**CHAPTER II**

LITERATURE SURVEY

2.1 Surfactant and Its Aggregation in Aqueous Solution

Surfactants are wetting agents that lower the surface tension of a liquid, allowing easier spreading, and lower the interfacial tension between two liquids. Surfactants are usually organic compounds that are amphiphilic, meaning they contain both lyophilic (solvent loving) and lyophobic (solvent hating) group. When the solvent is water, these terms become hydrophobic and hydrophilic. In this case, the hydrophobic hydrocarbon chains are termed "tails" and the hydrophilic groups "heads" (Rosen, 2004). Therefore, they are soluble in both organic solvents and water.

A surfactant can be classified by the presence of formally charged groups in its head. A nonionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic. In this dissertation, only one surfactant has been used for all studies, the cationic surfactant cetylpyridinium chloride, as shown in Figure 2.1.
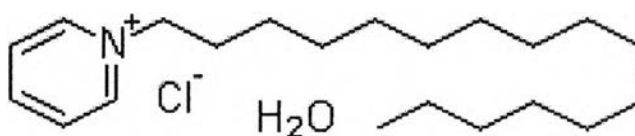
Figure 2.1 Molecular Structure of Cetylpyridinium Chloride.

Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Some of these aggregates are known as micelles. The

concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC shown in Figure 2.2.
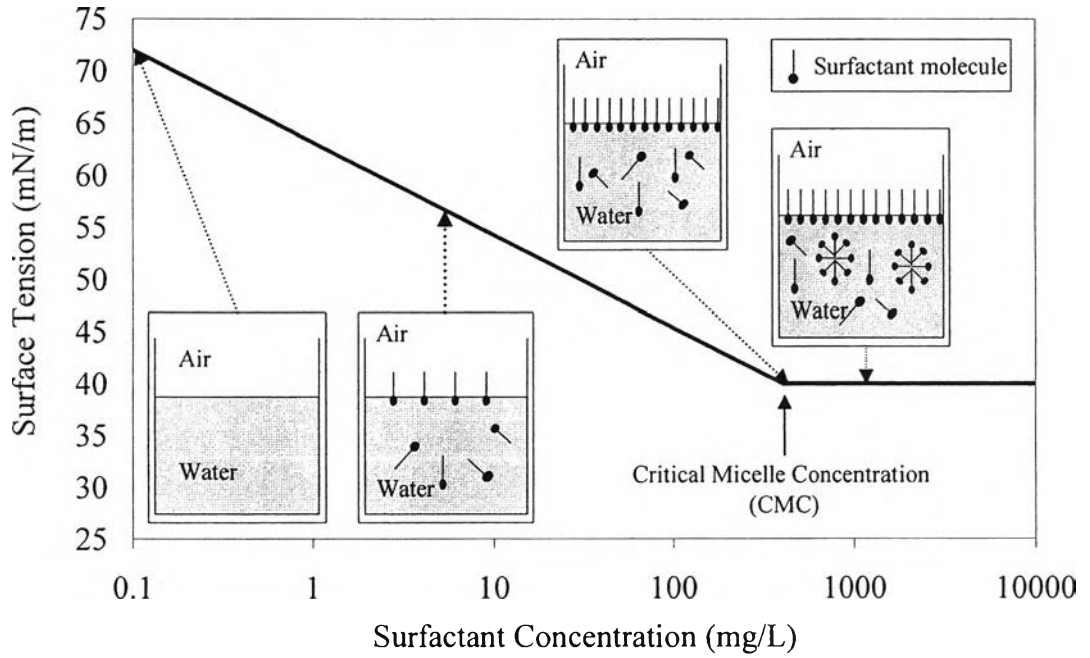
Figure 2.2 Determination of the critical micelle concentration of surfactant in water at 20 °C.
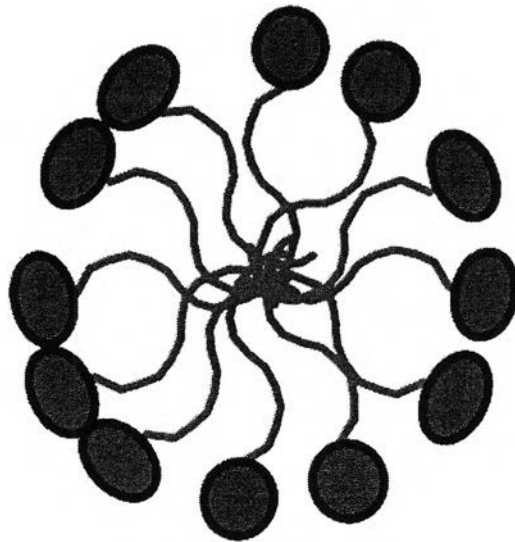
Figure 2.3 Typical micelle (spherical) structure.

