CHAPTER II
LITERATURE REVIEW

2.1 Characteristic of Surfactants

Surfactants or surface-active agents are a substance that has the property of adsorbing preferentially onto the surfaces or interfaces of the system, leading to a significant change in the surface or interfacial free energies at low surfactant concentrations (Rosen, 2004). Surfactants also have the important property of forming colloid-sized aggregates called micelles at a sufficient surfactant concentration. The lowest total surfactant concentration at which micelles are present is called the critical micelle concentration (CMC).

Surfactants are schizophrenic molecules that have two sides to their nature. One part is solvent-loving where the solvent is a polar solvent or water or lyophilic (hydrophilic) and the other one is solvent-hating or lyophobic (hydrophobic). The hydrophilic section is called the head while the hydrophobic section, usually a long hydrocarbon chain, is generally called the tail. The tail may be depicted either as a straight line or a wavy tail, as shown in Figure 2.1. Surfactants can form various types of aggregates, micelles in solutions and admicelles and hemimicelles on solid surfaces.
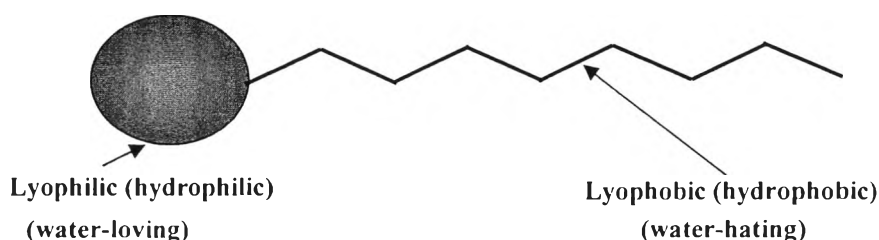

Lyophilic (hydrophilic)   Lyophobic (hydrophobic)
(water-loving)   (water-hating)

Figure 2.1 Surfactant structure.

Surfactants are classified according to the charge present in the hydrophilic portion of the molecule (after dissociation in aqueous solution). They can be categorized into 4 types (Rosen, 2004):

- Anionic: the surface-active portion of the molecule bears a negative charge, for example, $RCOO_3^-Na^+$ (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 of the molecule bears no apparent ionic charge, for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long-chain fatty acid).

2.2 Adsorption at the Solid/Liquid Interface of Surfactants

In an aqueous system, the hydrophobic group of the surfactant will be oriented toward the nonpolar phase, with the hydrophilic head in the aqueous phase. Since this orientation decreases the dissimilarity between the aqueous and the nonpolar phase, the interfacial tension between the two phases is decreased, and it will now be easier than in the absence of the surfactant to increase the area of the interface between them (Rosen and Dahanayake, 2000).

The adsorption of surfactants at the solid-liquid interface is strongly influenced by a number of factors (Rosen, 2004): (1) the nature of the chemical structure on the solid surface; (2) the molecular structure of the adsorbate (surfactant); and, (3) the environment of the aqueous phase – pH, electrolyte content, the presence of any additives such as short – chain polar solutes (alcohol, urea, etc.), and temperature.

2.2.1 Adsorption Isotherm

An adsorption isotherm relates to the concentration of adsorbate (surfactant) at the interface in equilibrium with its equilibrium concentration in the

bulk liquid phase. Since most of the information regarding the adsorption onto solid/liquid interface can be deduced from the adsorption isotherm, the isotherm is a usual method of describing adsorption at the solid/liquid interface. The results from surfactant adsorption experiments are usually expressed in the form of adsorption isotherm, which displays the amount of surfactant adsorbed as a function of equilibrium surfactant concentration (Rosen, 2004). The nature of the true adsorption mechanism may also be obtained from the adsorption isotherm (Rybinski and Schwuger, 1987).

