CHAPTER II

LITERATURE SURVEY

2.1 Natures of surfactants

A surfactant or surface-active agent has a characteristic molecular structure consisting of hydrophilic (water-loving) which is usually polar group and hydrophobic (water-hating) which is usually hydrocarbon or nonpolar group. One of important properties of surfactant was to adsorb onto the surface or interface of the system resulting to decreasing the surface or interfacial tension of the medium in which it is dissolved. The interface indicates a boundary between any two immiscible phases and the surface indicates an interface where one phase is a gas, usually air.

Depending on the nature of the hydrophilic group, surfactants are classified as anionic, cationic, nonionic and zwitterionic (Rosen, 1992). Anionic surfactant is a surfactant molecule whose polar group is negatively charged such as sodium dodecyl sulphate, ($CH_3(CH_2)_{11}SO_4^-Na^+$). Cationic surfactant is a surfactant molecule whose polar group is positively charged such as cetyltrimethyl ammonium bromide, ($CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$). Nonionic surfactant is a surfactant molecule whose polar group is not electrically charged such as polyoxyethylene alcohol, ($C_nH_{2n+1}(OCH_2CH_2)_mOH$). Zwitterionic surfactant is a surfactant molecule whose polar group contains both negatively and positively charged groups such as lauramidopropylbetaine, ($C_{11}H_{23}CONH(CH_2)_3N^+(CH_3)_2CH_2COO^-$) at neutral and alkaline solution pH.

A single molecule of surfactant is called monomer and at sufficiently concentration in solution, monomers or surfactant molecules will nucleate to form aggregates called micelles. This process is called micellization that is illustrated in Figure 2.1 and the lowest total surfactant concentration at which micelles are present is critical micelle concentration (CMC).

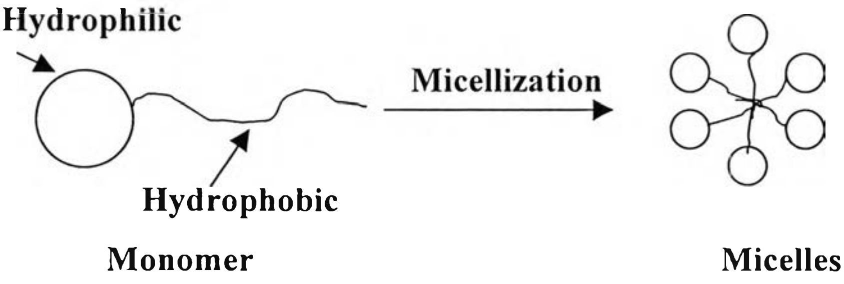


Figure 2.1 Schematic diagram of monomer, micelles and micellization

Surfactant solutions with concentrations above the CMC can dissolve considerably large quantities of organic materials than surfactant solutions with concentrations below the CMC. Since at the CMC, surfactant molecules form spherical micelles with the hydrophobic or hydrocarbon group on the interior and the hydrophilic group on the exterior. Therefore, oil or organic contaminants that are also hydrocarbon can solubilize at the center core of micelles. Furthermore, the solubilization increases as the number of micelles in the solution increases (Clarence and Neogi, 1985).

Normal micelles which have hydrophobic part in the interior and hydrophilic part in the external solvent are formed in aqueous solutions or water. Inverse micelles which have hydrophilic part in the interior and hydrophobic part on the outside are formed in nonpolar solvents. Figure 2.2 illustrates the picture of normal and reverse micelles (Rosen, 1992).

Normal micelles **Inverse micelles**

Figure 2.2 Schematic diagram of normal micelles and inverse micelles

Surfactants are widely used for many applications such as detergents, flotation, paints, cosmetics and enhanced oil recovery. Mixtures of different surfactants are used more than individual surfactants due to economical as well as beneficial effects. Mixtures of ionic and nonionic surfactants are commonly used in practical surfactant applications because the solution behaviors of these surfactants can be complementary. For instance, in laundry detergent formulations, anionic surfactants are used to maximize solubilization while nonionic surfactants are used to maximize water hardness tolerance. An addition of a nonionic surfactant to an ionic surfactant micelle can reduce the electrostatic repulsion between the charged surfactant heads and greatly facilitate mixed micelle formation (Shiloach and Blankschtein, 1998).

