



CHAPTER II LITERATURE SURVEY

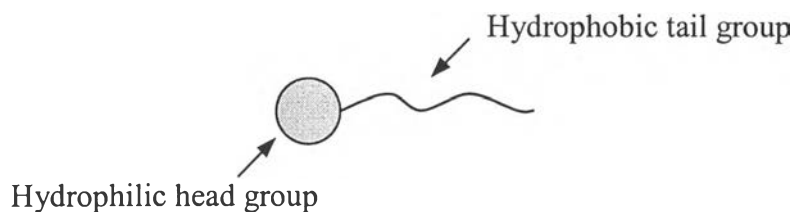
2.1 Introduction to Surfactants

Surfactants, a contracted term of surface active agents, are materials that tend to accumulate at the surfaces or interfaces. 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 surfactants is amphiphilic consisting of two structural groups, which are hydrophobic group and hydrophilic group. 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 is commonly a long chain hydrocarbon. In contrast, the hydrophilic group is usually referred as the “head group” and is an ionic or highly polar group.

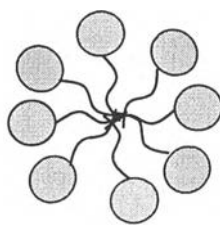
Surfactants can be classified as anionic, cationic, zwitterionic and nonionic surfactants by nature of the hydrophilic part. Anionic surfactants have a negative charge where as cationic surfactants have a positive charge in the hydrophilic portion. Zwitterionic surfactants carry both negative and positive charges in the head group. Nonionic surfactants have no apparent ionic charges in the hydrophilic parts. Mostly the hydrophilic portions of nonionic surfactant are the ethylene oxide groups (Rosen, 1989). Since this thesis was the study on cloud point property of nonionic surfactant, the description of nonionic surfactants will be further discussed in the section 2.2.

At low concentration of surfactant, the surfactant molecules form adsorbed monolayers at the surface. These surfactant monolayers can lower the surface tension of the medium in which they are dissolved. However, the surfactant molecules at higher concentration form organized aggregates called micelles. The micelles are formed at specific concentration of surfactant known as the 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 the polar head group to

maintain contact with the aqueous environment. Figure 2.1 presents the illustration of micelles showing the polar head group associates in the interior of aggregated micelle leaving hydrophilic parts to face the aqueous medium.



(a) a surfactant molecule



(b) a surfactant micelle

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

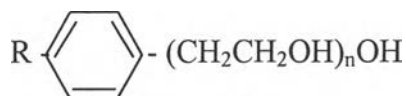
2.2 Nonionic Surfactants

Nonionic surfactants are usually prepared by the addition of ethylene oxide to the compounds that contain one or more active hydrogen atoms such as alkylphenols and fatty alcohols (Mackay, 1987). As the name implied, nonionic surfactants will not be ionized in the aqueous solution. Typically, their hydrophilic parts are normally the ethylene oxide head group or so called ethoxylated groups, $-(\text{OCH}_2\text{CH}_2)_n\text{OH}$. Moreover, nonionic surfactants are usually more gentle than ionic surfactants. They are used extensively in household and industrial products such as low-temperature detergents and emulsifiers (Rosen, 1989).

Although, there are many types of nonionic surfactants, only two types of them were used in this work *e.g.* alkylphenol ethoxylates and alcohol ethoxylates. The details of these two surfactants are discussed as following.

2.2.1 Alkylphenol Ethoxylates (APE)

The addition of ethylene oxide to an alkylphenol enables the manufacturer to produce a series of alkylphenol ethoxylates. Alkylphenol ethoxylates comprises the largest production volume among nonionic surfactants, with a wide scope of applications in both household and industrial products. For example, they are used in liquid dishwashing formulations and hard-surface cleaners. Nonylphenol ethoxylates are by far the most widely used base material with the combined octylphenol and dodecylphenol consumption at a somewhat lower volume (Schick, 1967). However, alkylphenol ethoxylates are more resistant to biodegrade than other nonionic surfactants. Furthermore, their biodegradation, as far as it takes place, are still in debates whether it gives toxic phenol derivatives and other toxic metabolic residues. Their structures can be shown in the following



where R represents hydrocarbon chain or hydrogen
and n represents number of moles of ethylene oxide.

2.2.2 Alcohol Ethoxylates (AE)

The fundamental reaction of alcohol ethoxylate production is the addition of ethylene oxide to the hydroxyl group of alcohol. The main advantages of alcohol ethoxylates (AE) over the alkylphenol ethoxylates (APE) are that AE surfactants are more easily biodegraded and their viscosities are lower than those APE surfactants. As a result of the recent emphasis on biodegradable surfactants, alcohol ethoxylates will be widely used for both household and industrial products (Mackey, 1987). They can be used in the formulation of household cleaners and used as an emulsion as well. Their structures can be represented as following



where R represents the hydrocarbon chain or hydrogen and n represents number of moles of ethylene oxide.

