



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Surfactants

Surfactants, abbreviation of the phrase surface-active agents, are substances that when they are presented at low concentration in a liquid (or system), the properties of liquid on the surface or interface can be altered significantly.

2.1.1 Structure of Surfactant

The structure of a surfactant includes a structural group that has strong attraction with a solvent, known as a lyophilic group (solvent-loving), together with a group that has less attraction with a solvent, called a lyophobic group (solvent-hating) (Rosen, 2004). In general, water is a common solvent. Therefore, the amphipathic structure of the surfactant consist of hydrophilic group (water-loving) and hydrophobic group (water-hating). The hydrophobic group is usually a long chain hydrocarbon residue, and less often a halogenated or oxygenated hydrocarbon or siloxane chain while hydrophilic group (usually called the head group) is an ionic or highly polar group depending on whether the head group has net charge or not (Porter, 1994). Hydrophobic and hydrophilic, provides the basis for characteristics useful in cleaner and detergency.

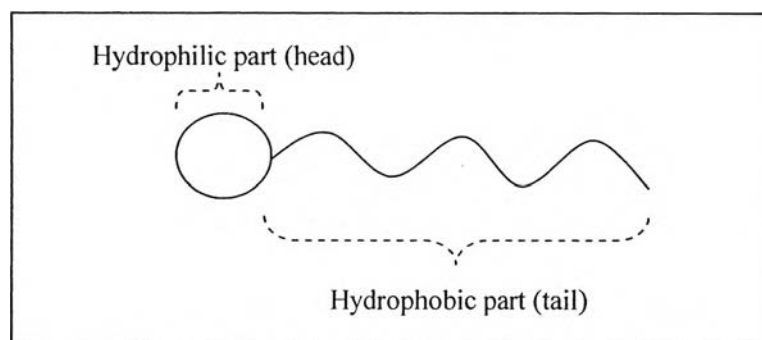


Figure 2.1 Schematic of surfactant monomer.

2.1.2 Types of Surfactant

Surfactants are generally characterized by the nature of the hydrophilic group as shown the following. (Rosen, 2004):

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

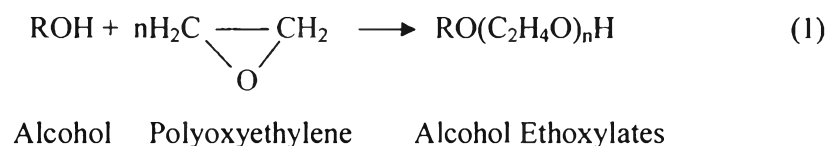
Cationic surfactant: The surface-active portion of the molecule bears a positive charge, for example, $\text{RNH}_3^+\text{Cl}^-$ (salt of a long-chain amine), $\text{RN}(\text{CH}_3)_3^+\text{Cl}^-$ (quaternary ammonium chloride).

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

Nonionic surfactant: The surface-active portion of the molecule bears a no apparent ionic charge. It is a class of synthetic surfactants that are prepared by attaching ethylene oxide molecule with a water-insoluble molecule, for example, $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long-chain fatty acid), $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$ (polyoxyethylenated alkylphenol).

2.1.3 Alcohol Ethoxylate Surfactant

Alcohol ethoxylate (AE) is one of the various types of nonionic surfactants of commercial importance, particularly a straight-chain alcohol together with ethylene oxide (Satkowski, 1967). Alcohol Ethoxylates can be produced from either oleochemical or petrochemical alcohols. The linearity of the hydrophobe can vary from highly linear (alcohol is derived from oleochemical sources and some petrochemical sources) to highly branched (from other petrochemical sources) (Rosen, 2004). The fundamental chemical reaction:



2.1.4 Micellization

A single molecule of a surfactant is called a monomer. The monomer or surfactant molecules will nucleate to form aggregate called micelles when concentration value is sufficient. This process is called micellization and the lowest total surfactant concentration at which micelles are form is called critical micelle concentration (CMC).



Figure 2.2 Schematic of a monomers and a micelle

Micelles are generally separated into two types, normal and inverse micelles. In water or aqueous solution, normal micelles are formed with the hydrophobic part in the interior and the hydrophilic part in the external, while inverse micelles are formed in a non-polar solvent with the hydrophilic part in the interior and the hydrophobic part in the exterior as shown in Figure 3.

