# CHAPTER II
# LITERATURE REVIEW

## 2.1 Surfactant

Surfactants are one of the most versatile products of the chemical industry, appearing in such diverse products as motor oils, pharmaceuticals, paints, cosmetics and detergents. For the last decade, extensive applications of surfactants have been moving toward high-technology areas as electronic printing, magnetic recording, biotechnology, microelectronic and environment separation processes.

A surfactant, which is a contraction of the term Surface Active Agent, is characterized by two distinct groups which differ greatly in their solubility relationships (Winsor, 1954). The structure of a surfactant molecule consists of a hydrophilic (water-loving) part which is usually an ionic or highly polar group and a hydrophobic (water-hating) part which is usually a long-chain hydrocarbon or non-polar group, or commonly and perhaps more pictorially as the head and the tail, respectively. Figure 2.1 illustrates a basic structure of surfactants. One of unique properties of surfactants is to adsorb onto the surface or interface of the system resulting in decreasing the surface or interfacial tension of the medium in which it is dissolved. The term interface indicates a boundary between any two immiscible phases. The term surface denotes an interface where one phase is gas, usually air (Rosen, 1989).

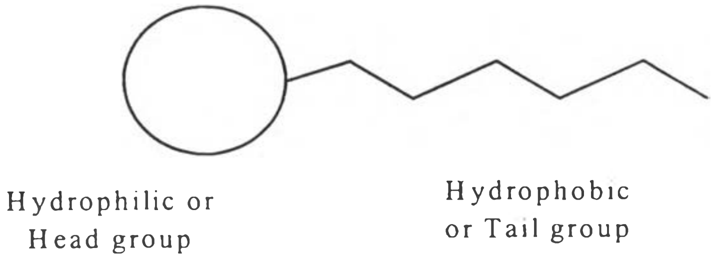


**Figure 2.1** Structure of surfactant molecule.

Depending on the nature of the hydrophilic group, surfactants are classified as anionic, cationic, zwitterionic and nonionic surfactants (Rosen, 1989).

1. Anionic surfactants will adsorb onto the positively hydrophilic surface because the surface-active portion of anionic surfactants has a negative charge.
2. Cationic surfactants will adsorb onto the negatively hydrophilic surface because the surface-active portion has a positive charge.
3. Zwitterionic surfactants, since they carry both positive and negative charges, can adsorb into both negatively and positively charged surfaces without changing the charge of the surface significantly.
4. Nonionic surfactants adsorb onto the surfaces with either the hydrophilic or the hydrophobic group oriented toward the surface, depending upon the nature of surface.

A single molecule of surfactant is called monomer and at sufficiently concentration in solution, monomers 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 called the critical micelle concentration (CMC).

There are two types of micelles which are normal and inverse (or reverse) micelles. For aqueous solution, normal micelles are formed with hydrophobic part in the interior and hydrophilic part in the external. In contrast, inverse micelles, are formed in a non-polar solvent with the hydrophilic part in the interior and hydrophobic part in the external. The picture of normal and inverse micelles is shown in Figure 2.3.

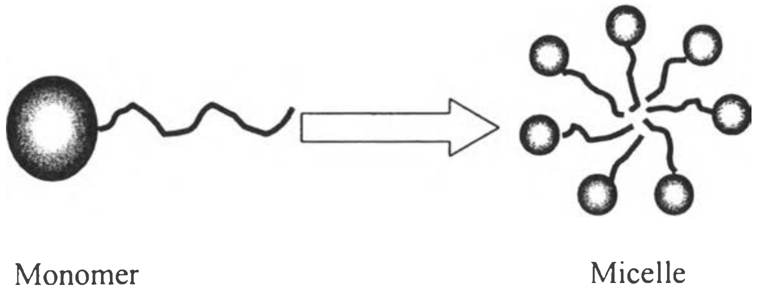
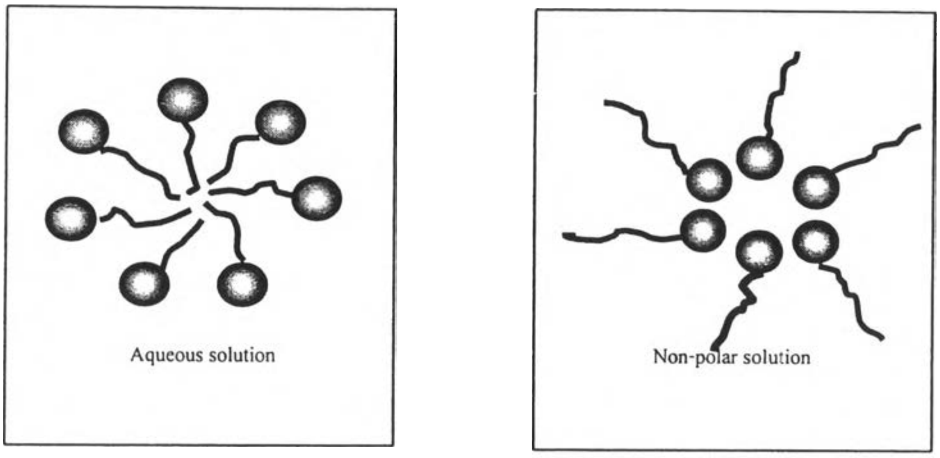


