



CHAPTER II

LITERATURE REVIEW

2.1 Contaminants in wastewater

2.1.1 Wastewater

Wastewater is water that has been quality-affected by some impurities. It is composed of liquid that may be disposed from domestic residences, commercial properties, industries, and/or agriculture. In most common use, wastewater is referred to municipal disposal, which contains a wide range of contaminant concentrations resulting from the mixing of wastewaters from different sources. Some contaminants may have no harm to health; unfortunately some do. Contaminants which have bad effects on the human body are described as toxicants.

2.1.2 Wastewater from industry

Heavy metals and hydrocarbon compounds are major types of contaminants in industrial wastewater. Aromatic hydrocarbons (AHs) and polyaromatic hydrocarbons (PAHs) are groups of the most difficult toxic organic compounds to be treated in petrochemical disposal. Because of they are composed of many benzene rings, the degradation is quite complex. Therefore, the removal of those compounds from wastewater is very important.

Table 2.1 Heavy metals and hydrocarbon contaminants in the Gulf of Thailand (EVS Environment Consultant, 1999).

Heavy Metals	Polyaromatic Hydrocarbons (PAHs)	
Cd	Acenaphthene	Benzo(k)fluoranthene
Cr	Acenaphthylene	Chrysene
Cr ⁶⁺	Acridine	Dibenz(a,h)anthracene
Cu	Anthracene	Fluoranthene
Fe	Benz(a)anthracene	Fluorene
Hg	Benzo(a)pyrene	Indeno(1,2,3-c,d)pyrene

Pb	Benzo(b)fluoranthene	Naphthalene
Zn	Benzo(g,h,i)perylene	Phenanthrene
		Pyrene

2.2 Adsorption

2.2.1 Theory

Adsorption and absorption are used in the separation of unwanted materials. The difference between these two methods is: adsorption is mostly defined as the process where one or more components (solute) of fluid, a gas or a liquid, accumulates on the surface of a solid (adsorbent). A solute is added to the surface of the adsorbent as a thin layer, not capable of getting inside. On the other hand, absorption is the process where the solute can enter the inside of the absorbent. However, both methods are very useful in the applications of the removal of organic compounds from water or organic solutions, colored impurities from organics, and various fermentation products from fermented effluents (Geankoplis, 2003).

2.2.2 Adsorption isotherm of surfactants at solid-liquid interface

There are a number of factors that are involved in the adsorption isotherm of surfactant at the solid-liquid interface: (1) nature of the solid sites whether it is polar or non-polar, charge density, etc.; (2) nature and structure of the adsorbed surfactant; and (3) systems of the aqueous phase, pH, ionic strength, temperature, etc. The adsorption isotherm of an ionic surfactant onto an oppositely charge interfaces is typically in an S-shape. On the other hand, the adsorption isotherm of a nonionic type is describes by Langmuir isotherm (Rosen, 2004). The S-shape adsorption isotherm is divided into four parts, as shown in Figure 1.

