CHAPTER II

LITERATURE REVIEW

2.1 Cloud Point Extraction (CPE)

As a nonionic surfactant solution is heated up to the temperature known as the cloud point, the surfactant solution turns cloudy and then separates into two phases—coacervate phase and dilute phase (Rosen, 1989). This cloud point phenomenon can be effectively applied to remove the volatile organic compounds (VOCs) from aqueous solution. In CPE, the contaminated VOCs tend to solubilize in the surfactant micelles and concentrated in the coacervate phase after phase separation, permitting the solute-free solution in the dilute phase to be discharged to a public water reservoir (Kimchuwanit *et al.*, 2000; Sakulwongyai *et al.*, 2000; Trakultamupatam *et al.*, 2002). Generally, this technique is wildly used in pre-concentration of metal ions or biomaterials from aqueous solutions, which is reviewed by many studies (Hinze and Pramauro, 1993; Quina and Hinze, 1999).

Typically, it has been reported that the cloud point extraction efficiency increases with increasing temperature, surfactant concentration, added electrolyte concentration, and solute hydrophobicity (Kimchuwanit *et al.*, 2000; Sakulwongyai *et al.*, 2000; Trakultamupatam *et al.*, 2002). However, due to cost of surfactant, the CPE process is not economically attractive unless the surfactant is recycled and reused.

2.2 Surfactant Regeneration Processes

There are a number of techniques available for surfactant regeneration as follows.

2.2.1 Air Stripping

Air stripping in a packed tower is conventionally utilized for the VOC removal from contaminated water. This process is applied in drinking water treatment, wastewater purification, and polluted ground water remediation (Gross and Termaath, 1985; Kutzer *et al.*, 1995; Linek *et al.*, 1998). In air stripping operation, two streams of solute-free air and contaminated aqueous solution are brought counter-currently to contact in the packed column. The VOCs are separated from the aqueous solution by partitioning of the VOCs from the liquid to the air stream. The effluent contaminated air stream has to be treated further by incinerator or granular activated carbon, while the exit solute-free liquid stream can be discharged to the environment. To apply this process for VOC removal from a concentrated surfactant solution, it has been reported that although low air-liquid flow rate ratio is applied, the contacting between air and surfactant solution can generate excessive foaming in the air stripping column, resulting in flooding and making the process inoperable (Lipe *et al.*, 1996).

2.2.2 Steam Stripping

Steam stripping process is the process that similar to air stripping process except that a hot steam is brought to contact with the contaminated liquid solution instead of air. After separation, the contaminated steam is condensed in the condenser and then the resulting condensate is treated further in the liquid-liquid separator where it is separated into two phases—organic phase and water phase. The treated water can be drained or recycle to the steam generator unit while the organic contaminants can be removed or recovery. Generally, many studies reported that the steam stripping is more attractive than the conventional air stripping process operating at atmospheric temperature and pressure (Hwang *et al.*, 1992a, 1992b; Ortiz-Del Castillo *et al.*, 2000). The advantage of the steam stripping is that it requires smaller column volume and lower operating cost, since the steam is commonly produced from other unit in the plant. However, to apply this process for coacervate regeneration, this process is also faced with an unfavorable foaming problem during the contacting of the vapor and surfactant streams in the column and the presence of surfactant may possibly cause the complication of the liquid-liquid separation in the separator unit.

2.2.3 Spraying

In spraying process, the contaminated aqueous solution containing the VOCs is pumped though a nozzle into a controlled chamber that can be operated under atmospheric or vacuum condition. The solution is dispersed as a small droplet in the chamber, which provides a high surface area for mass transfer (Lin *et al.*, 1977; Tackie and Rice, 1991). This process is favorable for separating the VOC in a water treatment process. However, if this process is applied for VOC removal from a contaminated surfactant solution, an excessive foaming may occur, leading to inoperable conditions in the process. To make this process becomes more attractive, an anti-foaming agent may be added to reduce foam, but the added chemical for foam reduction might increase an operating cost and requires the secondary unit to purify the solution.

