Chapter I

Introduction

Surfactant is a general term for surface active agents which include wetting agents, active ingredient in detergents, emulsifiers, dispersants, foaming agents, penetrating agents, and spreaders. The surfactant generally consists of two distinct moieties: a hydrophobic region, usually a long hydrocarbon chain, and a hydrophilic region such as an anion group or ethylene oxide residue. For this reason, it is an amphipathic molecule. The sodium salt of fatty acid (i.e., an ordinary soap) would be an example of the surfactants :

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{O}{\underset{}{C}}-O^-Na^+$$

$$\underbrace{\hspace{5cm}}_{\text{hydrophobic}} \qquad \underbrace{\hspace{1cm}}_{\text{hydrophilic}}$$

Types of surfactants

Depending on the chemical structure of the hydrophilic moiety bound to the hydrophobic portion(1), the surfactants may be classified as anionic, cationic, ampholytic or zwitterionic and nonionic .

1.<u>Anionic</u>, for example, Sodium 1-dodecanesulfonate
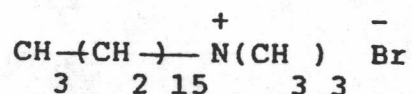
$$CH_3(CH_2)_{11}SO_3^-Na^+$$

2.<u>Cationic</u>, for example, Cetyltrimethyl ammonium bromide (CTAB).

$$CH_3\text{---}(CH_2)_{15}\text{---}\overset{+}{N}(CH_3)_3 \ \overset{-}{Br}$$

3.<u>Ampholytic or Zwitterionic</u>, for example, 3-(Dimethyl dodecylammonio)-propane-1-sulfonate

$$CH_3\text{---}(CH_2)_{11}\text{---}\overset{+}{N}(CH_3)_2\text{---}CH_2\text{---}CH_2\text{---}CH_2 \ \overset{-}{SO_3}$$
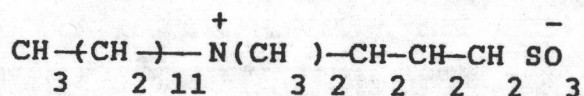
4.<u>Nonionic</u>, for example, Polyoxyethylene (3) decanol

$$CH_3\text{---}(CH_2)_9\text{---}O\text{---}(CH_2\text{---}CH_2\text{---}O)_3\text{---}H$$
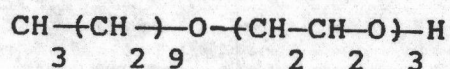
The above examples are the synthetic surfactants, however, there are surfactants which obtained from nature called the naturally occurring surfactants, for example, cholic acid .
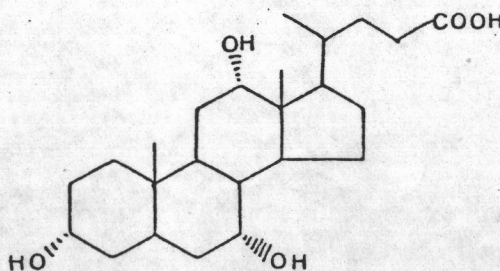
When surfactant dissolves in water,they can cluster with their hydrophobic parts in the centre of the cluster and their hydrophilic part on the outside, such an arrangement is called "a micelle". Generally, micelles at concentration close to their critical micelle concentration are roughly spherical(1,2). The structure of an ionic micelle in an aqueous solution is shown in Figure 1.