2.2.2 Surfactant Adsorption onto Nonpolar or Hydrophobic Surfaces

The adsorption of a surfactant onto hydrophobic surfaces is mainly by dispersion forces. The orientation of the adsorbate (surfactant) initially may be parallel to the surface of the solid or slightly tilted or L-shaped, with the hydrophobic group close to the surface and the hydrophilic group oriented toward the aqueous phase (Figure 2.2). As the adsorption continues with increasing surfactant concentration, the adsorbed surfactant molecules may become oriented more and more perpendicular to the surface with hydrophilic heads oriented toward the water. In some cases, the adsorption isotherm shows an inflection point that has been ascribed to a change in orientation of the surfactant from parallel to perpendicular (Rosen, 2004).
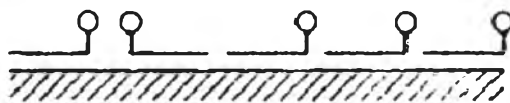

Figure 2.2 Adsorption via dispersion forces on a nonpolar surface (Rosen, 2004).

However, the adsorption of surfactant at the solid/liquid interfaces depends on the nature of solid substrates with many exceptions. In normally, hydrophobic surfaces can be briefly classified into two types (Ingram and Ottewill, 1990):

2.2.2.1 Uncharged Hydrophobic Substrates (Surfaces)

These can be considered as low-energy surfaces whereas the method of preparation is essentially critical not to produce ionizable groups on the surface which can become electrically charged on contact of the surface with water. Typical examples would be graphite, paraffin wax, polymers such as polystyrene, etc.

Conner and Ottewill (1971) studied the adsorption of hexadecyltrimetylammonium ions (HTAB) onto polystyrene without any ionic surface groups. Their results showed a slow rise in the amount adsorbed until just before the CMC, suggesting the formation of a monolayer on the surface with the hydrocarbon chains of the surfactant adsorbed on the hydrophobic surface and the ionic head groups exposed to the solution phase.

2.2.2.2 Charged Hydrophobic Substrates (Surfaces)

A good example of these charged hydrophobic substrates is hydrophobic with OH group silica or polymer lattices with relatively low surface charge densities, say 4 C/cm^2 or less. These materials are assumed to have the charges evenly spread over the surface and then there will be parts of the surfaces with charges which will attract water molecules by ion-dipole association and also become hydrophilic while the other areas still have low-energy hydrophobic patches.

An adsorption study on polystyrene particles with carboxylic acid groups was carried out by Connor (1968) and Chen (1974). The adsorption isotherms of hexadecyltrimetylammonium ($C_{16}TAB$), dodecyltrimetylammonium ($C_{12}TAB$), decyltrimetylammonium ($C_{10}TAB$), and octyltrimetylammonium (C_8TAB) ions obtained at pH 8.0 in the presence of potassium bromide showed higher adsorption with an increase in the chain length of surfactants. Besides, the adsorption isotherms appeared two striking features. Before the first striking features, the cationic head group adsorbed onto the negatively charged site of the polystyrene surface to balance the charges. At this plateau, then, the alkyl chain of surfactant was transferred from the aqueous phase to the hydrophobic surface in horizontal orientation and before the CMC in the second striking feature, the cationic head groups exposed to the aqueous phase and formed a close-packed monolayer.

Hoeft and Zollars (1996) studied the adsorption of single anionic surfactants on hydrophobic surfaces (polystyrene latex with various surface charge densities). For the effect of head group polarity of anionic surfactants: linear alkyl sulfonates (SLS) and linear alkyl sulfate (SLSN), it was found that the less polarity of SLSN possessed a lower diving force to adsorb on a surface as compared to SLS. This is again due to the small difference between the hydrophobic and hydrophilic character of the sulfonate surfactant chain in comparison with the sulfate surfactant. For this reason, it was expected that for any surface charge density, the adsorbed amount of SLS would likely be greater than that of SLSN for the same chain length at all bulk concentrations.

