



## CHAPTER IV

### RESULTS AND DISCUSSION

In this chapter, the time for toluene-surfactant and toluene-water solution system to reach equilibrium was experimentally obtained. The vapor-liquid phase equilibrium of toluene-water system for finding toluene partial pressure was studied. After that, the apparent Henry's law constant and solubilization constant were calculated. The vapor-liquid equilibrium partition coefficient of toluene and water were determined. Then, the results of the experiments are analyzed, and thermodynamic principles and mass transfer coefficient calculations of vacuum stripping are discussed.

#### **4.1 Equilibrium Time for Toluene-Water Solution and Toluene-Coacervate Phase Solution System**

The time to reach equilibrium in the batch operation was determined by measuring the concentration of the solute in vapor phase as a function of time. The surfactant concentration and amount of solution in the 22 ml headspace glass vials sealed with Teflon-faced silicone septa and clamp aluminum caps were determined to be constant throughout the experiment. The surfactant concentration in feed solution was held constant at 300 mM in every experiment. The toluene concentration was varied from 50 to 200 ppm in toluene-water solution system and 150 to 1000 ppm in coacervate phase solution system to cover the entire toluene concentration range used in subsequent experiments. The longest equilibrium time was around 300 minutes for toluene-water solution system and 100 minutes for coacervate phase solution system. Therefore, the systems were allowed to reach equilibrium for 360 minutes in toluene-water system and 150 minutes in toluene-coacervate phase system.

#### 4.2 The Correlation of Toluene Partial Pressure and the Responses of the GC Detector at Equilibrium Condition

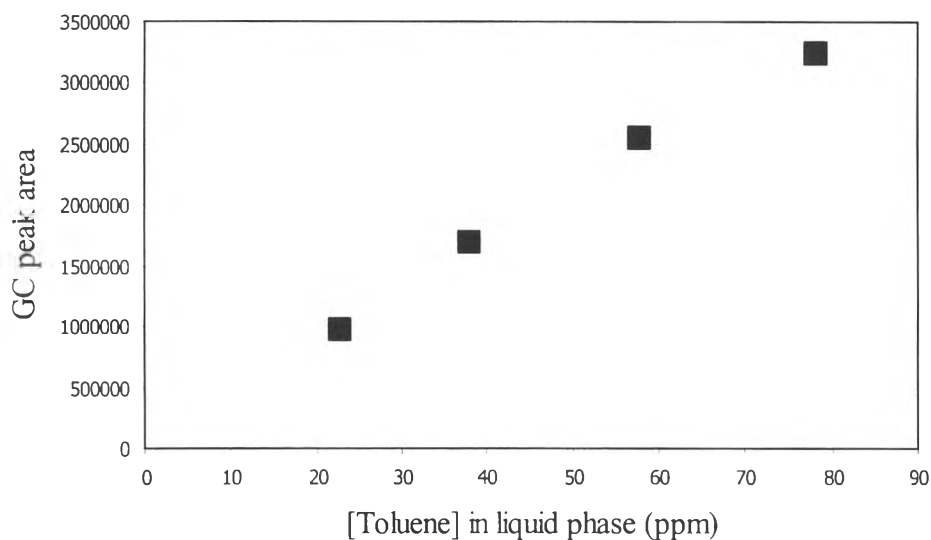
The relation between gas chromatographic responses of toluene concentration in vapor phase and toluene concentration in liquid phase in the toluene-water system can be found as shown in Figure 4.1. Coordinating with Henry's law constant for toluene in water solution (which sometimes called true Henry's law constant) that was equal to  $6.8 \times 10^{-5}$  atm/ppm, the correlation of toluene partial pressure and gas chromatographic responses can be found.

