



## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Properties of Studied Surfactant

##### 4.1.1 Cloud Point Temperature

To ensure that cloud point temperature (CPT) of studied surfactant is below operating temperature (40°C), it was essential to have completed information on the CPE of surfactant candidates; branched secondary AE surfactant as shown in Table 4.1.

The CPT was investigated entirely by visual observation on the temperature at the clear micellar solutions occur. After that phase solution was elucidated by Total Organic Compounds (TOC 5000A, Shimadzu). Normally, The CPT depends on both EO number and alkyl carbon number. The CPT increases with EO number but decreases with alkyl carbon number, while the branched structures of alkyl carbon make CPT lower than linear structure (Hung *et al.*, 2007; Taechangam *et al.*, 2008).

From Table 4.1, the numbers of carbon and the number of EO group of Tergitol TMN-6, and Tergitol 15-S-7 were almost the same so the CPT of these three nonionic surfactants will be similar (CPT of Tergitol TMN-6 was 36°C, CPT of Tergitol 15-S-7 was 37°C). Moreover, Tergitol TMN-6 and Tergitol 15-S-7 Shows the higher CPT than Triton X-114 because the number of carbon of Triton X-114 was higher than that of Tergitol TMN-6 and Tergitol 15-S-7.

**Table 4.1** Properties of Tergitol TMN-6 compared with Tergitol 15-S-7 nonionic surfactant

| Properties/Surfactants | Tergitol TMN-6                | Tergitol 15-S-7*     | Triton X-114** |
|------------------------|-------------------------------|----------------------|----------------|
| Type                   | Branched 2 <sup>nd</sup> , AE | 2 <sup>nd</sup> , AE | APE            |
| CPT, °C                | 36                            | 37                   | 25             |
| HLB                    | 13.1                          | 12.4                 | 12.3           |
| Number of carbon       | 12 to 14                      | 11 to 13             | 14 to 16       |
| Mole of EO group       | 8                             | 7                    | 7.5            |
| Molecular weight g/mol | 230.387                       | 515                  | 537            |
| Viscosity, CP (25°C)   | 71                            | 51                   | 260            |
| Density (25°C) g/ml    | 0.994                         | 0.992                | 1.058          |
| CMC, ppm               | 800                           | 38                   | 120            |

\*Data obtained from Kittisrisawai *et al.*, 2009.

\*\*Data obtained from Kungsanant *et al.*, 2008.

#### 4.1.2 Concentration of Surfactant in Coacervate Phase

After the phase separation, the concentration of both coacervate and dilute phase solution of branched secondary alcohol ethoxylate, Tergitol TMN-6 was measure by TOC. According to Table 4.2, the result shows that the concentration of coacervate phase of Tergitol TMN-6 was 354.6 mM which is lower than 450 mM-the surfactant concentration used in this experiment; so, it can be conclude that phase separation could not occur during the experimental (at 40°C).


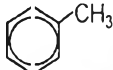
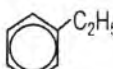
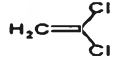
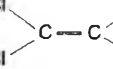
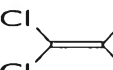
**Table 4.2** Concentration of surfactant in dilute and coacervate phase at 40°C

| Surfactant     | Dilute Phase conc. (mM) | Coacervate Phase conc. (mM) |
|----------------|-------------------------|-----------------------------|
| Tergitol TMN-6 | 10.4                    | 354.6                       |

## 4.2 Vapor-Liquid Equilibrium

In order to assess the performance of stripping processes for removing HVOCs from surfactant solution, the partitioning behavior of HVOCs among vapor, aqueous, and micellar phase must be investigated via the modified equilibrium partitioning in closed system (EPICS) method. The general properties of the studied HVOCs are shown in Table 4.3.

**Table 4.3** Molecular structures and the Henry's law constants (H) of the selected aromatic solutes

| HVOCs | Structure of VOCs   | log octanol-water partition coefficient, log $K_{ow}$ | Henry's law constant, H (atm/ppm) |
|-------|---|---|-----------------------------------|
| BEN   |  | 2.13  | $1.1 \times 10^{-04a}$            |
| TOL   |  | 2.69  | $1.2 \times 10^{-04a}$            |
| ETB   |  | 3.15  | $1.5 \times 10^{-04a}$            |
| DCE   |  | 1.32  | $3.7 \times 10^{-04a}$            |
| TCE   |  | 2.29  | $1.3 \times 10^{-04a}$            |
| PCE   |  | 3.4   | $2.0 \times 10^{-04a}$            |

<sup>a</sup> Data obtained from Kittirisawai *et al.*, (2009).

Generally, the presence of the micellar phase significantly reduces the volatilization of HVOCs. Thus, the total amount of HVOC accumulated in micellar phase plays a significant role in process design. In this study, the volatilization and

solubilization of HVOCs are reported in term of Henry's law constant (H) and solubilization constant ( $K_s$ ), respectively.

#### 4.2.1 The Partition Behavior of the HVOCs in Aqueous and Coacervate Phase Solution

To determine the equilibrium time of the HVOCs' partitioning in aqueous and coacervate phase solution, the concentration of the HVOCs in vapor phase was measured as a function of time. For aqueous system, the solution with various HVOCs concentration was added in 20 mL headspace glass vials with Teflon-coated septa and aluminum holed caps. The vials will be placed in the headspace-GC oven controlled at 40°C. The sample in vapor phase was collected and automatically measured as a function of time. For surfactant system, the surfactant concentration in feed solution was maintained at 450 mM in every experiment. The coacervate solution with various HVOCs concentrations was added in 20 mL headspace glass vials with Teflon-coated septa and aluminum holed caps. The equilibrium time was obtained by using the method similar to that in the aqueous system. From experiment, it was observed that the equilibrium was reached around 30 minutes with shaking. In order to guarantee this experiment reached equilibrium system, the systems were operated to reach equilibrium for 60 minutes.

