CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Surfactant

The term of "surfactant" is a contraction of surface-active agents. A surfactant 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 the surface or interfacial 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, 2004). Surfactants are among the most versatile products of the chemical industry, appearing in such diverse products such as pharmaceuticals, detergents, drilling muds, motor oils 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 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 as follows:

1. *Anionic.* The surface-active portion of the molecule bears a negative charge.

2. *Cationic.* The surface-active portion of the molecule bears a positive charge.

3. *Zwitterionic.* Both positive and negative charges may be present in the surface-active portion.

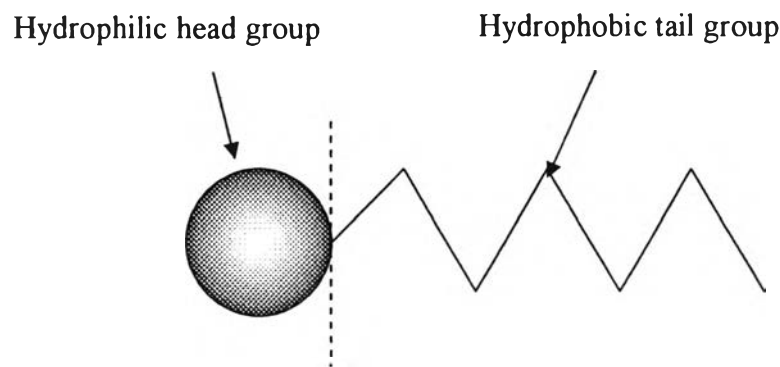4. *Nonionic.* The surface-active portion bears no apparent ionic charge.

Hydrophilic head group   Hydrophobic tail group

Figure 2.1 Schematic structure of the surfactant molecule monomer (Rosen, 2004).

One of the 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 core region and the hydrophilic groups exposed to the external aqueous solvent. These micelles may be spherical, rod-like, disk-like, or lamellae structures, depending upon the surfactant concentration and the physicochemical conditions such as pH, temperature and the presence of various electrolytes (Rosen, 2004). The interior region of normal micelles 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. The lowest surfactant concentration at which micelles are present is known as the critical micelle concentration (CMC). In a nonpolar solvent, inverse micelles occur with surfactant tail 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 surfactants, a surfactant micelle, and surfactants adsorbed at the air-water interface. If an 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 *et al.*, 1985).

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 frother or foam which is

skimmed off overhead. The presence of surfactant is 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 *et al.*, 2000).
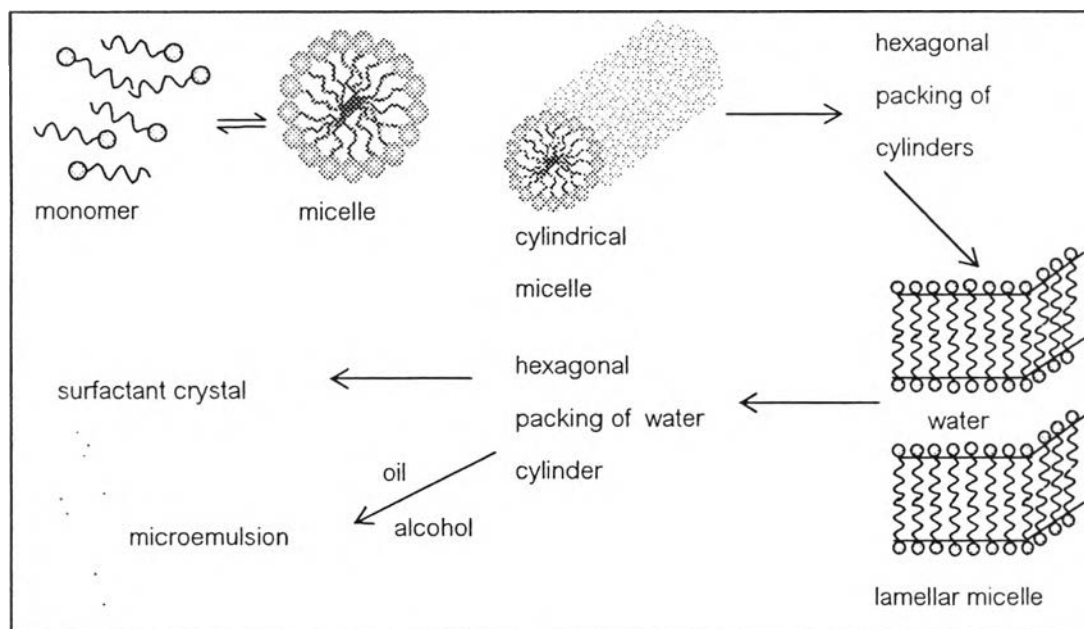