Aqueous
bulk
phase

Core

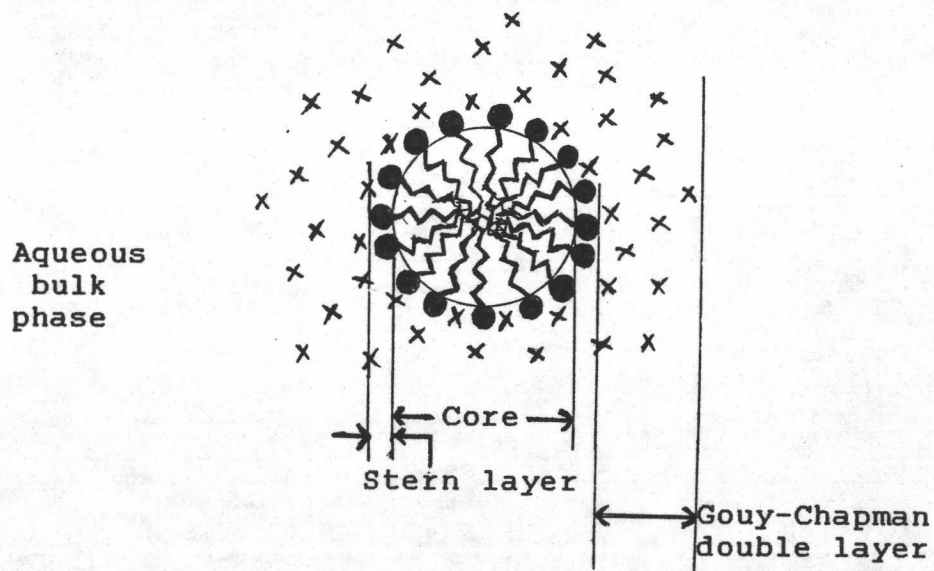Stern layer

Gouy-Chapman
double layer

Figure 1. Cross section of a spherical ionic micelle.

Figure 1. shows a typical ionic micelle in aqueous solution, which roughly spherical(1,2) with sequestering of the hydrophobic hydrocarbon chains away from the aqueous phase to form a micelle core. The polar groups are located at the hydrophobic-water interface. Water is associated with micelles most certainly with the polar head group or stern layer region, and probably penetrating a little into the hydrocarbon core. For ionic micelles such as cetyltrimethylammonium bromide, CTAB, most of the inorganic counterion (e.g., OH^-, Na^+ or Br^-) are located in stern layer. However, a sizable fraction (10-20%) of the ions, which varies with the type of the surfactant used, is located in the aqueous bulk or in the immediate surroundings of the micelle, or Gouy-Chapman layer. This arrangement leads to a large net charge in the micelle, if the aggregation number is 70-100, then the net charge can be 10 to 20 negative or positive groups, depending on the micelle.

Micelles are probably not truly spherical(2,3). The surfactant molecules pack together as closely as possible to eliminate as much water as possible from the structure. The degree of packing is affected by the repulsion of the polar head groups of the structure, which try to maintain as great as separation as possible. A compromise between these two opposing forces, the aggregation of the alkane chains and the repulsion of the head groups, are achieved by forming a structure with curve surface where the separation of head groups is maximized. Thus roughly spherical or cylindrical surface are possible.

Micellization

The formation of micelle(1,3) can be explained by the principle of the attractive and the repulsivse forces, namely ;

1. The attractive force is the hydrophobic interaction which composed of some distinct free energy factors, such as transferring of the hydrophobic portion of the surfactant from water to the alkane liquid state, and the increasing entropy of water molecule. Once a micelle is formed, a negative value of Giff's free energy of the system(ΔG°) will result.

2. The repulsive force is primarily due to repulsion of the ionic head groups. This force regulates the shape and size of micelle. Head group repulsion is the main factor contributing to the repulsive force in ionic micelles.

