



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; linear AE surfactant, Dehydol LS5 and the polyethoxylated secondary alcohol surfactant, Tergitol 15-S-7 as shown in Table 4.1.

The CPT was investigated entirely by visual observation on the temperature at the clear micellar solutions occur. After phase separation, the concentration of both coacervate and dilute phase solution was elucidated by TOC. 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 structure of alkyl carbon make CPT lower than linear structure (Hung *et al.*, 2007; Taechangam *et al.*, 2008).

In this thesis work, the numbers of carbon of two nonionic surfactants are similar; therefore the different of the CPT come from the effect of the number of EO and the structure of hydrophobic part. Tergitol 15-S-7 is the branched structure and its CPT lower than linear structure, Dehydol LS5. However, Tergitol 15-S-7 has the number of EO group higher than Dehydol LS5. Table 4.1 shows that the CPT of Tergitol 15-S-7 is 37°C whereas; the CPT of Dehydol LS5 is 18°C.

Table 4.1 Properties of Tergitol 15-S-7 and Dehydol LS5 nonionic surfactant

Properties/ Surfactant	Tergitol 15-S-7	Dehydol LS5
Type	2 nd , AE	linear AE
CPT, °C	37	18
HLB	12.4	10 to 11
Number of carbon	11 to 15	12 to 14
Mole EO group	7	5
Molecular weight	515	413.14
Viscosity, cP	51	n/a
Specific density at 25°C, g/ml	0.992	0.995
CMC at 1% wt solution, ppm	38	n/a
Coacervate phase conc., at 40°C, mM	222	~ 1200
Viscosity at coacervate conc., cP	37	700-1000*

* (Stable bubbles cause the fluctuation in viscosity measurement.)

4.1.2 Concentration of Surfactant in Coacervate Phase

After the phase separation, the concentration of both coacervate and dilute phase solution of branched AE, Tergitol 15-S-7 and linear AE, Dehydol LS5 was elucidated by TOC. According to Table 4.2, the result shows Tergitol 15-S-7 gives a much lower concentration of coacervate phase than Dehydol LS5.

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

Surfactant	Dilute conc. (mM)	Coacervate conc. (mM)
Tergitol 15-S-7	11.6	222.4
Dehydol LS5	N.A.	1200

In order to compare with previous study which used APE, Triton X-114, two AE surfactant candidates: the branched AE, Tergitol 15-S-7 and linear AE, Dehydol LS5 were chosen via 2 criteria. The first criterion is the CPT of new AE surfactant must be lower than the previous operating temperature (40°C). Another is the coacervate concentration should be lower than 450 mM (Kungsanant *et al.*, 2008). However, as shown in Table 4.1, the coacervate concentration of Dehydol LS5 is very high (1200 mM). Moreover, the solution at this point is very viscous. In the stripping process, it is difficult to form phase separation from the coexisting water phase due to the high viscosity of coacervate solution. Consequently, Tergitol 15-S-7 is selected for further study. In addition, the Tergitol 15-S-7 concentration was fixed at 450 mM throughout this thesis work due to the result of its in coacervate phase compare with previous work (Kungsanant *et al.*, 2008).

4.2 Vapor-Liquid Equilibrium

In order to assess the performance of stripping processes for removing VOCs from surfactant solution, the partitioning behavior of VOCs among vapor, aqueous, and micellar phase must be investigated via the modified equilibrium partitioning in closed systems (EPICS) method. Generally, the presence of the micellar phase significantly reduces the volatilization of VOCs. Thus, the total amount of VOC accumulated in micellar phase plays a significant role in process design. In this study, the volatilization and solubilization of VOCs are observed and reported in terms of Henry's law constant and solubilization constant, respectively.

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

To determine the equilibrium time of the VOCs' partitioning in aqueous and coacervate phase solution, the concentration of the VOCs in vapor phase was measured as a function of time. The surfactant concentration in feed solution was constant at 450 mM and 40°C in every experiment. The coacervate solution was in 22 ml headspace glass vials with Teflon-coated septa and aluminum holed caps. The

equilibrium time was 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 is the ratio of the distribution of the solute between the micelles and the aqueous phase and is calculated via Eqs (2.2).

Normally, the higher solubilization, the greater VOCs can be solubilized into coacervate phase solution. The K_s is independent of surfactant concentration except the micellar structure change via concentration (Vane *et al.*, 2000).

In this study, the hydrophobicity of VOCs is characterized by the octanol-water partition coefficient (K_{ow}). As mentioned in the literature review section, the higher K_{ow} , the higher hydrophobic of solute is and the more its tendency to solubilize in micelles which make the lower volatilization of VOCs to vapor phase (Taechangam *et al.*, 2008; Kungsanant *et al.*, 2008).

At concentration above CMC, the surfactant solution can be considered into 2 phase: aqueous and micellar phase. The interaction between the charges at head group of ionic surfactant and polar solutes can affect only in aqueous phase, resulted the correlation of K_{ow} and solubilization can be mistake due to ion/dipole interaction. Comparison to the nonionic surfactant and uncharged solute that used in this experiment, the Van der Waals forces are only the major force that affect in both octanol and aqueous phase, thus K_{ow} is supposed to perform the solubilization of the solutes in coacervate phase solution (Taechangam *et al.*, 2008).