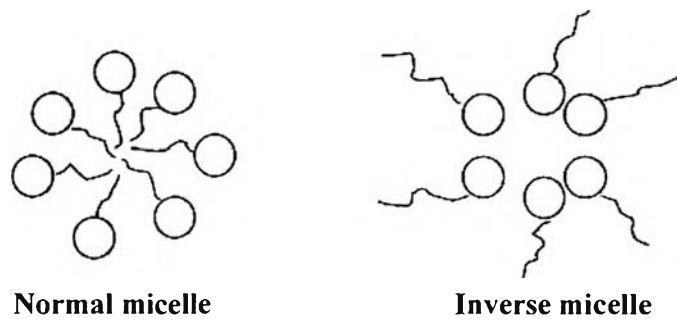


Figure 2.3 Schematic of normal micelle and inverse micelle

When increasing surfactant concentration, the formation of various association structures is form as shown in Figure 4. The surfactant molecules may form spherical, cylindrical, hexagonal, lamellar, or reverse micelle structures depending on

the physicochemical conditions, such as pH, temperature, and the presence of various electrolytes.

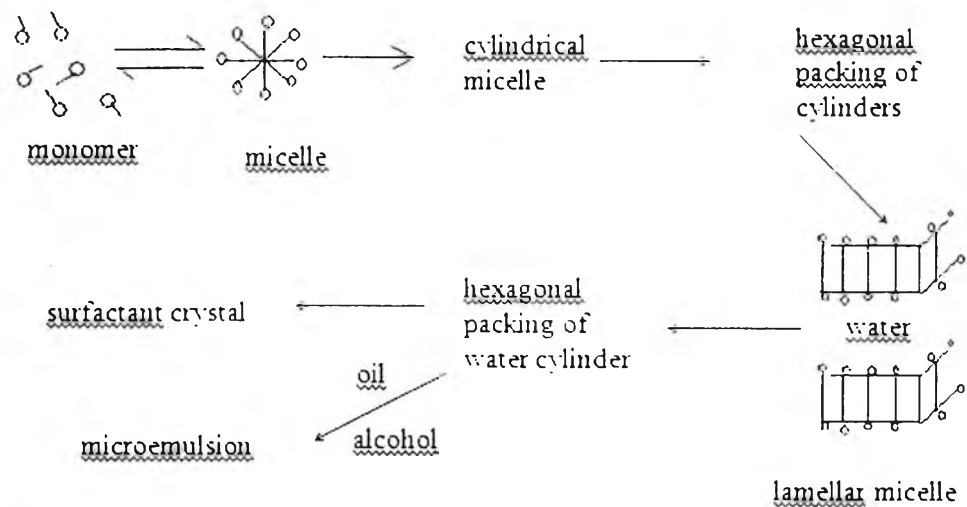


Figure 2.4 Schematic of a surfactant association structures with increasing surfactant Concentration.

2.2 Foam

2.2.1 Foam Formation

Foam is a gas dispersed in a liquid that is produced when air or another gas is introduced beneath the surface of a liquid that expands to enclose the gas with a film of liquid (Rosen, 2004). Foam would have no stability unless there were barriers to prevent coalescence when two gas bubbles touch. The barrier (liquid film) is produced by the presence of a water-soluble surfactant.

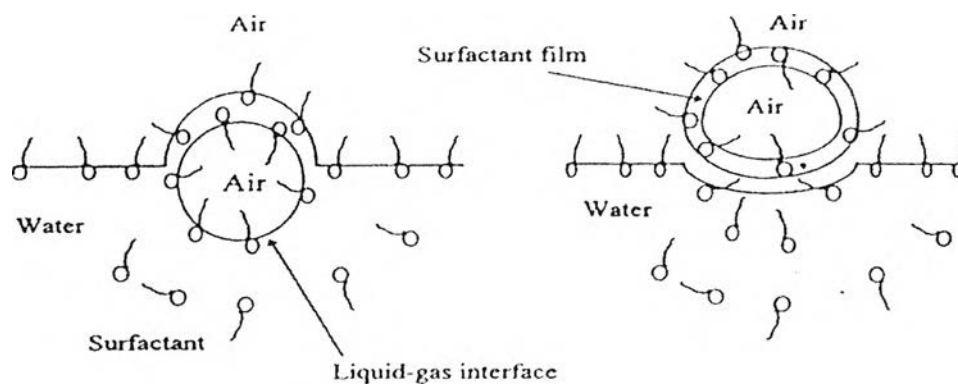


Figure 2.5 Schematic of foam formation.