Figure 2.2 Schematic illustrations of surfactant association structures
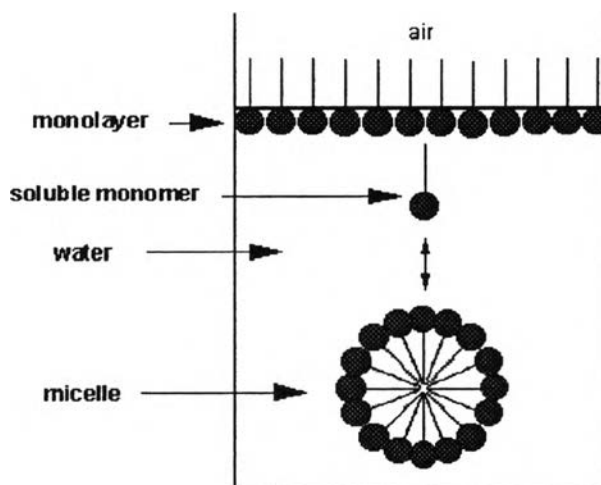(Sharma *et al.*, 1991).

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

2.2 Microemulsions

The term "microemulsions" was introduced by Hoar and Schulman (1943) 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 and Schechter, 1988). Some preferred the name "swollen micellar solutions" (Prince, 1977) or "solubilized micellar solutions" to describe precisely the same systems as those have called microemulsion by Hoar and Schulman (1943). A microemulsion is defined to be a thermodynamically stable dispersion system of water, immiscible oil and a surfactant which adsorbs on a monolayer at the interface between the two liquids. Microemulsions may contain electrolytes and one or more amphiphilic compounds (Winsor, 1968; Bourrel and Schechter, 1988).

A microemulsion system contains transparent dispersion of very small oil-in-water (O/W) or water-in-oil (W/O) droplets with particle diameters of 10-100 nm (0.01-0.1 μm) that are generally obtained upon mixing the ingredients gently (Rosen, 2004). 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. A 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).
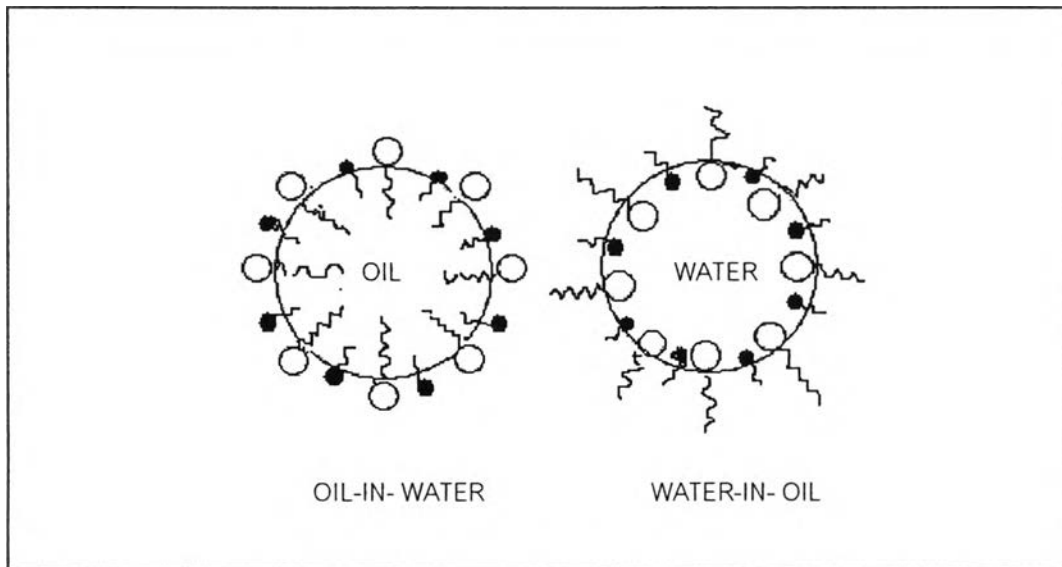
Figure 2.4 Schematic for oil-in-water (O/W) and water-in-oil (W/O) microemulsion
structures (the smaller molecules represent cosurfactant) (Rosen, 2004).

When a water-soluble surfactant is added to water under 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 an Winsor's type I microemulsion (Winsor, 1968).
Under the proper conditions, as a variable (e.g. salinity, temperature) is varied, this
system can transform from the two-phase system of the Winsor's 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 middle phase
containing high levels of both water and oil and most of the surfactant, as shown in
Figure 2.5. This system, known as a Winsor's type III microemulsion, 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. The condition corresponding to equal volumes of oil and water
being transferring from the excess phases to form the Winsor's type III
microemulsion approximately corresponds to the minimum equal interfacial tensions
between the excess phases and the middle phase. 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's type II

microemulsion, as shown in Figure 2.5. The factors that affect the phase transition of microemulsions are temperature, salinity, oil-to-water ratio, molecular structure of surfactant and cosurfactant and nature of oil (Winsor, 1968).