From Figure 4.1,

$$C_{\text{Tou}} (\text{ppm}) = 2.0 \times 10^{-5} \cdot \text{Area (vapor phase)} \quad \text{with } R^2 = 0.9939$$

Combining with true Henry's law constant

$$P_{\text{Tou}} (\text{atm}) = 1.4 \times 10^{-9} \cdot \text{Area (vapor phase)}$$

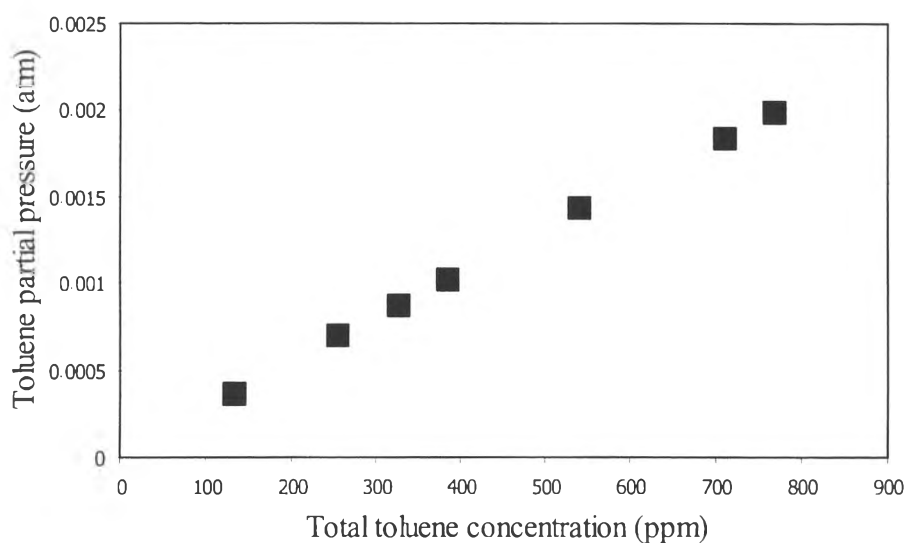


**Figure 4.1** Relation between GC peak area of toluene concentration in vapor phase and toluene concentration in liquid phase in toluene-water system at equilibrium condition.

### 4.3 Apparent Henry's Law Constant for Toluene in Coacervate Phase Solution

When surfactant concentration is above the CMC, the micellar phase was formed and organic solutes will be solubilized in the micelles. The presence of micellar phase can affect the Henry's law constant, therefore the true Henry's law constant is modified and occasionally called modified Henry's law constant or apparent Henry's law constant.

From the correlation of toluene partial pressure and gas chromatographic responses, the toluene concentration in vapor phase at equilibrium condition can be converted to the toluene partial pressure. The relationship between the toluene partial pressure and total toluene concentration in liquid phase was shown in Figure 4.2.



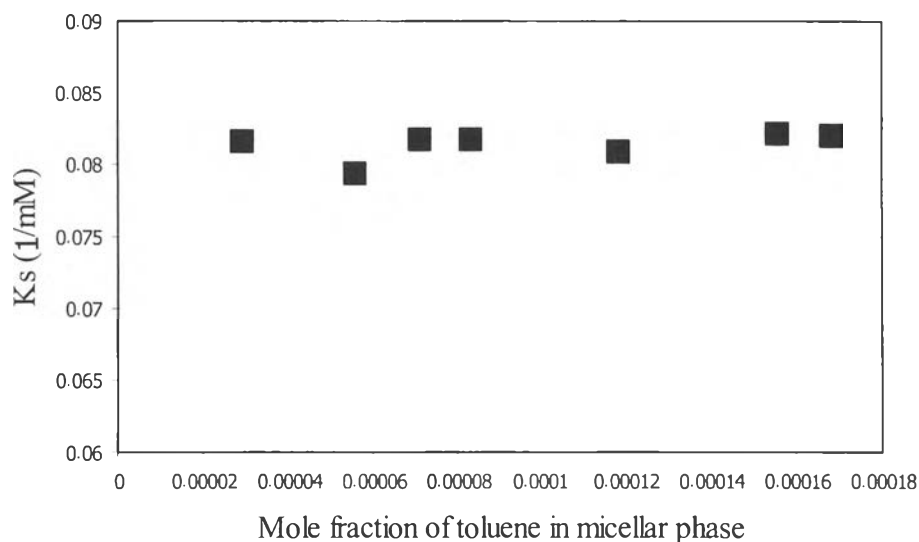
**Figure 4.2** Relation between toluene partial pressure and total toluene concentration in coacervate phase solution (300 mM OP(EO)<sub>7</sub>, 30°C) at equilibrium condition.