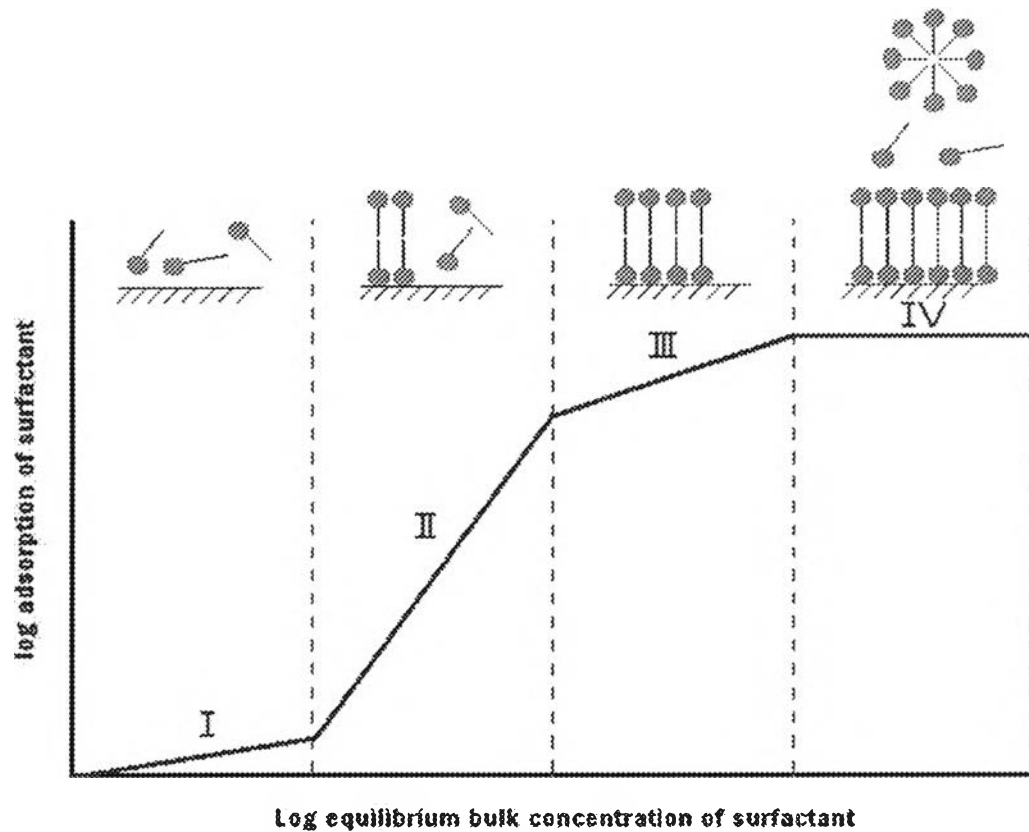


Figure 2.1 S-shaped adsorption isotherm of surfactant.

The first region (region I) is considered as the infinite dilution region and is referred to as the Henry's law region. A low concentration of surfactant results in a low amount adsorbed on the surface. The adsorption in this region is because of either the opposite charge attraction between ionic surfactant and the surface of the solid, or surfactant molecules lying prone on the surface of the solid in the nonionic type of surfactant.

In the second region (region II), there is a remarkable increase in the slope relative to the slope in Region I, which is a general indication of greater numbers of surfactant adsorbed. It is the consequence of hydrophobic interaction between the oncoming surfactant in the bulk solution and surfactant which have already been adsorbed onto the surface. This aggregation, which occurs at concentrations well below the critical micelle concentration (CMC) of surfactant, is called admicelles or hemimicelles, depending on whether their structures are formed as being local bilayers or local monolayers, respectively.

There is a decrease in the slope in region III, compared to region II. This results from the electrostatic repulsion between oncoming surfactant and surfactant which have already been adsorbed. At the end of region III, critical micelle concentration (CMC) occurs. It is the point where the surfactant reaches the maximum coverage; there is no further surfactant capable to adsorb onto the surface.

CMC is also the beginning point of region IV. It is the plateau adsorption region for increasing surfactant concentration. At the point of CMC, micelles begin to form and no more surfactant adsorption is observed.

The adsorption isotherm of a nonionic type of surfactant can be characterized by Langmuir isotherm which is based on four hypotheses.

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
2. Adsorbed molecules do not interact.
3. All adsorption occurs through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

The Langmuir equation is expressed as:

$$Q = \frac{Q_{\max} \cdot K \cdot c}{1 + K \cdot c} \quad (1)$$

where K = Langmuir equilibrium constant, c = aqueous concentration, Q = amount adsorbed, and Q_{\max} = maximum amount adsorbed. The Langmuir equation can be optimized by linear regression, commonly used linear regression methods are: Lineweaver-Burk, Eadie-Hofstee, Scatchard, and Langmuir.

The double reciprocal of the Langmuir equation yields the Lineweaver-Burk equation:

$$\frac{1}{Q} = \frac{1}{Q_{\max}} + \frac{1}{Q_{\max} \cdot K \cdot c} \quad (2)$$

A plot of $(1/Q)$ versus $(1/c)$ yields a slope = $1/(Q_{\max}K)$ and an intercept = $1/Q_{\max}$. The Lineweaver-Burk regression is very sensitive to data error and it is strongly reversed from fitting the data in the low concentration range. Another common linear form of the Langmuir equation is the Eadie-Hofstee equation:

$$Q = Q_{\max} - \frac{Q}{K \cdot c} \quad (3)$$

A plot of (Q) versus (Q/c) yields a slope = -1/K and an intercept = Q_{\max} . The Eadie-Hofstee regression has some bias toward fitting the data in the low concentration range. Note that if you invert the x and y axes, then this regression would convert into the Scatchard regression:

$$\frac{Q}{c} = K \cdot Q_{\max} - K \cdot Q \quad (4)$$

A plot of (Q/c) versus (Q) yields a slope = -K and an intercept = KQ_{\max} . The Scatchard regression is biased toward fitting the data in the high concentration range. The last linear regression commonly used is the Langmuir linear regression proposed by Langmuir himself:

$$\frac{c}{Q} = \frac{c}{Q_{\max}} + \frac{1}{Q_{\max} \cdot K} \quad (5)$$

A plot of (c/Q) versus (c) yields a slope = $1/Q_{\max}$ and an intercept = $1/(KQ_{\max})$. This regression is often erroneously called as the Langmuir linear regression when applied to adsorption isotherms. The Langmuir regression has very little sensitivity to data error. It has some bias toward fitting the data in the middle and high concentration range (Langmuir, 1916).

2.3 Adsolubilization

Water-insoluble organic compounds (solutes) adsorb into the adsorbed layer which sometimes takes place even if the solutes themselves hardly adsorb at the interface. This phenomenon is called surface solubilization or adsolubilization (Wu *et al.*, 1987 and Tsurumi *et al.*, 2006). The adsolubilization is mostly composed of three parts which are solid substrate (adsorbent), surfactant, and contaminant.