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 amphipathic nature, they tend to adsorb at interfaces. Thus, they can themselves act as collectors in flotation procedures (Sebba, 1989).

2.2 Emulsion systems

An emulsion is a significantly stable suspension of particles of liquid of a certain size within a second immiscible liquid (Rosen, 1992). Two immiscible pure liquid cannot form an emulsion and so a third component which is called the emulsifying agent needs to be introduced. A surfactant is typically used to form emulsion.

There are three types of emulsion.

1.Macroemulsion is an emulsion that is kinetically stabilized and generally milky-white in appearance when formed from colorless liquid. Moreover, it is an opaque emulsion with particles are greater than 400 nm which may be easily seen under a light microscope. It often tend to spontaneously separate into two or more phases without a significant temperature change.

2. Miniemulsion is a blue-white with particles size between 100-400 nm

3. Microemulsion is transparent dispersions with particles is less than 100 nm and may spontaneously separate as the result of a temperature change, but should return to their original state if returned to the original temperature. In addition, it looks clear and is kinetically stable.

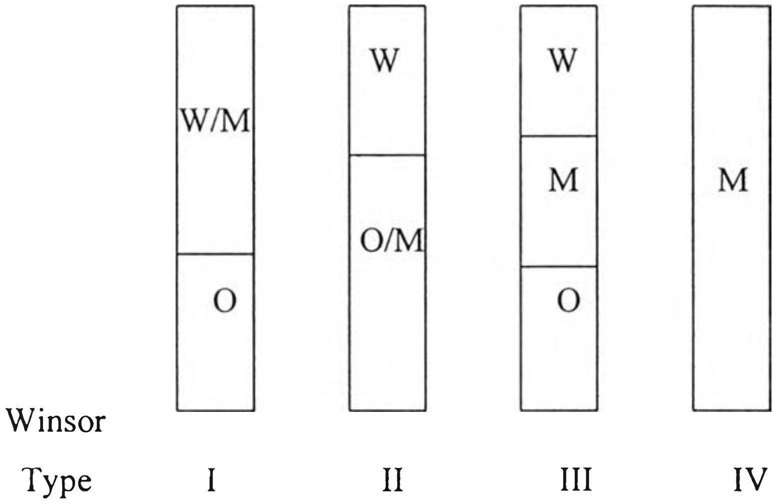
2.2.1 Characteristics of microemulsion

Microemulsions have been widely used in industrial and household application. Microemulsion were scientifically described for the first time in 1943 as special colloidal dispersions or a transparent or translucent system formed spontaneously upon mixing oil and water with a relatively large amount of ionic surfactant together with a cosurfactant by Hoar and Schulman.

Microemulsions are transparent and homogeneous mixtures of water and oil. They are stabilized by a fairly large amount of surfactant. Their spontaneous formation and long-lasting stability indicate that they are thermodynamically stable (Overbeek, 1978a,b). The formation of microemulsions generally involves a combination of three to five components which are oil, water, surfactant, cosurfactant and salt.

There are four types of microemulsion which are classified by Winsor (1954) as shown in Figure 2.3:

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



O = oil phase

W = water phase

M = microemulsion phase

Figure 2.3 Schematic diagram of types of microemulsions (Winsor, 1954)

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

Solans and Kunieda proposed the free energy of formation of microemulsion which consists of three contributions and is considered by Ruckenstein and Chi (1975)

1. interfacial free energy
2. energy of interaction between droplets
3. entropy of dispersion

