

## CHAPTER 2

### THEORETICAL ASPECTS AND LITERATURE REVIEWS

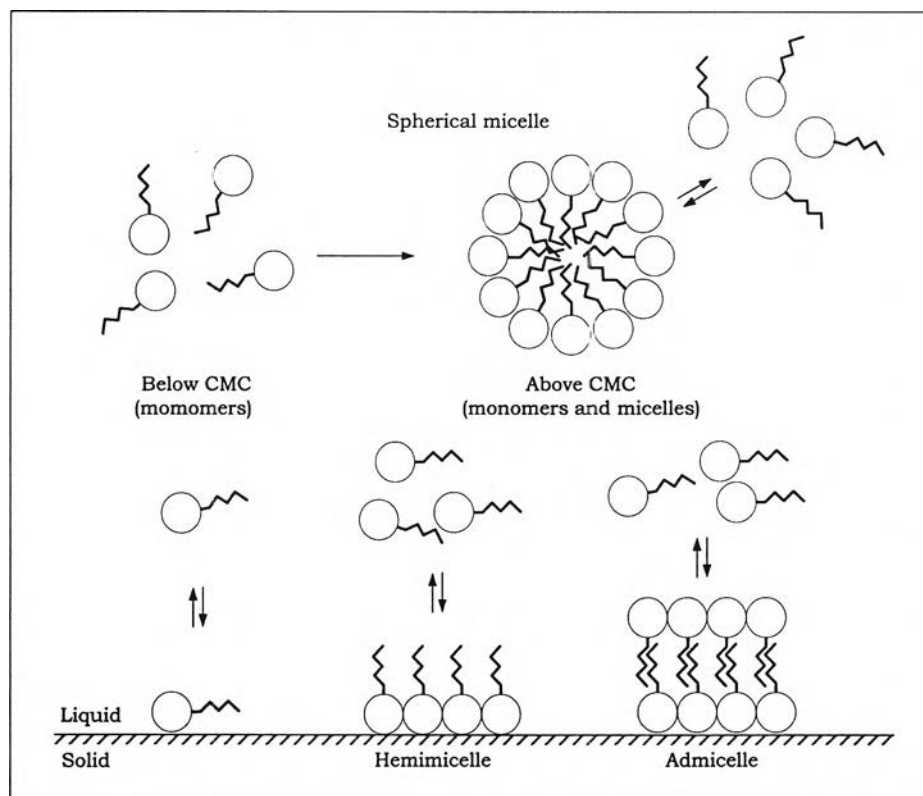
#### 2.1 Surfactant phenomena

Surfactants, which are commonly known as soaps or detergents, are called **amphiphiles** because of their unique and interesting chemical characteristics.

Surfactants are amphiphile molecules because they have both polar, hydrophilic head groups (water-like) and nonpolar, hydrophobic tail groups (oil-like) in the same molecule. Because of their amphiphile nature, surfactants will accumulate in interfacial regions (e.g.; water-oil, water-air, liquid-solid interfaces) and as a consequence will reduce the interfacial energy (Rosen, 1989). Surfactants are classified according to the nature of the hydrophilic portion of the molecule: anionic surfactants (negatively charged head groups), cationic surfactants (positively charged head groups), zwitterionic surfactants (negatively and positively charged head groups) and nonionic surfactants (non-charged head groups).

Depending on surfactant concentration in aqueous solution, surfactants are capable of forming many different types of aggregates. At low concentration, surfactants exist independent of one another in the solution phase and are called **monomers**. Surfactant monomers will aggregate at interfaces that are present in the system. When the surfactant concentration exceeds a certain level, surfactant monomers self-aggregate into spherical aggregates known as **micelles**. In a micelle, the individual monomers are

oriented with their hydrophilic head group facing the water or aqueous phase and their hydrophobic tail group oriented into the interior of the spherical aggregates. Micelles form when the surfactant concentration first exceeds the **critical micelle concentration (CMC)**, a value which varies for every surfactant. As additional surfactants are added above the CMC, the incremental surfactants go to form additional micelles (West and Harwell, 1992). Figure 2.1 shows the micelle formation of surfactants.