#### 4.2.2 Determination the Solubilization Constant, $K_s$

The solubilization,  $K_s$  was the ratio of the distribution of the solute between the micelles and the aqueous phase and was calculated via Eqs (2.2). The higher solubilization is the higher HVOCs can be solubilized into micellar phase. The  $K_s$  was independent of surfactant concentration except the micellar structure change via concentration (Vane *et al.*, 2000).

In this work, the solubilization constants of the HVOCs were conducted at 500-2000 ppm HVOCs in 450 mM tergitol TMN-6 at 40°C. The hydrophobicity of studied HVOCs is characterized by the octanol-water partition coefficient ( $K_{ow}$ ) were range from 1.32 to 3.40 as shown in Table 4.3. The higher  $K_{ow}$  gave higher hydrophobic of solute and the more its tendency to solubilize in

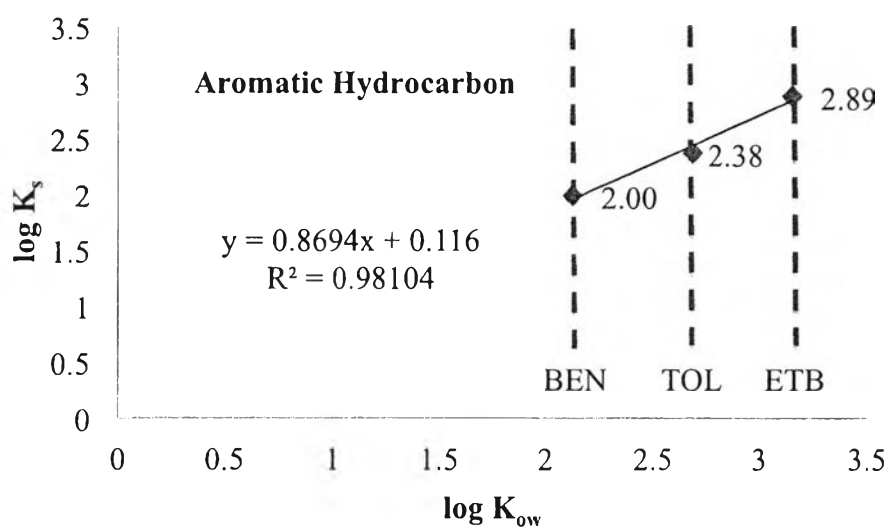
micelles which make the lower volatilization of HVOCs (Taechangam *et al.*, 2008; Kungsanant *et al.*, 2008).

Figure 4.1 presents the good linear logarithm correlation at equilibrium condition of aromatic hydrocarbon series. The r-square was 0.98104. The  $\log K_s$  value was increase with the increasing of alkyl group of aromatic hydrocarbon (BEN>TOL>ETB). The same trend is found in chlorinated hydrocarbon series, which corresponding to the increasing of the degree of chlorination (1,1-DCE>TCE>PCE) as shown in Figure 4.2. These phenomenon clearly confirm that the solubilization of HVOCs increase as a result of the increasing of the hydrophobic of HVOCs. This is because the surfactants can increase the mass transfer of the hydrophobic contaminant from bulk liquid phase by accumulating the hydrophobic compounds in micellar cores (Rosen, 2004).

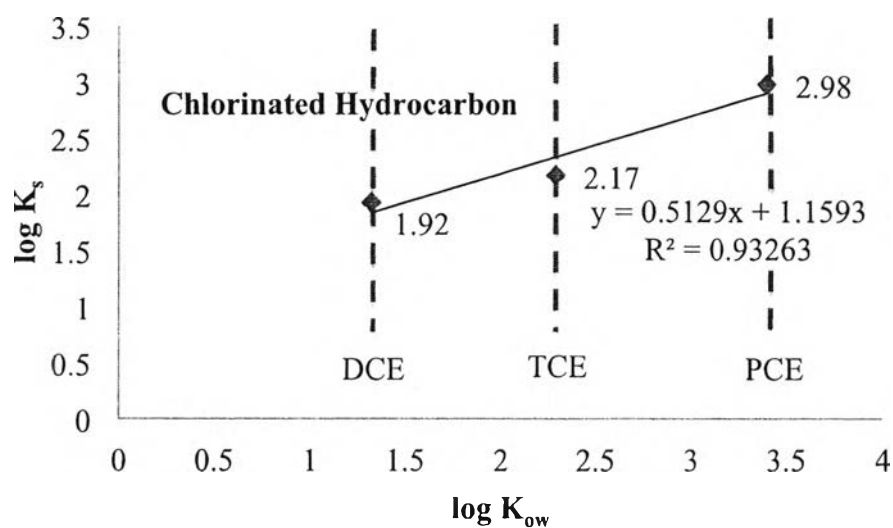
The correlation between  $\log K_s$  and  $\log K_{ow}$  at equilibrium condition of the six studied HVOCs: aromatic and chlorinated hydrocarbon series in coacervate solution displays on Figure 4.3. This demonstrates a good linear relationship with r-square equal to 0.88034 and also illustrates the dependence of  $\log K_s$  on HVOCs hydrophobicity.

