



## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Impact of Nonionic Surfactant in Environmental and Human Safety, and Trend in the Use of Alcohol Ethoxylate

Since surfactants are widely used in households, institutions, and industries application, large amount of surfactant usage is discharged to the public water reservoir. The two important types of nonionic surfactants are AE and APE. For APE, especially nonyl and octyl phenol ethoxylate are strongly disputed for the environmental acceptability. The presence of them in wastewater can be the cause of serious human illness (Jobling *et al.*, 1996; Nimrod and Benson, 1996; Pedersen *et al.*, 1999; Giesy *et al.*, 2000). As shown in Figure 2.1, APE can be biodegraded themselves to several degradation products (Ahel *et al.*, 1994; Talmage, 1994). Furthermore, some of them, mainly alkylphenols (APs) are more toxic than mother substances, APE, due to their great hydrophobic ability to accumulate in cell of aquatic organisms (Ahel *et al.*, 1994; Barber *et al.*, 2000; Barber *et al.*, 2007). From the potential toxic effects of some APE and their degradation products, alternative surfactants have been used in their place. Therefore, AE tend to be used in place of APE for residential and industrial uses.

The AE are widely accepted as the environmentally safe surfactants due to rapid biodegradation to harmless compounds, low to moderate foaming ability, superior cleaning of man-made fibers, and tolerance of water hardness than anionic surfactant.



molecular weight and the same average EO number. Their efficiency of surfactant on CPE was represented in term of the preconcentration factor. It is the ratio of the PAH concentration in the coacervate phase to its initial concentration before phase separation. The result illustrated preconcentration factor appeared in order of Tergitol 15-S-9 > Neodol 25-9 > Tergitol 15-S-7. It was due to the hydrophilicity order of surfactant.

Tergitol 15-S-7 or  $C_{11-15}H_{23-31}O(CH_2CH_2O)_{7.3}H$ , a polyethoxylated secondary alcohols nonionic surfactant, is a mixture of species with the alcohol group located at various positions along a chain of 11–15 carbon atoms with an average EO number of 7.3. There are many literatures studying the properties of Tergitol 15-S-7 to remove the contaminated polycyclic aromatic hydrocarbons in groundwater (Li *et al.*, 2002, 2003; Mar *et al.*, 2006; Hung *et al.*, 2007). Moreover, it has been used as an ingredient of a cleaner for general purpose cleaning, accepted by the Food Safety and Inspection Service of the US Department of Agriculture. Therefore, Tergitol 15-S-7 is used as a model of AEs surfactant in this study.

## 2.2 Cloud Point Phenomenon

Cloud point phenomenon occurs from the change of the clear micellar solution of a nonionic or zwitterionic surfactant from water-soluble to oil-soluble. Above the cloud point temperature (CPT), the surfactant will lose its water solubility almost completely, therefore, the surfactant molecules will separate out from the aqueous phase. As a result, the clear solution becomes turbid and phase separation occurs. So, the CPT is a specific temperature at which the nonionic or zwitterionic surfactant turns cloudy upon heating.

Generally, CPT of a nonionic surfactant can be affected by many factors: decreasing of ethylene oxide (EO) group, reducing its own concentrations, and lengthening of alkyl chain number; which normally reducing the CPT. In addition, the presence of electrolytes, salts and organic additives can also affect the CPT. For instance, CPT can be decreased by addition of polar compounds, anions that are water structure formers (hard bases,  $F^-$ ,  $OH^-$ ,  $SO_4^{2-}$ ,  $Cl^-$ , and  $PO_4^{3-}$ ) and certain cations ( $NH_4^+$ , alkali metal ions except for  $Li^+$ ), called salting-out effects. However,

CPT can be increased by addition of long chain nonpolar materials, anions, soft bases,  $\text{SCN}^-$ ,  $\text{I}^-$ ), and certain cations (polyvalent cations,  $\text{H}^+$ ,  $\text{Li}^+$ ), called salting-in effects (Huiber *et al.*, 1997, Taechagam *et al.*, 2008).

