

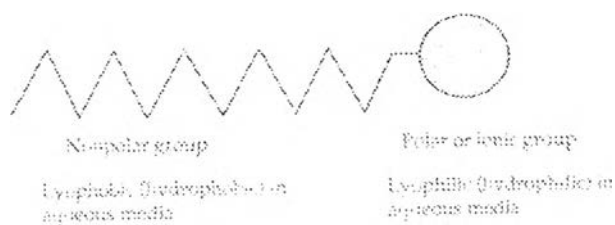


## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Characteristic of Surfactants

Surfactant (a contraction of the term “surface-active agent”) is a substance that, when presents at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and altering to a marked degree of the surface or interfacial free energies. A surfactant also has the property of forming colloid-sized aggregates called micelles at the sufficient high concentration. The lowest total surfactant concentration at which micelles are present is called critical micelle concentration (CMC).



**Figure 2.1** Generalized surfactant structure (Rosen and Dahanayake, 2000).

A surfactant has an amphipathic molecular structure; that is polar (hydrophilic [“water-loving”] or head group) at one end and non-polar (hydrophobic [“water-hating”] or tail group) at the other. The hydrophobic group is usually a long-chain hydrocarbon while the hydrophilic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants are classified as (Rosen, 2004):

1. *Anionic*. The hydrophilic group bears a negative charge.
2. *Cationic*. The hydrophilic group bears a positive charge.
3. *Zwitterionic*. Both positive and negative charges may be present in the surface-active portion.
4. *Nonionic*. The surface-active portion bears no apparent ionic charge.

## 2.2 Adsorption at the Solid/Liquid Interface of Surfactants

When the surfactant-containing solution is aqueous, 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 structure groups on the solid surface; (2) the molecular structure of the adsorbate; and, (3) the environment of the aqueous phase – its pH, its electrolyte content, the presence of any additives such as short – chain polar solutes, and its temperature. These factors determine the mechanism and the efficiency and effectiveness of adsorption.

### 2.2.1 Adsorption Isotherm

An adsorption isotherm relates the concentration of adsorbate at the interface to its equilibrium concentration in the liquid phase. Since most of the information regarding adsorption onto solid/liquid interface can be deduced from the adsorption isotherm, the isotherm is the usual method of describing adsorption at the solid/liquid interface (Rosen, 2004). The nature of the true adsorption mechanism may also be obtained from the adsorption isotherm (Rybinski and Schwuger, 1987).

### 2.2.2 Adsorption from Aqueous Solution onto Nonpolar, Hydrophobic Adsorbents

Adsorption onto these substrates is mainly by dispersion forces. The orientation of the adsorbate 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. As adsorption continues, the adsorbed 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).

Janczuk *et al.* (1997) suggested that, at high cetyltrimethylammonium bromide (CTAB) concentration in an aqueous solution, the adsorbed amount at the Teflon/water interface was close to that adsorbed at the water/air interface. Whereas at low concentration, the adsorbed amount at the Teflon/water interface was several times higher than at the water/air interface. This might be a result of the presence of a weak acid-base interaction across the Teflon/water interface, which played an important role in the mechanism of adsorption at low CTAB concentration.

The adsorption of CTAB onto the active carbon/water interface mainly took place through ion exchange, ion pairing, and hydrophobic bonding. The predominant mechanisms in the low CTAB concentrations were probably ion exchange and ion pairing. The hydrophobic bonding mechanism predominated with increasing CTAB concentration (Gurses *et al.*, 2003).

Wanless *et al.* (2004) investigated the adsorption of cetylpyridinium chloride (CPC) onto a ceramic glaze mixture composed of limestone, feldspar, quartz, and kaolin as a function of pH, ionic strength, and surfactant concentration. They discovered that the adsorption of small amounts of cationic CPC onto the primarily negatively charged surfaces of the particle at pH 7 and 9 resulted in strong attraction and flocculation due to hydrophobic interactions. After the addition of more CPC, the ceramic particles became hydrophilic again once a bilayered surfactant coating forms, because more surfactants were adsorbed but with the head groups oriented toward the solution.

