CHAPTER IV

TOLUENE REMOVAL FROM NONIONIC SURFACTANT COACERVATE PHASE SOLUTIONS BY VACUUM STRIPPING [*]

4.1 Abstract

Cloud point extraction (CPE) has been demonstrated to remove volatile aromatic pollutants from wastewater by using a nonionic surfactant as a separating agent. To make this process economically feasible, the surfactant in the concentrated or coacervate phase containing most of the original pollutant must be recycled and reused. This work proposes a vacuum stripping process to strip the volatile pollutant from the coacervate, leaving the concentrated surfactant solution to be recycled to the CPE process. An acrylic column was packed with glass Raschig rings and operated under rough vacuum in co-current mode to remove toluene from the coacervate phase containing the *t*-octylphenolpolyethoxylate ($OP(EO_7)$) nonionic surfactant. Co-current operation is necessary to avoid excessive foaming. In this study, although the apparent Henry's law constant of toluene was drastically reduced due to toluene solubilization in surfactant micelles, up to 90% of toluene was removed from 300 mM $OP(EO)_7$ surfactant solution using a 30.5-cm long column. The packed column can be operated without flooding and plugging, despite the viscous nature of the coacervate. The toluene removal increases with decreasing liquid loading rate, and column pressure, but with increasing number of distributor holes. The overall liquid phase volumetric mass transfer coefficient is reported for this system.

Keywords: Vacuum stripping; Co-current operation; Cloud point extraction

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4.2 Introduction

Contamination of ground and subsurface water by volatile organic compounds (VOCs) is a serious concern [1]. These contaminants can come from many sources, such as the leaking of organic compounds from underground storage tanks, poor disposal practices, application of agricultural chemicals, and accidental spills of VOCs. Removal of these contaminants is required for safety and public health reasons. Surfactant-based separation techniques have been proposed to economically eliminate these VOCs since they are more effective in terms of both separation efficiency and energy than conventional techniques [2, 3]. Moreover, surfactants are generally more environmentally friendly than other solvents utilized in liquid-liquid extraction [3–6].

In cloud point extraction (CPE), nonionic surfactants are utilized as the separating agent. When a nonionic surfactant solution containing organic solutes is heated above its cloud point, the solution separates into two phases, a coacervate phase and a dilute phase. The coacervate phase is a micellar rich phase; therefore, organic solutes tend to partition into micelles and are then concentrated in the coacervate phase [3–8]. CPE can be applied for various applications; for example, the extraction of organic compounds and biomaterials, and the pre-concentration of metal ions from an aqueous solution [3–6, 8–11].

Recently, a pilot scale CPE unit using a continuous rotating disk contactor demonstrated that 85-95% of volatile aromatic contaminants can be removed from water [10, 11]. It was found that over 90% of the total surfactants accumulated in the coacervate phase. Since the surfactant cost is a key determinant of the economic viability of the CPE process, it is important that the surfactants in the coacervate phase solution be recycled and reused [2, 3, 8].

Many processes have been used to remove VOCs from a surfactant solution; for instance, air or vacuum stripping, pervaporation, etc. [12–18]. Conventionally, air stripping in a packed column has been widely studied for VOC removal from water [19–21]. However, in an aqueous system containing surfactant, the direct contact between the air and the surfactant solution could generate a large amount of foam that causes a pressure drop and flooding, which can then lead to inoperable conditions. The amount of foam can be reduced by applying a lower ratio of air to liquid fed to the column; however, significant foaming was still observed in the air stripping column [13]. Moreover, adding an anti-foaming agent probably reduces the foaming, but the operating cost due to the cost of anti-foams and the lateral impurity clean-up is also increased [12, 16–18]. Alternatively, vacuum stripping can be utilized to remove VOCs from the surfactant solution. In this process, foaming is possibly reduced without adding chemicals because there is the absence of air flow at the vapor-liquid interface. Moreover, compared to air stripping, much less amount of exhausted gas is produced in vacuum stripping.

Vacuum stripping has been widely used for VOC removal from contaminated water in chemical and petrochemical industries, such as the removal of butane [22] and refrigerants [23] from water in a desalting process, carbon dioxide and oxygen from water [24, 25], volatile organic compounds from water streams [26], and emulsified organic liquid from water [27]. Generally, all of these processes are operated in counter-current mode because it provides a high mass transfer rate. In contrast, the mass transfer 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 [28]. It was 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 [29]; in general, co-current separation efficiency is lower than that of a counter-current separation, making the latter process much less popular [28]. However, flooding and limited liquid loading were found to be limitations of the counter-current operation, especially in a process containing surfactants; therefore, the co-current operation is suggested for use in recycling a contaminated surfactant solution [15]. This suggestion is supported by a study of gas vacuum stripping from an aqueous solution in a packed column [25]. It was found that a multistage co-current operation provided higher efficiency than a single stage counter-current operation. 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 [24]. From this point of view, co-current vacuum stripping was selected for investigation to remove VOCs from a concentrated surfactant solution.

In this study, toluene was selected as the model volatile organic contaminant. A packed column unit for co-current vacuum stripping was designed and built to remove toluene from a coacervate phase solution. The effects of feed flow rate, column pressure, and liquid distribution on the efficiency of vacuum stripping were investigated.

4.3 Experimental

4.3.1 Materials

In this study, a branched *t*-octylphenolpolyethoxylate, $OP(EO)_7$ having an average of seven moles of ethylene oxide per mole of octylphenol (Triton X-114) purchased from Dow Chemical, Inc. (South Charleston, WV, USA) was used as the nonionic surfactant. Reagent grade toluene, from J.T. Baker (Phillipsburg, NJ, USA), with a purity of 99.8% was used as the model VOC. All chemicals were used as received. Deionized (DI) water was used for making up the solution.

4.3.2 Apparatus: Vacuum Stripping Packed Column

A schematic of the vacuum stripping unit is shown in Figure 4.1. The cylindrical stripping column was 6.5-cm inside diameter and 30.5 cm in height and was made from acrylic fiber; there was also a 12.7-cm diameter acrylic water jacket. The stripping column was packed with 25.5-cm in height of 5 mm×5 mm glass Raschig rings. A 1-L glass feed tank was placed inside a 16.5-cm diameter acrylic water jacket. A product tank was made of stainless steel. The system was maintained under vacuum conditions by a rotary vane pump. The feed solution was sent to the stripping column using a peristaltic pump. The operating temperature was controlled at 30°C using a water circulating bath.