2.2.4 Pervaporation

Pervaporation is a separation process in which the VOC is separated from an aqueous solution by means of selective diffusion and then vaporization through a non-porous membrane. During operation, the liquid stream containing the VOCs is brought into one side of the porous polymeric membrane (retentate side) while another side (permeate side) is contacted with vacuum or gas purge. The VOCs transfer into the membrane, permeate through it, and evaporate into the vapor phase. The vapor is then condensed in the permeate side. This process is attractive for wastewater or ground water treatment processes because it does not have emission problems or require a sequential regeneration step (Vane *et al.*, 2001; Peng *et al.* 2003). To apply this process for surfactant regeneration, the problem of foaming is possibly eliminated but the surfactants can form gel on the membrane surface, resulting in lowering liquid flux or plugging in the membrane pore (Jiang *et al.*, 1997; Hitchens *et al.*, 2001; Vane and Alvarez, 2002).

2.2.5 Vacuum Stripping

Vacuum stripping has been widely used for decades to remove the VOCs from contaminated water in chemical and petrochemical industries, such as the removal of butane (Bajolle *et al.*, 1971) and refrigerants (Lin *et al.*, 1977) from water in a desalting process, carbon dioxide and oxygen from water (Lydersen, 1991; Rasquin *et al.*, 1977), VOCs from water streams (Rasquin *et al.*, 1978), and emulsified organic liquid from water (Tackie and Rice, 1991). This process is similar to the air stripping process except that the vacuum is applied in the packed column. The advantage of this process is that it requires small volume of packed column and produces less volume of the contaminated vapor in the effluent stream. To apply this process for recycle of the contaminated coacervate solution, the packed column is suggested to operate in co-current mode (Choori *et al*, 1998). It was reported that the co-current flow of the vapor and surfactant streams effectively reduces an excessive foaming and avoids flooding in the packed column.

However, co-current separation efficiency is generally lower than that of a counter-current separation, making the process much less popular (Treybal, 1981). The mass transfer of the VOC in a co-current process can be limited as a maximum of one transfer unit is possible before equilibrium is reached between the vapor and liquid phases (Treybal, 1981). A study reported that the mass transfer coefficient of the counter-current flow in a packed tower was three-fold higher than that of the co-current flow for carbon dioxide absorption into water (Ufford and Perona, 1973).

Nevertheless, a study observed that a multistage co-current operation provided higher efficiency than a single stage counter-current operation. In addition, flooding was found to be totally eliminated in the co-current operation; therefore, the column can be operated at a much higher liquid loading rate than that in the case of counter-current flow (Lydersen, 1991). From this point of view, co-current vacuum stripping was selected for investigation to remove VOCs from a concentrated nonionic surfactant solution.

2.3 VOC-Surfactant Equilibrium

2.3.1 Coacervate Characteristic

In CPE, it was found that over 90% of total surfactants was concentrated in the coacervate phase (Trakultamupatam *et al.*, 2004a, b). To recycle this solution in a co-current vacuum stripping process, the coacervate characteristic should be examined. Many researchers have investigated the structures of highly concentrated nonionic surfactant coacervate phases. Kato *et al.* (1995) measured the self-diffusion coefficient of the surfactant and found that, at high concentration, surfactants aggregates in the form of an entangled network called a worm-like micelle. In addition, the gradual "cross-linking" of the worm-like micelles occurs as temperature increases above the cloud point, and the worm-like micelles transform to a multiconnected network. A similar structure was also found in a study of the interaction between a solute and a nonionic surfactant, octylphenol ethoxylate ($OP(EO)_x$), where the EO varied from 4.5 to 12 moles (Qiao and Easteal, 1996), and where the surfactant forms rod-like micelle structures at high surfactant concentration. Another study reported that the solubilization of VOCs in a surfactant entangled network of a coacervate solution is similar to micelles (Sakulwongyai *et al.*, 2000). The reason is that there is a hydrophobic part enclosed with a hydrophilic region in a surfactant aggregate similar to a micelle structure. Therefore, the solubilization of the VOCs into coacervate phase can be explained in the same manner as solubilization of VOCs into micelles.