Figure 4.1-4.3 clearly confirm that the solubilization of HVOCs increase as a result of the increasing of hydrophobic of HVOCs. This is because the surfactants can increase the mass transfer of the hydrophobic contaminant from solid or non-aqueous liquid phase into aqueous phase by accumulating the hydrophobic compounds in their non-polar micellar cores (Rosen, 2004).

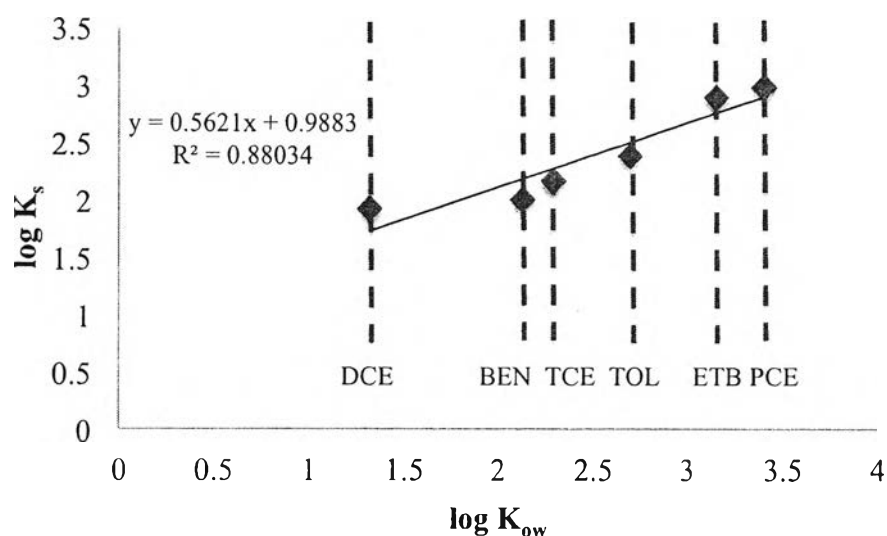
Comparing with the study of Li *et al.* (2002), which studied the solubilization of PAHs-naphthalene, fluorine, phenanthrene, and phyrene-in several type of nonionic surfactant, they showed the good relationship of the micelle-water partition coefficients ( $K_m$ ) and the  $K_{ow}$  in tergitol 15-S-7 surfactant solution. The r-square of  $\log K_m - \log K_{ow}$  was 0.99. The micelle-water partition coefficient is the ratio of solute in the micellar phase to solute in the aqueous phase. It is a parameter that can indicate the distribution of solute between the micellar phase and the aqueous phase as same as the  $K_s$ . This could be the one evidence to supported that  $K_{ow}$  could be used in predicting the efficiency of HVOCs' solubilization.



**Figure 4.1** Correlation between octanol-water partition coefficient ( $K_{ow}$ ) and solubilization constant ( $K_s$ ) of benzene (BEN), toluene (TOL), and ethyl benzene (ETB) in Tergitol TMN-6 solution (450 mM Tergitol TMN-6, 40°C) at equilibrium condition.



**Figure 4.2** Correlation between octanol-water partition coefficient ( $K_{ow}$ ) and solubilization constant ( $K_s$ ) of dichloroethylene (DCE), trichloroethylene (TCE), and perchloroethylene (PCE) in Tergitol TMN-6 solution (450 mM Tergitol TMN-6, 40°C) at equilibrium condition.



**Figure 4.3** Correlation between octanol-water partition coefficient ( $K_{ow}$ ) and solubilization constant ( $K_s$ ) of the studied HVOCs in Tergitol TMN-6 solution (450 mM Tergitol TMN-6, 40°C) at equilibrium condition.

When compare the result with previous work (Kittisrisawai *et al.*, 2009; Kungsanant *et al.*, 2008), we observed that the solubilization constant of all solutes in the branched AE nonionic surfactant solution (Tergitol TMN-6) was lower than that linear AE and linear APE nonionic surfactant solution (Tergitol 15-S-7 and Triton X-114) as respectively shown in Table 4.4. This is due to the much higher CMC of branched AE nonionic surfactant compared to that of the linear AE nonionic surfactant (Rosen, 2004). For the same surfactant concentration, the number of micelle in Tergitol TMN-6 solution will be lower than that in Tergitol 15-S-7 and Triton X-114. The aggregation numbers of branched AE nonionic surfactant also less than that of the linear AE nonionic surfactant (Rosen, 2004). Thus, it will be harder for solute to solubilized in Tergitol TMN-6 solution.

**Table 4.4** Solubilization constant ( $K_s$ ), and apparent Henry's law constant ( $H_{app}$ ) of all studied HVOCs in branched and linear nonionic surfactant

