CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Surfactants

Surfactants are among the most versatile products of the chemical industry, appearing in such diverse products such as motor oils, pharmaceuticals, detergents, drilling muds in prospecting for petroleum, and flotation agents used in ore processing. In the last decade surfactant applications have extended to such high-technology areas as electronic printing, magnetic recording, biotechnology, micro-electronics, and viral research (Rosen, 2004). 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 the surface or interfacial free energies of those surfaces (or interfaces). 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).

Surfactants have a characteristic molecular structure consisting of a hydrophilic (water-loving) part, which is made of a water soluble species such as an ionic or highly polar groups, and a hydrophobic (water-hating) part which is usually a long-chain hydrocarbon or non-polar group referred to as head and tail, respectively (as shown in Figure 2.1).
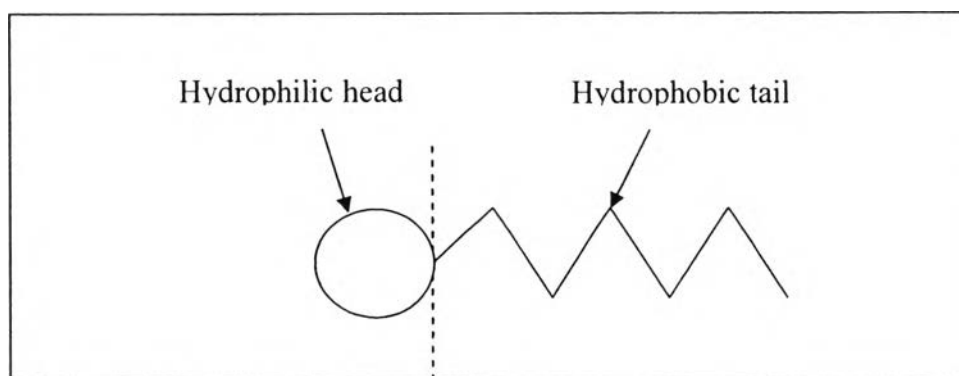
Hydrophilic head   Hydrophobic tail

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

Surfactants are classified into four main types according to the nature of the hydrophilic group: anionic, cationic, zwitterionic, and nonionic surfactants (Rosen, 2004).

1. *Anionic.* The surface-active portion of the molecule bears a negative charge; for example, $RCOO^-Na^+$ (soap), $RC_6H_4SO_3^-Na^+$ (alkylbenzene sulfonate).

2. *Cationic.* 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.* Both positive and negative charges may be present in the surface-active portion; for example, $RN^+H_2CH_2COO^-$ (long-chain amino acid), $RN^+(CH_3)_2CH_2CH_2SO_3^-$ (Sulfobetaine).

4. Nonionic. The surface-active portion bears no apparent ionic charge; for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long-chain fatty acid), $RC_6H_4(OC_2H_4)_xOH$ (polyoxyethylenated alkylphenol).

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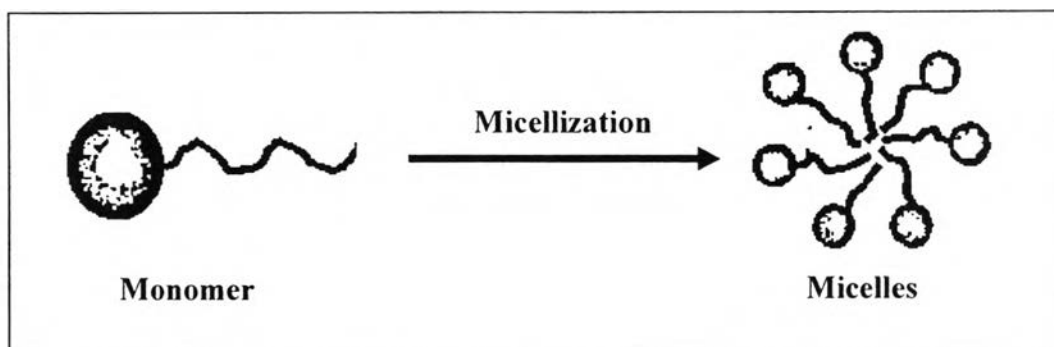
Figure 2.2 Schematic of a monomer, micelles, and micellization.

