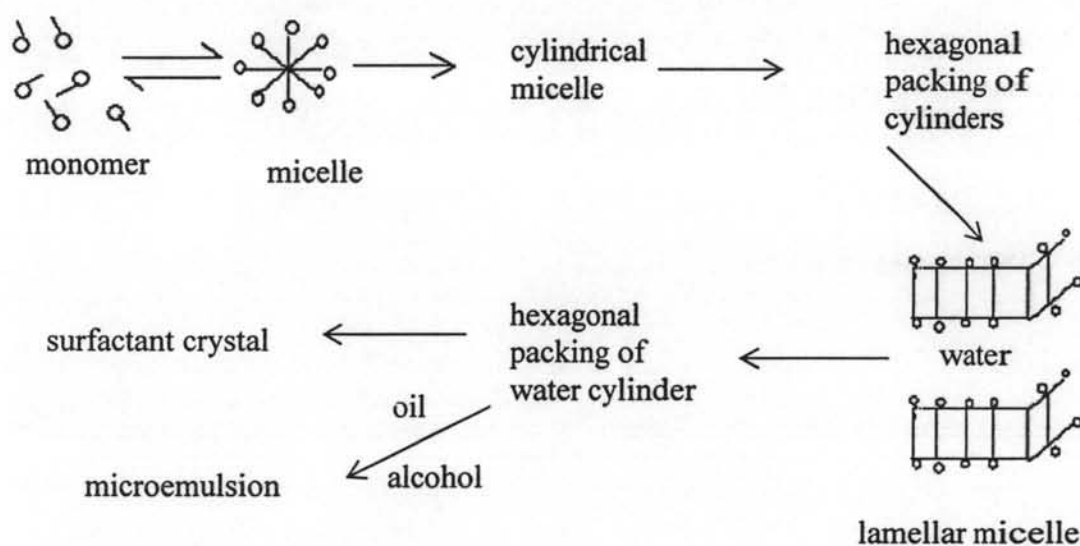

Figure 2.4 Schematic illustration of surfactant association structures (Sharma *et al.*, 1991).

Surfactants are used for variety of applications such as cleaning products, flotation agents, paints, cosmetics and enhance oil recovery. Mixtures of different surfactants are generally used more than individual surfactant due to economical as well as synergistic effects. Mixture of ionic and nonionic surfactants is commonly used in practical surfactant applications. For instance, in laundry detergent formulations, anionic surfactants are used to maximize solubilization while nonionic

surfactants are used to maximize water hardness tolerance. An addition of a nonionic surfactant to anionic surfactant system can reduce the electrostatic repulsion between the charge surfactant heads and greatly facilitate mixed micelle formation (Shiloach and Blankschtein, 1998).

Surfactants play an important role in separation procedures such as flotation. Flotation is one of interesting processes since it can serve as energy barrier, thus enabling fluid media to be stabilized in the form of very small globules thereby exposing an enormously increased interfacial area, where transfer from one phase to another can occure very rapidly. In addition because of their amphiphathic nature, they tend to adsorb at interfaces. Thus they can themselves act as collectors in flotation procedures (Sebba, 1989).

2.2 Emulsion

Emulsion is a significantly stable suspension of tiny particles of liquid within a second immiscible liquid. Normally, two immiscible pure liquids such as oil and water can not form an emulsion. The third component must be present in order to stabilize the suspension of one liquid in another. This third component is called as emulsifying agent and it is usually a surfactant. In fact, effective emulsify agents are usually mixtures of two or more substances (Rosen, 1989).

Based upon the size of the dispersed particles, the emulsion is classified into three types.

1. Macroemulsion is an emulsion that is kinetically stabilized and generally milky-white in appearance. Moreover, it is opaque emulsion with particle size greater than 400 nm which may be easily visible under a microscope. It often tends to spontaneously separate into two or more phases without a significant temperature change.

2. Microemulsion is a transparent dispersion with particle size less than 100 nm. It is a thermodynamically stable and has been intensively studied for the past few decade because of their various applications.