| HVOCs             | Surfactant Type               |                       |                              |                      |                            |                      |
|-------------------|-------------------------------|-----------------------|------------------------------|----------------------|----------------------------|----------------------|
|                   | Branched AE<br>Tergitol TMN-6 |                       | Linear AE<br>Tergitol 15-S-7 |                      | Linear APE<br>Triton X-114 |                      |
|                   | $K_s$                         | $H_{app}$             | $K_s$                        | $H_{app}$            | $K_s$                      | $H_{app}$            |
| Benzene           | 1.80                          | $6.03 \times 10^{-5}$ | 54                           | $4.4 \times 10^{-6}$ | 34                         | $6.8 \times 10^{-6}$ |
| Toluene           | 4.35                          | $3.98 \times 10^{-5}$ | 156                          | $1.6 \times 10^{-6}$ | 108                        | $2.2 \times 10^{-6}$ |
| Ethyl Benzene     | 14.16                         | $1.98 \times 10^{-5}$ | 310                          | $1.1 \times 10^{-6}$ | 294                        | $1.2 \times 10^{-6}$ |
| Dichloroethylene  | 1.51                          | $2.20 \times 10^{-4}$ | 45                           | $1.7 \times 10^{-5}$ | -                          | -                    |
| Trichloroethylene | 2.66                          | $5.89 \times 10^{-5}$ | 142                          | $2.1 \times 10^{-6}$ | 59                         | $4.9 \times 10^{-6}$ |
| Perchloroethylene | 17.29                         | $2.26 \times 10^{-5}$ | 500                          | $8.9 \times 10^{-6}$ | 113                        | $3.8 \times 10^{-6}$ |

#### 4.2.3 Determination of the Apparent Henry's Law Constant ( $H_{app}$ ) of HVOCs in Coacervate Phase Solution

Normally, the volatilization and Henry's law constant increases with increasing of the HVOCs hydrophobicity. The  $K_{ow}$  values increase in order to the increasing of the degree of alkylation as shown in Table 4.3. Nevertheless, the Henry's law constant of dichloroethylene was highest over the other due to its easiness of volatility nature. The Henry's law constant data of all studied HVOCs were illustrated in Table 4.3.

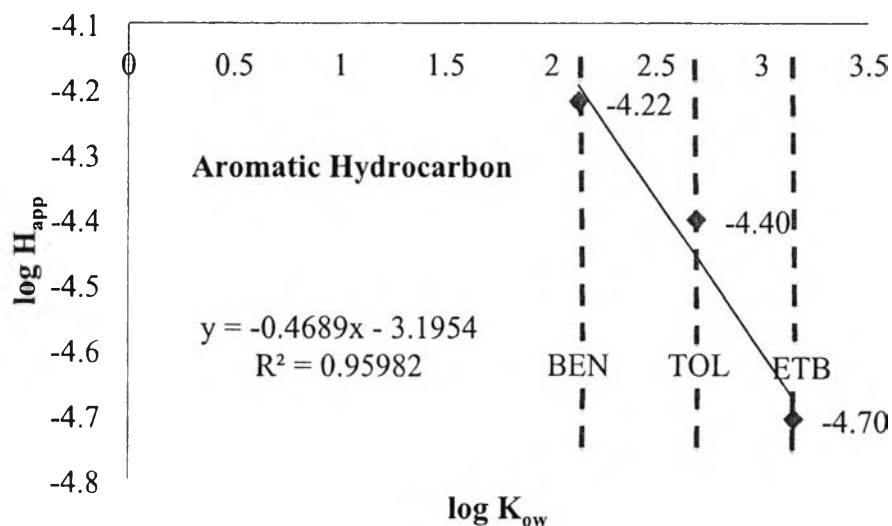
At surfactant concentration above CMC, the HVOCs in surfactant solution will be solubilized inside micelles, resulting in enhancing the solubility of HVOCs. However, the presence of micelles can decrease the volatilization of HVOCs which indicated in term of Henry's Law constant, so the Henry's Law constant must be modified to be "Apparent Henry's Law Constant" or  $H_{app}$ . The volatility of the HVOCs was conducted at 40°C by using 100-800 ppm HVOCs in water system and 500-2000 ppm HVOCs in 450 mM Tergitol TMN-6. The calculated apparent Henry's law constants of each solute are shown in Figure 4.4-4.6.



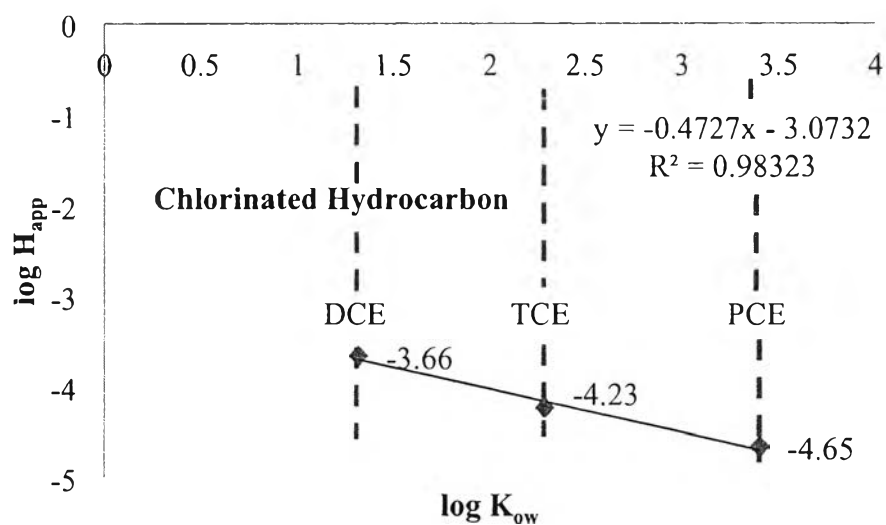
It should be noted that benzene has highest apparent Henry's law constant, so might be easiest to remove benzene from surfactant comparing with other HVOCs.

In addition, the Henry's law constant of all solutes decreases around one order of magnitude when surfactant is present in the solution. All solute illustrate the decrease of  $H_{app}$  along the increasing of hydrophobicity which means that the less of volatilization of HVOCs, despite the fact that the H values increase along the hydrophobicity of solute.

