CHAPTER II
LITERATURE REVIEW

2.1 Surfactant

A surfactant (a contraction of the term *surface-active agent*) is a substance that, when presents at low concentrations in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces). The term *interface* indicates a boundary between any two immiscible phases; the term *surface* denotes an interface where one phase is a gas, usually air (Rosen, 2004).

Surfactant are widely used in many products and applications such as metal treatments, ore flotation, cosmetic and pharmaceutical formulations, pesticides, cutting oils, detergent, motor oils, emulsion polymers (Hoeft and Zollars, 1996), flotation separation of plastic waste (Shibata *et al.*, 1996), membrane (Popescu, 1994), printing (Gerdes, 1997), soil remediation (Smith, 1996; Kibbey, 2000), food packaging film (Karbowiak, 2005), and corrosion prevention (Asefi, 2009).

2.1.1 Structure of Surfactant

Surfactants have a characteristic molecular structure consisting of a hydrophilic part, which is made of a water soluble species such as an ionic or highly polar group, and a hydrophobic part which is usually a long-chain hydrocarbon or non-polar group referred to as head and tail, respectively.

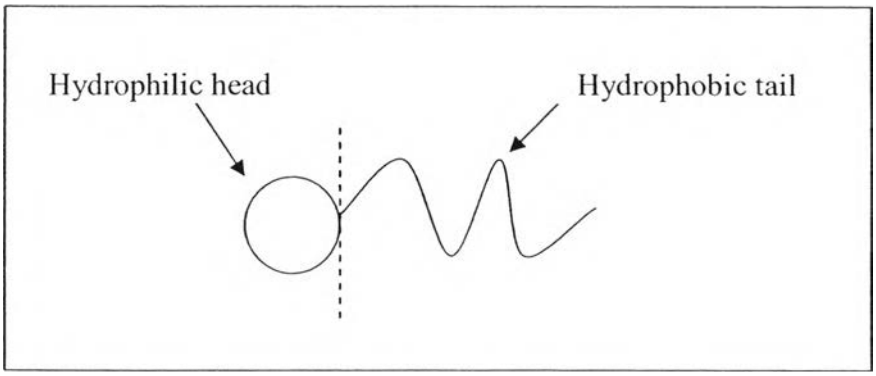

Figure 2.1 Schematic structure of surfactant molecule monomer.

2.1.2 Types of Surfactant

Surfactants are classified into four main types according to the nature of the hydrophilic group: anionic, cationic, zwitterionic, and nonionic surfactants (Rosen, 2004).

Anionic. The surface-active portion of the molecule bears a negative charge; for example, $RCOO^-Na^+$ (soap), $RC_6H_4SO_3^-Na^+$ (alkylbenzene sulfonate).

Cationic. The surface-active portion of the molecule bears a positive charge; for example, $RNH_3^+Cl^-$ (salt of a long-chain amine), $RN(CH_3)_3^+Cl^-$ (quaternary ammonium chloride).

Zwitterionic. Both positive and negative charges may be present in the surface-active portion; for example, $RN^+H_2CH_2COO^-$ (long-chain amino acid), $RN^+(CH_3)_2CH_2CH_2SO_3^-$ (Sulfobetaine).

Nonionic. The surface-active portion bears no apparent ionic charge; for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long-chain fatty acid), $RC_6H_4(OC_2H_4)_xOH$ (polyoxyethylenated alkylphenol).

2.1.3 Alcohol Ethoxylate Surfactant

Alcohol ethoxylates (AEs) which are the most widely used nonionic surfactants are one of the various types of nonionic surfactants of commercial importance, particularly a straight-chain alcohol together with ethylene oxide. Alcohol ethoxylates are "amphiphiles" containing hydrocarbon tails which prefer oil environments and ethoxylated alcohol groups which prefer water environments. They are prepared by the reaction of ethylene oxide with aliphatic or aromatic alcohols (Satkowski *et al.*, 1967; Cox, 1989).

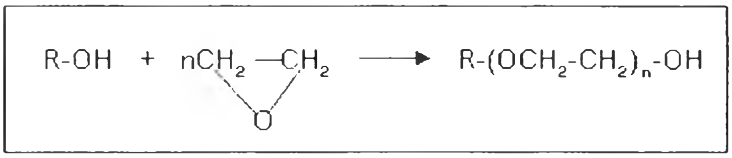

Figure 2.2 Reaction of ethoxylated alcohols.

The alcohols may be derived from either oleochemical or petrochemical sources. Oleochemical alcohol ethoxylates contain a highly linear hydrophobe, whereas the hydrophobe in petrochemical-based alcohol ethoxylates may range from highly linear to highly branched, depending on the method of manufacture (Varadaraj *et al.*, 1991; Rosen, 2004). Consequently, performance can be optimized by varying the average hydrophobic part, hydrophilic part, and distribution of the ethoxyethylene group (Cox, 1989; Hama *et al.*, 1997a, 1997b; Genova *et al.*, 2003; González-García *et al.*, 2004).

