

CHAPTER II

LITERATURE REVIEW

2.1 Surfactants

Surfactants are wetting agents that reduce the surface tension of water by adsorbing at the liquid-gas interface. They can reduce the interfacial tension between water and oil by adsorbing at the liquid-liquid interface as well.

The structure of surfactants consists of a head group, known as a hydrophilic group, that is water loving group. It has strong attraction for water but little attraction for solvent. For a tail group, known as a hydrophobic group, that is water hating group. It has strong attraction for a solvent but has little attraction for water (as shown in figure 2.1). There are four types of surfactants which are

1. Anionic Surfactants: The surface-active portion of the molecule bears a negative charge.
2. Cationic Surfactants: The surface-active portion bears a positive charge.
3. Zwitterionic Surfactants: Both positive and negative charges are present in the surface-active portion.
4. Nonionic Surfactants: The surface-active portion bears no apparent ionic charge.

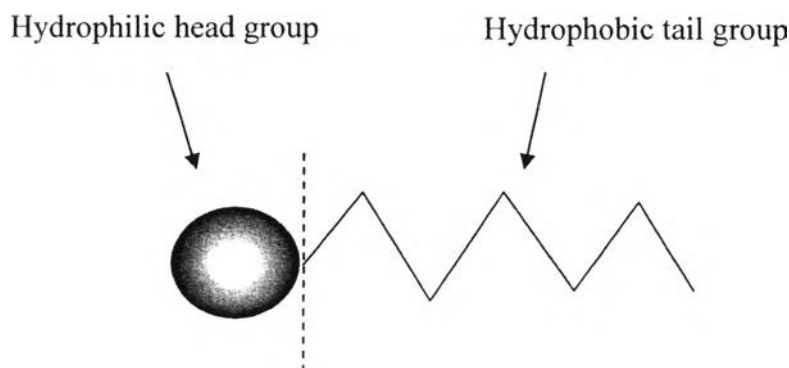


Figure 2.1 Schematic structure of the surfactant molecule monomer (Rosen, 2004).

A single molecule of surfactant is called monomer. At sufficient concentration, monomer can nucleate to form micelles. The lowest concentration which micelles are present is called critical micelle concentration ($C_{\mu C}$). Figure 2.2 shows schematically a surfactant solution containing dissolved monomeric surfactants, a surfactant micelle, and surfactants adsorbed at the air-water interface.

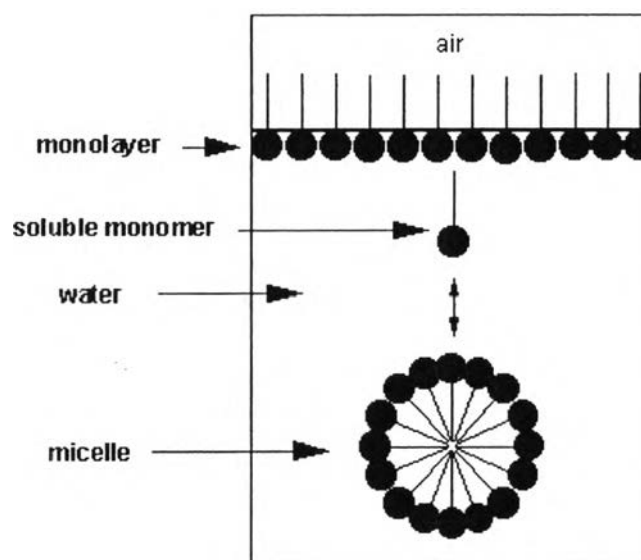


Figure 2.2 Schematic of an ionic surfactant solution showing monomeric surfactants in solution and adsorbed at the air/water interface and micelle aggregates (Prud'homme et al., 1996).

There are two types of micelle. In aqueous solution, normal micelles are formed with the hydrophobic group in the interior core region and the hydrophilic group exposed to the external aqueous solvent (as shown in figure 2.3). These micelles may be spherical, rod-like, disk-like, or lamelle structures depending upon the surfactant concentration and the presence of various electrolytes (Rosen, 2004). In non-polar solvent, reverse micelles are formed with the hydrophilic group in the interior and the hydrophobic group in the external.