3. Miniemulsion is a blue-white, with particle size between 100-400 nm.

2.2.1 Characteristics of Microemulsion

Microemulsions have been widely used in industrial and household application. Microemulsion was scientifically described for the first time in 1943 as special colloidal dispersions or a transparent or translucent system forms spontaneously upon mixing oil and water with a relatively large amount of ionic surfactant together with a cosurfactant by Hoar and Schulman (1943).

Microemulsions are transparent and homogeneous mixtures of water and oil. They are stabilized by a fairly large amount of surfactant. Their spontaneous formation and long-lasting stability indicate that they are thermodynamically stable (Overbeek, 1978a,b). The formation of microemulsions generally involves a combination of three to five components which are oil, water, surfactant, cosurfactant and salt.

There are four types of microemulsion which are classified by Winsor (1954) as shown in Figure 2.5

1. Winsor type I : oil-in-water microemulsion in equilibrium with excess oil phase
2. Winsor type II : water-in-oil microemulsion in equilibrium with excess water phase
3. Winsor type III : middle or microemulsion phase in equilibrium with an excess of both water and oil phase
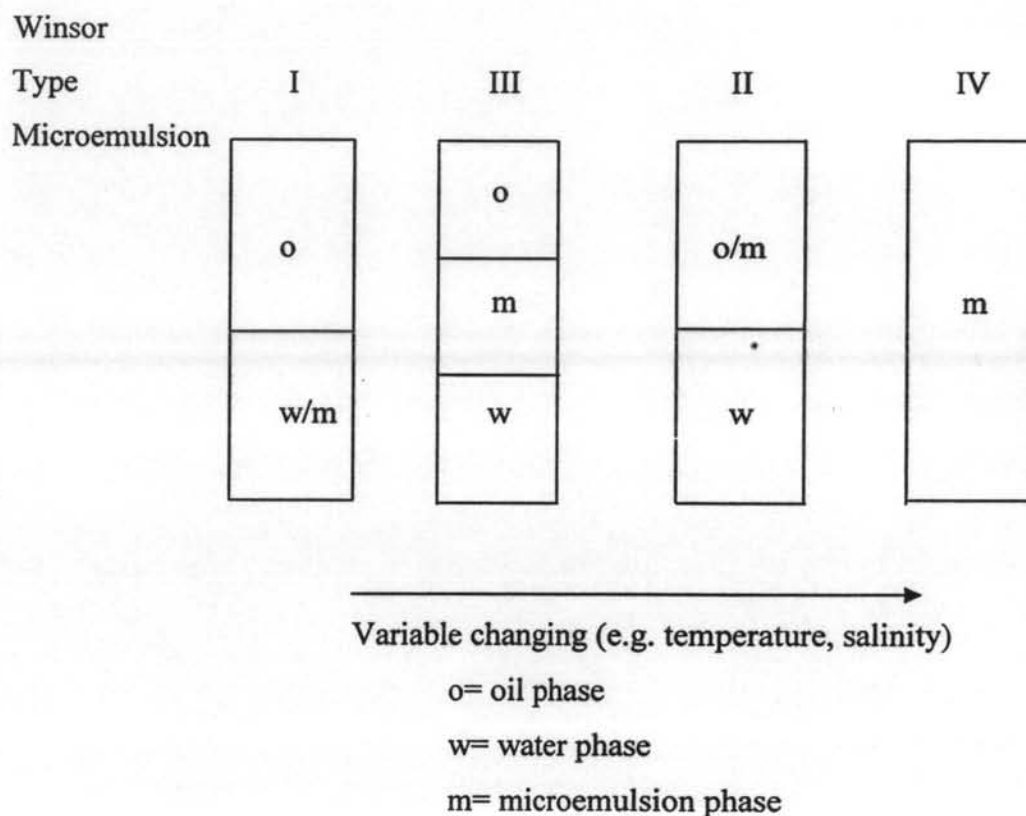4. Winsor type IV : single phase or microemulsion phase

Winsor
Type
Microemulsion

Variable changing (e.g. temperature, salinity)

o= oil phase

w= water phase

m= microemulsion phase

Figure 2.5 Schematic of type of microemulsions (Winsor, 1954).