2.3 The Cloud Point of Nonionic Surfactants

An aqueous solution of nonionic surfactant becomes cloudy when it is heated above a well-defined temperature known as cloud point (CP) or lower consolute temperature (LCT). At temperature above the cloud point, the solution is in a two-phase region of its phase diagram where the two liquid phases are in equilibrium. The example of phase diagram of nonionic surfactant is illustrated in Figure 2.2 (Clint, 1992). The solution in this region appears cloudy because it is an emulsion of one phase in another composing of very large micellar aggregations. Besides, this solution can be separated into two isotropic aqueous phases either by gravity or centrifugal force due to their density differences. These two phases are micellar-rich phase or coacervate phase and micellar-poor phase or dilute phase as shown in Figure 2.3. The coacervate phase contains high concentration of surfactant while the dilute phase has a surfactant concentration typically equal or slightly exceed 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).

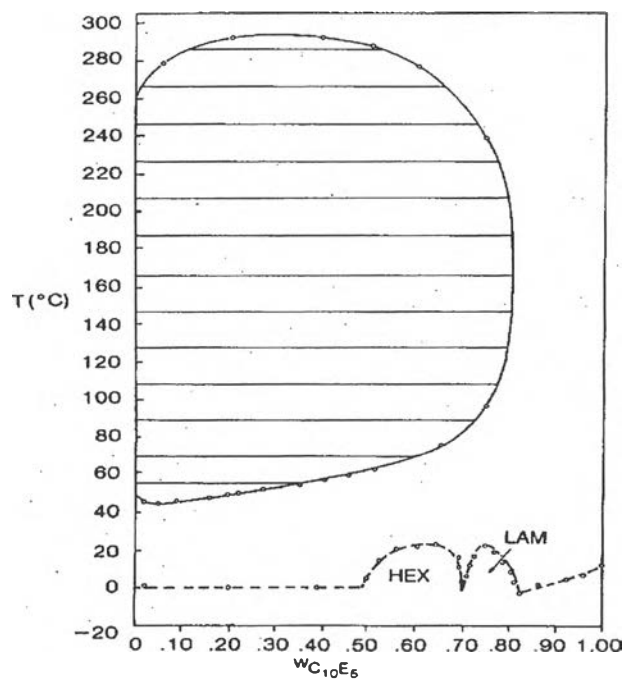


Figure 2.2 Phase diagram for the nonionic surfactant $C_{10}E_5$ in water showing the large closed-loop region where two liquid phases coexist (Clint, 1992).

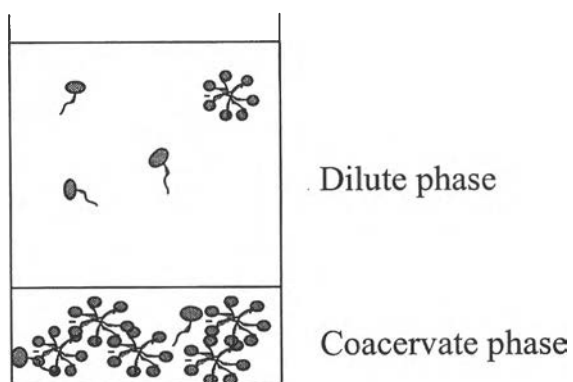


Figure 2.3 Phase partition of nonionic surfactant solution at temperature above the cloud point showing both dilute and coacervate phases.

2.4 The Mechanism of Phase Separation

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

As the temperature approaches the two-phase boundary, the intermicellar attraction is increased substantially (Corkill and Goodman, 1969). On the other hand, decreasing of the intermicellar repulsion makes a rapidly increase in micellar aggregation number of micelles. These surfactant aggregations are so large that the solution becomes visibly turbid.

In 1986, Claesson and co-workers stated that there are intermicellar repulsive forces at low temperature but these forces become attractive forces at temperature above LCT. The increasing interaction is a consequence of a strong entropy dominance. The water that hydrates the 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 an increase in entropy and enthalpy of the system. Thus, the phase separation occurs in order to reduce the entropy causing the increment in the 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 temperature, the nonionic surfactants are relatively more soluble in polar solvents such as water, while, at high temperature, they are more soluble in non polar solvents. 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 is gradually changed to the multiconnected network as the temperature is increased. In other words, the number of crosslinks of wormlike micelles increases with increasing temperature.

2.5 Parameters that Affect the Cloud Point Temperature

The cloud point temperature is depended on the surfactant structures. Moreover, the cloud point also can be influenced by the hydrophile-lipophile balance (HLB) of surfactants and other substances in the surfactant solution such as addition of other surfactants, salts, and other polar or non polar compounds.

At particular hydrophobic portion, the larger of ethylene oxide percentage in the hydrophilic part, the higher the cloud point. For example, highly hydrophilic chain (%EO > 75) often do not have a cloud point below the boiling point of 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, 1992).