**Figure 2.1** Example of surfactant micellization

When a solid phase is added to the surfactant solution, the surfactants will adsorb at the solid-liquid interface. At low surfactant concentrations, the surfactant begins to adsorb and form micelle-like structures called **hemimicelles** and **admicelles**, depending on whether the aggregates have one or two surfactant layers. Once the CMC is reached, additional surfactants do not increase the amount of adsorbed surfactants, but rather

increase the concentration of micelles in aqueous solution. Surfactant micelles, with hydrophilic head groups (polar moieties) at the exterior and hydrophobic tail groups (non-polar moieties) in the interior, exhibit certain unique properties. The polar exterior makes a micelle highly soluble in water, while the non-polar interior provides a hydrophobic sink for organic compounds, which can effectively increase the solubility of organic compounds. Therefore the solubility of organic contaminants increases with increasing micelle concentration in the solution, i.e., adding surfactant above the CMC.

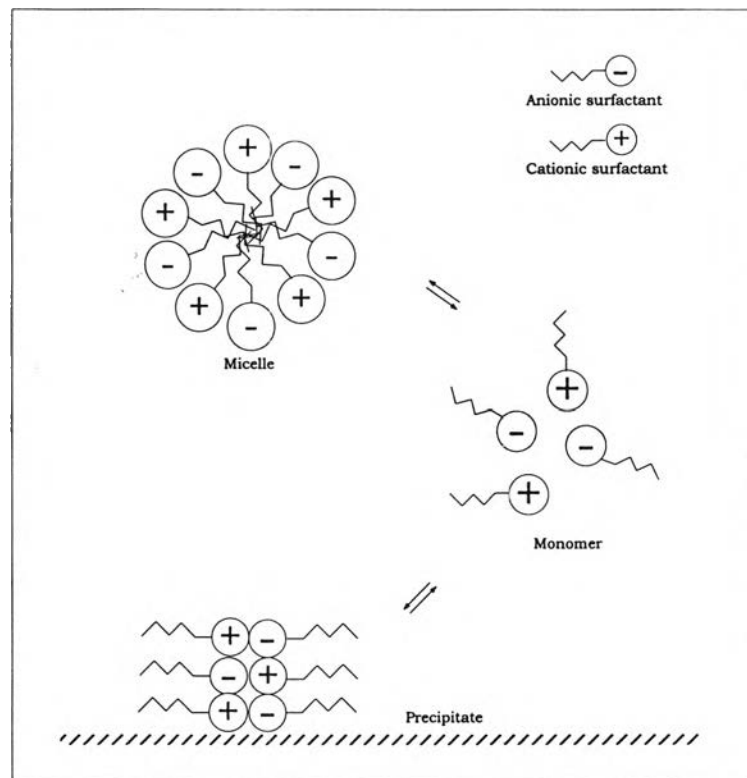
## **2.2 Mixed anionic and cationic surfactants**

Recently there has been a growing interest in research of mixed anionic and cationic surfactant systems, including the synergistic effects of mixed micelle formation, microemulsions, solubilization, and precipitation (Rosen et al., 1994; Shiao et al., 1994; Li et al., 1999; Li and Kunieda, 2000; Doan et al., 2002). Mixed anionic and cationic surfactant systems have many unique physicochemical properties that arise from the strong electrostatic interactions between the oppositely charged head groups. Mixed anionic and cationic surfactants exhibit the largest synergistic effect between surfactants such as lower CMC and surface tension relative to single surfactant systems (Bergstrom, 2000; Kang et al., 2001; Chen et al., 2002).

### **2.2.1 Precipitation of mixed anionic and cationic surfactants**

While mixtures of anionic and cationic surfactants exhibit the greatest synergism, their potential to precipitate and form liquid crystal phases has limited their use (Stellner et al., 1988; Meherteab, 1999). Figure 2.2 shows the equilibrium present in solution containing anionic and cationic surfactants under

conditions where the anionic and cationic surfactant form a precipitate with each other and micelles are present in solution. The precipitation phenomenon of mixed anionic and cationic surfactant systems has been studied by Scamehorn and co-workers (Stellner et al., 1988; Scamehorn and Harwell, 1992). They evaluated the precipitation phase boundaries of mixed anionic and cationic surfactants over a wide range of concentrations by considering regular solution theory and solubility relationships and developed a model to predict their results. Shiau et al. (1994) considered the effects of sodium chloride (NaCl) concentration and counterion binding on charged micelles in an effort to predict precipitation of the anionic surfactants by calcium.



