CHAPTER II
LITERATURE REVIEW

2.1 Nonionic Surfactants

Nonionic surfactants are usually prepared by an addition of ethylene oxide to the compound that contains one or more active hydrogen atoms such as alkylphenols and fatty alcohols (Schick, 1987). The hydrophilic parts of nonionic surfactant are normally 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 product such as low-temperature detergents and emulsifiers (Rosen, 1989).

There are many types of nonionic surfactants. Only two types of them were used in this work, which are alcohol ethoxylate (AE) and alkylphenol ethoxylate (APE). The fundamental 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 been widely used for both household and industrial products (Schick, 1987), for example, in the formulation of household cleaner and in use as an emulsion. APE comprises the largest production volume among other nonionic surfactants, with wide scope of applications. However, APE is more resistant to biodegrade and still in debates whether it gives toxic phenol derivatives and other toxic metabolite residues. Their structures can be shown as follows:

$$R - X - O - (CH_2CH_2O)_n - H$$

where R   represents hydrocarbon chain

n   represents number of moles of ethylene oxide

X   represents functional group

(X= benzene ring, in case of APE; and no X, in case of AE)
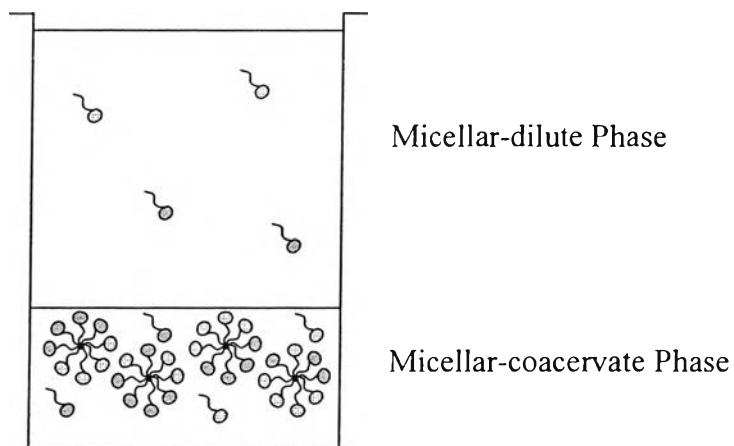
2.2 The Cloud Point of Nonionic Surfactants

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 temperature above the cloud point, nonionic surfactant solution separates into two-phase regions of its phase diagram where the two liquid phases are in equilibrium. Figure 2.1 shows an example of phase diagram of nonionic surfactant $C_{10}E_5$ in water. The solution appears cloudy because it is an emulsion of one phase in another composing of very large micellar aggregations. 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. Many factors affecting to the cloud point of solution were observed. The addition of polar organic solutes, such as fatty acid, aliphatic alcohols, and phenol, generally lowers the cloud point (Gu and Galera-Gomez, 1999). Adding anionic surfactant increases the cloud point (Gu and Galera-Gomez, 1995). The molecular structures of the nonionic surfactants show the significant effect with the cloud point. In general, the nonionic surfactant molecular structures consist of two parts. Hydrophilic head group or polar like part which typically are ethylene oxide groups and hydrophobic tail or non-polar like part which is alkyl chain length. It was found that lowering the number of ethylene oxide groups or lengthening the alkyl chain of the hydrophobic moiety of the nonionic surfactant will lower the cloud point (Gu and Sjoblom, 1992; Huibers *et al.*, 1997). Also, added electrolyte can reduce the cloud point due to the salting-out effect (Gu and Galera-Gomez, 1995). Figure 2.2 shows phase partition of nonionic surfactant above the cloud point.