A typical micelle in aqueous solution forms an aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic tail regions in the micelle centre (see Figure 2.3).

Micelles are often globular and roughly spherical in shape, but ellipsoids, cylinders, and bilayers are also possible. The shape and size of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength. The process of forming micelles is known as micellization.

Individual surfactant molecules that are in the colloid but are not part of a micelle are called "monomers." In water, the hydrophilic "heads" of surfactant molecules are always in contact with bulk solvent, regardless of whether the surfactants exist as monomers or as part of a micelle. However, the hydrophobic "tails" of surfactant molecules have less contact with water when they are part of a micelle. In a micelle, the hydrophobic tails of several surfactant molecules assemble into an oil-like core that has less contact with water. In contrast, surfactant monomers are surrounded by water molecules that create a "cage" of molecules connected by hydrogen bonds. This water cage is similar to a clathrate and has an ice-like crystal structure.

Micelles composed of ionic surfactants are surrounded by a "cloud" of ions. Because these ions have a charge opposite or counter to the charge of the ionic surfactant, they are called counterions. Although the bound counterions partially neutralize a charged micelle (by up to 90%), the effects of micelle charge may affect the structure of the surrounding solvent at appreciable distances from the micelle. Ionic micelles can influence many properties of the mixture, including its electrical conductivity. Adding salt to a colloid containing micelles can decrease the strength of electrostatic interactions and lead to the formation of larger ionic micelles.

2.2 Surfactant Adsorption Isotherm

The adsorption of ionic surfactant onto an oppositely charged solid surface has been extensively studied. When a mineral oxide surface is brought into contact with an aqueous solution, the adsorption of H_3O^+ or OH^- ions from the solution onto

the surface can cause variations in the surface charge. As the pH of the solution is lowered, the mineral oxide surface will usually become more positively charged (or less negatively charged) because of the adsorption of the H_3O^+ ions onto the surface, with the consequence of an increase in the adsorption of anionic surfactants and a decrease in the adsorption of cationic surfactants. The reverse is true when the pH of solution is raised.
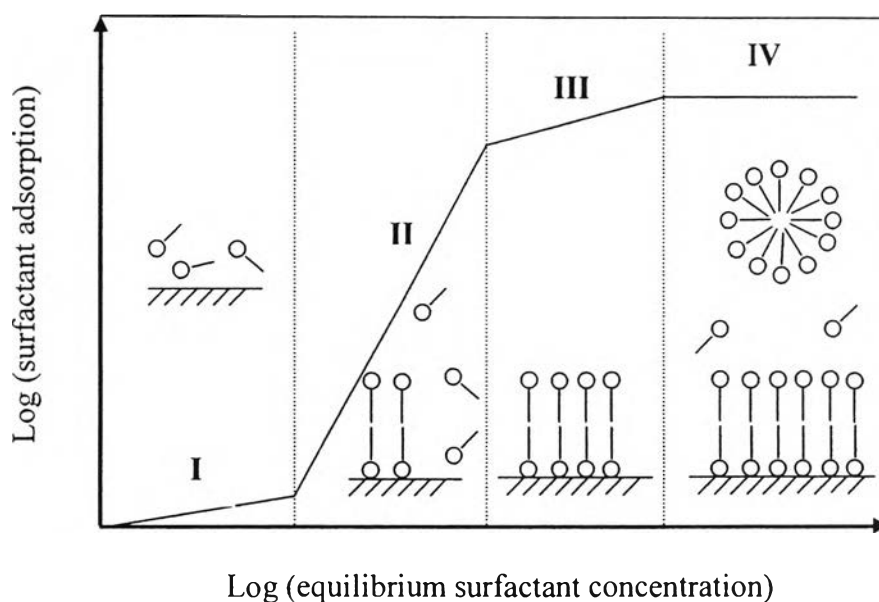
Figure 2.4 Adsorption isotherm for an ionic surfactant on an oppositely charged substrate.