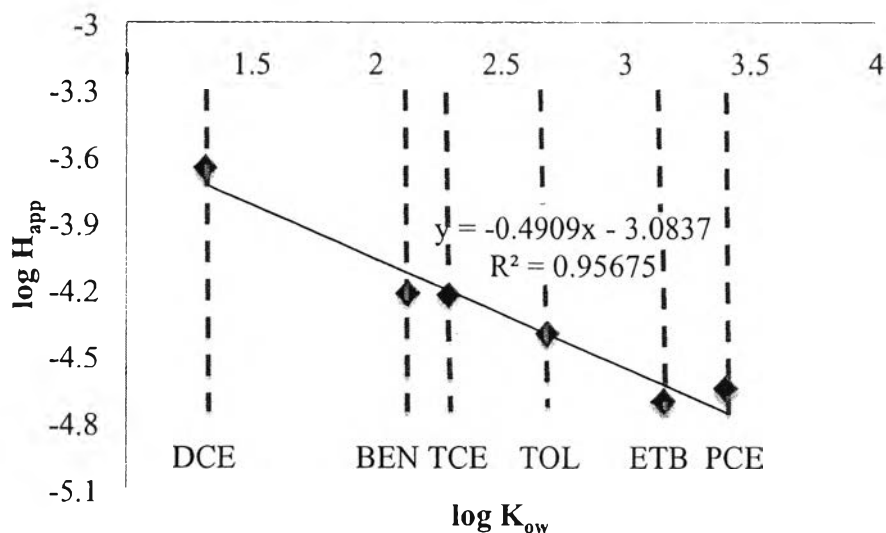
As investigated in the earlier, the increasing of hydrophobic of solutes ( $K_{ow}$ ) could increase the solubilization of HVOCs ( $K_s$ ) leading to the less volatilization of HVOCs in nonionic surfactant solution. This result was conversely with the relationship between H and  $K_{ow}$  (Table 4.3). Therefore, the phenomenon of  $H_{app}$  to the degree of hydrophobicity, which show in Figure 4.4-4.6, can be indicated that the effect of solubilization plays an important role in the volatility of HVOCs in surfactant solution. Figure also shows a good linear relationship between  $\log K_{ow}$  and  $\log H_{app}$  with the r-square was higher than 0.95.



**Figure 4.4** Correlation between octanol-water partition coefficient ( $K_{ow}$ ) and apparent Henry's law constant ( $H_{app}$ ) of benzene (BEN), toluene (TOL), and ethyl benzene (ETB) in Tergitol TMN-6 solution (450 mM Tergitol TMN-6, 40°C) at equilibrium condition.



**Figure 4.5** Correlation between octanol-water partition coefficient ( $K_{ow}$ ) and apparent Henry's law constant ( $H_{app}$ ) of dichloroethylene (DCE), trichloroethylene (TCE), and perchloroethylene (PCE) in Tergitol TMN-6 solution (450 mM Tergitol TMN-6, 40°C) at equilibrium condition.



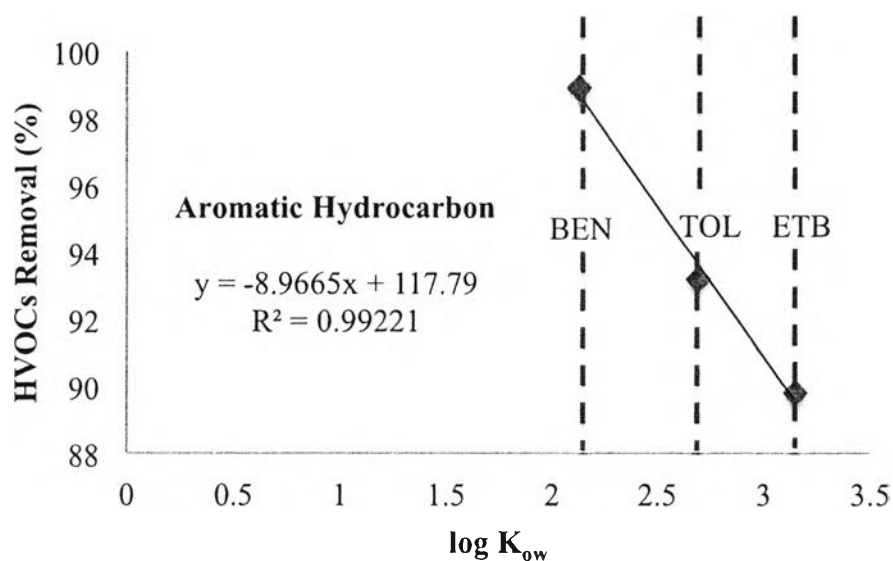
**Figure 4.6** Correlation between octanol-water partition coefficient ( $K_{ow}$ ) and apparent Henry's law constant ( $H_{app}$ ) of studied HVOCs in Tergitol TMN-6 solution (450 mM Tergitol TMN-6, 40°C) at equilibrium condition.

When compare the result with previous work (Kittisrisawai *et al.*, 2009; Kungsanant *et al.*, 2008), it can be seen that the apparent Henry's law constant of studied solutes in branched nonionic surfactant solution (Tergitol TMN-6) was much higher than that of linear AE and APE nonionic surfactant (Tergitol 15-S-7 and Triton X-114) as respectively shown in Table 4.4. This may be due to looser packing of the surfactant molecules in the micelles (Rosen, 2004). From this result, it can be observed that the solute, which solubilized in branched AE nonionic surfactant might be easier to evaporate from the micelle of surfactant solution than linear AE and APE nonionic surfactant (Tergitol 15-S-7 and Triton X-114).