2.3 The Cloud Point Extraction

The cloud point extraction (CPE) is a separation technique using the benign polyethoxylate nonionic surfactant as a separating agent (Clint, 1992; Hinze and Pramauro 1993; Quina and Hinze, 1999; Scamehorn et al., 2004). It has been shown
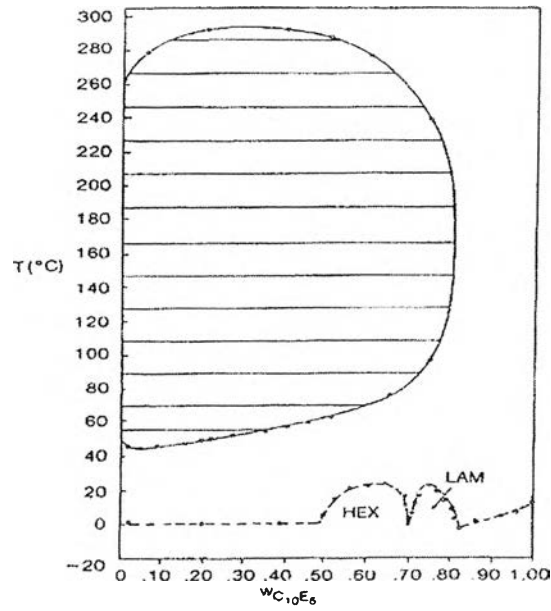
Figure 2.1 Phase diagram for the nonionic surfactant $C_{10}E_5$ in water showing the large closed-loop region where two liquid phases coexist (Clint, 1992).

Micellar-dilute Phase

Micellar-coacervate Phase

Figure 2.2 Phase partition of nonionic surfactant solution at temperature above cloud point showing both dilute and coacervate phase.

to be an alternative to traditional liquid-liquid extraction because of their efficiency, cost effectiveness and environmental friendliness without any usage of toxic and flammable organic solvent. When the nonionic surfactant solution at the concentration several times above its CMC, has the temperature higher than a certain temperature known as cloud point, either by heating or lowering the cloud point of the surfactant under the operating temperature, the phase separation will occur. Two micellar solutions are formed (Rosen, 1989; Clint, 1992; Hinze and Pramauro, 1993; Quina and Hinze, 1999). One is a concentrated surfactant micellar solution, known as a micellar rich phase or coacervate phase. The other is lean in surfactant micelles known as a micellar dilute phase. The organic solutes containing in the solution will tend to solubilize into surfactant micelles, associate with them during the phase separation and concentrate in the coacervate phase so that the dilute phase which containing less amount of organic pollutants can be released to the environment as shown in Figure 2.3. The phase separation is a reversible process. By cooling the solution below the cloud point, both two phases were transformed to a homogeneous solution.
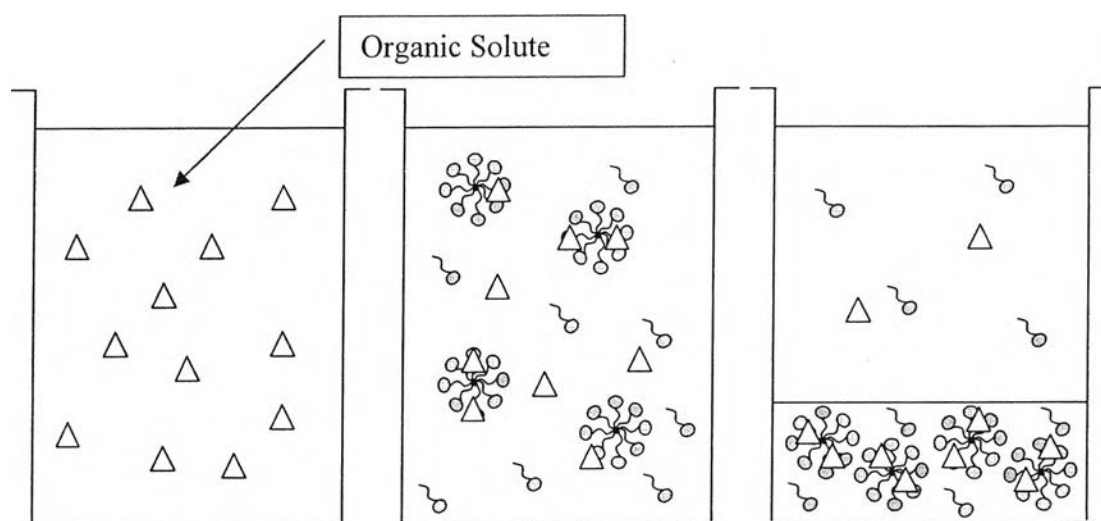
Figure 2.3 The schematic illustration of the cloud point extraction.

2.4 The 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 number 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 merge 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 (Corkhill and Goodman, 1969). In contrary, decreasing of the intermicellar repulsion makes aggregation number of micelles increase. 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 the cloud point. The increasing 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 contracting zone causes an increasing 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 is gradually changed to the multiconnected network as the temperature was increased. In other words, the number of crosslinks of wormlike micelles increases with increasing temperature.