Adsorption data have usually been presented as a log-log plot of the surfactant adsorption (amount of surfactant adsorbed per gram of adsorbent) versus the equilibrium concentration of the surfactant in bulk solution. Adsorption isotherms usually take on very characteristic shapes, depending upon the surfactant and substrate. Rosen (2004) described the adsorption isotherm of ionic surfactants onto an oppositely charged substrate and also sometimes – but not always – nonionic surfactants are typically S-shaped. (see Figure 2.4) In case of nonionic surfactants, an ethoxylated nonylphenol, for example, will exhibit a similar isotherm on silica, but will not adsorb sufficiently strongly to show all the details of such an isotherm on

alumina. Commonly, S-shaped isotherm can be divided into four regions as shown in Figure 2.4 and in each these regions corresponds to a different mechanism of surfactant adsorption.

In region I the surfactant adsorbs mainly by ion exchange and also the charge density, or potential at the Stern layer of the solid, remains almost constant. This region corresponds to very low adsorption densities and is sometimes referred to as the Henry's law region. The most important point is that there are no aggregates of adsorbed surfactants in this region and may not even be detectable because it occurs at such low surfactant concentrations.

In region II there is a marked increased in adsorption as the equilibrium concentration of surfactant increases. It is believed that this increase is caused by the interactions of the hydrophobic chains of oncoming surfactant ions with those of previously adsorbed surfactant and with themselves, which caused the adsorbed surfactants to form aggregates on the surface. This aggregation of the hydrophobic groups has been termed hemimicelle or admicelle depending upon whether the aggregates are viewed as monolayers or bilayers. The formation of these aggregates locally or patchwise at the interface is due to the heterogeneity of the surface. The original charged surface of the solid is neutralized by the adsorption of oppositely charged surfactant ions and eventually reverse, indicate the end of region II.

However, region III is characterized by a reduced slope in the adsorption isotherm not only because adsorption must overcome electrostatic repulsion between the oncoming ions and the identically charged head groups on the surfaces, but also because adsorption is now taking place on the more and more similarly charged surfaces. As the equilibrium concentration of surfactant further increases and eventually approaches the critical micelle concentration (CMC), adsorption is usually completed. The beginning of constant adsorption marks the onset of region IV.

Region IV is referred to as the plateau adsorption region and in this region the surface concentration of surfactant has reached saturation. The adsorption does not increase while the equilibrium concentration of surfactant is raised above the CMC. Further addition of surfactants only contributes to the formation of additional micelles in the bulk solution. In most systems the transition of region III/region IV occurs near the CMC of the surfactants.

2.3 Structure of Adsorbed Surfactant Aggregates at Solid/Aqueous Interface

Several studies have been done using AFM to image adsorbed surfactant structures *in situ*. Early studies of adsorbed surfactant structures were done by Manne and coworkers (Manne *et al.*, 1994 and Manne and Gaub, 1995). They showed that quaternary ammonium surfactants (mainly $C_{14}TAB$) formed surface aggregates at concentrations twice the CMC. Aggregate structures varied according to substrate. Spherical aggregates were reported on silica, cylindrical aggregates were found on mica and for graphite and MoS_2 surfaces hemi-cylinders were reported (Manne and Gaub, 1995). It must be noted that AFM does not provide the ability to discriminate hemi-spheres or hemi-cylinders from full spheres or cylinders.

Ducker and co-workers (Subramanian and Ducker, 2000; Ducker and Grant, 1996; Wanless *et al.*, 1997; Lamont and Ducker, 1998 and Liu and Ducker, 1999) have done extensive studies relating the effect of surface, counter-ion, and added electrolyte composition on the structure of adsorbed aggregates. They found a decrease in the adsorbed aggregate curvature as the surface hydrophobicity increases in zwitterionic systems (Ducker and Grant, 1997). This was attributed to a favorable decrease in the contact between the hydrophobic portion of the surfactant and water. Lamont and Ducker (Lamont and Ducker, 1998) also studied the effect of added salt on the organization of $C_{16}TAB$ adsorbed to mica. They found that added salt increases the curvature of the aggregate, and that the effect increases along the order Li^+, K^+, Cs^+. The more polarizable co-ion in this case increases curvature. This is in contrast to the effect of surfactant counter-ions, which decrease the curvature as the polarizability increases (Subramanian and Ducker, 2000). The cation effect is due to the adsorption of these co-ions to the solution-mica interface.