AEs biodegrade more readily than alkylphenol ethoxylates (Kibbey, 2000). AEs are more tolerant of high ionic strength and hard water than anionic surfactants and exhibit better stability in hot alkaline solutions than ethoxylated fatty acids. They also have excellent compatibility with enzymes in laundry formulations. They are also more water-soluble and have better wetting powers than corresponding fatty acid ethoxylates, somewhat better than the corresponding alkylphenol ethoxylates (APE), common commercial nonionic surfactant, for emulsification; are more water-soluble than linear alkyl sulfonate or LAS, common commercial anionic surfactant, for use in high active, heavy-duty liquid detergents free of phosphates; and are more effective detergency than LAS under cool washing conditions and on synthetic fabrics. AE are excellent detergents for removal of oily soil and are often used in laundry products, especially liquids. They are also excellent emulsifiers and suspending agents in numerous industrial applications such as soil remediation (Kibbey, 2000), where they compete with alkylphenol ethoxylates (Rosen, 2004).

2.1.4 Micelle Formation Property

A single molecule of a surfactant is called a monomer. When a concentration of surfactant is high enough, the monomers or surfactant molecules will nucleate to form aggregates called micelles. This process is called micellization, and the concentration at which this phenomenon occurs is called the *critical micelle concentration* (CMC).

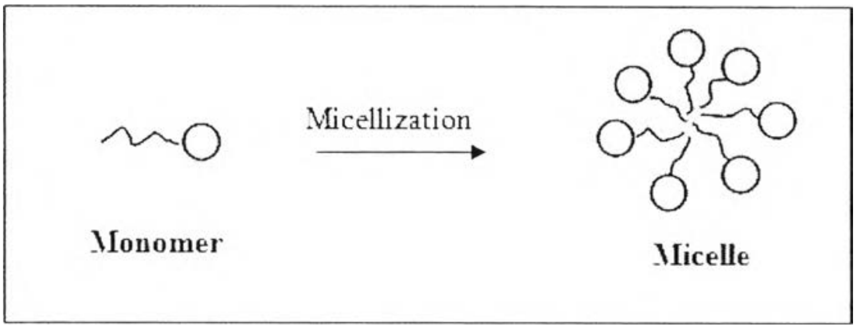

Figure 2.3 Schematic of a monomer and a micelle.

Many physical properties of solutions of surface-active agents change markedly when micelle formation commences; some physical properties increase or decrease, others tend to be constant (Cox, 1989; Varadaraj *et al.*, 1991; Hoeft and Zollars, 1996; Romero-Cano *et al.*, 1998; Piispanen *et al.*, 2003). Dependence of these properties on CMC is derived from concentration of monomer and/or micelle; it relates to monomer–micelle equilibrium. The equilibrium result from structures of surfactant; which are hydrophobic part mainly consisting of long alkyl chain and hydrophilic part which have either charge group in ionic surfactant or polar group in nonionic surfactant. For example, branching alkyl chain length disfavor micellization (or increase CMC) but enhance adsorption due to reach to meso-equilibrium faster and yielding higher effectiveness (lower γ_{CMC}) (Varadaraj *et al.*, 1991; Genova *et al.*, 2003).Increase in ethylene oxide content in AEs increase the CMC and γ_{CMC} (Cox, 1989).

Many techniques can be used for CMC determination such as UV-Vis spectrometry, surface tension determination, and contact angle measurement. Surface tension measurement is generally standard method for CMC determination (Romero-Cano *et al.*, 1998; Genova *et al.*, 2003).

2.2 Surface Tension

The interfacial (or surface) tension is a measure of the difference in nature of the two phases meeting at the interface (or surface). In other words, the interfacial tension between two phases is the interfacial free energy per unit area between them.

The interfacial free energy is the minimum amount of work required to create unit area of the interface or to expand it by unit area (Rosen, 2004).

$$W_{\min} = \gamma_{1} \times \Delta A \tag{1}$$

Surfactant can adsorb at some or all of the interfaces in the system and significantly changes the amount of work required to expand those interfaces. Therefore, they usually act to reduce interfacial (or surface) tension. Surface tension depends directly on the replacement of molecules of solvent at the interface by molecules of surfactant, and therefore on the surface (or interfacial) excess concentration of the surfactant, as shown by the Gibbs equation (Genova *et al.*, 2003).

Static surface tension can be determined by various techniques; Du Nouy ring, spinning drop, pendant drop, and Wilhelmy plate method (Cox, 1989; Varadaraj *et al.*, 1991; Hama *et al.*, 1997a, 1997b; Bahr *et al.*, 1999). Many parameters can be calculated from γ_{LV} by putting certain equations such as CMC, efficiency in surface tension reduction (π_{CMC}), effectiveness in surface tension reduction (pC_{20}), surface excess concentration (Γ_{max}), and minimum area per molecule at the liquid/vapor interface (a^{s}) (Varadaraj *et al.*, 1991; Rosen, 2004).

2.3 Surfactant Adsorption

Adsorption is the accumulation of atoms or molecules on the surface of a material. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the adsorbent's surface. In surfactant aqueous system, surfactant monomers firstly tend to adsorb at surface or interface which are water–air surface and water–container wall interface. These phenomena can be explained by electrical double layer model.