The formation of foam from a bulk involves the expansion of the surface area due to the work action upon the system. As surface tension is the work involved in creation a new system, the amount of new area formed will be greater. Therefore the surfactant is required for foam formation because it can reduce the surface tension of the new surface area as shown in Figure 5.

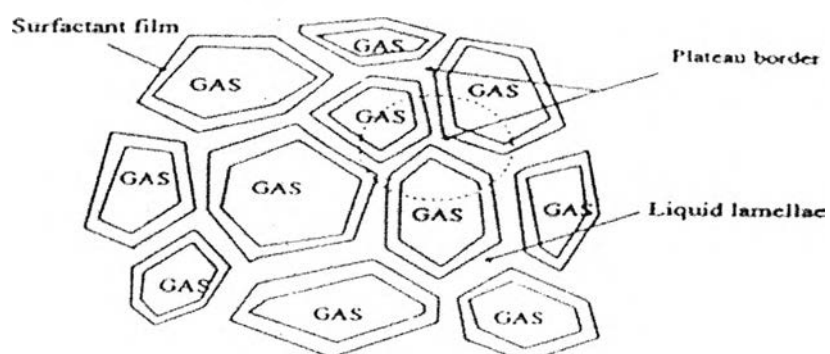


Figure 2.6 Schematic of foam structure.

2.2.2 Foam Structure

The structure of gas cell or foam consists of two-side of thin liquid films which called lamellae. When three or more bubbles meet, the lamellae are curved and concave to the gas cell that called the Plateau border or Gibbs triangle. Most of water will play an importance role in the drainage of water in foams (Rosen, 2004). Foam can be classified into two general categories:

- *Kugelschaums*: foam consists of nearly spherical bubbles separated by rather thick liquid films. Bubbles are fresh made and wet foam.
- *Polyederschaums*: foam contains mostly gas phase separated by thin films or larminar. Bubbles are polyhedrons, older foams and dryer foam.

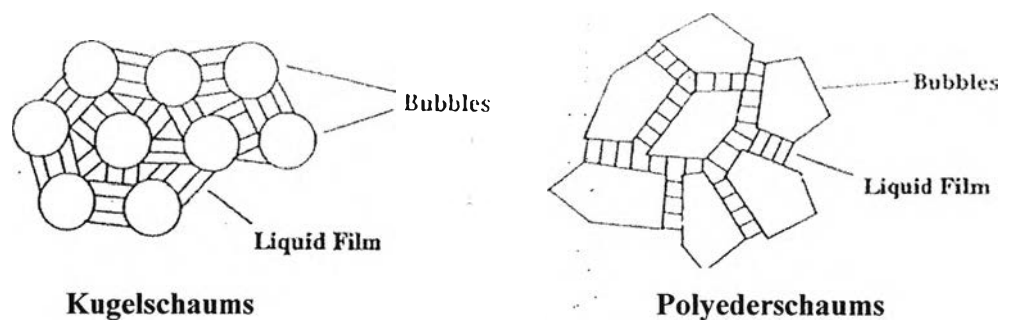


Figure 2.7 Schematic of two general foam structures.

Film elasticity indicates how easily the foam is formed that consists of two theories. First is *Gibbs effect*, the theory base on the change in surface tension with change in concentration of the surface-active solute and the second *Marangoni effect*, base on the change in surface tension with time. Both film elasticity theories postulate that elasticity is due to the local increase in surface tension with extension of film. When a local spot film thins and stretches (the area of film increase) in that region, its surface tension increase that causes liquid to flow toward the thinner section from the thicker portions. The thinning spot draws liquid from its perimeter and prevents further thinning of the film. In addition, the movement of surface material carries with it underlying material that helps “heal” and thicken a thinned spot by a surface transport mechanism (Rosen, 2004).

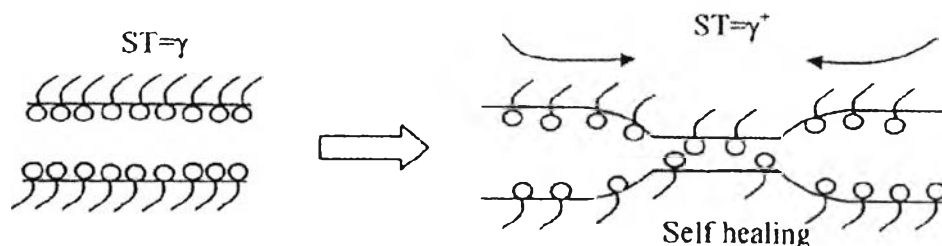


Figure 2.8 The stretch portion of foam lamella (film elasticity).