Winsor's
type   I   III   II   IV
Microemulsion

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        I              III             II              IV
   ┌─────────┐    ┌─────────┐    ┌─────────┐    ┌─────────┐
   │         │    │    o    │    │         │    │         │
   │    o    │    ├─────────┤    │   o/m   │    │         │
   │         │    │    m    │    │         │    │    m    │
   ├─────────┤    ├─────────┤    ├─────────┤    │         │
   │   w/m   │    │    w    │    │    w    │    │         │
   └─────────┘    └─────────┘    └─────────┘    └─────────┘
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increasing
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Variable changing (e.g. temperature for a nonionic surfactant system, salinity for an ionic surfactant system)

o= oil phase

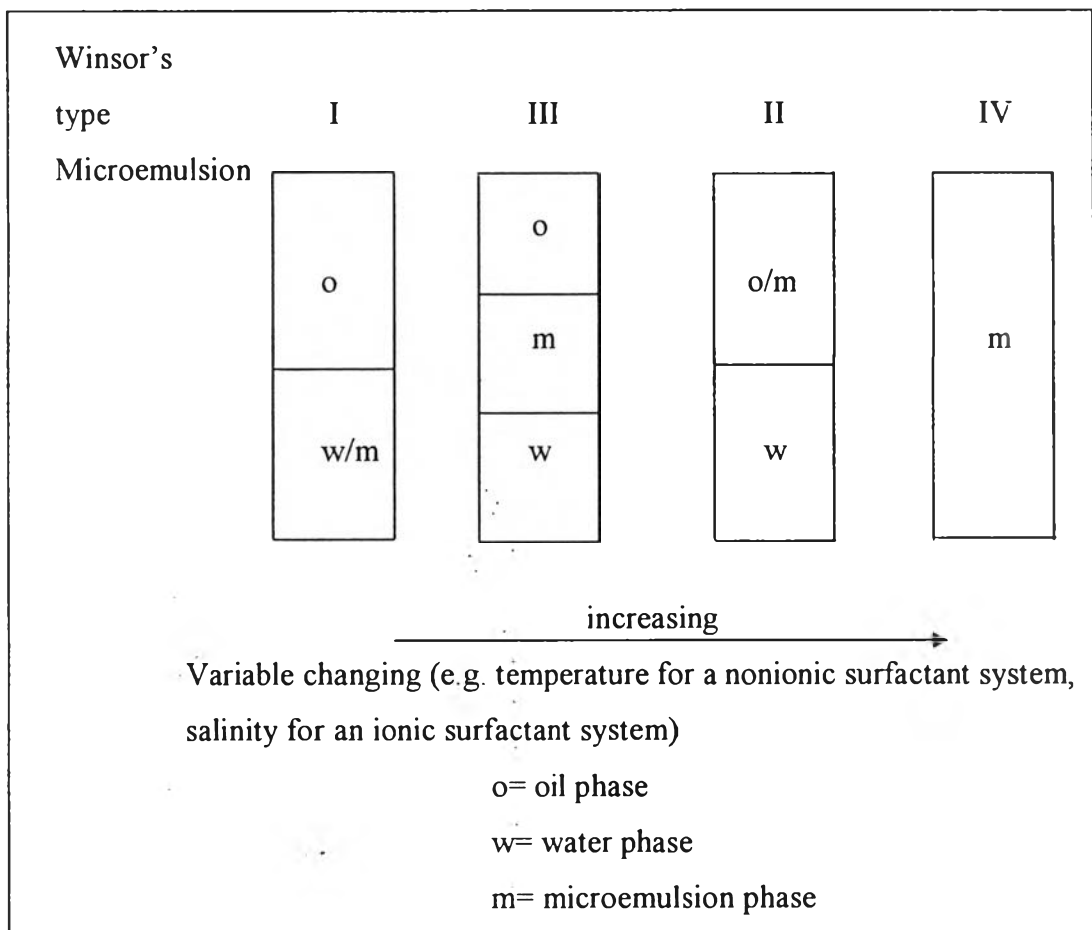w= water phase

m= microemulsion phase

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

Microemulsions have been found to have several potential applications including oil recovery and froth flotation for oil removal. Pondstabodee et al. (1998) reported that the oil removal efficiency of froth flotation was maximized when the system was in the Winsor's type III microemulsion region. 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 (Bourrel and Schechter, 1988; Scamehorn and Harwell, 2000).

