

## CHAPTER II

### BACKGROUND

#### 2.1 Theory

##### 2.1.1 Surfactant

Surfactants are one of the most versatile of the products used class chemicals in the chemical process industry under the various of names such as detergents, coagulant, dispersants, emulsifier, de-emulsifier, foaming agents and defoamer. They are appeared in such diverse products as detergents, paints, pharmaceuticals and motor oil. Of late, surfactant applications have been extended to high-technology areas such as electronic printing, magnetic recording, biotechnology, microelectronics and viral research.

“ Surfactant ” is an acronym of “ surface active agents ”; which literally means active at a surface.

Surface active agents have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a lyophobic group, together with a group that has strong attraction for the solvent, called the lyophilic group. This is known as an amphipathic structure. Due to the presence of two types of molecular groups, surfactant molecules which alters the interfacial properties of any two phases by concentration at the interface and thereby changing the interfacial free energy of the interface. If the surfactant is present in an aqueous solution, the lyophobic (solvent disliking) may cause distortion of the solvent liquid structure, increasing the free energy of the system. On the other hand, the

presence of lyophilic (hydrophilic group) prevents the surfactant from being expelled completely from the solvent as a separate phase, since that would require dehydration of the hydrophilic group. The amphipathic structure of the surfactant therefore caused not only concentration of the surfactant at the surface and reduction of the surface tension of the water, but also orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it.

The chemical structures of groupings suitable as the lyophobic and lyophilic portion of the surfactant molecule vary with the nature of the solvent and the conditions of use.

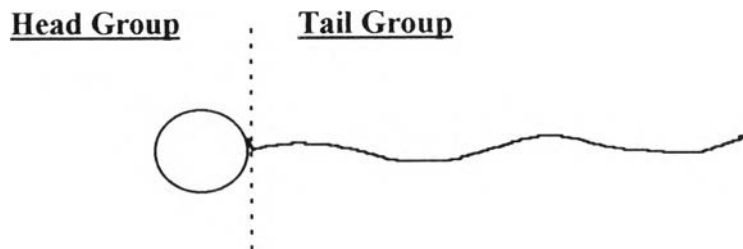
The hydrophobic group is usually a long-chain hydrocarbon residue, and less of the halogenated or oxygenated hydrocarbon or siloxane chain; the hydrophilic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants are classified as:

- Anionic: The surface active portion of the molecule bears a negative charge, for example:  $\text{R-C-O-Na}^+ \text{S}$  (alkylbenzene sulfonate)

- Cationic: The surface active portion bears a positive charge, for example:  $\text{RNH}_3^+ \text{Cl}^-$  (salt of a long-chain amine)

- Zwitterionic: Both positive and negative charges may be present in the surface active portion, for example:  $\text{RNH}_2\text{CH}_2\text{COO}^-$  (long-chain amino acid)

- Nonionic: The surface active portion bears no apparent ionic charge, for example:  $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$  (monoglyceride of long-chain fatty acid)



**Figure 2.1** General representation of a surfactant molecule.

Surfactant-enhanced carbon regeneration is a process which based on two important phenomena of surfactants in solution.