2.3.1 Solid substrates (adsorbents)

There are many types of solid substrates used nowadays, such as alumina, carbon black, clay, titanium dioxide, zeolite, silica, and so forth. They are usually divided into three main types based on their surface charge- positive charge

surface, negative charge surface, and hydrophobic surface. Alumina is an example of positive charge surface and carbon black is an example of hydrophobic surface.

2.3.1.1 Negative charge surface

Clay, titanium dioxide, zeolite, and silica are examples of negative charge surface. Esumi and Yamamoto (1997) investigated the adsorption of sodium dodecyl sulfate surfactant (SDS) and the adsolubilization of 2-naphthol on hydrotalcite, which is a type of clay. The result was that the amount of adsorbed SDS increased sharply and then reached a plateau with SDS concentration. Also the adsolubilized 2-naphthol increased considerably at low SDS concentration. In addition, the amount of adsolubilized 2-naphthol also increased because of an increase in the feed concentration. Adsolubilization of 2-naphthol and copper ions on laponite was experienced by using cationic surfactants (Esumi *et al.*, 1999). Dodecyl trimethylammonium bromide (DTAB) and 1,2-bis(dodecyldimethylammonio) ethane dibromide (2RenQ), which are cationic surfactants, retained a high sorption capacity for copper ions. 2-naphthol was completely solubilized by 2RenQ in a whole concentration region, although there was a decrease in adsolubilization above the CMC of DTAB. The effect of surfactant concentration and pH on the adsolubilization of weak acid at a kaolinite/water interface was studied by Talbot *et al.* (2002). 4-nitrophenol, a weak acid, was hardly adsorbed on naked kaolinite particles in the whole pH ranges (3-10). However, after cetylpyridinium chloride (a cationic surfactant) was added, the adsolubilization was increased. The influence of pH on adsolubilization was very much dependent upon surfactant coverage. The adsolubilization decreased with increasing pH. Therefore, as increasing surfactant concentrations induced the pH to increase, it resulted in the enhancement of the adsolubilization. Titanium dioxide was also one of the popularly used adsorbents. Esumi *et al.* (1998) investigated the adsorption of copper ions and 2-naphthol from aqueous solutions by anionic surfactant (SDS) adsorbed on titanium dioxide. Two types of titanium dioxide were used; one was untreated and the other was hydrophobic with dodecyl chain groups. The adsorption behavior of copper ions by the SDS adsorbed on the hydrophobic titanium dioxide was similar to that on the untreated titanium dioxide. 2-naphthol was adsolubilized more efficiently in the SDS adsorbed layer on hydrophobic titanium dioxide than on untreated titanium dioxide.

Esumi *et al.* (1998) also studied the adsolubilization of 2-naphthol in quaternary ammonium group surfactants on a titanium dioxide surface. The cationic surfactants used were dodecyltrimethylammonium chloride (DTAC) and 1,2-bis(dodecyltrimethyl ammonio) ethane dichloride (2RenQCl). The amount of adsorbed surfactants increased with increasing chain length of the ammonium groups. The amount of adsolubilized 2-naphthol increased with increasing surfactant concentration where the amount adsolubilized increased with increasing chain length of ammonium groups. Further, the adsorption of 2RenQCl enhanced the amount adsolubilized greater than by the adsorption of DTAC.

2.3.1.2 Silica

Silica, which is also called silicon dioxide (SiO_2), comprises two of the most abundant elements on the earth's crust; silicon and oxygen. Silica consumes about 59 percent of the earth's crust, and 95 percent of it is known as rocks. Silica is found in nature in several forms, including quartz and opal. In fact, 35 crystalline forms have been identified (Hart, 1927). Under ambient conditions, silica is formed when silicon is exposed to air (oxygen). A very thin layer of silica, so-called native oxide, is built on top of the silicon surface. Silica also has covalent bonding and forms a network structure (also known as lattice or continuous), as shown in Figure 2. Silica's network structure can be attacked by hydrofluoric acid (HF). HF is capable of breaking down the silica pattern (Iler, 1979).

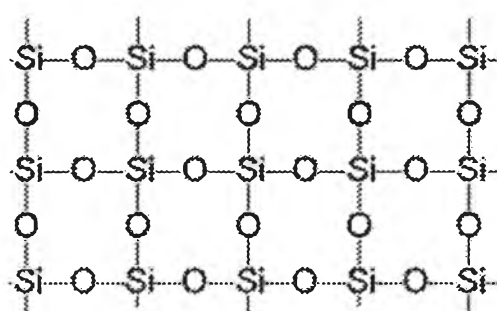


Figure 2.2 Structure of silicon dioxide (SiO_2) or silica.