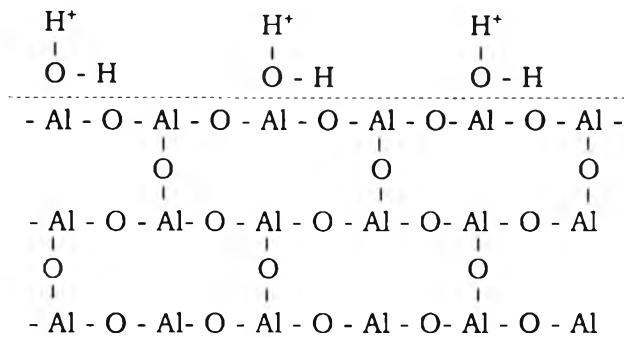
**Figure 2. 2** Precipitation of anionic and cationic surfactants (Adapted from Scamehorn and Harwell, 1992)

Since anionic and cationic surfactants tend to precipitate, many researcher have pursued ways of avoiding the precipitation of these mixtures. Li et al. (2000) investigated the solubilization and phase behavior of microemulsions with mixtures of anionic and cationic surfactants and alcohols. They found that alcohol addition was necessary to avoid liquid crystal formation, thereby allowing formation of middle phase microemulsions. However, alcohol addition is undesirable in environmental systems and consumer products. Thus recent research has attempted to find methods capable of forming alcohol-free microemulsions with mixed anionic and cationic surfactant systems, and evaluated the use of mixed anionic and cationic surfactants in environmental applications such as non-aqueous phase liquid (NAPL) removal in the subsurface. Doan et al. (2002) investigated the role of surfactant selection in designing alcohol-free microemulsion using mixed anionic and cationic surfactant microemulsions. They found that twin-head group anionic surfactants were less susceptible to precipitation in solution than single head group anionic surfactants due to increased solubility and steric constraints (as shown in Appendix A).

### **2.3 Aluminum oxide surface structure**

The crystal structure of alpha alumina oxide ( $\text{Al}_2\text{O}_3$ ) is made up of hexagonally packed oxygen atoms stacked on top of each other in an offset manner, with aluminum ions packed between the oxygen layers as shown in Figure 2.3. Upon contact with water, the crystal surface forms a layer of hydroxyl ions by a two-step process involving the chemical adsorption of a monolayer of water and its dissociation. Since the alumina surfaces are covered with hydroxyl groups, hydrogen and hydroxyl ions are the potential determining ions for alumina. There is also a physically adsorbed layer of water

molecules on top of the layer of hydroxyl ions. Therefore, the solution pH is critical for adsorption of ionic surfactants because it controls the charged of the alumina surface.



**Figure 2. 3** Schematic of crystal structure and surface layer of alpha aluminum oxide

The pH at which alumina has a net surface charge density of zero is called the point of zero charge (PZC). At a solution pH below the PZC, the alumina surfaces are positively charged; on the other hand, the alumina surfaces are negatively charged when the solution pH is above the PZC. The PZC of aluminum oxide at 25°C has been reported to be pH 9.1 (Sun and Jaffe, 1996). Alumina has been extensively studied as a positively charged adsorbent for anionic surfactants and mixed anionic and nonionic surfactants (Scamehorn et al., 1981; Lopata, 1988) and as a negatively charged adsorbent for cationic surfactants at solution pH of 10 and ionic strength 0.03 M NaCl (Fan et al., 1997)

## 2.4 Adsorption of ionic surfactants onto metal oxide surfaces

The adsorption of surfactants onto a solid interface is of great technological and scientific interest because of its potential use in commercial applications and environmental remediation. Examples of such applications are detergency, surfactant-

enhanced oil recovery, surfactant-enhanced subsurface remediation, surfactant-based separation processes, and surfactant-modified materials. In addition, the adsorption phenomenon is fundamentally important in understanding the solution and interfacial behavior of surfactants.

