CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Surfactant

A surfactant, which is a construction of the term Surface-active agent, is characterized by possessing in the same molecule two distinct groups which differ greatly in their solubility relationships (Winsor, 1948). Surfactants are among the most versatile products of the chemical industry such as the pharmaceuticals, the detergents, the drilling mud used in prospecting for petroleum, and the flotation agents. Surfactants are molecule consisting of hydrophilic (water-loving) and hydrophobic (water-hating) moieties: referred to as head and tails, respectively (as shown in Figure 2.1). The hydrophilic portion of the surfactant is made of a water soluble species such as ionic or a highly polar group as well as the hydrophobic portion of the surfactant is made of organic derivative groups. Depending on the nature of the hydrophilic group, surfactants are classified into four main types: anionic, cationic, zwitterionic, and nonionic (Rosen, 1989).
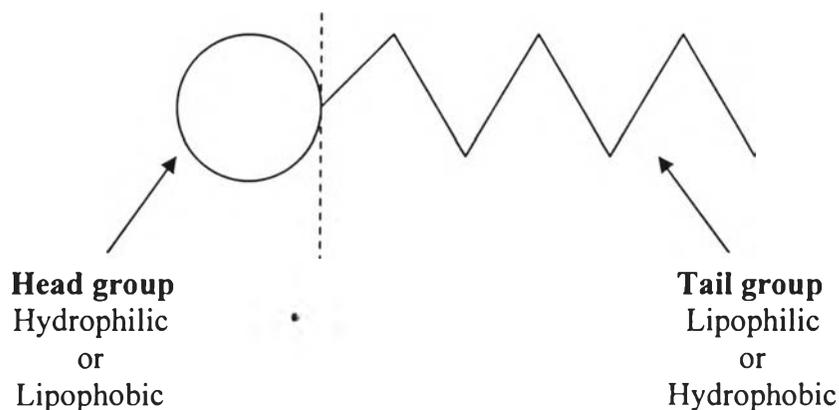

Head group
Hydrophilic
or
Lipophobic

Tail group
Lipophilic
or
Hydrophobic

Figure 2.1 Schematic of surfactant molecule monomer (Rosen, 1989).

The important characteristics of surfactant 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 of the surface or interface 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 (Rosen, 1989).

One of significant phenomena evidenced by surfactant molecules is the formation of micelle. In water or aqueous solutions, normal micelles occur with hydrophobic groups in the interior and hydrophilic exposed to the external aqueous solvent. These may be spherical, rod-like, disk-like, or lamellar structures by adjusting the proper physicochemical conditions such as pH, temperature and the presence of various electrolytes (Rosen, 1989). The interior of the micelle is often said to act like a very tiny oil droplet (no larger than a few nm in diameter). If oil is present in the system, these association structures can solubilize the oil, and can produce a clear, thermodynamically stable system. Depending on the nature of the oil phase and the oil-to-water ratio, the oil can be a continuous or disperse phase in the system (Sharma *et al.*, 1991). Moreover, the solubilization increases as the number of micelles in the solution increases (Clarence and Neogi, 1985). The lowest surfactant concentration at which micelles are present is critical micelle concentration (CMC). In nonpolar solvent, inverse micelles occur with surfactant head groups (often branched or twin-tailed) are on the outside in contact with similar groups of the surrounding solvent.

Surfactants play an important role in separation procedure such as flotation. Flotation involves bubble an insoluble gas (usually air) into an aqueous stream. Materials to be removed adhere to the bubbles as they rise through the process which is skimmed off overhead. Surfactant is useful to both facilitate adhesion of target material to the bubble surface and to 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, 2000).

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).