Figure 4.1 presents the correlation at equilibrium condition of aromatic, hydrocarbon series. The r-squared is 0.995. The $\log K_s$ values are in an increasing order of hydrophobic alkylation for aromatic hydrocarbon (BEN>TOL>ETB). The same trend is found in chlorinated hydrocarbon series, which corresponding to degree of chlorination (1,1-DCE>TCE>PCE) as shown in Figure 4.2.

The correlation at equilibrium condition of the 6 contaminated VOCs: aromatic and chlorinated hydrocarbon series in coacervate solution displays on Figure 4.3. The $\log K_{ow}$ of VOCs range of 1.32-3.40. The $\log K_s$ - $\log K_{ow}$ graph

demonstrates a good linear relationship ($R^2 = 0.90$). It illustrates the dependence of $\log K_s$ on VOCs hydrophobicity.

As illustrated in Figures 4.1-4.3, these phenomena clearly confirm that the solubilization of VOCs increases as a result of the increasing of hydrophobic of VOCs. 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 decreasing the interfacial tension and by accumulating the hydrophobic compounds in the micellar cores (Rosen, 2004).

Comparing with the study of Li *et al.* (2002), which studied the solubilization of PAHs—naphthalene, fluorine, phenanthrene, and pyrene—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-squared 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 VOCs' solubilization.

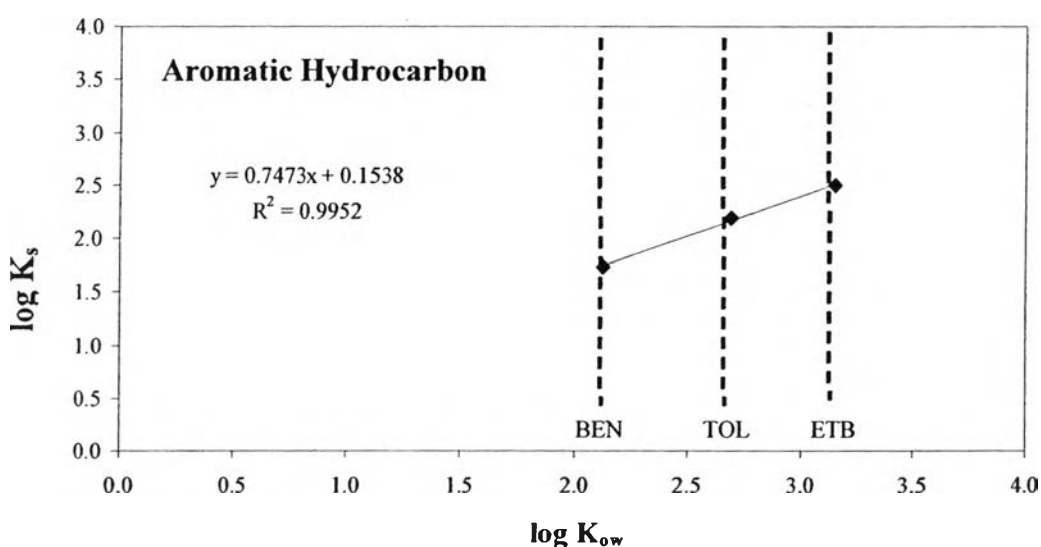


Figure 4.1 Correlation between octanol-water partition coefficient (K_{ow}) and solubilization constant, (K_s) of aromatic hydrocarbon in Tergitol 15-S-7, AE coacervate solution (450 mM Tergitol 15-S-7, 40°C) at equilibrium condition.

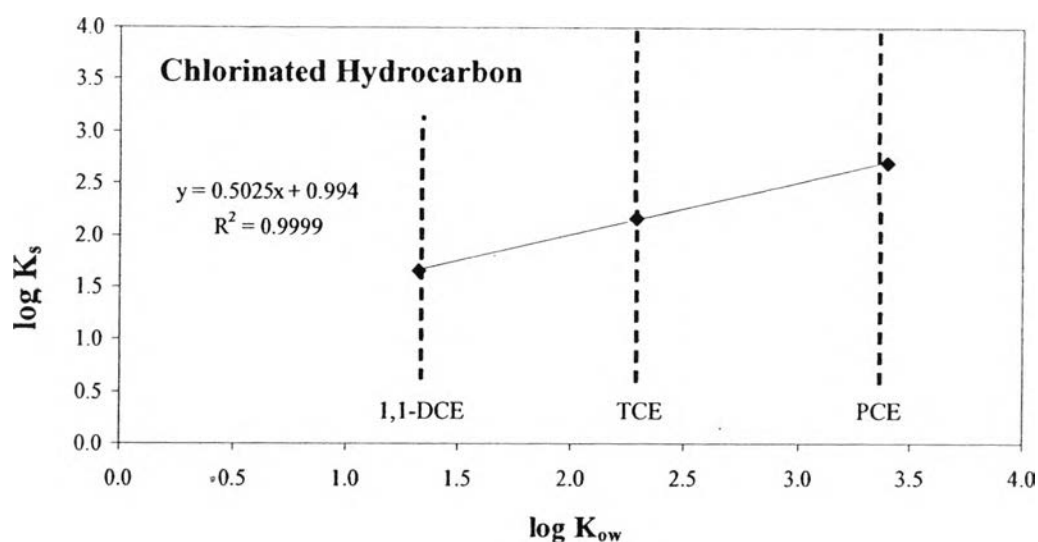


Figure 4.2 Correlation between octanol-water partition coefficient (K_{ow}) and solubilization constant, (K_s) of chlorinated hydrocarbon in Tergitol 15-S-7, AE coacervate solution (450 mM Tergitol 15-S-7, 40°C) at equilibrium condition.