**Figure 2.2** The formation of micelle (Rosen,1989).



Normal micelle

Reverse micelle

**Figure 2.3** Normal micelles and inverse micelles (Rosen, 1989).

The increasing solubility of a compound associated with the formation of micelles or inverted micelles has been termed "Solubilization" by McBain (1950). The presence of micelles in the solution system has a special advantage that organic compounds, such as oil and hydrocarbons, or water can solubilize more into the solution. It is because the organic compounds or water can dissolve into the center core of micelles. Furthermore, the solubilization increases as the number of micelles in the solution increases (Rosen,1989).

Surfactants play an important role in separation processes 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 occur very rapidly. In addition, because of their amphipathic 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 (Rosen, 1989). 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 emulsifying agents are usually mixtures of two or more substances.

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 during the past 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

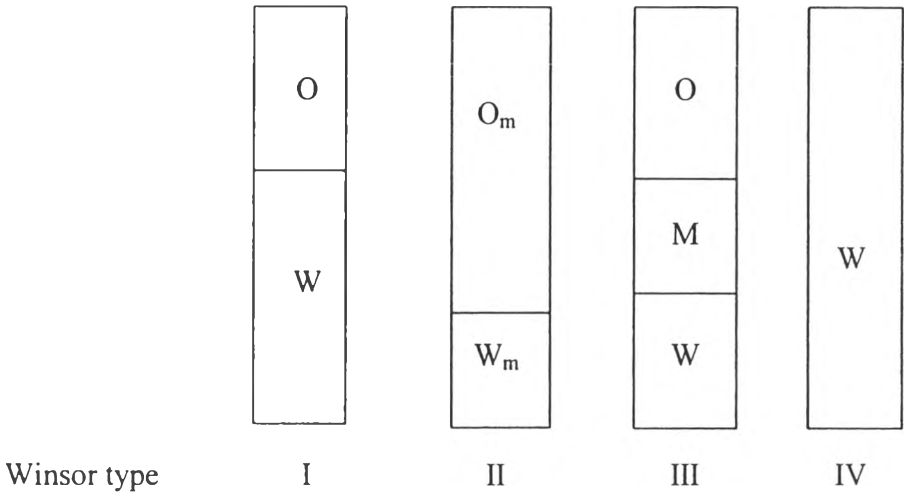
Microemulsions were scientifically described for the first time in 1943 as special colloidal dispersions or a transparent or translucent system formed spontaneously upon mixing oil and water with a relatively large amount of ionic surfactant together with a cosurfactant (Hoar and Schulman, ). Microemulsions are transparent dispersion containing two immiscible liquids with particles of 10-100 nm (0.01-0.1 μm) in diameters that are generally obtained upon mixing gently of oil and water in the presence of surfactants. They differ markedly from both macro- and miniemulsion in this respect, since these two types depend upon intense agitation for their formation (Rosen, 1989).

Microemulsions are generally prepared with more than one surfactant or with a mixture of a surfactant and a cosurfactant (e.g., a polar compound of intermediate chain length). Cosurfactant-free microemulsions can be also prepared (Holmberg, 1986). Unfortunately, microemulsion phases are not ubiquitous, but only found under certain carefully defined conditions. So in order to form microemulsions, the surfactant selection is an important step to obtain a proper balance between hydrophilic and hydrophobic properties for any particular oil. A study of the phase behavior, which is known as a map of the locations of in composition space, is a popular method to understand microemulsion.