2.3 Extended Surfactants

Extended surfactants are surfactants which groups of intermediate polarity, such as polypropyleneoxides or copolymers of propyleneoxides (PO) and ethyleneoxide (EO), are inserted between the hydrocarbon tail and hydrophilic head group. According to the unique molecular structure, the surfactant structure is extended out further into both the oil and water phases, offering a smoother transition between the hydrophilic and hydrophobic regions of the interface, which provides a more suitable environment for solubilizing hydrophilic and lipophilic molecules. Additionally, the Gibbs adsorption equation leads us to expect that a thickening of the interfacial region between the two phases should result in an increase in adsorption at the interface and a reduction of interfacial tension (IFT) (Witthayapanyanon et al., 2006). These surfactants are water-soluble and can be formulated in relatively high electrolyte concentrations without surfactant precipitation, despite of the relatively large molecular weight of these surfactants. Several researchers (Miñana-Pérez et al., 1995; Huang et al., 2004; Yanatatsaneejit et al., 2005a; Yanatatsaneejit et al., 2005b) have demonstrated the superior of these extended surfactants to enhance oil solubilization and microemulsions with highly hydrophobic oils.

In this study, ALFOTERRA® 145-5S ($C_{14-15}(PO)_5SO_4Na$) exhibits a unique extended surfactant structure allowing improved solubilization of oily materials in an aqueous medium. The monobranched alkyl hydrophobe allows for greater interaction with the oil phase while maintaining good solubility. These two factors give the surfactant unique emulsification properties and ultralow interfacial surface tension. ALFOTERRA® can be used in a wide variety of industrial and personal care applications such as enhancing oil recovery, soil remediation, drill cutting washing, oil/seed extraction, dry cleaning, industrial cleaning, personal care formulations (Sasol North America, 2008). Figure 2.6 shows the general structure of this extended surfactant.
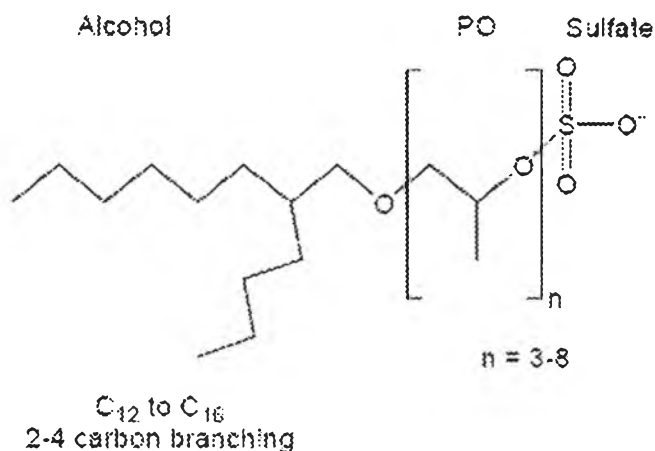
Figure 2.6 General structure of the ALFOTERRA® extended surfactant (Sasol North America, 2008).

2.4 Colloidal Gas Aphron (CGA)

CGA was first described by Sebba as microfoams with colloidal properties. The term of colloidal is used because of the small size of the bubbles generated (10-100 μm in diameter). CGA can be created by intense stirring (5,000-10,000 rpm) of a surfactant solution (Sebba, 1971 and 1987). The intense stirring of the surfactant solution causes air entrainment in microbubbles with a relatively high stability. The structure of CGA as proposed by Sebba (Sebba, 1987) composes of a gaseous inner core surrounded by a thin aqueous surfactant film or shell composed of two surfactant layers; moreover, there is a third surfactant layer that stabilizes this structure (see Figure 2.7). The attractive features of CGA have been reported that: 1) CGA has a large interfacial area per unit volume, as a result of its small size and high gas hold-up, 2) CGA exhibits relatively high stability, 3) flow properties of CGA are similar to those of pure water (e.g. can be pumped easily, without collapse, from one location to another), 4) the CGA phase can be separated easily from the bulk liquid phase due to its buoyancy, and 5) CGA possesses an extremely large interfacial area. As a consequence of these unique properties, CGA was employed in several studies such as flotation for the removal of biological and non-biological products (Hashim and Gupta, 1998; Basu and Malpani, 2001), protein recovery (Nobel and Varley,