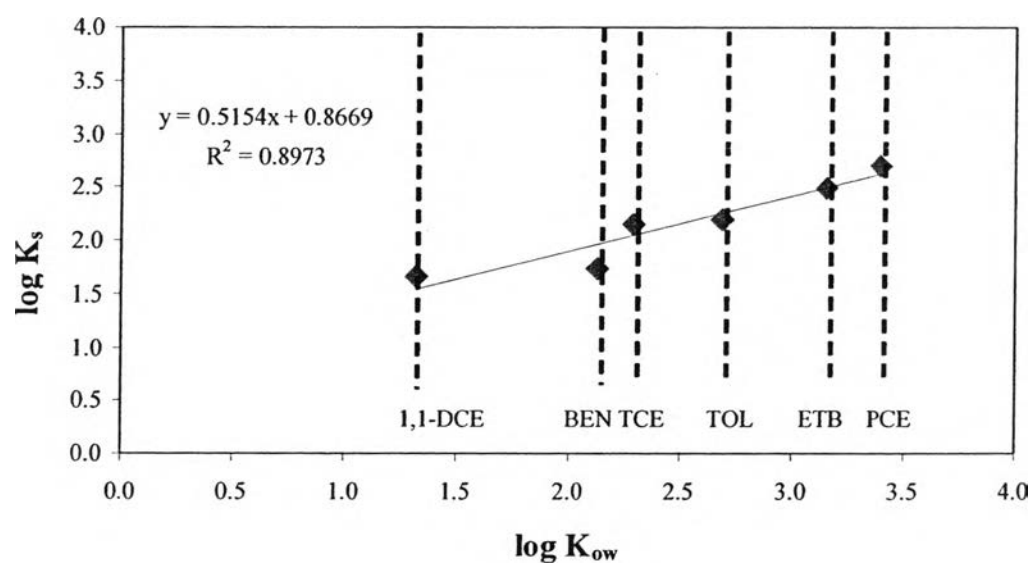


Figure 4.3 Correlation between octanol-water partition coefficient (K_{ow}) and solubilization constant, (K_s) of the VOCs in Tergitol 15-S-7, AE coacervate solution (450 mM Tergitol 15-S-7, 40°C) at equilibrium condition.

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

At concentration above CMC, the hydrophobic VOCs in surfactant solution will be solubilized in the hydrophobic cores of the micelles, resulting in enhancing the solubility of VOCs. The presence of micellar phase can be a reason of the decreasing of volatilization which is indicated in term of Henry's law constant, thus the Henry's law constant has to be modified and be called; "apparent Henry's law constant" or H_{app} .

Generally, the volatilization, H increases, when the hydrophobicity, K_{ow} values increase in order to the increasing of the degree of alkylation and chlorination, respectively. Nevertheless, the H of 1,1-DCE is higher over than the another due to its easiness of volatility nature. The relationship between H and K_{ow} of both aromatic and chlorinated hydrocarbon series is shown in Figure 4.4.

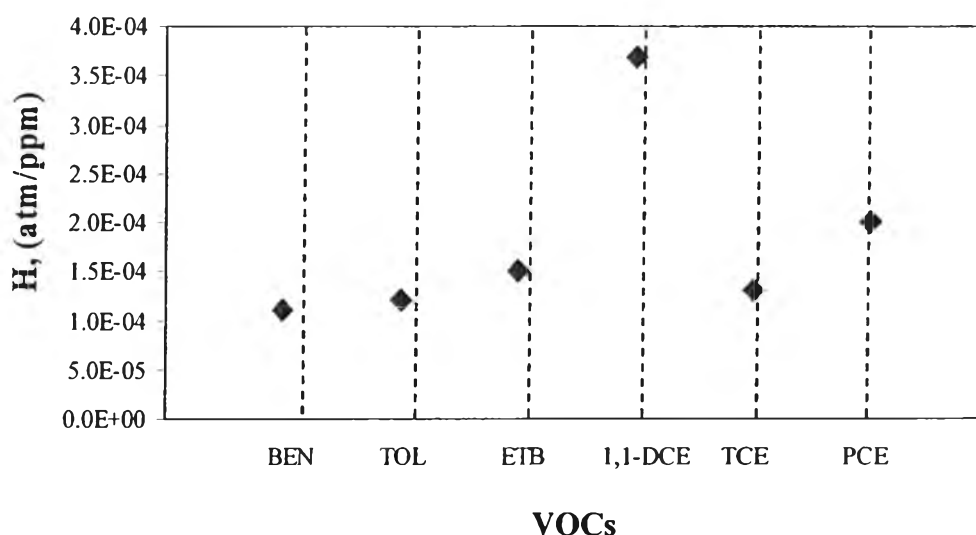


Figure 4.4 Henry's law constant of the VOCs in Tergitol 15-S-7, AE coacervate solution (450 mM Tergitol 15-S-7, 40°C) at equilibrium condition.

The volatilization of VOCs, H_{app} of each series—aromatic and chlorinated hydrocarbon series—in Tergitol 15-S-7, AE coacervate solution at equilibrium are calculated and plotted in Figure 4.5 and 4.6 with respect to their hydrophobicity, K_{ow} . The correlation between K_{ow} , and H_{app} of each hydrocarbon series show a very good linear relationship. The r-squared of $\log K_s$ - $\log K_{ow}$ of each

series are over than 0.92. In addition, the logarithms of H_{app} and $\log K_{ow}$ of six VOCs from both aromatic and chlorinated hydrocarbon series displays on Figure 4.7. The r -squared is also higher than 0.9. All of them illustrate the decrease of H_{app} along the increasing of hydrophobicity; means the less of volatilization of VOCs, despite the fact that the H values increase along the hydrophobic of VOCs.

