

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 as the motor oils we use in our automobiles, the pharmaceuticals we take when we are ill, the detergents we use in cleaning our laundry and our homes, the drilling muds used in prospecting for petroleum, and the flo-tation agents used in beneficiation of ores. The last decades have seen the extension of surfactant applications to such high-technology areas as electronic printing, mag-netic recording, biotechnology, micro-electronics, and viral research.

A surfactant (a contraction of the term *surface-active agent*) is a substance that, when present at low concentration 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 *inter-face* indicates a boundary between any two immiscible phrases; the term *surface* de-notes an interface where one phase is a gas, usually air (Rosen, 2004).

Surfactants have a characteristic molecular structure consisting of a hydro-philic (water-loving) part which is usually an ionic or highly polar group and a hy-drophobic (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).

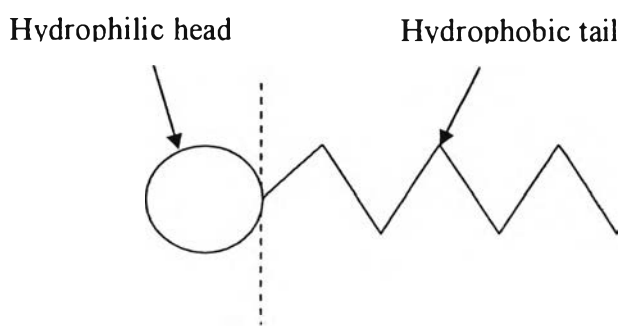


Figure 2.1 Schematic structure of surfactant molecule monomer (Withayapanyanon, 2003).

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

1. *Anionic*. The surface-active portion of the molecule bears a negative charge, for example, RCOONa^+ (soap), $\text{RC}_6\text{H}_4\text{SO}_3\text{Na}^+$ (alkylbenzene sulfonate).

2. *Cationic*. The surface-active portion bears a positive charge, for example, $\text{RNH}_3^+\text{Cl}^-$ (salt of a long-chain amine), $\text{RN}(\text{CH}_3)_3^+\text{Cl}^-$ (quaternary ammonium chloride).

3. *Zwitterionic*. Both positive and negative charges may be present in the surface-active portion, for example, $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$ (long-chain amino acid), $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$ (Sulfobetaine).

4. *Nonionic*. The surface-active portion bears no apparent ionic charge, for example, $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long-chain fatty acid), $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$ (polyoxyethylenated alkylphenol), $\text{R}(\text{OC}_2\text{H}_4)_x\text{OH}$ (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).

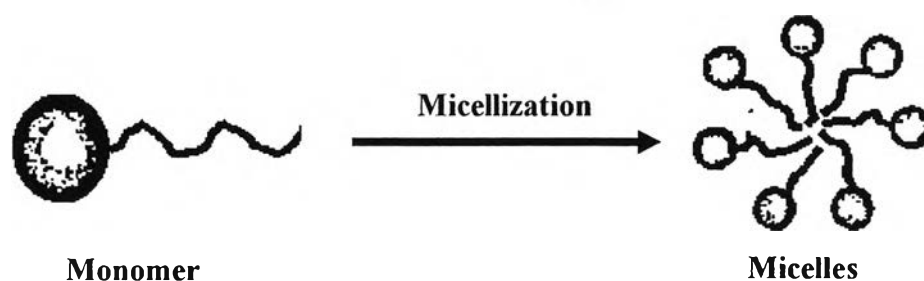


Figure 2.2 Schematic diagram of monomer, micelles and micellization.

One of significant phenomena associated with surfactant molecules is the formation of micelles which can be classified as normal and inverse (or reverse) micelles. In water or aqueous solution, normal micelles occur with the hydrophobic groups in the internal and the hydrophilic groups in the external. These may be spherical, rod-like, disk-like, or lamellar structures depending upon the physico-

chemical conditions such as pH, temperature and the presence of various electrolytes as shown in Figure 2.3. 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). In a nonpolar solvent, inverse micelles occur with the hydrophilic groups in the internal and the hydrophobic groups in the external. The schematic diagram of normal and inverse micelles is shown in Figure 2.4.