### **2.3 Principle of Cloud Point Extraction Process**

In CPE, as the nonionic surfactant solution is heated above CPT, the solution becomes turbid. Above the CPT, the surfactant solution separates into two phases, a surfactant-rich phase (coacervate phase) and an almost micelle-free dilute solution (dilute phase). The phase separation is reversible; therefore if the mixture is cooled to the temperature below the CPT, these two phases certainly merge to form a clear single phase again. CPE can be applied to remove the VOCs from contaminated water by phase partitioning above the CPT. The VOCs tend to be solubilized in the surfactant micelle, and then be concentrated in the coacervate phase whose volume is smaller. The small phase volume allows us to preconcentrate and easy to remove in another step.

The CPE process has many advantages such as cheaper, simpler, and more environmental friendly than conventional extraction processes using organic solvents (Zhu *et al.*, 2008). The CPE process can be applied not only for removing in the systems having 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 and 2004), but also for the systems having trace metal ions (Lemos *et al.*, 2007; Ohashi *et al.*, 2007; Zhu *et al.*, 2008).

### **2.4 Surfactant Regeneration Process: Co-Current Vacuum Stripping Using a Packed Column**

To make the CPE more economic attractive, the coacervate surfactant solution should be reused. There are many processes that can be used to remove the VOCs from contaminated coacervate surfactant solutions: for example, air stripping, stream stripping, spraying, pervaporation, and vacuum stripping (Lipe *et al.*, 1996;

Jiang *et al.*, 1997; Choori *et al.*, 1998; Hitchens *et al.*, 2001; Vane *et al.*, 2002). Generally, in conventional counter-current air stripping process or spraying, foam can be generated from the direct contact between the air and the liquid streams (Lipe *et al.*, 1996). A large amount of foam possibly causes a pressure drop and flooding in the operating column. Foam can be reduced by adding an anti-foaming agent, but this method requires the lateral unit of anti-foam and impurity clean-up. In pervaporation process, foam can be avoided; however, a gel layer can be generated by surfactants on the pervaporating membrane surface and possibly plugged the membrane (Hitchens *et al.*, 2001; Vane *et al.*, 2002). Consequently, to overcome these problems, a co-current vacuum stripping using a packed column is suggested to apply for VOCs removal from surfactant solution due to low foam formation in a packed column, and flooding is then eliminated.

Generally, a co-current vacuum stripping used widely use in many fields; majority in VOCs removal from contaminated water in chemical and petrochemical industries such as degassing for CO<sub>2</sub> and O<sub>2</sub> 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). Rasquin *et al.* (1997) reported that the multistage co-current operation can be accomplished most economically rather than a single stage counter-current operation. Moreover, it was found that the co-current vacuum stripping using a packed column could remove up to 90% of toluene from 300 mM Triton X-114, OP(EO)<sub>7</sub> coacervate phase solution without drastically flooding or foaming (Kungsanant *et al.*, 2008).

## 2.5 Hydrophobicity of Solutes

In this thesis work, the hydrophobicity of VOCs is represented in term of the octanol-water partition coefficient ( $K_{ow}$ ). It defined as the ratio of the equilibrium concentration of solute in an octanol phase to 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 VOCs to vapor phase (Taechangam *et al.*, 2008; Kungsanant *et al.*, 2008).

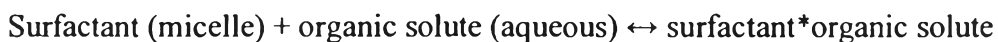
## 2.6 Vapor-Liquid Equilibrium of the VOCs in Aqueous Surfactant System

### 2.6.1 Micelle Formation

When surfactants 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 VOCs 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.