In 2005, Meerit evaluated the relationship between surfactant adsorption and wetting. This work studied three plastics; polytetrafluoroethylene

(PTFE), polyvinylchloride (PVC), and polycarbonate (PC). The surfactants used for this study were CPC and polyoxyethylene octyl phenyl ether (OP(EO)<sub>10</sub>). The results showed that the surfactant adsorption increased with increasing surfactant concentration and the surfactant adsorption could reduce not only the  $\gamma_{LV}$  but also the  $\gamma_{SL}$ . Moreover, when the solids became more polar, the difference between the natures of solid/liquid and liquid/air interfaces arose and the presence of electrolyte could not allow the surfactants to adsorb more at the solid/liquid interface. Thus, the  $\gamma_{SL}$  could not be reduced as effectively as the  $\gamma_{LV}$ , resulting in less efficient wetting. These surfactants also were studied by Puttharak in 2006 but they were adsorbed onto three high polar plastics – polymethyl methacrylate (PMMA), acrylonitrile butadiene styrene (ABS), and polyhexamethylene adipamide (Nylon66). For OP(EO)<sub>10</sub>, the  $\gamma_{SL}$  decreased with increasing surfactant concentration, whereas this phenomenon was not observed in the case of CPC. The opposite charge between the head group and the surfaces had an effect on the appearance of surfactant adsorption.

### 2.2.3 Synergism in Adsorption by Mixtures of Surfactants

Mixtures of two or more different types of surfactants often show a “synergistic” interaction; that is, the interfacial properties of the mixture are more pronounced than those of the individual components by themselves. As a result, in many industrial products and processes, mixtures of different types of surfactants, rather than individual materials, are used. A study of the adsorption of the individual surface active components in the mixture and of the interaction between them affords an understanding of the role of each and makes possible the selection in a rational, systematic manner of components for optimal properties (Rosen, 2004).

In 1996, Somasundaran *et al.* investigated the solution and interfacial behavior of surfactant mixtures by using a cationic surfactant, tetradecyl trimethyl ammonium chloride (TTAC), and a nonionic surfactant, pentadecylethoylated nonyl phenol (NP-15), with alumina as the substrate. Their results showed that TTAC adsorbed at the alumina-water interface as a result of electrostatic attraction whereas NP-15 did not. Interestingly, in the mixed surfactant system, the TTAC forced adsorption of the NP-15 as a result of hydrophobic interactions between the adsorbed

surfactant chains at the alumina-water interface. With an increase in TTAC content, the adsorption density of NP-15 increased and the isotherm shifted to lower surfactant concentrations. The adsorption of TTAC decreased under conditions of saturation adsorption due to the bulkiness of the coadsorbed NP-15 as well as competition for common adsorption sites. However, below saturation adsorption conditions, the adsorption of TTAC was increased due to synergistic interactions between the cationic and nonionic heads leading to reduced repulsion among the cationic headgroups.

Adsorption from aqueous solutions of mixtures of surfactants of CTAB and nonyl phenyl ethoxylates (NP-n) ( $n = 13, 20, 30$ ) on PTFE was studied in a wide concentration range by Desai and Dixit in 1996. They found that the adsorption of CTAB was enhanced by the presence of nonionic surfactants and vice versa in the pre-CMC region due to chain-chain interactions. The decrease in adsorption level of CTAB with an increase in mole fraction of nonionic surfactants in the region above the CMC has been attributed to the decrease in monomer concentration due to mixed micellization with nonionic surfactants. In case of adsorption of nonionic surfactants from the mixtures, adsorption increases in the presence of CTAB.

Soboleva *et al.* (2004) studied surfactant adsorption on quartz and the wetting of glass by aqueous solutions of tetradecyltrimethylammonium bromide (TTAB), OP(EO)<sub>10</sub>, and their mixtures. They found that the concentration and composition of mixed TTAB – OP(EO)<sub>10</sub> solutions affected the adsorption on quartz and the wetting of glass. At low surfactant concentrations, a synergistic adsorption of surfactant mixtures occurred and the contact angles increase to the values, which were equal for the solutions of pure TTAB and the mixtures. Adsorption layers on a quartz surface were enriched with OP(EO)<sub>10</sub> or TTAB at low or high OP(EO)<sub>10</sub> content in a solution, respectively. At high solution concentrations, aggregates were formed on the surface, and their composition slightly changes with solution concentration. It was assumed that, in the concentration range in which contact angles reached their maximal values and the predominant monolayer adsorption was replaced by the surface aggregation, the adsorption layer was formed at a fairly low

rate. This could be one of the causes for the reverse flow of the mixed TTAB-OP(EO)<sub>10</sub> solutions in capillaries observed in this concentration range.

#### 2.2.4 Structure of Adsorbed Surfactant Layer

There are several surface – specific techniques which are used 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 hemimicellar aggregates at the hydrophobic surface.