Both effects work in foam because gravity cause liquid to drain out of the thin lamellae (Figure 8 and 9), and hence the surface tension increase (few surfactant molecules) in the thin lamellae. There is now a restoring force from the Gibbs elasticity and Marangoni effect bringing surfactant molecules back into the region of high surface tension (Porter, 1994).

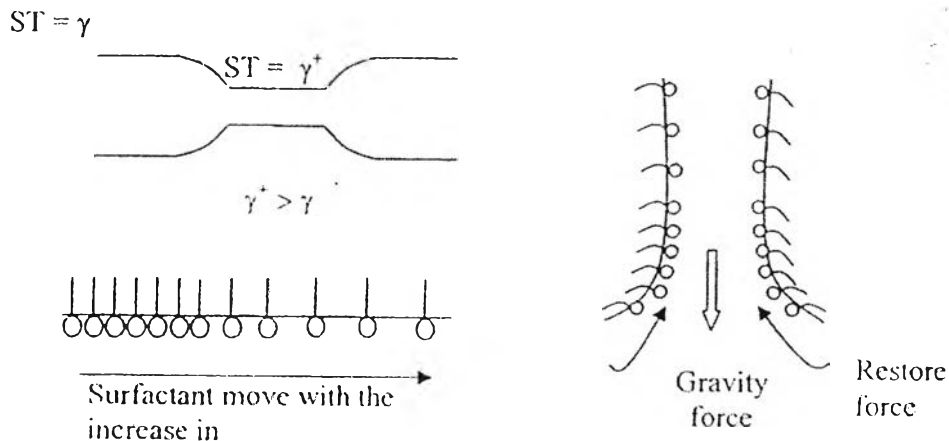


Figure 2.9 The Marangoni effect.

2.2.3 Foam Stability

Film drainage is the fact or that indicates how rapidly the foam formed breaks. Drainage of the film can occur under two influences. The first is drainage by gravity that is important mainly in very thick lamellae, such as are present when the foam is first formed. The bulk viscosity of the foaming solution is a major factor affecting the rate of drainage by gravity in thick lamellae. Thickeners are often added to increase the bulk viscosity when very stable foams are desired. At high concentration of surfactant the viscosity of the bulk solution is also high therefore the drainage rate in the lamellae is decreased with the amount of surfactant in the lamellae is increased.

The second is drainage by pressure difference that is more important when the lamellae are thin. This drainage is due to the differences in curvature of the surface of the lamellae. The lamella has a greater curvature than at the boundary in plateau border. There is a greater pressure across the interface in these regions than elsewhere in the foam. Since the gas cell is the same everywhere, the liquid pressure inside the lamellae at highly curved plateau border (A) must be lower than less curved regions (B). Thus, the continuous phase liquid drains from the thin film (B) to the adjoining plateau border (A) as shown in Figure 10.

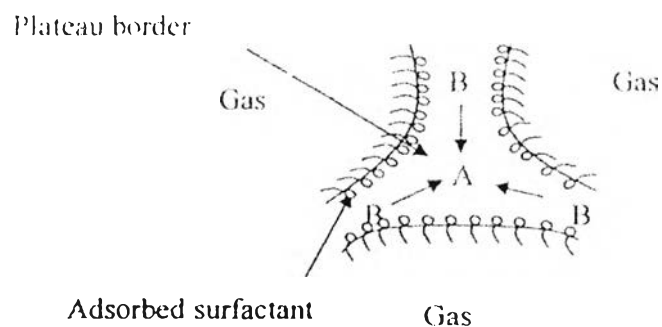


Figure 2.10 The liquid drainage in lamellae.

The different pressure (ΔP) is given by the expression;

$$\Delta P = \gamma \left(\frac{1}{R_A} + \frac{1}{R_B} \right) \quad (2)$$

Where γ = surface tension,

R_A and R_B = the radii of the curvature of the lamellae at point A and point B, respectively.

The greater the difference between R_A and R_B (i.e., the larger bubble size in the foam) and the greater the surface tension of the solution in the lamellae, the greater the pressure difference causing drainage (Rosen, 2004).

2.2.4 Application of Foam Test

2.2.4.1 Bartsch of Shaking Foam Test

The Bartsch (shaking test) and the Ross-Miles (pouring test) methods are most commonly applied simple test to compare the foam properties of solution. In shaking test a certain amount of solution is vigorously shaken in a locked cylinder.