The apparent Henry's law constant for toluene in coacervate phase solution or the ratio of partial pressure of toluene and total toluene concentration, obtained from the slope of Figure 4.2 that is  $3.0 \times 10^{-6}$  atm/ppm.

#### 4.4 The Solubilization Constant of Toluene in Coacervate Phase Solution

From equation 2.1 and 2.2, unsolubilized toluene concentration can be calculated from correlation coefficient between toluene partial pressure and linear responses of the GC detector, and true Henry's law constant. Then, the solubilized toluene concentration was determined by subtraction the total toluene concentration in liquid phase with unsolubilized toluene concentration. In addition, the concentration of surfactant in micellar form was assumed to be as the total surfactant concentration, since the CMC is very low when compare with the total surfactant concentration. The solubilization constant ( $K_s$ ) is then calculated and shown in Figure 4.3.

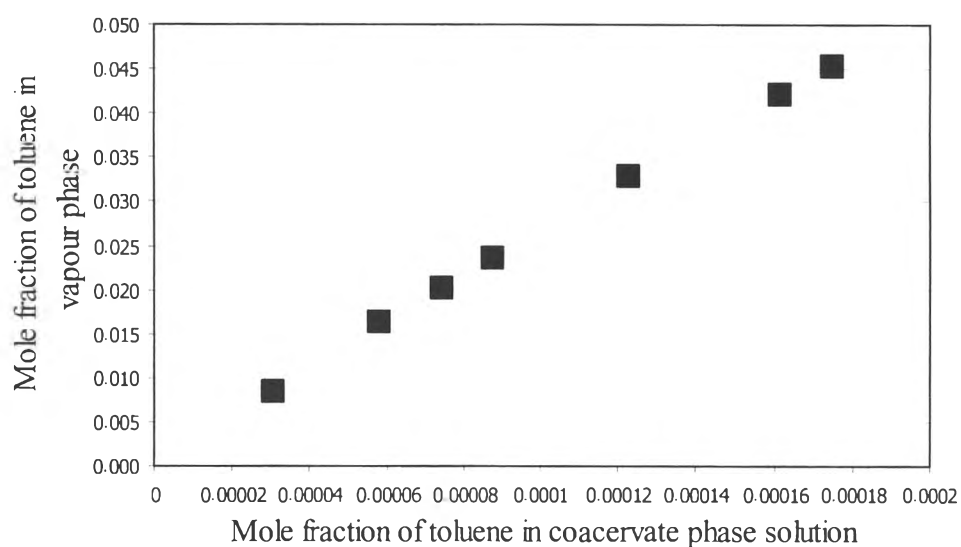
This result agrees with the work done by Choori et al. (1998). It was reported that, at a low solute concentration, the value of  $K_s$  is essentially equal to its infinite dilution value and is independent of solute concentration.



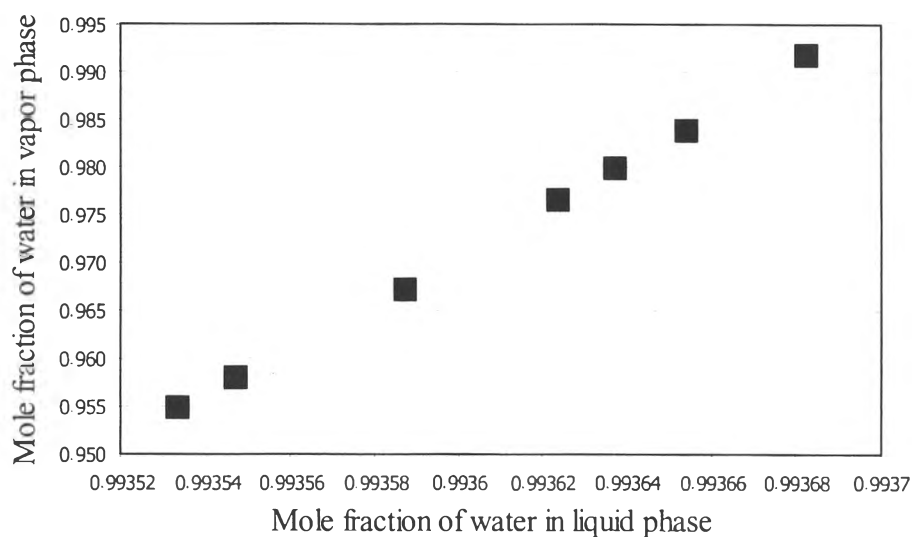
**Figure 4.3** Solubilization constant for toluene in 300 mM Triton x-114 solution as a function of toluene concentration at 30°C.