The use of surfactants also can remove water-based inks from a plastic film by using fundamental of surfactant adsorption. Gecol *et al.* (2004) studied the effect of calcium ion concentration and the length of surfactant hydrophobe on deinking from the plastic film. The results showed that either cationic or anionic surfactant was found to deink better as the number of carbons in the hydrophobe increased, with the largest hydrophobe yielding optimum deinking. The presence of calcium was found to decrease the effectiveness of all cationic, nonionic, and amphoteric surfactants because calcium ions compete with the surfactant for adsorption sites. The studied anionic surfactant was found to be effective for the removal of water-based ink from the plastic film only in the presence of calcium, probably because the calcium ions form a bridge between negatively charged ink and the anionic surfactant head group.

2.2.3 Structure of Adsorbed Surfactant Layer

There are several specific techniques available to study the structure of the surfactant layer at the solid/liquid interface; ellipsometry, neutron reflectivity, fluorescence spectroscopy, and atomic force microscopy (AFM). AFM can be used to image directly the structure of the surfactant aggregated at the solid/liquid interface (Garbassi *et al.*, 1994). It has been found that surfactants often form monolayer or hemimiceller aggregates on a hydrophobic surface.

Wanless *et al* (1997) used AFM to image the surfactant surface aggregation on graphite. For pure sodium dodecylsulfate (SDS), the surfactant

molecules were found to form parallel hemicylindrical surface aggregates over a concentration range from about one-third to at least ten times the CMC.

The existence of regular self-assembled structures (full or half cylinders, spheres or spheroids) at the solid/liquid interface for concentrations above the CMC was proved recently by using AFM imaging. These alignments depended on the concentration and the constitution of the surfactant's head group and on the hydrophilic or hydrophobic properties of the solid (Grosse and Estel, 2000). The AFM results showed the difference of adsorption of CTAB on hydrophilic (mica) and hydrophobic (graphite) surfaces. Hemicylinders dominated on the hydrophobic surface because a large contact area between the hydrophobic chains of the surfactant and the solid surface is thermodynamically favorable, whereas rods or full cylinders were found on hydrophilic surfaces. Nonionic surfactants were found to adsorb onto the surface of hydrophobic silica as a monolayer with head groups in contact with the aqueous solution. This aggregation was driven by a minimization of the area of the contact between water and the hydrophobic substrate. From the AFM images, the hydrophobic substrate was found not only to cause a lower curvature structure than in solution but also to produce an interface that is smoother than itself. To form a flat layer, either it must force the head groups closer together (by exerting a larger force than the charge-charge and/or hydration forces between the head groups) or the effective volume occupied by the hydrocarbon must change shape. Besides, most surfactants form hemicylindrical structures on graphite with a specific attractive interaction between graphite and alkyl chains of surfactants (Grant *et al.*, 1998). Atkin *et al.* (2003) explained that the tail length reached a critical length to successfully epitaxially adsorb and acted as template for hemicylindrical aggregation.

2.3 Wettability onto Solid Surface

Wettability enhancement onto a solid surface by using surfactant is important for many applications such as herbicide spraying, coating, adhesion textile dyeing, detergency, and printing. Generally, wetting, the displacement from a surface of one fluid by another, always involves three phases, at least two of which are

fluids: a gas and two immiscible liquids; a solid and two immiscible liquids; a gas, a liquid, and a solid; or even three immiscible liquids. Generally, wetting is applied to the displacement of air from a liquid or solid surface by water or an aqueous solution (Rosen, 2004).

Wetting is a surface property characteristic for all materials which yields a unique value for each compound. The surface tension value of a material can be utilized to determine the wettability of a material by specific liquids. Through the measurement of the contact angle between a solid surface and a droplet of liquid on the surface, the surface tension for the solid material can be calculated.