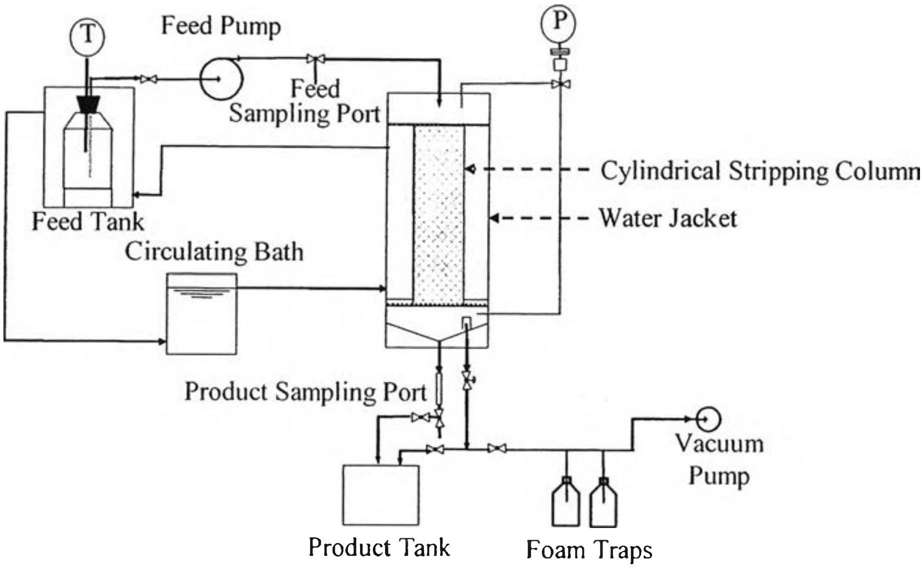

Figure 4.1 Schematic of the vacuum stripping unit.

4.3.3 Methods

4.3.3.1 Viscosity Determination

The viscosity of the surfactant solution containing the organic solute was measured by a Brookfield digital rheometer (DV-III, Brookfield Engineering Laboratories, Inc.). Spindle (RVDV-III) numbers 21 and 27 were used to determine the viscosity of the surfactant solution. The spindle's rotating speed was set at 250 rpm. The viscosity of each liquid sample was measured at least three times. Since toluene loss can occur during viscosity measurement, the toluene concentration was measured directly by taking 100 μL of the liquid sample from the viscosity meter and then analyzing by a gas chromatograph connected with a headspace autosampler (HSGC).

4.3.3.2 Equilibrium Data Determination

The partitioning behavior of toluene in water and the surfactant system was observed by modification of the Equilibrium Partitioning in Closed Systems (EPICS) method similar to work done by Jiang *et al.* [17] and

Valsaraj *et al.* [30]. To determine the equilibrium time, several identical 22-mL glass vials with Teflon-coated septa and aluminum holed caps containing 4 mL of toluene in DI water were placed in an isothermal water bath controlled at 30°C. One milliliter liquid samples were collected every 30 min by a gas-tight syringe. The liquid sample was transferred into the vial and immediately sealed with a Teflon-coated septum and an aluminum holed cap. Toluene concentration in liquid phase was measured by HSGC. Then, the time required to reach equilibrium was determined.

Subsequently, to find the Henry's law constant for the surfactant-free system, two sets of 12 identical 22-mL glass vials with Teflon-coated septa and aluminum holed caps containing 4 mL of toluene in aqueous solution were prepared. The toluene concentrations ranged from 50 to 200 ppm. The first set was placed in the isothermal water bath at 30°C, and the second set was incubated in the oven of the headspace autosampler at 30°C. After reaching equilibrium, the toluene concentration in the liquid phase of the first set was measured. The toluene concentration in the vapor phase of the second set was analyzed automatically by HSGC. Three samples were repeated for each toluene concentration. The equilibrium correlation between toluene concentration in vapor and in water phase was then obtained. For the surfactant containing system, the toluene concentrations were varied from 100 to 1 000 ppm in 300 mM $OP(EO)_7$. The experiments were conducted using the same procedure as those for the surfactant-free system, except that 100 μL of the liquid sample was collected after equilibrium, and four samples were repeated for each toluene concentration.

4.3.3.3 Continuous Operation

The vacuum in the stripping column, product tank, and foam traps was created by the rotary vane pump. Water at constant temperature was circulated through the water jacket of the feed tank and stripping column to control the system temperature. The temperature of the feed solution and the packed column was maintained at 30°C. After the column pressure was stable, the feed solution was pumped at the desired flow rate into the top of the column by the peristaltic pump.

The liquid flowed down the column and was kept in the product tank. The stripping packed column was operated in co-current mode with a vapor suction line attached at the bottom of the column. The foam trap was installed at the vapor exit before entering the pump in order to prevent the rotary vane pump from liquid-induced damage. The vacuum stripper was operated continuously, and liquid samples were collected by a gas-tight syringe every 20 min. The liquid sample in the feed stream was collected at the feed sampling port, and that in the product stream was collected at the product sampling port. The vacuum stripping unit reached steady state within 90 min as indicated by constant toluene concentrations. The solution from the inlet and the outlet streams after steady state were taken and analyzed for toluene concentration.

The operating conditions and studied variables in the vacuum stripping packed column were as follows: operating temperature, 30°C; surfactant concentration, 300 mM; toluene concentration, 300–1 000 ppm; feed flow rate, 1.1–9.8 mL/min; absolute column pressure, 38.6–125.0 Torr; and, number of distributor holes, 1–5 holes.

4.4 Background

The performance of co-current vacuum stripping using a packed column to remove toluene from a coacervate solution can be affected by the coacervate characteristics. Many researchers have investigated the structures of highly concentrated nonionic surfactant coacervate phases. Kato and coworkers [31] measured the self-diffusion coefficient of the surfactant and found that, at high concentration, surfactants aggregate in the form of an entangled network called a worm-like micelle. In addition, the gradual "cross-linking" of the worm-like micelles occurs as temperature increases above the cloud point, and the worm-like micelles transform to a multiconnected network. A similar structure was also found in a study of the interaction between a solute and a nonionic surfactant, octylphenol ethoxylate ($OP(EO)_x$), where the EO varied from 4.5 to 12 moles [32], and where the surfactant forms rod-like micelle structures at high surfactant concentration. Another study reported that the solubilization of VOCs in a surfactant entangled network of a coacervate solution is similar to micelles [33]. The reason is that there is a hydrophobic part enclosed with a hydrophilic region in a surfactant aggregate similar to a micelle structure. Therefore, the micellar solubilization model can be applied to explain the partitioning of the toluene in the concentrated $OP(EO)_7$ solution in this study.

The partitioning of the toluene between the bulk aqueous solution and the micellar pseudo-phase is called solubilization. This phenomenon is explained by a solubilization constant defined as follows [15]:

$$K_s = \frac{C_{sol}}{C_u(C_m + C_{sol})} \tag{1}$$

where K_s is the solubilization constant, C_{sol} is the solubilized toluene concentration in micelle, C_u is the unsolubilized toluene concentration in surfactant solution or toluene concentration in extra-micellar phase, and C_m is the surfactant micelle concentration. If the solubilized concentration of toluene in the micelle is very small compared to the surfactant concentration in the micelle ($C_{sol} << C_m$), equation (1) is simplified to:

$$K_s = \frac{C_{sol}}{C_u C_m} \tag{2}$$

Surfactant micelles show excellent performance in solubilizing organic compounds in aqueous solution. For this reason, surfactants have been applied in many surfactant remediation processes, such as liquid-liquid extraction [3–11] and micellar-enhanced ultrafiltration (MEUF) [13]. If appropriate solutes and solvents are selected, these processes have shown highly efficient removal of the organic compound from a contaminated solution. However, it could lead to lateral difficulty in the decontamination of surfactant solution for reuse; i.e., separation of the solubilized solute from the micellar surfactant can be difficult.