Surfactant adsorption onto metal oxide surfaces such as alumina is a complex process since solutes may adsorbed by ion exchange, ion pairing, and hydrophobic bonding mechanisms. Adsorption of surfactants onto metal oxide surfaces has been extensively studied including anionic surfactants onto positively charged surfaces (Scamehorn et al., 1981; Harwell et al., 1985) and cationic surfactants onto negatively charged surfaces (Goloub and Koopal, 1997)

The adsorption of surfactants at liquid-solid interfaces is usually characterized by adsorption isotherms. A plot of surfactant adsorption onto a solid surface versus the aqueous surfactant concentration at constant temperature is known as an adsorption isotherm. The surfactant concentration before and after adsorption is quantified to determine the amount of each species lost by adsorption.

$$\Gamma_i = \frac{(C_{i,b} - C_{i,a})V}{W_g} \quad (2.1)$$

where:

- $\Gamma_i$  = Adsorption density of surfactant i (mole/g)
- $V$  = Volume of sample (liter)
- $C_{i,b}$  = Concentration of surfactant at initial (mole/liter)
- $C_{i,a}$  = Concentration of surfactant at equilibrium (mole/liter)
- $W_g$  = Weight of aluminum oxide (g)

Equation 2.1 can be used to calculate the adsorption of the surfactant on the mineral oxide surface. In this equation, the adsorption of water or salt is assumed to be

negligible and the adsorption of the surfactant is assumed to have no effect on solution density (Lopata, 1988).

The adsorption isotherm of ionic surfactants onto metal oxide surfaces is typically an S-shaped isotherm (Somansudaran and Fuerstenau, 1966; Scamehorn et al., 1981). Normally the S-shaped isotherm can be divided into four regions, as shown in Figure 2.4. The designations for regions I, II and III first appeared in the work of Somansudaran and Fuerstuenau (1966).

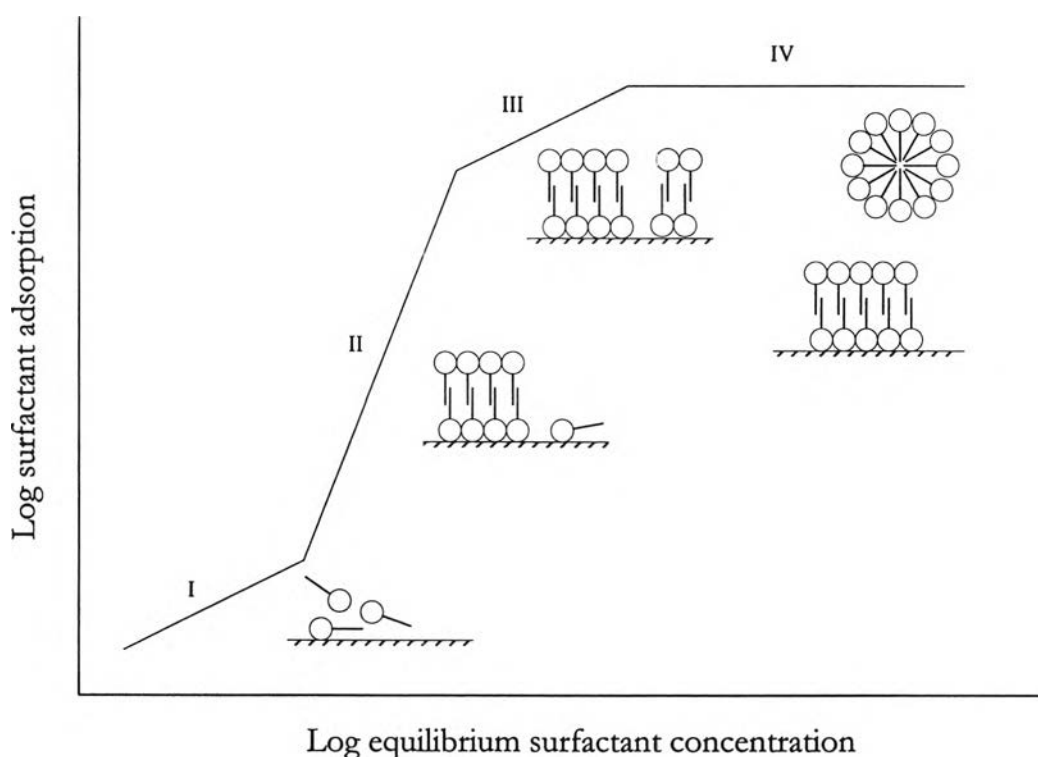


Figure 2. 4 Schematic presentation of typical surfactant adsorption isotherm

**Region I** corresponds to low surfactant concentration and low surfactant adsorption. This region is commonly referred to as the Henry's Law region because in this region, monoisomeric surfactants are generally adsorbed in a linear manner. In the Henry's Law region, surfactants are adsorbed mainly by ion exchange, with the



hydrophilic surfactant head groups adsorbing onto the solid surface. Adsorbed surfactants in this region are shown as being adsorbed alone and not forming any surfactant aggregates.