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

In an intermediate-salinity region, the Winsor type III system is composed of a middle-phase microemulsion in equilibrium with both excess oil and brine phases. 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 middlephase 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 as 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 Type I and Winsor Type II to Winsor Type III to microemulsion. The transition from Winsor Type I to Winsor Type III microemulsions has been attributed to coacervation of normal micelles (Shar, 1981), while the transition from Winsor Type II to Winsor 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 Type III systems are governed by both attractive force between droplet and interfacial bending stress.

Moreover, the transition of Winsor Type I-III-II influences the two interesting properties of microemulsion, which is solubilization and interfacial tension (IFT), due to the changing the microstructure. Figure 2.6 shows the relationship between the type of microemulsion and the interfacial tension. The region on the left hand side of the figure is the region of Winsor Type I microemulsion where oil-in-water (O/W) microemulsion exists along with an excess oil phase. The IFT between the excess oil phase and the micellar solution ($\gamma_{o/m}$) decreases with increasing salinity. When the middle phase is formed, the microemulsion with bicontinuous structure is in equilibrium with excess oil and excess water phases. IFT between the excess oil and excess middle phase ($\gamma_{o/m}$) and between the excess water and the middle phases ($\gamma_{w/m}$) further decrease. The point in the Winsor Type III microemulsion region, where the IFT between the excess oil and the middle phases ($\gamma_{o/m}$) equals the IFT between the excess water and the middle phases ($\gamma_{w/m}$), is known as the minimum IFT or optimum state.
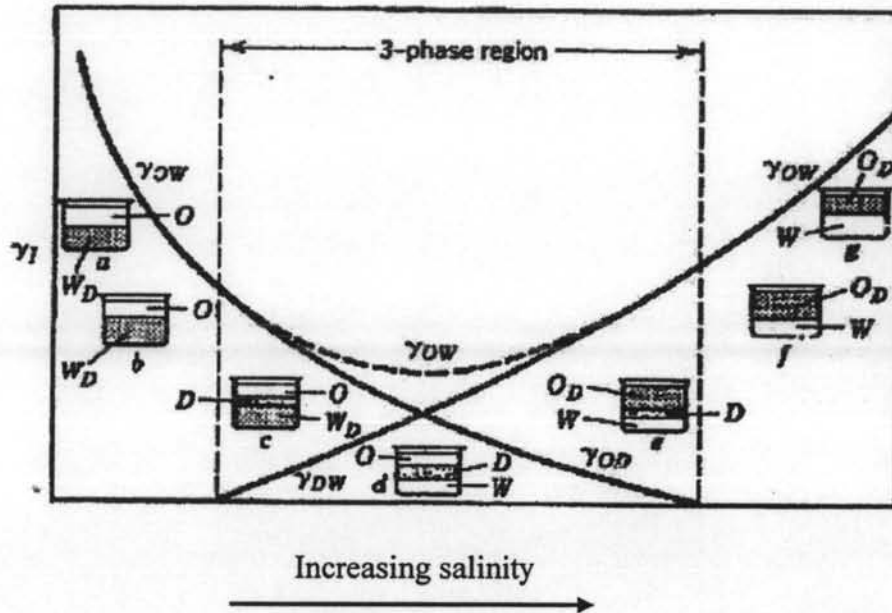
Figure 2.6 The transition of microemulsion structure and interfacial tension as a function of a salinity scan (Winsor, 1954).

Apart from the conventional salinity scan, the transition of a microemulsion system from O/W to W/O structure can also be done by changing any of the following variables in a systematic way:

1. Increasing alkyl chain length of 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 noionic 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 approach in applied in oil recovery to remove the resident oil in a porous medium. Many variables are considered to have a significant effect upon the 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 foam (Scamehorn, 2000).