The most studied phase equilibria of microemulsions are probably known as the Winsor-Type microemulsions (Winsor, 1954). There are four types of microemulsions as shown in Figure 2.4

1. *Winsor type I* : Oil in water microemulsion or oil-in-water microemulsions.in equilibrium with an excess oil phase
2. *Winsor type II* : Water in oil microemulsion in equilibrium with an excess water phase.
3. *Winsor type III* : The three phase system consists of non-droplet-type microemulsion (bicontinuous phase) in equilibrium with both excess oil and excess water phases. It is generally referred to as middle phase microemulsion.
4. *Winsor type IV* : The single phase of microemulsion phase appears.

A transformation from in the system Winsor's type I to type III to type II can be achieved by progressively changing temperature, salinity, the molecular structure of surfactant and cosurfactant, an oil to water ratio, or the structure of oil in a homologous series. This studied phase diagram is normally carried out by increasing the salinity or is known as a salinity scan, as illustrated in Figure 2.5. For example, a system by mixing equal volumes of surfactant solution and oil with a proper surfactant and cosurfactant. By increasing the salinity, one can simply visualize a progressive change in the phase diagram.



O = excess oil phase

$W_m$ = oil in water microemulsion

W = excess water phase

$O_m$ = water in oil microemulsion

M = middle phase microemulsion

Initial volume ratio of oil and water = 1:1

**Figure 2.4** Schematic diagram of types of microemulsions (Winsor, 1954).

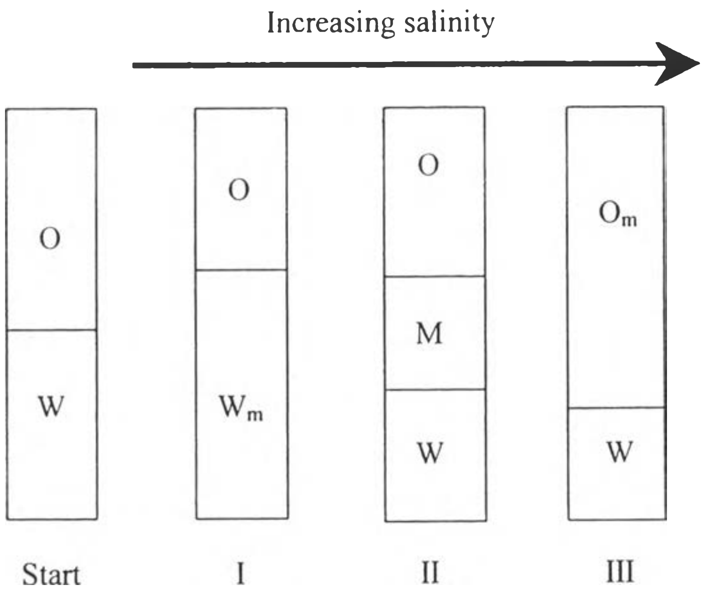


**Figure 2.5** Effect of salinity scan on phase diagram of microemulsion.

Moreover, the transition of Winsor's type I-III-II influences the two interesting properties of micreoemulsion, which is solubilization and interfacial tension (IFT), due to the changing of 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 Winsor's type I where oil-in-water (o/w) microemulsion exists along with an excess oil phase. IFT between the excess oil phase and the micellar solution ($\gamma_{o/m}$) decreases with increasing salinity. When the middle phase is formed, microemulsion becomes bicontinuous structure in equilibrium with excess oil and excess water phases. IFT between the excess oil and the middle phases ($\gamma_{o/m}$) and between the excess water and the middle phases ($\gamma_{w/m}$) further decrease. The point in the type III 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. If HLB is further decreased, Winsor's type III transforms to Winsor's type II microemulsion as shown on the right hand side of the figure. IFT between the excess water and the micellar phases ($\gamma_{w/m}$) increases rapidly.