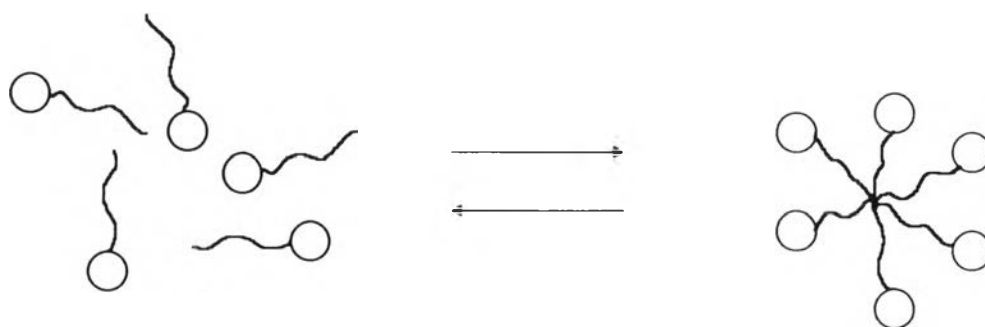
- : Micellization
- : Solubilization

### **2.1.2 Micelle formation by surfactants**

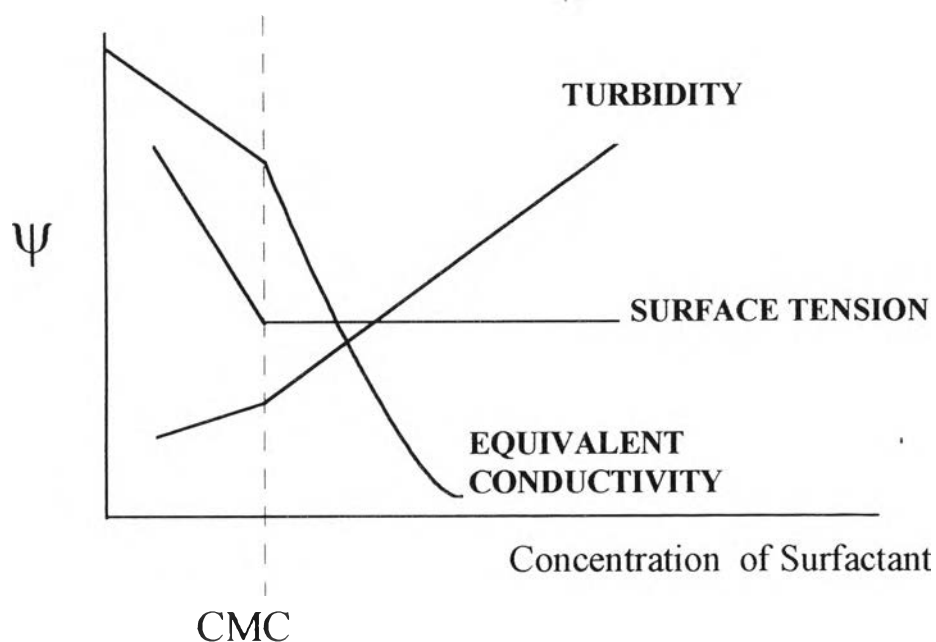
Micellization is the property that surface-active solutes have of forming colloidal-sized clusters in solution. Micelle formation, or micellization, is an important phenomenon not only because a number of important interfacial phenomena, such as detergency and solubilization, depend on the existence of micelles in solution, but because it affects other interfacial phenomena, such as surface or interfacial tension reduction, that do not directly involve micelles.

In an aqueous media, when surfactants are at low concentration, the hydrophobic groups distort the structure of the water and increase the free energy of the system. To minimize the free energy of the system, surfactant monomers should orient so that their hydrophobic groups directed away from the solvent. Therefore surfactant monomers concentrate at the surface by

replacing molecules of solvent at the interface, leading to surface tension reduction. If the surfactant concentration increase beyond the point at which the interface is completely covered with surfactant monomers, then the free energy of the system can be reduced by the aggregation of the surfactants monomers into clusters with their hydrophobic groups directed toward the interior of the clusters (micelles) and their hydrophobic groups directed toward the solvents. These clusters containing 50 to 200 monomers are called micelles. And this phenomenon is called micellization. At a specific concentration of monomers, the micellization begins to occur, is called critical micelle concentration (CMC). Above the critical micelle concentration, the total monomer concentration still remain at the CMC. And if surfactants are added in the solutions, it forms micelles instead of monomers. At the critical micelle concentration, bulk properties are unusual. Changing in almost measurable physical property such as electrical conductivity, surface tension, light scattering and refractive index have been observed.



**Figure 2.2** Micellization.



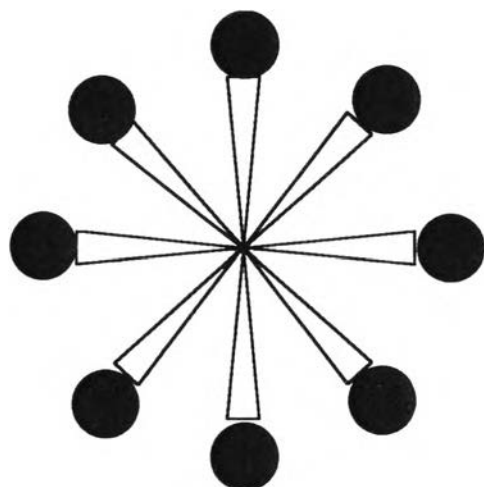
**Figure 2.3** Changes in some physical properties of surfactant solution.

A theory of micellar structure, based upon the geometry of various micellar shapes and the space occupied by the hydrophilic and hydrophobic groups of the surfactant molecules, has been developed by Israelachvili, Mitchell and Ningam (1976,1977) and Mitchell and Ninham(1981). The volume  $V_H$  occupied by hydrophobic groups in the micellar core, the length of the hydrophobic groups in the core  $l_c$  and the cross-sectional area  $a_o$ , occupied by the hydrophilic group at the micelle-solution interface are used to calculate a parameter,  $V_H/l_c a_o$ , which determines the shape of the micelle.