2.3.1 The Electrical Double Layer

The electrical double layer is a structure that describes the variation of electric potential near a surface. At any interface there is always an unequal distribution of electrical charges between the two phases. This unequal distribution causes one side of the interface to acquire a net charge of a particular sign and the other side to acquire a net charge of the opposite sign, giving rise to a potential across the interface (Rosen, 2004). The current classical electrical double layer is the Gouy–Chapman–Stern model, which combines the Helmholtz single adsorbed layer with the Gouy–Chapman diffuse layer.

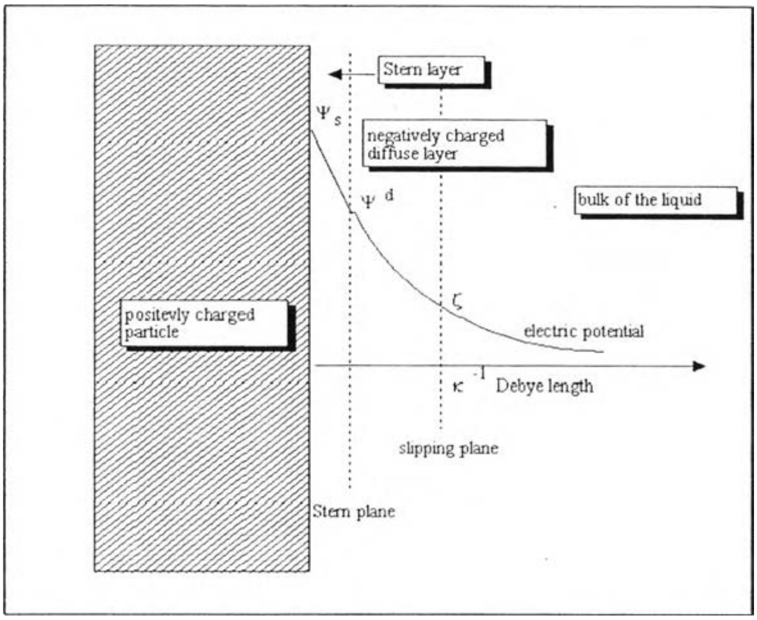

Figure 2.4 Stern model of the electrical double layer.

2.3.2 Adsorption of Surfactant at the Solid/Liquid Interface

The adsorption of surfactants at the solid/liquid interface is strongly influenced by a numbers of factor: (1) the nature of the structural groups on the solid surface (Scales *et al.*, 1986; Hoeft and Zollars, 1996; Romero-Cano *et al.*, 1998); (2) the molecular structure of the surfactant being adsorbed (the adsorbate) (Varadaraj *et al.*, 1991; Hoeft and Zollars, 1996; Hama *et al.*, 1997a; Romero-Cano *et al.*, 1998); and (3) the environment of aqueous phase. Together these factors determine the mechanism by which adsorption occurs, and the efficiency and effectiveness of adsorption.

There are a number of mechanisms by which surface–active solutes may adsorb onto solid substrates from aqueous solution as follow such as ion exchange, ion paring, acid–base interaction, and adsorption by polarization of π electrons, adsorption by dispersion forces, and hydrophobic bonding (Janczuk *et al.*, 1997; Rosen, 2004). In aqueous system, the surfactant structure formed depend upon the interaction of the surfactant molecules with the solid surface in such fashion as to minimize exposure of the hydrophobic groups to the aqueous phase (Rosen, 2004).

2.3.2.1 Adsorption Isotherm

Adsorption isotherm is a mathematical expression that relates the concentration of adsorbate at the interface to its equilibrium concentration in the liquid phase. It is the usual method of describing adsorption at the solid/liquid interface. A variety of analytical techniques are available for determining the change in concentration of the surfactant.

For dilute solution of surfactant, the surface concentration Γ, in μmol/m^2, of the surfactant may be calculated can be calculated from the concentrations of the solute in the liquid phase before and after the solution is mixed with the finely divided solid adsorbent (Rosen, 2004).

$$\Gamma = \frac{(C_i - C_f)\times V_{sol}}{1000\times W_{plastic}\times a_s} \tag{2}$$

where Γ = adsorption of surfactant, (μmole/m^2 plastic)

C_i = initial Surfactant solution concentration, (μM)

C_f = final Surfactant solution concentration, (μM)

V_{sol} = volume of solution, (ml)

$W_{plastic}$ = weight of plastic, (g)

a_s = specific surface area of plastic. (m^2/g)

For solid substrates that cannot be obtained in finely divided form, but can be obtained as a planar, smooth, nonporous surface on film, surface concentrations can sometimes be calculated from contact angles.

The adsorption isotherm can then be plotted in term of Γ as a function of C_i. The surface area per adsorbate molecule on the interface or adsorbent a^s in square angstrom(s) is

$$a^s = \frac{10^{23}}{N\Gamma} \tag{3}$$

where N is Avogadro's number, and Γ is in mol/1000 m^2.