Wanless *et al.* (1997) used AFM to image the surfactant surface aggregation on graphite. For pure sodium dodecylsulfate (SDS), the molecules associated into long, parallel hemicylindrical surface aggregates over a concentration range from about one-third to at least ten times the CMC.

Nonionic surfactants adsorbed onto 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 contact between water and the hydrophobic substrate. On graphite, the surfactant molecules aggregated a hemicylindrical structure with the head groups facing the solution (Grant *et al.*, 1998). Atkin *et al.* (2003) proposed that this was likely due to the tail length failing to reach a critical length to successfully adsorb epitaxially and act as a template for hemicylindrical aggregation.

Furthermore, Grosse and Estel (2000) explained that hemicylinders dominated on hydrophobic materials because a large contact area between the hydrophobic chains of the surfactant and the solid surface was thermodynamically favorable.

### 2.3 Wettability of Surfactant onto Solid Surface

Wettability of a surfactant onto a solid surface is important for many applications such as herbicides, coatings, 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. Commonly, however, wetting is applied to the displacement of air from a liquid or solid surface by water or an aqueous solution (Rosen, 2004).

Wettability 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 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 (Puttharak, 2006).

#### 2.3.1 Spreading Wetting

In wetting, a liquid spreads over the 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 the system,  $-\Delta G_w/a$ , can be estimated by this following equation:

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

If the quantity  $\gamma_{SV} - (\gamma_{SL} + \gamma_{LV})$  is positive, the system decreases in surface free energy during the spreading process, and the process can then occur spontaneously.

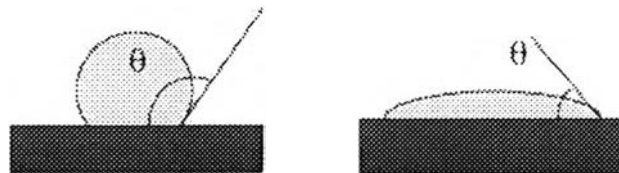
The quantity  $\gamma_{SV} - (\gamma_{SL} + \gamma_{LV})$  is then a measure of the driving force behind the spreading process and is usually called the spreading coefficient  $S_{L/S}$ , as defined by

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

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

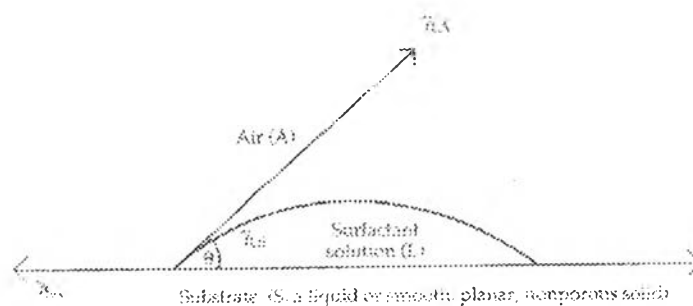
### 2.3.2 Contact Angle

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.



**Figure 2.3** Liquid droplet in equilibrium: definition of the contact angle.

The low values of contact angle indicate that the liquid spreads well (high wettability), while high values indicate less complete wetting (poor wettability). If the contact angle is less than 90 degrees the liquid is said 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”. Zero contact angles are possible, but they are always less than 180 degrees (Johnson and Dettre, 1993).



**Figure 2.4** Contact angle of a surfactant solution on a smooth, planar, nonporous solid, illustrating the relationship of various interfacial tensions (Rosen and Dahanayake, 2000).



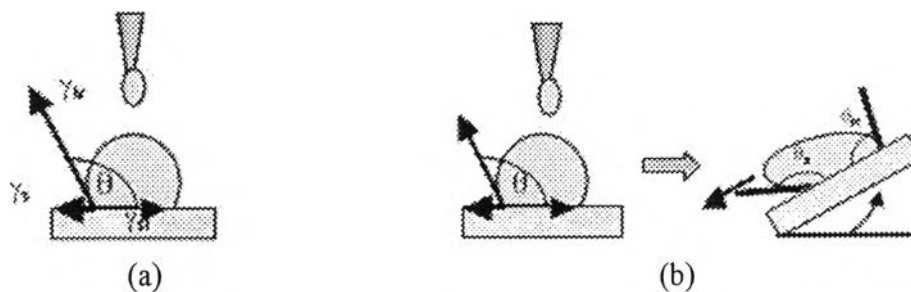
The contact angle is a function of the liquid's surface tension and the surface free energy of the substrate. The relationship between the contact angle and the interfacial tension is related to the Young's equation:

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}, \quad (2.3)$$

where  $\gamma$  represents the surface tension values between the corresponding interfaces. 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,  $\gamma_{sl}$ , the  $\gamma_{lv}$  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, lowering those interfacial tensions (Puttharak, 2006).