There are two types of micelles which are normal and inverse (or reverse) micelles. In water or an aqueous solution, normal micelles are formed with the hydrophobic part in the interior and the hydrophilic part in the external. On the other hand, inverse micelles are formed in a non-polar solvent with the hydrophilic part in the interior and the hydrophobic part in the exterior. A schematic of normal and inverse micelles is shown in Figure 2.3. The formation of various association structures with increasing surfactant concentration is shown in Figure 2.4. It is likely that surfactant molecules may form spherical, cylindrical, hexagonal, lamellar, or reverse micelle structures, depending on the 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 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).
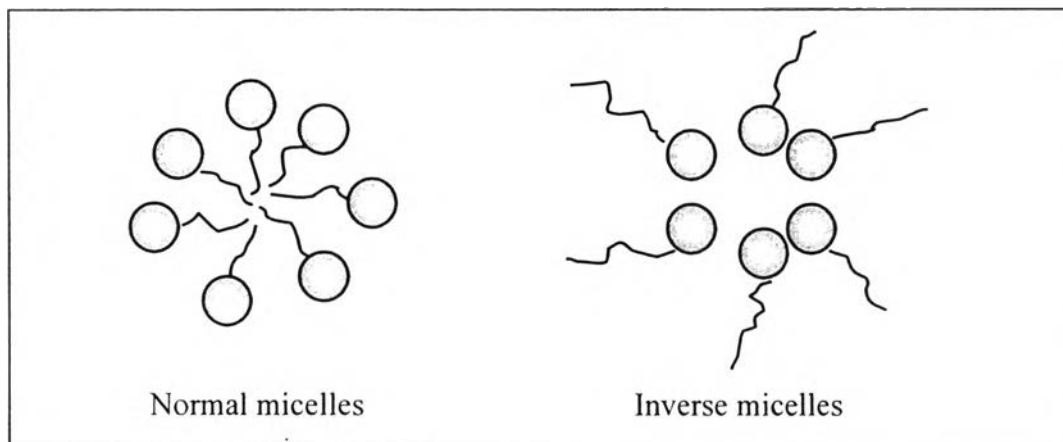
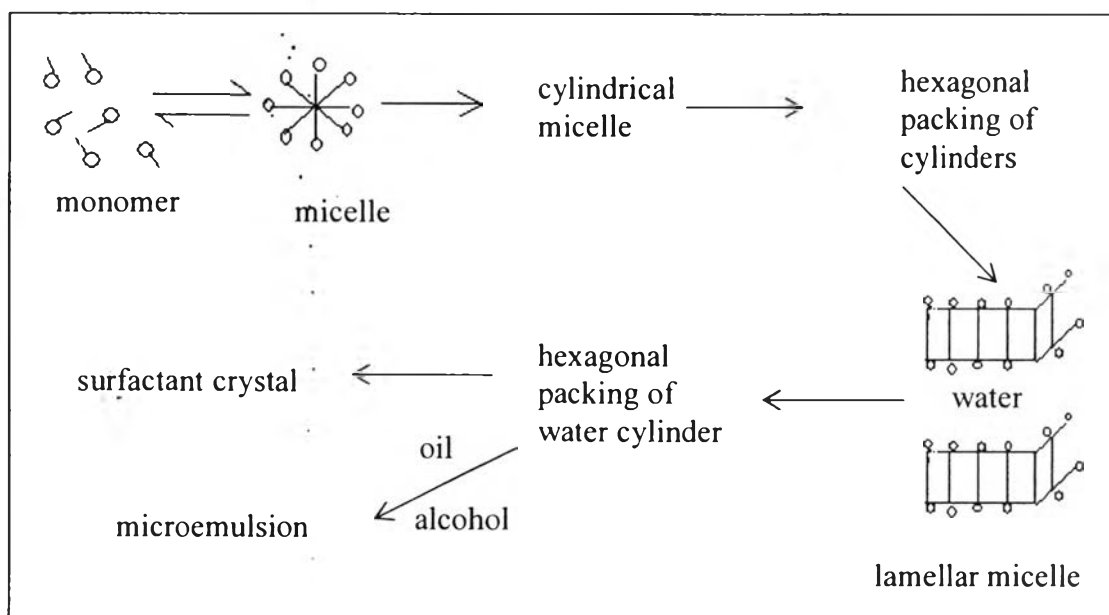**Figure 2.3** Schematic of normal micelles and inverse micelles.

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

Surfactants play an important role in separation procedures such as flotation. Flotation is an interesting process since it can serve as an energy barrier, thus enabling the fluid media to be stabilized in the form of very small globules and thereby exposing an enormously increased interfacial area where transfer from one phase to another can occur 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 Extended Surfactants

By definition, the oil and water phases of a surfactant-oil-water system are immiscible, and the role of the amphiphile is to reduce the miscibility gap, until the three components are eventually cosolubilized into a so-called microemulsion. The minimum interfacial tension was associated with a maximum solubilization of oil and water in the microemulsion phase (Perez et al., 1995).

