

CHAPTER II

LITERATURE REVIEW

2.1 Surfactants

A surfactant is a compound that lowers the surface tension of a liquid, increasing the contact between the liquid and another substance. There are a wide variety of these compounds that work with oil, water, and an assortment of other liquids. Many companies manufacture a range of surfactants for various purposes, ranging from soaps to inks. They are also sometimes referred to as “wetting agents.” (<http://www.wisegeek.org/what-is-a-surfactant.html>).

The general structure of a surfactant that has strong attraction with a solvent, known as a lyophilic group (solvent-loving), together with a group that has little attraction with the solvent, called the lyophobic group (solvent-hating). This is known as an amphipathic structure, as shown Figure 2.1. When the solvent is water, one usually calls a hydrophilic or head group and hydrophobic or tail group. Another important property of surfactants is to form aggregates, known as micelles, as shown Figure 2.2. The lowest surfactant concentration to form a micelle is called the critical micelle concentration (CMC) (Porter, M.R., 1994).

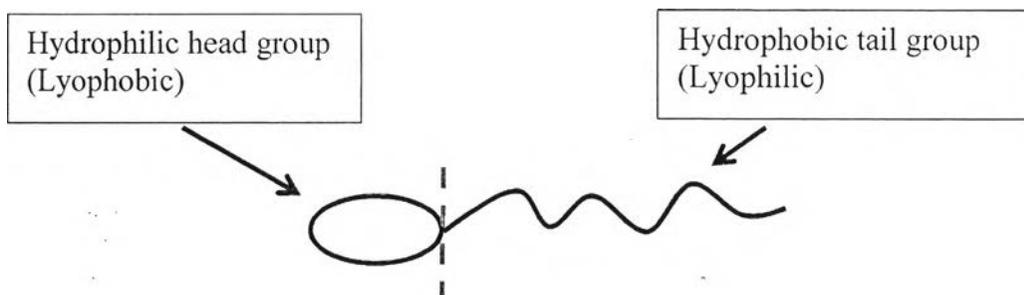


Figure 2.1 Schematic of a surfactant molecule.

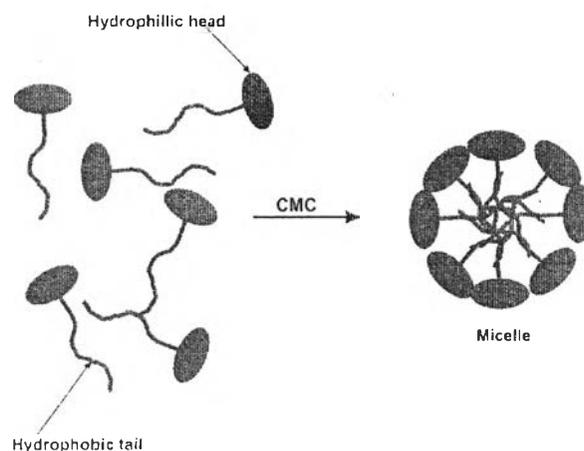


Figure 2.2 Show the structure of micelle.

Surfactants are generally classified according to the nature of the hydrophilic group as follows:

1. *Anionic surfactants*. The surface-active portion of the molecule bears a negative charge, for example, $\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+$ (alkylbenzene sulfonate), $\text{C}_{12}\text{H}_{25}\text{SO}_3^-\text{Na}^+$ (sodium dodecyl sulfate).

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

3. *Nonionic surfactants*. The surface-active portion of the molecule bears no apparent ionic charge, for example, $\text{RCOOCH}_2\text{CHOHCCH}_2\text{OH}$ (monoglyceride of long-chain fatty acid).

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

2.2 Foam

2.2.1 Foam Formation

Foam is a colloidal gas phase dispersed in a liquid phase. It is produced when air is introduced below the surface of a liquid and the liquid is

expanded to enclose the gas with a network of interconnected liquid films called lamellae (Rosen, 2004). There are two conditions to form foam. Firstly, surface activity of a foaming solution must be sufficiently high. Because the foam formation involves the expansion of air–water interface, the amount of newly created surface will be greater at a lower surface tension (Adamson and Gast, 1997). Therefore, a surfactant is required to reduce the surface tension and cause the formation of foam faster than its breakdown, as shown in Figure 2.3. Secondly, the liquid film must provide sufficiently high foam stability.

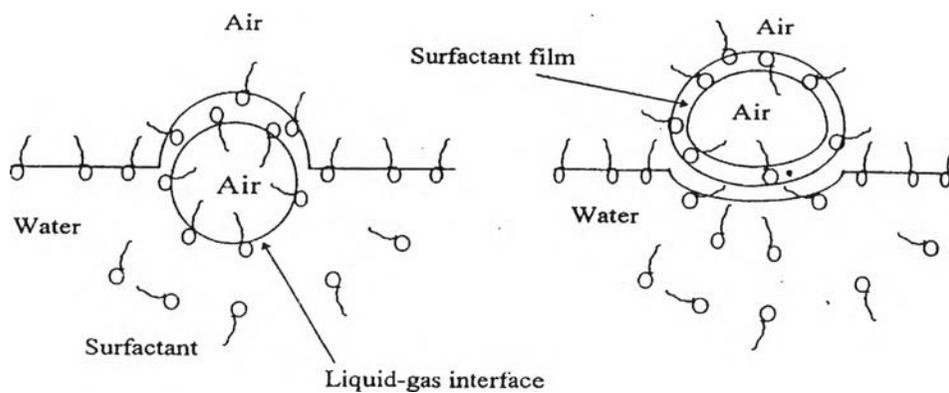


Figure 2.3 Formation of foam (Rosen, 2004).

2.2.2 Structure of Foam

Foam contains a high-volume fraction of gas dispersed in a liquid. The structure of gas cell consists of thin liquid film and there are two-side films which are called the lamellae of the foam where three bubbles generally meet. The joining area of the bubbles is called the Plateau border or Gibbs triangle, as shown in Figure 2.4. Most of the water in the foam is found in the plateau border. Thus, the plateau border will play an important role in the drainage of water (Adamson and Gast, 1997).

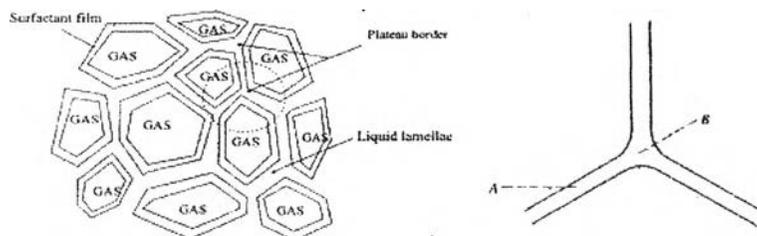


Figure 2.4 Plateau border at point of meeting of three bubbles (Rosen, 2004).

Foam can be categorized into two types as follows:

1. *Spherical Foam* (Kugelschaums). A fresh foam consists of nearly spherical gas bubbles separated by rather thick films of viscous liquid produced, as shown in Figure 2.5a. It is known as wet foam.