The adsorption of organic molecules on silica surface was reviewed by Parida *et al.* (2006). Adsorption of a dimeric (1,2-bis(dodecyldimethylammonio) ethane dibromide, 2RenQ), which is a cationic surfactant, on silica from its aqueous solution was investigated in the presence of

sodium bromide (NaBr) (Esumi *et al.*, 1996). The amount of adsorbed surfactant at saturation increased with increasing the amount of salt added. The adsolubilized 2-naphthol was also greater with adding NaBr. In addition, 2RenQ adsorbed on silica much stronger in the presence of added NaBr, keeping 2-naphthol in the adsorbed layers, than when no salt was added. The influence of pH and surfactant structure arrangement on the adsolubilization of toluene and acetophenone by cationic-modified silica was studied by Pradubmook *et al.* (2003) and Asvapathanagul *et al.* (2005). The surfactant used was cetyltrimethylammonium bromide (CTAB). The result was that the adsorption of the surfactant increased with an increase in pH. The adsolubilization in the single solute system of both toluene and acetophenone increased with increasing equilibrium concentration of the solute in the aqueous phase as well. At low surfactant adsorption, the structure, nature, or arrangement of the adsorbed CTAB onto the silica had a much stronger effect on the adsolubilization of the solutes than the actual adsorbed amount. This effect appeared to be less pronounced with increasing amounts of adsorbed CTAB. For toluene, pH had little effect on the adsolubilization. In contrast, the pH effect on acetophenone was much greater. In mixed solutes systems, the presence of acetophenone had little effect on toluene adsolubilization whereas the presence of toluene had a great effect on acetophenone adsolubilization. In addition, the presence of both solutes in the mixed solutes system was independent of pH. Okamoto *et al.* (2004) also confirmed that there was an increase in the adsolubilization of 2-naphthol and biphenol, in both single solute and mixed solute systems, with increasing pH of the solution. The used surfactant was hexadecyltrimethyl ammonium bromide (HTAB).

In order to maintain a suitable surface charge, the effect of the pH must be a concern. The isoelectric point (iep) is the pH at which the surface carries no net electrical charge. Silica has the isoelectric point around 2.5, alumina is 9.1, and titania is 6.8 (Yuan *et al.*, 2000). The pH of silica has to be controlled above 2.5 in order to adsorb a cationic surfactant, otherwise the anionic surfactant will be adsorbed in pH below isoelectric point. Nonionic type of surfactants can adsorb onto silica whatever the pH of the medium is but only a little on alumina. By changing the pH, the surfactant can be desorbed from the solid/liquid interface. This is the method to regenerate the solid substrate as well. Hydrophobic or ionized solute molecules

which do not adsorb onto the naked particles in the absence of surfactant, begin to be adsolubilized at very small surfactant coverage. This incorporation increases with increasing surfactant adsorption and aggregate formation at the solid/water interface up to a concentration close to but not necessarily equal to the equilibrium CMC. Above the CMC, as free micelles are formed in the solution, the solute is distributed between the adsorbed aggregates and the free micelles. At higher surfactant concentrations, the solute may be completely desorbed from the solid/water interface as the result of a near complete solubilization in the free micelles (Talbot *et al.*, 2002).

2.3.2 Surfactants

The word “surfactant” comes from “surface-active agent”. In the presence of low concentration in the system, it is capable of adsorbing onto the interface of the system and changes the properties of the interface itself. There are four types of commercially available surfactants- which are anionics, cationics, nonionics, and zwitterionics. In an anionic surfactant, some portion of the molecule appears to have a negative charge; for example RCOO^-Na^+ (soap) or $\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+$ (alkylbenzene sulfonate). In a cationic surfactant, some portion of molecule has a positive charge; for example $\text{RN}(\text{CH}_3)_3^+\text{Cl}^-$ (quaternary ammonium chloride). Zwitterionic may have both negative and positive charges in the surface-active portion; for example $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$ (long-chain aminoacid). For a nonionic surfactant, there is no apparent ionic charge in the molecule for example; $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride) (Rosen, 2004).

2.3.2.1 *EO/PO-based block copolymers*

Block copolymers are a special type of polymers in which each molecule is composed of two or more segments of simple polymers (blocks) joined in certain arrangements. These copolymers are classified by the number of blocks each molecule contains; block copolymers with two, three, and more blocks are called diblock, triblock, and multiblock copolymers respectively. Water-soluble block copolymers which have hydrophilic and hydrophobic moieties belong to a class of surfactant (Nakashima *et al.*, 2006).

