



CHAPTER II

LITERATURE REVIEW

2.1 Use of Surfactants in HVOCs Removal

Surfactants are compounds that lower the surface tension of a liquid, the interfacial tension between two liquids, or that between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants. Nowadays most of current researches continuously focus on the usage of chemical surfactant to treat the wastewater that contaminated with HVOCs. This is due to its high efficiency in treating the contaminant, low energy consumption, and environmental friendly.

2.2 Cloud Point Extraction (CPE)

As the nonionic surfactant solution is heated above cloud point temperature (CPT), the surfactant solution turn cloudy and then separates into two phases, a surfactant-rich phase (coacervate phase) and an almost micelle-free dilute solution (dilute phase). This cloud point phenomenon can be effectively applied to remove the hydrophobic volatile organic compounds (HVOCs) from aqueous solution. In CPE, the contaminated HVOCs tend to be solubilized 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).

The CPE process has many advantages such as cheaper, simpler, and more environmental friendly than conventional extraction process using organic solvents (Zhu *et al.*, 2008). In addition the CPE process can be applied to remove hydrophobic substances, *e.g.* PAHS (Li *et al.*, 2002, 2003; Hung *et al.*, 2007), biomaterials (Lopes *et al.*, 2007; Zhoua *et al.*, 2008), and VOCs (Li *et al.*, 2001; Trakultamupatam *et al.*, 2002, 2004), and for the system having trace metal ions (Lemos *et al.*, 2007; Ohashi *et al.*, 2007; Zhu *et al.*, 2008).

The cloud point extraction efficiency increase with increasing temperature, surfactant concentration, added electrolyte concentration, and solute hydrophobicity (Kimchuwanit *et al.*, 2000; Sakulwongyai *et al.*, 2000). However, due to cost of surfactant, the CPE process is not economically attractive unless the surfactant is recycled and reused.

The separation of HVOCs from wastewater by using coacervate phase of nonionic surfactant is considered to be a one of the proven method that has high efficiency. In this technique, heat is inserted to the nonionic surfactant solution until it reached the cloud point temperature of the surfactant. The solvent will turn cloudy and then be separated into two phases; the dilute phase, presented with very low concentration of surfactants, but very high volume, and the coacervate phase; presented with very high concentration of surfactants but very low volume. This method is effectively being applied to remove the HVOCs wastewater, which can be neglected out to the river (Kimchuwanit *et al.*, 2000; Sakulwongyai *et al.*, 2000; Trakultamupatam *et al.*, 2002). In addition, this method can also be applied to separate the metal ions from water or biological materials as well (Quina *et al.*, 1999).

Trakultamupatam and co-worker (2004) studied the separation of aromatic compounds from wastewater using the coacervate phase of Alkylphenol poly(ethoxylate)s nonionic surfactant, t-octylphenolpolyethoxylate (OP(OE)₇) in continuous rotating disk contactor. They found that the aromatic compound could be removed about 85-90 percent. Later on, Taechangam and co-worker (2008) continuously studied the capability of CPE to separate the chlorinated hydrocarbons and non-volatile group from water. The results of the study shown that, the capability for separation is about 100 percent. In addition, they could predict the separation capability by using the logarithms relation equation between the equilibrium constants and the octanol-water partition coefficient (K_{ow}) (Li *et al.*, 2003; Trakultamupatam *et al.*, 2004; Taechangam *et al.*, 2008).

From the above technique, their research group also studied the CPE techniques using many type of nonionic surfactant to separate different types of HVOCs, for example, the separation of the group of chlorinated hydrocarbons or the group of polycyclic aromatic hydrocarbons from water using nonionic surfactant

APEs type and AEs type with the separation efficiency in an average of 90 percent (Kimchuwanit *et al.*, 2000; Sakulwongyai *et al.*, 2000; Trakultamupatam *et al.*, 2002; Quina *et al.*, 1999). However, the surfactant-enhanced remediation is often not economically acceptable, since operation costs can be increased by up to 50% due to chemical costs of surfactant. Therefore, surfactant solution should be separated from contaminants and then reused.

