CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Structure and Behavior of Surfactants

Surfactants, an abbreviation for surface-active agents, are materials that tend to accumulate at surface and change the properties of those surfaces. A surfactant is amphiphile consisting of two distinct parts: one is hydrophilic or water-loving, which is usually ionic, highly polar group, or nonionic polar group. The other portion is hydrophobic or water-hating, which is usually a single or double hydrocarbon chain with various degrees of unsaturation or substitution.

Due to the presence of two structurally dissimilar groups within a single molecule, surfactants exist as individual molecules at very low concentration but they are favorable to form aggregate of molecules called micelles (as shown in Figure 2.1) when the concentration of the surfactant solute in the bulk solution exceeds a limiting values the so-called critical micelle concentration (CMC). Surfactants can be classified by the nature of their hydrophilic part as anionic, cationic, zwitterionic and nonionic surfactants.
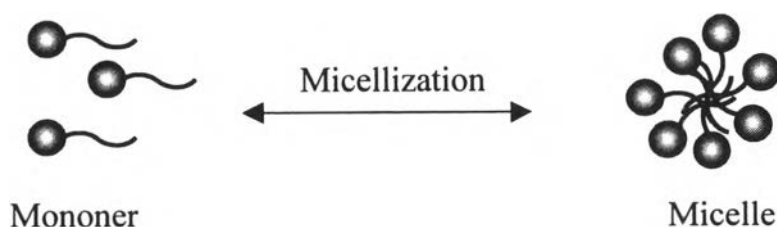

Mononer   Micelle

Figure 2.1 Micellization process.

2.2 Definition and Classification of Contact Angle

Contact angle is the angle between the substrate surface and the liquid droplet. The closer the contact angles to zero the better the wetting agent. A contact angle resting on a solid substrate is illustrated in Figure 2.2.
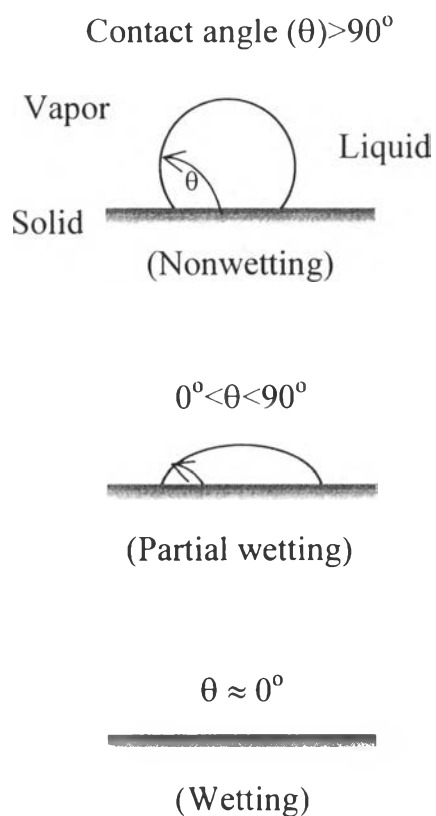
Contact angle $(\theta){>}90^{\circ}$

Vapor
Liquid
θ
Solid
(Nonwetting)

$0^{\circ}{<}\theta{<}90^{\circ}$

(Partial wetting)

$\theta \approx 0^{\circ}$

(Wetting)

Figure 2.2 Contact angles for nonwetting, partial wetting, and wetting (Lange, 1994).

There are, however, three different types of contact angle which can be measured. Firstly, an advancing contact angle, θ_A, is the angle obtained

when the liquid is being added to the droplet and then comes to rest on the initially dry and clean surface. Secondly, a receding contact angle, θ_R, is the angle obtained when the liquid is being withdrawn from the droplet resting on the surface, which is previously occupied by liquid. In addition, there is the equilibrium contact angle which is the direct consequence of Young's equation.