Generally, a pseudo-phase separation model is applied for describing the distribution of VOCs in a surfactant solution [34]. Since micelle formation is in rapid dynamic equilibrium, surfactant monomers can partition between the surfactant micelle and the extramicellar phase. The partial fugacity of the toluene equals the toluene partial pressure at these low pressures and is equal to the partial fugacity in the extramicellar phase and solubilized in the micelle. It is assumed that the partial fugacity of the toluene in the extramicellar solution is the same as that in water at the same toluene concentration; i.e., the Henry's law constant for the unsolubilized toluene is unaffected by the presence of micelles. Assuming that the solution is dilute enough to be in the Henry's law region, equating of partial fugacities yields:

$$p_t = HC_u \tag{3}$$

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

In this study, the equilibrium partitioning of toluene 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:

$$H_{App} = \frac{p_t}{(C_u + C_{sol})} \tag{4}$$

In the design of the stripping process, the impact of surfactant on the vapor-liquid equilibrium partitioning of the VOCs must be considered. It has been known that neglecting the effect of surfactant solubilization on the Henry's law constant causes underdesign of air stripping processes [12].

The solubilization constant and the Henry's law correlations of toluene, which are illustrated in equations (2), (3), and (4), respectively, are applied for the calculation of the vapor-liquid equilibrium partition coefficient of water, surfactant, and toluene between vapor and the coacervate solution as follows: for water:

$$K_w = \frac{y_w^*}{x_w^*} \tag{5}$$

for surfactant:

$$K_{surf} = \frac{y_{surf}^*}{x_{surf}^*} \tag{6}$$

for toluene:

$$K_t = \frac{y_t^*}{x_t^*} \tag{7}$$

where K_w, K_{surf}, and K_t are the vapor-liquid equilibrium partition coefficients of water, surfactant, and toluene; y_w^*, y_{surf}^*, and y_t^* are the equilibrium mole fractions of water, surfactant, and toluene in the vapor phase; x_w^* , x_{surf}^* , and x_t^* are the equilibrium mole fractions of water, surfactant, and toluene in the liquid phase, respectively.

From Dalton's law:

$$p_t = y_t^* P \tag{8}$$

where P is the total pressure in the system.

Combining equations (4), (7), and (8) yields:

$$p_t = (C_u + C_{sol})H_{App} = x_t^* C_T H_{App} \tag{9}$$

Substituting equation (2) into the above equation give:

$$K_t = \frac{HC_T}{P(1 + K_s C_m)} \tag{10}$$

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

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

$$F = L + V \tag{11}$$

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

$$z_t F = x_t^* L + y_t^* V \tag{12}$$

where z_t is the mole fraction of toluene in feed. Then, the equations (7) and (11) are substituted in equation (12), yielding:

$$x_t^* = \frac{z_t}{1 + \frac{V}{F}(K_t - 1)} \tag{13}$$

and, by applying equation (7), equation (13) is multiplied by K_t to obtain y_t^*.

$$y_t^* = \frac{z_t K_t}{1 + \frac{V}{F}(K_t - 1)} \tag{14}$$

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:

$$x_w^* = \frac{z_w}{1+\frac{V}{F}(K_w - 1)} \text{ and } y_w^* = \frac{z_w K_w}{1+\frac{V}{F}(K_w - 1)} \qquad (15), (16)$$

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

$$x_{surf}^* = \frac{z_{surf}}{1-\frac{V}{F}} \text{ and } y_{surf}^* = 0 \qquad (17), (18)$$

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.

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

$$-L_0 \frac{dx_t}{dz} = K_x a(x_t - x_t^*) \tag{19}$$

By integrating and rearranging the equation (19), the height of the packed bed (Z) is given as:

$$Z = \frac{L_0}{K_x a} \ln\left(\frac{x_{i,t} - x_t^*}{x_{f,t} - x_t^*}\right) \tag{20}$$

where Z is the height of packing, L_0 is the molar coacervate flux in packed column, $x_{i,t}$ and $x_{f,t}$ are the mole fractions of toluene in the inlet and outlet coacervate 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_t^* is the equilibrium mole fraction of toluene in the coacervate solution from the equilibrium flash calculation already described. This study assumed that x_t^* 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 coacervate streams, the $K_x a$ can then be calculated.

4.5 Results and Discussion

4.5.1 Viscosity of Coacervate Phase Solution

Because of its low CMC and cloud point temperature, $OP(EO)_7$ has shown excellent performance as a separating agent in CPE [5, 10, 11]. The coacervate solution obtained from CPE can contain surfactants at levels higher than 90 wt%. Moreover, in such a solution, the surfactants possibly aggregate in the form of rod-like micelles, whose viscosity is greater than those in the form of spherical micelles at the same concentration [32].

Concern about plugging of these viscous, concentrated solutions as they flow through the packed column caused us to measure viscosity of the coacervate. The effects of $OP(EO)_7$ and toluene concentration, and temperature on the solution viscosity were studied and are presented in Figures 4.2, 4.3, and 4.4, respectively. In Figure 4.2, the solution viscosity significantly increases with increasing $OP(EO)_7$ concentration from 300 to 630 mM. At higher surfactant concentration, the micelles in solution become denser and more aggregated, resulting in strengthening of the structural network of the solution, leading to higher viscosity. Figure 4.3 shows that an increase of the toluene concentration from 0 to 2 000 ppm causes a slight decrease in viscosity of a solution with 300 mM $OP(EO)_7$. As seen in Figure 4.4, it was found that an 80% reduction in the viscosity of a solution containing 630 mM $OP(EO)_7$ was observed when the temperature increased from 30 to 50°C. The reduction of viscosity of nonionic surfactant solutions with temperature has been reported due to a decrease in the length of the rod-like micelles [32]. The highest observed viscosity was 205 cP. Despite these high viscosities, no flooding or plugging was observed in vacuum stripping experiments in this work. However, uneven liquid flow patterns (channeling) can be observed due to high viscosities.

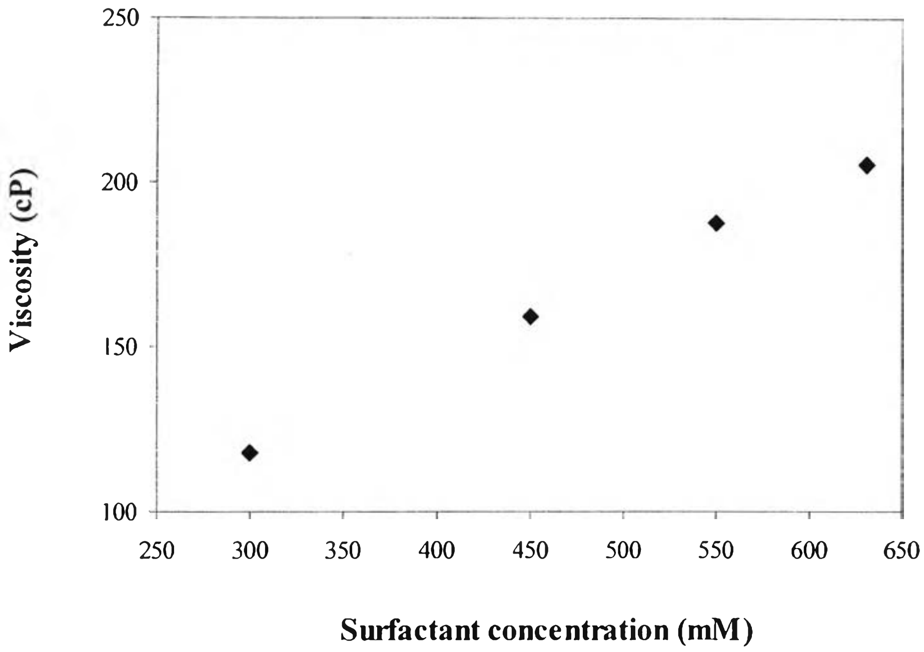

Figure 4.2 Variation of viscosity with surfactant concentration at 300 ppm toluene concentration and 30°C.