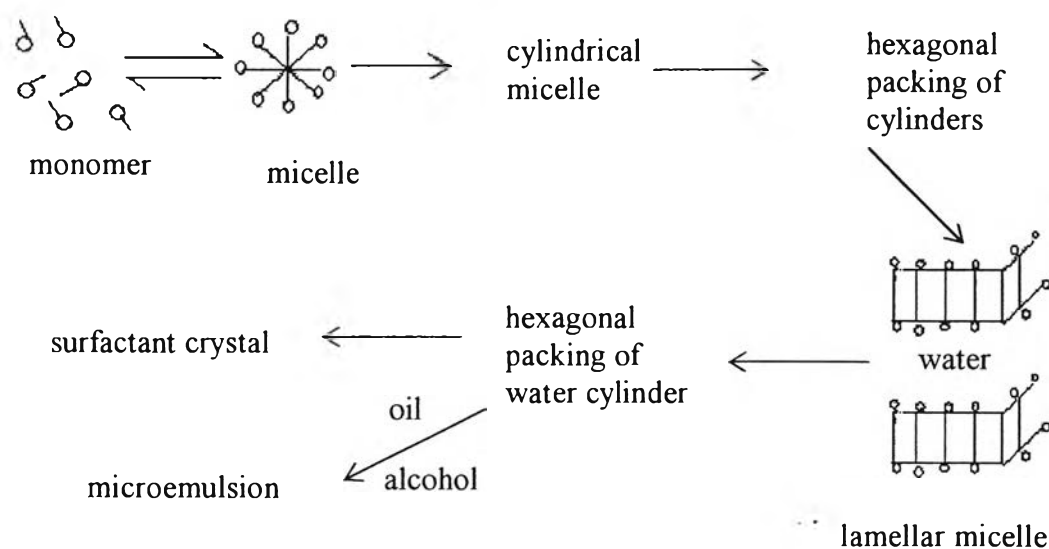


Figure 2.3 Schematic illustration of surfactant association structures (Sharma *et al.*, 1991).

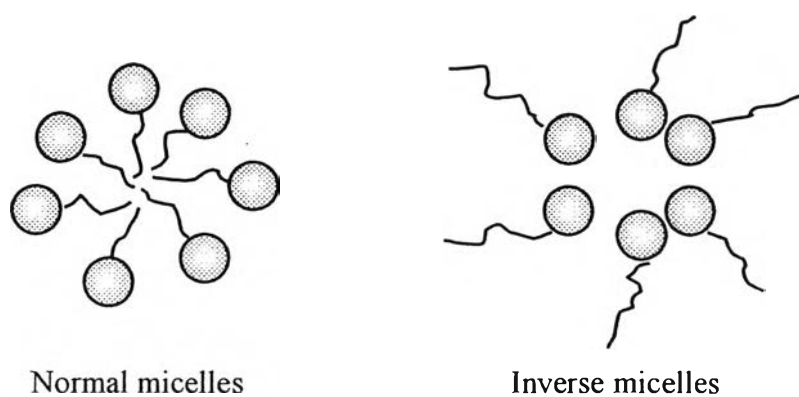


Figure 2.4 Schematic diagram of normal micelles and inverse micelles.

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 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 Microemulsion

Microemulsion is defined to be clear thermodynamically stable dispersions of water, immiscible oil and a surfactant which adsorbs on a monolayer at the interface between the two solvents. Microemulsion is a stable translucent micelle solution that may contain electrolytes and one or more amphiphilic compounds (Winsor, 1968; Bourrel, 1988).

Microemulsions are transparent dispersions containing two immiscible liquids with particles of 10-100 nm (0.01-0.1 μm) diameter that are generally obtained upon mixing the ingredients gently. Microemulsions may be water-external (O/W), oil-external (W/O), or both (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 2.5 illustrates schematically these two basic microemulsion structures.