Subramanian and Ducker (Subramanian and Ducker, 2000) have postulated that the "hard" or "soft" nature of the counter-ion dictates the curvature of the adsorbed structure. "Soft" ions are more polarizable and can more effectively shield head groups leading to a less curved structure. "Hard" ions on the other hand, are highly hydrated and cannot approach the head groups as closely. This leads to a less shielded repulsion between head groups and therefore more curved aggregates.

Velegol and co-workers (Velegol *et al.*, 2000) have also studied the effect of counter-ions and added electrolyte on surfactant adsorption to silica. They showed that changing the counter-ion from Br⁻ to Cl⁻ decreases the maximum adsorption by 60% and changes the structure of the adsorbed species from cylinders to spheres above the *cmc*. These structural changes are consistent with the "hard"/ "soft" theory mentioned above.

At low salt and surfactant concentrations, Koopal (Goloub *et al.*, 1996 and Goloub and Koopal, 1997) proposed that the initial adsorption of DPC and CPC occurs parallel to the surface. This occurs on a pyrogenic silica, which is more hydrophobic than a fully hydroxylated silica (Goloub and Koopal, 1997). This effect was also seen by Zajac and co-workers (Zajac *et al.*, 1996), for benzyldimethyl ammonium bromide on a hydroxylated silica in the absence of salt. At high salt (100 mM), however, chains were not parallel to the surface. Their study did not include intermediate salt concentrations. EPR studies have shown that a spin-labeled version of $C_{16}TAB$ also adsorbs flat at low surfactant concentrations and low pH (Bakker *et al.*, 1999).

As the surface excess increases, the surfactant-chains can interact with each other more favorably than with water (short-range hydrophobic effect). When this occurs the adsorption rises. The concentration where this tail association begins has been called the hemi-micelle concentration, HMC (Somasundaran and Fuerstenau, 1966). Neutron reflectivity studies of $C_{16}TAB$ adsorbed to amorphous silica, suggest that a defective bilayer of flattened micelles exist between ½ and ⅔ CMC (Rennie *et al.*, 1990 and McDermott *et al.*, 1994), whereas the cylindrical surfactant aggregates have been recently observed (by AFM) on mica at 0.8×CMC (See and O'Haver, 2004 and Saphanuchart *et al.*, 2007) for initial stage of surfactant adsorption. These aggregates have altered to bilayer the equilibrium condition has been approached.
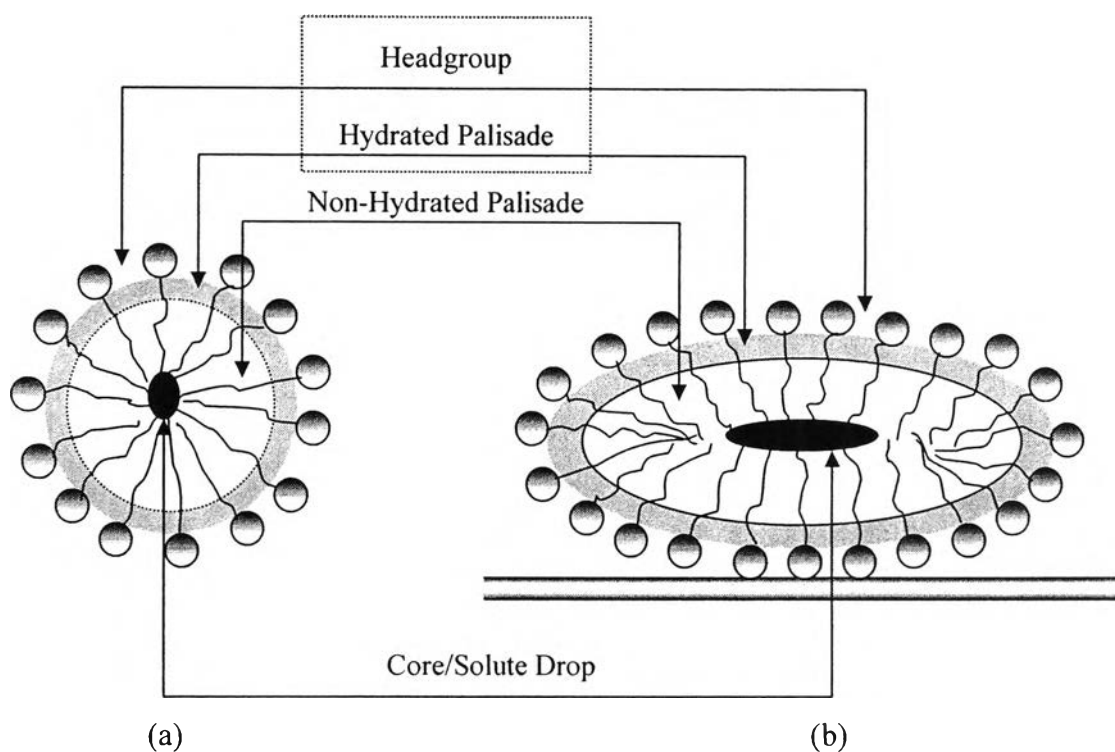
Figure 2.5 Typical micelle (a) and admicelle (b) structures with proposed loci of solubilization and adsolubilization.