**Region II** is characterized by a sharply increased isotherm slope relative to the slope in the Region I, which is a general indication of the onset of cooperative effects between adsorbed surfactants: as the surface coverage increases due to tail-tail interactions the tendency of surfactants to adsorb also increases. This increase in slope indicates the beginning of lateral interactions between surfactant molecules, resulting from interaction of the hydrophobic chains of oncoming surfactants with those of previous adsorbed surfactants, and with themselves. This aggregation, which occurs at concentrations well below the critical micelle concentration (CMC) of the surfactant, are called **admicelles** or **hemimicelles**, depending on whether their structures are formed as being local bilayers or local monolayers, respectively. The admicelle is considered as a bilayer with the lower layer of head groups adsorb onto the solid surface and the upper layer of head groups are facing to the solution. The hemimicelle is considered as a monolayer with the head group of surfactant adsorbs onto the solid surface while the tail group contacted with the solution.

**Region III** is characterized by a decrease in the isotherm slope relative to the slope in Region II, because adsorption now must overcome electrostatic repulsion between adjacent ions and the similarly charged solid surface or the beginning of admicelle formation on lower energy surface patches.

**Region IV** is the plateau adsorption region for increasing surfactant concentration. Generally, the equilibrium surfactant concentration at the transition point from Region III to Region IV is approximately at the CMC of the surfactant. In some systems, the Region III/Region IV transition point can be reached when the

surface of the adsorbent becomes saturated with adsorbed surfactants. For the adsorption of surfactants from the aqueous solution, this will correspond to bilayer completion for ionic surfactants adsorbed on oppositely charged surfaces or to monolayer completion for adsorption on hydrophobic surfaces. The pseudophase separation model for surfactant adsorption of isomerically pure surfactants is shown in the work of Harwell (1985).

Recently a new class of surfactants, known as twin-head surfactants (two-head surfactants with one-tail group) such as sodium hexadecyl diphenyloxide disulfonate. SHDPDS (as used in this study), have been widely studied for contaminant remediation (Rouse et al., 1993; Sun and Jaffe, 1996; Carter et al., 1998; Deshpande et al., 2000; Doan et al., 2002). Neupane and Park (1999) investigated the adsorption of gemini anionic surfactant, which has two heads and two tails surfactants (dialkylated disulfonated diphenyloxide, DADS-C12) and conventional anionic surfactants (sodium dodecylbenzene sulfonate, SDDBS) onto positively charged alumina. They found that the adsorption of gemini surfactants is higher than the conventional surfactants. They also studied in the partitioning of naphthalene by these surfactants onto the alumina for mobilization of organic contaminant in subsurface through a batch experiment study.

#### **2.4.1 Parameters affecting surfactant adsorption**

The adsorption of surfactants at solid-liquid interfaces is strongly influenced by a number of parameters: 1) the nature of the structural groups of the solid surface; 2) the molecular structure of surfactant being adsorbed; and 3) the environment of the aqueous solution e.g., pH, electrolyte content, and temperature. Together these parameters determined the mechanism, by which

the adsorption occurs, and the efficiency and effectiveness of surfactant adsorption (Rosen, 1989).

The nature of the structural group of the solid surface (aluminum oxide was used in this study) has already been mentioned above (Chapter 2.3). The other parameters that affect surfactant adsorption are equilibrium pH, ionic strength, and temperature.

#### **2.4.1.1 Equilibrium pH**

pH usually causes marked changes in the adsorption of ionic surfactants onto charged solid surfaces. As the pH of the aqueous solution is lowered, the alumina surface becomes more positive or less negative because of additional protons adsorbing from the solution phase. This consequently increases the adsorption of anionic surfactants and decreases the adsorption of cationic surfactants (Rosen, 1989). When anionic surfactants adsorb onto alumina, the equilibrium pH is usually higher than the initial solution pH because the anionic surfactants exchange the ions with the adsorbed counterions and hydroxyl ions on the alumina surface. Therefore, the equilibrium pH and the surfactant adsorption are closely related to surfactant adsorption.