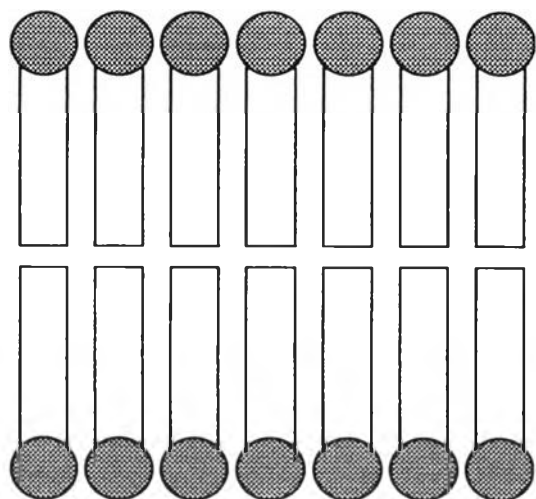
Value of $V_H/l_c a_o$	Structure of Micelle
0-1/3	Spherical in aqueous media
1/3-1/2	Cylindrical in aqueous media
1/2-1	Lamellar in aqueous media
> 1	Inverse (reversed) micelles in nonpolar media

when the value of the parameter  $V_H/l_c a_0$  reaches a value of approximately 1, the surfactant can form either normal lamellar micelles in aqueous media or reversed micelles in nonpolar media. As the value of the parameter gets larger and larger than 1, the reverse micelles in nonpolar media tend to become less asymmetrical and more spherical in shape.

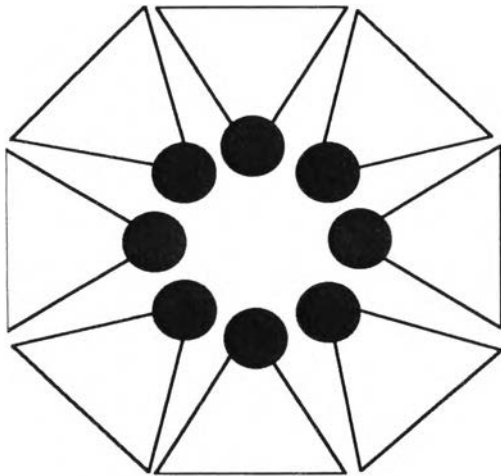
Example: As the hydrophobic groups becomes bulkier,  $V_H/l_c$  increases



**Normal Micelle**



**Bilayer Structure**



**Reverse Micelle**

**Figure 2.4** Model of micelle when  $V_H/l_c$  increases.

### 2.1.3 Micelle formation model

The two popular models for describing monomer-micelle equilibrium are the pseudo-phase separation model and the mass action model (Hiemenz, 1986 ; Rosen 1989).

The pseudo-phase separation model is based on the assumption of a constant monomer concentration at total surfactant concentrations at or above the CMC. This can be viewed as thermodynamically analogous to the vapor-liquid equilibrium. The monomer act as a vapor and micelle act as a liquid phase. The vapor pressure at the dew point is analogous to the monomer concentration at the CMC. All the surfactant interaction is in the dense phase that is the micelle.

The mass action model describes monomer-micelle equilibrium as a chemical reaction equilibrium between monomers and micelles. It considers the micelle as a reversible complex with a distribution coefficient. This is

treatment is exactly like a weak acid degree of dissociation calculation from freshman chemistry, except the stoichiometric coefficients are much larger.

Consider a simple nonionic surfactant monomers (A) forming a micelle:



The equilibrium constant of micellization ( $K_m$ ) is defined as follows:

$$K_m = [A_n] / [A]^n$$

where n : the aggregation number, which is the number of surfactant monomers in a micelle.

A: the surfactant monomer

\* where n is typically 50 to 100 for a spherical micelle.

#### 2.1.4 Solubilization

Solubilization is one of the important properties of surfactants that is directly related to micelle formation. It defines as the spontaneous dissolving of a substance (solid, liquid, or gas) by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material. Although both solvent-solute and solvent-insoluble materials may be dissolved by the solubilization mechanism, the importance of the phenomenon from the practical point of view is that it makes possible the dissolving of substances in solvents in which they are normally insoluble. (Rosen, 1989). This phenomenon