1999; Jauregi and Varley, 1999; Jarudilokkul *et al.*, 2004), bioremediation (Jauregi and Varley, 1999), and the enhancement of oxygen mass transfer (Dai *et al.*, 2004).
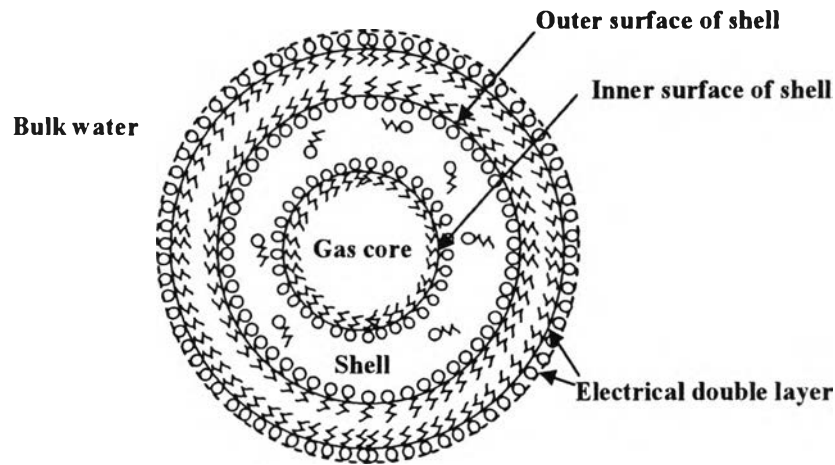

Figure 2.7 The structure of CGA proposed by Sebba (1987).

2.5 Foams

Foam is generated when a gas and a liquid are mixed together in a container, and then shaken; the gas phase has become a collection of bubbles that are dispersed in the continuous liquid phase, as shown in Figure 2.8. The gas phase is separated from the thin liquid film (lamellae). A foam structure can always be formed in a liquid if gas bubbles are generated faster than the drainage of liquid. However, the bubble coalescence can occur as soon as the liquid between them has drained away (Schramm and Wassmuth, 1994).Gas bubbles will ascend up and separate, more or less depending on Stokes' law. In pure water, gas bubbles coalescence very rapidly and also foam cannot be produced. The adsorption of surfactant molecules at a gas-liquid interface will enhance the thin film stability between the gas bubbles results in a stable foam structure. The presence of surfactant results in the reduction of surface tension, leading to a minimum of mechanical energy input requirement for increasing interfacial area. Moreover, the surfactant prevents bubble coalescence.
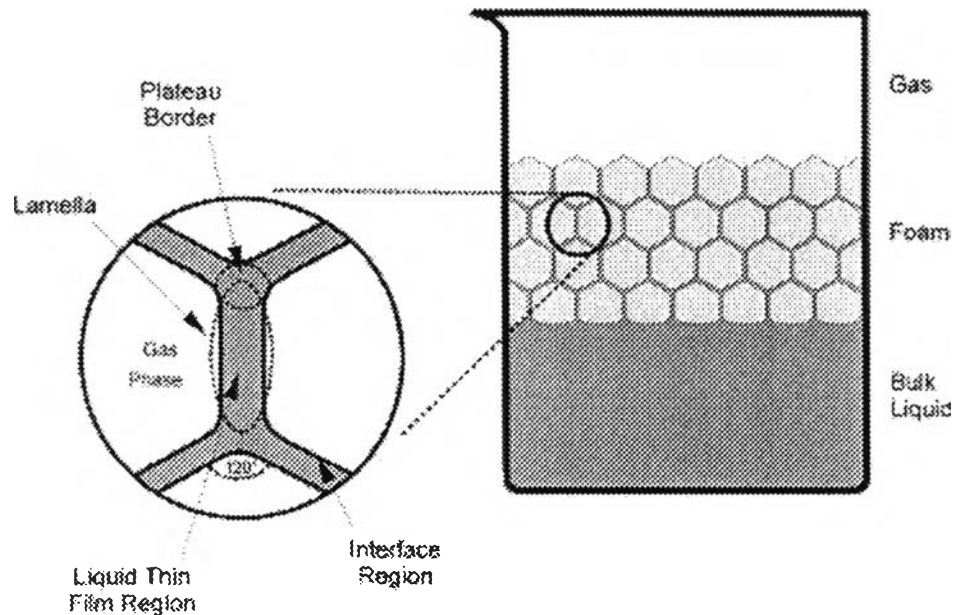
Figure 2.8 A generalized foam system showing aspects of a foam lamellae (Schramm and Wassmuth, 1994).

There are two significant factors in foaming which are how easily it foams (foamability) and how long the produced foams can exist (Wilson, 1996).

2.5.1 Foamability

Foamability is the foam-generating power of a liquid, and foamability is directly governed by physical properties such as viscosity, surface tension, and others within the liquid (Wilson, 1996).

2.5.2 Foam Stability

The static stability if foam is defined as the ability to resist bubble breakdown which causes the coalescence of gas bubbles or collapse. The liquid drains out from the foam lamellae, leading to the foam instabilities (Chambers, 1994). Actually, foams are thermodynamically unstable, the term stable mean relatively stable in a kinetic sense (Schramm and Wassmuth, 1994).