Analysis of the thermodynamic factors shows that the contribution of the interaction energy between droplets is negligible and that the free energy of formation can be zero or negative if the interfacial tension is very low (of the order of 10^{-2} – 10^{-3} mN/m), although not necessary negative. Since the interfacial tension between oil and water is low enough to be compensated by the entropy of dispersion. It can be concluded that microemulsions are thermodynamically stable. The ease of formation of an emulsion may be measured by the amount of work needs for its formation. So, the lower the interfacial tension, the less work is needed and the more readily the emulsion is formed. Two surfactants are almost always employed in the formation of microemulsions. They are called the surfactant which is usually water soluble or dispersible such as soap or a detergent and the cosurfactant which is an alcohol or low HLB (Hydrophile-Lipophile Balance) nonionic. The combination of the surfactant and the cosurfactant has emulsifying potential than only one surfactant (Solans and Kunieda, 1997).

Microemulsions as extraction vehicles offer several advantages in reduced toxicity and low energy requirements for the total process due to the reversibility of process (Friberg and Neogi, 1989). Because of low energy for preparation, spontaneous formation, clear appearance, thermodynamic stability and low viscosity, microemulsions are very attractive and suitable for many industrial applications such as microemulsions in biotechnology, pharmaceutical field, food, cosmetics, dyeing processes, enhanced oil recovery and extraction of contaminated solids.

2.2.2 Effect of electrolyte on microemulsion formation

A small amounts of neutral electrolyte added to ionic surfactant solution can increase the extent of solubilization of hydrocarbons that are solubilized in the inner core of the micelle and to decrease that of polar compounds that are solubilized in the outer portion of palisade layer (Rosen, 1992). Since an electrolyte can decrease the repulsion between the similarly charges ionic surfactant head groups, it can reduce CMC (Critical Micelle Concentration) and increase the aggregation number. Moreover the addition of electrolytes can reduce the surfactant monomers and thus increase solubilization in micelles.

2.2.3 Formation of liquid crystal

Liquid crystal formation may occur when there are strong chain-chain and head-head interactions between surfactant molecules due to long, straight chains and close-packed heads as illustrated in Figure 2.4. The liquid crystal formation usually limits the solubilization capacity of the solution because there is much less space available for solubilization in rigid liquid-crystal structures than in the more flexible types of micelles (Rosen, 1992). Some factors involving the liquid crystal formation also appear include the structure of the surfactant, the temperature, and the presence or absence of certain additives. Liquid crystals are usually highly viscous and behave as fluids. Liquid crystal aggregation is an intermediate between the crystalline solid and the amorphous liquid (Laughlin, 1994).

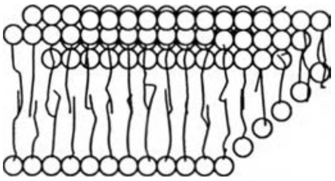


Figure 2.4 Schematic diagram of lamellar liquid crystal

2.3 Principles of froth flotation

Flotation is an important separation process that 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 (Somasundaran and Ramachandran, 1998). The success of flotation processes primarily depends on the tendency of surfactants to concentrate at the air-water interface and on their capability to make selected hydrophobic materials by means of adsorption on them or association with them.

In addition to the formation of a froth, the presence of a surfactant dramatically increases the dispersion of air in the flotation tank, reduces the coalescence of individual bubbles within the liquid, and decreases the rate at which the bubbles rise to the surface. All these factors greatly increase the possibility of particle-bubble contact and hence the rate of flotation. Absolutely pure liquid does not froth and the presence of a surfactant is necessary to induce frothing. When a surfactant is added to water, the surface tension of the solution decreases as a result of the heteropolar nature of the molecules, which leads to a preferential adsorption of these molecules at the air-water interface. The surfactant molecules are arranged at the interface such that the hydrophilic or polar group is situated in the water phase and the hydrophobic or hydrocarbon chain in the air phase. The degree of adsorption at the interface of these surfactant molecules is related to the decrease in surface tension by Gibbs adsorption equation (King, 1982).

$$\tau = -\frac{a}{RT} * \frac{d\gamma}{da} \qquad (2.1)$$

Where:

τ = the surface excess concentration of the surfactant

γ = the surface tension

a = the activity of the solute.