Various techniques can be used for determining equilibrium bulk surfactant concentration depending on the nature of surfactant such as UV-Vis spectrometry, and ion chromatography (Kronberg *et al.*, 1984a, 1984b; Hoeft and Zollars, 1996; Romero-Cano *et al.*, 1998; Janczuk *et al.*, 1997; Gurses *et al.*, 2003; Rosen, 2004). Alternatively, concentration of surfactant molecule is able to be determined by determining carbon in the surfactant structure with total organic carbon analyzer.

2.3.2.2 Langmuir Adsorption Isotherm

A type of adsorption isotherm commonly observed in adsorption from solutions of surfactants is the Langmuir-type isotherm (Rosen, 2004), express by

$$\Gamma = \frac{\Gamma_m C}{C + a} \tag{4}$$

where Γ_m = the surface concentration of the surfactant, in mol/cm^2, at monolayer adsorption,

C = the concentration of the surfactant in the liquid phase at adsorption equilibrium, in mol/l,

a = a constant [= 55.3exp(ΔG°/RT)], in mol/l, at absolute temperature T, in the vicinity of room temperature and where ΔG° is free energy of adsorption at infinite dilution.

This type of adsorption is valid in theory only under the following conditions:

1. The adsorbent is homogeneous.
2. Both solute and solvent have equal molar surface areas.
3. Both surface and bulk phases exhibit ideal behavior.
4. The adsorption film is monomolecular.

Many surfactant solutions show Langmuir-type behavior even when these restrictions are not met.

When adsorption follow the Langmuir equation, determination of the values of Γ_m and *a* permits calculation of the area per adsorbed molecule at surface saturation and the free energy of adsorption at infinite dilution. To determine whether adsorption is following the Langmuir equation and to permit calculation of the values of Γ_m and *a*, the equation is usually transformed into linear form by inverting it. Thus,

$$\frac{C}{\Gamma} = \frac{C}{\Gamma_m} + \frac{a}{\Gamma_m} \tag{5}$$

A plot of C/Γ versus C should be a straight line whose slope is $1/\Gamma_m$ and whose intercept with the ordinate is a/Γ_m. Examples of Langmuir-fitting curve were shown elsewhere (Hoeft and Zollars, 1996; Romero-Cano *et al.*, 1998; González-García, 2004).

2.3.2.3 Adsorption on Hydrophobic Surface

The adsorption of molecular chains such as surfactants onto solid/liquid interfaces especially hydrophobic surface is of a great interest because of its role in nature and industrial applications. Each improvement in the knowledge of this phenomenon has important consequences for different fields including industry, medicine, and biology (Puttharak, 2006).

An increase in the alkyl chain length increases the adsorption affinity, hence the adsorption of surfactants (Hoeft and Zollars, 1996; Rosen, 2004). For example, Hoeft and Zollars (1996) studied to adsorption of anionic surfactant—sulfate and sulfonate surfactants—with varied hydrophobic chain length (C_8 to C_{12}). They found that surfactants with shorter alkyl chain length give the higher adsorption compared with the corresponding surfactant and the same surfaces. On the other hand, an increase in hydrophilic chain length gives lower adsorption of surfactants (Scale *et al.*, 1986; Romero-Cano *et al.*, 1998; Rosen, 2004). Romero-Cano *et al.* (1998) studied the adsorption of nonionic surfactant with a series of polyethylene oxide (POE) group. They found that surfactant with lower number of POE group would adsorb more amount than one with higher number of POE group.

Surface charge density of surface affect on the adsorption as well. Hoeft and Zollars (1996) investigated the adsorption of a series of linear anionic surfactant on sulfonated polysterene latex with various charge densities. They found that, in the region of low surface charge density, the amount of adsorbed surfactant seem to increase with increasing surface charge density. This may probably derived from a result of configurational rearrangements of the adsorbed surfactant due to the charge on surfaces leading to an increase in surface area available for adsorption. However, surface with high surface charge density seemed to obtain low adsorption compared to one with low surface charge density. It might be because surface charges repel the surfactant that try to adsorb, the amount of surfactant adsorption, therefore, would be low. This result was in agreement with the study in nonionic surfactant (Romero-Cano *et al.*, 1998), that is, surface with low surface charge density give higher adsorption compared to one with high surface charge density.

2.3.2.4 Structure of Adsorbed Layer

Besides the industrial importance of surfactant adsorption, the structure of adsorbed layer and the forces involved are also of genuine scientific interest. The in-plane molecular organization of adsorbed surfactants at the solid/liquid interface or the structure of surfactant layer has been studied by atomic force microscopy (AFM). In addition, the technique can be used for measurements of force curves and, indirectly, thickness of adsorbed layers. Recently this technique has been used to study the equilibrium structure of anionic, cationic, zwitterionic, and nonionic surfactants adsorbed to a variety of surfaces (Grant *et al.*, 2000).

Grant *et al.* (2000) studied the structure of adsorbed surfactants on the surfaces with varied hydrophobicity. They found that the following general evolution of the adsorbed layer morphology with increasing surface hydrophobicity was observed: diffuse micellar coverage; dense micellar coverage; bilayer; and finally a monolayer structure at the most hydrophobic surface. In addition, they concluded that hydrophobic interaction was the main driving force for adsorption of ethylene oxide segments.