The basic operation of froth flotation to remove oil from wastewater is to introduce air at the bottom of a froth flotation column through a sinter glass disk, which can produce air bubbles (see Figure 2.7). The generated air bubbles rise through an oil-containing solution and carry the droplets of oil to the top of column. At the top of solution, air bubbles from foam or froth and it is collected in a launder. The treated water is withdrawn at the middle of column. There are two distinct zones in the flotation column, which are a solution zone and a froth zone. In a solution zone, air bubbles rise through and collect oil and hydrophobic particles are carried with the rising air bubbles to the froth zone. In a froth zone, most removed oil is concentrated and eventually the foam is skimmed off and broken as liquid. The use of froth flotation for the removal of insoluble organic contaminants from water. Froth flotation can be operated in batch and continuous modes.
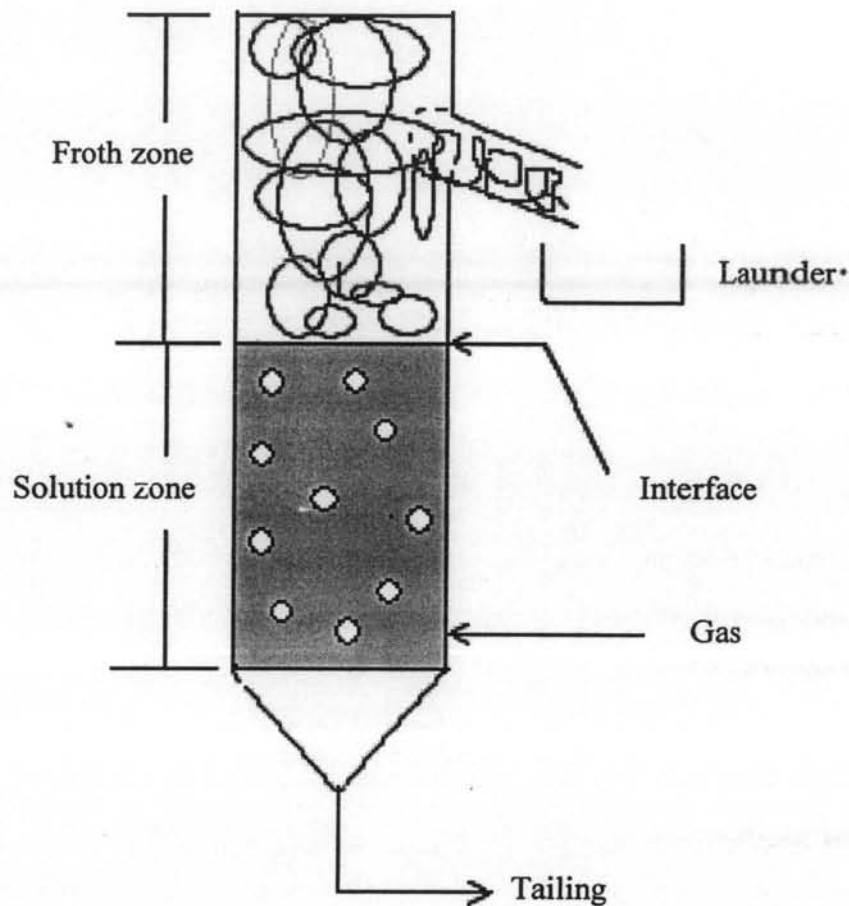
Figure 2.7 Schematic diagram of a froth flotation column (Pal and Masliyah, 1989).

In batch mode, the solution is transferred to the column at the outset and then air bubbles are passes through the column until a separation has been achieved or no further foaming occurs. The concentration of solution within the column and foam are continuously changing during the operation. The column is depleted of surfactant since it is swept up into the foam.