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

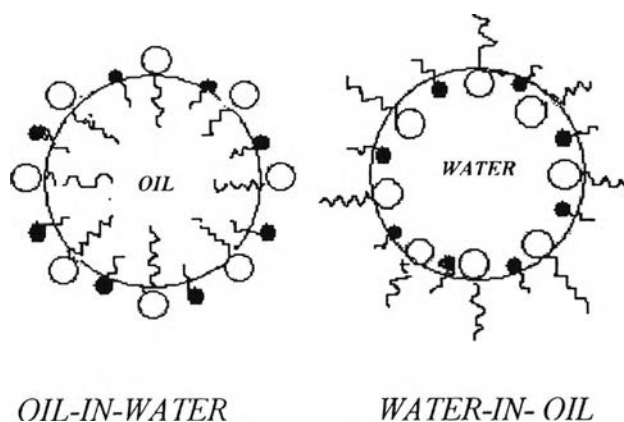


Figure 2.5 Schematic diagram for oil-in-water (O/W) and water-in-oil (W/O) microemulsion structures (the smaller molecules represent cosurfactant) (Rosen, 1989).

When a water-soluble surfactant is added to water under the proper conditions and above the CMC, the surfactant forms micelles which dissolve or solubilize oil, resulting in an increase in oil solubility in the aqueous phase. The aqueous phase in equilibrium with an excess oil is known as Winsor Type I microemulsion (Winsor, 1968). Under the proper conditions, as a variable (e.g. salinity, temperature) is changed, this system can transform from the two phase system of the Type I microemulsion and excess oil into a three phase system that consist of an excess oil phase, an excess water phase (both containing little surfactant) and a Winsor Type III microemulsion phase containing high levels of both water and oil and most of the surfactant as shown in Figure 7 (Puerto and Reed, 1983). This system attains ultra-low interfacial tension (IFT) (e.g. $< 10^{-4}$ mN/m) between the microemulsion phase and the excess water phase and between the microemulsion phase and the excess oil phase (Barakat *et al.*, 1983). The condition corresponding to equal volumes of oil and water being transferring from the excess phases to form the Winsor Type III microemulsion approximately corresponds to the minimum equal interfacial tensions between the excess phase and the middle phase. As the variable is further changed, the system becomes two phases again, and now the surfactant predominates in the oil phase in equilibrium with an excess water phase, so called a Winsor Type II microemulsion, as shown in Figure 2.6.

Hence, microemulsions can be classified into four types by Winsor (1968) as shown in Figure 2.6:

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 2.7 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 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 excess middle phase ($\gamma_{o/m}$) 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.