2.3.3 Adsorption of Surfactant at the Liquid/Vapor and Liquid/Liquid Interfaces

The direct determination of the amount of surfactant adsorbed per unit area of liquid/vapor (L/V) or liquid/liquid (L/L) interface, although possible, is not generally undertaken because of the difficulty of isolating the interfacial region from the bulk phase(s) for purposes of analysis when the interfacial region is small, and of measuring the interfacial area when it is large. Instead, the amount of material adsorbed per unit area of interface is calculated indirectly from surface or interfacial tension measurements (Varadaraj *et al.*, 1991; Hama *et al.*, 1997a). As a result, a plot of surface (or interfacial) tension as a function of (equilibrium) concentration of surfactant in one of the liquid phases, rather than an adsorption isotherm, is generally used to describe adsorption at these interfaces. From such a plot the amount of surfactant adsorbed per unit area of interface can readily be calculated by use of the Gibbs adsorption equation (Rosen, 2004).

2.3.4 Gibbs Adsorption Equation

The Gibbs adsorption equation, in its most general form,

$$d\gamma = -\sum_i \Gamma_i d\mu_i \tag{6}$$

where $d\gamma$ = the change in surface or interfacial tension of the solvent,
Γ_i = the surface excess concentration of any component of the system,
$d\mu_i$ = the change in chemical potential of any component of the system,

is fundamental to all adsorption processes where monolayers are formed (Rosen, 2004). At equilibrium between the interfacial and bulk phase concentration, $d\mu_i = RTd\ln a_i$, where a_i = the activity of any component in the bulk liquid phase, R = the gas constant, T = the absolute temperature, and for dilute solution (10^{-2} M or less) containing only on nonodissociating surface–active solute, the activity of the solvent of the solute can be replaced by its molar concentration C. Thus,

$$d\gamma = -RT\Gamma d\ln C \qquad (7)$$

which is the form in which the Gibbs equation is commonly used for solution of non-ionic surfactants containing no other materials.

For surface–active solutes the surface excess concentration, Γ can be considered to be equal to the actual surface concentration without significant error. The concentration of surfactant at the interface may therefore be calculated from surface or interfacial tension data by use of the appropriate Gibbs equation. Thus, for dilute solution of a nonionic surfactant, or for a 1:1 ionic surfactant in the presence of a swamping amount of electrolyte containing a common nonsurfactant ion,

$$\Gamma = -\frac{1}{2.303RT}\left(\frac{\partial\gamma}{\partial\log C}\right)_T \qquad (8)$$

and the surface concentration can be obtained from the slope of a plot of γ versus log C at constant temperature (when γ is in dyn/cm or ergs/cm^2 and R = 8.31 x 10^7 ergs mol^{-1} K^{-1}, then, Γ is in mol/cm^2; when γ is in m Nm^{-1} or m Jm^{-2} and R = 8.31 J mol^{-1} K^{-1}, Γ, is in mol/1000 m^2) (Rosen, 2004).

A typical plot for a dilute solution of an individual surfactant (surfactant are often used at concentrations of less than 1 x 10^{-2} M) is formed. The break in the curve occurs at the critical micelle concentration (CMC) (Cox, 1989; Varadaraj *et al.*, 1991; Piispanen *et al.*, 2003). Above this concentration the surface tension of the solution remains essentially constant since only the monomeric form contributes to reduction of the surface or interfacial tension.

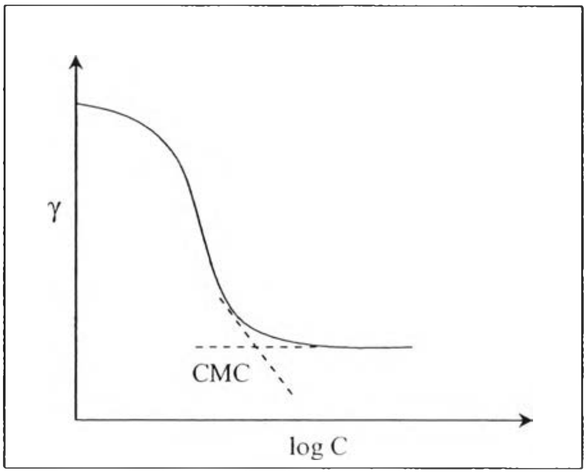

Figure 2.5 Plot of surface tension versus logarithm of the bulk phase concentration for an aqueous solution of a surfactant.

2.3.5 Point of Zero Charge (PZC)

The position of the PZC defines the affinity of the surface to the ionic species, especially ionic surfactants and polyelectrolytes, which are widely used to modify the surface properties. Then, the knowledge of the PZC of the materials of interest facilitates the choice of a surfactant for a specific purpose, e.g., in mineral process (flotation), or the choice of an adsorbent for removal of certain solutes, e.g., from wastewater, makes it possible to predict the pH effect on the phenomena and processes involving adsorption, etc. Therefore, determination of the PZC is an important element of the characterization of commercial adsorbents (Kosmulski, 2002).