As investigated in the earlier, the increasing of hydrophobic of solutes (K_{ow}), the solubilization of VOCs (K_s) increase, mean the less volatilization of VOCs in nonionic surfactant solution. This result is conversely with the relationship between H and K_{ow} (Figure 4.4). Therefore, the phenomenon of H_{app} to the degree of hydrophobicity, which show in Figure 4.5-4.7, can be indicated that the effect of solubilization is higher potential than the volatility nature properties of VOCs.

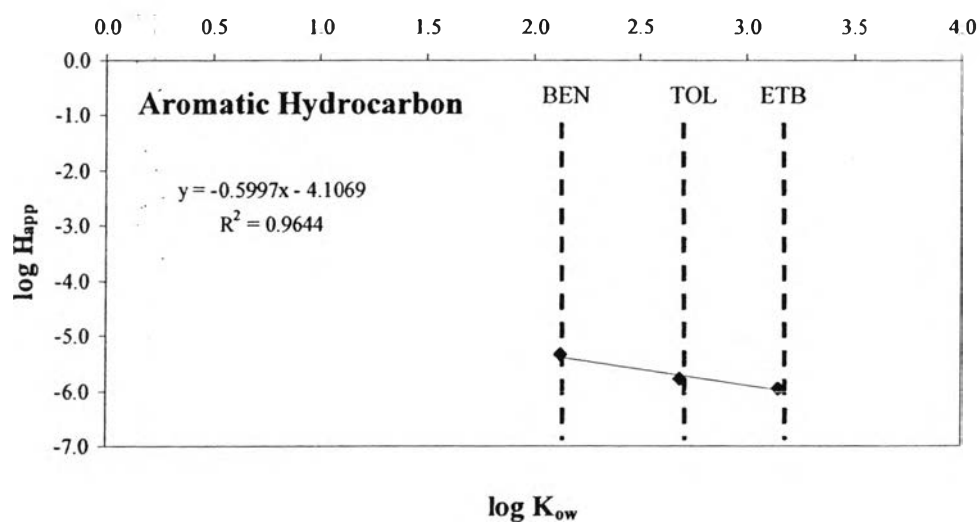


Figure 4.5 Correlation between octanol-water partition coefficient (K_{ow}) and apparent Henry's law constant, (H_{app}) of aromatic hydrocarbon in Tergitol 15-S-7, AE coacervate solution (450 mM Tergitol 15-S-7, 40°C) at equilibrium condition.

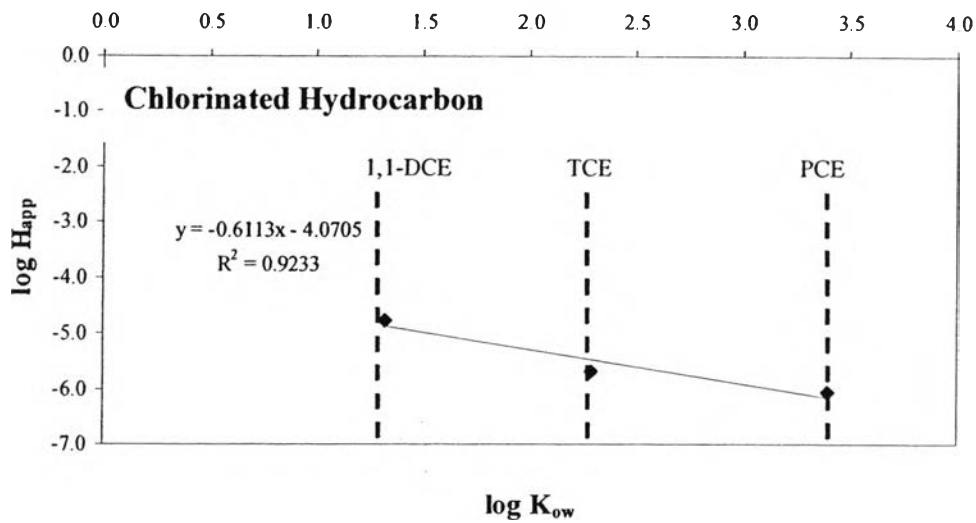


Figure 4.6 Correlation between octanol-water partition coefficient (K_{ow}) and apparent Henry's law constant, (H_{app}) of chlorinated hydrocarbon in Tergitol 15-S-7, AE coacervate solution (450 mM Tergitol 15-S-7, 40°C) at equilibrium condition.