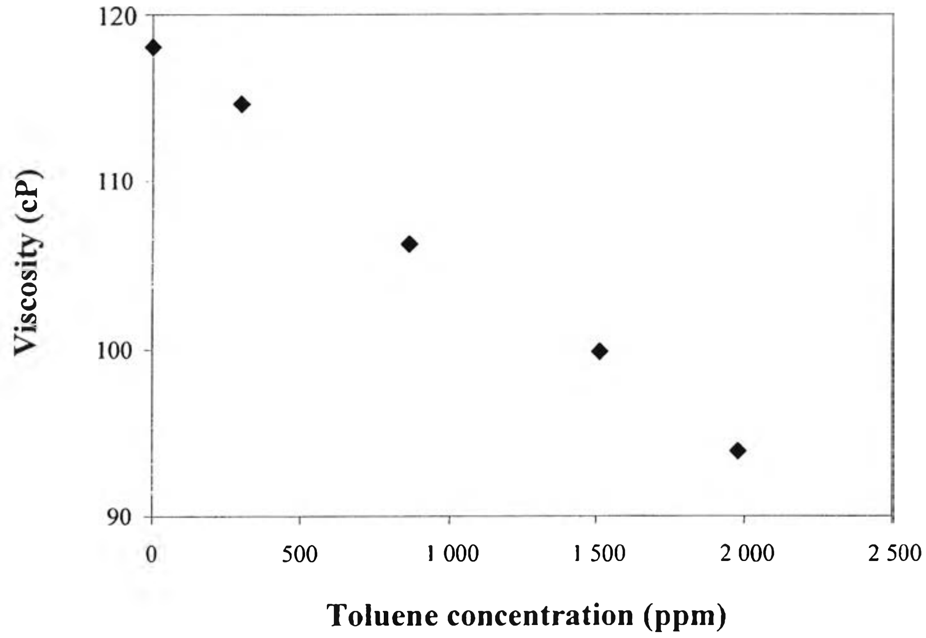

Figure 4.3 Variation of viscosity with toluene concentration at 300 mM $OP(EO)_7$ and 30°C.

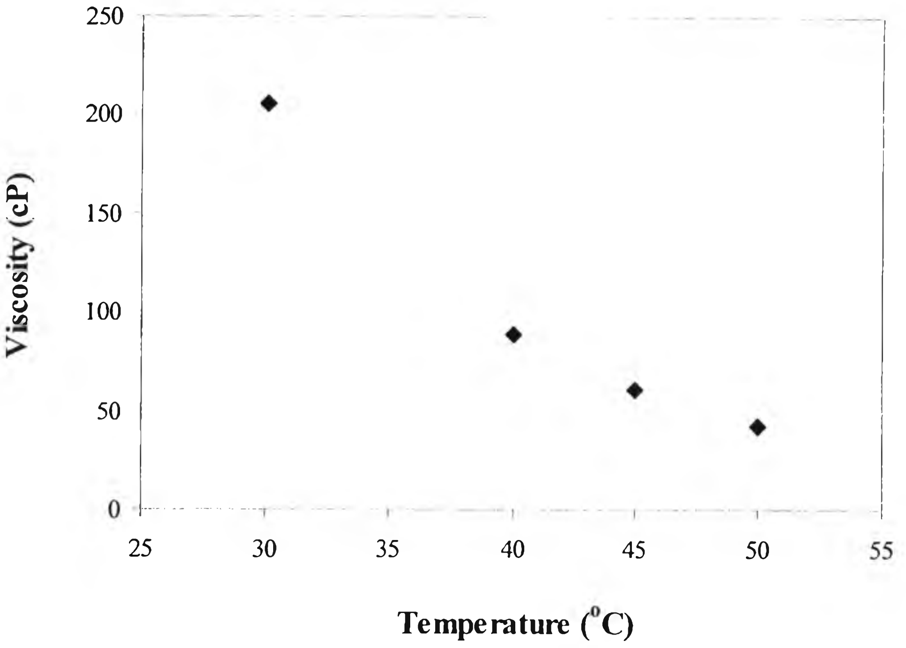

Figure 4.4 Variation of viscosity with temperature at 630 mM $OP(EO)_7$ and 300 ppm toluene concentration.

4.5.2 Partitioning of Toluene in Coacervate Phase Solutions

In batch experiments to determine the H_{App} or K_t, the initial toluene concentration was varied from 50 to 200 ppm for the surfactant-free system, and from 100 to 990 ppm for 300 mM $OP(EO)_7$ system. All experiments were conducted at 30°C. Without agitation, the time to reach equilibrium for the toluene-water and toluene-coacervate systems was 180 and 60 min, respectively. The equilibration time for toluene partitioning between vapor and liquid phases can be varied by adjusting the ratio of vapor-liquid volume in the container, container size, toluene and surfactant concentrations, and temperature. Moreover, the mass transfer of toluene can be accelerated by stirring or shaking.

Vane and Giroux [35] reported that the Henry's law constant for toluene in water at 30°C of $H = 6.8\times10^{-5}$ atm/ppm. The equilibrium headspace measurements showed linearly between the toluene concentration in the liquid phase and in the vapor phase for both water and the 300 mM $OP(EO)_7$ solution.

Comparison of the slope of GC peak area in vapor and in liquid phases to the published Henry's law constant allows conversion of the measured vapor peak areas to concentration yielding the data in Figure 4.5 and calculation of H_{App} from equation (4) for the surfactant solution. Equation (3) permits calculation of the unsolubilized toluene concentration (C_u) from vapor phase toluene concentrations. The difference between the total toluene concentration in the surfactant solution (C_{total}) and the C_u is the solubilized toluene concentration (C_{sol}). The total surfactant concentration minus the CMC is the surfactant micelle concentration (C_m), permitting calculation of the solubilization constant (K_s) from equation (1). Figure 4.6 shows K_s has little dependence on mole fraction of toluene in the micellar phase ($C_{sol}/(C_{sol}+C_m)$), which is not surprising since the largest measured mole fraction was 0.032 and all the data is near the infinite dilution range.

The apparent Henry's law constant is 2.3×10^{-6} atm/ppm, which is 3.4% of the true H. A reduction of the Henry's law constant in surfactant solution is commonly observed [12, 34–36]. This means that in the 300 mM $OP(EO)_7$ solution, approximately 3.4% of the toluene is unsolubilized and 96% is solubilized. Since the equilibrium toluene partial pressure is proportional to the unsolubilized toluene concentration, the presence of the surfactant greatly retards volatilization of the toluene and makes stripping more difficult.