Various techniques have been used for determining the PZC of materials such as CIP (common intersection point of potentiometric titration curves obtained at three or more ionic strengths); intersection (intersection point of potentiometric titration curves obtained at two ionic strengths); pH (natural pH of the dispersion); IEP (isoelectric point obtained by classical electrokinetic methods); acousto (isoelectric point obtained by the electroacoustic method; and potentiometric mass titration (Kosmulski, 2002, 2004, 2006, 2009).

2.4 Wetting

Wetting in its most general sense is the displacement from a surface of one fluid by another. Wetting, therefore, always involves three phases, at least two of which are fluids: a gas and two immiscible liquids, or a solid and two immiscible liquids, or a gas, a liquid, and a solid, or even three immiscible liquids. Commonly, however, the term wetting is applied to the displacement of air from a liquid or solid surface by water or an aqueous solution.

The term wetting agent is applied to any substance that increases the ability of water or an aqueous solution to displace air from a liquid or solid surface. Wetting is a process involving surfaces and interfaces, and the modification of the wetting power of water is a surface property shown to some degree by all surface-active agents (Rosen, 2004).

2.4.1 Type of Wetting

Wetting can be classified into 3 types, spreading wetting, adhesional wetting, and immersional wetting. The equilibria involved in these phenomena are well known. In spreading wetting, a liquid in contact with a substrate spreads over the substrate and displaces another fluid, such as air, from the surface. For the spreading to occur spontaneously, the surface free energy of the system must decrease during the spreading process. When the area of an interface increases, the surface free energy at that interface increases; when the area decreases, the surface free energy decreases (Rosen, 2004).

2.4.2 Spreading Coefficient

Spreading coefficient (S_{LS}) is quantity that act as driving force for spreading process, and relate to corresponding interfacial (or surface) tension as following equation (Rosen, 2004);

$$S_{LS} = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}) \tag{9}$$

where γ_{SV} is interfacial tension at substrate/vapor interface,
γ_{SL} is interfacial tension at substrate/liquid interface,
γ_{LV} is interfacial tension at liquid/vapor interface.

If S_{LS} is positive, spreading can occur spontaneously; if S_{LS} is negative, the liquid will not spread spontaneously over the substrate.

Bahr *et al.* (1999) studied the spreading behavior of microdrops of surfactant solutions at solid surfaces to determine the influence of different factors, including drop lifetimes, surface tension dynamics, and surface energies.

Due to the depletion effect, the measured contact angle does not necessarily have to significantly smaller for a surfactant solution drop (with a start concentration equal to or above the CMC) than for a corresponding drop of pure water. This effect was pronounced in the surfactant with CMC lower than 5×10^{-5} M when using 4 μl droplet. Surfactant droplets with below CMC show spreading delay, despite prespread to 1 min, whereas the delay was not found in drop with more than 10 CMC. The spreading behaviour on a more hydrophilic surface was faster than the less ones because a smaller adsorption is needed to produce the necessary surface pressure to drive the spreading. Despite, it often takes a longer time to reach a steady-state wetting (Stoebe *et al.*, 1996; Bahr *et al.*, 1999).

For Roughness effect, no significant difference in the spreading rates was found. Apparently, as the roughness grows, the increase in the pulling force due to elongation of the triple contact line is cancelled by increased viscous drag. The only exception might be if the average peak–to–valley distances turn out to be less than the thick ness of the stagnant layer of liquid, in which case the flow hydronamics would be insensitive to the underlying surface relief (Bahr *et al.*, 1999).

When the substrate is a solid, the spreading coefficient is usually evaluated by indirect means, since surface and interfacial tensions of solids cannot easily be measured directly. S_{LS} can be alternatively determined by measuring contact angle (Rosen, 2004).

2.4.3 Contact Angle

The contact angle is a quantitative measure of the wetting of a solid by a liquid; it is indirect means for evaluating spreading coefficient (Rosen, 2004). It is 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°) of contact angle indicate that less complete wetting (poor wettability). If value is zero contact angle indicate that "complete wetting" (Jirawatanaporn, 2009).

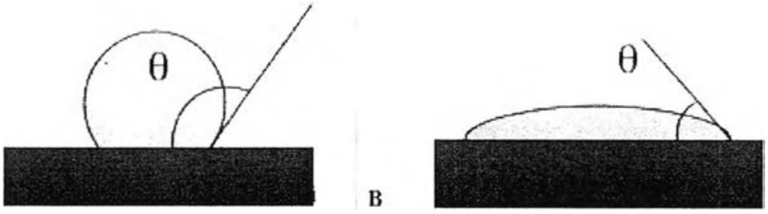

Figure 2.6 The contact angle of liquid droplet at equilibrium.

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 (Rosen, 2004):

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \qquad (10)$$

where γ_{SV}, γ_{SL}, and 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, 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 (Rosen, 2004).

2.4.3.1 Measurement of Contact Angle

Many experimental techniques are available for wettability, such as, capillary penetration techniques, the adhering gas bubble method, the Wilhelmy plate method, Draves method, and the sessile drop technique (Norling and Brukl, 1986; Scale *et al.*, 1986; Varadaraj *et al.*, 1991; Varadaraj *et al.*, 1994; Hama *et al.*, 1997a; Hama *et al.*, 1997b; Janczuk *et al.*, 1997; Luangpirom *et al.*, 2001; Szymczyk and Janczuk, 2006). 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" (Luangpirom *et al.*, 2001).