The understanding of wettability was initiated by Young in 1805 (Marmur, 1996) where the static contact angle is related to the free energies of the liquid/vapor (γ_{LV}), solid/liquid (γ_{SL}), and solid/vapor (γ_{SV}) interfaces through Young's equation. This equation can be derived using the principle of energy minimization as well as a force balance along the surface at the contact line,

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \qquad (1)$$

where θ is the equilibrium contact angle. This is only valid for a liquid drop resting at equilibrium on a smooth, flat, homogeneous, impermeable, and nondeformable surface, which can be used as a model for explaining wetting phenomena in most systems. However, it is unfortunate that evaluation of the various interfacial tensions required is not always straightforward and liquid/vapor interfacial tension can be measured. On the other hand, the solid/liquid and solid/vapor interfacial tension are not experimentally and directly accessible. (Lange, 1994).

An approach to deduce γ_{SV} and γ_{SL} was based on the determination of the so-called critical surface tension, γ_C, as introduced by Zisman and coworker (1964). They realized that there is an approximately linear relation between γ_{LV} of the homologous series of the test liquids and their contact angles θ with a solid surface. γ_C is defined as the linear exploration of γ_{LV} for

$\theta = 0$ and is interpreted as a measure for γ_{SV} of the solid surface. This Zisman approach works reasonably well only for nonpolar solid surfaces in contact with nonpolar liquid of low surface tension.

2.3 Contact Angle Measurement

There are three main techniques for measuring the contact angle, i.e. sessile drop, Wilhelmy plate, and incline plane methods.

In the sessile drop method, a drop is placed on a horizontal solid surface so that the edge of the drop is viewed by using a goniometer or computer program (Junczuk *et al.*, 1997; Nakae *et al.*, 1998). This allows the tangent to be determined precisely at the point of contact between the drop and the surface. Several measurements are often made on both sides of the drop and the average is taken. It is commonly claimed that the accuracy of this method is ±1 or better (Johnson and Dettre, 1993). However, measurement reported from independent laboratories using this method for the same solid/liquid system have a discrepancy around 5° (Neumaan and Good, 1979). The major advantages of this method are rapid and convenience but the error can be made by the operator (Johnson and Dettre, 1993).

In the Wilhelmy plate method, a thin plate is mounted vertically above the liquid. The measurement is begun when the plate is suspended with the bottom edge nearly touching the surface of the liquid. Later, the liquid is raised until it touches the plate. The force on the plate is measured as it cycled slowly down and up. The contact angle can be calculated from the force exerted by a fluid/fluid interface on a solid surface (Johnson and Dettre, 1993). Major advantage of the Wilhelmy plate method is that it is independent of the person making the measurement. This method is suitable for dynamic contact angle measurement. Although this method is valuable, it has several drawbacks that can restrict the usefulness of the procedure. The method

requires the sample to have constant plate perimeter; to be smooth, homogeneous, and morphological at all surfaces; and not be swelled by the liquid (Erbil *et al.*, 1999).

In the incline plane method, the solid sample is placed on a motor-driven inclined plane. When the plane of solid surface reaches the critical slope, the drop starts to slide. The measured contact angle at the downhill edge of the drop approaches θ_A and the uphill edge approaches θ_R. However, Good and Mitta (1993) cautioned against this method because it yields values of advancing and receding angles that are strongly dependent on the drop size.

2.4 Wetting and Its Modifications by Surfactant

The presence of a surfactant at an interface affects the surface properties of the liquid phase. For example, if a surfactant is added to water, it will interfere with the ability of the water molecules to engage in hydrogen bonding with each other at the air/water interface. This results in a reduction in surface tension, which is why a needle floats on pure water but sinks when surfactant is added. Surfactant alignment in a vapor/liquid/solid system is illustrated in Figure 2.3.