2.3 Surfactant Regeneration Process

There are many techniques that available for surfactant regeneration as follow

2.3.1 Air Stripping

Air stripping is the transferring of volatile components of a liquid into an air stream. It is conventionally utilized for volatile components from contaminated water. This process is applied in drinking water treatment, waste water purification, and polluted ground water remediation (Gross and Termaath, 1985; Kutzer *et al.*, 1995; Linex *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 HVOCs are separated from the aqueous solution by partitioning of the HVOCs 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 environmental. To apply this process for HVOCs 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).

2.3.2 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

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 remove 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.*, 1992; 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.

2.3.3 Spraying

In spraying process, the contaminated aqueous solution containing the HVOCs is pumped through 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.*, 1997; Tackie and Rice, 1991). This process is favorable for separating the HVOC in a water treatment process. However, if this process is applied for HVOC 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.

2.3.4 Vacuum Stripping

Vacuum stripping has been widely used in many fields; majority in HVOCs removal 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, degassing for CO₂ and O₂ from water in a packed column (Rasquin *et al.*, 1997), removal of trichloroethylene from surfactant solutions by flash vacuum stripping in a packed column (Lydersen *et al.*, 1991; Choori *et al.*, 1998), 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 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 HVOC 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).

In 1997, Rasquin *et al.* reported that multistage co-current operation can be accomplished most economically rather than a single stage counter-current operation and it was found that the co-current vacuum stripping using a packed column could remove up to 90% of toluene from 300mM Triton X-114. 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).

Nevertheless, in 2008 Kungsanant *et al.* reported that the single stage vacuum packed column can successfully strip the toluene from a coacervate solution in co-current operation, with up to 90% removal observed. The viscous coacervate solution can flow passing the packing materials without plugging. Co-current flow of vapor and liquid is necessary to avoid unacceptable foaming which limits the separation to a maximum of that of one equilibrium stage no matter how long the

column is. From this point of view, co-current vacuum stripping was selected for investigation to remove HVOCs from a concentrated nonionic surfactant solution.

The process of recycling the surfactant is often limited by foaming of surfactant compounds. Many current researches mainly focus on solving these limitations, for example, Ahn and Kim studied the recovery of surfactants in soil washing processes using activated carbon. There were 4 types of nonionic surfactant; Tween 40, Tween 80, Brij 30 and Brij 35 applying in the removal of. After treatment, the surfactants were recycled by means of absorption with activated carbon. They found that about 85-89 percent of surfactants were recovered (Kimchuwani *et al.*, 2000; Sakulwongyai *et al.*, 2000). However, the separation and adsorption with activated carbon performance in this process should be carefully concerned. If the surfactant that chosen for separation has very good quality, the recycling process can be more complicated. To choose the surfactant for this process, the user needs to be careful.

Vacuum stripping is considered to be another method that widely used, to, separate the HVOCs from waste water in petrochemical and chemical industries, for example, use to eliminate butane (Kimchuwani *et al.*, 2000) or remove the coolant from wastewater (Lin *et al.*, 1977), remove the carbon dioxide and oxygen from the water (Sakulwongyai *et al.*, 2000; Trakultamupatam *et al.*, 2002), remove organic substances from water (Tackie *et al.*, 1977). The vacuum stripping is more advantage than the air stripping in term of using smaller chamber. This method was successfully applied in removal of HVOCs in the group of aromatic compounds from surfactant solution by operating under the vacuum with the same flow direction of vapor and liquid. Choori and co-worker (1998) studied the separation HVOCs from anionic surfactant using this method and found that the co-current between the vapor and the liquid phase could reduce the foam forming flooding and flooding in stripping packed column. Later, Kungsanant and co-worker (2008 and 2009) studied about the separation of aromatic compounds and Chlorinated Hydrocarbons from the coacervate phase of APES nonionic surfactant, t-octylphenolpolyethoxylate (OP(OE)₇), using the co-current packed Rashching ring column operated under vacuum. They found that the coacervate surfactant has high concentration and high stickiness. However, the same flow direction of vapor and liquid could reduce the

problem of obstruction, foam forming and flooding of the liquid in the packed column. Moreover, they found that 90 percent of HVOCs could be removed from 450 mM OP(OE)₇ within single stage operation.