2.5 The Studies of Cloud Point Extraction

The used of cloud point extraction technique seems more advantageous as the clouding is reversible and transparent solution are obtained after cooling (Materna and Szymanowski, 2002). The first utilization of cloud point extraction was carried out by Watanabe (1982) to extract and preconcentrate the metal ions. 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 reported that the use of CPE method for removing organic compounds was of interest 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). Kimchuwanit and co-workers also proved that the efficiency can be improved by raising the operating temperature. In 2000, Sakulwongyai *et al.* examined the removal of chlorinated ethanes, which are tetrachloroethane, trichloroethane, and dichloroethane from wastewater. They observed 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.

Essentially all reported cloud point extractions were carried out in batch experiment on a laboratory scale (Hinze and Pramauro, 1993; Wang *et al.*, 2002; Li and Chen, 2003). In order for this technology to become commercialized, scale-up to continuous, multi-stage units will be necessary. Also, recovery and reuse of the surfactant is crucial for economical operation. These two engineering problems are far from trivial; the viscous coacervate phase may cause plugging of extractors or strippers and efficient liquid-liquid contact at surface may be difficult to attain in an extractor due to the stickiness and viscous nature of the coacervate phase. Recently, CPE technique has been successfully scaled up to remove aromatic contaminants from wastewater stream continuously in a multi-stage rotating disc contactor (RDC)

(Trakultamupatam *et al.*, 2004). Figure 2.4 shows the integrated flow diagram of the multistage cloud point extraction process including a surfactant recovery unit. The contaminated feed water and a surfactant solvent solution are fed to a temperature controllable extractor where two streams are mechanically mixed at the temperature above the cloud point. As a result, phase separation takes place. The heavy coacervate phase, which contains the majority of polluted solutes, settles down at the bottom of the extractor as an extract phase due to a density difference. The dilute phase, which is lighter, will rise up to the top of the extractor as a raffinate phase and can be discharged to the environment.

Many researchers have studied the CPE of organic contaminants in batch experiments, but little work has been done with volatile organic compounds (VOCs) except for our studies, despite their great environmental concern in industrial wastewater or polluted groundwater. It is believed that this is due to the experimental difficulty of making accurate measurements on these systems due to leakage of these compounds because of volatilization. In 2002, the batch CPE study of the aromatic VOCs, (benzene, toluene, and ethylbenzene) from wastewater utilized octylphenolpolyethoxylate as a nonionic surfactant (Trakultamupatam *et al.*, 2002). The influences of temperature, concentration of total surfactant, added electrolyte, and degree of alkylation of aromatic solutes on the extraction efficiency were investigated. Subsequently, toluene and ethylbenzene were selected as toxic compounds when the CPE was scaled up using RDC for removal of volatile aromatic contaminants from wastewater (Trakultamupatam *et al.*, 2004). In that work, the concentration of solutes in the coacervate phase increased as agitator speed, wastewater/surfactant solution flow rate ratio, degree of alkylation of the aromatic solutes, operating temperature, and electrolyte concentration increased. Vacuum stripping in continuous bench-scale unit was reported to successfully strip the VOCs (toluene) from a concentrated surfactant solution (Choori *et al.*, 1998). Detailed studies in our laboratory are further demonstrating the feasibility of vacuum stripping the micellar rich phase from CPE in a continuous, packed bed stripper (Kungsanant *et al.*, 2008) so that the solute-free micellar rich stream can be recycled for reuse in the CPE unit.
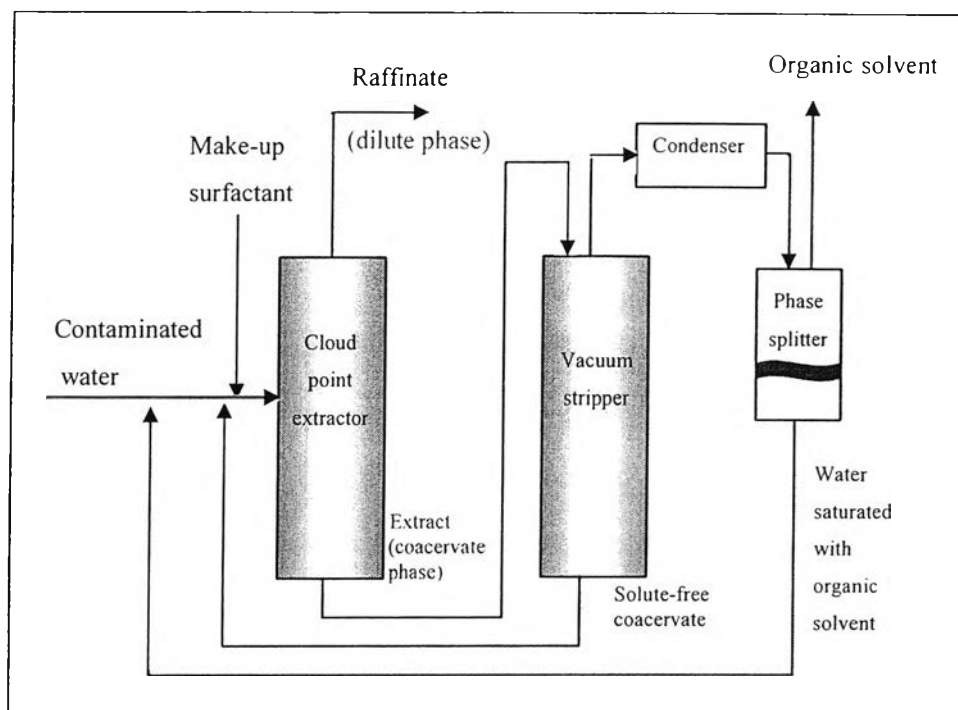
Figure 2.4 The integrated schematic of the cloud point extractor including a surfactant recovery unit