2.3.1 Spreading Wetting

In wetting, a liquid spreads over the surface of a substrate and displaces another fluid from the surface. For the spreading to occur spontaneously, the surface free energy of the system must decrease during the spreading process. The total decrease in surface free energy per unit area of system, $-\Delta G_w/a$, can be expressed by the following equation:

$$-\Delta G_w /a = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}) \tag{2.1}$$

If the term of $\gamma_{SV} - (\gamma_{SL} + \gamma_{LV})$ is positive, indicating that the free energy of the system decreases and consequently, the spreading process can occur spontaneously.

The quantity of $\gamma_{SV} - (\gamma_{SL} + \gamma_{LV})$ can be considered as the driving force behind the spreading process and is usually called the spreading coefficient, $S_{L/S}$, as defined by

$$S_{L/S} = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}) \tag{2.2}$$

If the $S_{L/S}$ is positive, spreading can occur spontaneously; if the $S_{L/S}$ is negative, the liquid will not spread spontaneously over the substrate (Rosen, 2004).

Liquid spreading and wetting behaviors on solid surfaces are dependent on surfactant physical chemistry and concentration at gas–liquid interfaces

and gas (or liquid)–liquid–solid contact lines. A great deal is known about surfactants and their concentration-dependent effects on interfacial tension (Grotberg and Gaver, 1996). Eckmann *et al.* (2001) studied wetting characteristics of aqueous surfactant solutions on different surfaces of glass, acrylic and stainless steel. The results demonstrated that a particular surfactant delivered to the interface at a certain concentration could significantly change the wetting potential of the liquid onto the solid. The studied surfactants were found not only to lower interfacial tension but also to reduce static, advancing, and receding contact angles and the spreading coefficient in a concentration dependent fashion that was quite similar when normalized to the effect on surface tension.

2.3.2 Contact Angle

The contact angle is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three-phase boundary where a liquid, gas, and solid intersect (see Figure 2.3).
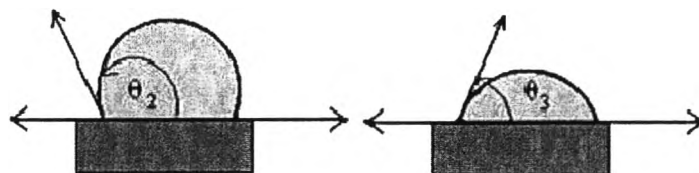

Figure 2.3 Liquid droplet in equilibrium: definition of contact angle (http://www.pharmainfo.net/reviews/mercury-intrusion-porosimetry-tool-pharma ceutical-particle-characterization).

The low values of contact angle indicate that the liquid spreads well (high wettability), while the high values indicate less complete wetting (poor wettability). If the contact angle is less than 90 degrees, the liquid is considered to "wet" the solid. If it is greater than 90 degrees, it is said to be "non-wetting". A zero contact angle represents "complete wetting". The contact angle is always less than 180 degrees (Johnson and Dettre, 1993).

The contact angle is a function of the liquid's surface tension and the surface free energy of the substrate. The relationship between the contact angle and

the interfacial tension is related to the Young's equation (Young, 1805), as shown in Equation 2.3 and Figure 2.4:

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}, \tag{2.3}$$

where θ is the contact angle, γ_{SV} is the solid/vapor interfacial tension, γ_{SL} is the solid/liquid interfacial tension, and γ_{LV} is the liquid/vapor interfacial tension (which is normally called the surface tension). However, this equation is only valid for finite contact angles in the case of mechanical equilibrium, so it does not apply when spreading takes place. Thus, to encourage wetting, both γ_{SL} and γ_{LV} should be made as small as possible. This is done in practice by adding a surfactant to the liquid phase. The surfactant adsorbs to both the liquid/solid and liquid/vapor interfaces, lowing those interfacial tensions (Rosen, 2004). Surface pressures are useful since they represent the difference between γ_{SL} and γ_{LV} for pure water and that for the surfactant solution and are defined as follows:

$$\Pi_{SL} = \gamma^o_{SL} - \gamma_{SL} \tag{2.4}$$

$$\Pi_{LV} = \gamma^o_{LV} - \gamma_{LV} \tag{2.5}$$

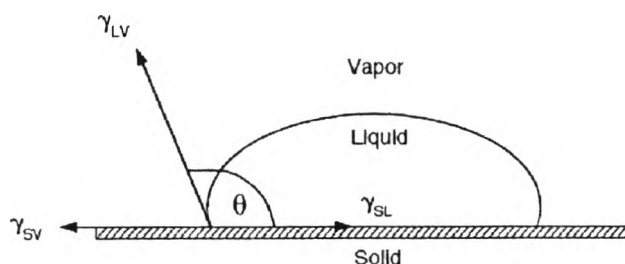where the superscript o refers to surfactant-free solution or pure water in this study.

Figure 2.4 Illustration of contact angle of a surfactant solution on solid surface and the relationship of interfacial tensions of three surfaces (Luepakdeesakoon et al., 2006).

When the solid substrate is nonpolar, low-energy surface, the contact angle can be used to determine the surface excess concentration of the surfactant at solid/liquid interface, Γ_{SL}.

For pure water, Equation (2.3) can be written as:

$$\gamma^{\circ}_{LV} \cos \theta^{\circ} = \gamma_{SV} - \gamma^{\circ}_{SL} \qquad (2.6)$$

where θ° is the contact angle for pure water.

For the surfactant solution:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}, \qquad (2.7)$$

subtracting Equation (2.6) from Equation (2.7) and using Equation (2.4) defining surface pressure:

$$\Pi_{SL} = \gamma_{LV} \cos \theta - \gamma^{\circ}_{LV} \cos \theta^{\circ}. \qquad (2.8)$$

γ_{SV} at the solid/vapor interface is the same for pure water (Equation (2.6)) and the dilute surfactant solution (Equation (2.7)) since only advancing contact angles are considered and the solid surface is in equilibrium with air saturated with water in both cases.

Since adsorption of surfactant at interfaces is responsible for reduction of γ_{LV} and γ_{SL}, we are interested in quantifying the adsorption levels. From the Gibbs equation [Rosen, 2004] at the solid/liquid surface for an anionic or cationic surfactant with the definition at surface pressure (Equation (2.4)):

$$\Gamma_{SL} = \frac{1}{2RT} \frac{d\Pi_{SL}}{d\ln C_S} \qquad (2.9)$$

where C_S is the surfactant concentration in solution.

Similarly at the liquid/vapor interface, combining the Gibbs equation with the definition at surface pressure (Equation (2.5)), for anionic or cationic surfactants,

$$\Gamma_{LV} = -\frac{1}{2RT}\frac{d\gamma_{LV}}{d\ln C_S}$$

(2.10)

Equations (2.9) and (2.10) assume that the surfactant partial fugacity or activity is proportional to concentration, so only applies to dilute solutions below the CMC. The vapor/liquid interface typically exhibits a constant adsorption (Γ_{SL}) or constant slope of γ_{SL} vs. $\ln C_S$ from about 20% of the CMC to the CMC as a Gibbs close-packed monolayer is attained. Whether a solid surface becomes saturated as the CMC is approached depends on the nature of the solid. The value of Γ_{SL} can therefore, under these conditions, be determined from the slope of Π_{SL} versus $\ln C_S$ plot at constant temperature (Rosen, 2004).

Balasuwatthi *et al.* (2004) investigated the contact angle of a saturated aqueous surfactant solution on the precipitate of that surfactant measured by using the sessile drop method. The results revealed the sodium and calcium salts of alkyl sulfates (C_{12}, C_{14}, and C_{18}) had advancing contact angles higher than those of alkyl trimethylammonium bromides (C_{14}, C_{16}, and C_{18}). For the effect of pH, the contact angles of fatty acid (C_{12} and C_{16}) solutions did not show any dependence on pH between a pH of 4 and 10.