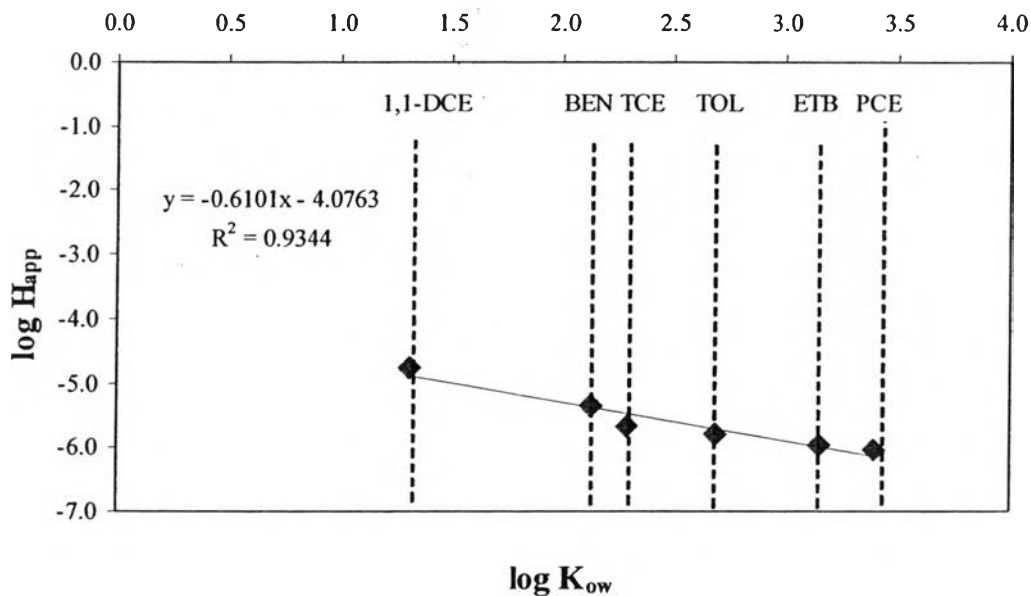

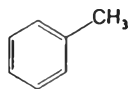
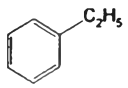
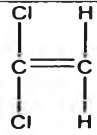
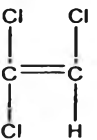
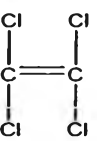


Figure 4.7 Correlation between octanol-water partition coefficient (K_{ow}) and apparent Henry's law constant, (H_{app}) of the VOCs in Tergitol 15-S-7, AE coacervate solution (450 mM Tergitol 15-S-7, 40°C) at equilibrium condition.

The molecular structure, the volatilization and solubilization constant of all VOCs in batch experiments: condition: 20–800 ppm VOC in water, 100–2000 ppm VOC in 450 mM Tergitol 15-S-7, and 40°C is shown in Table 4.3.

Table 4.3 Molecular structure, Henry's law constant (H), apparent Henry's law constant (H_{app}), and solubilization constant (K_s) of all VOCs in batch experiments

VOCs	Structure of VOCs	log octanol-water partition coefficient, $\log K_{ow}$	Henry's law constant, H (atm/ppm)	Solubilization constant, K_s (M^{-1})	Apparent Henry's law constant, H_{app} (atm/ppm)
BEN		2.13	1.1×10^{-04b}	54	4.4×10^{-06}
TOL		2.69	1.2×10^{-04a}	156	1.6×10^{-06}
ETB		3.15	1.5×10^{-04b}	310	1.1×10^{-06}
1,1-DCE		1.32	3.7×10^{-04d}	45	1.7×10^{-05}
TCE		2.29	1.3×10^{-04a}	142	2.1×10^{-06}
PCE		3.4	2.0×10^{-04a}	500	8.9×10^{-06}

^a Data obtained from Vane *et al.*, (2000).

^b Data obtained from Robbins *et al.*, (1993).

^c Data obtained from Howe *et al.*, (1988).

^d Data obtained from Staudinger *et al.*, (2001).

4.3 Continuous Operation

In this thesis work, the stripping column was operated at co-current mode; 1.0 mL/min feed flow rate, 59 absolute torr column pressure, 3-hole distributor, and 40°C, which was reported in the previous work to be the optimum operation (Kungsanant *et al.*, 2008). The concentration of each VOC is 2000 ppm in 450 mM Tergitol 15-S-7. There is no significant foaming and flooding of coacervate solution was observed in the stripping 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 %VOCs removal, and the overall liquid phase volumetric mass transfer coefficient (K_{xa}).

The K_{xa} is a 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 VOCs removal (%) and K_{ow} of each series—aromatic and chlorinated hydrocarbon series are displayed in Figures 4.8-4.9. The r-squared of VOCs removal (%) - $\log K_{ow}$ of them are 0.96 and 0.97, respectively. Figure 4.8 shows that the percentage of VOCs removal are in a decreasing order of hydrophobic alkylation for aromatic hydrocarbon (BEN < TOL < ETB). The same trend is found in chlorinated hydrocarbon series, which corresponding to degree of chlorination (1,1-DCE < TCE < PCE) in Figure 4.9.

Furthermore, the correlation between VOCs removal (%) and K_{ow} from both aromatic and hydrocarbon series is displayed in Figure 4.10. The r-squared of this graph is 0.81. The graph illustrates that VOCs removal decreases in the order: ETB < PCE < TOL < TCE < BEN < 1,1-DCE. The efficiency of VOCs removal is higher than 60.6% for both series. The greatest efficiency of vacuum stripping to remove VOC is 98.1% at 1,1-DCE. This is because it is the highest volatilization (H_{app}). On the other hand, the lowest efficiency is 60.6% at ETB due to the hardest to strip VOC from coacervate solution to vapor phase.

