

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

Surfactants have many applications in various fields of industry, agriculture, and household. Some applications are connected with adsorption abilities of surfactants having amphiphilic character and the others exploit the abilities of surfactants to form micelles (Materna and Szymanowski, 2002).

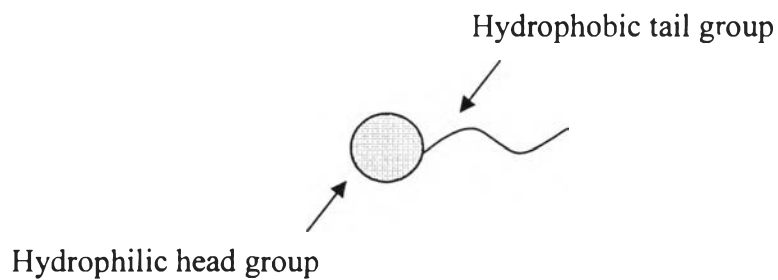
2.1 Introduction to Surfactants

Surfactants, a contraction of the term *surface-active agent*, are materials that tend to accumulate at the surface or interface. These surfaces normally refer to the boundary between the two immiscible phases, which can be solid/liquid, liquid/liquid, or liquid/gas (Clint, 1992). Typically, the molecular structure of surfactant is amphiphilic consisting of two structural groups, which are hydrophilic group and hydrophobic group, as shown in Figure 2.1(a). The hydrophobic group has very little attraction for the aqueous solvent, *i.e.*, water while hydrophilic group has a strong attraction for the water (Rosen, 1989). The hydrophobic group is usually called the “tail group” and commonly a long chain hydrocarbon. In contrast, hydrophilic group is usually referred to as “head group”. It is an ionic or highly polar group.

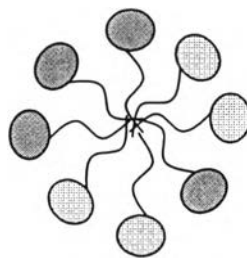
Depending on the nature of the hydrophilic group, surfactants are classified as anionic, cationic, zwitterionic, and nonionic. Anionic surfactants have a negative charge while cationic surfactants have a positive charge in the hydrophilic portion. Zwitterionic surfactants carry both negative and positive charge in the hydrophilic portion. Nonionic surfactants have no apparent ionic charges in the hydrophilic portion. Most of hydrophilic portions of nonionic surfactants are ethylene oxide groups.

At low surfactant concentration, surfactant molecules form adsorbed monolayer at the surface. This monolayer can decrease surface tension of media, which are dissolved in. When surfactant has higher concentration, the surfactant molecules will form organized aggregate, called micelle, at specific concentration of

surfactant known as critical micelle concentration (CMC). The formation of micelles is generally viewed as a compromise between the tendency for alkyl chains to avoid energetically unfavorable contacts with water and the preference for polar head group to maintain contact with the aqueous environment. Figure 2.1 shows the schematic sketch of a surfactant molecule and a surfactant micelle.



(a) a surfactant molecule



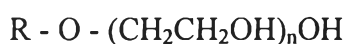
(b) a surfactant micelle

Figure 2.1 The schematic sketch of (a) a surfactant molecule and (b) a surfactant micelle.

2.2 Nonionic Surfactants

Nonionic surfactants are usually prepared by addition of ethylene oxide to the compound that contains one or more active hydrogen atoms such as alkylphenols and fatty alcohols (Mackay, 1987). The hydrophilic parts of nonionic surfactant are normally an ethylene oxide (EO) head group or so called ethoxylate group. Nonionic surfactants are gentler than ionic surfactants and will not be ionized in the aqueous solution. They have been used extensively in household and industrial products such as low-temperature detergents and emulsifiers (Rosen, 1989).

Nonionic surfactants can be separated into many types such as alcohol ethoxylate (AE) and alkyl phenol ethoxylate (APE). AE is a nonionic surfactant used in this work. The fundamentals of AE production is an addition of ethylene oxide to hydroxyl group of alcohol. AE can be easier biodegraded and has lower viscosity than those APE surfactants. As a result of the recent emphasis on biodegradable surfactants, alcohol ethoxylates have widely been used for both household and industrial products (Mackey, 1987). They can be used in the formulation of household cleaner and used as an emulsion as well. Their structures can be shown in the following.



where R represents hydrocarbon chain.

and n represents number of moles of ethylene oxide.