2.3.3 Adsorption and Wetting

Lucassen-Reynders (1963) developed the relation of surfactant adsorption to equilibrium wetting analyzing method, which is a combination of the Gibbs adsorption equation with Young's equation to yield:

$$\frac{d(\gamma_{LV}\cos\theta)}{d\gamma_{LV}} = \frac{\Gamma_{SV} - \Gamma_{SL}}{\Gamma_{LV}},$$

(2.11)

where Γ_{SV}, Γ_{SL}, and Γ_{LV} represent the surface excess concentrations of the surfactant at the solid/vapor, solid/liquid, and liquid/vapor interfaces, respectively. If the Γ_{SV} for a surfactant is assumed to be zero, a plot of $\gamma_{LV}\cos\theta$, the adhesion tension, versus γ_{LV}, should have a slope of - (Γ_{SL}/Γ_{LV}). When the slope of the plot is negative, wetting is improved by the presence of the surfactant; when it is positive, wetting is impaired by its presence (Rosen, 2004).

For hydrophobic surfaces such as paraffin and Teflon, the slope was usually close to -1. The linear relationship between $\gamma_{LV}\cos\theta$ and γ_{LV} for the Teflon/CTAB aqueous solution drop-air system was studied by Janczuk *et al.* (1997). The slope was equal to -1 in the range of high CTAB concentrations. It was indicated that the CTAB adsorption at the Teflon/water interface is the same as that at the water/air interface, even though in the range of low CTAB concentrations, the slope was considerably lower than -1.

In 2003, Dutschk and co-workers studied the dynamic wetting behavior of aqueous solutions of three surfactants – anionic (sodium dodecyl sulfate, SDS), cationic (dodecyltrimethylammonium bromide, DTAB), and nonionic (pentaethylene glycol monododecyl ether, $C_{12}E_5$) – on polymer surfaces. The results showed that the ionic surfactant solutions did not spread on the very low-energy surfaces (highly hydrophobic surfaces) at any concentrations and could spread over the moderately hydrophobic surfaces. For the nonionic surfactant, $C_{12}E_5$, the wetting behavior was quite different. This surfactant was found to enhance spreading in aqueous solutions on both highly and moderately hydrophobic surfaces.

The relationship between the adsorption and the wetting of cationic surfactant (cetylpyridinium chloride, CPC) on very low polar plastics – PTFE, PVC, and PC was studied by Meerit in 2005. For all plastics, the Γ_{LV} was much higher than the Γ_{SL} and there was no significant effect when an electrolyte was added. For the high polar plastics – PMMA, ABS, and Nylon66, the slopes of adhesion tension plot were very close to zero in the absence of electrolyte, indicating that the Γ_{LV} was much higher than the Γ_{SL} (Puttharak, 2006). Both works indicate that the cationic surfactant molecules can adsorb less at the solid/liquid interface.

2.3.4 Critical Surface Tension and Surface Energy of Polymers

The surface energy of solids (γ_{SV}) is another way of characterizing a solid surface. In addition, the contact angles relating to interfacial forces by Young's equation are a classical method of describing the adhesion of a liquid to a solid. Strictly speaking, the surface energy (γ_{SV}) cannot be determined from contact angle measurement alone, because there are three variables in Young's equation. These extra variables are removed by employing a theory which explains their interactions. There are several theories in use, from the Girifalco-Good-Fowkes-Young equation (Thünemann, 2000) to the Lewis acid/base theory (http://www.firsttenangstorm. com/pdfdocs/DyneSolutions.pdf).

A rather simple method of estimating the surface energy of solids was developed by Zisman and co-workers (Fox and Zisman, 1950 and Zisman, 1964). They introduced an empirical relation of contact angle data on polymers by measuring the contact angles for a series of pure liquids on the same polymer samples, and plotted cos θ vs. γ_L of the different liquids (Zisman plot), the graphical points fell close to a straight line or collected around it in a narrow rectilinear band:

$$\cos \theta = 1 - \beta(\gamma_L - \gamma_c). \qquad (2.12)$$

Each line extrapolates to $\theta = 0$ at a certain γ_L value, which it was called the "critical surface tension of solid", γ_c. They proposed that as γ_L decreases toward γ_c (but not γ_{SV}), however the γ_L is different from 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 (Erbil, 1997).