2.4 Hydrophobicity of Solutes

In this thesis work, the hydrophobicity of HVOCs is expressed in term of the octanol-water partition coefficient (K_{ow}). This parameter is defined as the ratio of the equilibrium concentration of solute in an octanol phase to that in a water phase at a constant temperature. Octanol is an organic solvent that is used as a represent for natural organic substance. This parameter is used in many environmental studies to indicate the fate of chemicals in the environment. As with solubility, K_{ow} is a function of the presence of electrolytes and for dissociating chemicals it is a function of pH (Mackay, 2006).

Generally, the higher hydrophobic of solute (higher K_{ow}) is, the greater its tendency to solubilize in micelles which is the cause of the lower volatilization of HVOCs to vapor phase (Taechangam *et al.*, 2008; Kungsanant *et al.*, 2008).

2.5 Vapor-Liquid Equilibrium of Solute in Aqueous Surfactant System

2.5.1 Micelle Formation

When surfactant are continuously added into aqueous solution until it exceeds a certain threshold value, called a critical micelle concentration (CMC), surfactant monomers tend to aggregate to form micelles in colloidal-size, which have a hydrophobic region enclosed with the hydrophilic surface. This phenomenon is called micelle formation or micellization. The hydrophobic HVOCs in contaminated aqueous solution can be incorporated in the hydrophobic cores of the micelles; as a result, their aqueous solubility can be enhanced. Micellization of surfactant is an important phenomenon in detergency and solubilization process.

2.5.2 Solubilization

When a hydrophobic organic molecule is added to a micellar solution it tends to concentrated in a nonpolar interior of micelles, which are oil-like (hydrophobic) region, rather than going into the more polar aqueous phase, this phenomenon called solubilization. Treating the micelle as a pseudo-phase in which the surfactant and solubilized substances reside, the distribution of the solute between the micelles and the aqueous phase is defined as follows:

Surfactant (micelle) + organic solute (aqueous) \longleftrightarrow surfactant*organic solute

$$K_s = \frac{C_{sol}}{C_u(C_m + C_{sol})} \quad (2.1)$$

Where K_s is the solubilization constant, C_{sol} is the solubilized organic solute concentration in micelle, C_u is the unsolubilized organic solute concentration in surfactant solution, and C_m is the surfactant micelle concentration.

In ground water treatment processes, where the concentration of solutes in the micellar phase is usually much smaller than the concentration of surfactant in the micellar phase ($C_{sol} \ll C_m$), thus C_{sol} can be ignored. Thus, Eq. (2.1) is simplified to:

$$K_s = \frac{C_{sol}}{C_u C_m} \quad (2.2)$$

Where:

$$C_{sol} = C_{total\ solute} - C_u$$

$$C_m = C_{total\ surfactant} - CMC$$

$C_{total\ solute}$ is total organic solute concentration, and $C_{total\ surfactant}$ is total surfactant concentration.

At low solute concentration, the value of K_s can be estimated as its infinite dilution value and is independent of solute concentration (Choori *et al.*, 1998).

2.5.3 Vapor-Liquid Partitioning of the HVOCs

In dilute aqueous solution, the Henry's law can be applied to describe the equilibrium partitioning of the HVOCs between the vapor and liquid phases, which is expressed as:

$$p_t = HC_u \quad (2.3)$$

Where H is the Henry's law constant of HVOC at controlled temperature and p_t is the partial pressure of the HVOC in vapor phase.

In this study, the equilibrium partitioning of HVOC 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:

$$H_{App} = \frac{p_t}{C_u + C_{sol}} \quad (2.4)$$

2.5.4 The Vapor-Liquid Equilibrium Partition Coefficient, K_i

The vapor-liquid equilibrium partition coefficient is applied for mass transfer calculation in continuous operation. In dimensionless form, it is defined as:

$$K_i = \frac{y_i^*}{x_i^*} \quad (2.5)$$

Where: y_i^* = mole fraction of component "i" in the vapor phase at equilibrium condition.

x_i^* = mole fraction of component "i" in the liquid phase at equilibrium condition.