There are several investigations of wetting modifications by surfactant. Shiao *et al.* (1998) reported the effect of chain length compatibility of sodium alkyl sulfate/alkanol mixtures on contact angle. The spreading coefficient is maximum, the contact angle and the surface tension are minimum when the chain length of the surfactant is equal to that of the alkanol. This can be explained by the closer packing of the monolayer expected for matched surfactant/alkanol pairs. Chesters *et al.* (1998) reported that a key element in the wetting behavior appears to be the boundary condition arising from a surfactant balance at the contact line, which gives rise to surfactant accumulation and hence to surface immobilization which tends to

be self-maintaining (hysteresis) and surfactant concentration many orders of magnitude greater than the equilibrium level can be maintained near the contact line, disproportionally reducing static contact angle.
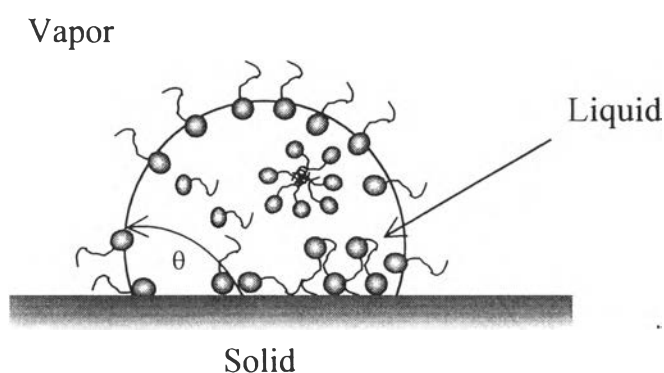
Vapor

Liquid

θ

Solid

Figure 2.3 Surfactant alignment in a vapor/liquid/solid system.

Bahr *et al.* (1999) suggested the existence of two spreading regimes exhibiting different spreading characteristics. Firstly, nondiffusive regime where the spreading is very rapid and controlled to different extents by inertia, gravity and capillarity depending on the drop size, impact energy, and interfacial tension balance. Secondly, diffusion-controlled regime is characterized by slower concentration dependent spreading rates that are mainly controlled by the diffusive transport of surfactant to the expanding liquid -vapor interface. Bigelow and Brockway (1956) reported that the most important factor in determining the oleophobic properties of fatty acids film and similar polar organic compounds adsorbed on solid surfaces is the density of the adsorbed molecules on the surfaces. Decreases in the densities of the films are accompanied by decreasing in their oleophobic properties. The length of the adsorbed polar molecules is not a major factor in determining the oleophobic properties of the films. However, the roughness of the substrate

surface may be large compared with the dimensions of the polar molecules, and increasing the length of the molecules may improve their ability to form film having the required surface characteristics.

Christenson and Yaminsky (1997) has explained the correlation between contact angle hysteresis and the range of the hydrophobic attraction. Surfaces which show a small difference between advancing and receding contact angles of a sessile water droplet exhibit no long-range force. These surfaces are stable and no rearrangement, mobility or desorption of hydrophobic groups can occur. Pitt *et al.* (1996) found that increasing the number of tails lowers the limiting value of the surface tension. Branching the tails also tends to lead to lower limiting values of the surface tension due to the increase in methyl groups.

2.5 Factors Affecting Contact Angle and Wettability

There are a number of factors affecting contact angle, for examples, methods of measurement, drop evaporation, surface roughness, surface heterogeneity, temperature, pH, and drop contamination.

Ebril *et al.* (1999) reported that the distortion of the drop surface caused by a needle could make the contact angle incorrect. If the needle enters the drop at the point very close to the solid, it may obscure the drop profile. If the needle passes through the upper surface of the drop, there will be some capillary rise of the liquid up to the needle and distortion of the surface. However, it has been claimed that this capillary rise does not perturb the liquid in the region of the contact line with the solid (Neumann and Good, 1979).