#### 4.5 The Vapor-Liquid Equilibrium Partition Coefficient (K) for Toluene and Water in Coacervate Phase Solution

From equilibrium data which were calculated from section 4.2 to 4.4, the partition coefficient of toluene and water can be calculate from equation 2.15 and 2.21, respectively as shown in Figure 4.4 and 4.5.



**Figure 4.4** The vapor-liquid equilibrium partition coefficient for toluene in coacervate phase solution (300 mM OP(EO)<sub>7</sub>) at 30°C.



**Figure 4.5** The vapor-liquid equilibrium partition coefficient for water in coacervate phase solution (300 mM OP(EO)<sub>7</sub>) at 30°C.

From Figure 4.4 and 4.5, the result can be concluded that vapor-liquid equilibrium partition coefficient for toluene and water in coacervate phase solution tend to be constant at around 262.8 and 1.0734, respectively.

#### 4.6 The Co-Current Flash Vacuum Stripping Operation

In this thesis, the vacuum stripping unit was designed to operate for co-current continuous operation since it has been suggested that this mode of operation can reduce or inhibit the foam formation. As expected, no significant foaming was observed. However, a little foam was observed at the liquid distributor, while foaming at the other parts of the packed column was not noticed. Furthermore, the highly viscous coacervate solution flows pass the packing materials without plugging the column. Therefore, this thesis has demonstrated that the vacuum stripping operation can be applied to the coacervate solution. Moderate pressure drop (0-78 torr/m) was observed across the packed column. This was probably because of the high viscosity of coacervate phase solution.

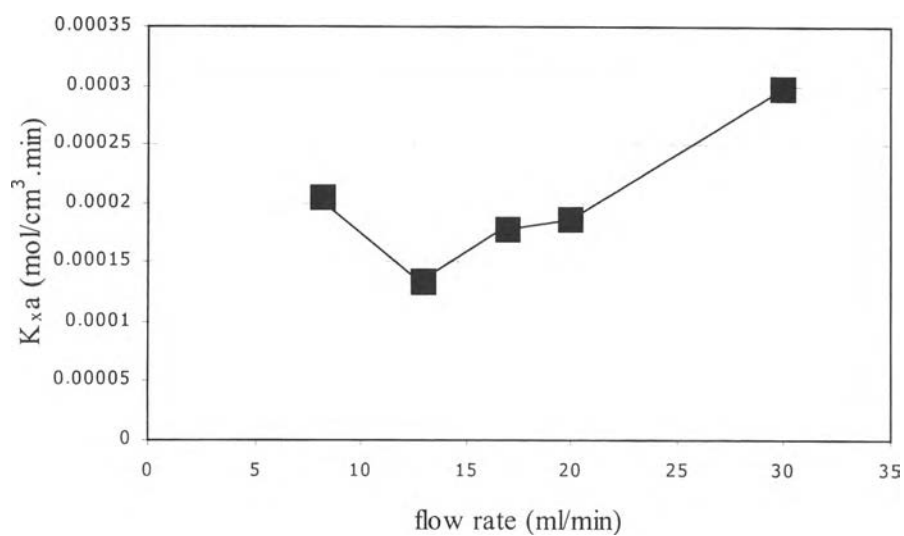
For the percent removal of toluene from coacervate phase solution as shown in Table C6 and C7 in appendix C, 20-45% of toluene were removed when the liquid flow rate was decreased from 30 ml/min to 8.2 ml/min, and 12-50% of toluene removal were observed when column pressure was varied from 130 torr to 43 torr.