2.3 Cloud Point of Nonionic Surfactants

An aqueous solution of nonionic surfactants becomes cloudy when it is heated above a well-defined temperature known as cloud point (CP) or lower consolute temperature (LCT). At temperatures above the cloud point, nonionic surfactant solution separates in two-phase regions of its phase diagram where the two liquid phases are in equilibrium. Figure 2.2 shows an example of phase diagram of nonionic surfactant C₁₀EO₅ in water. The solution appears cloudy because it is an

emulsion of one phase in another composing of very large micellar aggregations. Moreover, this solution can be separated into two isotropic aqueous phases by either gravity or centrifugal force due to their density differences. These two phases are called micellar-rich phase or coacervate phase and micellar-dilute phase. The coacervate phase contains high concentration of surfactant while the dilute phase has a surfactant concentration typically equal or slightly exceeds the critical micelle concentration (CMC) (Scamehorn and Harwell, 1989). In addition, this phase separation is a reversible process; hence cooling the solution below the cloud point causes both two phases come together and form a homogeneous solution once again (Clint, 1992). Figure 2.3 shows phase partition of nonionic surfactant above the cloud point.

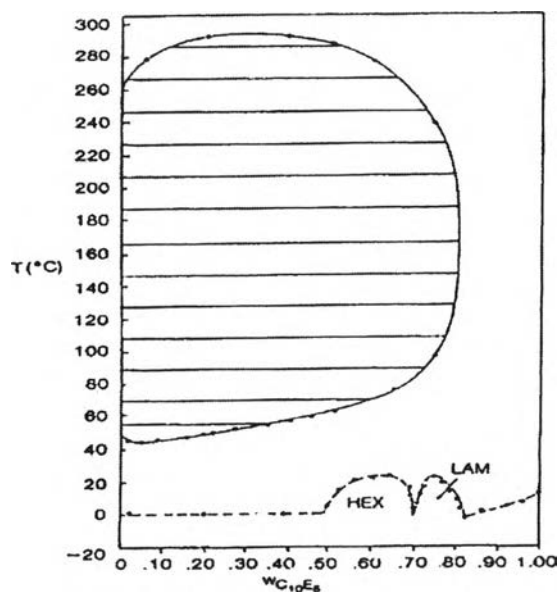


Figure 2.2 Phase diagram for the nonionic surfactant C₁₀EO₅ in water showing the large closed-loop region where two liquid phases coexist (Clint, 1992).

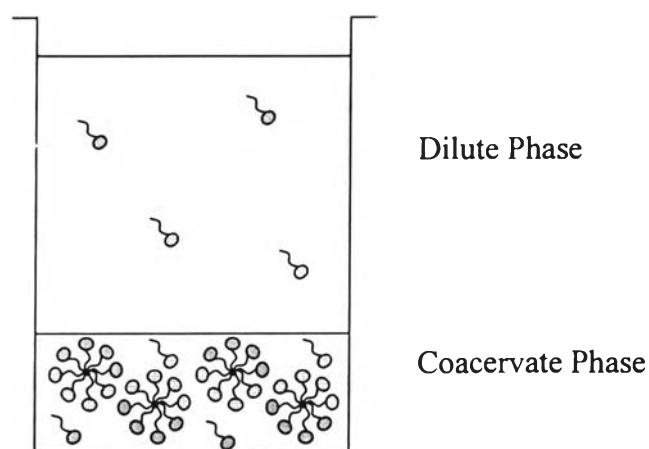


Figure 2.3 Phase partition of nonionic surfactant solution at temperatures above cloud point showing both dilute and coacervate phases.

2.4 Mechanism of Phase Separation

The cloudy behavior of nonionic surfactant solution attributes to the dehydration of ethylene oxide polar head groups. This dehydration process involves in breaking of hydrogen bond between hydrophilic head groups and water molecules (Akita and Takeuchi, 1995). During the dehydration process, both aggregation numbers of micelles and intermicellar attraction are increased. On the other hand, intermicellar repulsion is decreased as temperature increased. This is because micelles of surfactant have more hydrophobicity enough to come together and then form a micelle-rich phase or coacervate phase at temperatures above the cloud point.

As the temperature approaches the two-phase boundary, the intermicellar attraction is increased substantially (Corkill and Goodman, 1969). In contrary, decreasing of the intermicellar repulsion makes aggregation numbers of micelles increase. These surfactant aggregations are so large that the solution becomes visibly turbid.