The interplay of the two effects leads to overall ΔG^o of micellization. To understand the factor involved in the formation of a micelle, the free energy of a monomer surfactant molecule must be considered as a function of the state of association. The free energy may be broken down into two main terms: a hydrophobic contribution that favors association and a term marking the repulsion between head groups of the surfactant that limits the size of the assembly. This consideration is, however, concerned mainly with ionic micelle. With non-ionic micelles, the hydrophobic term is similar to the one in ionic micelles. Nevertheless, the repulsion terms are more difficult to express in non-ionic micelles. The shape of the micelle is important because this feature influences the pack of the head groups and, hence, the repulsion energy term. The free energy(3) of transferring of a monomer surfactant from the aqueous phase to the micelle, ΔG^o, is broken down into two parts:

$$\Delta G^o = \Delta G_a + \Delta G_r$$

where ΔG_a and ΔG_r represent the attractive and repulsive fractions of ΔG, respectively. Thermodynamically, micelle will be form when the free energy of micelle formation (ΔG^o) have the negative value. Micellization will occur when the attractive force have more effect over the repulsion ones, hence, ΔG_a has negative value more over the positive value of ΔG_r, then the value of ΔG^o will less than zero. The negative value of ΔG^o shows the chance of micelle formation.

As mentioned above, the attractive factor or the hydrophobic interaction will relate to the numbers of methylene groups(3) in hydrocarbon chain and the numbers of surfactants in micelle, which relates to concentration of surfactant. The first minimum concentration, which micelle is formed, called "critical micelle concentration (cmc)" and the number of surfactant molecules in micelle called " aggregation number (N) " . Both critical micelle concentration and aggregation number have no specific values(1) but depends on other factors , for examples, temperature, pressure, structure of surfactants, and any substances in the solution.

The critical micelle concentration of surfactant is physically observable from the discontinuities or changes in slope of the curves of surface tension, electrical conductance, etc., which is plotted with the concentration of surfactant. The quantity of micelles which present in the system becomes appreciable at this point also.

The micellar catalysis of organic reaction has been widely studied in recent years(1-4). One of the reasons for the intensive study of micellar catalysis is the belief that the reaction in micelle may be a useful model for the enzyme-catalysed reaction in a biological system. The micellar catalysis(1-6) is generally attributed to the concentration of reagents within the smaller volume of the micelle.

From a study of Manger, F.M. et.al.(7), they proposed the kinetic model for the micellar catalysis to be mimic to the model of enzyme-catalysed process. The kinetic model was shown in Scheme 1 .

$$M + S \underset{\longleftarrow}{\overset{K}{\longrightarrow}} [MS]$$

$$\downarrow k_w \qquad\qquad \downarrow k_m$$
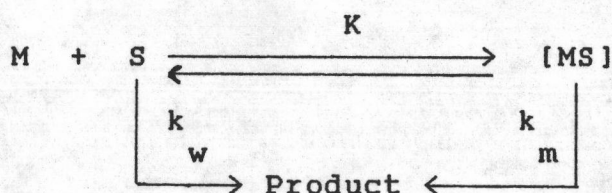
$$\longrightarrow \text{Product} \longleftarrow$$

Scheme 1

Where M is a micelle, S is a substrate, [MS] is The micelle-substrate complex, K is the equilibrium or binding constant, k_m and k_w are rate constants for product formation with and without micelle, respectively. This model leads to equation 1(1,7).

$$\frac{1}{(k_w - k_{obs})} = \frac{1}{(k_w - k_m)} + \frac{1}{(k_w - k_m)} \frac{N}{K} \frac{1}{(C_D - cmc)} \qquad (1)$$

Where k_{obs} is the observed pseudo first-order rate constant, and C_D is the total concentration of surfactant. This equation is used with the assumptions as following :

1. It has been assumed that the substrate does not form complex to each surfactant molecule.

2. The ratio of a micelle to a substrate in complex must be 1:1 .

3. The substrate does not change the micellization and cmc .

4. The micellar structure will be changed if the surfactant concentration is changed.

5. The other reagents can partition between micelle and water as well (Scheme 1).

However, the plot of $1/(k_w - k_{obs})$ VS $1/(C_D - cmc)$ in proper range of C_D will give the straight line only if the behavior of reaction obeys the Scheme 1 . In this case, C_D must be higher than cmc and k_{obs} must be larger than k_w too. From the equation 1, k_m will be obtained from the intercept and K/N from the slope. Those two values will be useful for the next calculation step.