In continuous mode, the solution is fed continuously into the column at a particular rate. At the same time, foam and liquid are removed continuously during the operation leading to the generation of a steady state. The concentrations of surfactant and oil in the column are maintained at constant levels same as the concentrations of them that extracted into the foam.
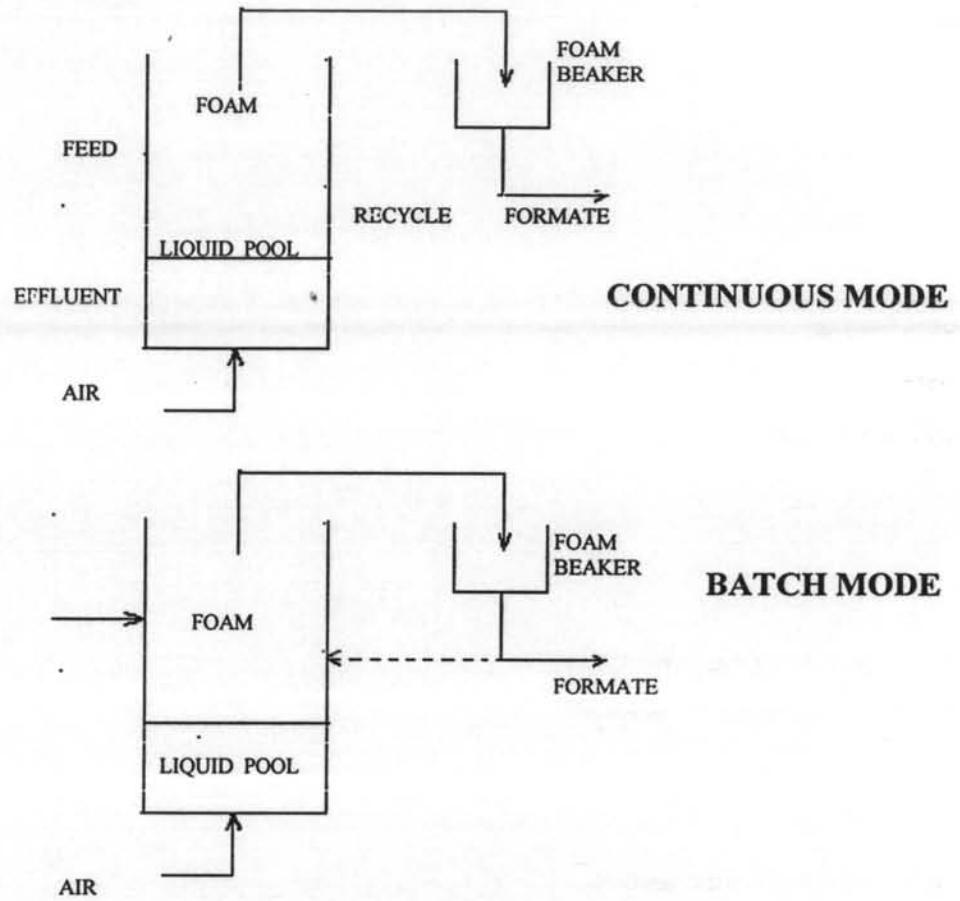
Figure 2.8 Configurations for froth flotation operation (Carleson, 1989).

In addition to the formation of a froth, the presence of a surfactant dramatically increases the dispersion of air in the flotation tank, reduces the coalescence of individual bubbles within the liquid, and decreases the rate at which the bubbles rise to the surface. All these factors greatly increase the possibility of particle-bubble contact and hence the rate of flotation. Absolutely pure liquid does not froth and presence of a surfactant is necessary to induce frothing.When a surfactant is added to water, the surface tension of the solution decreases as a result of the heteropolar nature of the moleculesat the air-water interface. The surfactant molecules are arranged at the interface such that the hydrophilic or polar group is situated in the water phase and the hydrophobic or hydrocarbon chain in the air phase. The degree of adsorption at the interface of these surfactant molecules is related to the decrease in surface tension (King, 1982).