The microemulsion system contains transparent dispersion of very small oil-in-water (O/W) or water-in-oil (W/O) droplets with particles of 10-100 nm (0.01-0.1 µm) diameter that are generally obtained upon mixing the ingredients gently (Rosen, 1989). 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 2.2 illustrates schematically these two basic microemulsion structures.
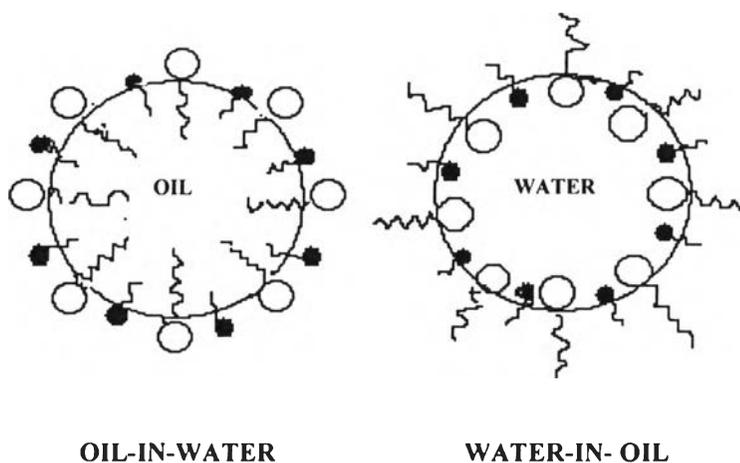

OIL-IN-WATER   WATER-IN- OIL

Figure 2.2 Schematic diagram for oil-in-water (O/W) and water-in-oil (W/O) microemulsion structures(the smaller molecules represent cosurfactant).

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. It is believed that the ultra low interfacial tension of Winsor type III microemulsion can maximize the separation efficiency of froth flotation system.

When water-soluble surfactant is added to water and under the proper conditions and above the CMC, the surfactant forms micelles which dissolve or

solubilize oil, represent in an increase in oil solubility in the aqueous phase. The aqueous phase in equilibrium with excess oil is known as Winsor type I microemulsion (Winsor, 1968). Under the proper conditions, as some variables (e.g. salinity, temperature) is changed, this system can change from the two phase system composed of the 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 Winsor type III microemulsion phase containing high levels of both water and oil and most of the surfactant in the system as shown in Figure 3 (Puerto and Reed, 1983). This system attains ultra low interfacial tension (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 phase to form the microemulsion approximately corresponds to minimum equal interfacial tensions between the excess phases (Shiau, 1994). As the adjustable variables are changed further, the system becomes two phases again, and now the surfactant predominates in the oil phase in equilibrium with an excess water phase, so called Winsor type II microemulsion, as shown in Figure 2.3.
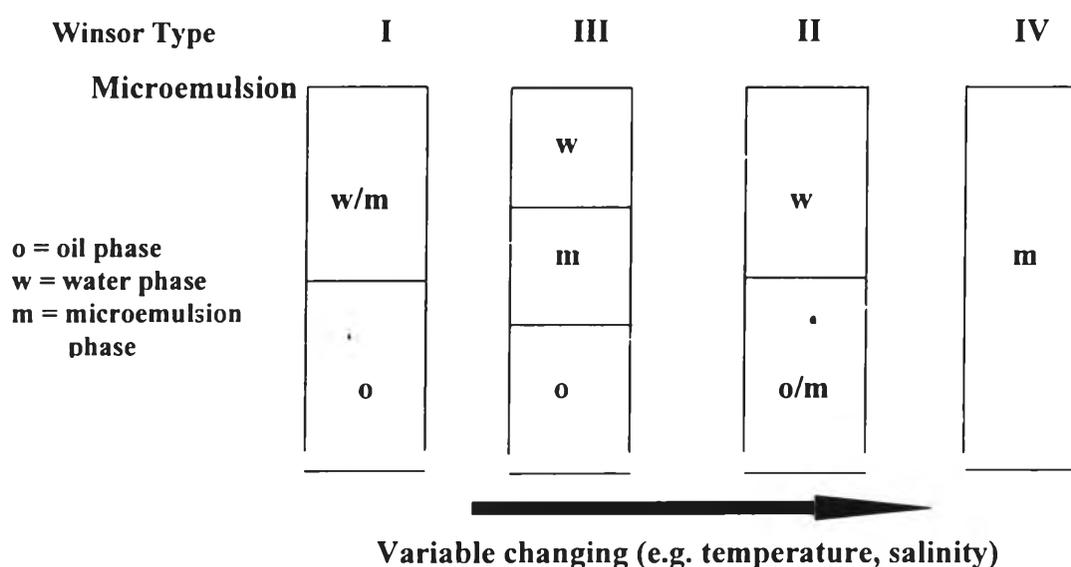

Figure 2.3   Demonstration of microemulsion phase behavior for a model system (Winsor, 1968).