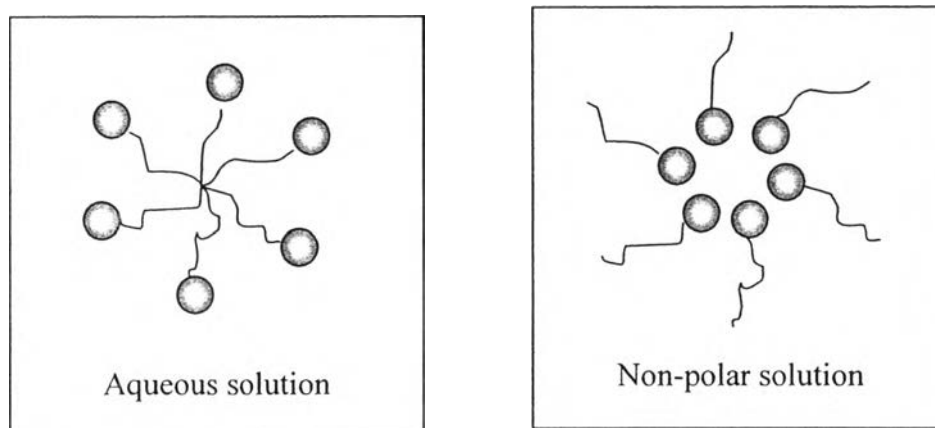


Figure 2.3 Normal micelle and reverse micelle (Bourrel et al., 1988).

Surfactants play an important role in various industry such as detergent, pharmaceutical or separation process including Froth flotation. Froth flotation involves bubbling an insoluble gas (usually air) into an aqueous stream. Impurities are removed by adherence the bubbles that rise up and accumulate at the top of a column. At this point, impurities and foams are skimmed off. 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).

2.2 Microemulsions

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

It can be prepared by mixing either more than one surfactant or a surfactant and a cosurfactant. This combination is required to balance properties between hydrophilic and hydrophobic. This balance can be determined by mixing an oil and water in various proportions between surfactant and surfactant or surfactant and cosurfactant to get Winsor's type I, III, II and IV respectively.

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, the system transforms from Winsor type I to Winsor's type III. This system consists of an excess oil phase, an excess water phase and a middle phase that 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. After that, the system becomes two phases again that is excess water phase or we called "Winsor's type II", as shown in figure 2.4. 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).

Microemulsion is very useful in several applications including froth flotation technology for oil removal. Pondstabodee et al., (1998) reported that the efficiency of oil removal was maximized when the system was in Winsor's type III microemulsion region. This condition was found to minimize interfacial tension between the water and oil phase. For improving the efficiency of oil removal, the proper condition, where interfacial tensions are substantially reduced, is chosen (Scamehorn and Harwell, 2000).