A review of the work carried out before 1987 has been published (Bourrel and Schechter, 1988), and explains different ways to improve solubilization. At equal interfacial coverage, the best way to enhance the interactions on both sides of the interface is to use a surfactant with both a larger hydrophobic and a larger hydrophilic groups; the word "larger" actually means that a greater interaction results from it, as expected from a simple length increase. There is neither a theoretical nor an experimental problem on the water side of the interface, since the surfactant average number of ethylene oxide groups per molecule (EON) and the salinity formulation variables allow precise monitoring of what is happening in nonionic and ionic surfactant systems, respectively. The problem is on the oil side, i.e. with the surfactant hydrophobic group. In effect, a larger interaction between this hydrophobic group and the oil phase is expected to result from an increase in length and/or an increase in linearity (if it is branched). However, such an increase has two direct effects on the system. On the one hand, longer tail surfactants are less soluble in water, and at some point the solubility becomes lower than the critical micelle concentration (CMC) and the so-called Kraft point of the ionic surfactant is reached (Rosen, 2004); if no micelle can form, no microemulsion can form, and the surfactant actually precipitates. On the other hand, a longer tail tends to produce more organized solubilization structures, so-called mesophases or liquid crystals, rather than microemulsions. The melting of the liquid crystals can be achieved without changing the temperature by adding short chain alcohols, but this results in general in a decrease in solubilization, since the al-

cohol molecules adsorbed at the interface displace the surfactant molecules, and reduce the overall number of interactions per unit area (Bourrel and Schechter, 1988).

In order to overcome the dilemma between a longer tail that increases the solubilization and lesser solubility of the surfactant, which places an upper limit at say 20 methylene groups per molecule, the so-called lipophilic linker feature was proposed (Graciaa, Lachaise, Cucuphat, and Salager, 1993). This consists of forming an apparently longer tail surfactant at the interface by linking the surfactant and a lipophilic additive that is introduced separately into the system, and thus does not affect the surfactant solubility. In order to avoid gel-like structures, a proper but not-so-good fit is found between the surfactant tail and the additive, for instance by mixing linear and branched chains.

Fig. 2.5 indicates the role of the lipophilic linker, which is a slightly polar oil, such as a long-chain alcohol (more than 8 carbon atoms), or phenol. It cannot be considered as a conventional co-surfactant component of the interfacial layer, since it was found to perform better when it adsorbed less at the interface. It seems to be located in the oil layer adjacent to the interfacial layer, as evidenced in recent oil segregation studies (Graciaa, Lachaise, Cucuphat, and Salager, 1993). As a consequence of their polar group, the lipophilic linker molecules are likely to have an average orientation perpendicular to the interface. This preferred orientation tends to organize the oil layers located next to the interface (as illustrated in Fig. 2.5), thus providing extra interactions with the surfactant molecules. The lipophilic linker is then some kind of intermediate between the surfactant layer (adsorbed at the interface) and the bulk oil phase, where molecules are oriented at random. The lipophilic linker role is out of the scope of Winsor's R, since the increase in interaction on the oil side is not compensated on the water side. This increase is believed to be due to the extension of the surfactant interaction with oil through the intermediary role of the lipophilic linker.

Following this finding, the lipophilic linker additive was seen as a substance able to produce a layer of intermediate polarity and of some thickness in the oil phase located in the neighborhood of the interface. It was then conjectured that such an intermediate polarity region could be incorporated intramolecularly, i.e. inside the surfactant molecule, without precipitation. This idea gave birth to the so-called extended

surfactants, which contain an intermediate polarity part located between the conventional hydrophile and lipophile groups (Perez *et al.,* 1995).

The so-called extended surfactant has a poly-propylene oxide chain inserted in between the conventional alkyl and ether sulfate groups (as shown in Figure 2.6). Thus, the surfactant and film thickness is increased, and the interfacial tension is expected to increase (per the Chun-Huh relationship). These surfactants exhibit a critical micelle concentration and a cloud point that changes with number of propylene oxide groups per molecule.
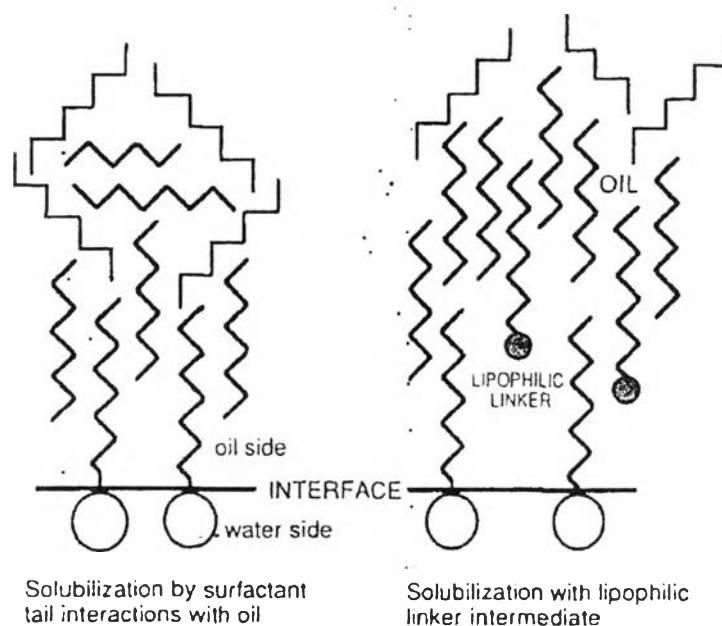