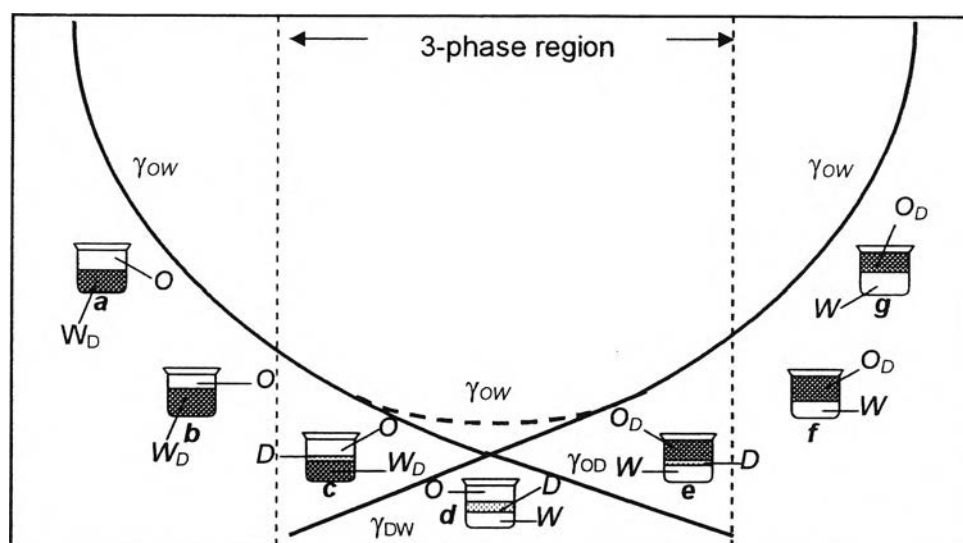


Figure 2.7 Transition of microemulsion structure and interfacial tension as a function of a salinity scan.

A part from the conventional salinity scan, the transition of a Winsor type system from O/W to W/O structure can also be produced 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 nonionic 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 area, microemulsion has been applied in oil recovery to remove the resident oil in a porous medium. Various variables have been investigated to have a significant effect on recovery including the surfactant concentration, interfacial tension, salinity, oil to water ratio, optimal surfactant structure, and cosurfactant concentration.

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

2.3 Froth Flotation

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

Flotation involves bubble and soluble gas (usually air) into an aqueous stream. Materials to be removed adhere to the bubbles as they rise through the process unit and are concentrated in the foam (called a froth in this case), which is skimmed off overhead. Surfactant is useful to both facilitate adhesion of target mate-

rial to the bubble surface and to acts as a froth promoter/stabilizer. (Feng and Aldrich, 2000).

Figure 2.8 represents a basic unit of froth flotation process to remove oil from wastewater. In froth flotation, there is a driving force that causes oil droplets from the solution to attach to the surface of the air bubbles rising through the froth flotation column. Air is introduced at the bottom of the froth flotation column through a porous sparger. The generated air bubbles rise through a pool of aqueous oil slurry. At the top of the pool, air bubbles form froth and it is collected in a launder. Hence, there are two distinct zones in the flotation column that consists of a bubbly zone and a froth zone. At the bottom of the column, the tailing 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 pick-up some of the undesirable hydrophilic particles. In a froth zone, oil is removed in form of froth by rising through the top of the column and then froth is skimmed off and broken as liquid (Pal and Masliyah, 1990).

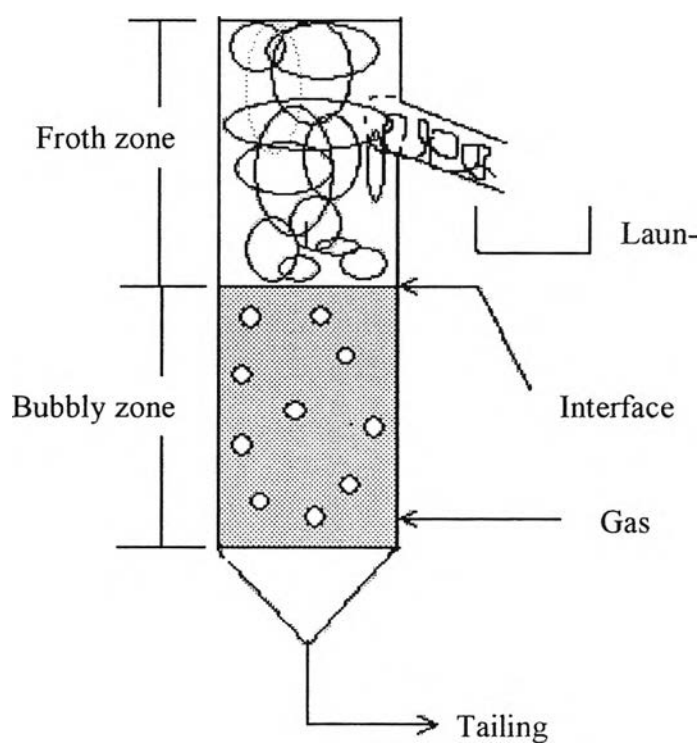


Figure 2.8 Schematic diagram of a froth flotation column (Pal and Masliyah, 1989).