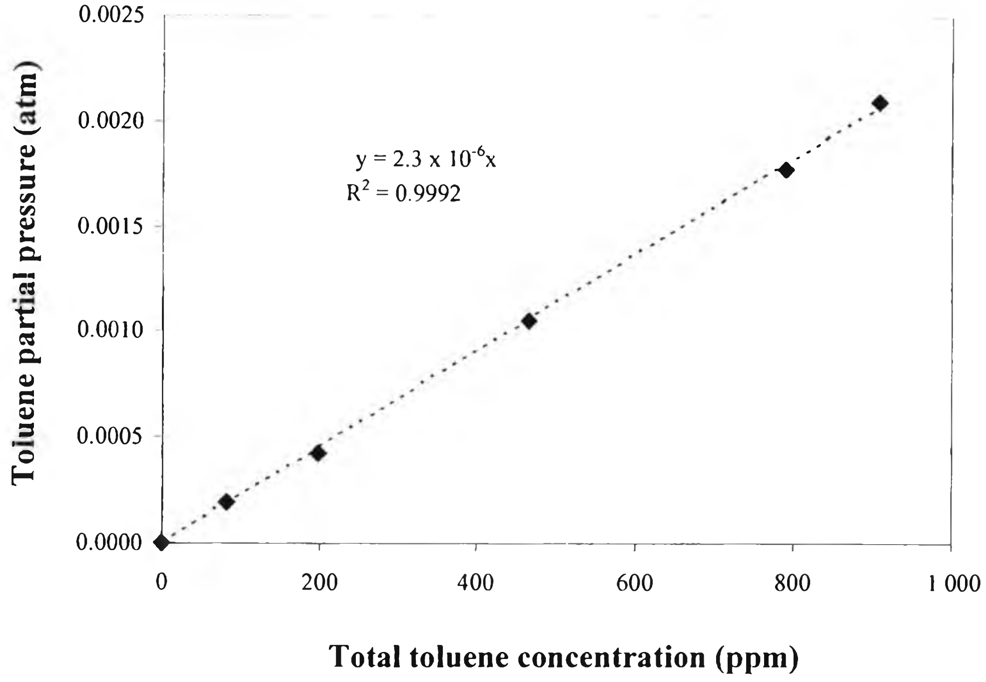

Figure 4.5 Relationship between toluene partial pressure and total toluene concentration in coacervate phase solution at equilibrium condition (300 mM OP(EO)$_7$ and 30°C).

4.5.3 Solubilization of Toluene in Coacervate Phase Solution

In order to calculate the solubilization constant (K_s), the Henry's law and apparent Henry's law relationships are applied to obtain the relation between C_{total} and C_u. If the C_{total} is known, C_u can be calculated from equation (4). Subsequently, C_{sol} can be calculated from the difference between C_{total} and C_u, and then leads to obtain K_s from equation (1). The results are expressed in Figure 4.6 where K_s is relatively constant over the entire range of the studied toluene concentration in micellar solution. At infinite dilution, K_s was determined to be 87 M^{-1} for the toluene in 300 mM OP(EO)$_7$ at 30°C. This parameter is used in converting the H to H_{App}.

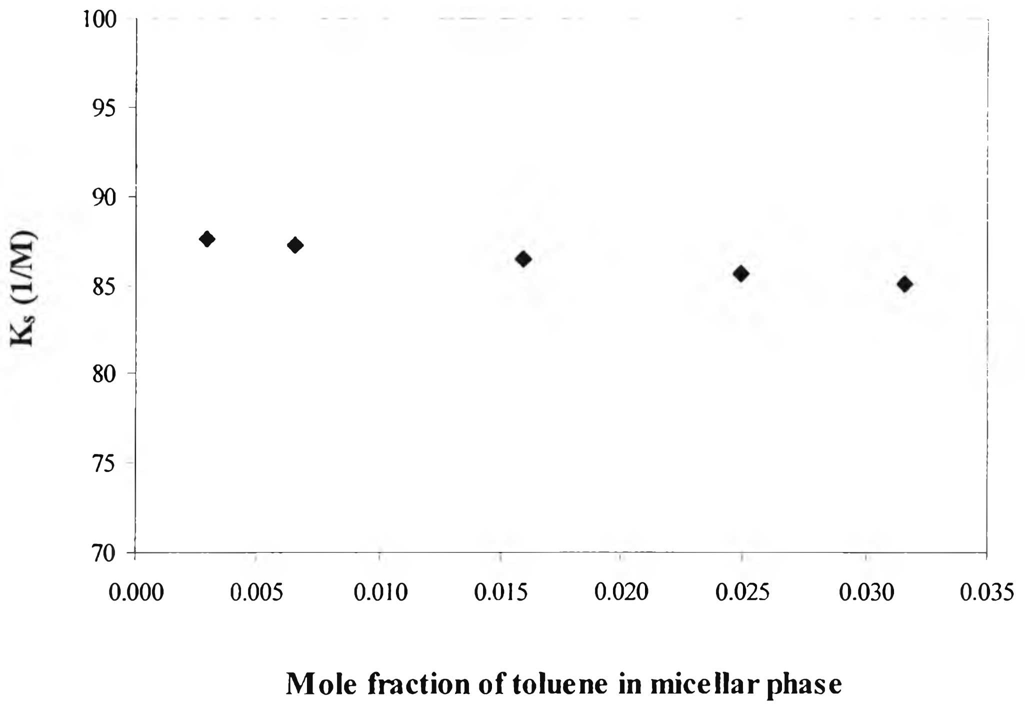

Figure 4.6 Solubilization constant for toluene in 300 mM $OP(EO)_7$ as a function of toluene mole fraction in the micellar phase at 30°C.

4.5.4 Effect of Feed Flow Rate on Vacuum Stripping of Toluene

After we obtained the equilibrium parameters, the stripping column was tested to remove toluene from coacervate phase solutions. With the column pressure of 53 Torr and operating temperature of 30°C, the toluene removal was reduced from 56 to 22% as the feed flow rate increased from 1.1 to 9.8 mL/min (Figure 4.7). As expected, the removal of toluene is significantly reduced if the feed flow rate increases. However, beyond the 5 mL/min feed flow rate, only a slight effect on toluene removal was observed. A by-passing flow pattern and dry packing sections were observed at a 1.1-mL/min feed flow rate. As the liquid flow rate increased from 1.1 to 5.0 mL/min, a larger wet surface area of the packing was observed. This flow behavior was also observed in a study of the co-current downflow of air and water in a rectangular cross-section packed bed [37]. At low liquid loading, the liquid flowed as small rivulets down the packed bed, which appeared to be stable. Larger sized rivulets were observed at higher liquid flow rates. Although a better liquid distribution was observed in the present study, a significant reduction of toluene removal with increasing liquid flow rate was obtained. This might possibly be due to the shorter vapor-liquid contact time in the packed column.

If the feed flow rate reached 7.0 mL/min, foam was generated and occupied the entire packed bed. The amount of foam was significant, particularly when the flow rate was higher than 9.8 mL/min. The large amount of generated foam caused an increase the column pressure drop, leading to undesired operating conditions. When foaming occurred, a 5 Torr/ft pressure drop was observed across the packed bed. The high amount of foam was probably caused by turbulence due to the high feed flow rate in the packed bed. In addition, the foam generated in the flow rate of 7.0–9.8 mL/min resulted in low percentage of toluene removal. The reason is that foam possibly covered the voids between pieces of packing, resulting in a lower vapor-liquid contact area.