The evaporation may cause the contact angle to decrease and the liquid front to retreat, so the measured contact angle is incorrect. In practice, a closed chamber can be used to ensure saturation of vapor and also minimize

the evapolation effect. Chantra *et al.* (1996) studied the effect of varying the solid/liquid contact angle on the drop evaporation. It was found that addition of a surfactant to water droplet reduces surface tension and increases its spreading on a solid. As the results, heat transfer area from the solid to the liquid/vapor interface is enhanced and droplet evaporation is reduced. Bourges-Monnter and Shanahan (1995) reported the evaporation of water and n-decane drops on various substrates. In stage II, the drop height and contact angle decreases while contact radius remains constant and stage III, the height and contact radius decreases while contact angle remains constant. Later, Shanahan (1995) developed a simple theory for stick-slip behavior during drop evaporation, in which the wetting front remains static for most of the time but from time to time moves quite abruptly. The slip/stick behaviors of many liquids are also reported by Kwok *et al.* (1997,1998). This slip/stick behavior could be due to non-inertness of the surface. An energy barrier for the drop front exists, which results in sticking and causes contact angle to increase at constant radius. However, as most liquid is supplied into the sessile drop, the drop front posses enough to overcome the energy barrier, results in slipping, which causes contact angle to decrease suddenly. Therefore, the contact angle measurement when this phenomenon occurs cannot be used for interpretation in terms of surface energy.

On a rough and chemically homogenous surface, the capillary attraction or capillary depression of grooves in the surface can effect the value of contact angle. For contact angle less than 90°, each liquid will wet the rough surface of a given solid better than the corresponding smooth surface. For contact angle greater than 90°, on the other hand, the wettability of such liquid on the rough surface is worse than the ideally smooth solid surface. Zisman (1964) stated that pure water on smooth surface of paraffin produces an advancing contact angle between 105 and 110° while rough surface results in the angles greater than 110°. Later, Rosen (1989) reported that surface

roughness reduced contact angle when a value on a smooth surface is less than 90° and increases the contact angle when the value greater than 90°. Lin *et al.* (1995) and Delich *et al.* (1996,1997) reported that the contact angle can be modified by surface heterogeneity depending on a position where the three phase lines are located.

The temperature dependence of contact angle is not well understood or documented, although it has been reported that the contact angles decrease with increasing temperature. Adamson (1990) reported that the temperature derivatives of contact angle is negative with $|\,d\theta/dT\,| \approx 0.1$ deg K^{-1} for many systems at low temperatures (5-100°C). Ruijter *et al.* (1998) reported that the relaxation of the contact angle depends on the temperature. Molecular kinetics, hydrodynamic, and combined approaches were used to model the data. It was shown that parameters from the molecular kinetic model seem to be more physical in the experiments, indicating that the dissipation near the wetting line is more important than the flow in the wedge.

Basu *et al.* (1998) reported that the dynamic and static contact angles of bitumen decrease above a certain NaCl concentration for a particular pH when compared the results with no-salt case. The dynamic and static contact angles of bitumen decrease significantly with increasing NaCl concentration at high pH and decrease with increasing pH.

Contamination of a droplet by adsorption of impurities from the gas phase tends to reduce contact angle (Rosen, 1989).

2.6 Adsorption Isotherm of Surfactant

The most simple and widely used method to gain insight into a particular adsorption system is to study its adsorption isotherms and to apply a proper theoretical model. It is possible to get information on the capability of solid to retain surfactant and the arrangement of the adsorbed molecules at an

