CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Background

Surfactants, which are commonly known as soaps or detergents, are amphiphile molecules because of their unique and interesting characteristic. Their molecular structure consists of both polar, hydrophilic head groups (water-like) and nonpolar, hydrophobic tail groups (oil-like). Due to this nature, surfactants will accumulate at interfacial regions (e.g. water-oil, water-air and liquid-solid interfaces) which result in a reduction of the interfacial energy (Rosen, 1989). According to the nature of the hydrophilic portion of the molecule, surfactants are classified as anionic surfactants (negatively charged head groups), cationic surfactant (positively charged head groups), zwitterionic surfactant (negatively and positively charged head groups) and nonionic surfactant (non charged head groups).

Surfactants are capable of forming many different types of aggregates in aqueous solution depending on surfactant concentration temperature, additive, etc.. For individual molecule of surfactants existing in a solution, it is called as a monomer. 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 cluster known as micelles. In a micelle, the individual monomer is oriented by arranging its hydrophilic head group facing the water or aqueous phase and its hydrophobic tail group oriented into the interior of the spherical aggregates. The first micelle will be formed when the surfactant concentration exceeds the critical micelle concentration (CMC). This value varies from type to type of surfactant.

As additional surfactant is added above the CMC, number of micelles increases (West and Harwell, 1992). The surfactant micellization is shown in figure 2.1.
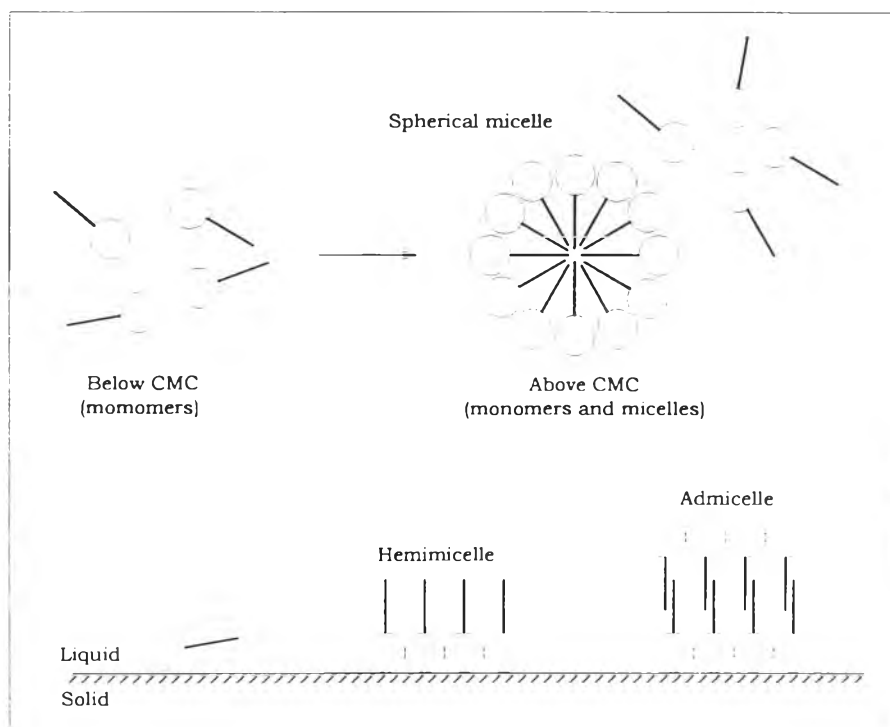
Figure 2.1 Example of surfactant micellization (adapted from West and Harwell, 1992).