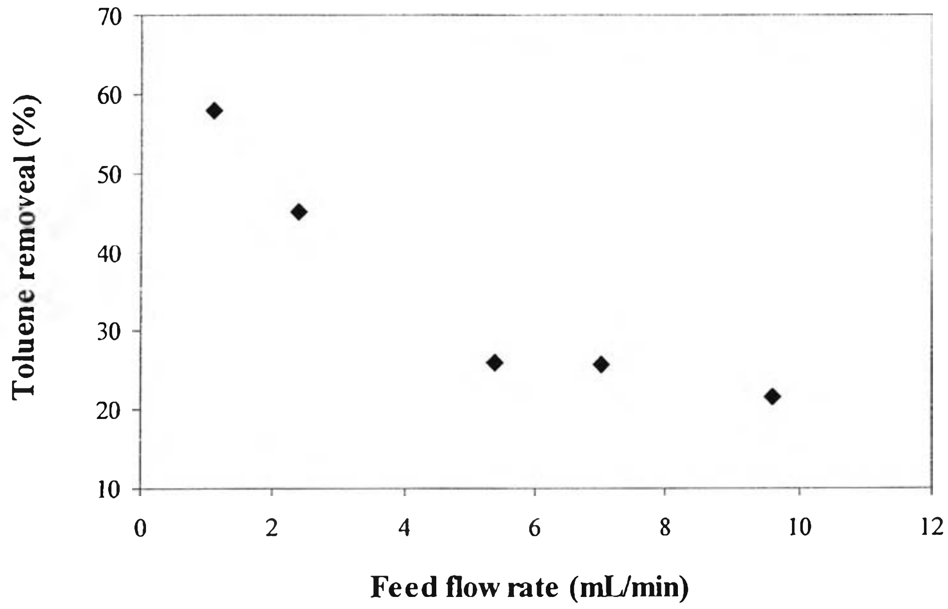

Figure 4.7 Toluene removal as a function of feed flow rate: 300 mM OP(EO)$_7$ feed, 300 ppm toluene feed, 53 Torr column pressure, 1-hole distributor, and 30°C.

4.5.5 Effect of Column Pressure on Vacuum Stripping of Toluene

To avoid the foaming problem, the feed flow rate at 1.1 mL/min was set to remove toluene from 300 mM $OP(EO)_7$ coacervate solution at different column pressures. As shown in Figure 4.8, the toluene removal is as high as 68% at the column pressure of 38 Torr, and the removal efficiency then decreases as the column pressure increases. The toluene removal is about 40% when the column pressure is 70 Torr. By decreasing the column pressure, the driving force of toluene transferring from the surfactant solution to the vapor phase was increased. It should be noted that the operating pressure should not be reduced lower than the vapor pressure of water at any operating temperature in order to prevent the back-mixing of water vapor and the stripped toluene at the exit stream [25].

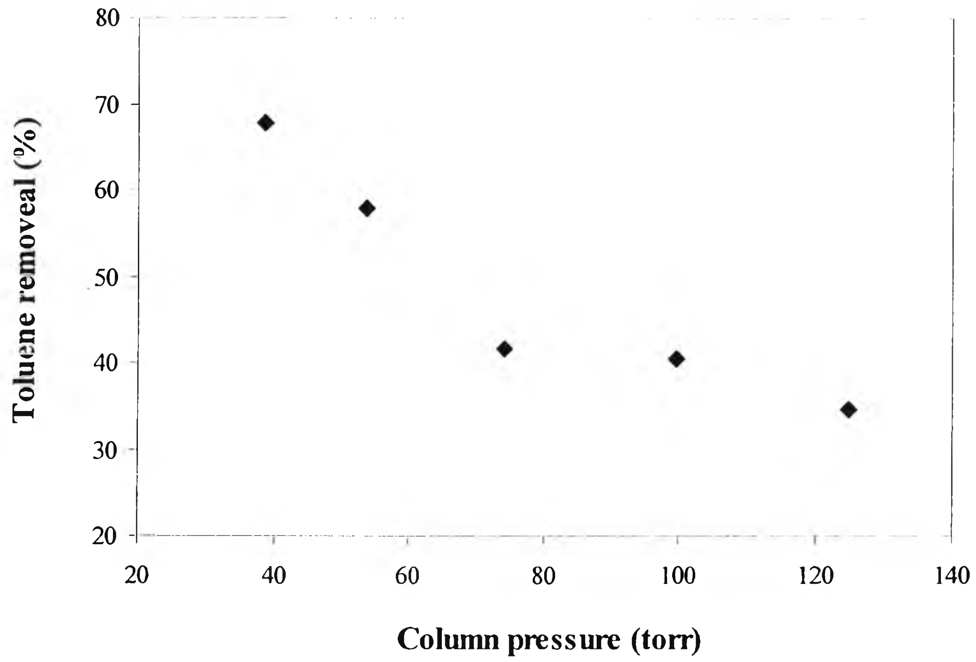

Figure 4.8 Toluene removal as a function of column pressure: 300 mM $OP(EO)_7$ feed, 300 ppm toluene feed, 1.1 mL/min feed flow rate, 38 Torr column pressure, 1-hole distributor, and 30°C.

4.5.6 Effect of Liquid Distribution on Vacuum Stripping of Toluene

As mentioned earlier, the coacervate phase solution was very viscous due to a high concentration of surfactant. When a 1-hole liquid distributor was used, the wall effect and liquid channeling problems in the packed bed were occasionally observed, especially at the feed flow rate range of 1.1–5.0 mL/min. The improper distribution of the coacervate solution is possibly due to the fact that some surfactants adsorb at the interface and alter the physical properties of solution, which could retard the liquid motion and cause coalescence of the liquid stream in the packed column [38]. Unfortunately, a conventional high performance distributor, such as a spray nozzle, is not suitable for the solution containing surfactant since it can easily generate foam. Thus, a circular acrylic plate with a diameter of 3-cm was used as the distributor. The entrance hole was made of a 0.4-cm ID stainless-steel hollow tube connected at the center of the plate. The exit holes were 0.1-cm ID stainless-steel hollow tubes connected at the edge of the plate. During operation, the feed coacervate stream was delivered to the inlet hole and was then spread as a rivulet when it passed through the multi-hole distributor. The distributors with the number of distributor holes varied from 2 to 5 holes are illustrated in Figure 4.9. The effect of a number of holes in distributor was investigated at constant 1.1 mL/min feed flow rate, 300 mM $OP(EO)_7$ concentration, and 38 Torr column pressure. The results are shown in Figure 4.10. It was found that the toluene removal was increased from 68 to 88%, when the number of distributor holes was increased from 1 to 3. For the 4 and 5 holes of liquid distributor the removal of toluene was slightly increased. The increasing number of distributor holes provided more uniform distribution of the surfactant solution on to the top cross-sectional area of the packed column. Therefore, the viscous surfactant solution was more easily spread out over the entire packing surface, resulting in a larger effective surface area for mass transfer.