interface (Gonzalez-Garcia *et al.*, 2000). Adsorption isotherm can be divided into 4 regions as shown in Figure 2.4.
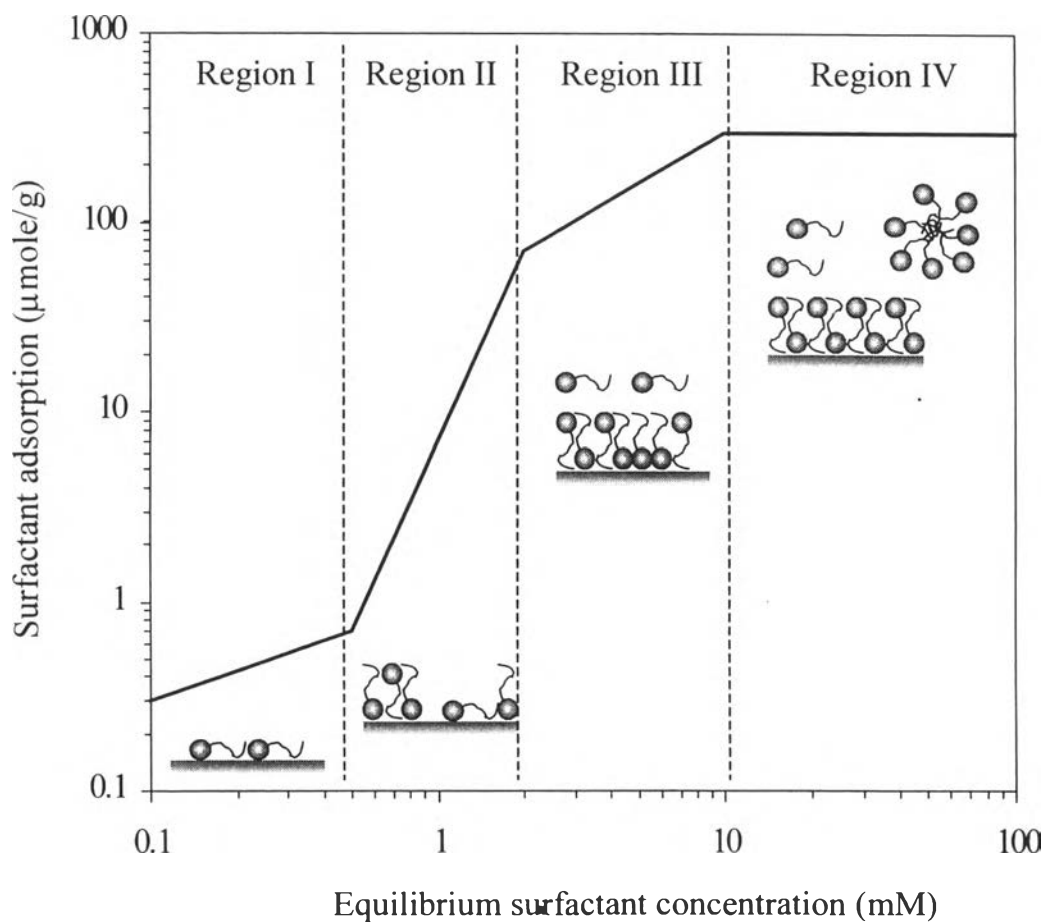

Figure 2.4 Typical surfactant adsorption isotherm (Rosen, 1989).

In region I, at very low concentrations, the surfactant is adsorbed on surface. There is no orientation and the molecule lies flat on the surface.

In region II, called hemimicelle formation or cooperative adsorption, there is a marked increase in adsorption resulting from interaction between the hydrophobic groups.

In region III, the slope of the isotherm reduced because there is not

enough room for them to lie flat and so they begin to orient. The orientation depending upon the nature of the hydrophilic group and the surface.

In region IV, adsorption in this fashion is usually complete when the surface is covered with a monolayer for hydrophobic surfaces or bilayer of surfactant for hydrophilic surfaces. In many cases this occurs approximately at the CMC of the surfactant.

In practice many solids are intermediate in hydrophilic/hydrophobic character, and the steps in the adsorption curve are smoothed out.

2.7 Adsorption of Surfactants at Solid/Liquid Interface

Adsorption of Surfactants at solid/liquid interfaces depends on many factors, i.e. the nature of solid surface, the structure of surfactant, and pH of the system. Many researchers investigated the adsorption of surfactants on hydrophilic or polar surface and hydrophobic or nonpolar surface (Zettlemoyer, 1968; Vogler, 1998)

Adsorption of nonionic surfactants on hydrophilic solid surfaces results in rise in their hydrophobicity and contact angles. Maximum hydrophobicity is achieved upon monolayer coverage. Formation of second layer of molecules oriented into solution by their hydrophilic parts layer is not formed in this case. A decrease in contact angles may be explained by forces of hydrophobic attraction are decayed ar even replaced by the forces of hydrophillic repulsion.