#### **2.4.1.2 Ionic strength**

Counter ions that are present in the surfactant solution are also present in the surfactant admicelles at the solid-liquid interface. Counter ions can affect the adsorbed surfactant by reducing electrostatic repulsion between ionic surfactant head groups. When counter ions are present in the system, the admicelles are formed more easily because of the repulsion between ionic surfactants is lower. Admicelle patches with the complete bilayer are also capable of forming a larger

aggregation number of surfactant molecule. As concentration of counterions in solution increases, the maximum surfactant adsorption increases.

#### **2.4.1.3 Temperature**

Temperature increases generally causes a decrease in the efficiency and effectiveness of ionic surfactant adsorption. The effect of temperature is relatively small compared to that of pH. However, a rise in temperature usually results in an increase in the adsorption of non-ionic surfactants containing a polyelectrolyte chain as the hydrophobic group.

### **2.5 Mixed anionic and cationic surfactant adsorption**

The solution properties of surfactant mixtures with oppositely charged head groups usually experiences deviation from ideal mixing (e.g., mixtures of anionic surfactants). Mixed anionic and cationic surfactant systems are expected to exhibit the greatest diversion from ideal mixing behavior (Harwell and Scamehorn, 1992). There have been few studies on the adsorption of mixed anionic and cationic surfactants onto solid surface (Huang et al., 1989 and Capovilla et al., 1991). The one reason for a small number of studies of the mixed anionic and cationic surfactants is their tendency to precipitate.

Huang et al. (1989) studied the adsorption of mixed anionic and cationic surfactants onto silica gel. They found that the adsorption of cationic surfactants was enhanced by the amount of anionic surfactants present in the system and the adsorption of cationic surfactants with addition of anionic surfactants to the system exactly equaled to adsorbed anionic surfactants. They suggested that each adsorbed surfactant can co-

adsorb with a cationic surfactant as an ion-pair onto uncharged silica gel through Van der Waals interactions.

### 2.5.1 The effect to micelle formation of surfactant mixtures

The CMC of the single surfactant system is the aqueous surfactant concentration in equilibrium with the maximum surfactant adsorption. For mixed surfactant systems, when the surfactant solution is a mixture of surfactant molecules, the CMC of the mixed surfactants does not correspond to the care of either individual surfactant component. The CMC of mixed surfactant systems can be predicted by the pseudophase separation model. If the micelles are treated as a pseudophase and the formation of mixed micelles is treated with either ideal solution theory (for surfactant systems with similar head groups) or non-ideal solution theory (for surfactants with different head groups), the concentration of the surfactant monomer of different surfactant components can be predicted as a function of overall surfactant concentration. For a binary surfactant system at constant weight fraction of surfactant 1 to surfactant 2, and as the total surfactant concentration increases, the individual surfactant concentration does not remain constant but changes continuously (Harwell and Scamehorn, 1992). This is important to the application for surfactant adsorption of mixed surfactant systems.

Capovilla et al. (1995) investigated the formation of mixed anionic and cationic surfactant bilayers on laponite clay suspensions through the adsorption of anionic surfactants by aqueous flocculated suspensions of laponite clay that had been cationic-exchanged by cationic surfactant. The results from their experiments showed that anionic surfactants favor tail-tail adsorption through

Van der Waals interactions with a monolayer of adsorbed cationic surfactants onto laponite clay. The schematic representation of anionic and cationic surfactant bilayers at laponite clay interfaces shows that the lower layer cationic surfactant head groups adsorb onto the negatively charged clay and the head group of the upper layer of anionic surfactant is in contact with the solution, as shown in Appendix A (Figure 1.2). They also found that ionic strength and the structure of cationic surfactants affect the maximum adsorption and the stability of mixed surfactant bilayers.

## 2.6 Solubilization

In pump-and-treat remediation, the amount of groundwater removed from the subsurface to extract the contaminant depends on the aqueous solubility of the contaminant. When surfactant is added into the aqueous phase, the organic interior of micelle acts as an organic pseudophase into which the organic contaminants can be partitioned. This process is known as solubilization.