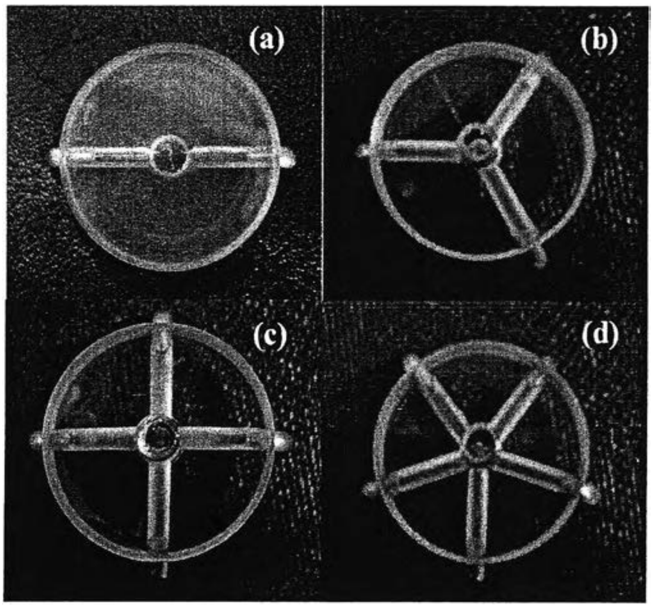

Figure 4.9 Photographs of the packed column distributors with different numbers of exit holes; (a) 2 holes, (b) 3 holes, (c) 4 holes, and (d) 5 holes.

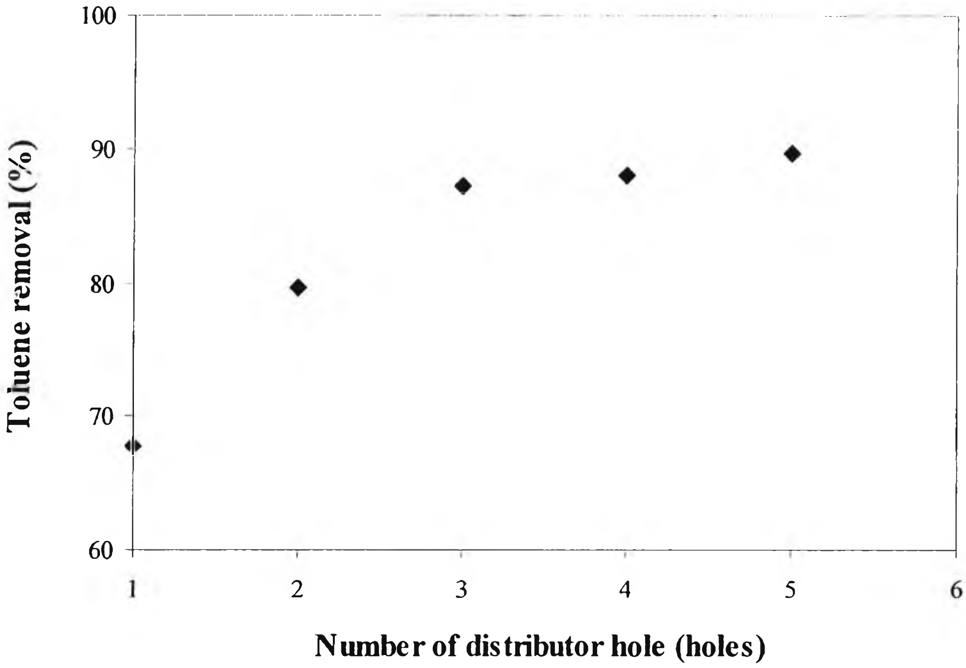

Figure 4.10 Toluene removal as a function of number of holes in the distributor: 300 mM $OP(EO)_7$ feed, 300 ppm toluene feed, 1.1 mL/min feed flow rate, 38 Torr column pressure, and 30°C.

4.5.7 Mass Transfer Coefficient for Co-current Vacuum Stripping

Mass transfer rates of toluene removal from coacervate solution are required to quantitatively describe the dynamics of the co-current vacuum stripping unit. Many models have been proposed and developed for VOC mass transfer determination in counter-current air [12–14, 19–21, 39–41] or vacuum stripping using a packed column [22, 23, 25–27]. For example, Onda's correlations have been used for determining the mass transfer coefficient of VOC removal from water [20, 39, 40]. The Surfactant Air Stripping Model (SASM) was designed for examining the VOC mass transfer in surfactant recovery [13, 14]. The mass transfer coefficient obtained from these models was found to vary with many parameters, such as types and sizes of packing, vapor and liquid flow rates, density and viscosity of liquid solution, and also the VOC Henry's law constants. However, in co-current vacuum stripping, the mass flow rate of vapor phase generated by the applied vacuum is very low and could not be measured here. Thus, those models cannot be applied.

In this work, the model for the mass transfer coefficient of toluene removal from a coacervate solution in co-current vacuum stripping using a packed column is defined in equation (20). In the equation, the initial and final toluene concentration data were obtained directly from the analysis of toluene in the inlet and outlet coacervate streams. The equilibrium mole fraction of toluene (x_t^*) was determined from flash calculation illustrated in equation (13).

There are few studies available for co-current stripping mass transfer calculations. In this work, two additional assumptions were made. First, the liquid flow rate considered in the flash calculation was assumed to be constant through the column due to the small amount of toluene and water vaporization; hence, the liquid-to-feed ratio, $\frac{L}{F}$, was almost one, and the vapor-to-feed ratio, $\frac{V}{F}$, was close to zero. Second, the vapor-liquid equilibrium partition coefficient of water (K_w) was assumed to be equal to one. Based on this assumption, the K_w was calculated from the ratio of mole fraction of water in vapor phase to that in coacervate solution. Because of its higher volatility and lower fraction in coacervate solution compared to water, toluene vaporized rapidly and then reached equilibrium, whereas the vaporization of water still continued; thereby, the amount of water in vapor phase was much greater than that of toluene. Then, the mole fraction in the vapor phase was dominated by water. In liquid phase, since the total mole of surfactant was still relatively low when compared to the total mole of water, the mole fraction of water was close to one (>0.99) for all experiments. Therefore, the K_w calculated at steady state condition was reasonably equal to one. This value, as well as the vapor-liquid equilibrium partition coefficients of toluene and surfactant, were then substituted into flash correlation and rearranged. The equation was then solved by iterating $\frac{V}{F}$ value with the target of $\sum x - \sum y = 0$ until the overall summation approached zero. Following these calculations, the equilibrium mole fraction of toluene was obtained and then applied for the calculation of the overall liquid phase volumetric mass transfer coefficient ($K_x a$) of toluene in equation (20). The $K_x a$ was significantly increased with increasing feed flow rate from 1.1 to 9.8 mL/min, as shown in Figure 4.11. Even though a high value of $K_x a$ was observed at high flow rate, the percentage of toluene removal was somewhat low. This might be due to the short contact time between the vapor and liquid phases, resulting in a reduction of separation performance. The value of $K_x a$ was reduced when the toluene driving force was decreased (Figure 4.12) and $K_x a$ was slightly increased if the liquid distribution was improved (Figure 4.13).