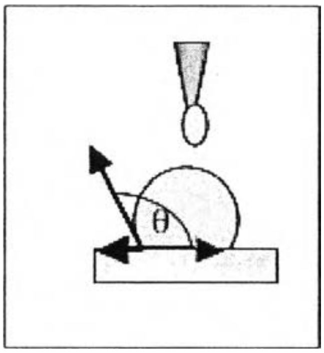

Figure 2.7 The contact angle by the sessile drop technique.

In contact angle measurement, the volume of drop of surfactant in the range of 1 μl to 6 μl was not affect on the spreading and contact angle. In addition, no effect of the volume on the initial spreading rate was observed (Bahr, 1999).

Norling and Brukl (1986) studied the feasibility of increasing the wettability of poly(vinyl siloxanes) elastomer by incorporating commercial nonionic surfactants with a series of polyoxyethylene (POE) group, and determined a systematic structure–property relationship of those surfactants. The results showed that the minimum contact angle occurred at optimum POE chain length. Therefore, it indicated that the contact angle was a strong function of the surfactant HLB number and that a clear minimum contact angle occurred at a specific HLB number.

Scales *et al.* (1986) examined the effect of a series of nonionic surfactants (EO5, EO9, and EO30) on the wettability on quartz surface with varied hydrophobicity. They found that contact angle increased with increasing EO group. For specific surfactants, the contact angle decreased with increasing hydrophobicity. In addition, they found that temperature affect in contact angle on polydisperse surfactant greater than on monodisperse surfactant. It might be because the polydisperse surfactant has low activation energy needed to complete association of the adsorbed layer to be occur.

Varadaraj *et al.* (1994) studied effect of surfactant type and structure on hydrophobic granular surface by using the capillary penetration wetting technique. The results indicated that both the surfactant type and hydrocarbon chain branching influenced significantly on the rate and effectiveness of wetting rates (mg/s) for ethoxylates > sulfates > ethoxysulfates; wetting effectiveness (mg) for sulfates > ethoxylates. For a given surfactant type, hydrocarbon chain branching was observed to increase wetting rate and effectiveness.

Hama *et al.* (1997a) investigated influence of the structure of hydrophobic groups and polyoxyethylene (POE) chain length of the ethoxylate ester on interfacial properties. For range of EO number in this study, EO6 to EO15, EO9-to-EO15 range of C10- to C14-EFME show favorable wettability. Among them, C12-EFME shows the best wettability (lowest wetting times).

Genova *et al.* (2003) studied effect of hydrophobic structure on the performance of alcohol ethoxylates derived from oleochemical alcohol and oxo-alcohols derived from kerosene, butylene, or coal by the Fischer–Tropsch process. They found that increasing substitution at the C2 carbon increases the amount of unethoxylated alcohol in the ethoxylate due to hindrance of ethoxylation by alcohol but decreases wetting time

Piispanen *et al.* (2004) investigated the wetting properties of the sugar-based surfactants compared with water and nonylphenol ethoxylates with POE group of 6, 10, and 20 units. A wetting property scale of 0 to 6 was used, where 6 stands for the best possible wetting property, and the results were 5, 3, 1, and 0, for NPE-6, NPE-10, NPE-20, and pure water, respectively.

2.4.3.2 Wetting by Aqueous Surfactant Solution

Water has a considerably high surface tension; hence, it does not readily spread over solids that have surface free energy of 72 mN/m or lower. The addition of surfactant is, therefore, often necessary to enable water to wet on solid surface. Surfactant can improve wetting through altering the surface properties of the liquid phase by its presence at the interface (Puttharak, 2006).

An equilibrium wetting can be related to adsorption, as developed by Lucassen–Reynders, by combining the Gibbs adsorption equation with Young's equation (Rosen, 2004);

$$\frac{\partial(\gamma_{LV}\cos\theta)}{\partial\gamma_{LV}} = \frac{\Gamma_{SV}-\Gamma_{SL}}{\Gamma_{LV}} \tag{11}$$

Γ_{ij} represents the surface excess concentration of the surfactant at the ij interface. The slope of a plot of $\gamma_{LV}\cos\theta$ versus γ_{LV} consequently provides information at the three interfaces (Janczuk, 1997; Szymczyk and Janczuk, 2006; Szymczyk and Janczuk, 2008).

The surfactants increasingly less adsorbing at solid/liquid interface with increasing hydrophilicity of surface were also observed by Gau and Zografi (1990). In their works, advancing contact angle of aqueous solutions of the nonionic surfactants, polyoxyethylene ether, surfactants were measured on surfaces prepared from PS surface, PMMA surface, latex particles as well as paraffin. They discovered that wetting of surfactant solutions is less efficient relative to pure liquid for

PS and PMMA due to less adsorption at solid/liquid interface compared with adsorption at liquid/vapor interface.

2.4.3.3 Critical Surface tension

The critical surface tension of a solid surface is an indication of its relative water-hating or water-loving character. A low critical surface tension means that the surface has a low energy per unit area. The quantity is based on experiments with a series of pure liquids. These experiments have to be conducted on a flat, non-porous solid sample (Puttharak, 2006).