2. *Polyhedral Gas Cells* (Polyederschaums). After a long period of time, foam contains mostly gas phase separated by thin films with polyhedral shape as shown in Figure 2.5b. It is considered as dryer foams.

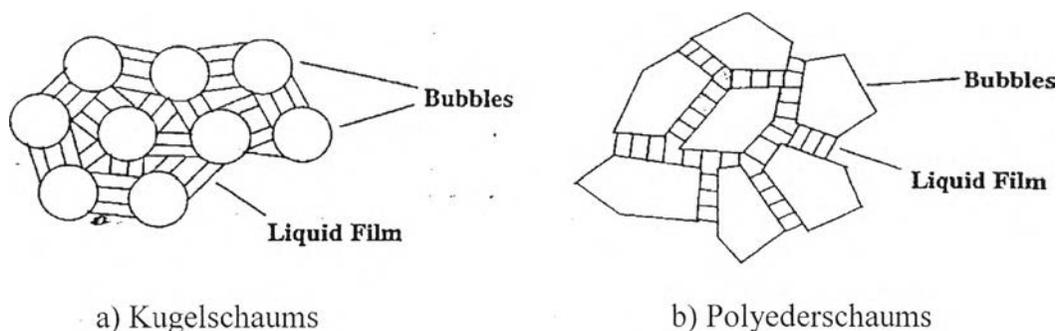


Figure 2.5 Structure of foam (Rosen, 2004).

In a foam fractionation column, foam structure is changed along the column due to the liquid film drainage process. The spherical structure (low gas content) near the base of the column (bubble zone) is changed into polyhedral foam (high gas content) at the upper part of the column, as shown in Figure 2.6.

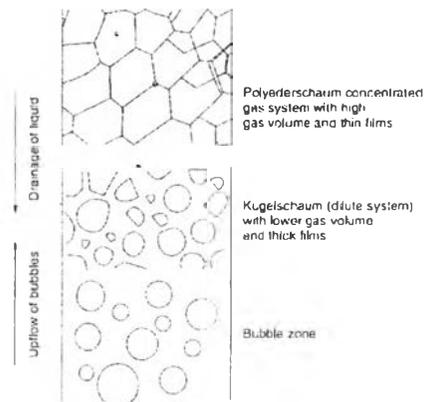


Figure 2.6 Schematic of foam structure in a column (Tadros, 2005).

2.2.3 Foam Stability

The foam stability depends on various factors including liquid film drainage and thin film stability. Another effect of foam stability is originated from the gas pressure inside the bubble is inversely proportional to the size of the bubble. Therefore, gas molecule will diffuse from a smaller to a larger bubble, causing bubble coalescence. This phenomenon is called Ostwald ripening or disproportionation. With polyhedral foam with planar liquid lamella, the pressure difference between the bubbles is not large and hence the Ostwald ripening effect is not responsible for the foam instability.

2.2.3.1 *Liquid Film Stability*

The stability of thin liquid film (lamellae) of foam consists of two factors: surface elasticity and disjoining pressure. The surface elasticity or Gibbs elasticity, E , is defined as the increase in surface tension, γ , as the surface area, A , is increased (Schramm, 2005) in Equation 2.1.

$$E = A \frac{d\gamma}{dA} \quad (2.1)$$

For a foam lamella, there are two such surfaces and the elasticity becomes equation 2.2.

$$E = 2 \frac{d\gamma}{d \ln A} \quad (2.2)$$

The Gibbs elasticity was introduced as a variable resistance to surface deformation during thinning and is a measure of the ability of the film to adjust its surface tension in an instant stress (Tadros, 2005). When a foam lamella is stretched, the surfactant concentration at the newly create surface is suddenly lowered, thus resulting in an increased surface tension and thus, restoring force as depicted in Figure 2.7 (Holmberg *et al.*, 2003).

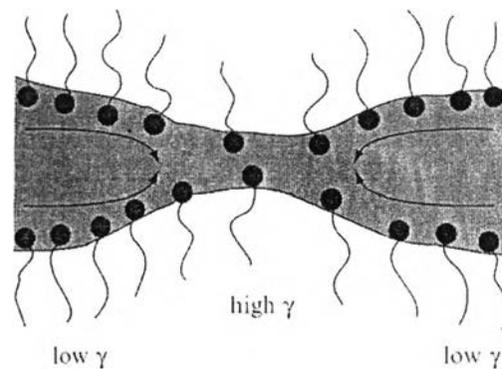


Figure 2.7 Surface elasticity of foam film (Holmberg *et al.*, 2003).

However, the Gibbs elasticity applies to the case where there are insufficient surfactant molecules in the bulk solution (liquid lamellae) to diffuse to the new surface and lower the surface tension. In other word, it can apply only for the case that the surface diffusion of adsorbed surfactant must be faster than the surfactant diffusion from the bulk. This is clearly not the case with most surfactant films (Tadros, 2005). In order to obtain film elasticity, the diffusion of the surface active component from the bulk (from the interior of the lamella film) to the newly created surface is not allowed before the film retracts because it will destroy the surface tension gradient and prevent restoring force. That is a reason why surfactants with very high CMC (high fraction of unimer) will not produce stable foam because the high bulk concentrations promote the surfactant diffusion from the interior of the lamella film (Holmberg *et al.*, 2003).

For the second factor, disjoining pressure , if the foam films remain stable during the drainage process, they may approach a very thin film in the

range of 100 nm where the surface force becomes significant. The gas bubbles and the liquid films between them would be stabilized by the surface forces created when the two charged interfaces approach each other and their electrical double layers overlap. The surface force is called disjoining pressure, Π , which is the sum of three forces including electrostatic double layer repulsion (Π_{el}), van der waals attraction (Π_{vdW}), and steric force (Π_{st}) (Tadros, 2005), as shown in Equation 2.3.

$$\Pi = \Pi_{el} + \Pi_{vdW} + \Pi_{st} \quad (2.3)$$

At low electrolyte concentrations, the double layer repulsion Π_{el} can counterbalance the Laplace capillary pressure (capillary suction effect at Plateau border), $P_c = \Pi_{el}$. When the capillary pressure is counterbalance, the draining liquid film reaches equilibrium state. This is a main mechanism for prevent thin foam film from rupture (Wang and Yoon, 2008) and foam collapse (Tadros, 2005). Besides, an equilibrium film has a lower probability of rupture than a draining film of much larger thickness (Wang and Narsimhan, 2007).

2.2.3.2 *Liquid Film Drainage*

Liquid film drainage is an important factor, effect of the foam stability. During lamellae liquid draining off, the foam may collapse immediately or reach metastable state depending on liquid film drainage. The foam will reach the metastable state with an equilibrium film if the time scale of the liquid film drainage is much shorter than the film rupture time (Wang and Narsimhan, 2007). This implies that fast liquid film drainage and high thin liquid film stability lead to the equilibrium film. After reaching equilibrium, the foam stability is mainly affected by the disjoining pressure as mentioned above.