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

Surfactant micelles, with hydrophilic head group (polar moieties) at the exterior and hydrophobic tail group (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 provide a hydrophobic sink for organic compounds, which can effectively increase the solubility of organic compounds (Rosen, 1989). Therefore solubility of the organic contaminant increases with an increase in the micelle concentration in the solution.
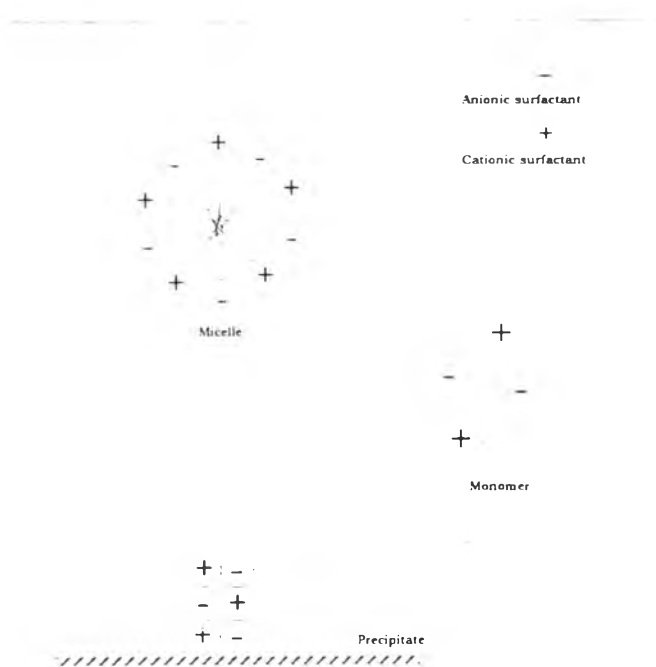
2.2 Mixed anionic and cationic surfactants

There has been a growing interest in research of mixed anionic and cationic surfactants system in this decade including the synergistic effects of mixed micelle formation, microemulsions, solubilization and precipitation (Rosen et al., 1994; Shiau et al., 1994; Li et al., 1999; Li and Kunieda, 2000 and Doan et al., 2002). Mixed anionic and cationic surfactants systems have many unique physicochemical properties which 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 component systems (Bergstrom, 2001; Kang et al., 2001; Chen et al., 2002).

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

the anionic and cationic surfactants form a precipitate with each other and micelles are present in solution.

The precipitation phenomenon of mixed anionic and cationic surfactants system has been studied by Scamehorn and co-worker (Stellner et al., 1988; Scamehorn and Harwell, 1992 and Shiau et al., 1994). 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. They 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 (Scamehorn and Harwell, 1992)

Since mixtures of anionic and cationic surfactants have a potential to precipitate, phase behavior of an individual mixture of anionic and cationic surfactants is necessary to investigate for future application to avoid the precipitation of these mixtures. Li et al. (2000) investigated the solublilization and phase behavior of microemulsion 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 surfactants systems and subsequencely, to evaluate the use of mixed anionic and cationic surfactants in environmental applications such as non aqueous phase liquid removal in the subsurface. Doan et al. (2002) investigated the role of surfactant selection in designing alcohol-free microemulsion by mixed anionic and cationic surfactants microemulsion. They found that twin-head group surfactants were less susceptible to precipitate in a solution than single head group surfactants due to an increase in solubility and steric constraints.

2.3 Adsorption of surfactant on metal oxide surface

The adsorption of surfactants onto a solid interface is of great technological and scientific interest because of its advantages for commercial applications and environmental remediation (Mazari et al., 1993). Examples of such applications include 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 on metal oxide surface such as silica is a complex process since solutes may be adsorbed by ion exchange, ion pairing, and hydrophobic bonding mechanism. Adsorption of surfactants onto metal oxide surfaces has been extensively studied including cationic surfactants onto negatively charge surface (Goloub and Koopal, 1997) and anionic surfactants onto positively charged surfaces (Scamehorn et al., 1981 and Harwell et al., 1985).

Adsorption of surfactant onto 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 (Scamehorn, et al., 1981). The surfactant concentration before and after adsorption is quantified to determine the amount of each species lost by adsorption.

The adsorption of the surfactant on the mineral oxide surface can be expressed and calculated by equation 2.1. In this equation, the adsorption of water or salt is assumed to be negligible and the adsorption of surfactant is assumed to have no effect on the solution density (Lopata, 1988).

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

where

Γ_i = Adsorption of surfactant i (mole/g)

V   = Volume of sample (liter)

$C_{i,b}$ = Initial concentration of surfactant (mole/liter)

$C_{i,a}$ = Equilibrium concentration of surfactant (mole/liter)

W_g = Weight of metal oxide (g)

The adsorption can also be expressed as molecules/surface area as calculated from equation 2.2 by Scamehorn, et al. (1981).

$$\Gamma_{moleules\,/\,nm^2} = \Gamma_{mole\,/\,gram} \, x \, Avogadro's\_number_{molecules\,/\,mole} \, x \, \frac{1}{SSA} \, x \, \frac{1_{m^2}}{10^{18}_{nm^2}} \quad (2.2)$$

Where: SSA = Specific surface area of the adsorbent, m^2/g.