An interesting type of block copolymers, which are popularly used as surfactant, is EO/PO-based block copolymers. They are the nonionic type,

which is composed of poly(ethylene oxide) as hydrophilic blocks and poly(propylene oxide) as hydrophobic blocks. These block copolymers can be classified into two main types; diblock and triblock copolymers. Pluronics is a triblock copolymers PEO-PPO-PEO, where the hydrophilic poly(ethylene oxide) forms the end blocks and the hydrophobic poly(propylene oxide) forms the middle blocks. These copolymers are sold under the trade name Pluronics (BASF), and also as the Poloxamers, Synperonics, Epans, Slovaniks, Proxanols, and so forth (Nakashima *et al.*, 2006). Pluronics is considered non-toxic and is usually used in the surfactant area. The surface tension of Pluronics is decreased linearly, because of an increase in concentrations. Nevertheless, there is a change in the slope at one concentration and then the slope is slowly decreased again until there is no slope change at critical micelle concentration (CMC). CMC of copolymers are shown in Figure 3. The first changing in the slope results from the configuration arrangement to be more compact (Gosa *et al.*, 2002). The structures of EO/PO-based block copolymers are shown in Figure 4.

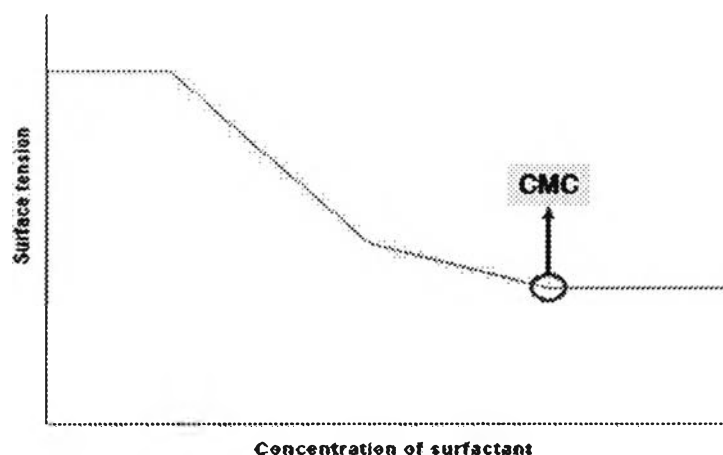


Figure 2.3 The tested CMC of copolymers.

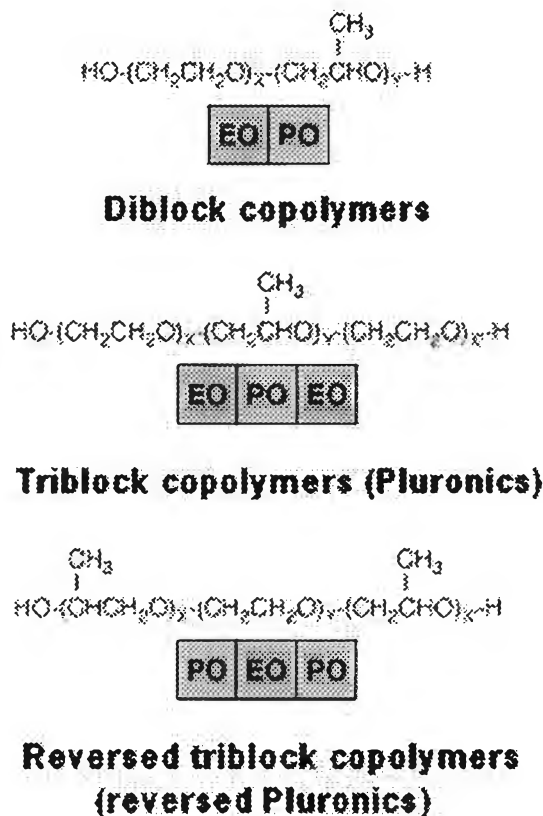


Figure 2.4 Structures of EO/PO-based block copolymers.

2.3.2.2 Adsorption of EO/PO-based block copolymers

Block copolymers are also capable of adsorbing onto the solid surface. The adsorption of block copolymers depends on their molecular characteristics, natures of the block copolymers, the adsorbing surface, and the solvent. Because of their amphiphilic nature, they are adsorbed onto the surface as trains, tails, and loops as shown in Figure 2.5 (Bahadur, 2001). The adsorption of homopolymers onto the hydrophilic surface, the adsorbed arrangements of trains, tails, and loops are all occur. In contrast, in the adsorption of diblock and triblock polymers onto hydrophilic surface, the hydrophilic part of polymers adsorb onto the solid surface as a train, leaving the hydrophobic part pointing out toward the solution as a tail.