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

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 upon recovery including the surfactant concentration, interfacial tension, salinity, oil to water ratio, optimal surfactant structure, and cosurfactant concentration.

2.3 Froth Flotation

Flotation is one of adsorptive bubble separations which are 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.

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 material to the bubble surface and to as a froth promoter/stabilizer.

The accumulation of surfactants at the air/water interface, and the resulting lowering of the excess Gibbs free energy of the interface, is the principal phenomenon in formation of stable foams. When the surfactants adsorbed on the surface of a solid are also adsorbed at the air interface, the surfactant-treated solid can demonstrate improved adhesion to the surface of a bubble. The adhesion of a particulate material to a bubble rising through a liquid is the basis of the froth flotation process (Scamehorn, 2000).

A basic unit of froth flotation technique is to remove oil from wastewater. In froth flotation as illustrated in Figure 2.4, there is a driving force that causes oil droplets floated from the solution to attach to the surface of the air bubbles rising through the froth flotation column. Air is launched 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. 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. 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).
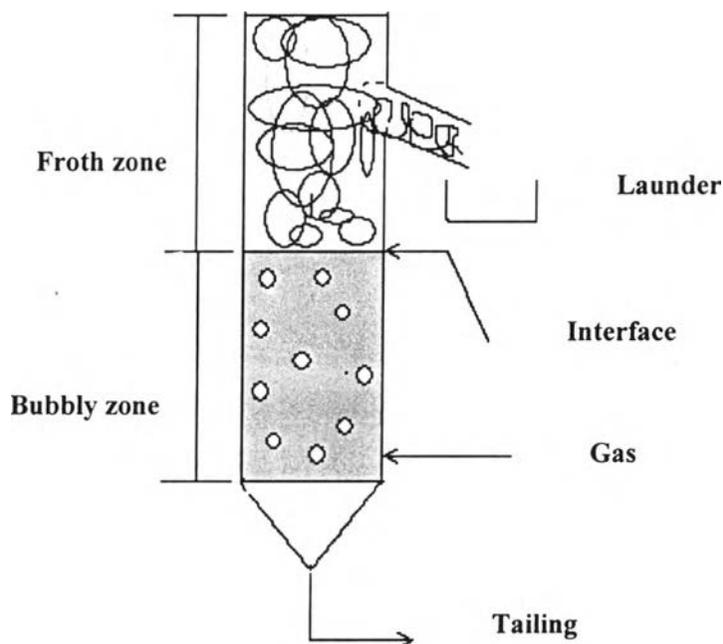

Figure 2.4 Schematic diagram of a froth flotation column (Pal and Masliyah, 1989).