Piispanen *et al.* (2004) studied the foam property of the surfactants were determined by comparison with NPE-6, NPE-10, and NPE-20. Those of surfactants were used as references and measured by using simple shaking test. This test, aqueous solutions of the surfactants and reference surfactants (40 mL; 0.1 wt/vol% surfactant) were prepared. The solution was poured into a 100-mL graduated cylinder. The cylinder containing the solution was turned upside down a total of 10 times at a rate of 1 turn per 2 s. The foam produced (in mm) was measured immediately and after 1 min. These data were used for estimating the foamability and foam stability of the surfactants. According to Ross-Miles foaming tests, nonylphenol ethoxylates show a maximal foamability when the polyoxyethylene chain constitutes around 75 wt.% of the surfactant. For the reference surfactants, the results reported that, NPE-6, NPE-10, and NPE-20, have compositions of 58, 69, and 81.5 wt.%, respectively. Indeed, we found that NPE-6 has relatively low foamability, whereas NPE-10 and NPE-20 both exhibit high foamabilities.

Mousli *et al.* (2007) investigated the effect of dodecanesulfonamide on foam properties by the Bartsch method and compared to commercial surfactant, linear alkylbenzenesulfonate (LAS). The samples, dodecanesulfonamidoacetic acid (measured at 25°C) and n-ethanoldodacanesulfonamides (measured at 45°C), was poured into a 100 mL graduated cylinder and turned up-side down a total of ten times at a ratio one turn every 2 sec. the foaming power measured the height foam immediately after agitation every concentrations, and the stability of foam from the evolution of the foam height versus time. The results of surface tension and CMC found that the better were the pure primary isomer of sodium salt of dodecanesulfonamidoacetic acid (29.19 mN/m), and those of mixture of secondary isomer of N-ethanoldodacanesulfonamides (the lowest 22 mN/m). the branching chain effect leads to lower surface tension because branch chain of surfactants oppose the cohesion of the molecules. According to the Bartsch method, the results obtained show only three products possess foaming properties; primary-N-ethanoldodacanesulfonamides, primary-sodium salt of dodecanesulfonamidoacetic acid and secondary sodium salt of dodecanesulfonamidoacetic acid, and LAS was used for reference. The primary n-ethanoldodacanesulfonamides showed lower (weak) foaming power than the other sulfonamides because the foaming power is related to the solubility of surfactant. So, this sample leads to the formation of unstable foam (temporary, wet foam). From this test, the better foaming power is secondary sodium salt of dodecanesulfonamidoacetic acid, it can be considered as metastable foam (dry foam). The stability of foam, the change of foam height versus the time, the result shown that primary-n-ethanoldodacanesulfonamides is not only low foaming power but there is low foam stability. The secondary sodium salt of dodecanesulfonamidoacetic acid is a surfactant that shows good surface properties with regard to the low surface tension and good foaming power.

Shama *et al.* (2007) investigated the effect of dilute aqueous nonionic fluorinated, surfactant $C_8H_{17}SO_2N(C_3H_7)(CH_2CH_2O)_nH$ abbreviated as $C_8H_{17}EO_n$ ($n= 10$ and 20), on the stability of foam by shaking test. The samples prepared in water at concentrations 0.1 wt.% and 1 wt.% of both $C_8H_{17}EO_{10}$ and $C_8H_{17}EO_{20}$, taken in clean and dry glass bottles and stirred for few hours at room temperature. The results found that the foam stability increase with increasing surfactant concentration.

The different liquid drainage rate in foam films indicate difference of foam stability but in the first of this test found that the stability of foam at concentration 0.1 wt% and 1 wt.% is the same. This indicated that in both concentrations, the liquid drainage is the same. Until the drainage is almost completed, the foam films become dry and it's influenced by the interfacial dynamics. The comparison of the foam stability between $C_8H_{17}EO_{10}$ and $C_8H_{17}EO_{20}$ at fixed concentration, 1 wt.%, found that the foam stability $C_8H_{17}EO_{10}$ is higher than $C_8H_{17}EO_{20}$. This study can be explained by the micellar structure because the viscosity of solution depends on the micellar structure. In generally, the large size of head group or hydrophilic form spherical micelles, whereas the small size of head group forms long cylindrical micelles. So, the hydrophilic head group size of the $C_8H_{17}EO_{20}$ tends to form spherical micelles that less viscous aqueous solution than $C_8H_{17}EO_{10}$ that forms long cylindrical micelles. Thus, the difference in the foaming properties depending on the surfactant nature can be explained on the basis of micellar structure.