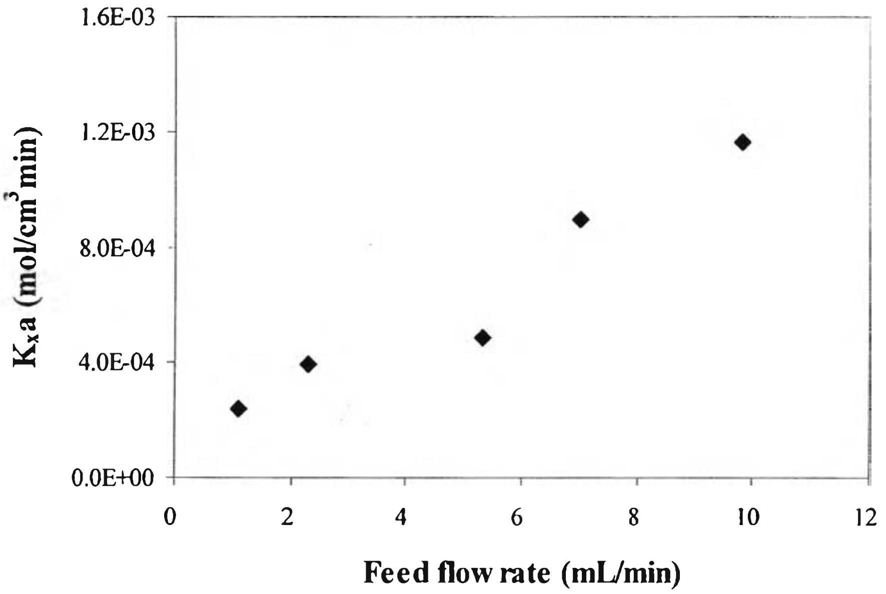

Figure 4.11 Overall liquid phase volumetric mass transfer coefficient (K_xa) as a function of feed flow rate: 300 mM OP(EO)$_7$ feed, 300 ppm toluene feed, 53 Torr column pressure, 1-hole distributor, and 30°C.

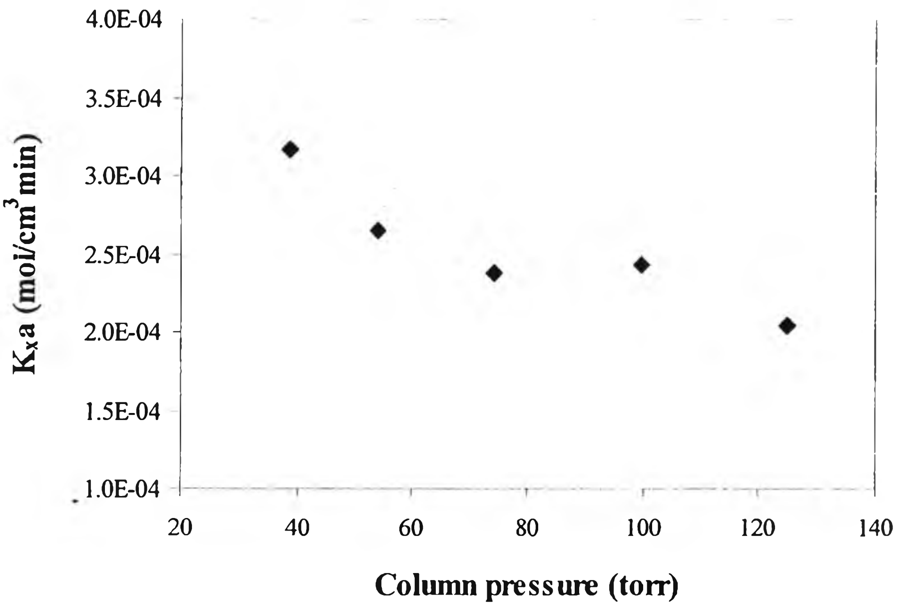

Figure 4.12 Overall liquid phase volumetric mass transfer coefficient (K_xa) as a function of column pressure: 300 mM OP(EO)$_7$ feed, 300 ppm toluene feed, 1.1 mL/min feed flow rate, 1-hole distributor, and 30°C.

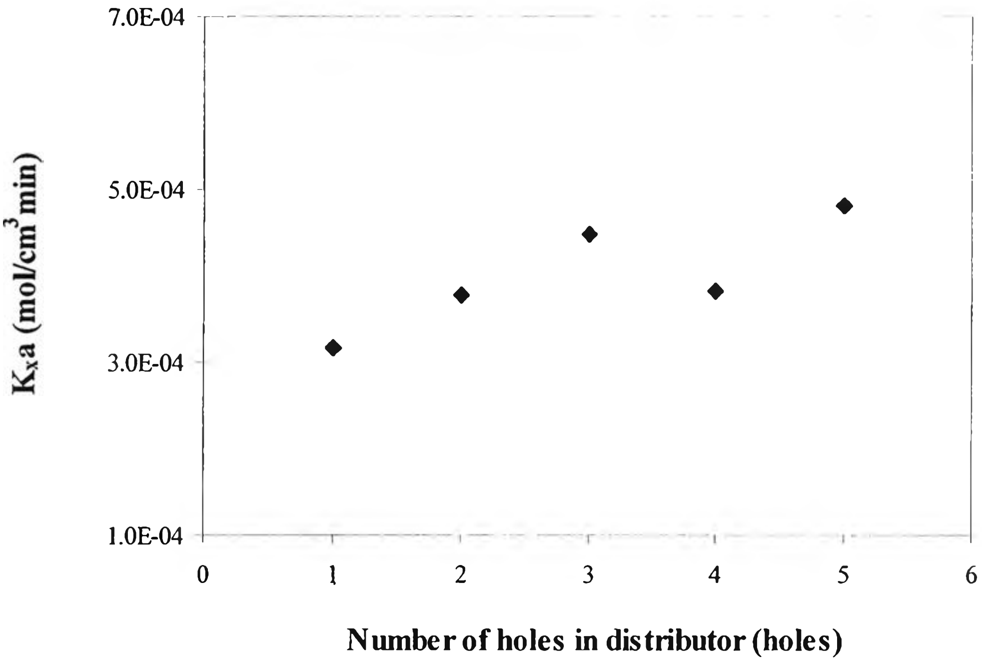

Figure 4.13 Overall liquid phase volumetric mass transfer coefficient (K_xa) as a function of number of holes in distributor: 300 mM $OP(EO)_7$ feed, 300 ppm toluene feed, 1.1 mL/min feed flow rate, 38 Torr column pressure, and 30°C.

4.6 Conclusions

This work demonstrates 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. Due to the solubilization of toluene in surfactant micelles, the Henry's law constant of toluene in 300 mM $OP(EO)_7$ is 96% less than that in water. If the feed flow rate is decreased from 9.8 to 1.1 mL/min, the toluene removal efficiency increases by 34%. But, when the feed flow rate is higher than 7.0 mL/min, significant amount of foam is observed. However, foam can be avoided by controlling the feed flow rate to be less than 5.0 mL/min without adding anti-foam chemicals. By reducing the column pressure from

70 to 38 Torr, the toluene removal is increased by 28%. The toluene removal increases by 22% when increasing the number of holes in the liquid distributor plate from one to five. The results are also reported in terms of an overall liquid phase volumetric mass transfer coefficient which can be used in design of a commercial stripping unit.

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