Froth flotation technique can be operated in both batch and continuous modes as illustrated in Figure 2.5. In a batch operation, the solution is transferred to the column at the outset. After that air bubbles are passed 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 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 same as the concentrations of them that extracted into the froth.
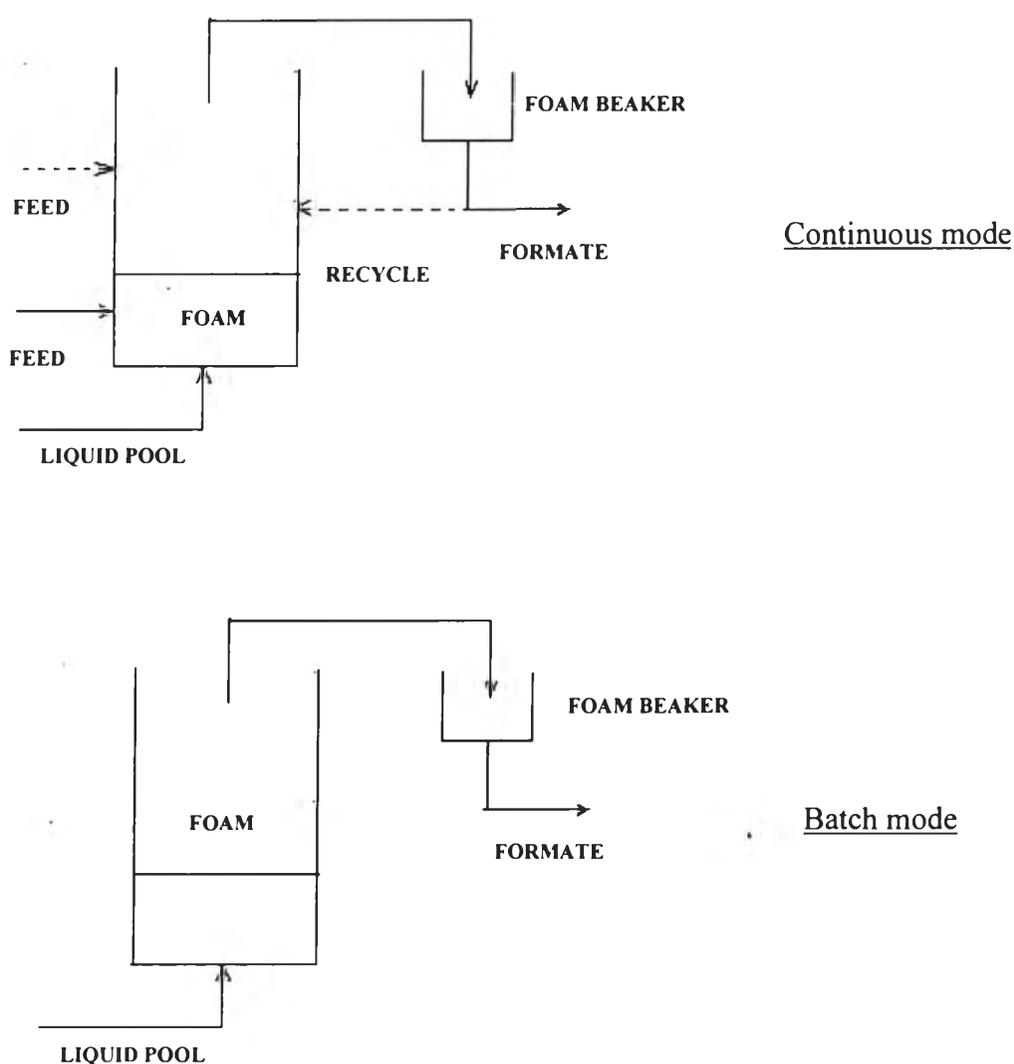

Figure 2.5 Experimental configurations for froth flotation (Carleson, 1989).

2.4 Colloidal Gas Aphrons (CGAs)

Colloidal Gas Aphrons (CGAs) are micro-bubbles (10-100 mm) encapsulated in a soapy film. They are creatd by intense strring at 5000-10000 rpm. The attractive features of CGA have been reported that:

1. CGA have large interfacial area per unit volume; a result of their small size (aphron diameters are typically 10– 100 mm) and high gas hold-up (typically 50%).

2. CGA exhibit relatively high stability (e.g., time for half the initial volume of liquid to drain from the aphron phase, after stirring is stopped).

3. Flow properties of these dispersions are similar to those of water (e.g., can be pumped easily, without collapse, from one location to another).

4. The aphron phase separates easily from the bulk liquid phase due to its buoyancy.

The identification of these properties has led researchers to consider CGA for various applications, such as removal of metals (Ciriello, 1982) and dyes (Roy *et al.*, 1992), flotation of cells (Subramaniam *et al.*, 1990; Hashim *et al.*, 1998), protein recovery (Noble *et al.*, 1998; Jauregi and Varley, 1998), and mass transfer in bioreactors (Bredwell and Worden, 1998).