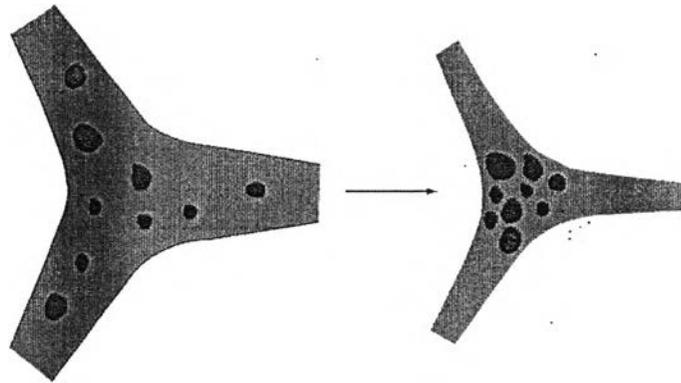


Figure 2.8 Reduction of foam film drainage by particle trapped in the plateau border (Holmberg *et al.*, 2003).

The liquid drainage of the film can be determined by considering two forces acting on foam. The first is the gravitational force causing drainage of the liquid between the air bubbles. It is dominant in very thick lamellae when the foam is first formed. The drainage can be reduced by either increasing the viscosity of the bulk liquid or by adding particles (Holmberg *et al.*, 2003). These particles can be trapped into the plateau border leading to a local increase in viscosity, as shown in Figure 2.8. Thickeners are often added to increase the bulk viscosity when very stable foams are desirable. At a high concentration of surfactant, the viscosity of the bulk solution is also high and, therefore, the drainage rate in the lamellae decreases.

The second is capillary suction force originated from the fact that hydrostatic pressure in the plateau border is lower than in the lamellae. This force is more dominant for polyhedral foam with thin liquid film because the drainage due to gravitational force will gradually be replaced by the drainage due to the capillary suction (Holmberg *et al.*, 2003). Since the curvature in the lamellae is much greater than that at the plateau borders, there is a greater pressure across the interface in these regions than elsewhere in the foam. Since the gas pressure inside on individual gas cell is everywhere the same, the liquid pressure inside the lamellae at the highly curved Plateau Border (point A) must be lower than in the adjacent, less curved regions (point B). Thus, the continuous phase liquid drains from the thin film

(point B) to the adjoining Plateau Borders (point A), as shown in Figure 2.5b. The difference pressure (ΔP) can be expressed by the following Equation 2.4:

$$\Delta P = \gamma [1/R_A + 1/R_B] \quad (2.4)$$

where γ is surface tension, R_A and R_B are the radii of the curvature of the lamellae at point A and B, respectively. The greater the difference between R_A and R_B , the greater the pressure difference causing drainages (Rosen, 2004).

In the process of water drainage, foam is always under dynamic conditions and the Marangoni effect takes surfactant diffusion from the bulk solution to the newly created surface into account in order to describe a mechanism retarding the liquid film drainage (film thinning) and providing foam stability. The viscous drag from the bulk results in the formation of a surfactant concentration gradient on a bubble surface as illustrated in Figure 2.9 (Tan *et al.*, 2006). This surface tension gradient causes the spreading of surfactant molecules from regions of low to high surface tension at the air-liquid interface, leading to the movement of the underlying layer of liquid in the film. This is opposite to the drainage direction of the thin liquid film, resulting in retardation, thus providing transient stability to the foam. At a very high surfactant concentration, the surface tension difference present on the bubble surface diminishes due to the fast adsorption of surfactant molecules from the bulk to regions of high surface tension on the bubble and the Marangoni effect is diminished. This may cause the foam to collapse. The maximum in foamability at intermediate concentrations is likely to be related to the influence of bulk surfactant concentration on the Marangoni effect (Pugh, 1996). On the one hand, at low surfactant concentrations, the surface tension gradient present on the surface is not large enough to cause significant Marangoni flow. An optimal concentration range exists where maximum foamability occurs (Tan *et al.*, 2006). Moreover, bulk diffusion coefficient is one of the relevant parameters in the drainage of surfactant solution (Buzzacchi *et al.*, 2006).

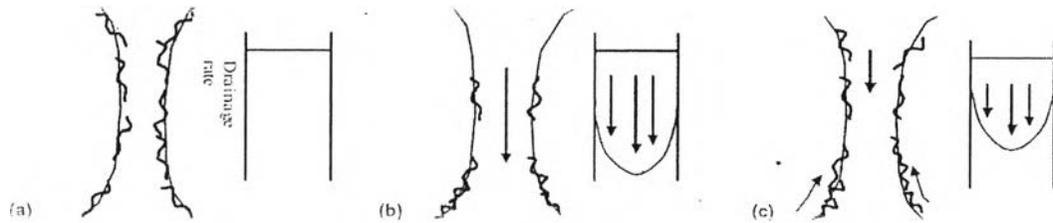


Figure 2.9 (a) Surfactants at the air–liquid interface in the absence of thin film drainage. (b) Surface tension gradient on the surface is created as the surfactants are displaced due to the bulk viscous drag force in the presence of drainage. (c) The Marangoni effect results in a decrease in the net drainage rate (Tan *et al.*, 2006).

2.3 Surfactant Adsorption at Air–Water Interface

The reduction in surface tension results from a strong adsorption of the surfactant molecules at the air–water interface. The surface excess concentration of surfactant is related to the surfactant concentration of the bulk liquid as described by the Gibbs adsorption equation. For a dilute solution of a surfactant, the adsorption is related to the change in surface tension as described by Equation 2.5.

$$\Gamma = - \frac{1}{nRT} \frac{d\gamma}{d \ln C} \quad (2.5)$$

where Γ is the surfactant surface excess concentration, γ is the bulk surface tension, C is the bulk surfactant concentration, R is the gas constant, n is equal to 2 and 1 for ionic surfactant in absence and presence of large excess of simple sodium salt (i.e. NaCl), respectively, and T is the absolute temperature (Rosen, 2004).

At below the CMC, the surface excess concentration (slope of γ -log C) increases as the bulk concentration increases. For surfactant concentrations below but near the CMC, the slope of the curve is essentially constant (Rosen, 2004), indicating that the surface excess concentration of surfactant has reached a constant maximum value (Γ_m), often in the order of 3×10^{-10} mol/cm².

2.4 Adsorptive Bubble Separation

The adsorptive bubble separation methods based on the selective adsorption or attachment of materials on the surfaces of gas bubbles rising through a solution or suspension (Lemlich, 1972). If a material to be removed (colligend) is non-surface active, a suitable surfactant (collector) has to be added to interact with it and bring it to adsorb at the bubble surface. (Sebba, 1962). The colligend is transferred from the solution into foam or froth and are removed from the liquid.