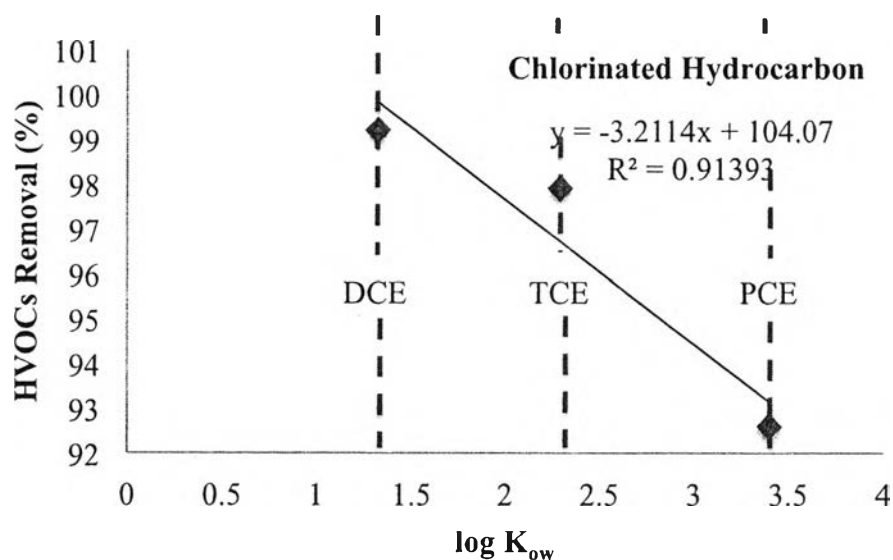
### 4.3 Continuous Operation

In this thesis work, the stripping column was operated at co-current mode with 1.1 mL/min feed flow rate, 59 absolute torr column pressure, 3-hole distributor, and 40°C which is the optimum operation conditions reported in the previous work (Kungsanant *et al.*, 2008). The concentration of each HVOC was 2000 ppm in 450 mM of Tergitol TMN-6. There was no significant foaming and flooding of coacervate solution observed in the column along the experiments. The steady state time of aromatic and chlorinated hydrocarbon series in vacuum stripping is around 60 minutes. In addition, the vacuum stripping performance is reported in term of HVOCs removal, and the overall liquid phase mass transfer coefficient ( $K_{xa}$ ). The  $K_{xa}$  is parameter that indicated the mass transfer rate of solute from one phase to another phase, in this case from coacervate phase to vapor phase. It can show the efficiency of the operating design.

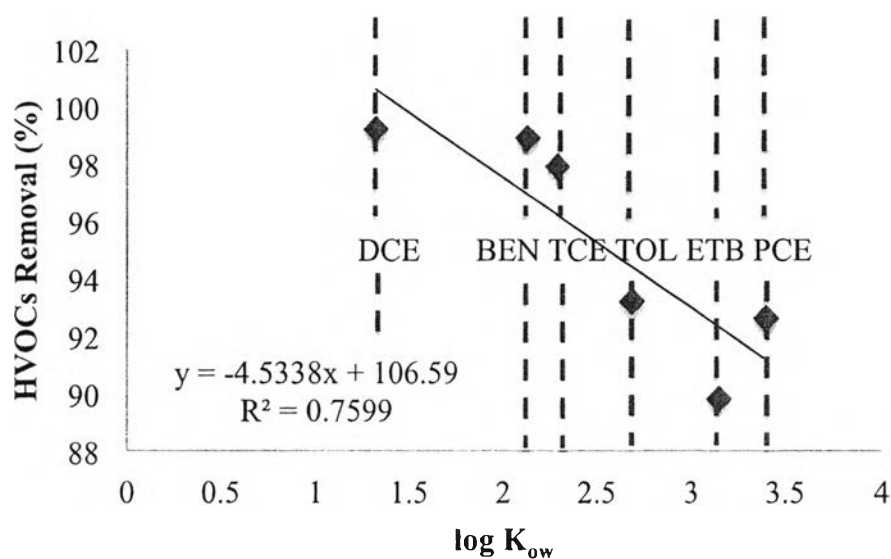
The corresponding of the HVOCs removal (%) and the  $K_{ow}$  of each series; aromatic and chlorinated hydrocarbon series are displayed in Figure 4.7 and 4.8. The r-square of HVOCs removal (%) and  $\log K_{ow}$  of both series are 0.9922 and 0.9139, respectively. Figure 4.7 Shows that the percentages of HVOCs removal of aromatic hydrocarbons are decreased as the degree of alkylation increase (BEN>TOL>ETB). The same trend is observed in chlorinated hydrocarbon series, which corresponding to degree of chlorination (1,1-DCE>TCE>PCE) as shown in Figure 4.8.



**Figure 4.7** Correlation between HVOCs removal (%) and octanol-water partition coefficient ( $K_{ow}$ ) of benzene (BEN), toluene (TOL), and ethyl benzene (ETB) in Tergitol TMN-6 solution (2000 ppm HVOCs in 450 mM Tergitol TMN-6, 40°C).