Froth flotation can be used in several applications such as removal of oil from wastewater, mineral separation, removing ink from paper fibers. Surfactants used as flotation reagents include those that function as collectors, depressants, frothers, flocculants, dispersants, and filtering aids (Fuerstenau and Herrera-Urbina, 1989). Surfactants act as collectors and surfactants tend to strongly adsorb at the air/water interface with the hydrophobic or tail group in the air and the hydrophilic or head group in the water. The hydrophilic region is favorable for organic solutes which tend to co-adsorb at the air bubble surface.

In froth flotation, there is a driving force that causes oil droplets floated from the solution to adhere to the surface of the air bubbles rising through the liquid column. Air is introduced at the bottom of froth flotation column through a porous sparger that can produce air bubbles. The generated air bubbles rise through an oil solution and carry molecules of oil to the top of column. At the top of the solution, air bubbles form foam or froth and it is collected in a launder that is illustrated in Figure 2.5. There are two distinct zones in flotation column which are a bubbly zone and a froth zone. In a bubbly zone, air bubbles collect oil or hydrophobic particles and carry them to the froth zone. In a froth zone, there is a removed oil in forms of foam or froth rising through a top of column after that foam is broken as liquid. Flotation can be operated in batch and continuous modes that is shown in Figure 2.6.