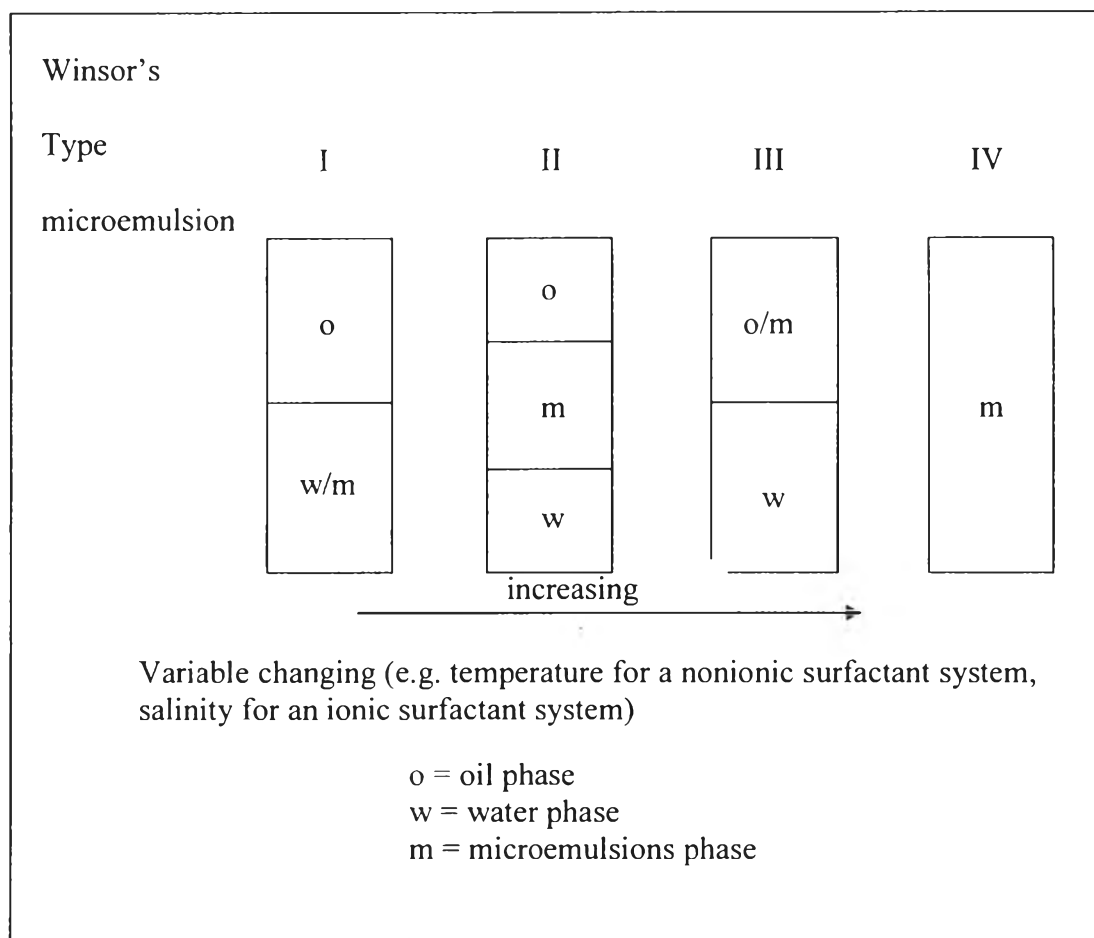


Figure 2.4 Demonstration of microemulsion phase behavior for a model system (Winsor, 1968).

2.3 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. 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).

In pure water, gas bubbles coalesce very rapidly so foam cannot be produced easily. Surfactants play an important role for foam producing by adsorption at gas-liquid interface resulting in a stable foam structure. The advantages of presenting surfactant are reduction of surface tension, reduction mechanical energy requirement for increasing interfacial area and preventing bubble coalescence.

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

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). Foam stability is expressed as foam volume at equilibrium divide by the gas flow rate (Beneventi, 2001).

Foam Stability

The static stability of 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).

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).

2.4 Multistage 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). Materials are removed by adherence to the air bubbles that skimmed off at the top of the column. The skimmed foams contain high concentration of removal material as compare with feed solution. There are four basic steps in the flotation process to treat oily wastewater, beginning with bubble generation in oily water, contact between oil droplets suspend in the water and gas bubbles, attachment of oil droplets to gas bubbles and rising of the bubble-droplets to assembly at the water surface where the oil is removed. The use of froth flotation for the removal of oil from water is shown in figure 2.5.