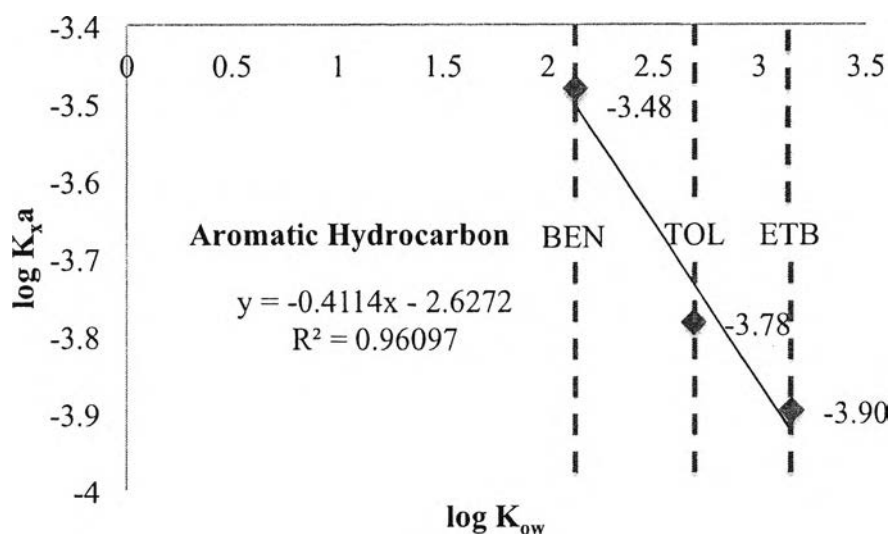


**Figure 4.8** Correlation between HVOCs removal (%) and octanol-water partition coefficient ( $K_{ow}$ ) of dichloroethylene (DCE), trichloroethylene (TCE), and perchloroethylene (PCE) in Tergitol TMN-6 solution (2000 ppm HVOCs in 450 mM Tergitol TMN-6, 40°C).

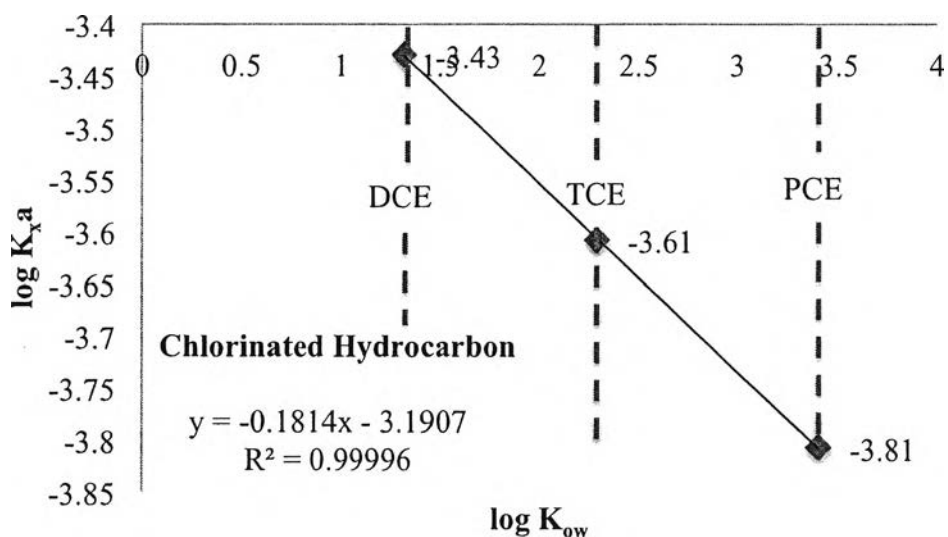


**Figure 4.9** Correlation between HVOCs removal (%) and octanol-water partition coefficient ( $K_{ow}$ ) of studied HVOCs in Tergitol TMN-6 solution (2000 ppm HVOCs in 450 mM Tergitol TMN-6, 40°C).

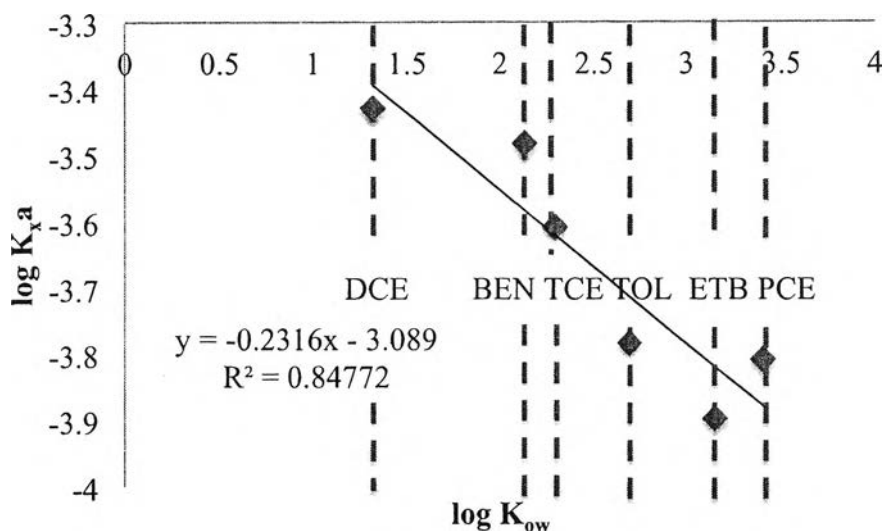
Furthermore, the correlation between HVOCs removal (%) and  $K_{ow}$  from both aromatic and chlorinated hydrocarbon series is displayed in Figure 4.9. The  $r$ -square of this plot is 0.7599. The plot illustrates that HVOCs removal decrease in order; 1,1-DCE > BEN > TCE > TOL > PCE > ETB. The efficiency of HVOCs removal is higher than 89% for both series. The greatest efficiency of vacuum stripping to remove HVOC is 99.2 % for 1,1-DEC, which is correspondent with its highest volatility result ( $H_{app}$ ). On the other hand, the lowest efficiency is 89.8% for ETB due to the hardest to strip HVOCs from coacervate solution to vapor phase.