Although, from a thermodynamic point of view, the critical surface tension of solid (γ_c) is not identical to its surface energy (γ_{SV}), but from a practical point of view, the numbers are very similar. Therefore many workers use critical wetting tension as a usable approximation to surface energy (http://www.firsttenang stroms.com/pdfdocs/DyneSolutions.pdf).

Hence, 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 or surface character is similar to vapor character. These experiments have to be conducted on a flat, non-porous solid sample with different types of pure liquids, as shown in Figure 2.5.
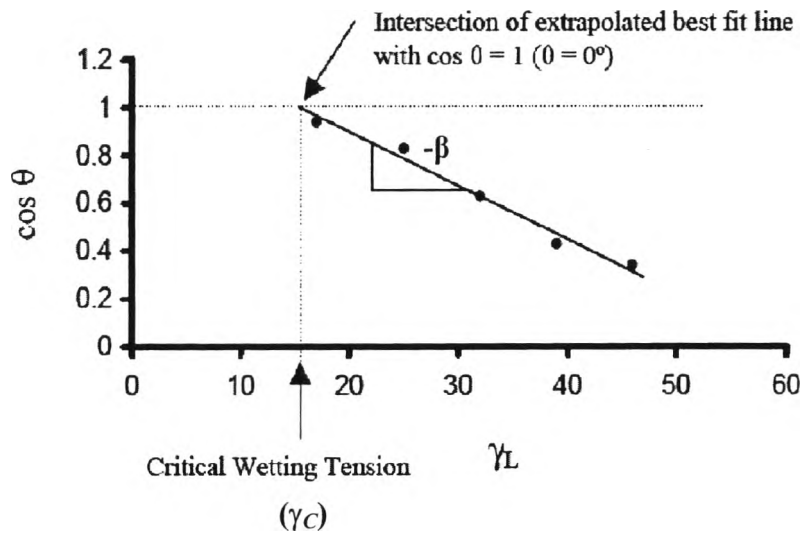

Figure 2.5 Zisman Plot (http://www.firsttenangstroms.com/pdfdocs/DyneSolu tions.pdf).

The critical surface tension is obtained from the Zisman plot, in which the cos θ of the wetting angle for a series of pure liquids is plotted against the surface tension, γ_L, of each pure liquid. These plots give the best empirical fit of experimental data. The intercept of these curves with the cos θ = 1 axis 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 surfaces and estimating contact angles, since β in the Zisman's equation (see Equation 2.12) 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 with 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

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 of surfactant on plastic surfaces and its relation to wetting phenomena. The results 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.

In 2005, Meerit found that the deviation of the Zisman plot did not appear in the case of CPC, sodium octyl benzene sulfonate (SOBS), or polyoxyethylene octyl phenyl ether $(OP(EO)_{10})$ on PTFE, PVC, and PC. Whereas the deviation of the Zisman plot appeared in the case of CPC on PMMA, ABS, and Nylon66 when NaCl was added 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 (Puttharak, 2006).

In addition, in 2006 to 2010, the study of relation of wetting and adsorption by Szymczyk *et al.* (2006 and 2010) and Zdziennicka *et al.* (2008 and 2010) on PTFE was found that the relation of θ and γ_{LV} (Zisman plot) was not linear, Thus, they used the adhesion tension plot to determine the critical surface tension instead of Zisman equation due to the linear relationship of this plot, but it is somewhat higher than the IFT at solid/vapor (γ_{SV}) obtained the basis of contact angle measured for n-alkanes using the Fowkes equation (Jańczuk et al., 1997).