Solubilization by surfactant
tail interactions with oil

Solubilization with lipophilic
linker intermediate

Figure 2.5 Illustration of the role of the lipophilic linker in improving solubilization (Perez *et al.,* 1995).
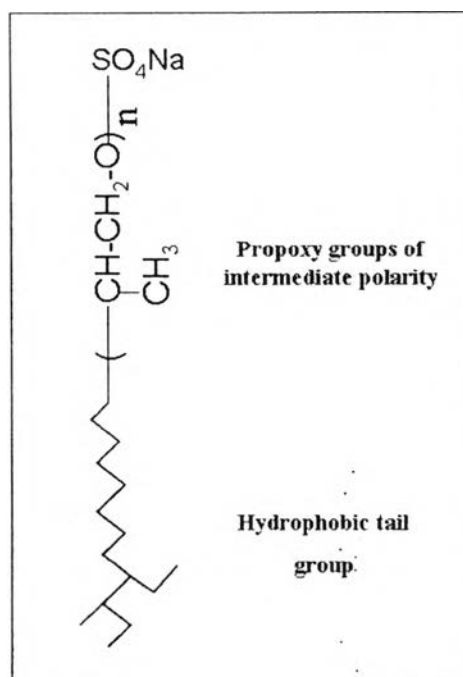
Figure 2.6 Schematic structure of extended surfactant molecule monomer.

2.3 Microemulsion

Emulsion is a significantly stable suspension of small particles of a first liquid with certain sizes within a second, immiscible liquid (Rosen, 2004). In order to stabilize the system, a third component, which is called the emulsifying agent, must be present. It is usually a surface-active agent. Based on the size of the dispersed particles, the emulsion is categorized into three types: macroemulsion (>400 nm), microemulsion (<100 nm), and nanoemulsion (100-400 nm).

Microemulsion was scientifically described for the first time in 1943 by Hoar and Schulman as special colloidal dispersions or a transparent or translucent system formed spontaneously upon the mixing of oil and water with a relatively large amount of an ionic surfactant together with a cosurfactant (Hoar and Schulman, 1943). Microemulsion is defined as a clear thermodynamically stable dispersion of water, immiscible oil, and a surfactant which adsorbs on a monolayer at the interface between the two solvents.

Microemulsion is transparent dispersions containing two immiscible liquids with particles of 10-100 nm (0.01-0.1 μm) in diameter that are generally obtained when mixing the ingredients gently. Microemulsion may be water-external (O/W), oil-external (W/O), or both (Rosen, 2004). The oil-in-water (O/W) 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 this case, the "discontinuous" (inner phase); the aqueous phase is the "continuous" (outer) phase. The water-in-oil (W/O) type is a dispersion of water or an aqueous solution (W) in a water-immiscible liquid (O). Figure 2.7 illustrates schematically these two basic microemulsion structures.

A microemulsion possesses superior characteristics as having a relatively large interfacial area, ultra-low interfacial tension, and a large solubilization capacity for both water-soluble and oil-soluble compounds, as compared to other colloidal systems (Bourrel and Schechter, 1988).
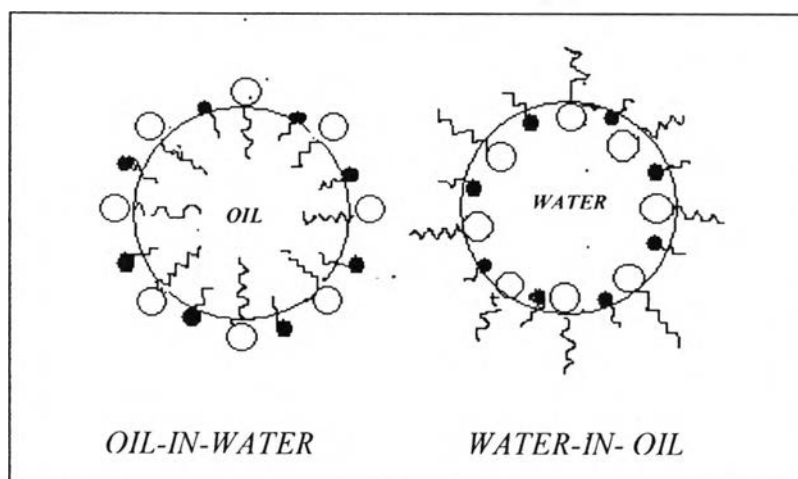

Figure 2.7 Schematic for oil-in-water (O/W) and water-in-oil (W/O) microemulsion structures (the smaller molecules represent a cosurfactant)(Rosen, 1989).