Similarity, the relation between K_{xa} and $\log K_{ow}$ of aromatic and chlorinated hydrocarbon series are shown in Figures 4.11 to 4.12. The r-squared of $\log K_{xa}$ - \log

K_{ow} of them are higher than 0.93. The graphs illustrate that the K_{xa} drop in the order of: BEN<TOL<ETB and 1,1-DCE<TCE<PCE along the increasing of hydrophobic of aromatic and chlorinated hydrocarbon (K_{ow}), respectively. The r-squared of K_{xa} and K_{ow} of the six VOCs graph is 0.83. The graph indicates that the K_{xa} decreases as a result of the increasing of hydrophobic of VOCs as well as the tendency of VOCs removal (%) and $\log K_{ow}$.

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

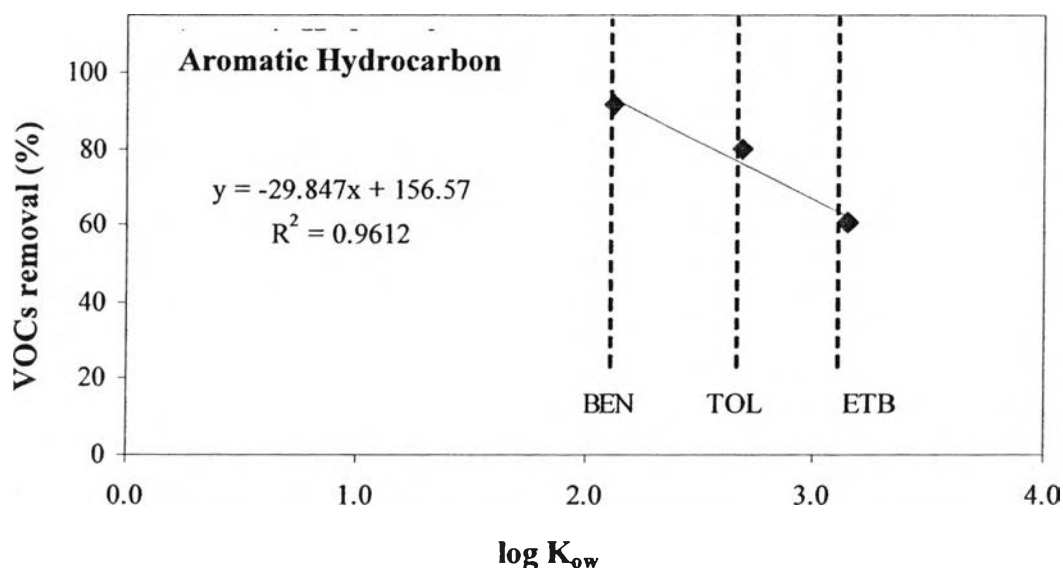


Figure 4.8 C correlation between VOCs removal (%) and octanol-water partition coefficient (K_{ow}) of aromatic hydrocarbon in Tergitol 15-S-7, AE coacervate solution (2000 ppm VOC in 450 mM Tergitol 15-S-7, 40°C).

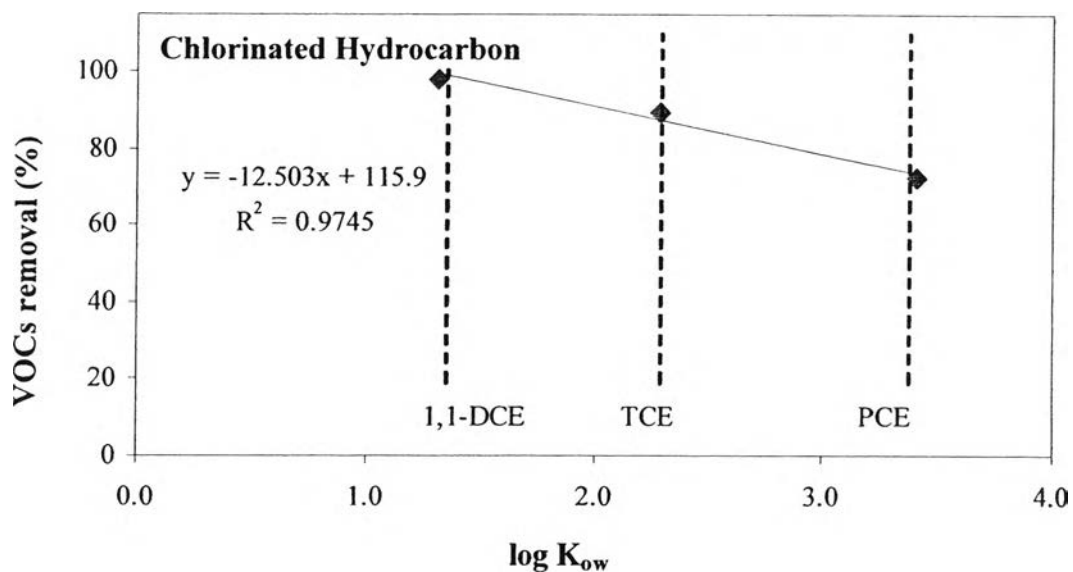


Figure 4.9 Correlation between VOCs removal (%) and octanol-water partition coefficient (K_{ow}) of chlorinated hydrocarbon in Tergitol 15-S-7, AE coacervate solution (2000 ppm VOC in 450 mM Tergitol 15-S-7, 40°C).