The most widely accepted classification of the various adsorptive bubble separation methods is shown in Figure 2.10 (Perry and Green, 2007). Among the methods of foam separation, foam fractionation usually implies the removal of dissolved (or sometimes colloidal) materials (Perry and Green, 2007). On the other hand, flotation usually implies the removal of solid particulate materials. For removal of ions, several categories of the flotation are as follows (Lazaridis *et al.*, 2004):

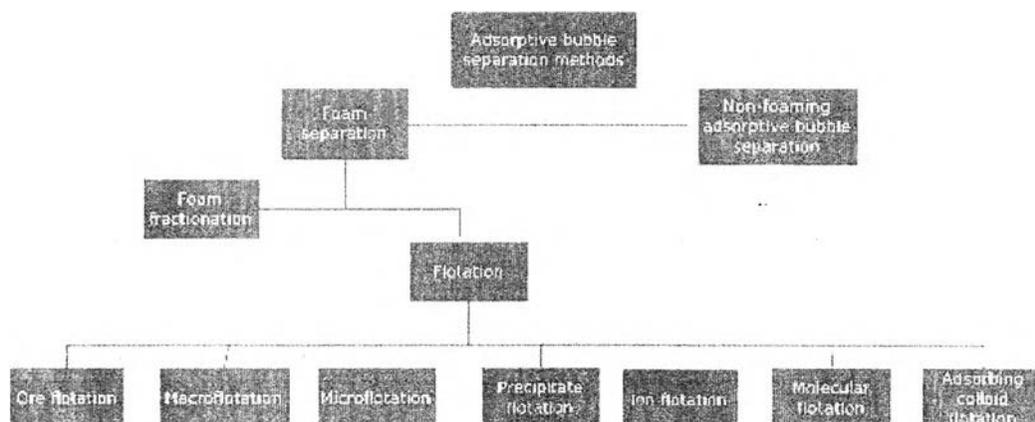


Figure 2.10 Classification for the adsorptive bubble separation methods.

1. *Ion Flotation*. Non-surface active ions are removed from an aqueous solution by adding an oppositely charged ionic surfactant to form ion pairs or soluble complexes which are adsorbed at the solution–vapor interface (Doyle, 2003). Here the added surfactant performs the dual roles of frother and collector (Rubio *et al.*, 2002).

2. *Precipitate Flotation*. The ions removed are immobilized as surface active precipitates (fine particle) by adding the collectors or another species in a sufficient amount which can reach their solubility products. The precipitates are themselves floatable and removed by attachment at the bubble surface of froth (Doyle, 2003; Alexandrova and Grigorov, 1996).

3. *Sorptive Flotation or Adsorptive Particulate Flotation*. The ions removed are scavenged from aqueous solution into bonding agent (i.e. sorbent). After the sorption, the metal-loaded sorbent particles are separated from the treated and clean solution by adsorption on the rising bubbles (Zamboulis *et al.*, 2004).

4. *Foam Fractionation*. This method is similar to ion flotation but uses an excess of a surfactant (for frothing) or a proper frother to produce a stable foam (Rubio *et al.* 2002).

5. *Adsorbing Colloid Flotation*. This method involves the removal of metal ions by adsorption onto or co-precipitation with a precipitate acting as a carrier. The loaded carrier is then floated, usually assisted with a suitable “collector” surfactant (Jurkiewicz, 2006; Huang and Wang, 1988).

Among the three flotation techniques: ion, precipitate, and sorptive flotation, ion flotation showed the highest copper recovery with the lowest residual copper concentration (Lazaridis *et al.*, 2004).

2.4.1 Principles of Foam Fractionation

Foam fractionation is an adsorptive bubble separation process in which a surface active species, which can adsorb preferentially at the bubble surface, are separated selectively from a liquid solution, depending on the difference in surface activity of the individual species. It can be used to remove dissolved materials from a homogeneous solution, i.e., pollutants from wastewater and groundwater (John and Edward, 1996). This process offers many advantages for the treatment of industrial wastewaters as compared to the other treatment processes: low space and energy requirement; simplicity in design, operation and scale-up; low capital and operating costs (Wong *et al.*, 2001). Not only surfactants are removed by the adsorption at the air–liquid interfaces, but other matters that can form a complex with the surfactants tend to also be concentrated (Yapijakis and Wang, 2005).

In a foam fractionation operation (see Figure 2.11), air is introduced beneath the solution surface at the bottom of the foam fractionation column to generate rising pneumatic foam. The surface active solutes, which can adsorb at the bubble surface of the generated foam, are carried upward with the rising foam and then leave the column. Not only material adsorption on bubble surface, most liquid must be separated from the foam by liquid film drainage, causing the liquid to be drained off at the bottom and material enrichment at the top of the column. Once the foam collapses, concentration of the solute in collapsed foam solution called foamate is higher than that in feed, depending on degree of liquid film drainage, bubble surface area flux, and adsorption density.

During the liquid film drainage process, the mass transfer between internal reflux liquid (draining liquid) which is a surfactant rich stream and upward entrained liquid in foam phase which is a surfactant lean stream (Darton *et al.*, 2004). If most surfactant molecules can be recovered back from the draining liquid, insignificant amount of surfactant molecules are left as residue in effluent. Hence, the liquid drainage is necessary for inducing separation and enrichment to occur because it reduces the liquid content in the foam phase without significant withdrawing of surfactant molecules from the foam phase. However, foam collapse must be avoided during the liquid film drainage because of releasing of the adsorbed surfactant molecules. This is a role of surfactant to provide sufficiently high foam film stability with fast liquid film drainage.

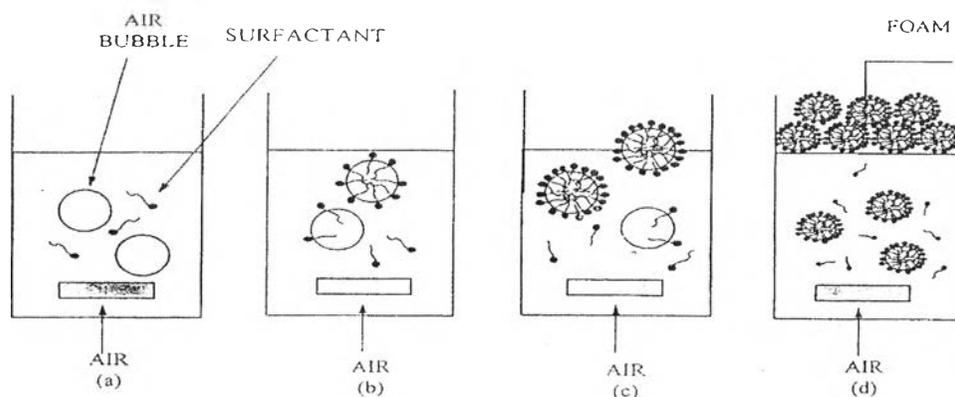


Figure 2.11 Principle of foam fractionation.

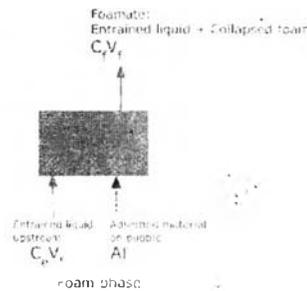


Figure 2.12 Material balance around foam phase.