2.4 Solubilization and Adsolubilization

The surfactant aggregates (micelle and admicelle) provide a microenvironment conductive to the partitioning of solute molecules which are otherwise sparingly soluble in the aqueous solution, a phenomenon known as solubilization and adsolubilization, respectively (Rosen, 2004, Nagarajan, 1996 and O'Haver *et al.*, 1995). It is generally agreed that the primary locations for solubilization of neutral organic solutes in surfactant aggregates have been divided into three main parts by polarity (O'Haver *et al.*, 1995; Kittiyanan *et al.*, 1996 and Dickson and O'Haver, 2002) (see Figure 2.5), which are (1) headgroup region (2) hydrated palisade region and (3) non-hydrated palisade region. These proposed locations of various solutes solubilized in the surfactant aggregates have been elucidated by NMR spectroscopy (Hedin *et al.*, 1999; Mata *et al.*, 2006; Lindblom *et al.*, 1973 and Goldenberg *et al.*, 1993).

The outer region is the most polar, consists of the surfactant headgroups, and forms the surfactant aggregate/water (and surfactant aggregate/solid for admicelle) interface. The inner region (surfactant tail region) is referred to as the palisade region. This region is divided into two sections by degree of water penetration, which are (1) hydrated palisade region, consists of the carbons near the headgroups and also characterized by water molecules that have penetrated the surfactant aggregates (Wennerstroem and Lindman, 1979; Novaki and Seoud, 2000 and Bruce et al., 2002). This region is intermediate in polarity (2) non-hydrated palisade region consisting of the hydrocarbon chains and is totally non-polar in nature (Rosen, 2004). Within the micelle, the palisade region consists of intertwined, randomly oriented hydrocarbon groups, forming a liquid-like region having a viscosity approximately an order of magnitude greater than that of liquid hydrocarbons of similar chain length (Zana, 1986), whereas the palisade region of admicelle is also similar but denser (Dunaway et al., 1995 and O'Haver et al., 1995). Sometimes, when the micelles solubilize very large amount of highly hydrophobic solutes, the micelles tend to radially expand and pure solute droplets are then formed in the micelles (Hedin et al., 1999 and Doi et al., 2004). It is thus additionally proposed another region as non-hydrated core/solute drop region as shown in Figure 2.5. The non-hydrated palisade region combined with the core/solute drop region is usually called "core" region because both of them are dried similarly. Various studies have indicated that organic solutes partition into the regions of the surfactant aggregates that possess similar polarity (Nagarajan, 1996; Rosen, 2004, Dunaway et al., 1996 and O'Hvaer et al., 1995). Thus, alkanes or other nonpolar solutes partition primarily to the core region, while polar components partition to the hydrated palisade or headgroup region.