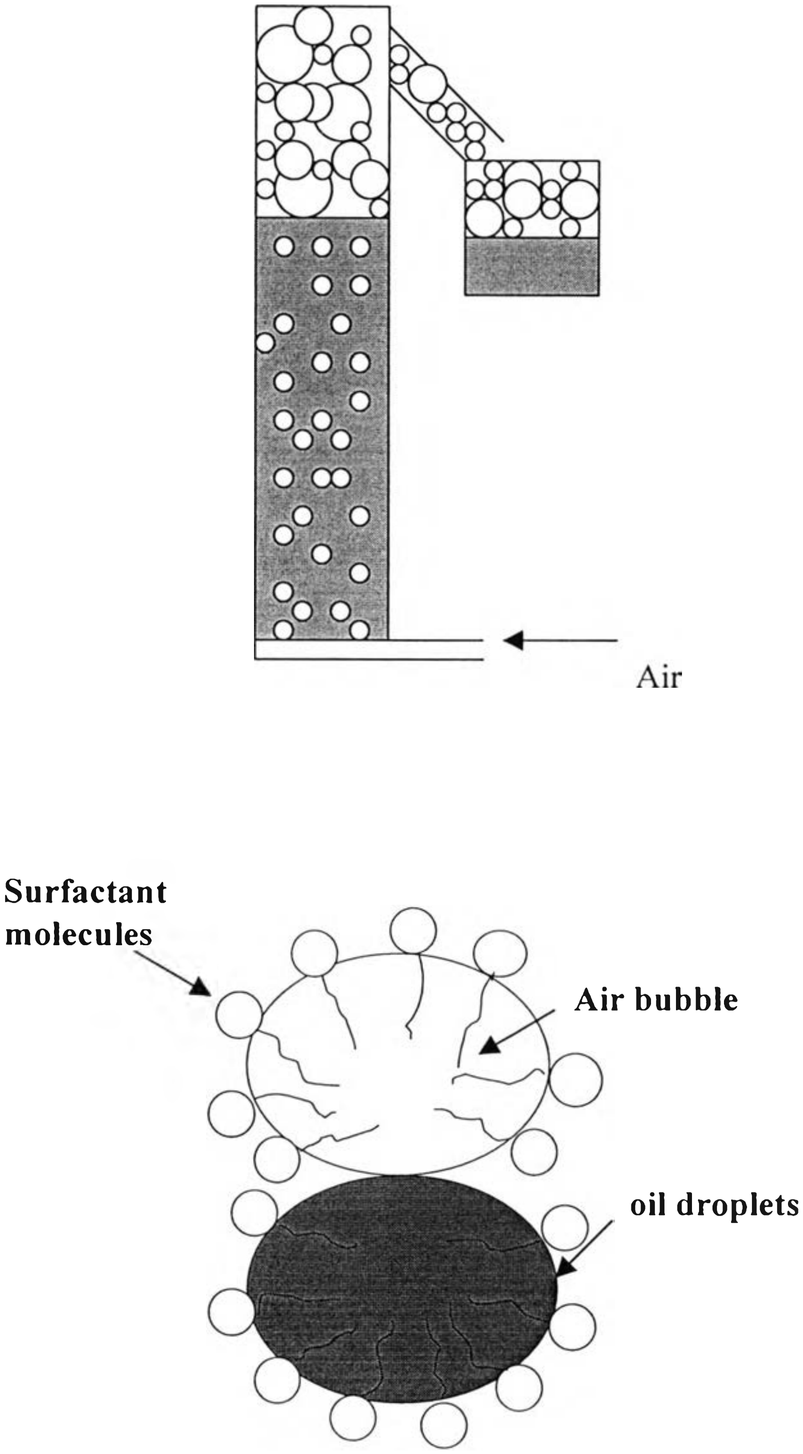
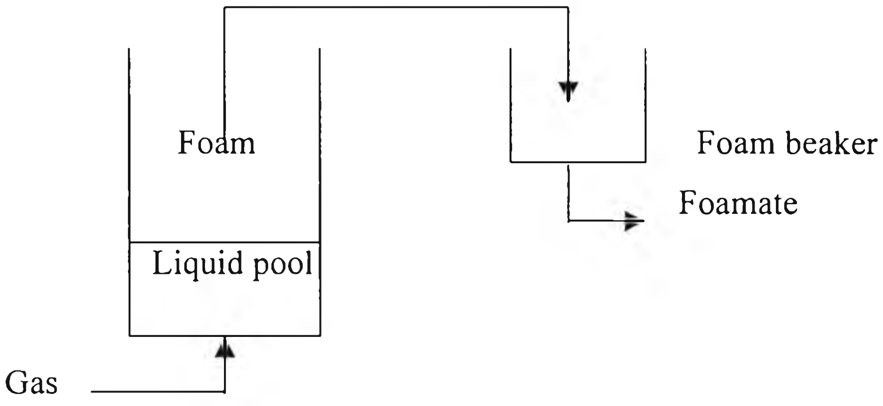
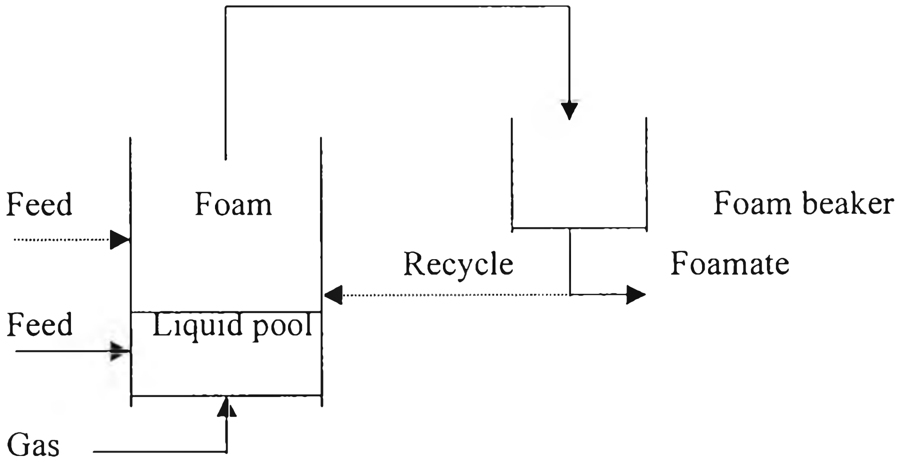


Figure 2.5 Schematic diagram of froth flotation column in batch mode and mechanism of oil removal



Batch Mode



Continuous Mode

Figure 2.6 Experimental configurations for foam or froth separation (Carleson, 1989)

In batch mode, the solution is transferred to the column at the outset and then air bubbles are passes through the column until a separation has been achieved or no further foaming occurs. The concentration of solution within the column and foam are continuously changing during the operation. The column is depleted of surfactant since it is swept up into the foam.