2.4.2 Mole Balance in Foam Fractionation Column

A mole balance of a surfactant in the collapsed foam at the top of column under steady state condition, which is the molar flow rate of foamate ($C_f V_f$) is equal to the sum of the mass transfer by the bulk liquid and the adsorptive transports (Darton *et al*, 2004), as shown in Figure 2.12:

$$C_f V_f = C_e V_e + A\Gamma \quad (2.6)$$

where V_f is the volumetric flow rate of collapsed foam, C_e is the surfactant concentration in the bulk liquid or in the effluent, C_f is the surfactant concentration in the collapsed foam, A is the flow rate of the interfacial area of the generated foam, and Γ is the surface excess concentration. The term $A\Gamma$ indicates the amount of surface adsorption on the bubble surface, known as the adsorptive transport. By performing overall mole balance ($V_i C_i = V_f C_f + V_e C_e$) under steady state condition, the input moles of the surfactant is equal to the sum of the moles of the surfactant in the foamate and in the effluent, as shown in Equation 2.7:

$$C_i V_i = C_e V_e + C_f V_f + A\Gamma \quad (2.7)$$

where V_i and V_e are the volumetric flow rates of the feed and the effluent, respectively. We can rearrange Equation 2.7 to obtain the mole balance in terms of residual factor by dividing Equation 2.7 with $C_i V_i$ to yield the following:

$$\frac{C_e}{C_i} = \left[1 - \frac{A\Gamma}{C_i V_i} \right] \quad (2.8)$$

The process separation performance of the foam fractionation column is usually assessed by using % surfactant recovery; enrichment ratio; and separation factor, described as follow:

$$\% \text{ Surfactant recovery} = \frac{C_f V_f}{C_i V_i} \times 100 \quad (2.9)$$

$$\text{Enrichment ratio} = \frac{C_f}{C_i} \quad (2.10)$$

$$\text{Separation factor} = \frac{C_f}{C_e} \quad (2.11)$$

Equation 2.6 suggests that an increase in the surfactant recovery is governed by both bulk liquid transport and adsorptive transport. A reduction in $A\Gamma$ is responsible for an increase in the residual factor (C_e/C_i), as described by Equation 2.8, as well as for a decrease in surfactant recovery, as described by Equation 2.6. With aid of Equation 2.8 and overall mass balance ($V_i = V_f + V_e$) under steady state condition, the bulk liquid transport term ($C_e V_f$), normalized by feed molar flow rate ($C_i V_i$), can be expressed as

$$\text{Normalized bulk liquid transport} = \left(1 - \frac{A\Gamma}{C_i V_i} \right) \left(\frac{V_f}{V_i} \right) \quad (2.12)$$

Equation 2.12 suggests that the normalized bulk liquid transport is an upward stream of lamella liquid with unadsorbed molecules. Thus, the bulk liquid transport increases amount of unadsorbed material in foamate. At larger value of normalized adsorptive transport ($A\Gamma/C_i V_i$), Equation 2.12 suggests that less amount of surfactants are transferred by the bulk liquid even at large foamate volumetric ratio (V_f/V_i) as shown in Figure 2.13.

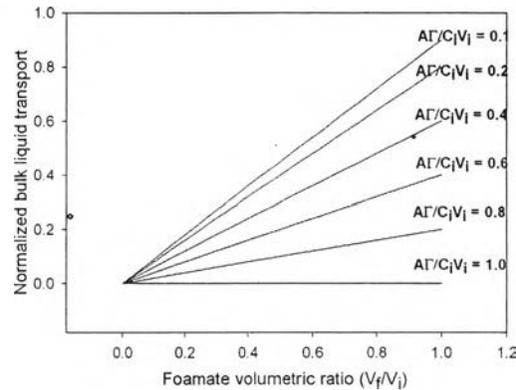


Figure 2.13 Dependence of normalized bulk liquid transport on foamate volumetric ratio as described by Equation 2.12.

Combing Equation 2.6, 2.8, and 2.9, one can obtain % surfactant recovery as a function of foamate volumetric ratio and normalized adsorptive transport ($A\Gamma/C_iV_i$) as shown in Equation 2.13

$$\% \text{ Surfactant recovery} = \left[\frac{V_f}{V_i} + \frac{A\Gamma}{C_iV_i} - \left(\frac{V_f}{V_i} \right) \left(\frac{A\Gamma}{C_iV_i} \right) \right] \times 100 \quad (2.13)$$

Equation 2.13 suggests that the surfactant recovery is mainly governed by the adsorptive transport at low bulk liquid transport and by the bulk liquid transport at low adsorptive transport as illustrated in Figure 2.14. At normalized adsorptive transport approaching unity, the lamellae liquid contains no surfactant and thus liquid film drainage or liquid entrainment does not affect the surfactant recovery. On the other hand, at significantly low normalized adsorptive transport, the lamellae liquid contain a significant amount of surfactant and thus the surfactant recovery should be decreased with an increase in liquid film drainage and increased with increasing liquid entrainment in foam.

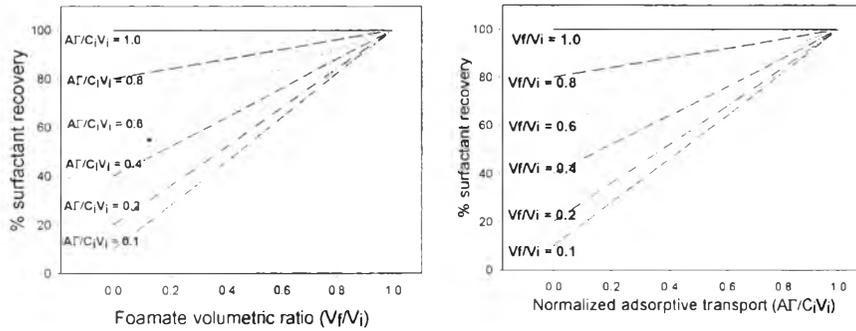


Figure 2.14 Dependence of % surfactant recovery on foamate volumetric ratio and normalized adsorptive transport as described by Equation 2.13.

By applying the overall mole balance, mass balance, and Equation 2.8, the enrichment ratio and separation factor as a function of normalized adsorptive transport ($A\Gamma/C_iV_i$) and foamate volumetric ratio (V_f/V_i) can be described as follow:

$$\text{Enrichment ratio} = 1 + \left(\frac{1}{\left(\frac{V_f}{V_i}\right)} - 1 \right) \left(\frac{A\Gamma}{C_iV_i} \right) \quad (2.14)$$

$$\text{Separation factor} = 1 + \frac{\frac{A\Gamma}{C_iV_i}}{\left(1 - \frac{A\Gamma}{C_iV_i}\right)\left(\frac{V_f}{V_i}\right)} = 1 + \frac{\text{Normalized Adsorptive}}{\text{Normalized Bulk liquid}} \quad (2.15)$$

Equations 2.14 and 2.15 suggest that the bulk liquid transport will contribute to the surfactant recovery but does nothing in terms of true separation and will actually reduce the enrichment ratio and separation factor due to dilution of adsorbed molecules by entrained liquid. On the other hand, the adsorptive transport mechanism is responsible for an increase in enrichment ratio and separation factor.