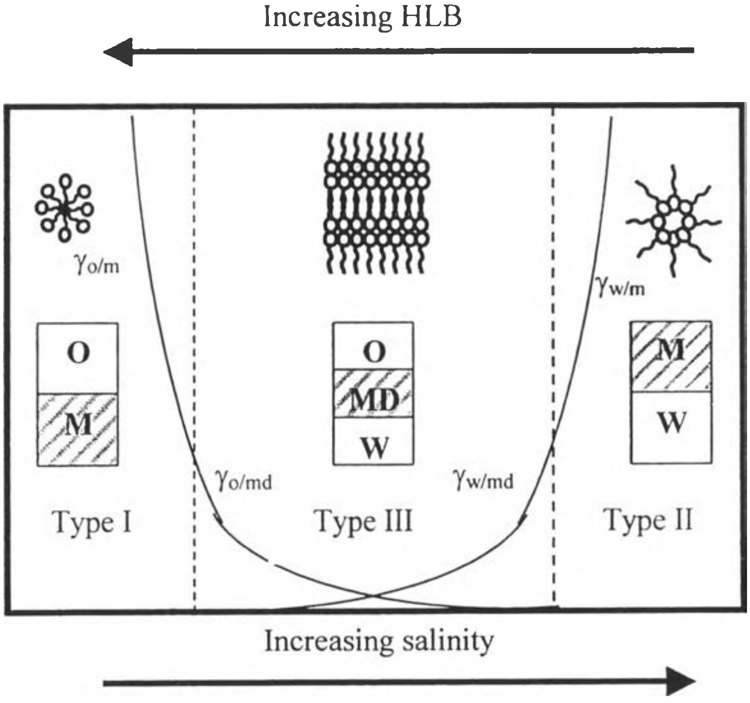


**Figure 2.6** The transition of microemulsion structure and interfacial tension as a function of salinity scan and HLB.

The correlation between interfacial tension and solubilization parameter (SP) is followed by Chun-Huh relationship, as shown in equation 2.1, and Figure 2.7. Figure 2.7 illustrates the change in solubilization parameters observed and the interfacial tension over the same range of salinity. It showed a direct correlation between the amount of oil (or water) solubilized and the interfacial tension, which it displays against the excess oil (or water) phase It can concluded that the higher the solubilization, the lower the interfacial tension is founded inside a middle phase microemulsion (Winsor type III) region.

$$S = \sqrt{\frac{C}{IFT}} \qquad 2.1$$

where, S = solubilization ratio; C = constant; IFT = interfacial tension,

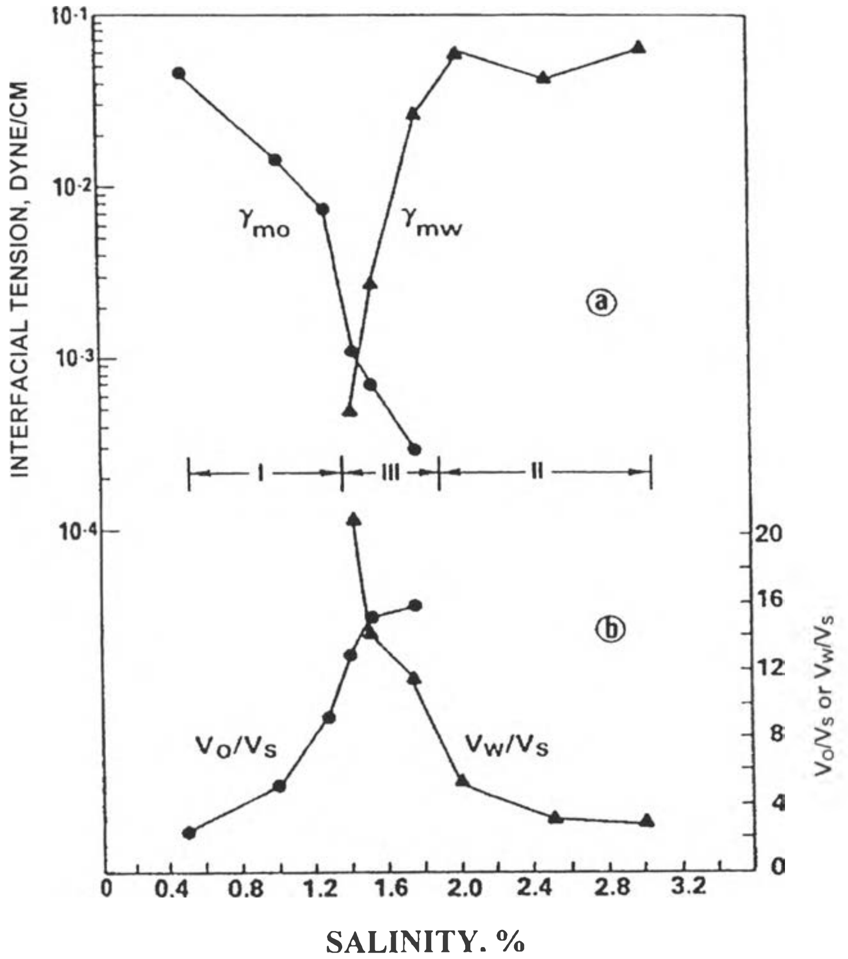


**Figure 2.7** Interfacial tensions (a) and solubilization parameters (b) as a function of salinity for the system MEA C12 OXS/TAA, oil, water NaCl (Bourrels , 1988).