The most studied phase equilibria of microemulsions is probably known as the Winsor-Type microemulsion (Winsor, 1954). There are four types of microemulsions, as shown in Figure 2.8:

1. Winsor Type I: oil-in-water microemulsion in equilibrium with excess oil

2. Winsor Type II: water-in-oil microemulsion in equilibrium with excess water

3. Winsor Type III: middle, or microemulsion, phase in equilibrium with an excess of both water and oil

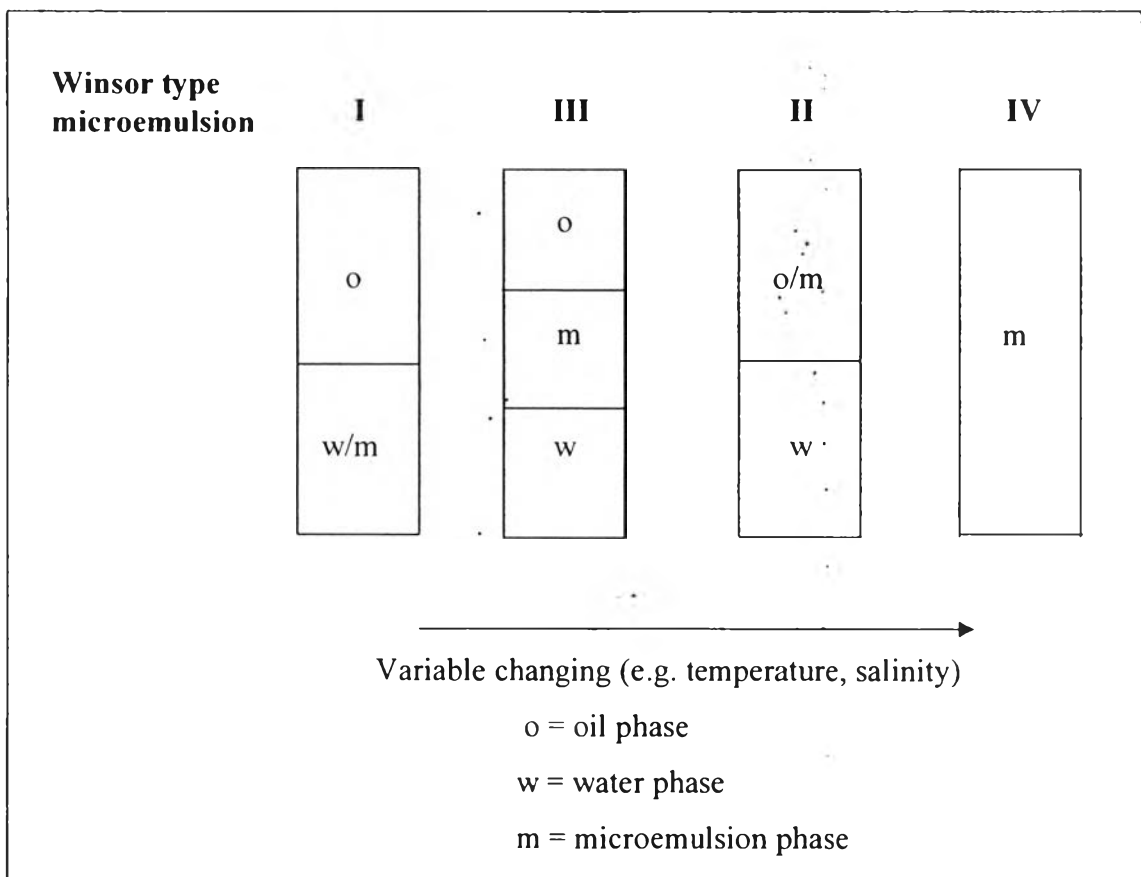4. Winsor Type IV: single phase or microemulsion phase

Figure 2.8 Microemulsion phase behavior for a model system (Winsor, 1968).

A transformation in the system from Winsor's Type I to Type III to Type II can be achieved by progressively changing temperature, salinity, the molecular structure of the surfactant and cosurfactant, the oil-to-water ratio, or the structure of oil in a homologous series. This studied phase diagram is normally carried out by increasing salinity (known as a salinity scan), as illustrated in Figure 2.8.