For multistage foam fractionation, it can be modeled as single-stage foam fractionation columns connected in series. There are two main features of the multistage foam fractionation described as follow:

1. A residual surfactant containing in the draining liquid from an upper stage can be recovered back into foam phase and hence the residual surfactant concentration can be lower, leading to higher separation factor.

2. The enrichment of the surfactant between stages is obtained if fraction of liquid recovered back into foam phase is relatively lower. This is due to

the fact that the liquid recovered back can make making a dilution of the recovered surfactant.

2.4.3 Literature Review on Surfactant Recovery Using Foam

Fractionation

Grieves and Wood, (1964) found that temperature had subtle effect on the separation performance of continuous foam fractionation. Tharapiwattananon *et al.*, (1996) investigated a single continuous mode of foam fractionation to remove surfactants from water. The enrichment ratio of surfactant decreased with increasing air flow rate and surfactant concentration, but with decreasing pore size of the sparger. Kumpabooth *et al.*, (1999) found that the foam flow rate, foam wetness and surfactant recovery increased but the enrichment ratio decreased with increasing salt concentration. Yamagiwa *et al.*, (2001) found that the external foam reflux was essential for enhancing separation efficiency of foam fractionation when treating a highly foaming solution of poly(Vinyl Alcohol).

For multistage mode, Boonyasuwat *et al.* (2003) studied the recovery of cetylpyridinium chloride (CPC), a cationic surfactant, and sodium dodecyl sulfate (SDS), an anionic surfactant, from water by using multistage foam fractionation with various numbers of stages ranging from 1 to 4. The separation efficiency of multistage foam fractionation for the recovery of CPC from water was found to be much higher than that in a single-stage system, especially in terms of the enrichment ratio and % recovery of the CPC (Boonyasuwat *et al.*, 2003). Darton *et al.* (2004) found that the effect of liquid reflux was revealed to be important in separation efficiency of multistage foam fractionation. Chuyingsakultip, (2004) investigated the effects of feed position, recycle ratio, and tray spacing on separation efficiency of CPC. The results showed that feed position is important for process performance and the optimum feed position is the top stage; however, the recycle ratio and tray spacing affected slightly the separation efficiency. Triroj, (2005) investigated the recovery of surfactants from mixed surfactant solution (CPC and Triton X-100). It was found that both surfactant recovery and enrichment ratio of Triton X-100 from the mixed solution were higher than those of the CPC due to preferential adsorption of Triton X-100.

2.5 Ion Foam Fractionation

2.5.1 Principle of Foam Fractionation for Ion Separation

Foam fractionation for ion separation can also be called ion flotation. Ion flotation, first described by Sebba, (1962), is a separation technology for recovering and removing metal ions from a dilute aqueous solution. The ion foam fractionation uses an excess of a surfactant (for frothing) or a proper frother to produce a stable foam (Rubio et al., 2002). The basic principle relies on the direct interaction between ionic surfactant and an oppositely charged metal ion. The mechanisms of ion flotation and ion foam fractionation process can be summarized into two ways (Doyle, 2003; Yuan *et al.*, 2008). The first is adsorption. The surfactant and metal ions adsorb as monolayer at the air–water interface through the electrostatic adsorption, producing a foam layer, as shown in Figure 2.15. The second is conglutination. First, soluble metal–surfactant complex called sublimate is formed in the liquid and then conglutinate on the bubbles, producing a foam layer. After the formation of heavy-metal-containing foam by the two possible mechanisms, the foam are carried upwards with rising air to the foam exit at the top of the column as described before in section 2.2.5.1. The collapsed foam simply contains both surfactant and heavy metal at very high concentrations due to liquid film drainage mechanism.

2.5.2 Kinetics of Ion Foam Fractionation

A serious limitation of batch ion flotation processes has been their relative slow operation due to slow kinetics of ion flotation (Doyle, 2003). It takes thirty to hundreds minutes to reach 100 % removal of ion for batch test. For continuous foam fractionation, the recovery efficiency depends on the residence time within the column. In some case, it is necessary to use more than one column connected in series to achieve reasonable high recovery efficiency. Although equilibrium adsorption densities in nonturbulent systems determined by surface tension relaxation experiments can be several minutes, the turbulence encountered in typical flotation systems is likely to reduce appreciably the time needed to achieve

equilibrium adsorption densities. Morgan *et al.* (1992) estimated that it would take only about 0.1 s to achieve the equilibrium adsorption. Liu (2001) estimated that it would take about 0.2, 2 and 8 s to reach the equilibrium adsorption for copper flotation with dodecylsulfate, tetradecylsulfate and hexadecylsulfate, respectively. Both of these results suggest that even bubbles with relatively short residence times in ion flotation systems can have equilibrium adsorption densities. If the adsorption density of collector and colligend at the vapor–solution interface are at equilibrium with the solution, the residence time of solution needed to achieve complete removal could only be improved by increasing the interfacial area flux (Doyle, 2003).

Because the molar flow rate of fomite depends on the surface area of gas bubbles, it might be advantageous to have extremely small bubbles produced by a porous material (Doyle, 2003). However, smaller bubbles result in wetter foams for a given gas flow rate, leading to a lower enrichment ratio. A longer residence time of the foam by having a longer foam height is needed for increasing liquid film drainage. The problem of ion flotation equipment is that most of the solution in the column would be unable to interact with the bubbles because the bubbles would already be saturated with the collector and ion during the first few tenths of a meter of the column. Consequently, a tall column may offer little or no enhancement in solution throughput over a short column of the same diameter (Doyle, 2003).

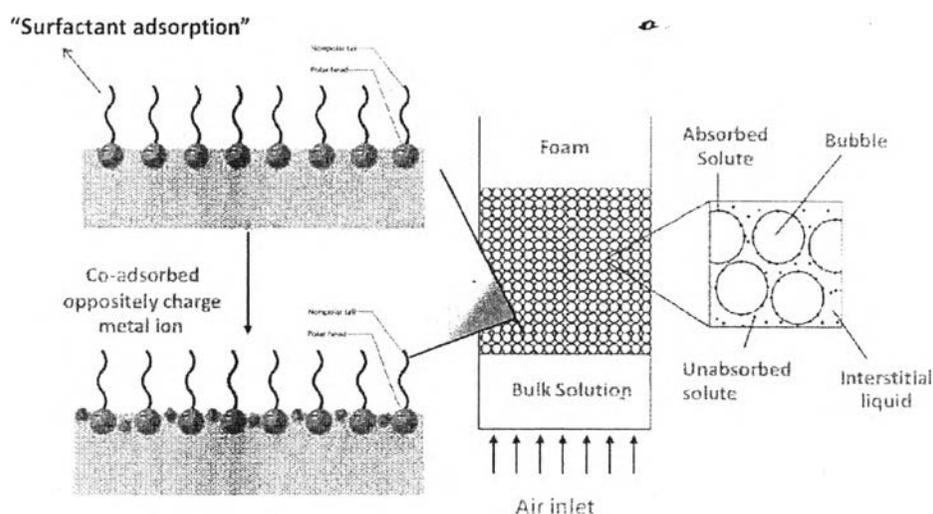
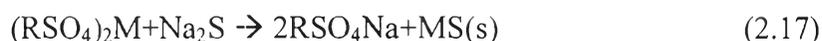
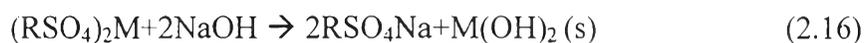