2.2.4.2 Ross–Miles Foam Test

In the Ross-Miles method, a definite amount of solution is poured from the upper vessel through an orifice of definite diameter onto a bed of the same solution located in the cylinder at a standard distance from the orifice.

Hama *et al.* (1997) studied nonionic surfactant on foam property using Ross-Miles method. From the his previous paper, the effect of ethoxylate structure of ethoxylated fatty methyl esters (EFME) on surfactant properties, studied the degree of the hydrophobic structure groups (fatty acid methyl ester of various alkyl chain lengths) and polyoxyethylene (POE chain length). The results found that ethoxylated methyl laurate (C12-EFME) with about 60 to 70 %EO (number 7-11 EO) content showed to be the most suitable as a base surfactant for household detergents. So, this paper studied methoxypolyoxyethylene dodecanoate (ethoxylated fatty methyl esters, C12-EFME) compared with polyoxyethylene dodecylether (alcohol ethoxylate, AE). The both samples was varied different EO adduct distribution such as for EFME (narrow C12-EFME and broad C12-EFME) and for AE (C12-NRE, narrow range ethoxylate and C12-BRE, broad range ethoxylate). The results shown that EFME shows lower water solubility and cloud point than AE because the terminal-end of

the EO chain is blocked by a methyl group for EFME. From the Ross-Miles method, Foamability values show C12-NRE > narrow C12-EFME > C12-BRE > broad C12-EFME. The presence of the terminal methyl group and ester bond may lower the foaming ability. However, Narrow has foam stability than broad distribution. For broad distribution, unreacted raw material and the fractions with few EO units tend to hinder foam breaking.

Piispanen *et al.* (2003) studied foam properties by the standardized Ross-Miles test on surfactants that are derived from dehydroabiatic acid; Monomethyl PEG-550 ester of dehydroabiatic acid (DeHab(EO)12), Monomethyl PEG-750 ester of dehydroabiatic acid (DeHab(EO)17) and Monomethyl PEG-2000 ester of dehydroabiatic acid (DeHab(EO)45). Foamability and foam stability were investigated at room temperature ($\sim 22^{\circ}\text{C}$). An aqueous surfactant solution (200 mL) of surfactant DeHab(EO)12 and DeHab(EO)17 were poured into a column with 50 mL of surfactant solution in the bottom, at concentration 0.1 and 1 wt/vol % that above the CMC (≈ 0.007 wt.%) for compound DeHab(EO)12 and DeHab(EO)17. The results shown that the foamability (at $t=0$) and foam stability increase when the EO chain length is increased from 12 to 17 units and with concentration. The foamability and foam stability of DeHab(EO)17 have higher values than DeHab(EO)12 because the foaming behavior is dependent on the size of the EO group in relation to the size of the hydrophobic group. The foamability for DeHab(EO)45 is extremely low because of the high surface tension at the solubility limit and because of the large head group, which prevents packing a planar interface.

The differences in the behavior cannot be explained by difference in the CMC, but rather are related to the packing at the interface. The better interfacial packing results a higher surface elasticity, which increase the foam stability. Drummond *et al.* studied in comparison to sugar surfactant with dodecyl chain (lactose monododecanoate), the foamability and foam stability were higher for the sugar surfactant. The foam behavior for the sugar surfactant is less dependent on the concentration and is unchanged when the concentration is lowered from 1 wt.% to 0.1 wt.% (Piispanen, 2003).

2.2.4.3 Pneumatic Foam Test

Due to at high surfactant concentrations the lifetime of metastable foam can be many hours or even days. Thus, $t_{1/2}$ parameter for comparison of foam stability may require measurement over a long time period. Therefore, Lunkenheimer *et al* studied the R5 parameter is use as test at a reliable and simultaneously quick evaluation of foam stability.

The parameter R5 defined, as the ratio of the height of the foam at 5 min after formation to the initial height as:

$$R5 = \frac{h_5}{h_0} 100, \quad (3)$$

This equation is proposed for the evaluation foam stability. As foams have R5 higher than 50% can be considered as metastable, if lower value indicates low stability (Lunkenheimer, 2003).