Moreover, the transition of Winsor Type I-III-II influences the two interesting properties of microemulsion, solubilization and interfacial tension (IFT), due to the changing of the microstructures. Figure 2.9 shows the relationship between the type of microemulsion and the interfacial tension. The region on the left hand side of the figure is Winsor Type I where a lower-phase 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 becomes a bicontinuous structure in equilibrium with excess oil and excess water phases. The 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 decreases. 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 optimum salinity which is defined as the salinity at which equal volumes of brine and oil are solubilized in the middle phase microemulsion. The region on the right hand side of the figure is Winsor Type II which consists of an upper-phase water-in-oil (W/O) microemulsionin equilibrium with excess water phase.
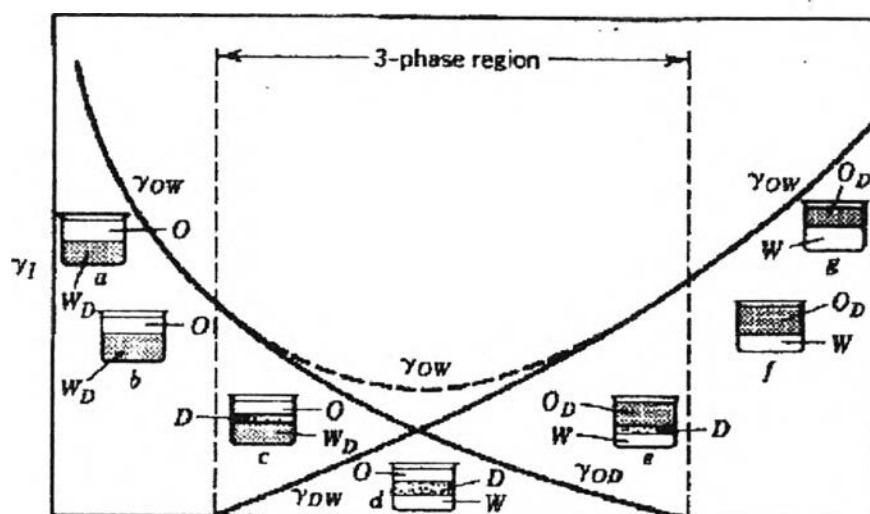

Figure 2.9 Transition of the microemulsion structure and the interfacial tension as a function of a salinity scan.

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, microemulsion has other special characteristics, such as spontaneous formation and a 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 IFT of Winsor Type III microemulsion can maximize the separation efficiency of a froth flotation system.

A research project was reported to investigate the advantages of performing flotation with a surfactant amount in the region of microemulsion formation between oil and water phases. The results indicated that if the system formed a Winsor Type III microemulsion, the flotation efficiency was maximized (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).

2.4 Froth Flotation

Flotation is an adsorptive bubble separation process, which a desired species is preferentially adsorbed at the interface between a dispersed phase (bubbles) and a continuous phase (Scamehorn and Harwell, 1989). Flotation involves bubbles and a soluble gas (usually air) in an aqueous stream. Materials to be removed adhere to the bubbles introduced into the system as they rise through the solution in a flotation tank and are concentrated in the foam (called a froth in this case), which is skimmed off overhead. A surfactant is needed to both facilitate the adhesion of target material to the bubble surface and to act as a froth promoter/stabilizer (Feng and Aldrich, 2000).

Flotation is an important separation process where 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. The success of flotation processes primarily depends on the tendency of surfactants to concentrate at the air-water interface and on the ca-

pability to make selected hydrophobic materials by means of adsorption on them or association with them.

The basic operation of froth flotation to remove oil from wastewater is shown in Figure 2.10. 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 solution, air bubbles form froth and it is collected in a launder. The tailing stream is withdrawn at the bottom of the column. Hence, there are two distinct zones in the flotation column, a bubbly zone and a froth zone. In the bubbly zone, the rising air bubbles 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 the froth zone, oil is accumulated in the form of froth rising through the top of the column and then the froth is skimmed off and broken as a liquid (Pal and Masliyah, 1990). Figure 2.11 shows how stable organic compounds including oils can be removed by froth flotation. In addition, froth flotation can be used for the removal of insoluble organic contaminants from water.