It has been postulated that the location of the solubilized/adsolubilized solutes can be determined by examining the graph of the partition coefficient plotted against the mole fraction of solute in the surfactant aggregates (Dunaway et al., 1996, O'Haver et al., 1995, Mata et al., 2006, Kittiyanan et al., 1996). The following trends have been proposed concerning the locus of solubilization and partition coefficients: (1) if the solute partitions primarily to the non-hydrated (core) region, the partition coefficients will increase as solute mole fraction in the surfactant

aggregates increases; (2) if the solute partitions primarily to the hydrated region (hydrated palisade or headgroup region), the partition coefficients will decrease as the solute mole fraction in the surfactant aggregates increases; and (3) if the solute partitions to both the hydrated and the non-hydrated regions, the partition coefficient will remain constant as solute mole fraction in the surfactant aggregates increases. It is possible that this data can roughly distinguish solute partitioning between the hydrated region and solute in the non-hydrated regions of the micelle/admicelle.
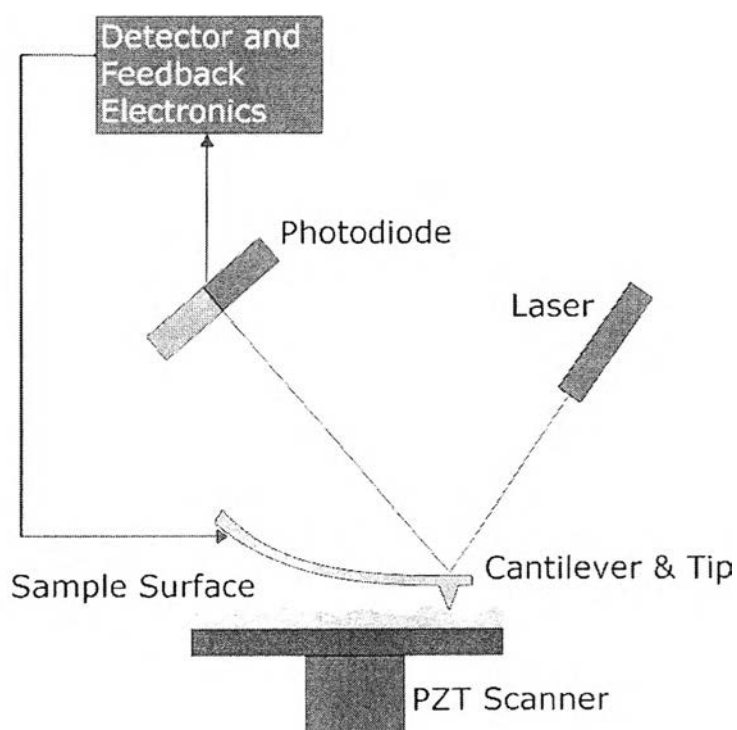
2.5. Atomic Force Microscopy

The AFM first appeared in 1986 as an evolution from scanning tunneling microscopy (Scales, 1999; Wiesendanger, 1994; Sarid, 1991 and Merris *et al.*, 1999). It takes on many different forms and configurations and, indeed, the AFM is just one type of scanning probe microscope (SPM) that is used in the characterization of interfaces. AFM's mode of operation is applicable to both conductive and non-conductive surfaces and to fluid and non-fluid environments. This has established uses for the AFM in a wide range of scientific and engineering endeavors. In the last few years, AFM has undergone extensive development but imaging is still its main caveat of use. Its popularity as a tool for imaging surfaces is almost certainly related to the imaging environment and substrate preparation requirements. The AFM can be used on a vast range of surfaces, with the only real head and that the thickness of the sample be less than approximately 0.5 cm. Even the latter restriction is being obviated in many new commercial AFM head designs.

The surface can be imaged in air, water, vacuum, or some other fluid environment that retains compatibility with the materials of construction of the instrument. Sample preparation is therefore sub-critical relative to techniques such as transmission and scanning electron microscopy. As with nearly all techniques, the AFM is not a panacea of all ills and it has a number of limitations to go with its many advantages. These will be explored, along with its many advantages. For example, a clear disadvantage of the AFM technique is that it is purely a surface or topological technique. A consequence of this is that imaging of soft or motile surfaces is inherently difficult. Imaging artifacts are also of concern.