The adsorption isotherm of ionic surfactants onto metal oxide surface is typically **an S-Shaped** isotherm (Somasudaran and Fuerstenau, 1966; Scamehorn et al., 1981). Normally the S-shaped isotherm can be divided into four regions, as shown in Figure 2.3. The designations for regions I, II and III first appeared in the work of Somansudaran and Fuerstuenau (1966).
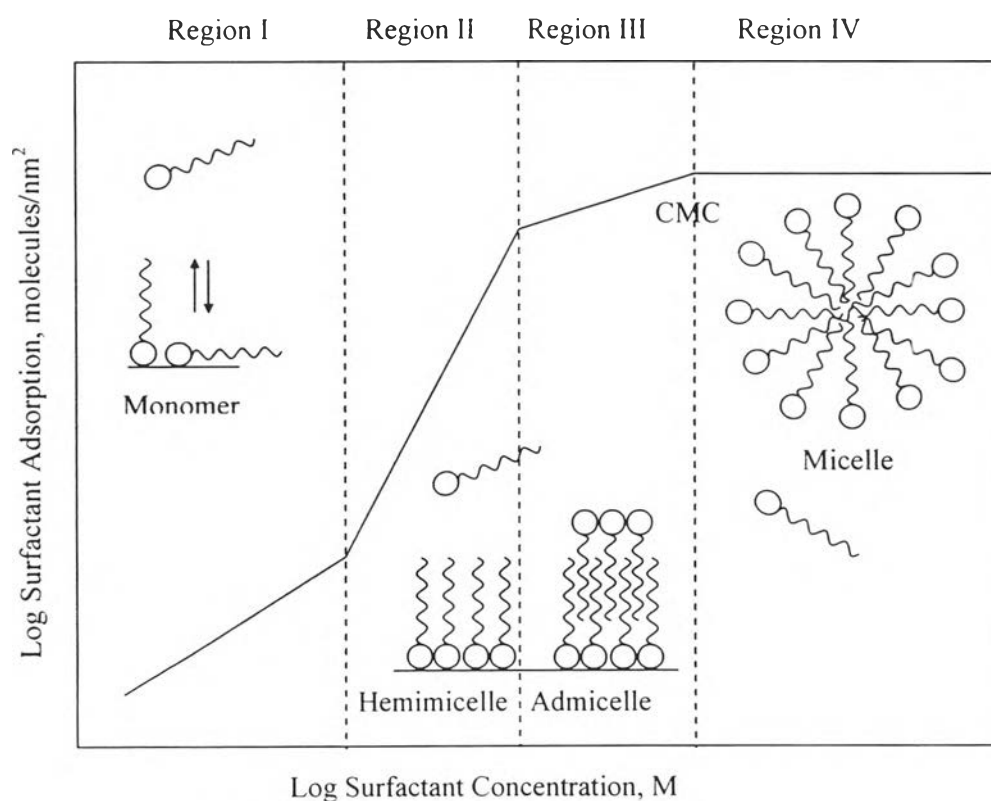
Figure 2.3 Schematic presentation of typical surfactant adsorption isotherm (adapted from Somansudaran and Fuerstuenau, 1966)

Region I corresponds to low surfactant concentration and low surfactant adsorption. This region is commonly referred as the Henry's law region because in this region monoisomeric surfactants generally adsorb in a linear manner. In the Henry's law region, surfactants adsorb mainly by ion exchange, with the hydrophilic surfactant head group more adsorbing on 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 absorb also increases. This increase in slope indicates the beginning of lateral interaction 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 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 lower layer of head groups adsorb on solid phase and an upper layer of head group are facing to the solution. The hemimicelle is considered as monolayer having the head group of surfactant adsorbs on the solid surface while the tail group is contacted with aqueous 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 the Region III to Region IV as transition point is approximately at the critical micelle concentration (CMC) of the surfactant. In some systems, the transition point of the Region III/ Region IV can be reached when the surface of the adsorbent becomes saturated with adsorbed surfactants. For the adsorption of surfactants from aqueous solutions, this will correspond to bilayer completion for ionic surfactants adsorbed on oppositely charged surfaces or to monolayer completion for adsorption on hydrophobic surfaces. The psuedophase separation model for surfactant adsorption for isomerically pure surfactant reported by Harwell (1985).