Gas bubbles and oil drops must contact, then attach, for flotation to occur. As oil and gas are both less dense than water, (except for some very heavy oils), they will both rise if placed in water. The gas bubble size, bubble size distribution and degree of dispersion affect the performance of flotation process significantly. A range of gas bubbles is beneficial because the smaller bubbles can capture the smaller oil droplets and the larger ones the larger droplets. Naturally too, the longer the residence time of the gas bubbles in the flotation tanks, the greater the number of gas bubble-oil droplet collisions (contact efficiency), the greater the quantity of the oil that ought to be removed, but clearly water throughput is also an important consideration (Moosai *et al.*, 2003).
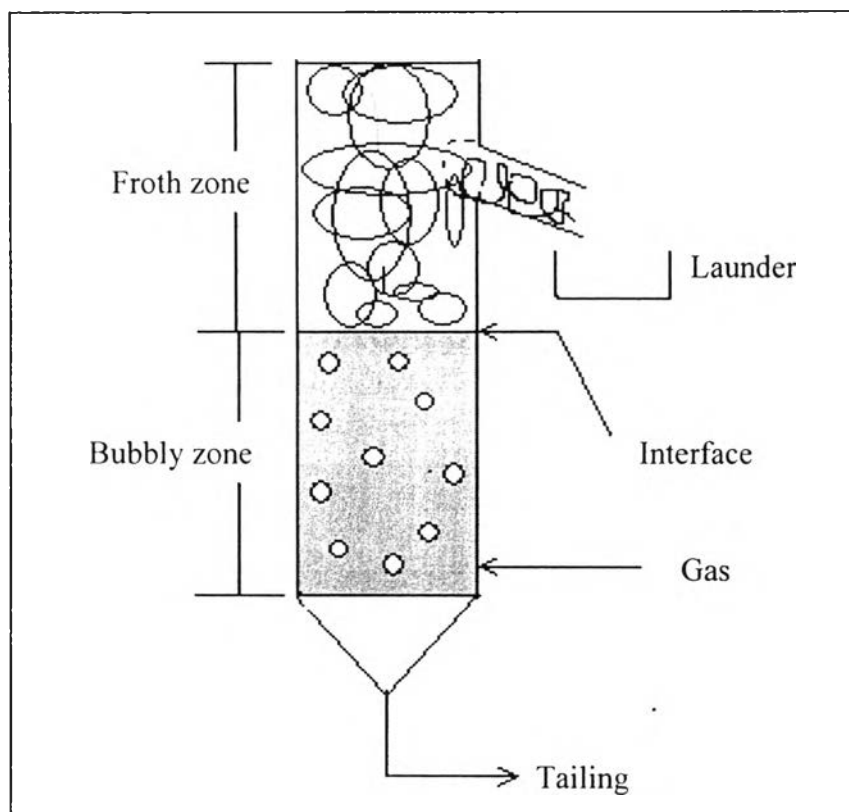
Figure 2.10 Schematic of a froth flotation column (Pal and Masliyah, 1989).
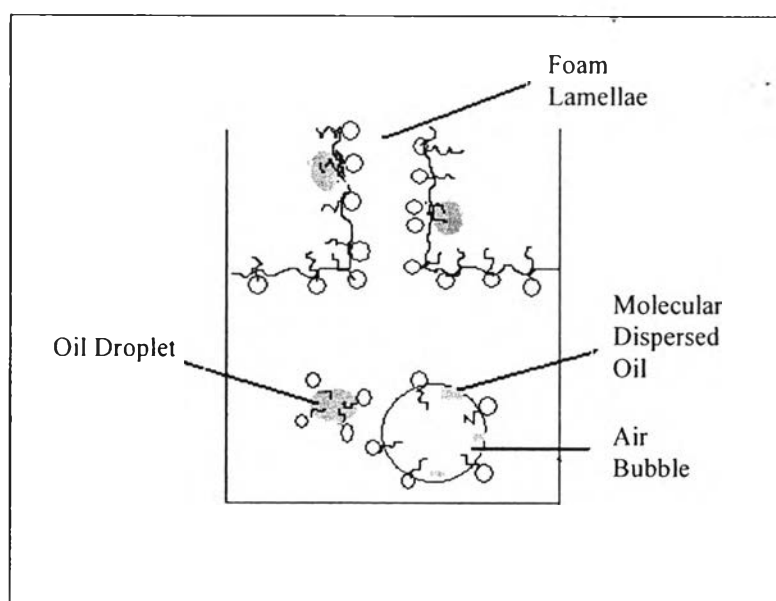

Figure 2.11 Schematic of froth flotation removal of oil from water (Wungrattanaso-pon, 1995).

Wungrattanasopon *et al.* (1996) studied the effects of cetyl pyridinium chloride (CPC) and sodium dodecyl sulfate (SDS) surfactants, and NaCl on the efficiency of *tert*-butylphenol (TBP) removal by using the foam flotation process. This process was operated in a batch mode. It was found that the TBP removal was maximized when the surfactant concentration was around the critical micelle concentration (CMC). 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.