There are several factors affecting the stability of the foam which relate to foam breakdown and collapse. The rate of deterioration of a liquid foam is governed by the relatives activities of three interactive physical phenomena:

gravitational separation (drainage), flocculation and coalescence, and Oswald ripening (disproportionation) (Wilson, 1996).

The gravitational separation relates with the ascending of gas bubbles through the foam mass (a phenomenon is well known as creaming). At the same time, liquid drains out from the produced foam under the influence of gravity through the lamellae and Plateau borders between the bubbles. The rate of liquid drainage is related to the viscosity of the liquid phase of the foam and the presence of any thickeners or a secondary disperse phase.

The coalescence relates with the thinning and ultimate rupture of the foam lamellae which separating two or more bubbles, after that rearrange to form a larger bubble. This phenomenon usually occurs with the thinning of the lamellae due to prolonged drainage.

The disproportionation, or Oswald ripening is the loss of gas by diffusion from a small bubble with high Laplace pressure to a larger bubble with lower pressure.

In order to quantify foam stability, foam half-life is measured. Foam half-life is the time needed for foam to drain its half liquid volume. A longer half-life time represents higher stability of produced foam. Foam stability is affected by several factors including type and concentration of surfactant, salinity, viscosity and temperature. In addition, foam half-life is reportedly a function of column height (Chambers, 1994).

2.6 Froth Flotation

Flotation is one of adsorptive bubble separations which are a process where a species is adsorbed at the interfacial boundary between a dispersed phase (bubbles) and a continuous phase. Flotation involves the removal of particulates 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 a vessel and are concentrated in the foam (called a froth in this case), which is skimmed off overhead. The presence of a surfactant is useful to both

facilitate adhesion of a target material to the bubble surface and to acts as a froth promoter/stabilizer. (Feng and Aldrich, 2000).

The accumulation of surfactants at the air/water interface, resulting in lowering the excess Gibbs free energy at 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 on bubbles rising through a liquid is the basis of the froth flotation process (Scamehorn and Harwell, 2000).

Figure 2.9 shows a basic configuration of froth flotation process. In froth flotation operation to remove oil from water, there is a driving force that causes oil droplets from the solution to attach to the surface of the air bubbles rising through a 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 bubbly zone and a froth zone. For continuous froth flotation operation, a feed solution is generally introduced continuously at the top of the froth flotation column while the treated stream is 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 picked-up some of the undesirable hydrophilic particles. For an oil-containing wastewater, oil is carried with foam or froth accumulating at the top of the column and then froth is skimmed off and broken as liquid (Pal and Maliyah, 1990).
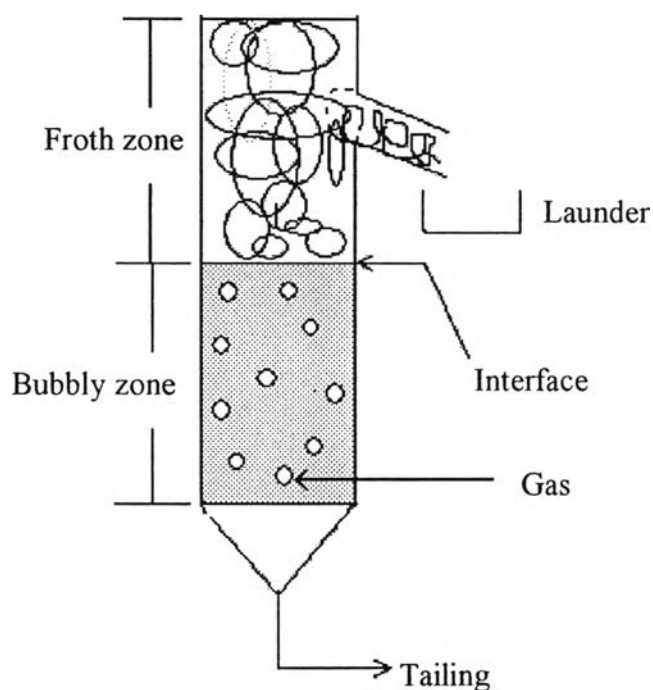
Figure 2.9 Schematic of a froth flotation column (Pal and Maliyah, 1990).

Froth flotation technique can be operated in both batch and continuous modes. In batch mode of operation, solution is transferred to the column at the outset. After that air is introduced through the column until no further foaming occurs due to the depletion of surfactant. The surfactant concentrations in the solution within the column and in the collapsed foam are continuously changing during the operation. In a continuous mode of 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 (Carleson, 1989). Because of 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 constant concentrations of them in the froth.