In the aqueous system, the extent to which a solute will concentrate in a micelle can be related to the octanol-water partitioning coefficient ( $K_{ow}$ ) of the organic solutes (Edwards et al., 1991). In general, the larger the  $K_{ow}$  (hydrophobicity) of an organic solute the greater the tendency of the compound to concentrate in the micelle. Thus, micelles in an aqueous solution represent an increased solubilization capacity of the mobile aqueous phase for the organic solute over pure water.

Carter et al. (1998) evaluated various methods of increasing the solubility enhancement of Dowfax components (alkylated diphenyloxide disulfonate and can be mono- or disulfonated), such as using a co-surfactant, adding an electrolyte, and forming

middle phase microemulsions. The result showed that the surfactant alkyl chain length increased with increases in the solubility enhancement and the middle-phase microemulsions greatly increased the solubility enhancement.

## 2.7 Adsolubilization

Effective utilization of adsorbed surfactant aggregates for processes such as admicellar polymerization, admicellar chromatography, and ultra thin film formation, necessitate a more complete understanding of the internal structure and capabilities of these adsorbed layers.

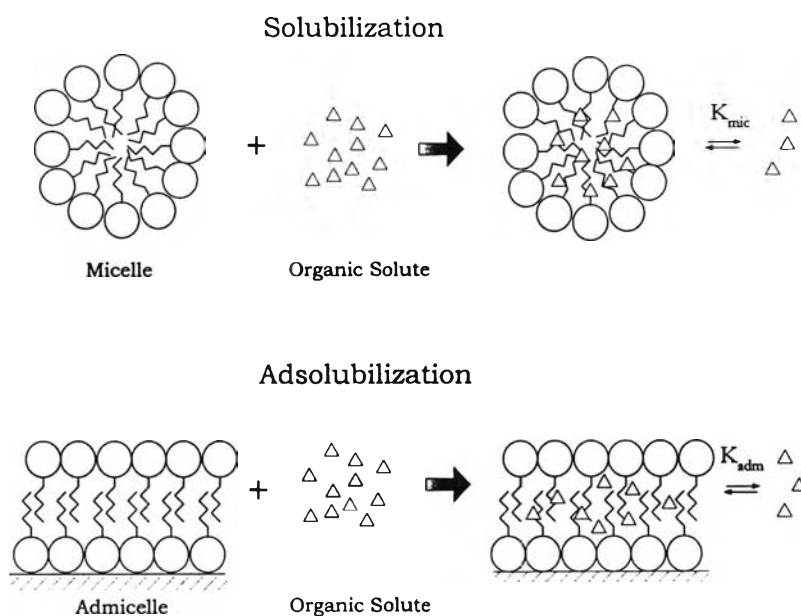
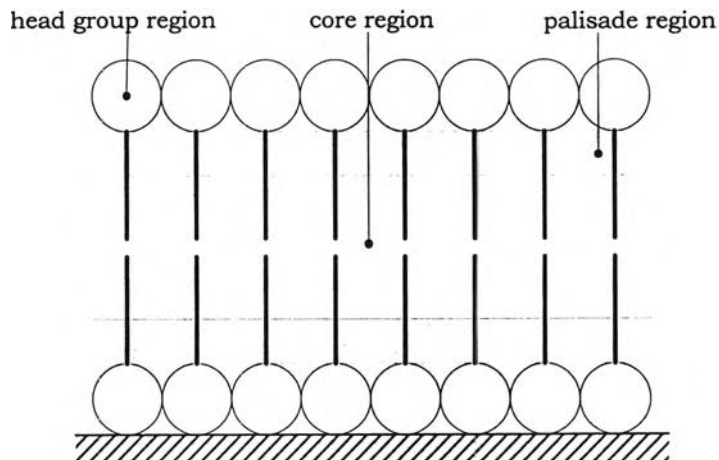


Figure 2. 5 Phenomena of solubilization and adsolubilization

The hydrophobic core of an admicelle provides an ideal site for solubilizing organic solutes. This process is known as **adsolubilization**. Normally, adsolubilization is the partition of organic solutes into the interior of adsorbed surfactant aggregates.

This phenomenon is the surface analog of **solubilization**, where the adsorbed surfactant bilayer plays the role of the micelle. The phenomena of solubilization and adsolubilization are shown in Figure 2.5.