In continuous mode, the solution is fed continuously into the column at a particular rate. At the same time, foam and liquid are removed continuously during the operation leading to the generation of a steady state. The concentrations of surfactant and oil in the column are maintained at constant levels same as the concentrations of them that extracted into the foam

Flotation column is static, simple and compact in design, has no parts moving in an abrasive medium and efficiently utilize operating and volume. It also has other advantages such as low power requirement (in absence of rotating parts), low capital cost, a high aerated volume and the possibility of air flow rate and bubble size distribution control (Rubinstein, 1995).

Flotation involves the removal of particulate by frothing, whereas foam fractionation involves the separation of soluble species by foams (Carleson, 1989).

Wungrattanasopon *et al.* (1996) studied the effects of two types of surfactants of SDS (Sodium Dodecyl Sulphate) and CPC (Cetyl Pyridinium Chloride) and NaCl on the removal efficiency of tert-butylphenol (TBP) that acted as a toxic pollutant by using foam flotation process. It was conducted that TBP removal was maximum when the surfactant concentration was around the CMC. Without the addition of NaCl, CPC give higher TBP removal than SDS did. However, the addition of NaCl to the feed solution resulted in a significant reduction of the ability of CPC to remove TBP while it improved the ability of SDS to remove TBP.

2.4 Chlorobenzene as a hazardous substance

Chlorobenzene and its derivatives are classified as hazardous substance. However, they are widely used in several applications including solvents in paints, a raw material in the manufacture of phenol and aniline, an insecticide for termites, a degreasing agent for metals and as a heat transfer medium. (Martin *et al.*, 1992)

Ortho-dichlorobenzene which is an aromatic substance is one kind of chlorobenzene. It is a starting material to produce 3,4 dichloroaniline that is a raw material in the herbicide manufacturer. It can damage human's health such as depression of central nervous system, anesthesia and liver damage. It is a representative of pollutants in groundwater and rank twenty-fifth in the EPA list of organic priority pollutants. Therefore, it is necessary to remove its from waster water before it is discharged into public water or reused in industrial processes.

In the previous work, Pongstabodee *et al.* (1998) and Ratanarojanatam (1997) also used ODCB as an oil to study the phase behavior of microemulsion and the removal of ODCB from wastewater by froth flotation.

Pongstabodee *et al.* (1998) investigated the effect of salinity on the phase behavior of microemulsion for three surfactants which were CPC (Cetyl Pyridinium Chloride), SDS (Sodium Dodecyl Sulfate) and Dow-fax 8390 (Mono and di-hexadecyl diphenyloxide disulfonate, sodium salt). The results showed that as salinity increased, the systems transferred from Winsor type I or oil in water microemulsion to Winsor type III or middle phase microemulsion. The salinity range which affected the phase behavior decreased with increasing surfactant concentration. The effect of cosurfactant (pentanol) was also studied and the results indicated that an addition of pentanol promoted phase transformations. Varying oil/water ratio to very large or very small caused a formation of liquid crystalline. For the froth flotation experiment, the removal of ODCB increased when salinity increased and the system was in Winsor type III. The ability of CPC to remove ODCB was greater than DADS and SDS respectively under the same range of salinity.

Ratanarojanatam (1997) studied the formation of microemulsion system depended on the mixed surfactants concentration and the SDS weight fraction (Xsds). As Xsds increased, the surfactant could transfer from Winsor type II to Winsor type III and to Winsor type I system. An increase of surfactant concentration caused the formation of the Winsor type III system. For the froth flotation, the solutions under the Winsor type III system gave the highest percentage of ODCB removal.