2.4 Mixed anionic and cationic surfactants adsorption

The solution properties of surfactant mixtures with oppositely charged head groups usually indicated deviation from ideal mixing (e.g. mixture of anionic surfactants). Mixed anionic and cationic surfactants systems are expected to exhibit the greatest diversion form ideal mixing behavior (Harwell and Scamehorn, 1992). There have been few studies on the adsorption of mixed anionic and cationic surfactants (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 surfactant was enhanced by the amount of anionic surfactant present in the system and the adsorption of cationic surfactants with an addition of anionic surfactants to the system exactly equaled to the adsorption of anionic surfactants. They suggested that each adsorbed surfactant can

co-adsorb with cationic surfactants as ion-pairs on non charged silica gel through Van der Waals interactions.

Capovilla et al. (1991) 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 which had been cationic-exchanged by cationic surfactants. The results from their experiments showed that surfactant favored tail-tail adsorption of anionic surfactants through Van der Waals interactions with monolayer of adsorbed cationic surfactants onto laponite clay. The anionic and cationic surfactants bilayers at laponite clay interfaces showed the lower layer cationic surfactant head group adsorbed onto negatively charged clay surface and the upper layer of anionic surfactant head group contact with the solution. They also found that ionic strength and the structure of cationic surfactants affected maximum adsorption and the stability of mixed surfactant bilayers.

2.4.1   The effect to micelle formation of surfactant mixtures

Since the transition point of the amount of adsorbed surfactants onto solid interface and surfactant concentration at equilibrium is the CMC of the surfactant. 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 system 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 system.
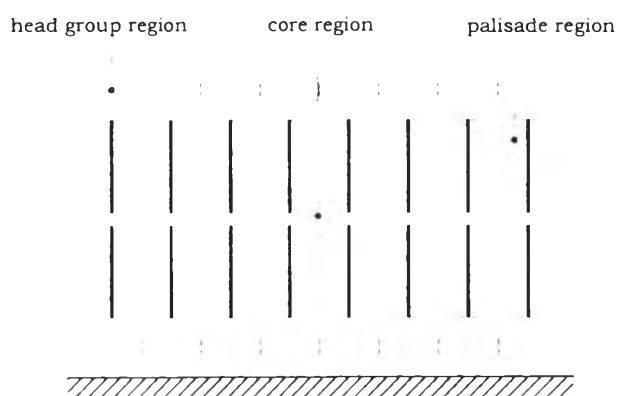
2.5 Adsolubilization

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. The hydrophobic core of an admicelle provides an ideal site for solubilizing organic solutes. This process is known as **adsolublization**. Normally, the partition of organic solutes into the interior of adsorbed surfactant aggregates or micelle is a phenomenon known as **solubilization**, while a term "adsolubilization" explains a phenomenon of the partition of organic solute into bilayer of adsorbed surfactant on solid surface. The phenomena of solubilization and adsolubilization are shown in Figure 2.4.
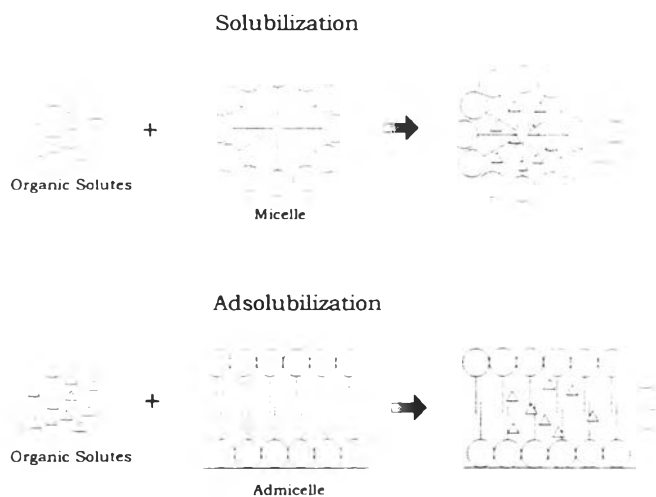
Figure 2.4 Phenomena of solubilization and adsolubilization

Similar in a 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 nonpolar nature, which consists of the hydrocarbon chain of surfactant tail group. The palisade region is the region between surfactant head group and the core region. This region has intermediate polarity which consists of the carbon near head groups, and is characterized by water molecules that have penetrated the admicelle. The bilayer structure of surfactant admicelles are shown in Figure 2.5

Figure 2.5 The bilayer structure of surfactant admicelles at the solid-liquid interface

Many studies have investigated the organic solutes partition to the regions of admicelle. O' Haver et al. (1989) studied the adsolubilization of alkane and alcohol into surfactant admicelles onto alumina surface. For alcohol system, 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 ratios of alcohol to surfactant admicelles to the value which is similar to the ratio of alcohol to surfactant molecule in micelles. For alkanes, the adsolubilization into surfactant admicelles was very high degree. In addition, the adsolubilization of alkane increased with an increase in the surfactant adsorption. From this result they predicted that the adsolubilization of alkane was approximately the same as the solubilization of alkane into surfactant micelles. This indicates that interior of admicelles is similar to the interior of micelles.