Figure 2.15 Co-adsorption of surfactant and metal mechanism for ion separation in ion foam fractionation

2.5.3 Recovery of Metal Product from Foamate

For ion flotation to be economically viable, both the metal and the collector can be recovered from the foam (Sreenivasarao and Doyle, 1997). The chemical precipitation in forms of hydroxides and sulfides and electrolysis are available to recover heavy metals and surfactants from the collapsed foam. The precipitation reactions of hydroxides and sulfides are represented as:



However, the recovery efficiency of metals from the foamate by the chemical precipitation was found to be much lower than that calculated from the solubility products because of the complexation of the heavy metal cations and dodecylsulfate (Doyle, 2003).

Electrolysis seems to be more promising for recovering metals and regenerating collector. This process has been used to decompose precious metal-collector complexes (Doyle, 2003). For ion flotation with dodecylsulfate with divalent cation, the relevant cathodic reaction would be



The anode reaction would be oxidative decomposition of water:



Because the later reaction acidifies the solution, conditioning of recovered stream is needed by adding base (i.e. NaOH). A conceptual diagram of foam fractionation of ions integrated with the recovering unit (FF-Electrolysis) can be depicted in Figure 2.16. The FF-Electrolysis process requires electrical energy (for air compressor, pump, and electrolysis unit) and chemicals (for make-up surfactant and NaOH). The current efficiencies were reportedly around 60–65%,

with no detectable change in dodecylsulfate (Sreenivasarao and Doyle, 1996). Therefore, this process is expected to consume small amount of chemicals and to create a small amount of CO₂ per unit of treated wastewater.

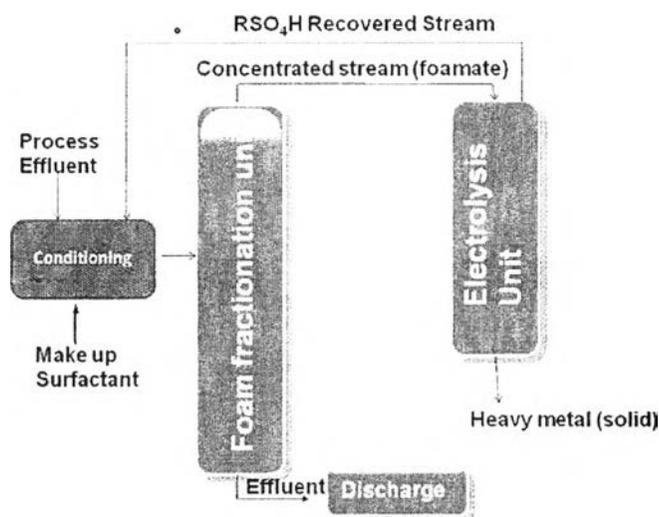


Figure 2.16 A conceptual diagram of foam fractionation of ions integrated with the recovering unit (FF-Electrolysis) (Doyle, 2003).

However, there are two main problems, affecting the accomplishment of this process:

1. To reduce work load on metal recovery unit (electrolysis), the volumetric flow rate of foamate should be minimized while the concentration of the metal in effluent meets the discharge standards. Hence, the produced foam should provide high foam film stability and high liquid film drainage.
2. To reduce consumption of make-up surfactant, % surfactant recovery should be high.

2.5.4 Literature Review on Ion Foam Fractionation and Ion Flotation

Although ion foam fractionation has many attractive features for removing metal ions from dilute solutions (Doyle, 2003), there are about 30 publication papers available in the past ten years (1999 – 2009). A few of them were carried out in continuous mode of operation and most of them were tested on

laboratory scale. Many of them focused on selective flotation under mixed metal ions (Lazaridis *et al.*, 2004; Qu *et al.*, 2008; Doyle, 2003; Moussavi and Javidnejad, 2007; Polat and Erdogan, 2007).

For most of batch ion foam fractionation studies, to achieve high removal, operational time of thirty to hundreds minutes was required because of the slow flotation kinetics as described earlier. The slow flotation the kinetics observed in batch mode but invisible for continuous or semi batch operation because the backflux term would be lower in the latter than in the former (Liu and Doyle, 2001a). However, some auxiliary ligands can be used to accelerate kinetic of ion flotation due to enhanced Gibbs free energy for moving metal ions from the bulk solution to adsorb at the air–water interface (Charewicz *et al.*, 1999; Liu and Doyle, 2003). Beside slow operation, another main problem of batch mode was that almost complete removal (>99%) always yielded a large volume of wet foam with a low enrichment ratio while a dry foam provide a lower removal efficiency (<90%) (Scorzelli *et al.*, 1999; Polat and Erdogan, 2007).

Qu *et al.* (2008) investigated the use of continuous foam fractionation to recover valuable surfactant (SDS) and metal ion (Cd^{2+}) in the permeate of micellar-enhanced ultrafiltration (MEUF) with an initial cadmium concentration of 10 ppm. It was found that, after the optimization of process parameters with the surfactant concentration of 500 ppm, an enrichment ratio of 3.1 was achieved with 52% recovery of SDS, and 99.35% removal of cadmium. However, an enrichment ratio for the metal was low about 6.7. The effect of ethanol as co-surfactant was also investigated. Adding ethanol resulted in the increase of surfactant removal, but the enrichment ratios of Cd and SDS dropped dramatically and the removal of Cd slightly decreased. This is may be due to the enhanced stability with smaller bubbles. Temperature had a little effect on the Cd^{2+} removal.

Selective separation of mixed metals by ion flotation technique was investigated (Liu and Doyle, 2001b). The selectivity was found to be controlled by the difference among their Gibbs free energy associated with moving metal ions from the bulk solution to the air–water interface. In other word, a solute with higher affinity to the surfactants preferentially adsorbs on the bubble surface, whereas a solute without affinity (i.e., non-target solute) exists only in the interstitial liquid

located in foam lamellae. Therefore, the selectivity of a target ion can be enhanced using chelating agent to increase the Gibbs free energy gap among metal ions (Charewicz *et al.*, 1999; Doyle, 2003). An incomplete draining of the interstitial water results in the contamination of ion of interest in foamate by accompanying non-target solutes. In order to increase the selectivity, liquid film drainage should be enhanced to remove unfavorable solutes existing in the interstitial water (Kinoshita *et al.*, 2007). The main application of selective flotation is to recover precious metal ions (i.e. gold) from mixed metal ion solution. Adjusting pH value and addition of inorganic ions can also change the affinity of metal ion to surfactant due to the transition or complexation of metal species (Moussavi and Javidnejad, 2007).