The structure of CGA was first proposed by Sebba (1987). Sebba claimed that CGA are not like conventional bubbles, which are surrounded by a surfactant monolayer, but are gas bubbles surrounded by three surfactant layers (see Figure 2.6). This theory was based on several experimental observations, including stability measurements. Sebba (1987) claimed that CGA can last for minutes or for hours, if stirring is maintained, without coalescence being appreciable. According to Sebba (1987), this is a result of the multilayer surfactant film surrounding the gas bubble, which delays coalescence. The evidence for the proposed CGA structure by Sebba (1987) is inconclusive. The current literature on CGA is mainly focused on the application of CGA, with the structure of CGA assumed to be that proposed by Sebba (1987).
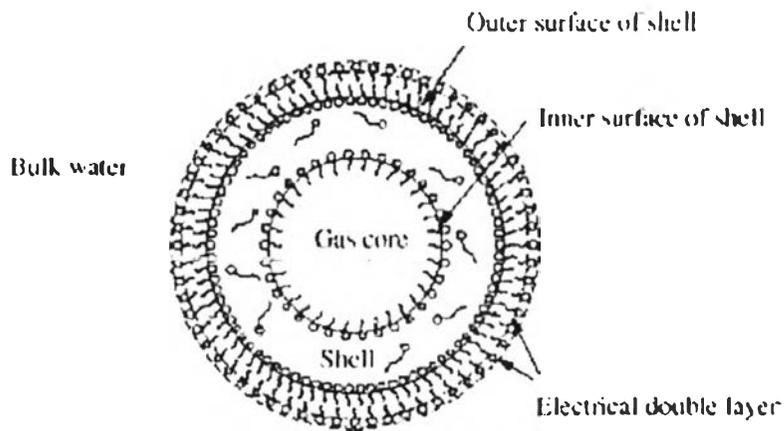
Figure 2.6 Structure of CGA proposed by Sebba (1987).

Wungrattanasopon *et al.* (1996) studied the effect of two types of surfactants, cetyl pyridinium (CPC) and sodium dodecyl sulfate (SDS), and NaCl on the removal efficiency of tert-butylphenol (TBP) by using foam flotation process. This process was operated in the batch mode. It was found that the TBP removal was a maximum when the surfactant concentration approached the 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.

Hashim *et al.* (1997) studied the recovery of fine cellulose fibres from paper mill wastewater. CGAs were used to separate fine fibres from lean slurry of cellulosic pulp in a flotation column. The pulp fibres were recovered as foamate from the top. Sodium dodecyl sulphate at a concentration of 2.0 kg/m^3 was used as a surfactant to generate the CGAs in a spinning disc apparatus. The results indicated that up to 70% flotation efficiency could be obtained within a short column height of 0.3-0.35 m. This technique can be applied to recover fine cellulosic pulp from paper machine backwater

Pongsatabodee *et al.* (1998) investigated the removal of ortho-dichlorobenzene (ODCB) from water by batch froth flotation under the Windsor Type III microemulsion. The cationic surfactant studied was more effective than either the monosulfate or the disulfate anionic surfactants studied. The oil flotation

efficiency increased as the initial surfactant concentration increased, the salinity increased, and the oil/water ratio decreased.

Ratanarojanatum (1995) studied the effect of mixed surfactants, sodium dodecyl sulfate (SDS) and nonylphenol polyethoxylate $(NP(EO)_{10})$ on the removal of ODCB. The Winsor's type III system gave a higher percentage of ODCB removal than the 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% corresponding to the surfactant removal of 65% was obtained.

Phoochinda (1999) focused on the effect of NaCl added to mixed surfactants SDS and $NP(EO)_{10}$ on microemulsion formation and efficiency of flotation for removing ODCB from water. It was found that small amount of NaCl added to mixed surfactants could improve microemulsion formation. At high concentration of NaCl, precipitation and liquid crystal limit the solubilization capacity of solution appeared. The mixed surfactants of 3 and 5 wt% of SDS and $NP(EO)_{10}$ were selected for froth flotation experiments. The prepared solution, i.e. water and middle phase (w-m), water and oil phase (w-o) and water, middle and 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 the w-o and w-m systems. The effect of NaCl in the w-m-o system was studied and the study showed that the addition of 0.5 wt% of NaCl increased the ODCB removal. The effect of volume of each phase was also studied. The results showed that when the volume of the oil phase decreased and volume of the water phase increased in the w-o system, the ODCB removal decreased. When the volume of the middle phase increased and volume of the water phase decreased in the w-m system, the ODCB removal increased.