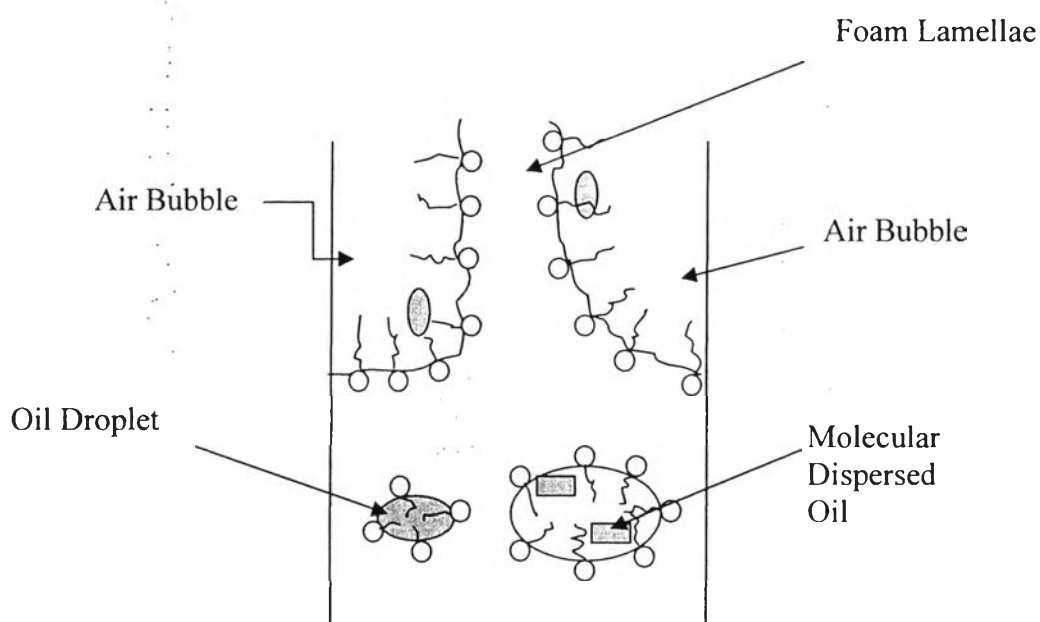


Figure 2.5 Schametic of the foam flotation process (Pongstabodee *et al.*, 1998).

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 adherence of a particulate material on bubbles rising through a liquid is the basic of the froth flotation process (Scamehorn and Harwell, 2000).

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).

In froth flotation operation for removing oil from water, there is a driving force that causes oil droplets from the solution to attach 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 froth zone, as shown in figure 2.6. 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 froth flotation 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. 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).

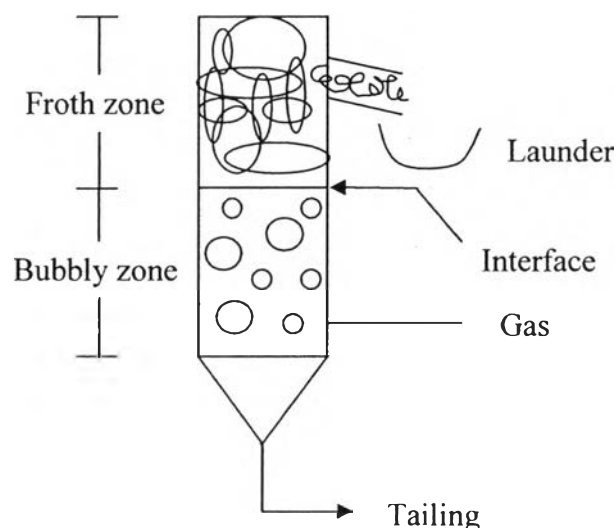


Figure 2.6 Schematic of a froth flotation column (Pal and Maliyah, 1990).

There are two modes to operate froth flotation process, batch and continuous modes. In batch mode, Solution is transferred to the column at the outset. Af-

ter 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, 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).

Pondsatabodee *et al.*, (1998) studied about removing ortho-dichlorobenzene (ODCB) from water by batch froth flotation under Winsor's type III microemulsion. The result indicated that the removal efficiency of ODCB increased as the 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.

Boonyasuwat *et al.*, (2009) studies the recovery of surfactants using a multistage foam fractionators for three types of surfactants: cationic (cetyl pyridinium chloride, CPC); anionic (sodium dodecyl sulfate, SDS); and nonionic (polyoxyethylene (20) sorbitan monolaurate, Span80). The system was operated at a constant temperature of 25°C with a surfactant concentration in the range of 50 to 100% of CMC (critical micelle concentration). For any surfactant system, the enrichment ratio of surfactant increased with increasing foam height and number of stages but decreased with increasing effects of the air flow rate and feed concentration. For all studied surfactants, the removal efficiency of the surfactant was not significantly affected by changing the air flow rate, foam height, and feed concentration in the studied ranges. An increase in the stage number, both the enrichment ratio and the removal of surfactant increased substantially for all three studied surfactants. In term of the enrichment ratio and removal was found to lie in the following order: CPC > Span80 > SDS.

Yanatatsaneejit *et al.*, (2005a) studied the effect of microemulsion condition and foam characteristics to froth flotation performance in removal of emulsified ethybenzene in water. Dihexyl sulfosuccinate (Aerosol MA or AMA) was used as a surfactant. This experimental was focus on Winsor's type III microemulsion which corresponded to ultralow interfacial tension between oil and water phases. At 0.3 wt% AMA and 3 wt% NaCl, the highest oil removal was obtained. The results demon-

strated that both interfacial tension and foam characteristics influenced the efficiency of oil removal in the froth flotation process.

Yanatatsaneejit *et al.*, (2005b) investigated the effect of air flow rate, oil-to-water ratio and equilibration time in removal ethylbenzene from water. Dihexyl sulfosuccinate (Aerosol MA or AMA) was used as a surfactant. Oil removal, surfactant removal and enrichment ratio were used to evaluate the performance of froth flotation process. From the result, at 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 but the oil removal slightly decreased. The feed solution was induced a state closer to equilibrium by agitation for 40 min. The result shown that, the ethylbenzene removal is nearly as high as that with the equilibrium feed solution.