The addition of either anionic or cationic surfactants can increase the cloud point due to the increasing in the repulsion force between the surface of mixed micelles. Moreover, the addition of another nonionic surfactants can also change the cloud point and the new cloud point for this mixed surfactant is in between the cloud points of the two pure surfactants(Rosen, 1989).

In 1995, Kamaromy-Hiller and co-workers indicated that the presence of electrolytes in the nonionic surfactant solution change the cloud point, which is called the salting effect. For example, addition of sodium chloride (NaCl) or chloride ions (Cl⁻) depress the cloud point due to the salting-out effect. This salting-out effect is the decreasing of the availability of non associated water molecules for dehydration of hydrophilic chains. On the other hand, added iodide ions raise the cloud point. The iodide ions can produce more available water molecules to interact with head groups and this is called salting-in effect. In 1995, Gu and Galera-Gomez showed that the cloud point decreases dramatically when the electrolytes are added, and the cloud point is in the order, LaCl₃ > MgCl₂ > NaCl, which implied that polyvalent cations or counterions are more active than the univalent cation.

Furthermore, the addition of non polar compounds, *e.g.* saturated aliphatic hydrocarbon increases the cloud point while adding of polar compounds, *e.g.* phenol, decreases the cloud point. The increment of the cloud point on addition of non-polar compounds may be due to the non-polar solubilize increase the size of micelles. As the sizes of micelles are larger, the area of micelle-water interfaces is increased resulting in higher dehydration the hydrophilic chains. In contrast, the polar compounds can decrease the dehydration of hydrophilic chains as a result of competition for the hydratable sites by polar solubilize. Moreover, Gu and Galera-Gomez (1999) indicated that the effect of added organic compounds on the cloud point is depended on their solubilities in water.

2.6 The Cloud Point Extraction

To apply the phase separation between surfactant-rich 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 phases partitioning system rather than to solvent extraction. When a nonionic surfactant solution containing solute is heated, the phase separation occurs and the solute will partition between dilute and coacervate phases as shown in Figure 2.4. In general, non polar organic solute is solubized and concentrated at the coacervate phase while leaving the purified water at the dilute phase.

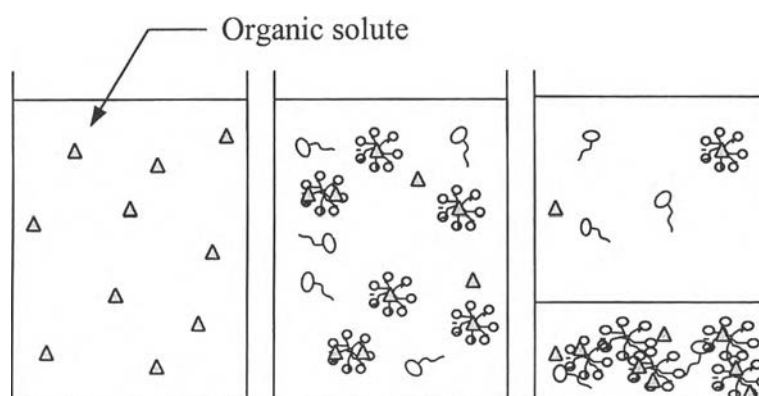


Figure 2.4 The schematic illustration of the cloud point extraction.

This CPE technique can be applied to extract many desired chemical; for example, Saitoh and Hinze (1995) studied the CPE of hydrophobic protein. Recently, the CPE method for organic compounds has been interested due to the environmental concern (Quina and Hinze, 1999). When an organic compound is subjected to a nonionic surfactant solution, the organic solute tends to solubilize in the micelles at temperature below its cloud point. The amount of organic solubilize is depended on the affinity to the surfactant micelles. After heating, the organic solutes will mainly partition to the coacervate phase, while only a small amount of solutes will stay in the dilute phase.

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

Sakulwongyai *et al.*, (2000) examined the removal of chlorinated ethanes, which are tetrachloroethane, trichloroethane, and dichloroethane, from wastewater. They showed that the surfactant aggregates 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. In other words, the amount of solute extracted depends on the solubility of solute, which decrease with increasing the degree of chlorination.

In many surfactant extraction processes, surfactant should be recovered after the operation to reduce the cost. For the extraction of organic solutes that has high volatility enough such as toluene, nonionic surfactant can be reused by using vacuum, steam or gas stripper to remove organic solutes. Unlike the nonionic surfactant, ionic surfactant can be recovery by precipitation. The regeneration of surfactant is not studied here because of the difficulty of experiment due to solute loss by volatilization. However, there have been literature studies of surfactant regeneration for extraction of less volatile organic solute such as phenolics.

Although there have been studies on the CPE of organic compounds, there have been a few works studied on the removal of volatile organic compounds such as toluene. In this work, the study is focused on the removal of toluene from contaminated water using alkyl phenol ethoxylates and alcohol ethoxylates. The experimental procedure was set up in a batch system to examine the effects of temperature and nonionic surfactant structures as well. The results of this experiment can serve to promote fundamental data for the applications of the cloud point extraction technique.