Zisman and co-workers introduced and empirical relation of contact angle data on polymers. They measures the contact angles for series of liquid on the same polymer sample, and plotted cosθ vs γ_{LV} of the liquid (Zisman plot), the graphical points fell close to a straight line or collected around it in a narrow rectilinear band:

$$\cos\theta = 1 - \beta(\gamma_{LV} - \gamma_C) \qquad (12)$$

Each line extrapolates to zero θ at a certain γ_{LV} value, which Zisman has called the "critical surface tension of liquid", γ_C. They proposed that as γ_{LV} decreased toward to γ_C, γ_{SL} will approach to zero, and when γ_{SL} reachs zero, γ_{LV} will be equal to γ_C (but not γ_{SV}), however the γ_C is different form the γ_{SV}. Where Van der Waals forces are dominant, γ_C of the polymeric solid is independent of the nature of liquid and is a characteristic of the solid alone (Ellison and Zisman, 1954; Bernett and Zisman, 1959a; Bernett and Zisman, 1959b; Janczuk, 1997).

Ellison and Zisman (1954) studied the wettability of polymer surface of PET, nylon, and PS by dynamic contact angle measurement (advancing and receding contact angle) using pure liquid, for example, water, glycerol and formamide. It was revealed that hydrophilicity of surface affected on the wettability, that is, the more hydrophilicity, the greater wettability. Besides, the given γ_C derived from Zisman plot support their results.

Surfactant solutions with a range of concentration could be used to determine the γ_C of polymer surface. Bernett and Zisman (1959a) used a variety of pure anionic, cationic, and nonionic surfactants for determining γ_C from Zisman plot. The given curves were found the break in slope close to the CMC but were slightly lower which was not found in micelle-producing liquids. In addition, other phenomena might be involved in such discontinuities (Bernett and Zisman, 1959b).

The critical surface tension is obtained from the Zisman plot, in which the cosine θ of the wetting angle for a series of liquids is plotted against the surface tension γ_{LV} of the liquid. These plots give the best empirical fit of experimental data. The intercept of these curves with the $\cos\theta = 1$ is known as the critical surface tension, γ_C, perfect wetting (Johnson and Dettre, 1993).

The critical surface tension concept is useful in classifying the surface and estimating contact angles, since β is approximately 0.03 to 0.04. However, the value of γ_C is often uncertain since the extrapolation is quite long and considerable curvature of the empirical line is present for solids on which a wide range of liquids form non-zero contact angles. Hence, Zisman and Good warned researchers not to construct Zisman plots using binary solutions. This is because with the additional components at an interface, one of them may be adsorbed or interpenetrated at the interface more strongly and there will not be any simple relation for such situations (Erbil, 1997).

Supalasate (2004) studied the adsorption surfactant on plastic surfaces and its relation to wetting phenomena. The result showed that the adsorption of surfactant at the solid/liquid interface caused the Zisman plot to deviate. The deviation of the Zisman plot appeared in the case of CPC on polystyrene and polyethylene terephthalate. It could indicate that the polarity of plastics has an effect on the wettability of CPC.

Meerit (2005) found that deviation of the Zisman plot did not appear in case of CPC, sodium octyl benzene sulfonate (NaOBS), and $OP(EO)_{10}$ on PTFE, PVC, and PC. Whereas the deviation of the Zisman plot appeared in the case of CPC on PMMA, ABS, and Nylon 66 when NaCl presented because of these reasons; (1) the anchor-like structure of CPC limited the movement; (2) the addition of NaCl might not be able to allow more CPC to adsorb on the surface; and, (3) CPC had the opposite charge to the surfaces so it adsorbed on the surface in horizontal appearance and lowered the adsorption area.

Szymczyk *et al.* (2005) determined the influence of the concentration and composition of aqueous solution of mixtures of cationic surfactants and nonionic surfactant, on the wettability of polytetrafluoroethylene (PTFE). According to Zisman plot, there is no linear dependence between cosθ and the surface tension of aqueous solution of CTAB and TX100 mixtures for all studied systems, but a linear dependence exists between the adhesional tension and surface tension for PTFE in the whole concentration range, the slope of which is -1, that suggests that the surface excess of the surfactant concentration at the PTFE–solution interface is the same as that at the solution–air interface for a given bulk concentration. On the basis of the surface tension of PTFE and the Young equation and thermodynamic analysis of the adhesion work of aqueous solution of surfactant to the polymer surface it was found that in the case of PTFE the changes of the contact angle as a function of the mixture of nonionic and cationic surfactants concentration resulted only from changes of the polar component of solution surface tension.

Szymczyk *et al.* (2006) determined the critical surface tension of PTFE and PMMA surfaces by aqueous solution of CTAB and CPyB mixture by contact angle measurement using sessile drop method. The given value was higher than for that of the surface tension of PTFE but lower than for PMMA. It was found that for the studied surfaces, the changes of the contact angles of the solution of mixture resulted only from the decrease of the polar component of the solution surface tension.