2.3.2 Solubilization

For the surfactant solution containing the VOCs, the pseudo-phase separation model is applied for describing the partitioning of the VOCs between the micellar pseudo-phase, the extramicellar phase, and the vapor phase in a surfactant system (Anderson, 1992). The partitioning of the VOCs between the bulk extramicellar phase and the micellar pseudo-phase is explained by a solubilization constant defined as follows (Choori *et al*, 1998):

$$K_s = \frac{C_{sol}}{C_u(C_m + C_{sol})} \tag{1}$$

where K_s is the solubilization constant, C_{sol} is the solubilized concentration of the VOCs in micelle, C_u is the unsolubilized concentration of the VOCs in surfactant solution or the VOCs concentration in extra-micellar phase, and C_m is the surfactant micelle concentration. If the solubilized concentration of the VOCs in the micelle is very small compared to the surfactant concentration in the micelle ($C_{sol} << C_m$), equation (1) is simplified to:

$$K_s = \frac{C_{sol}}{C_u C_m} \tag{2}$$

Surfactant micelles show excellent performance in solubilizing organic compounds in aqueous solution. For this reason, surfactants have been applied in many surfactant remediation processes, such as liquid-liquid extraction (Hasegawa *et al.*, 1997) and micellar-enhanced ultrafiltration (MEUF) (Lipe *et al.*, 1996). If appropriate solutes and solvents are selected, these processes have shown highly efficient removal of the organic compound from a contaminated solution. However, it could lead to lateral difficulty in the decontamination of surfactant solution for reuse; i.e., separation of the solubilized solute from the micellar surfactant can be difficult.

2.3.3 Vapor-Liquid Equilibrium

2.3.3.1 Henry's Law

A pseudo-phase separation model is applied for describing the distribution of VOCs in a surfactant solution (Anderson, 1992). Since micelle formation is in rapid dynamic equilibrium, surfactant monomers can partition between the surfactant micelle and the extramicellar phase. The partial fugacity of the VOC equals the VOC partial pressure at these low pressures and is equal to the partial fugacity in the extramicellar phase and solubilized in the micelle. It is assumed that the partial fugacity of the VOC in the extramicellar solution is the same as that in water at the same VOC concentration; i.e., the Henry's law constant for the unsolubilized VOC is unaffected by the presence of micelles. Assuming that the solution is dilute enough to be in the Henry's law region, equating of partial fugacities yields:

$$p = HC_u \tag{3}$$

where H is the Henry's law constant of VOC at controlled temperature and p is the partial pressure of the VOC in vapor phase.

In this study, the equilibrium partitioning of VOC between vapor and the coacervate solution is determined by modifying the Henry's law constant to become the *apparent* Henry's law constant. The apparent Henry's law constant (H_{App}) is expressed as:

$$H_{App} = \frac{p}{(C_u + C_{sol})} \tag{4}$$

In the design of the stripping process, the impact of surfactant on the vapor-liquid equilibrium partitioning of the VOCs must be considered. It has been known that neglecting the effect of surfactant solubilization on the Henry's law constant causes underdesign of air stripping processes (Kibbey *et al.*, 2001).

2.3.3.2 Vapor-Liquid Equilibrium Partition Coefficient

In order to calculate the mass transfer for the VOC, it is necessary to know their equilibrium compositions in vapor and liquid phases, which could be indicated by the vapor-liquid equilibrium partition coefficient. Thus, the solubilization constant and the Henry's law correlations of VOC, which are illustrated in equations (2), (3), and (4), respectively, are applied for the calculation of the vapor-liquid equilibrium partition coefficient of water, surfactant, and VOC between vapor and the coacervate solution as follows:

for water,

$$K_w = \frac{y_w^*}{x_w^*} \tag{5}$$

for surfactant,

$$K_{surf} = \frac{y^*_{surf}}{x^*_{surf}} \tag{6}$$

and for VOC,

$$K_{voc} = \frac{y^*_{voc}}{x^*_{voc}} \tag{7}$$

where K_w, K_{surf}, and K_{voc} are the vapor-liquid equilibrium partition coefficients of water, surfactant, and VOC; y^*_w, y^*_{surf}, and y^*_{voc} are the equilibrium mole fractions of water, surfactant, and VOC in the vapor phase; x^*_w, x^*_{surf}, and x^*_{voc} are the equilibrium mole fractions of water, surfactant, and VOC in the liquid phase, respectively.

from Dalton's law,

$$p = y^*_{voc} P \tag{8}$$

where P is the total pressure in the system.
Combining equations (4), (7), and (8) yields:

$$p = (C_u + C_{sol})H_{App} = x^*_{voc} C_T H_{App} \tag{9}$$

Substituting equation (2) into the above equation gives

$$K_{voc} = \frac{HC_T}{P(1 + K_s C_m)} \tag{10}$$

where C_T is the total concentration of all components in the liquid phase.