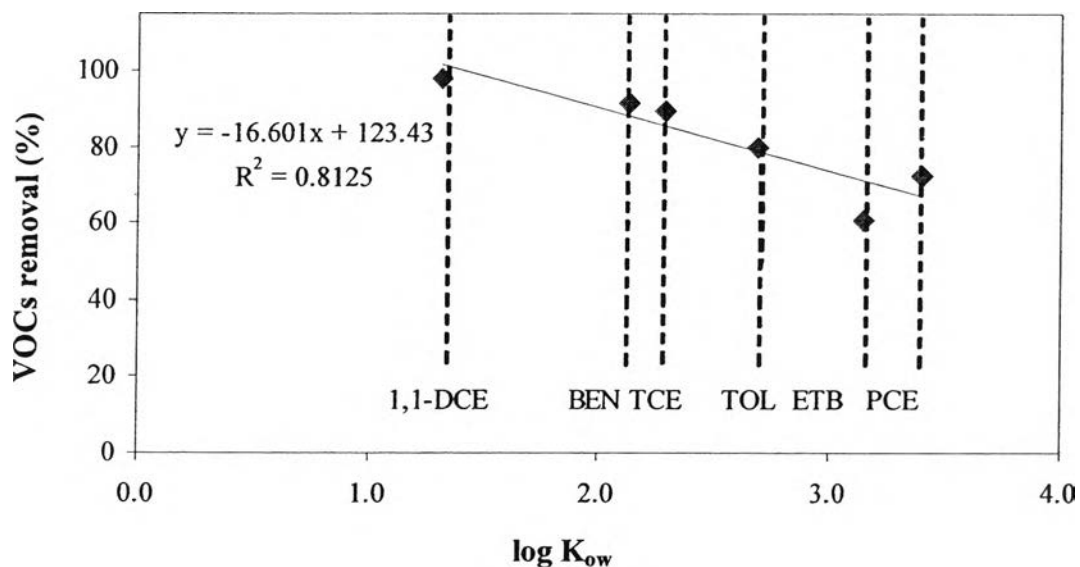


Figure 4.10 Correlation between VOCs removal (%) and octanol-water partition coefficient (K_{ow}) of the VOCs in Tergitol 15-S-7, AE coacervate solution (2000 ppm VOC in 450 mM Tergitol 15-S-7, 40°C).

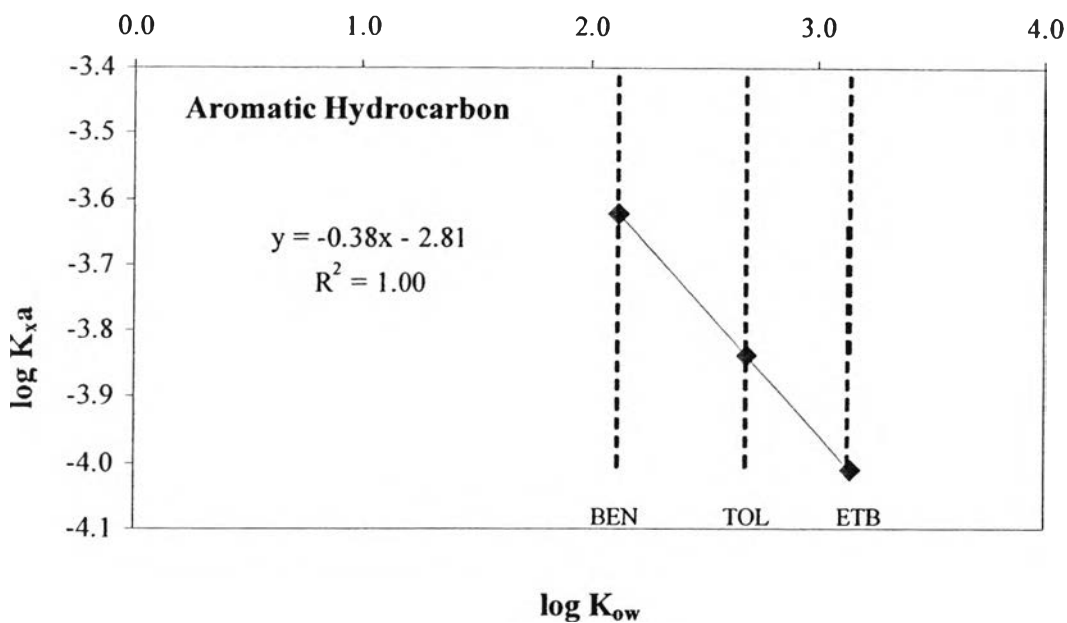


Figure 4.11 Correlation between the overall liquid phase volumetric mass transfer coefficient, K_{xa} (mol/cm³min) and octanol-water partition coefficient (K_{ow}) of aromatic hydrocarbon in Tergitol 15-S-7, AE coacervate solution (2000 ppm VOC in 450 mM Tergitol 15-S-7, 40°C).