In 1986, Claesson and co-workers stated that there were intermicellar repulsive forces at low temperatures but these forces became attractive forces at temperature above the cloud point. The increase of interaction is a consequence of strong entropy dominance. The water that hydrates hydrophilic chains is higher

structured (lower entropy and enthalpy) than bulk water. When the hydration layers of two approaching chains overlap, the partial exclusion of water from the contacting zone causes increase in entropy and enthalpy of the system. Thus, the phase separation occurs in order to reduce the entropy which causes the increment of surfactant concentration.

Friberg and Lindman (1992) suggested that the oxyethylene segments (EO) in the nonionic surfactants changed their conformation if temperature or concentration was changed. At low temperatures, the nonionic surfactants are relatively more soluble in polar solvents such as water, while they are more soluble in non polar solvents at high temperatures. The change in the conformation makes the EO chains less polar, causing the phase separation to occur.

In 1995, Kato *et al.*, proposed that the entangled network among the micelles was gradually changed to the multi-connected network as the temperature was increased. In other words, the number of cross-links of wormlike micelles increases with increasing temperature.

2.5 Parameters Affecting Cloud Point

Since cloud point is strongly depended on the molecular structure of nonionic surfactant, it can also be influenced by the hydrophile-lipophile balance (HLB) of surfactants. Several trends in cloud point with surfactant molecular structure are commonly known: cloud point increases with the relative ethylene oxide content and decreases with increasing alkyl carbon chain length (Huibers *et al.*, 1997). At particular hydrophobic portion, the larger of ethylene oxide percentage is the hydrophilic part, the higher the cloud point. For example, highly hydrophilic chain (%EO > 75) often does not have a cloud point below the boiling point of the water (Rosen, 1989). On the other hand, the cloud point is lowered by increasing the alkyl chain length at specific hydrophilic head group (Gu and Galera-Gomez, 1999)

The other substances added into the surfactant solution such as other surfactants, electrolyte, and other polar or non polar compounds also affected the cloud point. The addition of either anionic or cationic surfactants can increase the cloud point due to increasing of repulsive force between the surfaces of mixed

micelles. Moreover, the addition of other nonionic surfactants can also change the cloud point and the new cloud point for this mixed surfactant is in between the cloud point of the two pure surfactants (Rosen, 1989).

In 1997, Huibers D.T. and co-workers notified that cloud point of aqueous surfactants solutions can be strongly influenced by the presence of other materials. For example, cloud point can be decreased by the introduction of polar compounds, anions that are water structure former (hard bases, F^- , OH^- , SO_4^{2-} , Cl^- , and PO_4^{3-}), and certain cations (NH_4^+ , alkali metal ions except for Li^+). Cloud point can be increased by an addition of long chain non-polar material, anions that are water structure breakers (large, polarizable anions, soft bases, SCN^- , I^-), and certain cations (polyvalent cations, H^+ , Li^+).

Addition of non-polar compounds, *e.g.* saturated aliphatic hydrocarbons, increases the cloud point while adding polar compounds, *e.g.* phenol, decreases the cloud point. The increment of the cloud point by an addition of non-polar compounds may be because the non-polar solubilize made a micelle size increase. As the micelle size increased, the area of micelle-water interface increased, and then the dehydration of hydrophilic chain was higher. In contrary, the polar compounds can decrease the dehydration of hydrophilic chains as a result of competition for the hydration regions by polar solubilize. Moreover, Gu and Galera-Gomez (1999) indicated that the effect of added organic compounds on the cloud point was depended on their solubilities in water.

In 1995, Komaromy-Hiller and co-workers indicated that presence of electrolytes in the nonionic surfactant solution change the cloud point, which called salting effect. For example, addition of sodium chloride (NaCl) or chloride ions (Cl^-) depress the cloud point due to the salting-out effect. Salting-out effect is the decreasing of availability of non-associated water molecules for dehydration of hydrophilic chains. In contrary, addition of iodide ions (I^-) raise the cloud point because iodide ion can produce more available water molecules to interact with the head groups which called salting-in effect. In 1995, Gu and Galera-Gomez showed that the cloud point decreases dramatically when the electrolytes are added, in the order $LaCl_3 > MgCl_2 > NaCl$, which implied that polyvalent cations or counterions are more active than the univalent cation.