When cationic surfactants adsorbed on the negatively charged surface, at low concentration, can destabilize wetting films and large contact angles are formed. At high concentration, both film surfaces become positively charged, thus resulting in the forces of electrostatic repulsion and complete wetting take places. Adsorption of anionic surfactants on same charged surface can change only potential of the film/gas interface. Addition of electrolyte, 0.1 KCl, in

NaDS solution results in variation of the film/substrate potential and decrease contact angles from 20° to complete wetting.

2.8 Applications and Related Works

The understanding of wetting behavior can be applied to numerous practical applications, i.e. foaming, deposition of printing ink from paper, floatation, coating, enhanced oil recovery, detergency, and surface characterization.

Foam breaking and inhibition of foam formation are important industrial processes. Garrett (1993) stated that hydrophobic particles can bridge lamella surfaces, and if the contact angle which the foaming solution makes with the solid is sufficiently. this can lead to film rapture as particles become dewetted by the aqueous surfactants.

Averyard *et al.* (1993) studied foaming behavior of aqueous solution of surfactants (SDS, CTAB, and AOT) in the presence and absence of hydrophobic particles and dodecane. It was found that dodecane alone is an effective foam breaker for CTAB solutions and foam reduction by particles alone or in the presence of dodecane can change the contact angle (θ_1) of the surfactant solution with solid in air. The presence of dodecane reduces the value of θ_1 required for effective foam breaking. The contact angles were used in conjunction with interfacial tension to estimate the extent of adsorption of surfactant on the particles. Adsorption at the solid/aqueous solution interface is very similar to that at the air/solution interface and a little less than at oil/solution interface. Later the relation of the contact angles of solid on film and foam stability was reported (Averyard *et al.*, 1994). It was found that spherical glass beads and cylindrical rods with contact angles more than 90° rapidly rapture single soap films. The stabilizing effect was

attributed to collection of particles in the plateau border regions of the foams and the concomitant reduction in the rate of film drainage.

Alexandrova and Grigorov (1998) reported that the surfactant changes the three-phase contact angle (wetting properties) of copper minerals, pyrite and molybdenite which it leads to a significant reduction in deleterious froths.

In enhanced oil recovery, oil becomes more wetting at high pH due to the zwitterionic nature of the crude oil/water interface caused by acidic and basic groups at the interface. The experimental and calculated wetting behavior agreed well where regions of water wetting occur at higher pH. Changes in wetting behavior observed here as a function of pH are explained most likely due to reaction of acids and bases present in crude oil (Teeters *et al.*, 1992).

Guy *et al.* (1996) used the contact angle to characterize solid surface of five different coal types ranking from brown to low volatile bituminous in the presence of water and also used several organic liquids. It was found that a critical interfacial tension (γ_C) exists, below which wetting properties of the organic liquids are equivalent. Above γ_C the wettability of the coal increases. At a fixed interfacial tension, θ_A and θ_R decrease as the rank of the coal increases.