2.6 The Theory of Coacervate Solubilization Equilibrium Constant Calculation

In aqueous surfactant solution, the ability of micelles to solubilize solutes is usually described by a solubilization equilibrium constant (K_m), which is defined by

$$K_m = X_m / C_u = [O]_{mic} / (C_u ([surfactant]_{mic} + [O]_{mic})) \qquad (1)$$

where X_m is the mole fraction of solute in micelles, C_u is the concentration of unsolubilized organic solute, $[O]_{mic}$ is the solute concentration solubilized in surfactant micelles and $[surfactant]_{mic}$ is the surfactant concentration in micellar form. Eq. (1) describes the solubilization of the solute into the micelles in the dilute phase.

In CPE, in order to determine the tendency of the organic solute to solubilize into the surfactant aggregates in the coacervate phase, a coacervate

solubilization equilibrium constant (K_c) can be defined in analogy to K_m (Sakulwongyai *et al.*, 2000).

$$K_c = X_c / C_u = [O]_{agg,c} / (C_u ([surfactant]_{agg,c} + [O]_{agg,c})) \qquad (2)$$

where X_c is the mole fraction of solute in the coacervate aggregate, C_u is the concentration of unsolubilized organic solute in the coacervate phase, $[O]_{agg,c}$ is the solute concentration associated with surfactant aggregate in the coacervate phase, and $[surfactant]_{agg,c}$ is the surfactant concentration in the aggregate in the coacervate phase. The value of C_u is assumed to be equal in the dilute phase and the coacervate phase and so is the same in Eq. (1) and Eq. (2). This assumes that the solute is dilute enough to obey Henry's law and that the Henry's law constant is the same in both dilute and coacervate phases since both are aqueous solutions.

From material balances:

$$[O]_{agg,c} = [O]_c - C_u \qquad (3)$$

$$[surfactant]_{agg,c} = [surfactant]_c - CMC \qquad (4)$$

where $[O]_c$ and $[surfactant]_c$ are the total solute and surfactant concentration in the coacervate phase, respectively. The CMC is assumed to be equal to the monomeric surfactant concentration in the coacervate phase. Then,

$$K_c = ([O]_c - C_u) / (C_u ([O]_c - C_u + [surfactant]_c - CMC)) \qquad (5)$$

By analogy, when considering the dilute phase,

$$K_m = ([O]_{dil} - C_u) / (C_u ([O]_{dil} - C_u + [surfactant]_{dil} - CMC)) \qquad (6)$$

where $[O]_{dil}$ and $[surfactant]_{dil}$ are the total solute and surfactant concentration in the dilute phase. In a previous literature (Sakulwongyai *et al.*, 2000), the researchers had used dialysis experiments to prove that K_m in the dilute phase is very close to K_c. With an assumption of $K_m = K_c$, these two equations can be solved for K_c and C_u.