In the study, for water:

$$K_w = \frac{y_w^*}{x_w^*} \quad (2.6)$$

For surfactant:

$$K_{surf} = \frac{y_{surf}^*}{x_{surf}^*} \quad (2.7)$$

For solute (HVOCs):

$$K_{HVOCs} = \frac{y_{HVOCs}^*}{x_{HVOCs}^*} \quad (2.8)$$

Where K_w , K_{surf} , and K_{HVOCs} are the vapor–liquid equilibrium partition coefficients of water, surfactant, and solute; y_w^* , y_{surf}^* , and y_{HVOCs}^* are the equilibrium mole fractions of water, surfactant, and solute in the vapor phase; X_w^* , X_{surf}^* , and X_{HVOCs}^* are the equilibrium mole fractions of water, surfactant, and solute in the liquid phase, respectively.

From Dalton's law, K_{HVOCs} is expressed as:

$$P_{HVOCs} = P y_{HVOCs}^* \quad (2.9)$$

Where P is the total pressure in the system.

Combining Eqs.(2.4), (2.8), and (2.9) yields:

$$P_{HVOCs} = (C_u + C_{sol}) H_{App} = X_{HVOCs}^* C_T H_{App} \quad (2.10)$$

Substituting Eq. (2.2) into the above equation gives:

$$K_{HVOCs} = \frac{H C_T}{P(1 + K_S C_m)} \quad (2.11)$$

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

2.6 Flash Calculation

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

$$F = L + V \quad (2.12)$$

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 solute balance in flash vacuum stripping at constant vapor and liquid flow rate is expressed as:

$$z_{HVOCs}F = x_{HVOCs}^*L + y_{HVOCs}^*V \quad (2.13)$$

Where z_{HVOCs} is the mole fraction of toluene in feed. Then, Eqs. (2.8) and (2.12) are substituted in Eq. (2.13), yielding:

$$x_{HVOCs}^* = \frac{z_{HVOCs}}{1 + \frac{V}{F}(K_{HVOCs} - 1)} \quad (2.14)$$

And, by applying Eq. (2.8), Eq. (2.14) is multiplied by K_{HVOCs} to

$$y_{HVOCs}^* = \frac{z_{HVOCs}K_{HVOCs}}{1 + \frac{V}{F}(K_{HVOCs} - 1)} \quad (2.15)$$

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,

$$x_w^* = \frac{z_w}{1 + \frac{V}{F}(K_w - 1)} \text{ and } y_w^* = \frac{z_w K_w}{1 + \frac{V}{F}(K_w - 1)} \quad (2.16)$$

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

$$x_{surf}^* = \frac{z_{surf}}{1-\bar{V}} \text{ and } y_{surf}^* = 0 \quad (2.17)$$

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.

2.7 Mass Transfer Calculation

The efficiency of the packed column used in co-current vacuum stripping to remove solute from coacervate solution was described by evaluating the overall mass transfer coefficient of solute 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 solute 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, solute 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 solute transfer per unit volume of packed column is a function of the overall mass transfer coefficient, the interfacial contact area of packing, and the solute concentration gradient existing across the liquid phase. This relationship was applied to the solute mass balance on the liquid phase in a differential volume of packed column.

Which is expressed as:

$$-L_0 \frac{dx_{HVOCs}}{dz} = K_x a (x_{HVOCs} - x_{HVOCs}^*) \quad (2.18)$$

Integrating and rearranging above equation, the height of the packed bed (Z) is given as:

$$Z = \frac{L_0}{K_x a} \ln \left(\frac{x_{i,HVOCs} - x_{HVOCs}^*}{x_{f,HVOCs} - x_{HVOCs}^*} \right) \quad (2.19)$$

where Z is the height of packing, L_0 is the molar cocervate flux in packed column, $x_{i,HVOCs}$ and $x_{f,HVOCs}$ are the mole fractions of toluene in the inlet and outlet cocervate streams, K_x is the overall liquid phase mass transfer coefficient of toluene, 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 toluene, and x_{HVOCs}^* is the equilibrium mole fraction of toluene in the cocervate solution from the equilibrium flash calculation already described.

This study assumed that x_{HVOCs}^* remains constant along the column. When the initial and final mole fraction data of toluene are known by directly analyzing the toluene concentration in the inlet and outlet cocervate streams, the $K_x a$ can then be calculated.