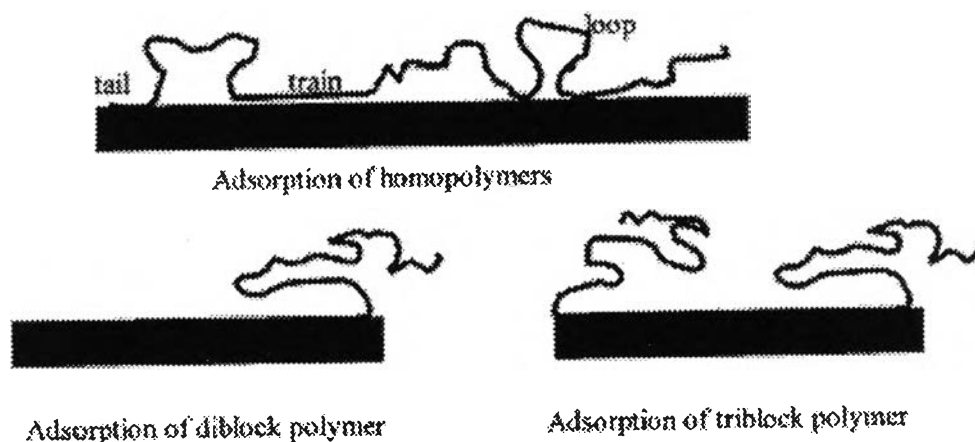


Figure 2.5 Homopolymer, diblock polymer, and triblock polymer adsorption at interfaces.

Mathur and Moudgil (1997) reported that the EO-based type of surfactant prefers to adsorb onto silica surface. In contrast, it is difficult to adsorb onto the other adsorbents such as Titania, Alumina, Ferrous oxide, and Magnesium oxide due to the reason of hydrogen bonding in Bronsted-Lewis theory.

Tsurumi *et al.* (2006) also confirmed that Pluronics, which had higher hydrophobicity, had more preference to adsorb onto silica. Also Pluronics tended to desorb more difficultly on silica, compared to other conventional surfactants. Moreover, the amount of adsorbed Pluronics onto silica was in opposite trend with respect to an increase in the HLB value (hydrophilic-lipophilic balance). The adsolubilization of 2-naphthol into an adsorbed layer of poly(ethylene oxide) poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymers (Pluronics) on hydrophilic silica was investigated. Four kinds of Pluronics (P103, P105, P123, and F108) were used in order to understand the effect of the hydrophobicity of the surfactants on the adsolubilization. The order of the adsorption in the saturation level was found to be $P123 \approx P103 > P105 \gg F108$. Indeed, this order was parallel to the order of the adsolubilization amount of 2-naphthol. The adsolubilization amount increased gradually at lower surfactant concentration regions, reached a maximum, and then decreased with increasing concentration of the Pluronics. The maximum amount appeared at critical polymolecular micelle concentration of each of the Pluronics.

2.3.2.3 EO/PO-based block copolymer micellization

The micellization of EO/PO-based block copolymers results from the hydrophobic interaction of poly(propylene oxide) blocks. In contrast, the CMC of copolymers shows a large decrease with PPO block length. The influence of the PEO block length is less pronounced than that of the PPO block (Bahadur, 2001). Nagarajan *et al.* (1996) compared the solubilization of hydrocarbons in diblock (PEO-PPO) and triblock (PEO-PPO-PEO) copolymers. It was reported that for identical molecular weight diblock and triblock copolymers ($\text{EO}_{200}\text{PO}_{64}$ and $\text{EO}_{100}\text{PO}_{64}\text{EO}_{100}$), the amount of hydrocarbons solubilized in the diblock was much larger than in the triblock copolymers. In contrast, for half the molecular weight $\text{EO}_{100}\text{PO}_{32}$ and $\text{EO}_{100}\text{PO}_{64}\text{EO}_{100}$, the same amount of hydrocarbons solubilized was observed between the diblock and triblock copolymers. In addition, both the diblock copolymer and triblock copolymer micelles preferred to solubilize the aromatic compounds more than the aliphatic compounds, compared to low molecular weight surfactant micelles. The solubilization of hydrocarbons by three types of Pluronics aggregation-spherical, cylindrical, and lamellar- was also predicted by Nagarajan (1999).

Nagarajan *et al.* (1985) investigated that the block copolymers micelles had much higher selectivity over the aromatic compounds more than aliphatic compounds comparing to other conventional surfactants. Because of the Flory-Huggins interaction parameter, which showed the interaction between the organic solutes and the adsorbed tails of surfactants, was less in the hydrophobic tails of copolymers than the hydrophobic tails of other conventional surfactants, meaning these aromatic compounds preferred to be in the copolymer tails more than tails of conventional surfactants.

2.3.2.4 Temperature dependence of EO/PO-based block copolymers

The aqueous system of EO/PO-based block copolymers is quite special, showing dramatic temperature dependence with the possibility of either polymers dispersing individually in the solvent or aggregating into micelles. This is because both PEO and PPO are relatively hydrophilic at low temperature. In water, PEO-PPO-PEO and PPO-PEO-PPO copolymers appear as independent polymer chains, so-called unimers. Therefore, EO/PO-based block copolymers is preferable in

water at low temperature (because of polarity), but as the temperature is increased the copolymers begin to prefer to dissolve in oil (Mortensen, 2001). It was shown that CMC of EO/PO-based block copolymer surfactant is dependent on temperature as well. The micellization of block copolymers is a consequence of hydrophobic interaction (PPO blocks). Therefore, when the temperature is raised, the hydrophobicity of PPO blocks is also increased. It results in a decrease in CMC. D'Errico *et al.* (2004) studied the phase behavior (temperature with respect to concentration) of two binary system (Pluronic 25R4 (PO₁₉EO₃₃PO₁₉) and Pluronic 25R2 (PO₂₁EO₁₄PO₂₁)) in aqueous solution, which resulted from the temperature changes. Although at low temperature the mixtures were dissolved in aqueous phase, it was reported that as the temperature increased, the mixtures split into water-rich and copolymer-rich solutions in equilibrium.