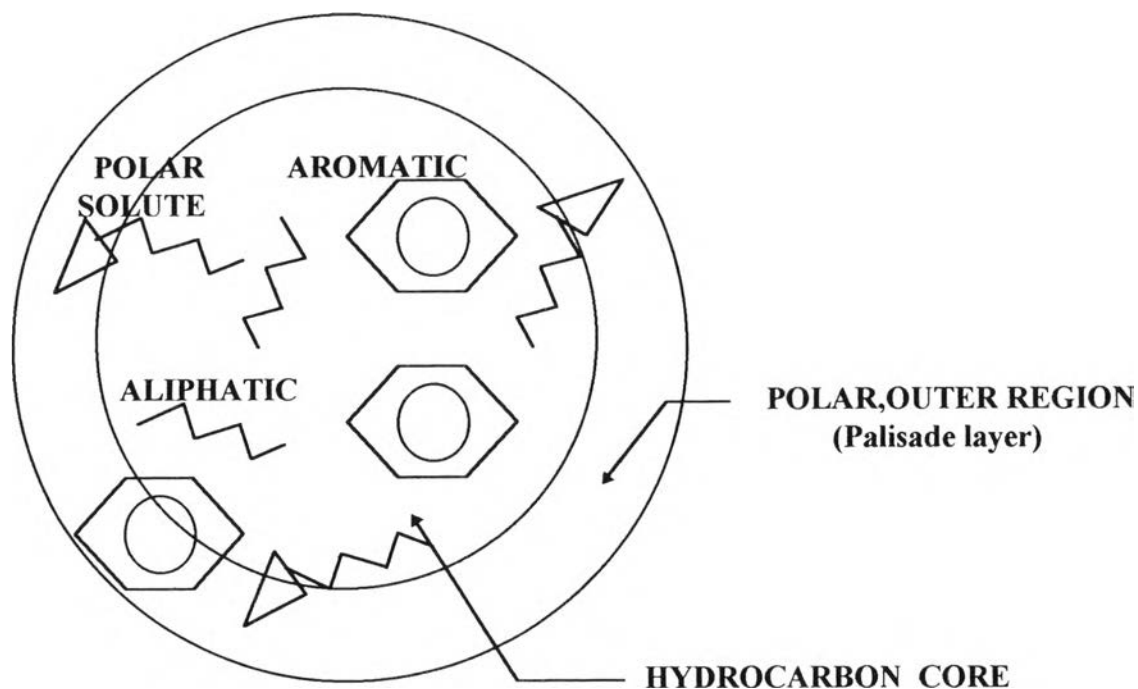
has been widely exploited in industry as well as household application including detergency, pharmaceuticals, agriculture, emulsion polymerization, cosmetics, insecticides etc.

When a surfactant is present in an aqueous solution in concentration greater than its CMC, it forms micelles of 20 to 200 molecules. In this experiment, SDS has a CMC of  $8.3 \times 10^{-3}$  M. and forms roughly spherical micelles containing about 70 surfactant molecules (Lianos, 1984).

The exact location in the micelle at which solubilization occurs (i.e, the locus of solubilization) varies with the nature of the material solubilized and is of importance in that it reflects the type of interaction occurring between surfactant and solubilize.

An organic compound can be solubilized in five locations of varying polarity within the micelle by using X-ray Diffraction, NMR spectrometry etc. as shown in figure 2.5

1. On the surface of the micelle, at the micelle-solvent interface.
2. Between the hydrophilic head groups (e.g. in polyoxyethylenated materials.)
3. In the so-called palisade layer of the micelle between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups and the outer core of the micelle interior.
4. More deeply in palisade layer.
5. In the inner core of the micelle.



**Figure 2.5** Solubilization by micelle.

Saturated aliphatic and alicyclic hydrocarbons and other types of molecules that are not polarized or not easily polarizable are solubilized, in aqueous medium in the inner core of the micelle between the end of the hydrophobic groups of the surfactant molecules. Their UV and NMR spectra indicate a completely nonpolar environment on solubilization.

Polarizable hydrocarbon, such as short chain arenes ( benzene, isopropylbenzene ), have been shown to be solubilized in quaternary ammonium solutions initially by absorption at the micelle-water interface, replacing water molecules that may have penetrated into the outer core of micelle close to the polar heads, but solubilization of additional material is either deep in the palisade layer or located in the inner core of the micelle. In polyoxyethylenated nonionics, benzene may be solubilized between the polyoxyethylene chains of the hydrophobic groups.

Large polar molecules, such as long-chain alcohols or polar dyestuffs, are believed to be solubilized in aqueous medium, mainly between the individual molecules of surfactant in the palisade layer with the polar groups of the solubilize oriented toward the polar groups of the surfactants and the nonpolar portions oriented toward the interior of the micelle. Depth of penetration in the palisade layer depends on the ratio of polar to nonpolar structures in the solubilize molecules. In polyoxyethylenated materials the locus of solubilization for polar dyestuffs may change with change in the length of polyoxyethylene chain, more of the solubilize being solubilized in the vicinity of the oxyethylene groups as the length of the polyoxyethylene chain increase.