#### **4.7 Effect of Liquid Flow Rate on Overall Volumetric Mass Transfer Coefficient ( $K_x a$ ), Number of Transfer Unit (NTU), and Height of Transfer Unit (HTU)**

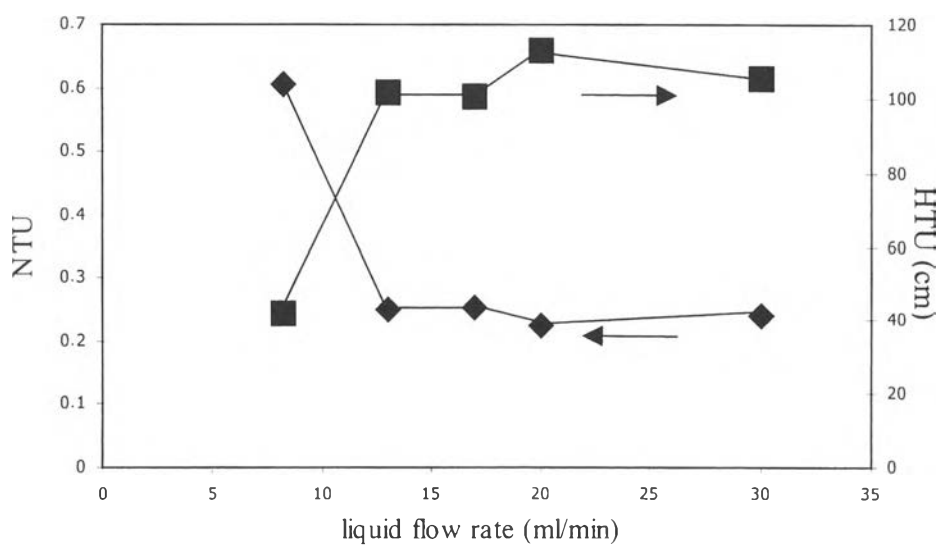
The effect of liquid flow rate was studied in 300 mM coacervate phase solution, which used OP(EO)<sub>7</sub> as nonionic surfactant and toluene as a pollutant. The results were given in Figure 4.6 and 4.7.

At liquid flow rate lower than 13 ml/min, channeling was occurred because liquid flow rate was quite low and feed distributor was not appropriate for using with viscous liquid. And this resulted in the reduction of  $K_x a$  of toluene with an increasing in liquid flow rate. However, above this liquid flow rate, channeling was eliminated, as a result, the effective contacting area was increased, leading to higher  $K_x a$  values.

As shown in Figure 4.7 at liquid flow rate higher than 13 ml/min, the efficiency of the packed column should be less than at lower liquid flow rate. So, NTU was expected to be decreased while HTU was increased. However, the NTU and HTU are relatively consistent with the liquid flow rate because the effective contacting area is increased, resulting in constant efficiency of the column.



**Figure 4.6** Overall volumetric mass transfer coefficient ( $K_{x,a}$ ) as a function of liquid flow rate (initial system: 300 ppm toluene, 300 mM surfactant solution, 55 torr column pressure, and 30°C).

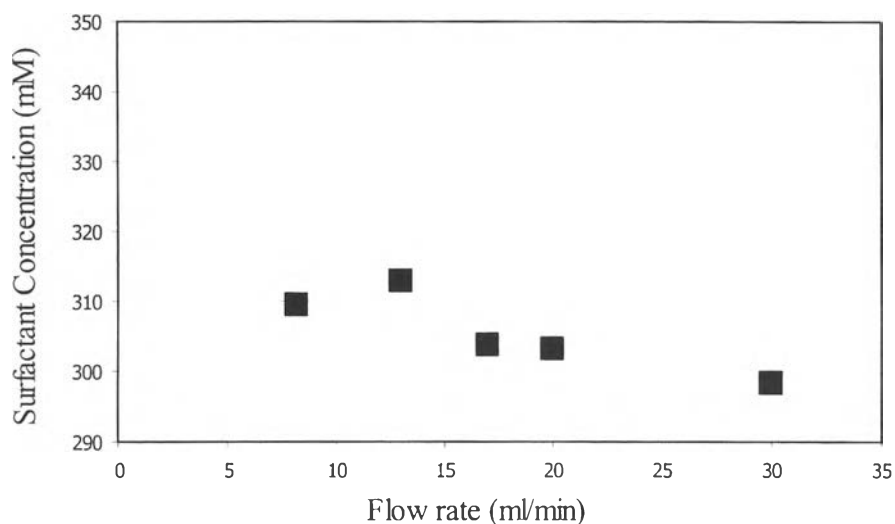


**Figure 4.7** Number of transfer unit (NTU) and height of transfer unit (HTU) as a function of liquid flow rate (initial system: 300 ppm toluene, 300 mM surfactant solution, 55 torr column pressure, and 30°C).