Yanatatsaneejit *et al.*, (2008) Showed that there were many factor to achieve high performance of froth flotation process such as ultralow interfacial tension between excess oil phase and excess water phase, high foam production rate and foam stability. To obtain an ultralow interfacial tension, a Winsor's type III microemulsion or middle phase had to be formed. In this research, 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 microemulsion with diesel oil. The result showed that, increasing in surfactant concentration decreased interfacial tension (IFT), and also increased foam stability. The minimum IFT was found at 5 wt% NaCl but this condition cannot be operated due to poor foam characteristic. Both IFT and foam characteristics should be optimized to achieve high efficiency of oil removal in froth flotation.

Surfactants can be present at low concentrations in effluent wastewater from various industrial operations. Its concentration must sometimes be reduced in order to meet environmental standards in discharging these waters to the environment. Also, recovery of the surfactant for reuse is sometimes economical and desirable. Boonyasuwat *et al.*, (2003) studied Anionic and cationic surfactant recovery from water using a multistage foam fractionator. In this study, the recovery of a cationic surfactant (cetylpyridinium chloride, CPC) and an anionic surfactant (sodium dodecylsulfate, SDS) from water by multistage foam fractionation in a bubble-cap tray column was investigated with one to four stages operated in steady-state mode for surfactant

concentrations less than the critical micelle concentration (CMC). From the result, enrichment ratios as high as 120.23 were observed and increased with decreasing superficial air flow rate, increasing foam height of the top tray, increasing feed liquid flow rate, decreasing feed surfactant concentration and increasing number of stages. The fractional surfactant removal can be as high as 100% and increases with decreasing air flow rate, increasing foam height per tray, increasing feed liquid flow rate, increasing feed surfactant concentration and increasing number of stages. Scale-up of foam fractionation for recovery or removal of surfactant from water to a multi-tray column was successful.

Boonyasuwat et al., (2005) found that the air flow rate, foam height, feed flow rate and number of stages effect to surfactant recovery from water using a multistage foam fractionator. In this study, the recovery of the cationic surfactant (cetylpyridinium chloride or CPC) from water by multistage foam fractionation in a bubble-cap tray column was investigated with one to four stages operated in steady-state mode for surfactant concentrations less than or equal to the critical micelle concentration. Both enrichment ratio and surfactant removal fraction increase with increasing feed flow rate, foam height and number of stages but they decrease with increasing CPC feed concentration and air flow rate. This study has demonstrated that the multistage foam fractionator used in this study can achieve almost quantitative removal of the surfactant with high enrichment ratio and short residence time. Multistage foam fractionation is demonstrated to be an extremely effective method of reducing surfactant concentrations from low to even lower concentrations in wastewater.

Chungchamroenkit *et al.*, (2009) showed that froth flotation can be applied to separate hydrophobic particles from hydrophilic ones in aqueous solution with the use of an appropriate surfactant. In this work, carbon black was separated from silica gel by means of froth flotation. Since the point of zero charge, or PZC, of three carbon black (3.5) close to that PZC of silica gel (4.1), a nonionic surfactant (ethoxylated alcohol) was selected as the separating agent. Based on experimental results using a surfactant concentration of 62 μM or 75% of its critical micelle concentration (CMC), up to 70% of carbon black recovery was achieved with a carbon black enrichment ratio around 3.5. Added electrolyte (NaCl) showed a negligible effect on

the separation efficiency. The presence of the surfactant was found to provide both a higher mass transfer surface area and to reduce the coalescence of air bubbles in the froth flotation column.

Wungrattanasopon *et al.*, (1996) studied using of foam flotation to remove tert-Butylphenol from water. The surfactants cetyl pyridinium chloride (CPC) and sodium dodecyl sulfate (SDS) were used in a study of an adsorptive bubble flotation process in batch mode to remove tert-butylphenol (TBP) from water. The TBP removal is maximized when the surfactant concentration is around the critical micelle concentration (CMC). Since micelles form above the CMC, this indicate that the higher the surfactant monomer concentration, the better the removal, but the micelles compete with the air/water interface for the TBP, resulting in micelle reducing removal efficiency. The addition of NaCl to the feed solution results in a significant reduction of the ability of CPC to remove TBP, while it improves the ability of SDS to remove TBP.