The optimum state is designated as a number of properties which can be either a maximum or a minimum under practically the same conditions. Moreover, microemulsions have other special characteristics such as spontaneous formation and relatively large interfacial area as compared to other colloidal systems. These intriguing properties of microemulsion are useful for many industrial applications. It is believed that the ultra-low interfacial tension of Winsor type III microemulsion can maximize the separation efficiency of froth flotation system.

Mono- and di-hexadecyl diphenyloxide disulfonate sodium salt (DOWFAX 8390) surfactants have a robust nature for enhanced subsurface remediation. However, these surfactants are not as effective as others in enhancing contaminant solubility. Carter *et al* (1998) investigated various methods of increasing the solubility enhancement of the DOWFAX components. An introduction of a cosurfactant and adding electrolyte to form middle-phase microemulsions was found to be effective methods. The results demonstrated that an increase in the alkyl chain slight increased in contaminant solubility. Middle-phase microemulsion increased contaminant solubility by one to two order of magnitudes over DOWFAX surfactant alone, and by three to four order of magnitude as comparsed to pure water.

Wu (2000) used binary surfactant systems and nonalcoholic hydrotropes to formulate alcohol-free DPDS middle-phase microemulsions for low temperature environmental applications. The mixed surfactant system consisted of mono-chain DPDS and di-tail AOT. Octanoic acid and L-tartaric acid were used as nonalcoholic hydrotrope. For the system of C16MADS-AOT/ PCE microemulsions, the salinity scan for C16MADS-AOT with octanoic acid PCE middle-phase could be produced whereas with tartaric acid the middle-phase did not occur. By using DOWFAX 8390 instead of C16MADS, the middle of the three-phase region had an optimal solubilization parameter of 3,200 g/mol, which was larger than the previous C16MADS-AOT systems. However, for the DOWFAX 8390/PCE microemulsion, the requirement for $CaCl_2$ was too much to form middle phases. The higher optimal hardness, the wider three-phase region, and the smaller optimal solubilization parameter (about half of that of PCE microemulsion) were obtained from the decane middle-phase system. Based on the equivalent alkane carbon number (EACN), decane (EACN of 10) is obviously more hydrophobic than PCE (EACN of 2.9).

Both the supersolubilization and the middle-phase microemulsion regions were found to solubilize significantly more PCE than their corresponding micellar solutions. Maximum PCE solubilization was achieved with middle-phase microemulsion systems. For the C16MADS-AOT system, the supersolubilization region showed an improvement of the PCE solubilization of 8.7 times over the original system while the middle phase region gave the PCE solubilization about 13 times the value for the untreated system.

## 2.3 Froth Flotation

Adsorptive bubble separation is a process where a species is adsorbed at the interface between a dispersed phase (bubbles) and a continuous phase water. 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 particulate by frothing, whereas foam fractionation involves the separation of soluble species by foams (Scamehorn and Harwell, 1989).

Flotation is an important separation process that surfactants play a critical role because their interaction with the particle surface essentially determines the hydrophobicity of the particles and their probability of attachment to bubbles during collisions in the flotation cell (Somasundaran and Ramachandran, 1998). The success of flotation processes primarily depends on the tendency of surfactants to concentrate at the air-water interface and on the capability to make selected hydrophobic materials by means of adsorption on them or association with them.

In addition to the formation of froth, the presence of a surfactant dramatically increases the dispersion of air, 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 efficiency of froth flotation increases. Absolutely pure liquid does not generate froth and the presence of a surfactant is necessary to induce frothing. When a surfactant is added to solution, the surfactant molecules arrange themselve at the interface such that the hydrophilic or polar group is toward into solution phase and the hydrophobic or hydrocarbon chain in the air phase. As the surfactant molecules concentrate at the interface, they will reduce the interfacial tension leading to preferential adsorption of substance at the air-water interface.

Froth flotation has been widely using in many applications such as mineral separation and recovery ions from water and it has been recently applied for wastewater treatment. Surfactants used as flotation reagents include those that function as collectors, depressants, frothers, flocculants, dispersants, and filtering aids.