The effects of various chemical species were also investigated. The effect of added NaCl and Na₂SO₄ on ion flotation for cadmium removal was investigated (Scorzelli *et al.*, 1999). It was found that adding either NaCl or Na₂SO₄ resulted in drastic reduction on either floatability of cadmium or % metal recovery. It can be concluded that adding species that can alter metal ions to be less chemical affinity with surfactant results in dramatic decrease in separation efficiency and increasing the final concentration of effluent.

Three main physico-chemical factors affecting the performance of foam fractionation should be taken into consideration. The first is the surface activity and adsorption density of the metal-surfactant complex. The second is the characteristics of foam and foam film including liquid film drainage, foam film stability, and the surface area of foam. Lastly, the chemical affinity of metal-containing species (i.e. positive and negative complex; free metal ion) is directly affected by the other soluble species which can react with the metal ion (Kinoshita *et al.*, 2007).

2.5.5 Literature Review on Removal of Trace Cd²⁺ using Continuous Multistage Ion Foam Fractionation

In this research consist of three parts: Firstly, Part I describe the effect of feed SDS/Cd molar ratio. A continuous multistage ion foam fractionation column with bubble-cap trays was employed to remove cadmium ions from simulated wastewater having cadmium ions at a low level (10 mg/L). In this study,

study, sodium dodecyl sulfate (SDS) was used to generate the foam. An increase in feed SDS/Cd molar ratio enhanced the removal of Cd. However, the SDS concentration above a certain level resulted in wetter foams, leading to having a high volume of generated foam that lowered both the enrichment ratio and separation factor of the Cd. The SDS recovery tended to increase with increasing feed SDS/Cd molar ratio. The molar ratio of SDS/Cd in foamate was found to be close to the theoretical adsorption molar ratio of 2/1 on the air–water interface of foam when the system was operated at a feed SDS/Cd molar ratio in the range of 2/1–7/1. Ion foam fractionation has been demonstrated in this study to be a promising technique for high heavy metal removal (more than 99%) for a feed having a low heavy metal concentration in the ppm (mg/L) level. And the second part describes the effects of operational parameters. A multistage ion foam fractionation column with bubble-cap trays was employed to study the removal of cadmium ions from simulated wastewater having low Cd concentrations (10–30 mg/L), examining the effects of foam height, air flow rate, feed flow rate, and feed Cd concentration. Sodium dodecyl sulfate (SDS) was used to generate foam in this study. An increase in foam height, which reduces liquid hold-up in the generated foam, resulted in the enhancement of the enrichment ratios of both SDS and Cd while the removal and residual factor of Cd showed insignificant change. An increase in air flow rate increased the foam generation rate, foamate volumetric ratio, and the removal efficiency of Cd but decreased the enrichment ratios of both Cd and SDS. The separation factors of both Cd and SDS decreased with increasing feed flow rate, which is mainly attributable to both the effects of the enhancement of foamate volumetric ratio and the increases in both SDS and Cd input rates. An increase in feed Cd concentration was found to increase Cd effluent concentration and SDS removal but to decrease the enrichment ratios of both Cd and SDS because of the increasing liquid entrainment in the produced foam. In the last section, a multistage foam fractionation column with 5 bubble-cap trays was used to remove cadmium (Cd) at a low concentration (mg/L) with sodium dodecyl sulfate (SDS) used to generate foam. The effects of anions (NO_3^- , Cl^- , and SO_4^{2-}) and cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) were investigated by addition of sodium salts and nitrate salts, respectively. The addition of each studied cation was found to increase the residual

factor of Cd (Cd concentration in effluent/Cd concentration in feed) due to the effect of the competitive adsorption of added counterions with Cd^{2+} at the air–water interface of foam at a relatively high concentration of cation whereas, for all studied sodium salts, the residual factor of Cd decreased slightly with increasing counterion concentration at low concentrations. However, the added anions had a little effect. The effect of added cations and anions on the reduction of Cd removal are in the following order: $\text{Ca}^{2+} > \text{Mg}^{2+} \gg \text{K}^+ > \text{Na}^+$ and $\text{SO}_4^{2-} \approx \text{Cl}^- > \text{NO}_3^-$, respectively. The SDS recovery was found to increase significantly with increasing added salt concentration because the repulsion force among the head groups of SDS is greatly reduced by the co-adsorption of the counterions from added salt, leading to increasing SDS adsorption at the air–water interface of foam. The added salts of divalent cations were found to affect both Cd and SDS separation performance more than those of monovalent cations (Rujirawanich *et al.*, 2010).

2.5.6 Literature Review on Selective Removal of Heavy Metals using Ion Flotation

In this research was studied about a thermodynamic approach was taken to model the removal of cupric ion from sodium dodecylsulfate (SDS)–Cu, sodium tetradecylsulfate (STS)–Cu and sodium hexadecylsulfate (SHS)–Cu ion flotation systems (Zhendong Liu *et al.*, 2000). They found that we have used the equilibrium adsorption densities, predicted from experimental equilibrium surface tension measurements, to calculate the amount of copper that is removed in a specific time interval of batch ion flotation, and hence build up a model for the copper removal kinetics. Provided the bubble diameter was treated as a variable that increased with increasing surface tension, the kinetics predicted by the thermodynamic model agreed well with the experimentally measured kinetics for the copper dodecyl-, tetradecyl- and hexadecyl-sulfate systems. These findings provide quantitative guidelines for optimizing ion flotation processes. When selecting a collector for a specific application, it is clear that a longer alkyl chain allows faster removal of the cation, and attainment of lower ultimate concentrations of cations (in a continuous or semi-batch operation, where drained foam is continually removed from the flotation column, the backflux term would be lower than in the batch

operation considered here). However, because the higher molecular weight alkylsulfates have a lower solubility than have the lower molecular weight ones, they are less suitable for treating solutions that have relatively high initial cation concentrations. For these, it would be preferable to remove the bulk of the cation by ion flotation with a relatively low molecular weight surfactant, or by a more conventional separation process such as solvent extraction, and then have a final 'polishing' ion flotation step with a high molecular weight collector, to get down to very low concentrations of cation. The estimates made here of the time taken to achieve equilibrium adsorption density indicate that there is little point in using long flotation columns for ion flotation. The same volume of solution could be treated faster in a shallow, broader tank through which a higher flowrate of air can be passed. If ion flotation is also controlled by thermodynamic adsorption densities in other systems, the work presented here indicates that straightforward equilibrium surface tension measurements would be an effective way of screening different collectors for their suitability for a given ion flotation separation. This would be much faster and simpler than performing ion flotation tests.