#### 4.8 Effect of Liquid Flow Rate on Surfactant Concentration in the Effluent Stream

As seen in Figure 4.8, there was no significant change in surfactant concentration in the effluent stream as liquid flow rate further decreased from 30 ml/min to 17 ml/min. And at the liquid flow rate lower than 17 ml/min surfactant concentration was slightly increased. This was probably because of the vaporization of toluene and water, but not the high molecular weight surfactant.



**Figure 4.8** Surfactant concentration in product stream as a function of liquid flow rate (initial system: 300 ppm toluene, 300 mM surfactant solution, 55 torr column pressure, and 30°C).

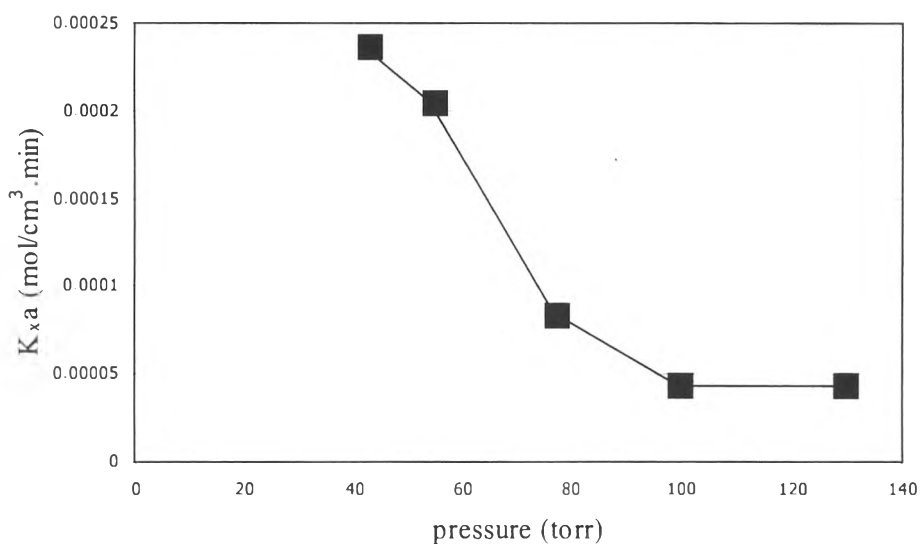
#### 4.9 Effect of Pressure on Overall Volumetric Mass Transfer Coefficient ( $K_x a$ ), Number of Transfer Unit (NTU), and Height of Transfer Unit (HTU)

Figure 4.9 and 4.10 respectively show the effect of pressure on  $K_x a$ , and NTU and HTU of the system at 8.2 ml/min liquid flow rate.  $K_x a$  of toluene increased with decreasing pressure. At pressure greater than 100 torr, the effect of pressure on  $K_x a$  was insignificant. However, at lower pressure,  $K_x a$  increased substantially when