2.9 Phase Boundary and Precipitation

Phase boundary represents the minimum or maximum concentration of an additive required to form an infinitesimal amount of precipitate in the aqueous surfactant solution at constant temperature at various surfactant concentrations. The boundary separates concentration regimes in which precipitation occurs at equilibrium from regimes where no precipitate is present. Phase boundary can represent the hardness tolerance or minimum concentration of multivalent cation required to precipitate anionic surfactant.
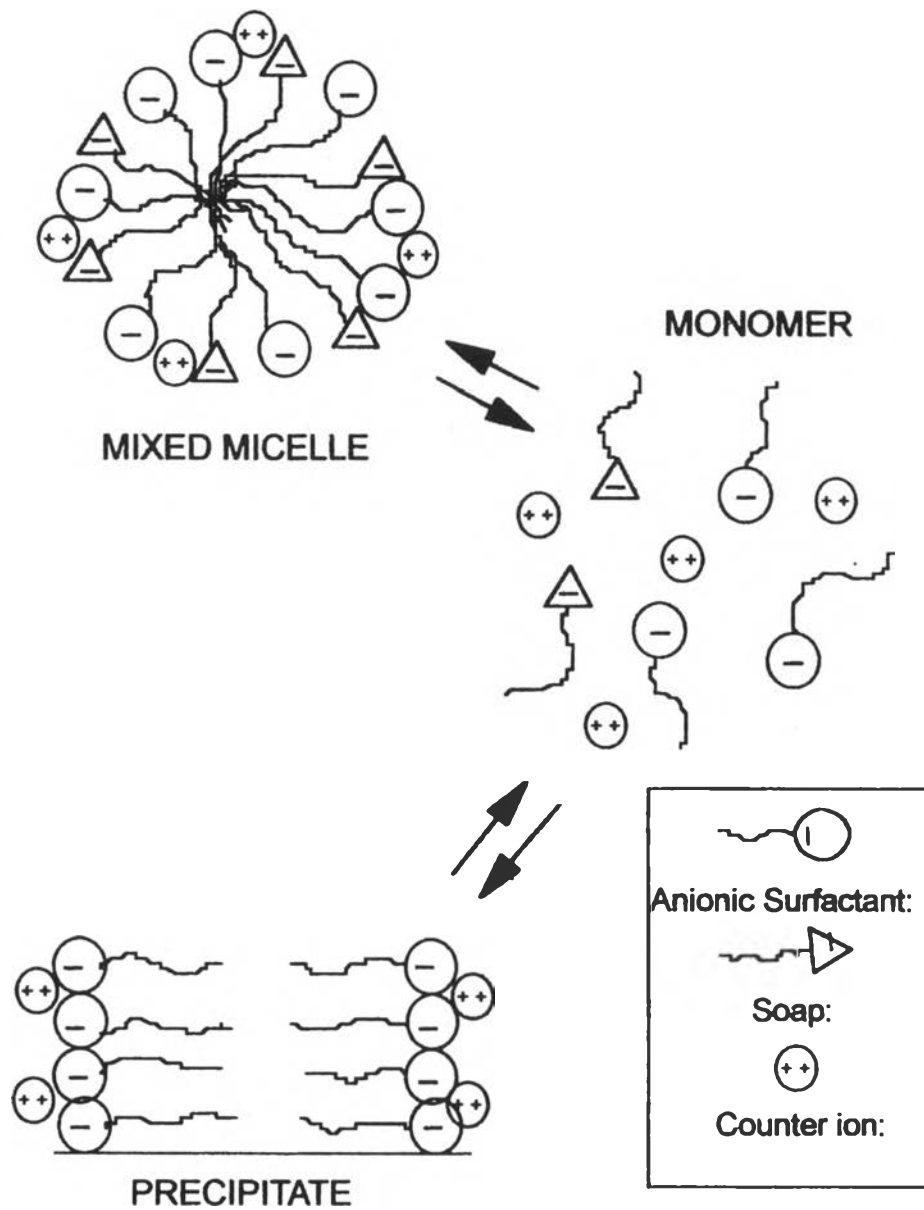
Figure 2.5 Schematic of Equilibrium existing in system (Rodriguez *et al.*, 1998).

At equilibrium, surfactant precipitation will occur if the product of the surfactant activity and the counterion activity equals the solubility product of the surfactant salt. Below the CMC, when no micelles are present, surfactant precipitation can be described by activity based solubility product written between the surfactant and counterion. Above the CMC, where micelles exist, the solubility product must be written between the unbound (unassociated) counterion and the monomeric (unassociated) surfactant activity.

At low surfactant concentration below the CMC, the minimum Ca^{2+} concentration required to cause precipitation decreases as the surfactant concentration increases to satisfy the solubility product relationship since all the surfactant and calcium are unassociated. Above the CMC, the hardness tolerance increases with increasing NaDS concentration as shown in Figure 2.5. This is due to the micelles formed above the CMC binding with calcium, making it unavailable for precipitation. Another reason is when more NaDS is added to the system, a higher concentration of unbound sodium is present in solution, lowering the CMC, increasing the fraction of surfactant which is present in micelles instead of monomeric form.