Ratanarojanatam (1997) investigated the effect of mixed surfactants, sodium dodecyl sulfate (SDS) and nonylphenol polyethoxylate ($NP(EO)_{10}$), on the removal of ortho-dichlorobenzene (ODCB). The Winsor Type III system gave a higher percentage of ODCB removal than Type II or Type I. For the system containing a surfactant concentration of 7% and a weight fraction of SDS of 0.8, the highest ODCB removal (91%) was obtained, corresponding to the surfactant removal of 65%.

Pondstabodee *et al.* (1998) studied the removal of ODCB from water by batch froth flotation under the Winsor Type III microemulsion condition. The experimental results indicated that the cationic surfactant was more effective than either the monosulfate or the disulfonate anionic surfactants. The oil removal efficiency increased as the initial surfactant concentration and the salinity increased (causing a Winsor Type I to III transition for these systems) but as the oil/water ratio decreased.

Phoochinda (1999) focused on the effect of NaCl added to the mixed surfactants SDS and $NP(EO)_{10}$ on the microemulsion formation and the efficiency of flotation for removing ODCB from water. It was found that a small amount of NaCl added to the mixed surfactants could improve the microemulsion formation. However, precipitation and liquid crystals that limit the solubilization capacity of the solution appeared at a high NaCl concentration. The mixed surfactant concentrations of 3 and 5 wt% were selected for the froth flotation experiments. The prepared solutions, i.e. water excess and middle phases (w-m), water excess and oil excess phases (w-o), and water excess, middle and oil excess phases (w-m-o) were transferred to a 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 m-o and w-m systems. The effect of NaCl in the w-m-o system was studied and showed that adding 0.5 wt%

NaCl increased the ODCB removal. The effect of each phase volume 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) investigated the removal of diesel oil from aqueous emulsions by using batch flotation. The stability of these emulsions was characterized and operational 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 oil content, air flow rate, surfactant dosage, and the air distributor sinter were also studied. Regarding the effect of pH on the diesel removal, it was concluded that when pH increased, the diesel oil-water emulsion stability constant (K_s) increased as a result of the unstable microemulsion system, leading to the rapid destruction of the emulsion, and enhancing the diesel oil removal efficiency. 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, octadecyl amine chloride (ODAC) and cetyl trimethyl ammonium chloride (CTMAC), but less so with the anionic surfactant, SDS. Under the optimal conditions, up to 99% of the diesel oil removal could be obtained. This resulted in a residual diesel oil concentration of less than 10 ppm.

Withayapanyanon (2003) 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 of froth flotation using a 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 microemulsions with ethylbenzene. Results showed that at 3% NaCl and 0.3% AMA, the system provided the maximum oil removal (99.55%), but did not correspond to the minimum interfacial tension found in a 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. Foamability and foam sta-

bility were found to be other parameters involving in the oil removal efficiency in the froth flotation process.

Watcharasing (2004) investigated the relationship between the ultra-low IFT and the efficiency of diesel oil removal from water by using the continuous froth flotation technique. Branched alcohol propoxylate sulfate, sodium salt (Alfoterra 145-5PO), and sodium dodecyl sulfate (SDS) were used for both the microemulsion formation and the froth flotation studies. Surfactant concentration, salinity, and oil-to-water ratio were varied in the microemulsion formation experiments in order to determine the compositions required to obtain an ultra-low IFT. From the results, the oil removal efficiency of the froth flotation process did not correspond to the min-mum IFT of the system, indicating that the ultra-low IFT alone cannot be used as a sole criteria for a froth flotation operation. Furthermore, 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%).

Lapee-e (2006) investigated the relationship between the ultra-low IFT and the efficiency of cutting oil removal from water by using continuous froth flotation. Branched alcohol propoxylate sulfate, sodium salt (Alfoterra 145-5PO Sulfate), and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) were used for the microemulsion formation. Surfactant concentration, salinity, and oil-to-water ratio were varied in the microemulsion formation experiment in order to determine the compositions required to obtain the ultra-low IFT. The effects of surfactant concentration, salinity, foam height, air flow rate, hydraulic retention time (HRT), and polyelectrolyte on the oil removal were investigated in the froth flotation experiments. The results showed that the maximum oil removal efficiency of the froth flotation process did not correspond to the minimum IFT of the system. Foam stability was revealed to be another crucial factor in the froth flotation operation, as Watcharasing (2004) found. Sodium dode-cyl sulphate (SDS) was added to increase foam stability and foamability in the con-tinuous froth flotation experiments. The system with 0.1 wt% SDS, 5 wt% NaCl, 0.15 L/min air flow rate, 30 cm foam height, and 60 min HRT gave a maximum oil removal of 96%.