Ratanarojanatam (1995) focused on the use of the mixed surfactants of sodium dodecyl sulfate (SDS) and nonylphenol polyethoxylate (NP(EO)$_{10}$) to remove ortho-dichlorobenzene (ODCB). The mixed surfactants were used to prepare the microemulsion solutions between water and ODCB. The Winsor Type III system gave a higher percentage of ODCB removal than the Winsor Type II and I system. For the system containing a total surfactant concentration of 7% and weight fraction of SDS of 0.8, the highest of ODCB removal of 91% was obtained corresponding to the surfactant removal of 65%.

Wungrattanasopon *et al.* (1996) studied the effects of type, concentration of surfactant and NaCl on the removal efficiency of tert-butylphenol (TBP) by using foam flotation process. This process was operated in the batch mode. Cetyl pyridinum chloride (CPC) and sodium dodecyl sulfate (SDS) were used as surfactant to remove TBP from water in a flotation process. The TBP removal was maximized when the surfactant concentration was around the critical micelle concentration (CMC). The addition of NaCl affected the surfactant monolayer and micelle formation. It enhanced the removal ability of SDS, while reduced the removal ability of CPC.

Phoochinda (1997) investigated the effect of NaCl added to mixed surfactants on microemulsion formation and the flotation efficiency for removing ODCB from water. It was found that small amount of NaCl added to the mixed surfactants could improve microemulsion formation. However, precipitation and liquid crystal that limit the solubilization capacity appeared at high NaCl concentrations. The mixed surfactant concentrations of 3 and 5% by weight of mixed surfactants were selected for froth flotation experiment. The water phase with the middle phase (w-m), the water phase with the oil phase (w-o), and the water phase, the middle phase and the oil phase (w-m-o) were transfer 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 those in the w-o and w-m systems. Moreover, the effect of NaCl in the w-m-o system was studied and showed that adding 0.5 by weight of NaCl increased the ODCB removal but adding more than 1.0 by weight of NaCl decreased the ODCB removal. The effect of the volume of each phase was also studied. The results showed that when the volume of the oil phase decreased and the

volume of water phase increased in the w-o system, the ODCB removal decreased. When the volume of the middle phase increased and the volume of water phase decreased in the w-m system, the ODCB removal increased.

Pongstabodee *et al.* (1998) studied the removal of ODCB by froth flotation under Winsor Type III conditions. From the experimental results, it indicated that the removal efficiency of ODCB increased as the surfactant concentration increased, salinity increased (causing Winsor Type I to Winsor Type III transition for the system) and oil/water ratio decreased. The cationic surfactant was more effective than either the monosulfate or the disulfate anionic surfactant.

Phoochinda (1999) focused on the effect of NaCl added to mixed surfactants of SDS and $NP(EO)_{10}$ 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 $NP(EO)_{10}$ were selected for froth flotation experiments. The prepared solution, i.e. water excess and middle phase (w-m), water excess and oil excess phase (w-o) and water excess phase, middle phases and oil excess phase (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.

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. The 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 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.

In the year 2004, Watcharasing investigated the relationship between the ultra-low IFT and the efficiency of diesel removal from water by using continuous froth flotation technique. Branched alcohol propoxylate sulfate, sodium salt (Alfoterra 145-5PO) and sodium dodecyl sulfate (SDS) were used for both microemulsion formation and froth flotation studies. Surfactant concentration, salinity, and oil to water ratio were varied in the microemulsion formation experiment in order to determine the compositions required to obtain ultra-low IFT. From the results, the oil removal efficiency of the froth flotation process did not correspond to the minimum IFT of the system indicating that the ultra low IFT alone cannot be used as a sole criteria for froth flotation operation. Foam stability was revealed to be another crucial factor in the froth flotation operation. The system with 0.1 wt% Alfoterra, 0.5 wt% SDS, 4 wt% NaCl, 1:19 oil:water ratio, 0.15 L/min air flow rate, 26 cm foam height, and 49 min HRT gave the maximum oil removal (90.37 %).