Similar in nature to a micelle, the admicelle is characterized into three-regions. The outer region has the most polar or ionic nature, which consists of the surfactant head group. The inner region or the core region is non-polar in nature, which consist of the hydrocarbon chain of surfactant tail groups. The palisade region is the region between surfactant head groups and the core region. This region is intermediate in polarity and consists of the carbon near head groups, and is also characterized by water molecules that have penetrated the admicelle. The bilayer structure of surfactant is admicelles shown in Figure 2.6.



**Figure 2. 6** The bilayer structure of surfactant admicelles at the solid-liquid interface

Many studies have investigated organic solute partitioning into regions of the admicelles. O' Haver et al. (1989) studied the adsolubilization of alkane and alcohol into surfactant admicelles on alumina surfaces. For alcohol systems, the ratios of alcohol to surfactant admicelles were very high at low surfactant coverage; the adsolubilization of



alcohol increased up to the CMC, and slightly decreased in the plateau adsorption. They also found that the surfactant adsorption increased with decreasing ratio of alcohol to surfactant admicelles to a value that similar to the ratio of alcohol to surfactant molecule in micelles. For alkanes, the adsolubilization into surfactant admicelles was very high. In addition, surfactant adsorption increased with increasing adsolubilization of alkane. From this result, they predicted that the adsolubilization of alkane is approximately the same as the solubilization of alkane into surfactant micelles. This indicated that the interior of admicelles is similar to the interior of micelles.

Lee et al. (1990) showed that the adsolubilization and solubilization of alkane was very similar. They explained the result of alcohol adsolubilization by a two-site model. The model assumed that adsolubilization of a polar solute such as alcohol occurs both in the palisade region and in the hydrophobic perimeter of disk-like admicelles (which are not present in surfactant micelle). Since the fraction of adsolubilized alcohols at the perimeter of admicelles can be significant at low surfactant coverage, the ratios of adsolubilized alcohols to adsorbed surfactant were very high at low surfactant adsorption. For adsolubilization of non-polar alcohol, they found that as the surfactant coverage increased, the availability of the hydrophobic perimeter surface decreased along with the admicellar partitioning coefficient ( $K_{adm}$ ), thereby approaching the micellar partitioning coefficient ( $K_{mic}$ ).

As mentioned, it has been suggested that the admicellar partition coefficient can be used to elucidate the locus of solubilization in the surfactant micelles (Edwards et al., 1991; Rouse et al., 1993; Nayyar et al., 1994). Due to the analogy between micelles and admicelles, the partition coefficient of solubilized micelles can be applied to adsolubilized admicelles. Through the solubilization and the partition coefficients, the following trends have been observed: 1) If the solute partitions primarily to the core, the partition

coefficient increases with increasing mole fraction of the solute solubilization, 2) If the solute partitions to the palisade layer, the partition coefficient decreases with increasing mole fraction of the solute solubilization, and 3) If the solute partition into both the core and palisade region, the partition coefficient remains relatively constant with the mole fraction of solute solubilization (Dickson and O'Haver, 2002).

Kitiyanan et al. (1996) investigated adsolubilization of styrene and isoprene by cationic surfactants onto silica. They calculated the partition coefficient of the organic solutes into admicelles. The partition coefficient for styrene remained constant with the increasing mole fraction of styrene, while the partition coefficient for isoprene decreased with increasing mole fraction of isoprene. They concluded that styrene was partitioned primarily both into the core and palisade layer of admicelles, and isoprene was partitioned primarily to the palisade layer.

Additional research investigated the fundamental aspects of adsolubilization for organic solutes into admicelles (Wu et al., 1987; Esumi, 2001) and adsolubilization of organic solutes by mixed surfactant systems (Esumi et al. 2000 and 2001). Moreover, many researchers are interested in the effect of various parameters to maximum adsolubilization of organic solutes. Factors investigated included the effects of surfactant concentration, solution pH (Esumi et al., 1996), electrolyte concentration (Pradubmook et al., 2003), and structure of organic solute (Dickson and O'Haver, 2002). The results of these research efforts indicate that the amount of adsorbed surfactants can be changed by controlling both the amount of surfactants present at the solid-liquid interface and the structure of the adsorbed layer or adsorbent.