Investigation of past work

Hegarty,A.F. et.al.(8,9) investigated the mechanism of hydrolysis of a peptide bond by an enzymatic process. They wanted to mimic the active site of enzyme, which has either carboxylic or hydroxylic group . The carboxylic group as the substituent at ortho(o-) or para(p-) position

in N-aryl of phenyl N-arylcarbamate was hydrolysed in an ordinary basic solution. At pH below 11, they discovered that the reaction would be accelerated when a carboxylic group at o-position acted as a nucleophile. This led to the formation of the cyclic intermediate instead of hydroxyl ions in the solution(9). Beside the carboxylic group, other groups such as amide, hydroxyl groups can cause the formation of cyclic intermediates too(8,9). The reaction mechanism was proposed as shown in Scheme 2 .
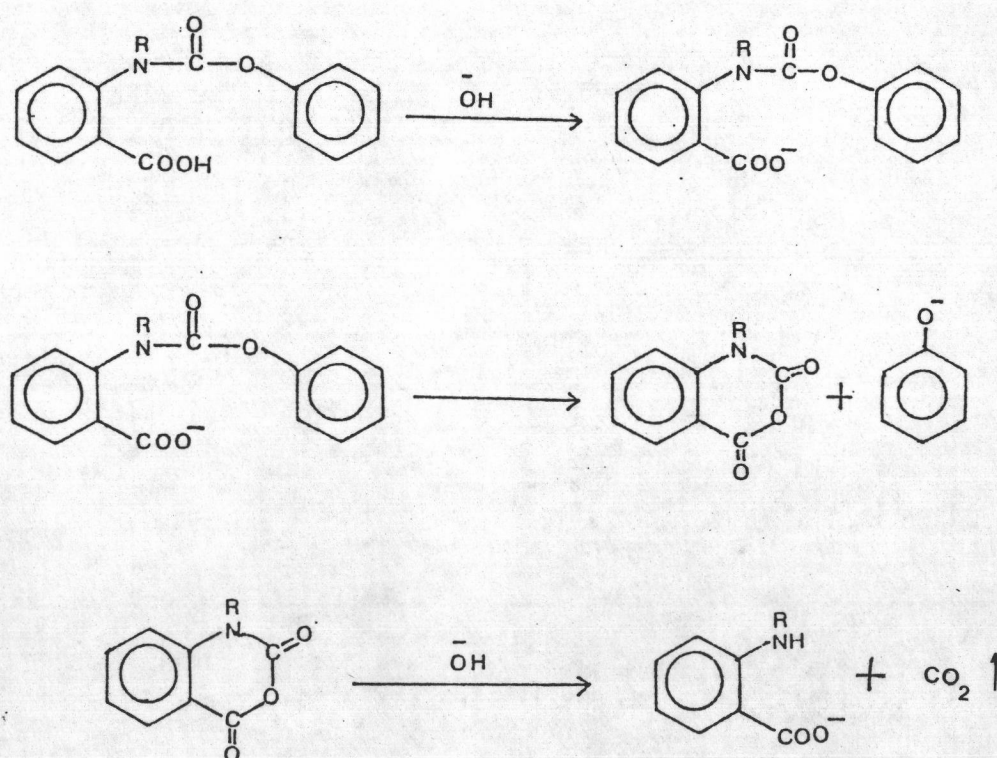
Scheme 2.

As mentioned before, micelle can mimic enzyme to some degrees(1). The hydrolysis of carbamates in micellar environment is concerned to study the micellar effect as in the same reaction as Hegarty did. Furthermore, the correlation between the structure and the rate of reaction will be also studied.

Since the reaction is basic hydrolysis, the hydroxyl ion ($\overline{OH}$) is therefore the reactive species in the reaction. In order to attract $\overline{OH}$ and to stabilize the intermediate, the cetyltrimethylammonium bromide(CTAB) is proposed to use as the cationic surfactant to form the cationic micelles.