Lee et al. (1990) also showed 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 polar solute such as alcohol adsolubilized both in the palisade region and in the hydrophobic perimeter of disk-like admicelles (which is not present in surfactant micelle). Since the fraction of alcohols adsolubilized at the perimeter of admicelles can be significant at low surfactant coverage, the ratios of adsolubilized alcohols to adsorbed surfactant are very high at the low surfactant adsorption. For adsolubilization of non-polar alcohol, they found that as the surfactant coverage increased, the availability of hydrophobic perimeter surface decreased and the admicellar partitioning coefficient decreased, thereby approaching the micellar partitioning coefficient.

As mentioned, it had been suggested that 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 solubilzation and the partition coefficient, the following trends have been observed: 1) If the solute partition primary to the core, the partition coefficient increases with an increase in 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. 3) If the solute partition into both the core and palisade region, the partition coefficient remains relatively constant with the mole fraction of solute solubilzation.

Kitiyanan et al. (1996) investigated adsolubilization of styrene and isoprene of 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 the increasing mole fraction of isoprene. As this results, they concluded that styrene was partition primary both into the core and palisade layer of admicelles while isoprene was partition primary only to the palisade layer.

Additional research investigated the fundamental aspects of adsolubilization for organics solute into admicelles (Wu et al., 1987; Esumi, 2001) and adsolubilization of organic solutes by mixed surfactant system (Esumi et al. 2000 and 2001). Moreover, many researches are interested in the effect of various parameters to maximize adsolubilization of organic solute. Factors investigated the effect on adsolubilization were 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 investigations indicate that the amount of adsorbed surfactant can be changed by controlling both amount of surfactant presence at the solid-liquid interface and the structure of adsorbed layer or adsorbent.

2.6 Column Study

Equilibrium sorption parameters may be determined in the laboratory by conducting batch or column studies. The relative advantage of conducting batch studies is that a variety of factors (chemical concentration, pH, background ions, etc.) can be analyzed with limited effort. However, column studies more closely mimic the field scale by virtue of their continuous flow nature, the solid to liquid ratio in the column, the potential surface access limitations introduced by the first two factors, etc. At the same time, column studies are much more labor intensive. The use of batch studies as preliminary screening tools and column studies to confirm observations made in the batch studies is suggested as a reasonable approach.

Sorption parameters can also be determined from column studies in the laboratory. The results of the column study include a breakthrough curve (a plot of chemical concentration versus time or, in normalized terms, relative concentration versus pore volumes). While conducting the column breakthrough study, the breakthrough of conservative (non-adsorbing) chemical should be evaluated.

Several analyses can be used in determining the r_f (or K_p) from the column data. The first approach would be to utilize the definition of the retardation factor. Under ideal conditions, the retardation factor corresponds to the centroid of the breakthrough curve,

i.e., the value of the pore volume, where the relative concentration of the chemical breakthrough curve is 0.5, would correspond to the retardation factor.

Another approach for determining r_f values from column data would be to utilize mass balance considerations of the chemical adsorbed during the column study. Knowing the influent concentration of the chemical and monitoring the concentration of the chemical exciting the column, the mass of chemical adsorbed can be calculated from area above the plot between concentration and volume). At such time when the concentration of chemical exiting the column is equal to the concentration entering the column ($C/C_0 = 1.0$), the column study can be considered to be at a steady state condition. The mass of chemical adsorbed to the soil can be determined from mass balance that total mass entering column minus mass exiting column minus mass in pore water in the column. Given the mass of chemical sorbed and the mass of soil (as determined when packing the column), a value of q (mass of chemical adsorbed to the soil normalized by the mass of soil) can be determined. The chemical concentration causing this level of adsorption is the initial concentration (which is constant throughout the column). Therefore, the column can be treated as a single point isotherm and a value of K_p can be determined. Utilizing this approach, along with additional parameters determined during the packing of the column such as bulk density (ρ_b) and porosity (η), the value of r_f can be determined (Knox et al., 1993).