Small polar molecules in aqueous medium are generally solubilized close to the surface in the palisade layer or by adsorption at the micelle-water interface. The spectra of these materials after solubilization indicate that they are in a completely, or almost completely, polar environment. Short-chain phenols, when solubilized in polyoxyethylenated nonionics, appear to be located between the polyoxyethylene chains.

In concentrated aqueous surfactants solutions, although the shape of micelles may be very different from that in dilute solution, the locus of solubilization for a particular type of solubilize appears to be analogous to that in dilute solutions, that is, polar molecules are solubilized mainly in the outer regions of the micellar structures, whereas nonpolar solubilizes are contained in the inner portions.

Like surfactant monomers, organic solutes also distribute between aqueous phase and micellar phase. The solubilization equilibrium constant is defined as follows:

$$K = X_o/C_o$$

where  $X_o = C_s/(C_m+C_s)$

$K$  = solubilization equilibrium constant

$C_o$  = the concentration of unsolubilized organic solute in the aqueous phase

$C_s$  = the concentration of solubilized solute in the micelle

$C_m$  = the concentration of surfactant in micelle form

### **2.1.5 Adsorption of surfactant on activated carbon**

Adsorption isotherms for well-purified monofunctional anionic and cationic surfactants are similar on activated carbon and are of the Langmuir type. They appear to show surface saturation in the vicinity of the critical micelle concentration of the adsorbate, with an orientation of the adsorbate perpendicular to the substrate. Adsorption onto these substrates is mainly by dispersion forces. The orientation of adsorbate initially may be parallel to the surface of the solid or slightly tilted or L-shaped, with the hydrophobic groups close to the surface and the hydrophilic group oriented toward the aqueous phase. As adsorption continues, the adsorbed molecules may become oriented more and more perpendicular to the surface with hydrophilic heads oriented toward the water.

The rate of adsorption has been shown to be a function of the position of the hydrophilic group in the molecules, with surfactants containing the hydrophilic group in a central location in the molecule adsorbing faster than those in which the hydrophilic group is terminally located. Moreover, the rate of adsorption on carbon also has been shown to be dependent on the presence in the aqueous phase of additives that affect the structure of water.

Neutral electrolyte addition increases both efficiency of adsorption of ionic surfactants, by decreasing the electrical repulsion between the similarly charged adsorbed ions and oncoming ions, and the effectiveness of adsorption, probably by decreasing the electrical repulsion between the similarly charged adsorbed ions, permitting closer packing. The addition of small amounts of cationic to aqueous solution of anionic, or small amounts of metal carboxylates to cationic solutions, has also been shown to increase the adsorption of the predominant ionic surfactant.

## **2.2 Previous work**

### **2.2.1 SECR in liquid phase**

In previous studies for SECR to treat carbon used in a liquid phase applications, Blakeburn and Scamehorn (1989) found that a regenerant stream containing a cationic surfactant can remove of approximately 80% tert-butylphenol with a reasonable volume of surfactant solution. Removal of the last 20% of the adsorbate from the carbon is very difficult due to these adsorbate being chemisorbed instead of physically adsorbed. The residual surfactant can be washed off by a water flush step using a large volume of water.

Bhummasobhana et.al (1995) also studied the effect of regeneration and flushing conditions on the breakthrough of the solute (phenol) in subsequent adsorption cycles, and hence, on effective adsorption capacity upon repeated usage. It showed that the reduction of the effective carbon adsorption capacity is less if a higher regenerant concentration of surfactant, more pore volumes of regenerant, or more pore volumes of water flush solution are used.

Bhummasobhana et.al also investigated the activated carbon regenerated by the SECR in liquid phase application can be effective in subsequent adsorptions.

### **2.2.2 SECR in vapor phase**

In a previous study of the use of SECR to treat activated carbon used in a vapor phase application, Roberts et al.(1989), studied solutes toluene and amyl acetate, and used an anionic surfactant in regenerant solution. SECR did not have serious effects on the performance of the carbon over nine regenerant cycles. However, detailed breakthrough curves were not regenerated. Roberts et al. also found that the regeneration step was equilibrium limited for removal of toluene, but mass transfer effects were important for amyl acetate because of its high molecular weight. The water flush was found to be nearly equilibrium limited.

These three previous studies have demonstrated the general features of SECR in liquid and vapor phase applications. The purpose of this study is to measure breakthrough curves for adsorption of model organic solute (trichloroethylene) from air in an adsorption cycle following a regeneration/flush process under varying condition to quantify the effect of the regenerant process on effective adsorption capacity on repeated usage.