**Figure 4.10** Correlation between the overall liquid phase volumetric mass transfer coefficient,  $K_{xa}$  ( $\text{mol}/\text{cm}^3 \text{ min}$ ) and partition coefficient ( $K_{ow}$ ) of benzene (BEN), toluene (TOL), and ethyl benzene (ETB) in Tergitol TMN-6 solution (2000 ppm HVOCs in 450 mM Tergitol TMN-6, 40°C).



**Figure 4.11** Correlation between the overall liquid phase volumetric mass transfer coefficient,  $K_{xa}$  ( $\text{mol}/\text{cm}^3 \text{ min}$ ) and partition coefficient ( $K_{ow}$ ) of dichloroethylene (DCE), trichloroethylene (TCE), and perchloroethylene (PCE) in Tergitol TMN-6 solution (2000 ppm HVOCs in 450 mM Tergitol TMN-6, 40°C).



**Figure 4.12** Correlation between the overall liquid phase volumetric mass transfer coefficient,  $K_{xa}$  ( $\text{mol}/\text{cm}^3 \text{ min}$ ) and partition coefficient ( $K_{ow}$ ) of studied HVOCs in Tergitol TMN-6 solution (2000 ppm HVOCs in 450 mM Tergitol TMN-6,  $40^\circ\text{C}$ ).

Similarity, the relation between  $K_{xa}$  and  $\log K_{ow}$  of the aromatic and the chlorinated hydrocarbon series are shown in Figure 4.10 and 4.11. The  $r$ -square of  $\log K_{xa}$ - $\log K_{ow}$  of both series are higher than 0.95. The plot illustrate that the  $K_{xa}$  drop in along the increasing of hydrophobicity  $K_{ow}$  of solute:  $\text{BEN} < \text{TOL} < \text{ETB}$  and  $1,1\text{-DCE} < \text{TCE} < \text{PCE}$ . Figure 4.12 show the correlation between  $K_{xa}$  and  $\log K_{ow}$  of both aromatic and chlorinated hydrocarbon, the  $r$ -square of the correlation between the  $K_{xa}$  and the  $K_{ow}$  of the six solutes is 0.84108. The plot indicates that the  $K_{xa}$  decrease as a result of the increasing of hydrophobicity of HVOCs as well as the trend of HVOCs removal (%) and  $\log K_{ow}$ .

According to the corresponding of the HVOCs removal (%), the  $K_{xa}$ , and the  $K_{ow}$ , the results clearly show that the lower  $K_{ow}$  facilitate the greater HVOCs removal from the surfactant solution as a result of the higher mass transfer rate. The reason is that an increase in HVOCs hydrophobicity affect in enhancing solubilization of HVOCs in the surfactant micelles (Kungsanant *et al.*, 2008).

**Table 4.5** Overall liquid phase mass transfer coefficient ( $K_{x,a}$ ), and % HVOCs removal of all studied HVOCs in branched nonionic surfactant and linear nonionic surfactant

| HVOCs             | Surfactant Structure      |                                     |                           |                                     |
|-------------------|---------------------------|-------------------------------------|---------------------------|-------------------------------------|
|                   | Branched (Tergitol TMN-6) |                                     | Linear (Tergitol 15-S-7)* |                                     |
|                   | Removal (%)               | $K_{x,a}$ (mol/cm <sup>3</sup> min) | Removal (%)               | $K_{x,a}$ (mol/cm <sup>3</sup> min) |
| Benzene           | 98.9                      | $3.30 \times 10^{-4}$               | 91.4                      | $2.38 \times 10^{-4}$               |
| Toluene           | 93.2                      | $1.65 \times 10^{-4}$               | 79.8                      | $1.45 \times 10^{-4}$               |
| Ethyl Benzene     | 89.8                      | $1.27 \times 10^{-4}$               | 60.6                      | $9.74 \times 10^{-5}$               |
| Dichloroethylene  | 99.2                      | $3.72 \times 10^{-4}$               | 98.1                      | $2.85 \times 10^{-4}$               |
| Trichloroethylene | 97.9                      | $2.47 \times 10^{-4}$               | 89.7                      | $2.36 \times 10^{-4}$               |
| Perchloroethylene | 92.6                      | $1.56 \times 10^{-4}$               | 72.3                      | $1.26 \times 10^{-4}$               |

\* Data obtained from Kittisrisawai *et al.*, (2009).

Table 4.5 shows the comparison of the  $K_{x,a}$ , and the percentage of HVOCs removal of all studied HVOCs observed in Tergitol TMN-6 to those observed in Tergitol 15-S-7. It should be noted that at least 89.8% of all six HVOCs could be removed from 450 mM branched nonionic surfactant coacervate solution (Tergitol TMN-6) by the single stage vacuum stripping.

When compare the result with previous work (Kittisrisawai *et al.*, 2009; Kungsanant *et al.*, 2008), Table 4.5 shows that the  $K_{x,a}$ , and the percentage of HVOCs removal of the HVOCs observed in branched nonionic surfactant was higher than those observed in linear nonionic surfactant because of the looser packing of the surfactant molecules (Rosen, 2004). So, it might be easier for contaminated to transfer to the gas phase and remove out from the micelle.