Lunkenheimer *et al.* (2003) studied the foamability of solution and the stability of the foam formed by using a simple and quick pneumatic test as called R5. This paper investigated aqueous solutions of sodium dodecyl sulfate (SDS), n-octyl- β -D-glucopyranoside, hexadecyltrimethylammonium bromide (CTAB). The solution 50 mL was poured into the column in such manner that no foam was formed. After that, the gas from the syringe was introduced into the solution through the sintered glass at the bottom of column. The change of R5 values with SDS concentrations resembled that of $t_{1/2} = f(c)$ dependence. For SDS solution of concentration $< 1 \times 10^{-3}$ M (showed low stability-from $t_{1/2}$ method), the values of the R5 are below 50% whereas at concentrations $> 2 \times 10^{-3}$ M (metastable foam $t_{1/2} \approx 10^4$ s), the R5 has a value of *ca.* 80%. For n-octyl- β -D-glucopyranoside and CTAB have a similar character, there is a transition region from low stability to high stability. This transition occurs within a narrow concentrations range and followed by a plateau at concentration close to CMC.

Watcharasing S. (2004) studied the effect of SDS concentration in mixed surfactant system; [Alfoterra]=0.10 wt.%, [NaCl]= 3 wt.%, and Oil:water=1:19

on foam properties using pneumatic foam test method. Foamability is defined as the ratio of maximum foam height to initial solution height whereas foam stability ($t_{1/2}$) is the time required for the foam volume to collapse by half. The results found that increasing SDS concentration increased foamability until at higher sufficiently SDS concentration the foamability decreased slightly. For the foam stability of the system, foam stability increases with increasing SDS concentration.

Aside from The Bartsch (shaking test), the Ross–Miles (pouring test), and pneumatic foam test methods, there is also other method to evaluate foam properties as shown in Genova *et al.* (2003).

Genova *et al.* (2003) investigated the effect of hydrophobe structure of alcohol ethoxylates (oleochemical alcohol and oxo alcohol) on foam performance by Schlag foam apparatus (German Standard Test DIN S3 902). It was found that the overall linearity of the parent alcohol and the degree of substitution at the C2 carbon are two importances for performance of hydrophobe structure. The linearity of the parent alcohol from high to low follow that oleochemical alcohol, Fisher-Tropsch oxo, conventional oxo and butylene base isotridecyl oxo alcohol. The degree of substitution at the C2 carbon from high to low follow that butylene base isotridecyl oxo, conventional oxo Fisher-Tropsch oxo and oleochemical alcohol. The free alcohol in the alcohol ethoxylate increased with increasing degree of substitution at the C2 carbon. On foam properties, 100 mL of alcohol ethoxylate solution was equilibrated at 49°C in a 1000-mL graduated cylinder. The solution was agitated by a perforated stainless steel plunger attached to a motorized arm. Foam values were recorded after 30 s and again 5 min. It was found that the foam volume decrease as the degree of substitution at the C2 carbon of the parent alcohol increase because increasing of substitution of the C2 carbon increase free alcohol and free alcohol is foamicidal. So, alcohol ethoxylates based on butylenes based oxo-alcohol has a lower initial foam height than others. In the presence of soil, isotridecyl alcohol ethoxylate has a higher foam volume than the others after 5 min. this may be related to lower interfacial tension and emulsify vegetable oil that make it less foamicidal.

2.3 Wetting

2.3.1 Wetting of Solid Surface

Wetting of solid surfaces by surfactants is important property in many practical applications such as oil recovery, coating, printing and detergency and that is also used as an analytical technique to characterize surfaces. The aqueous solution of surfactants is used to enhance the ability of aqueous solutions to wet and spread over solid surfaces since they can modify the solid/liquid and liquid/vapor interfacial tension (Balasuwatthi, 2004). Commonly, the term of wetting is applied to the displacement of air from a liquid or solid surface by water or an aqueous solution (Rosen, 2004). The tendency for fluids to wet can be indicate by the contact angle.

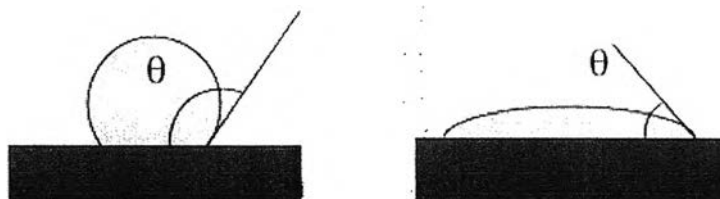


Figure 2.11 The contact angle of liquid droplet at equilibrium.