The removal of phenol, which is one of the toxic organic compounds, by surfactant (SDS)-modified alumina, was investigated by Adak *et al.* (2006) in the presence of various additives. The presence of different ions (Cl⁻, NO₃⁻, SO₄²⁻, HPO₄²⁻, Fe³⁺ and Mg²⁺) and humic acid on the phenol removal were studied. It was shown that the removal of phenol followed second order kinetics. While the pH was maintained at 6.7 ± 0.1, it was observed that the removal efficiency was increased because of the presence of anions and was decreased a little because of the presence of cations. Temperature and humic acid had no effect at all on the removal of phenol. Esumi *et al.* (2000) studied adsolubilized 2-naphthol in SDS-modified alumina. The system was controlled at pH 3.5 in the presence of NaCl 10 mmol/dm³. It was reported that the adsolubilized amount of 2-naphthol increased sharply and reached a maximum, then decreased with surfactant concentration. The difference in adsolubilized amount of 2-naphthol was not the result of the partition of 2-naphthol between SDS adsorbed layer and SDS micelles, but was because of the difference of SDS adsorption states such as the monolayer and admicelles. The partitioning of naphthalene to anionic surfactants adsorbed on alumina in the aqueous phase was studied by Neupane *et al.* (2000). Three anionic surfactants with different molecular structures were used: a conventional (sodium dodecylbenzene sulfonate, SDDBS), a gemini (dialkylated disulfonated diphenyl oxide with alkyl chain length

of 12, DADS-C12), and a dianionic (monoalkylated disulfonated diphenyl oxide with alkyl chain length of 12, MADS-C12). It was found that the maximum mass of adsorbed DADSC12 onto aluminum oxide was higher than that of SDDBS. At lower surfactant concentrations, the uptake of naphthalene by the adsorbed gemini surfactant was similar to that of the adsorbed conventional surfactant for equivalent masses adsorbed. However, the adsorption efficiency diminished for the gemini surfactant at higher concentrations. The adsolubilization of naphthalene to the dianionic surfactant-treated aluminum oxide was much lower than that of the gemini surfactant and the conventional surfactant-treated alumina. The adsolubilization of phenanthrene, in both experimental and modeling, were also studied in the presence of the anionic surfactant SDS (Jain *et al.*, 1999). It was concluded that the experimental data and modeled prediction came into agreement. Phenanthrene was able to be solubilize into a layer of surfactant-modified alumina as the data predicted.

2.4 Atomic force microscope (AFM)

2.4.1 Principle

The atomic force microscope (AFM) or scanning force microscope (SFM) is a very high-resolution type of scanning probe microscope, with demonstrated resolution of fractions of a nanometer. The AFM consists of a microscale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever. Typically, the deflection is measured using a laser spot reflected from the top of the cantilever into an array of photodiodes. The deflection signal is collected and translated into image. If the tip were scanned at a constant height, there would be a risk that the tip would collide with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. The AFM can be operated in a number of modes, depending on the application. In general, possible imaging modes are divided into static (also called Contact) modes and a variety of dynamic (or non-contact) modes.

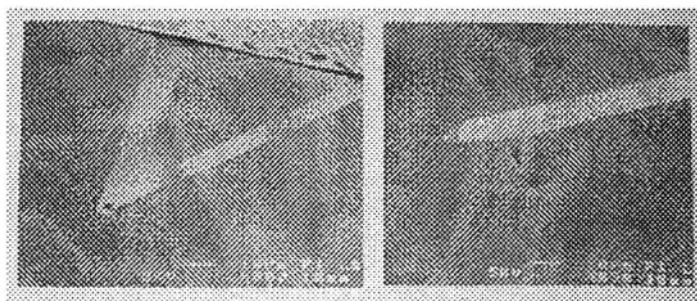


Figure 2.6 Two types of cantilevered probes: silicon nitride (left), and crystal silicon (right) (Ref: MMAFM-2; Veeco Nanoscope V (Digital Instruments, Santa Barbar, CA) manuscript).