Pondsatabodee *et al.* (1998) studied the removal of ortho-dichlorobenzene (ODCB) from water by batch froth flotation under the Winsor's type III microemulsion condition. From the results, the ODCB removal efficiency increased

as the initial surfactant concentration increased; the salinity increased causing a transition of a Winsor's type I to Type III. The cationic surfactant (CPC) was more effective to remove ODCB than either monosulfate or the disulfate anionic surfactants.

To enhance the formation of microemulsions with ODCB, Chavadej *et al.* (2004) focused on the use of mixed anionic and nonionic surfactants; sodium dodecyl sulfate (SDS) and nonylphenol polyethoxylate $(NP(EO)_{10})$. The optimum condition was achieved at 5% total surfactant concentration with the fraction of SDS of 0.5. From the results of froth flotation experiment, under the Winsor's type III microemulsion condition, the system had a higher oil removal than those under the Winsor's type I or II microemulsion condition. The highest oil removal of 91% was achieved at 7% total surfactant concentration and a weight fraction of SDS of 0.8. Moreover, the selectivity of oil-to-water in the overhead froth was much higher than that of the feed under the Winsor's type III microemulsion condition. In addition, the maximum oil removal was achieved when the system was in the Winsor's type III microemulsion region.

Chavadej *et al.* (2004), studied the relation of Winsor's type III microemulsion and the removal of ortho-dichlorobenzene (ODCB) by using mixed surfactant systems, sodium dodecyl sulfate (SDS) and nonylphenol polyethoxylate $(NP(EO)_{10})$. Froth flotation experiments were studied at 3 wt.% and 5 wt.% total surfactant concentrations. The results in this study confirmed that the highest oil removal corresponded to the formation of Winsor's type III microemulsion. In addition, the combination of two phases of the Winsor's type III microemulsion system was studied to identify which phase was the main source of the removed oil. The results revealed that most the removed oil came from the excess oil phase instead of the middle phase. Moreover, the optimum salinity was found to be 0.5%.

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. It was concluded that when pH increased, the

diesel-water emulsion stability constant (K_s) increased as a result of the emulsion unstable, leading to rapid destruction of the emulsion, and enhancing the diesel removal efficiency. The emulsion was gradually destabilized by the increase in the amount of NaCl. The oil could be removed more effectively with the cationic surfactants, octadecyl amine chloride (ODAC) and cetyl trimethyl ammonium chloride (CTMAC), but less with the anionic surfactant, SDS. Under the optimal conditions, up to 99% of the diesel could be removed.

Samuthjarindr (2001) studied the relationship between foam stability and froth flotation efficiency in oily wastewater treatment. Sodium dodecyl benzenesulfonate (SDBS) and a cationic polyelectrolyte, Novous CE 2680 were used as a 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 using a continuous froth flotation unit. From the experimental results, 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 0.5 CMC of the surfactant was used, the oil removal efficiency increased to 77.5%.

Yanatatsaneejit *et al.* (2005a) investigated the relationship of the froth flotation performance in removal of emulsified ethylbenzene in water under the microemulsion conditions and with foam characteristics. The surfactant used was dihexyl sulfosuccinate (Aerosol MA or AMA) which can form microemulsions with ethylbenzene. The phase study was focused on Winsor's type III microemulsions with etylbenzene which generally correspond to ultralow interfacial tension between oil and water phases. The lowest interfacial tension was obtained at 1 wt.% AMA and 3 wt.% NaCl, while the interfacial tension was not substantially influenced by oil-to-water ratio. The highest oil removal was achieved in froth flotation with

0.3 wt.% AMA and 3 wt.% NaCl. No separation was experienced when the NaCl concentration exceeded 4 wt.% due to the poor foamability of the froth formed under these conditions. Therefore, the results demonstrated that both interfacial tension and foam characteristics influenced the efficiency of oil removal in the froth flotation process.

In another paper of this series (Yanatatsaneejit *et al.*, 2005b), dihexyl sulfosuccinate (Aerosol MA or AMA) was used to prepare microemulsions with ethylbenzene which were used to run froth flotation experiments to remove emulsified ethylbenzene from water. Oil removal, surfactant removal, and enrichment ratio were used to evaluate the performance of froth flotation. In this study, the effects of air flow rate, oil-to-water ratio, and equilibration time were investigated. A very high air flow rate was found to create more turbulence in the froth flotation column, resulting in low oil removal. As the oil-to-water ratio decreased, the enrichment ratio increased whereas the oil removal slightly decreased. The froth flotation column with a feed solution in which the oil and water had been allowed to equilibrate was found to yield much a higher ethylbenzene removal than that with a nonequilibrium feed solution. When the feed solution was agitated for 40 min to induce a state closer to equilibrium than with no mixing, the ethylbenzene removal is nearly as high as that with the equilibrium feed solution.