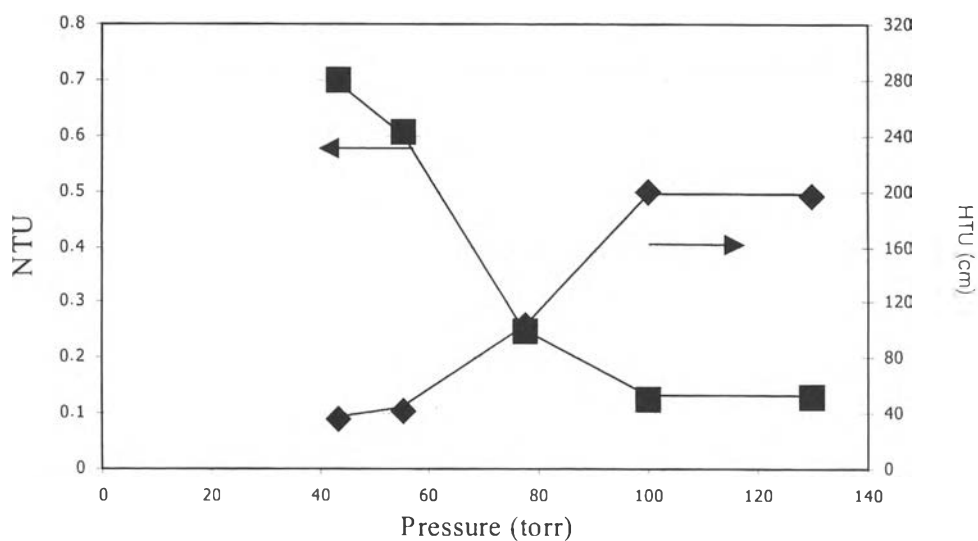
pressure was decreased. This was probably because of increasing in driving force of toluene. Since the vapor pressure of toluene at 30°C is around 40 torr, when pressure is reduced near this value, the driving force to vapor phase of toluene is greatly increased. As illustrated in Figure 4.10 the results show the same way that, NTU was increased rapidly, while HTU was decreased substantially when pressure was lower than 100 torr.

#### 4.10 Effect of Pressure on Surfactant Concentration in the Effluent Stream

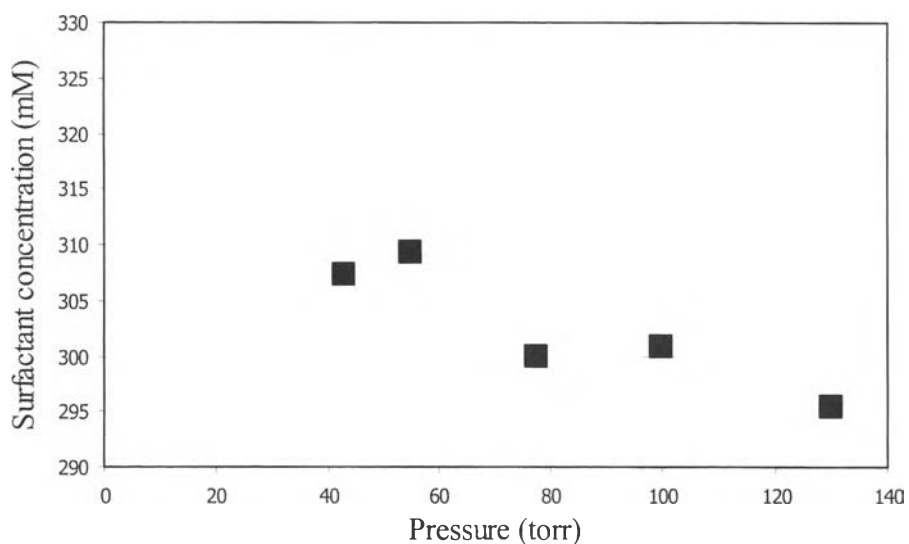
Figure 4.11 indicates that as the pressure decrease from 130 to 77.5 torr, the surfactant concentration in the product stream remained essentially constant. And at the pressure lower than 77.5 torr, the surfactant concentration was slightly increased. This was probably because of the vaporization of toluene and water, but not the high molecular weight surfactant.



**Figure 4.9** Overall volumetric mass transfer coefficient ( $K_{x,a}$ ) as a function of pressure (initial system: 300 ppm toluene, 300 mM surfactant solution, 8.2 ml/min liquid flow rate, and 30°C).



**Figure 4.10** Number of transfer unit (NTU) and height of transfer unit (HTU) as a function of pressure (initial system: 300 ppm toluene, 300 mM surfactant solution, 8.2 ml/min liquid flow rate, and 30°C).



**Figure 4.11** Surfactant concentration in product stream as a function of pressure (initial system: 300 ppm toluene, 300 mM surfactant solution, 8.2 ml/min liquid flow rate, and 30°C).