2.4.2 Tapping mode (dynamic mode)

In the dynamic mode, the cantilever is externally oscillated at or close to its resonance frequency. The oscillation amplitude, phase and resonance frequency are modified by tip-sample interaction forces; these changes in oscillation with respect to the external reference oscillation provide information about the sample's characteristics. In tapping mode the cantilever is driven to oscillate up and down at near its resonance frequency. The amplitude of this oscillation is greater than 10 nm, typically 100 to 200 nm. Due to the interaction of forces acting on the cantilever when the tip comes close to the surface, Van der Waals force or dipole-dipole interaction, electrostatic forces, etc cause the amplitude of this oscillation to decrease as the tip gets closer to the sample. A Tapping AFM image is therefore produced by imaging the force of the oscillating contacts of the tip with the sample surface. This is an improvement on conventional contact AFM, in which the cantilever just drags across the surface at constant force and can result in surface damage.

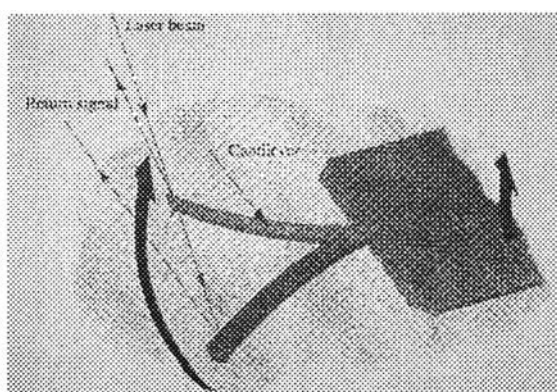


Figure 2.7 Tapping cantilever in free air (Ref: MMAFM-2; Veeco Nanoscope V (Digital Instruments, Santa Barbar, CA) manuscript).

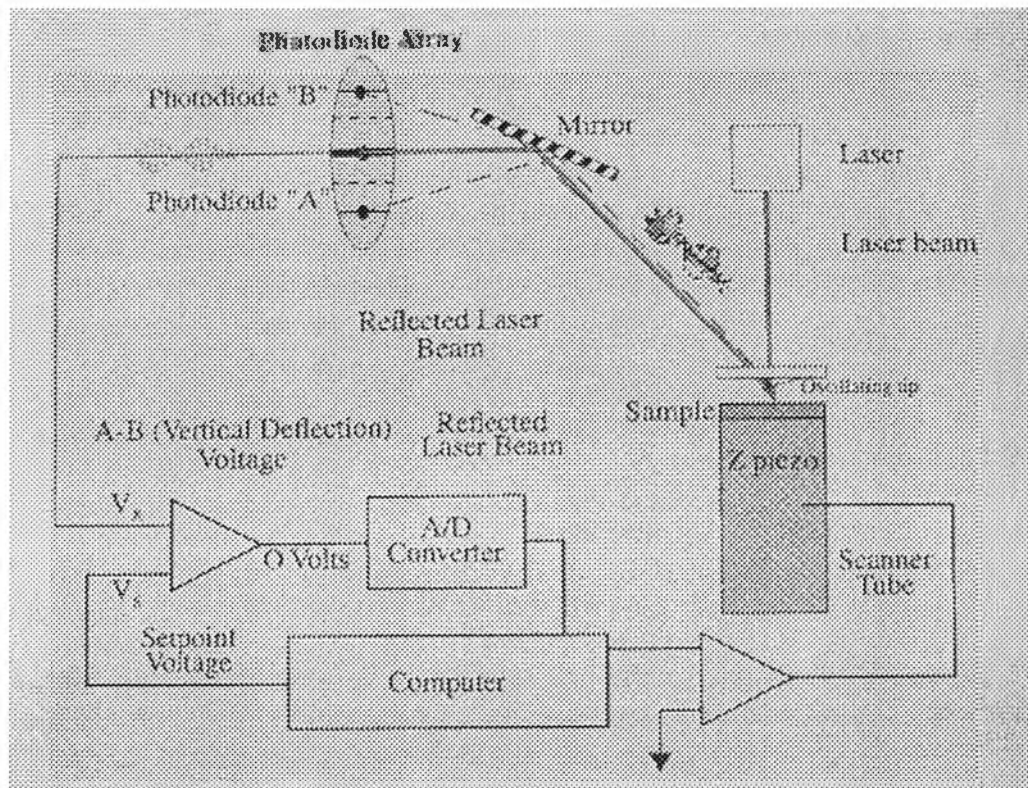


Figure 2.8 Tapping mode concept (Ref: MMAFM-2; Veeco Nanoscope V (Digital Instruments, Santa Barbar, CA) manuscript. .

An atomic force microscope (AFM) was used to quantify directly the adhesive interactions between a silica sphere and a planar silica surface. Electrostatic double layer interactions had also been quantified through analysis of approach curves (Bowen *et al.*, 1999). The surfaces of the sphere and planar surface were treated prior to measurements either by ethanol washing or by plasma treatment. The result showed that the magnitudes of the adhesion forces were substantially less for the plasma treated surfaces. The adhesion forces did not vary systematically with the loading force. The results showed that the adhesion of such surfaces was a complex phenomenon and that non-DLVO interactions probably played a substantial overall role.