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. 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 form 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 flotation column, which are a bubbly zone and a froth zone. In a bubbly zone, air bubbles collect oil and hydrophobic particles and finally carry them 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 is shown in Figure 2.8. Froth flotation can be operated in batch and continuous modes.

Koutlemani *et al.* (1994) investigated foam flotation technique for recovering cobalt ions ($Co^{2+}$) from aqueous solutions. The study was carried out under acidic conditions where the ionic form of $Co^{2+}$ was predominant. Three surfactants, sodium dodecyl sulfate (SDS), cetyl pridinium chloride (CPC), and dodecylamine (DA), were used as collectors. Only SDS was found an appreciable caption of floating $Co^{2+}$ (recoveries over 90%). All of them, however, produced highly hydrated froths; part of the ion removal was due to hydraulic entrainment leading to rather low recoveries and separation efficiencies. It was concluded that the stabilization of froth would probably lead to a greatly improved $Co^{2+}$ recovery. The volumetric gas flow rate was found to affect the process in relation to the amount of surfactant added and the column diameter.

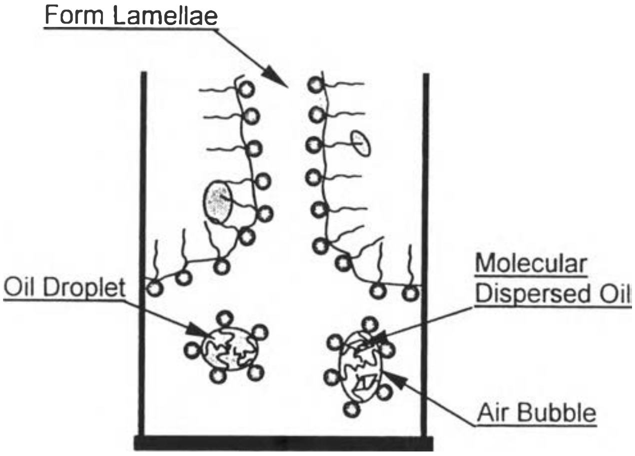


**Figure 2.8** Schematic of the froth flotation process.

Another application of flotation technique, which was used to recovery surfactant from water, was investigated by Tharapiwattananon *et al.* (1996). A simple continuous mode of foam flotation was used with three types of surfactants, sodium dodecyl sulfate (SDS), cetyl pyridinium chloride (CPC), and sodium n-hexadecyl di-phenyloxide disulfonate (Dowfax 8390 or DADS). The result showed that the surfactant concentration in the collapsed foam was 21.5 times the feed concentration. For example, CPC concentration in water could be reduced by 90% in one stage. The cationic surfactant was easier to remove from water than the anionic surfactant. The operating parameters (air flow rate, foam height, feed liquid surfactant concentration, and size of bubble) influenced an enrichment ratio and the surfactant recovery rate. However, the liquid height had little effect on the separation process.

Wungrattanasopon *et al.* (1996) studied the effect 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 pyridinium 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.

Pongstabodee *et al.* (1998) studied the removal of ortho-dichlorobenzene (ODCB) by froth flotation under Winsor's type III conditions. From the experimental results, it indicated that the removal efficiency of ODCB increased as the surfactant concentration increased, salinity increased (causing a Winsor's type I to 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.

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's type III system gave a higher percentage of ODCB removal than the Winsor's type II and I. For the system containing a total surfactant concentration of 7% and weight fraction of SDS of 0.8, the heighest of ODCB removal of 91% was obtained corresponding to the surfactant removal of 65%.

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 amounts 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 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 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 the water phase increased in the w-o system, the

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

Feng and Aldrich (2000) discussed the removal of diesel from aqueous emulsions by using flotation. The stability of these emulsions was characterized and factors such as pH and salinity affecting the stability of emulsion were investigated. Moreover, they studied the effects of anionic and cationic surfactants, original diesel content, air-flow rate, surfactant concentration and the air distributor sinter size. From the experimental results, it was concluded that when pH exceeded 11, the emulsion stability decreased rapidly, leading to very rapid destruction of the emulsion and the removal of diesel by flotation increased rapidly. An addition of the electrolyte (NaCl) was found to have some influence on its stability. The cationic surfactant such as octadecyl amine chloride (ODAC) and cetyl trimethyl ammonium chloride (CTMAC) were effective collectors than the anionic surfactant which was sodium dodecyl sulfate (SDS). Under the optimal conditions, approximately 99% of the diesel removal could be obtained. The residual diesel concentration in the effluent was less than 10 ppm.