2.4 Mass Transfer Determination

2.4.1 Flash Calculation

The equilibrium components in the vapor and coacervate solution existing in the co-current vacuum stripping are quantified from a single stage equilibrium flash calculation. The overall balance is:

$$F = L + V \tag{11}$$

where F is the total molar feed flow rate, L is the total molar flow rate in the liquid product, and V is the total molar flow rate in the vapor phase. The VOC balance in flash vacuum stripping at constant vapor and liquid flow rate is expressed as:

$$z_{voc}F = x^{*}_{voc}L + y^{*}_{voc}V \tag{12}$$

where z_{voc} is the mole fraction of VOC in feed. Then, the equations (7) and (11) are substituted in equation (12), yielding:

$$x^{*}_{voc} = \frac{z_{voc}}{1+\frac{V}{F}(K_{voc}-1)} \tag{13}$$

and, by applying equation (7), equation (13) is multiplied by K_{voc} to obtain y^{*}_{voc}.

$$y^{*}_{voc} = \frac{z_{voc}K_{voc}}{1+\frac{V}{F}(K_{voc}-1)} \tag{14}$$

The equilibrium mole fractions of water and surfactant in the vapor and coacervate solution are calculated by the same methods, which are shown as:

for water,

$$x_w^* = \frac{z_w}{1+\frac{V}{F}(K_w - 1)} \text{ and } y_w^* = \frac{z_w K_w}{1+\frac{V}{F}(K_w - 1)} \quad (15), (16)$$

for surfactant, since surfactant has a high molecular weight, then the vaporization of surfactant is negligible and the K_{surf} becomes zero. Therefore,

$$x_{surf}^* = \frac{z_{surf}}{1-\frac{V}{F}} \text{ and } y_{surf}^* = 0 \quad (17), (18)$$

where z_w and z_{surf} are the mole fractions of water and surfactant in feed respectively. The criterion used to solve the flash calculation is that the $\frac{V}{F}$ is calculated by iteration until it satisfies that $\sum x - \sum y = 0$, where $\sum x$ and $\sum y$ are the total equilibrium mole fractions of all components in coacervate solution and vapor phase, respectively. Consequently, the final equilibrium compositions in both the vapor and coacervate solution after flashing are obtained simultaneously.

2.4.2 Mass Transfer Calculation in Vacuum Stripping Column

The efficiency of the packed column used in co-current vacuum stripping to remove VOC from coacervate solution was described by evaluating the overall mass transfer coefficient of VOC between the vapor and liquid phases. At steady state, the packed column was determined as a series of differential volume of height dz. The flow rates of the vapor and coacervate streams flowing through the packing material in this dz section were assumed to be constant. When the coacervate solution flows through the packing material, the vaporization of VOC from the coacervate film over the packing surface to the vacuum atmosphere can be explained by two-film theory. Theoretically, considering the liquid and vapor interface, VOC diffuses from the bulk of the coacervate solution to the interface, then across the interface, and finally diffuses from the interface to the bulk of the vapor phase. The rate of VOC transfer per unit volume of packed column is a function of the overall liquid phase mass transfer coefficient, the interfacial contact area of packing, and the VOC concentration gradient existing across the liquid phase. This relationship was applied to the VOC mass balance on the liquid phase in a differential volume of packed column, which is expressed as:

$$-L_0\frac{dx_{voc}}{dz} = K_x a(x_{voc} - x_{voc}^*) \tag{19}$$

By integrating and rearranging the equation (19), the height of the packed bed (Z) is given as:

$$Z = \frac{L_0}{K_x a}\ln\left(\frac{x_{i,voc} - x_{voc}^*}{x_{f,voc} - x_{voc}^*}\right) \tag{20}$$

where Z is the height of packing, L_0 is the molar coacervate flux in packed column, $x_{i,voc}$ and $x_{f,voc}$ are the mole fractions of VOC in the inlet and outlet coacervate streams, K_x is the overall liquid phase mass transfer coefficient of VOC, a is the effective interfacial area of packing per unit packed volume, $K_x a$ is the overall liquid phase volumetric mass transfer coefficient of VOC, and x_{voc}^* is the equilibrium mole fraction of VOC in the coacervate solution from the equilibrium flash calculation already described. This study assumed that x_{voc}^* remains constant along the column. When the initial and final mole fraction data of VOC are known by directly analyzing the VOC concentration in the inlet and outlet coacervate streams, the $K_x a$ can then be calculated.