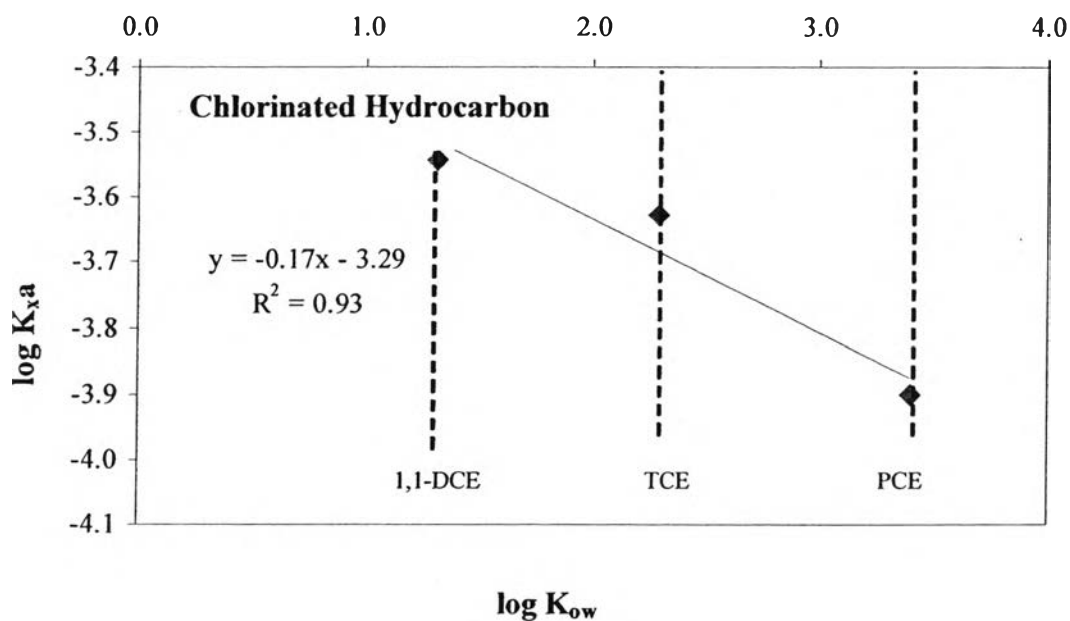


Figure 4.12 Correlation between the overall liquid phase volumetric mass transfer coefficient, K_{xa} (mol/cm³min) and octanol-water partition coefficient (K_{ow}) of chlorinated hydrocarbon in Tergitol 15-S-7, AE coacervate solution (2000 ppm VOC in 450 mM Tergitol 15-S-7, 40°C).

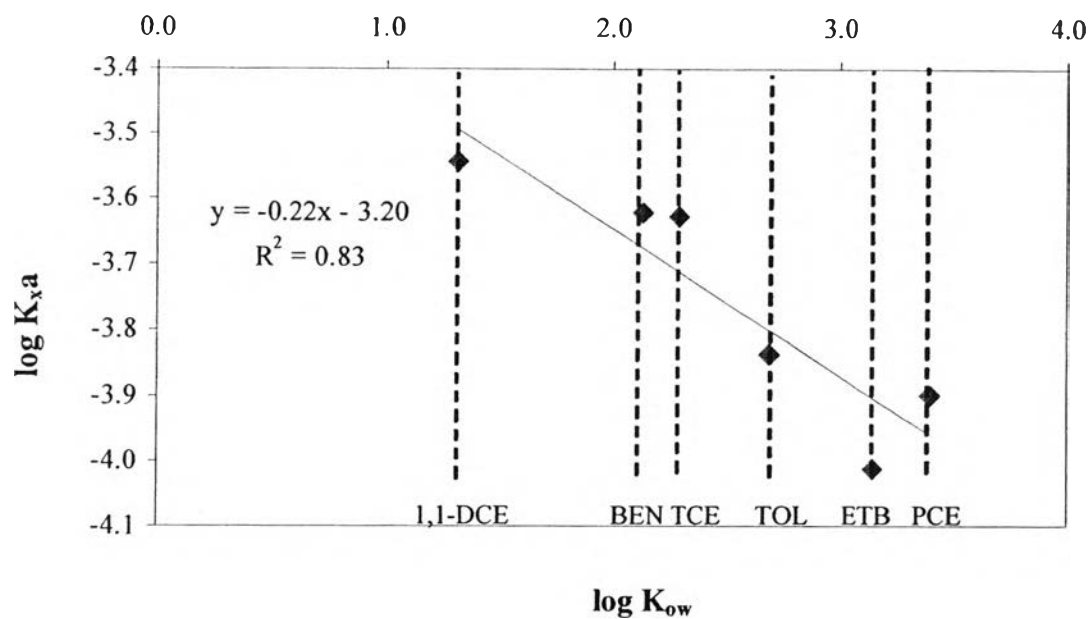

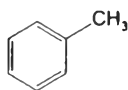
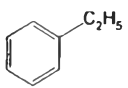
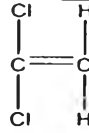
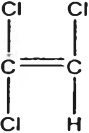
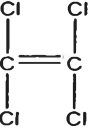


Figure 4.13 Correlation between the overall liquid phase volumetric mass transfer coefficient, K_{xa} ($\text{mol}/\text{cm}^3\text{min}$) and octanol-water partition coefficient (K_{ow}) of the VOCs in Tergitol 15-S-7, AE coacervate solution (2000 ppm VOC in 450 mM Tergitol 15-S-7, 40°C).

Table 4.4 shows the molecular structure, %VOCs removal, and the overall liquid phase volumetric mass transfer coefficient of all VOCs in continuous operation.

Table 4.4 Molecular structure, %VOCs removal, and the overall liquid phase volumetric mass transfer coefficient of all VOCs in continuous operation

VOCs	Structure of VOCs	log octanol-water partition coefficient, log K_{ow}	VOCs removal (%)	The overall liquid phase volumetric mass transfer coefficient, $K_L a$ (mol/cm ³ min)
BEN		2.13	91.41	2.38×10^{-04}
TOL		2.69	79.81	1.45×10^{-04}
ETB		3.15	60.61	9.74×10^{-05}
1,1-DCE		1.32	98.10	2.85×10^{-04}
TCE		2.29	89.70	2.36×10^{-04}
PCE		3.4	72.25	1.26×10^{-04}