2.6 Cloud Point Extraction

To apply the phase separation between coacervate and dilute phases, the cloud point extraction (CPE) or also called liquid-coacervate extraction has been studied (Frank and Willie, 1999). The cloud point extraction is similar to an aqueous two phase partitioning system rather than to solvent extraction. When a nonionic surfactant solution containing organic solute is heated, the phase separation occurs and the solute is partitioned between dilute and coacervate phases. In general, non-polar organic solute is solubilized and concentrated at the coacervate phase while the dilute phase that remains only trace amounts of organic solute can be released to the environment, as shown in Figure 2.4.

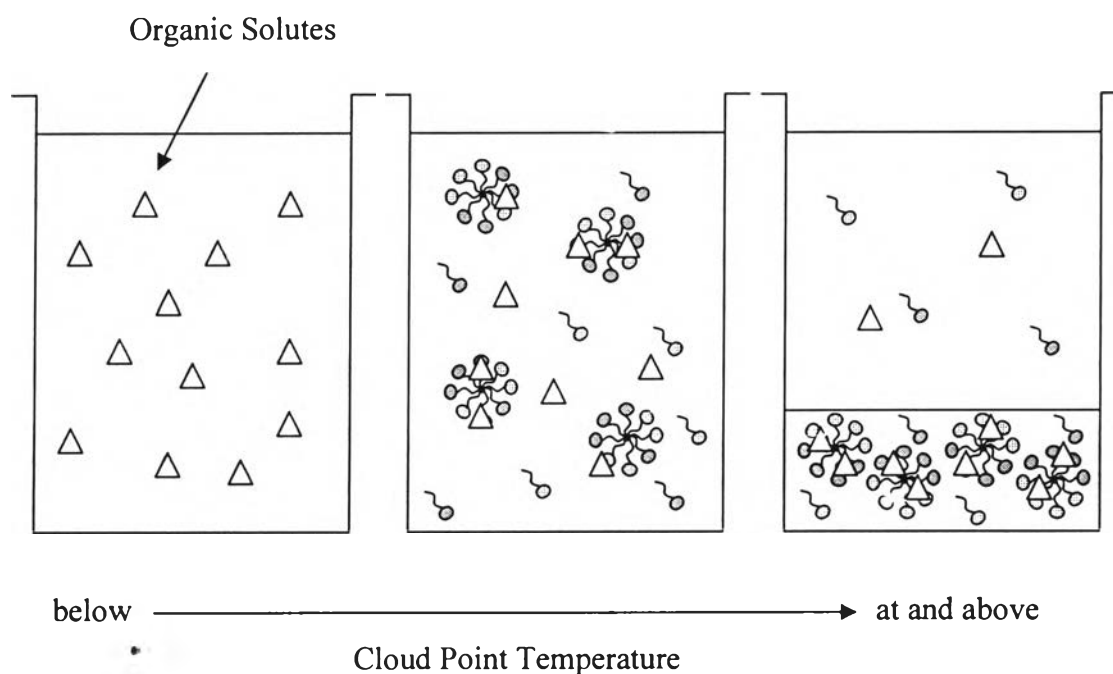


Figure 2.4 The schematic illustration of the cloud point extraction.

The used of cloud point technique seems more advantageous as the clouding is reversible and transparent solution are obtained after cooling (Materna and Szymanowski, 2002). CPE technique can also be applied to extract many desired chemicals. In 1995, Saitoh and Hinze studied the CPE of hydrophobic protein. In

1999, Quina and Hinze showed that CPE method for organic compounds has been interesting due to the environmental concern.

Akita and Takeuchi (1995) suggested that adding sodium chloride (NaCl) and phenol increased the efficiency of CPE for removal of pyridines. They also found that the higher concentration of surfactant can improve the efficiency of CPE, as a result of the higher capacity. These results were confirmed by Kimchuwanit *et al.* (1995). Moreover, Kimchuwanit and co-workers also showed that the efficiency can be improved by raising the operating temperature.

In 2000, Sakulwongyai *et al.*, examined the removal of chlorinated ethanes, which are *tetra*-chloroethane, *tri*-chloroethane, and *di*-chloroethane, from wastewater. They showed that the surfactant aggregated in the coacervate phase are the micelle-like in structure due to the equality of the solubilization equilibrium constant and the coacervate equilibrium constant. Furthermore, they also concluded that the amount of solute removal for higher ethane chlorination is higher than the lower ethane chlorination.