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 showed 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 the cationic surfactants, which were octadecyl amine chloride (ODAC) and cetyl trimethyl ammonium chloride (CTMAC), but less so with the 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.

Jauregi *et al.* (2000) investigated dispersion and structural features of CGA utilizing a range of novel predictive for prediction of aphron size and drainage rate and experimental electron microscopy and X-ray diffraction methods. Results indicate structural differences between foams and CGA, which may have been caused by a multilayer structure of the latter as suggested by the electron and X-ray diffraction analysis.

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

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 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's 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.

Jarudilokkul *et al.* (2004) studied protein separation by CGAs using nonionic surfactant. It was found that Tween 20 was a suitable surfactant. The stability of CGA was investigated by varying surfactant concentration, motor stirring speed, stirring time and concentration of NaCl as additive. The optimal condition for CGA preparation was 10 mM Tween 20 in distilled water, stirring speed of 5500 rpm and stirring time of 5 min. To simplify, lysozyme and β-casein of different pI values were employed as substitutes of protein in wastewater. Factors affecting protein separation such as initial protein concentration, CGA volume ratio and pH were examined. It was demonstrated that hydrophobicity of Tween affected CGA stability and the electrostatic interaction between CGAs and proteins played an important role in the separation.

Jauregi *et al.* (2004) studied the recovery of lactoferrin and lactoperoxidase from sweet whey was studied using CGAs, which are surfactant-stabilized microbubbles (10-100μm). CGAs are generated by intense stirring (8000 rpm for 10 min) of the anionic surfactant AOT (sodium bis-2-ethylhexyl sulfosuccinate). A volume of CGAs (10-30 mL) is mixed with a given volume of whey (1-10 mL), and the mixture is allowed to separate into two phases: the aphron (top) phase and the liquid (bottom) phase. Each of the phases is analyzed by SDS-PAGE and surfactant colorimetric assay. A statistical experimental design has been developed to assess the effect of different process parameters including pH, ionic strength, the concentration

of surfactant in the CGAs generating solution, the volume of CGAs and the volume of whey on separation efficiency. As expected pH, ionic strength and the volume of whey (i.e. the amount of total protein in the starting material) are the main factors influencing the partitioning of the Lf,Lp fraction into the aphron phase. Moreover, it has been demonstrated that best separation performance was achieved at pH 4 and ionic strength 0.1 mol/L i.e., with conditions favoring electrostatic interactions between target proteins and CGAs (recovery was 90% and the concentration of lactoferrin and lactoperoxidase in the aphron phase was 25 times higher than that in the liquid phase), whereas conditions favoring hydrophobic interactions (pH close to pI and high ionic strength) led to lower performance. However, under these conditions, as confirmed by zeta potential measurements, the adsorption of both target proteins and contaminant proteins is favored. Thus, low selectivity is achieved at all of the studied conditions. These results confirm the initial hypothesis that CGAs act as ion exchangers and that the selectivity of the process can be manipulated by changing main operating parameters such as type of surfactant, pH and ionic strength.

In 2004, Watcharasing investigated the relationship between the ultra-low IFT and the efficiency of diesel removal from wastewater by 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. The effects of surfactant concentration, salinity, oil to water ratio, foam height, air flow rate, and HRT on the oil removal were investigated. 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 sole criteria for froth flotation operation. Foam stability was revealed to be another crucial factor in the froth flotation operation. The system with 0.1 wt% Alfoterra, 0.5 wt% SDS, 4 wt% NaCl, oil to water ratio 1:19 at air flow rate 0.15 L/min, foam height 56 cm, and HRT 22 min gave the maximum oil removal (83.86%).