Atomic Force Microscopy (AFM) can be used to investigate the structure and morphology of the surface. This is a powerful technique that allows the generation of topographic images of the surface with atomic resolution

The principle behind AFM is similar to that of an old record player. A sharp tip (like needle) makes contact with the surface and moves up and down in response to the surface features (see Figure 2.6). This tip is connected to a small cantilever. The tip is scanned over the sample and the features on the surface cause the cantilever to bend up and down. This deflection of the cantilever is monitored by shining a small laser beam on the back of the cantilever and measuring the change in the reflected position of the laser beam. Several forces typically contribute to the deflection of an AFM cantilever. The force most commonly associated with atomic force microscopy is an inter-atomic force called the van der Waals force. The dependence of the van der Waals force upon the distance between the tip and the sample is shown in Figure 2.7.

Figure 2.6 Principle of Atomic Force Microscopy.
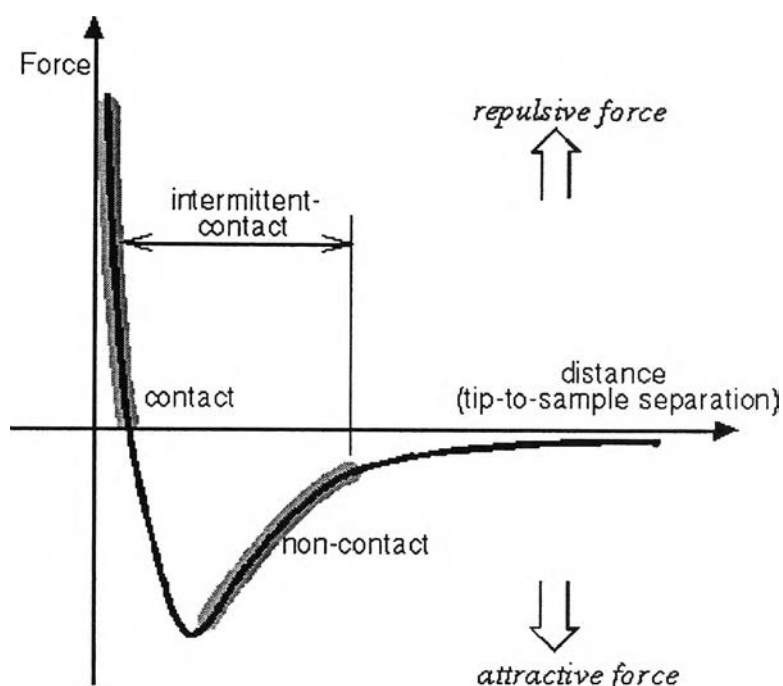
Figure 2.7 Inter-atomic force vs. distance curve.

A feed back loop is used to deepen the deflected laser beam signal constant by adjusting the sample height at each position. This change in height is recorded to give a topographic image of the surface. In order to collect an image, the cantilever is scanned back and forth over the sample and the signal from the z-piezometers are recorded as the tip is moved to keep the photodiode signal constant at the setpoint level. The size of the scan is set in the scan parameters anywhere from about 1 nm to 125 microns. The scan speed and direction are also controlled by software parameters.

To investigate soft structure of surfactant aggregates at solid/liquid interface, contact mode AFM has been used generally (Manne *et al.*, 1994). In contact mode AFM, also known as repulsive mode, and AFM tip makes soft physical contact with the sample. The tip is attached to the end of a cantilever with a low spring constant, lower than the effective spring constant holding the atoms of the sample together. The slope of the van der Waals curve is very steep in the repulsive or contact regime. As a result, the repulsive van der Waals force balances almost any force that attempts to push the atom closer together. In AFM this means that when

the cantilever pushes the tip against the sample, the cantilever bends rather than forcing the tip atoms closer to the sample atoms. In addition to the repulsive van der Waals force, capillary forces arise when water wicks its way around the tip, applying a strong attractive force that holds the tip in contact with the surface.

As long as the tip is in contact with the sample, the capillary force should be constant because the distance between the tip and the sample is virtually incompressible. The variable force in contact AFM is the force exerted by the cantilever. The total force that the tip exerts on the sample is the sum of the capillary plus cantilever forces, and must be balanced by the repulsive van der Waals force for contact-modeAFM.