Froth flotation technique can be operated in both batch and continuous modes as illustrated in Figure 2.9. In a batch operation, the solution is transferred to the column at the outset. After that air is introduced through the column until no further foaming occurs or a separation has been achieved. Some of the coalesced foam may be returned to the foam column similar to that in a batch distillation column. The concentration of solution within the column and foam are continuously changing during the operation as well as the concentration of surfactant. In a continuous operation, the entering liquid may be introduced into the liquid pool or into the foam section of the column. Overhead product is drawn off at the top of the column and underflow from the liquid pool. Some of the overhead may be recycled analogous to a distillation column (Carleson, 1989). Because of the solution is fed continuously into the column at a specific rate as well as froth and liquid are removed continuously

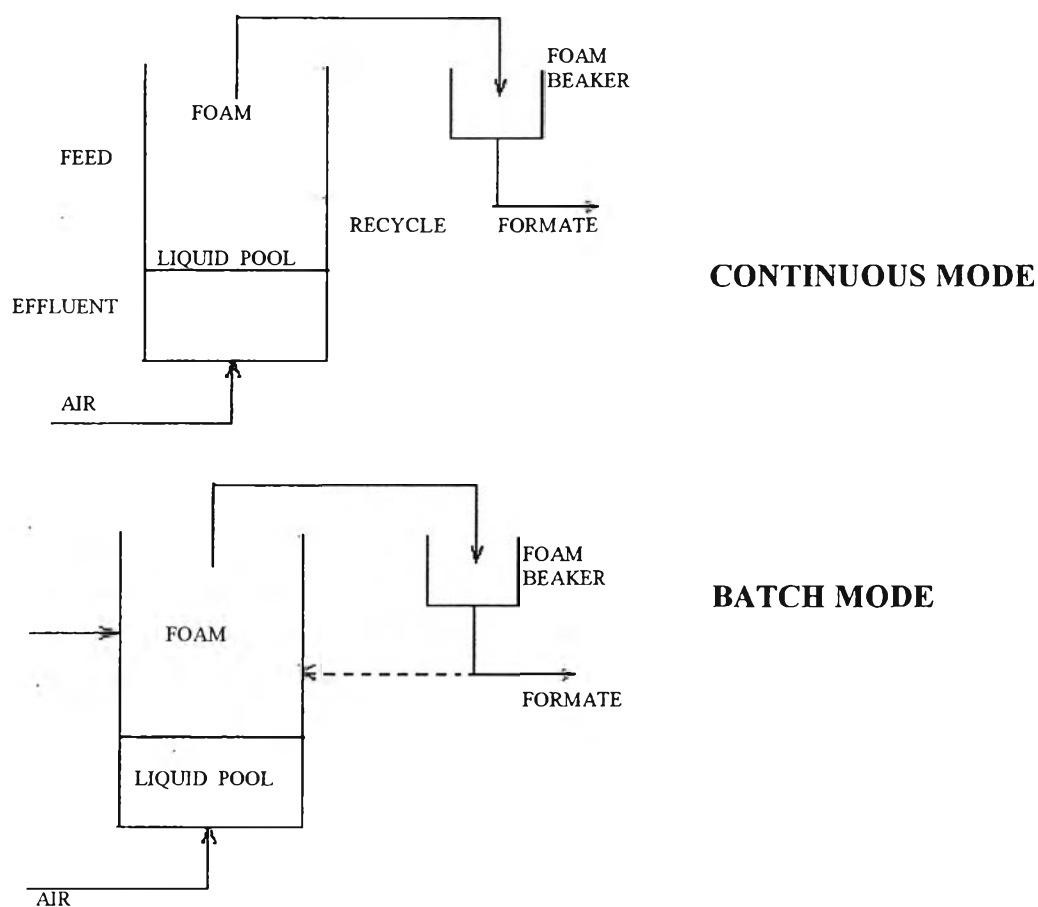


Figure 2.9 Configurations for froth flotation operation (Carleson, 1989).

during the operation leading to the generation of a steady state, the concentrations of surfactant and oil in the liquid column are maintained at constant levels as same as the concentrations of them that extracted into the froth.