### 2.6.2 Solubilization

When a hydrophobic organic molecule is added to a micellar solution, it tends to concentrate 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:



Where the transfer of the solute into the micelle is treated as a binding phenomenon, for which the equilibrium solubilization constant ( $K_s$ ) is

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

Where  $C_{sol}$  is the solubilized organic solute concentration;  $C_u$  is the unsolubilized organic solute concentration, and  $C_m$  is the surfactant concentration in the micelle form.

In the 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:

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

$$\begin{aligned} \text{Where: } C_{sol} &= C_{\text{Total solute}} - C_u \\ C_m &= C_{\text{Total surfactant}} - \text{CMC} \end{aligned}$$

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

### 2.6.3 Vapor-Liquid Partitioning of the VOCs

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

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

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

However, in coacervate solution, the effect of surfactant micelles on the equilibrium partitioning of VOCs should be considered by modifying the Henry's law constant to the apparent Henry's law constant shown as follows:

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

#### 2.6.4 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 this study, for water:

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

For surfactant:

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

For solute (VOCs):

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

Where  $K_w$ ,  $K_{\text{surf}}$ , and  $K_{\text{VOCs}}$  are the vapor-liquid equilibrium partition coefficients of water surfactant, and solute;  $y_w^*$ ,  $y_{\text{surf}}^*$ , and  $y_{\text{VOCs}}^*$  are the equilibrium mole fractions of water, surfactant, and solute in the vapor phase;



$x_w^*$ ,  $x_{surf}^*$ , and  $x_{VOCs}^*$  are the equilibrium mole fractions of water, surfactant, and solute in the liquid phase, respectively.

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

$$p_{VOCs} = Py_{VOCs}^* \quad (2.9)$$

Where P is the total pressure in the system.

$$p_{VOCs} = (C_u + C_{sol})H_{App} = x_{VOCs}^* C_T H_{App} \quad (2.10)$$

$$K_{VOCs} = \frac{HC_T}{P(1 + K_s C_m)} \quad (2.11)$$

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

## 2.7 Flash Calculation

In co-current vacuum stripping, the equilibrium components in vapor and liquid are calculated from single stage equilibrium flash calculation.

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:

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

Where  $z_{\text{VOCs}}$  is the mole fraction of solute in feed solution. Then, Eqs (2.8) and (2.12) are substituted in Eq. (2.13), yielding:

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

Eqs (2.14) is multiplied through by  $K_{\text{VOCs}}$  to obtain  $y_{\text{VOCs}}^*$ ,

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

The equilibrium mole fractions of water, and surfactant in the vapor and coacervate phase are calculated by the same method, which are expressed as:

For water,

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

For surfactant,

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

Where  $z_w$  and  $z_{\text{surf}}$  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.

## 2.8 Mass Transfer Calculation in Co-Current Vacuum Stripping

The efficiency of the vacuum stripping is evaluated by determining the mass transfer coefficient of the VOC between the vapor and liquid phases. Theoretically, the mass transfer coefficient is a function of temperature, pressure, liquid and vapor flow rates, physical properties of liquid and vapor, packing size and type, and concentrations of solute (VOC) and surfactant.

For a diluted liquid solution, the mass balance of solute (VOC) on the liquid phase across a differential volume in a packed column is defined as:

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

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

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

Where Z is the height of packing,  $L_0$  is the molar coacervate flux in packed column,  $x_{i,\text{VOCs}}$  and  $x_{f,\text{VOCs}}$  are the mole fractions of solute in the inlet and outlet coacervate streams,  $K_x$  is the overall liquid phase mass transfer coefficient of solute,  $a$  is the effective interfacial area of packing per unit packed volume,  $K_x a$  is the overall liquid phase volumetric mass transfer coefficient of solute, and  $x_{\text{VOCs}}^*$  is the equilibrium mole fraction of solute in the coacervate solution from the equilibrium flash calculation already described.

In this work, it assumed that  $x_{\text{VOCs}}^{\circ}$  remains constant along the column. When the initial and final mole fraction data of solute are known by directly analyzing the toluene concentration in the inlet and outlet cocervate streams, the  $K_x a$  can then be calculated.