Yanatatsaneejit (2004) found that to achieve high performance for froth flotation operation, the combination of the ultralow interfacial tension between excess oil phase and excess water phase and the high foam production rate as well as high stability of foam produced had to be obtained. To obtain an ultralow interfacial tension, a Winsor's type III microemulsion or middle phase had to be formed. In this study, branched alcohol propoxylate sulfate sodium salt with 14-15 carbon number and 4 PO groups ($C_{14-15}(PO)_4SO_4Na$) was used to form microemulsions with diesel. From the results in this work, an increase in surfactant concentration decreased interfacial tension (IFT), and increased foam stability. To improve Winsor's type III microemulsion formation, NaCl was added and the minimum IFT was achieved at 5 wt.% NaCl. However, this optimum salinity was not possible to be operated in froth flotation experiment due to poor foam characteristics. The results indicated that

both IFT and foam characteristics should be optimized to achieve high efficiency of oil removal in froth flotation operation. Unlike the ethylbenzene work (Yanatatsaneejit *et al.* 2005a), the agitated solution before operated in the flotation column yielded the lowest diesel removal efficiency because of the poor foam characteristics.

2.7 Studied Oils in this Work

2.7.1 Diesel oil

Diesel oil is a petroleum fraction which is composed primarily of aliphatic (linear of unbranched) hydrocarbons. Diesel oil is classed as middle distillates and is more dense than gasoline, thus providing more energy per unit volume than gasoline. It is a complex combination of hydrocarbons produced by the distillation of crude oil. Diesel oil consists of hydrocarbons having carbon numbers in the range of C_9-C_{20} and its boiling point is in the range of approximately 163-357°C.

Diesel oil is one of the most important transportation fuels in the growing transportation around the world. Because diesel engines possess more thermally-efficient than gasoline engines, it is anticipated that diesel oil demand and utilization will still rise substantially (Song *et al.*, 2000). According to its widespread usage in several industrial processes such as metal manufacture and machining, food processors as well as petroleum refinery plant, diesel oil is often found in several wastewaters (Patterson, 1975). Apart from the contamination of groundwater by diesel oil leakage, several industrial wastewaters have been found to contain significant amounts of oils including diesel oil.

2.7.2 Motor oil

Motor oil is among the most frequently spilled oils, because of their widespread usage with vehicles and machinery (Johnson, 1986). Motor oils are complex mixtures of predominantly hydrocarbons. Generally, motor oils contain

several hydrocarbons having low molecular weights as low as 250 molecular weight units (Daltons) for low viscosity motor oils and molecular weights as high as 1,000 Daltons for high viscosity motor oils (Kirk-Othmer, 1981; Johnson, 1986; Vartanian, 1991). Physical properties, such as viscosity and viscosity-temperature-pressure characteristics, depend largely on the relative distribution of paraffins, naphthenes, and aromatic compounds. The compositions in a typical motor oil are approximately 15% paraffins (alkanes), 54% naphthenes (cyclo paraffins), and 31% aromatic compounds. Several additives are present to meet the expected service conditions. These additives include a detergent, dispersant, oxidation inhibitor, rust inhibitor, pour-point depressant, and viscosity improver (Vartanian, 1991).

Used motor oils are a very dangerous pollutant since they contain several carcinogenic substances such as polyaromatic hydrocarbons (PAH). The PAHs accumulation in used motor oils results from the combustion of petrol (Irwin, 1997). Used motor oil also contains a high level of metals, so disposal by burning is not an exceptable solution because heavy metals are disperse to the atmosphere after incineration process (Vazquez-Duhalt et al., 1986).

2.7.3 Cutting oil

Cutting oil is a emulsionable fluid which is composed of an oil/water microemulsion: a complex mixture of water, oils, organics, surfactants, co-surfactants, and other additives. Cutting oil is widely used in metal-working processes to lubricate and refrigerate workpieces during drilling and cutting. There are two main types of metal working fluids: water-based and oil-based coolants. After long use, cutting oils accumulate large amounts of solid particles as well as the changes in their chemical and physical properties, resulting in the deterioration of lubricating and refrigerating properties. The spent motor oils have been reportedly found to contain heavy metals, biocides, microorganisms and harmful decomposition products (Perez et al., 2006). After a number of operations, the cutting oils have to be discarded without proper handling of the spent motor oils, both underground water and surface water may be subject to be contaminated. Therefore, treatment of cutting oil is necessary before discharging to the environment. (Hadj-Ziane and Moulay,

2004). According to, environment regulations, the acceptable concentrations of hydrocarbons in effluents must below 10 ppm (Rios *et al.*, 1998).