### 2.3.3 Contact Angle Measurement

Contact angles are measured on macroscopic, smooth, nonporous, planar substrates by simply placing a droplet of the liquid or solution on the substrate and determining the contact angle (Rosen, 2004). This study uses the static or sessile drop method because the major advantages of this method are speed and convenience. A drop of liquid or solution is placed on a horizontal solid surface and observed in cross section through a macroscope. A goniometer in the eyepiece is used to measure the angle. The angle of vision is just slightly off horizontal so the edge of the drop and its reflected image are both visible. This allows the tangent to be determined precisely at the point of contact between the drop and the surface. Agreement between different individuals measuring the same drop will be about 1-2 degrees. Several measurements are often made on both sides of the drop and the numbers averaged. This compensates for any deviation of the surface from the horizontal. In this method, the drop is not moving when the measurement is made, these angles are sometimes called advanced or receded angles (Johnson and Dettre, 1993).



**Figure 2.5** (a) Sessile drop method, and (b) schematic of advancing angles,  $\theta_a$  and receding angles,  $\theta_r$  (<http://www.uweb.engr.washington.edu/research/tutorials/contact.html>).

#### 2.3.4 Adsorption and Wetting

Lucassen and Raynder have developed the relation of adsorption to equilibrium wetting analyzing method, which is a combination of the Gibbs adsorption equation with Young's equation yields:

$$\frac{d(\gamma_{LV} \cos\theta)}{d\gamma_{LV}} = \frac{\Gamma_{SV} - \Gamma_{SL}}{\Gamma_{LV}}, \quad (2.4)$$

where  $\Gamma_{SV}$ ,  $\Gamma_{SL}$ , and  $\Gamma_{LV}$  represent the surface excess concentration of the surfactant at solid/vapor, solid/liquid, and liquid/vapor interfaces, respectively. If the  $\Gamma_{SV}$  for a surfactant is assumed to be zero, a plot of  $\gamma_{LV} \cos\theta$ , the adhesion tension, versus  $\gamma_{LV}$ , should have a slope of  $-(\Gamma_{SL}/\Gamma_{LV})$ . 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 is usually close to -1. The linear relationship between  $\gamma_{LV} \cos\theta$  and  $\gamma_{LV}$  for the Teflon/CTAB aqueous solution drop-air system was studied by Janczuk *et al.* (1996). The slope was equal to about -1 in the range of high CTAB concentration. It was indicated that CTAB adsorption at the Teflon/water interface was the same at the water/air interface, even though, in the range of low CTAB concentration, the slope was considerably lower than -1.

In 1990, Gau and Zografí studied the relationship between adsorption and wetting of nonionic surfactant solutions – penta(oxyethylene) dodecyl mono-

ether, C<sub>10</sub>E<sub>5</sub>, and penta(oxyethylene) decyl monoether, C<sub>10</sub>E<sub>5</sub> – on several polymer surfaces. From the adhesion tension plots for paraffin, the  $\Gamma_{SL}$  was essentially equal to  $\Gamma_{LV}$  over the entire concentration range, whereas for PS and PMMA, the ratio of  $\Gamma_{SL}$  to  $\Gamma_{LV}$  became increasingly less than 1, indicative of increasingly less efficient wetting as the solid became more polar.

In 2003, Dutshk *et al.* studied the dynamic wetting behavior of aqueous solutions of cationic dodecyltrimethylammonium bromide (DTAB) and nonionic pentaethylene glycol monododecyl ether (C<sub>12</sub>E<sub>5</sub>) on polymer surfaces. The results showed that the ionic surfactant solution did not spread on low energy surfaces at any concentrations and spread over moderately hydrophobic surfaces. As to the nonionic C<sub>12</sub>E<sub>5</sub>, the wetting behavior was quite different. This surfactant was found to enhance spreading in aqueous solutions on both highly hydrophobic and moderately hydrophobic surfaces.