Chavadej *et al.*, (2004) investigated the relationship between surfactant phase behavior and efficiency of the flotation of ortho-dichlorobenzene. Uses of anionic/nonionic surfactant mixture here permit examination of a wide range of conditions compare to the use of only anionic surfactants. Optimum oil flotation corresponds to a Winsor Type III microemulsion, which also corresponds to minimum interfacial tensions between oil and water and to maximum solubilization of water and of oil into a surfactant-rich microemulsion phase. In this work, high selectivity for oil compared to water in the overhead froth was demonstrated, a necessary criterion for an effective separation.

Chavadej *et al.*, (2004) indicated that the exact relationship between the equilibrium microemulsion characteristics and the froth flotation operation is still not clear. The Winsor type III microemulsion also corresponds to a minimum in interfacial tension between liquid phases at equilibrium. In order to elucidate which aspect of the microemulsion is responsible for flotation of oil, flotation experiments were performed with three different combinations of phases: water and middle phases (w-m); water and oil phases (w-o); and water, middle and oil phases (w-m-o). It was found that most oil was recovered when in the Winsor Type III microemulsion region is in the excess oil phase (not the middle phase), the reason why the Winsor

Type III microemulsion results in excellent oil removal in flotation operation is probably the ultralow interfacial tensions present and the formation of the middle phase is incidental.

Watcharasing *et al.*, (2008) investigated the relationship between the froth characteristics, the system interfacial tension (IFT), and the efficiency of diesel oil removal by froth flotation under colloidal gas aphyron (CGA) conditions. Branched alcohol propoxylate sulfate sodium salt ($C_{14-15}(PO_4)SO_4Na$) as an extended surfactant, was used to form CGA and microemulsion with diesel oil. For the CGA studies, the effects of salinity, surfactant concentration, stirring speed and stirring time were investigated. The results showed that the use of CGA enhanced the process performance of froth flotation in term of both the removal and the enrichment ratio of diesel oil since CGA increased both froth formation and stability. The froth flotation column which was operated at an air flow rate of 0.3 l/min with the feed solution prepared under non-equilibrium and the CGA conditions at 0.1 wt.% $C_{14-15}(PO_4)SO_4Na$, 3 wt.% NaCl, with a stirring speed of 5000 rpm and a stirring time of 5 min gave the highest oil removal of 97%.

Watcharasing *et al.*, (2008) studied the relationship between interfacial tension (IFT) and foam characteristics and the efficiency of diesel oil removal from water in a continuous froth flotation. Unlike the batch system, only Branched alcohol propoxylate sulfate sodium salt ($C_{14-15}(PO_4)SO_4Na$) and NaCl present in the solution yielded such poor foam characteristics so sodium dodecyl sulfate (SDS) was used as a froth promoter to improve the foam stability. Foam formation, stability and production rate were found to be crucial parameters to the froth flotation efficiency. The continuous froth flotation system offers a high diesel oil removal of 96% in the single stage unit.

Watcharasing *et al.*, (2009) studied the effect of air bubble parameters in a flotation column and the surfactant concentration to the efficiency of motor oil removal from water by continuous froth flotation. Branched alcohol propoxylate sulfate sodium salt ($C_{14-15}(PO_4)SO_4Na$) was used to form microemulsions with motor oil. An increase in surfactant concentration was found to reduce the size and rising velocity of air bubbles in the froth flotation column, whereas the specific surface area, bubble surface area flux, bubble number flux and residence time of the air bubbles

increased with increasing surfactant concentration. The maximum removal of both motor oil and surfactant was found to correspond to the $C_{\mu C}$. Beyond the $C_{\mu C}$, the oil removal decreased with increasing the surfactant concentration because increasing the micelle concentration results in increasing oil stabilization.

2.5 Studied Oil in This Work

Motor oil

Motor oil, or engine oil, is an oil used for lubrication of various internal combustion engines. The main function is for lubrication moving parts, motor oil also cleans, inhibits corrosion, improves sealing and cools the engine by carrying heat away from moving parts. Generally, motor oils contain several hydrocarbons having 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 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 dispersal by burning is not an expectable solution because heavy metals are dispersed to the atmosphere after incineration process (Vazquez-Duhalt et al., 1986).