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

Ratanarojanatam *et al.* (1997) studied the effect of mixed surfactants, sodium dodecyl sulfate (SDS) and nonylphenol polyethoxylate (NP(EO)₁₀), on the removal of σ -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 of 91% was obtained corresponding to the surfactant removal of 65%.

Pondstabodee *et al.* (1998) investigated the removal of σ -dichlorobenzene (ODCB) from water by batch froth flotation under the Winsor Type III microemulsion. It was found that the cationic surfactant was more effective than either the monosulfate or the disulfonate anionic surfactants. The oil flotation efficiency increased as the initial surfactant concentration increased, as the salinity increased (causing a Winsor Type I to III transition for these system), and as the oil/water ratio decreased.

Phoochinda *et al.* (1999) focused on the effect of NaCl added to mixed surfactants of SDS and NP(EO)₁₀ on the microemulsion formation and the efficiency of flotation for removing ODCB from water. It was found that small amounts of NaCl added to mixed surfactants could improve the microemulsion formation. However, precipitation and liquid crystal that limit the solubilization capacity of solution appeared at high NaCl concentration. The mixed surfactants concentrations of 3 and 5 wt.% were selected for froth flotation experiment. 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 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 by weight of NaCl increased ODCB removal. The effect of each phase was also studied. The results showed that when the volume of oil phase decreased and the volume of water phase increased in the w-o system, ODCB removal decreased. When the volume of middle phase increased and the volume of water phase decreased in the w-m system, ODCB removal increased.

Feng and Aldrich (2000) investigated the removal of diesel from aqueous emulsions by using batch flotation. The stability of these emulsions was characterized and factors such as pH and salinity affecting the stability of the emulsion were investigated. In addition, the effects of anionic and cationic surfactants, original diesel content, air-flow rate, surfactant dosage, and the air distributor sinter were investigated. In terms of the effect of pH on the diesel removal, it was concluded that when pH increased, the diesel-water emulsion stability constant (K_s) increased as a result of the unstable leading to rapid destruction of the emulsion, and enhancing the diesel removal efficiency. For the effect of NaCl concentration, it was found that the emulsion was gradually destabilized by the increase in the amount of NaCl. It was found that, the oil could be removed effectively with cationic surfactants, which were octadecyl amine chloride (ODAC) and cetyl trimethyl ammonium chloride (CTMAC), but less so with anionic surfactant, which was SDS. Under the optimal condition, up to 99% of the diesel could be removed. This amounted to a residual diesel concentration of less than 10 ppm.

Withayapanyanon *et al.* (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 by the batch mode. A single surfactant (sodium di-1,3-dimethylbutyl sulfosuccinate, AMA) and mixed surfactants (sodium bis-2-ethylhexylsulfosuccinate, AOT, and mono- and dihexadecyl diphenyloxide disulfonate sodium salt, Dowfax 8390) were selected to form microemulsion with ethylbenzene. Results showed that at 3% NaCl, 0.3% AMA, the system provided the

maximum oil removal (99.55%) but did not correspond to the minimum interfacial tension found in Winsor 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.

Watcharasing *et al.* (2004) 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. 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%).

In the year 2005, Lapee-e investigated the relationship between the ultra-low interfacial tension (IFT) and the efficiency of cutting oil removal from water by using continuous froth flotation. Branched alcohol propoxylate sulfate, sodium salt (Alfoterra 145-5PO) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) were used for 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 experiment. From the results, 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. Sodium dodecyl sulphate (SDS) was added to increase foam stability and foamability in the continuous froth

flotation experiment. 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 the maximum oil removal of 96%.