2.3.2 Contact Angle

The contact angle is a quantitative measure of the wetting of a solid by a liquid. It's defined geometrically as the angle formed by a liquid at three-phase boundary system. The low values (near "0") of contact angle indicate that the liquid spreads well (high wettability), while high values ($> 90^\circ$) of contact angle indicate that less complete wetting (poor wettability). If value is zero contact angle indicate that "complete wetting".

The relationship between the interfacial tensions of the surfaces at the three-phase boundary of solid, liquid and vapor system at equilibrium is described by the Young 's equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \quad (4)$$

Where γ_{SV} , γ_{SL} , γ_{LV} are solid/vapor, solid/liquid and liquid/vapor interfacial tensions, respectively, and Θ is the equilibrium contact angle.

This equation is only valid for finite contact angle in case of mechanical equilibrium, so it does not apply when spreading take place. Thus to encourage wetting, γ_{SL} , γ_{LV} should be made as small as possible. This is done by adding a surfactant to the liquid phase. The surfactant absorbs to both the liquid/solid and liquid/vapor interfaces to lower those interfacial tension (Puttharak, 2006).

For systems which fail to attain equilibrium, Spreading Coefficient (S) is the free energy change per unit area of the spreading of liquid film on the solid, as defined instead of contact angle:

$$S_{L/S} = \gamma_{SA} - (\gamma_{SL} + \gamma_{LA}) \quad (5)$$

The positive values of spreading coefficient indicate that spreading can occur spontaneously, if the values are negative the liquid will not spread spontaneously over the substrate (Rosen, 2004). From Young's Equation, $S=0$ corresponds to $\cos\Theta$ attaining its maximum value of unity ($\Theta=0$) and corresponds to the on set of complete wetting (Puttharak, 2006).

2.3.3 Contact Angle Measurement

Many experimental techniques are available for contact angle measurement, such as, capillary penetration techniques, the adhering gas bubble method, the Wilhelmy plate method and the sessile drop technique. In the sessile drop technique, contact angles are measured directly by depositing a liquid drop on a solid surface and placing a tangent to the drop at its base by computer program. The resulting "static advancing contact angle" represents the "equilibrium contact angle".

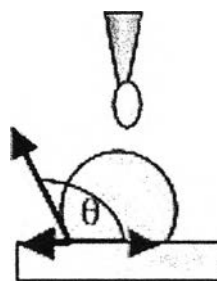


Figure 2.12 The contact angle by the sessile drop technique.

Piispanen *et al.* (2003) studied the contact angle of surfactants derived from dehydroabiatic acid, Monomethyl PEG-550 ester of dehydroabiatic acid (DeHab(EO)12) and Monomethyl PEG-750 ester of dehydroabiatic acid (DeHab(EO)17) at concentration above the CMC on a hydrophobized glass slide by using Wilhelmy plate method. The advancing contact angle was continuously measured while immersing the plate into the solution, and the receding contact angle was measured while withdrawing the plate from the solution. It found that the contact angle is dependent only on the surface tension of the solution but this is perhaps true for structurally similar substances. The contact angle at concentration above the CMC for Monomethyl PEG-550 ester of dehydroabiatic acid and Monomethyl PEG-750 ester of dehydroabiatic acid were much lower than those of C_{12} -maltose and LABA (N-lauryl lactobionamide). At the same surface tensions Monomethyl PEG-550 ester of dehydroabiatic acid and Monomethyl PEG-750 ester of dehydroabiatic acid were better wetting abilities than TEDAd [tetra(ethyleneoxide) dodecyl amide] and $C_{12}E_5$ (polyoxyethylene-based ether surfactant) because it might be better packing of the dehydroabiatic hydrophobe on the surface.

Piispanen *et al.* (2004) studied the wetting abilities of the surfactants were determined by comparison with NPE-6, NPE-10, NPE-20 and pure water. Those of surfactants were used as references and measured by using a goniometer, four or five repetitions. This test, a droplet 10 μ L of surfactant solution (1 wt/vol %) was put on the fresh (Parafilm "M"[®] laboratory Film; American National Can, Chicago, IL). The diameter of the droplet was measured after 1 min. For the references, it reported that the referent surfactant solutions were defined as the values scale of 0-6, where 6

show that the best possible wetting ability. The wetting properties of the references were the values 5, 3, 1, and 0 for NPE-6, NPE-10, NPE-20 and pure water, respectively and then used those for comparison.