The relationship between the adsorption and the wetting of CPC on nonpolar polymers – PTFE, PVC, and PC was studied by Meerit in 2005. For all polymers, the  $\Gamma_{LV}$  was much higher than the  $\Gamma_{SL}$  and there was no significant effect when an electrolyte was added. Whereas on high polar plastics – PMMA, ABS, and Nylon66, the slopes were very close to zero in the absence of an electrolyte which indicated that the surfactant molecules adsorbed less on the solid/liquid interface (Puttharak, 2006).

For the nonionic surfactant system, OP(EO)<sub>10</sub>, on both of these nonpolar and polar polymers, the  $\Gamma_{LV}$  was much higher than the  $\Gamma_{SL}$  (Meerit, 2005, and Puttharak, 2006).

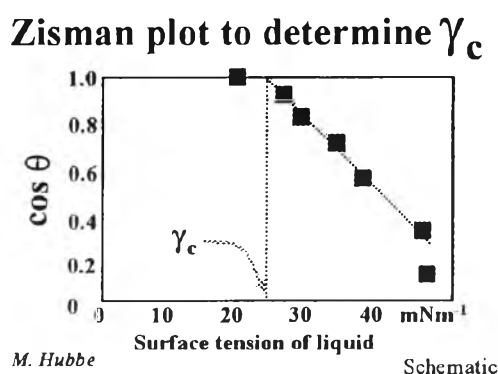
### 2.3.5 Critical Surface Tension of Polymers

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 an empirical relation of contact angle data on polymers. They measured the contact angles for series of liquids on the same polymer sample, and plotted  $\cos\theta$  vs.  $\gamma_L$  of the liquids (Zisman plot), the graphical points fell close to a straight line or collected around it in a narrow rectilinear band:

$$\cos\theta = 1 - \beta(\gamma_L - \gamma_C). \quad (2.5)$$

Each line extrapolates to zero  $\theta$  at a certain  $\gamma_L$  value, which Zisman has called the “critical surface tension of solid”,  $\gamma_C$ . they proposed that as  $\gamma_L$  decreases toward  $\gamma_C$ ,  $\gamma_{SL}$  will approach zero, and when  $\gamma_{SL}$  reaches zero,  $\gamma_L$  will be equal to  $\gamma_C$  (but not  $\gamma_{SV}$ ), however the  $\gamma_C$  is different from the  $\gamma_{SV}$ . Where van der Waals forces are dominant,  $\gamma_C$  of the polymeric solid is independent of the nature of liquid and is a characteristic of the solid alone (Erbil, 1997).



**Figure 2.6** Zisman plot (<http://www4.ncsu.edu/~hubbe/Defnits/CritSrfT.htm>).

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

The critical surface tension concept is useful in classifying the surfaces and estimating contact angles, since  $\beta$  is approximately 0.03 to 0.04. However, the value of  $\gamma_C$  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).

Supalassate (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 (NaOBS), and OP(EO)<sub>10</sub> 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 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 (Puttharak, 2006).

### 2.3.6 Synergism in Wetting by Mixtures of Surfactants

The interaction of two different types of surfactants with each other either in a mixed monolayer at an interface or in mixed micelles in aqueous solution, can result in the synergistic enhancement of their interfacial properties. Such an enhancement can result in improved performance properties, such as wetting, foaming, solubilization, and so on.

Bogdanova *et al.* (2003) investigated the wetting of polystyrene, low-energy solid surfaces with aqueous solutions of binary mixtures of cationic surfactant CTAB and nonionic surfactant OP(EO)<sub>10</sub> at molar fractions of the cationic surfactant of 0.2, 0.5, and 0.8. The region of low concentration exhibited an insignificant decrease in the contact angles. The contact angles decreased with an increase in the concentration. And at concentrations higher than the CMC, the contact angle value

remained unchanged. In the entire region of concentrations studied, wetting of the solid substrates with solutions of OP(EO)<sub>10</sub> and OP(EO)<sub>10</sub>-CTAB mixtures was better than for solutions of CTAB; OP(EO)<sub>10</sub> possessed the highest wetting efficiency, and the efficiency of the wetting action of the mixtures decreased with an increase in the molar fraction of the cationic surfactant because the hydrophobic portion of the cationic surfactant oriented toward the aqueous solution. They concluded that in a narrow concentration range, the non-additive effect of wetting was observed: wetting of the solid surfaces with solutions of the mixtures is better than what would be expected from the additive behavior of the components. The magnitude of the effect depended on the surface energy of the solid substrate, total surfactant concentration in a mixture, and molar fraction of the cationic component.