CHAPTER III

SCALING UP CLOUD POINT EXTRACTION OF AROMATIC CONTAMINANTS FROM WASTEWATER IN A CONTINUOUS ROTATING DISC CONTACTOR: PART 1. EFFECT OF DISC ROTATION SPEED AND WASTEWATER/SURFACTANT RATIO

ABSTRACT

When an aqueous solution containing nonionic surfactant is heated above the cloud point, the solution separates into two phases. A micellar-rich phase or coacervate, and a micellar-dilute phase are formed. Aromatic contaminants presented in the original solution tend to solubilize into the micelles in the coacervate phase and concentrate there – this is the basis of the separation process known as cloud point extraction (CPE). In this study, CPE was scaled up from single stage batch experiments to multistage continuous operation in a rotating disc contactor (RDC) to remove the aromatic contaminants, toluene and ethylbenzene, from wastewater. A nonionic surfactant, t-octylphenolpolyethoxylate, was utilized as the separating agent. The concentration of solutes in the coacervate phase increases as agitator speed, wastewater/surfactant solution flowrate ratio and degree of alkylation of the aromatic solutes increase. The overall volumetric mass transfer coefficient (Ka) and the number of transfer unit (NTU) in the RDC increase with increasing rotation speed of the rotor disc. In this pilot scale, multistage continuous operation, the toluene partition ratio and concentration of toluene in the coacervate phase are two times greater than that observed in a single stage, equilibrium batch experiment with the same initial condition.

INTRODUCTION

Environmental contamination due to wastewater discharges containing a trace amount of aromatic compounds can cause severe problems because of the toxicity of either known or suspected carcinogens or mutagens (1). A novel class of separation processes known as surfactant-based separations has been shown to be effective techniques in environmental clean-up (2-5). These techniques involve biodegradable, non-toxic separating agents (surfactants) and include technologies such as surfactant enhanced oil recovery, foam fractionation, and froth flotation. Cloud point extraction (CPE) is one of the surfactant-based separation technologies, which is effective and economical in the removal of organic compounds from polluted water (1, 6-18). An aqueous solution of nonionic surfactant undergoes a phase separation when it is at a temperature above its cloud point, attained either by heating or by adjustment of surfactant structure or additives to lower the cloud point of the surfactant below the operating temperature. Above the cloud point, two isotropic micellar phases are formed; one phase is generally less in volume and contains most of surfactant micelles and is known as a micellar-rich or coacervate phase. The other phase is an aqueous solution lean in surfactant micelles, known as a micellar-dilute or dilute phase. When nonionic surfactant is added to polluted water above the cloud point, the organic solutes contained in the solution will solubilize into surfactant micelles. After the phase separation, surfactant and pollutants are concentrated in the coacervate phase. The dilute phase, which contains a low concentration of organic pollutant, can be discharged to the environment as the effluent water. If a single stage results in insufficient purification, multiple stages can be used as in traditional liquid-liquid extraction as investigated in this paper. The CPE is a special case of a class liquid-liquid extractions, known as aqueous biphasic extractions (19).

From our previous work, we have shown in batch experiments that CPE is a promising technique to remove aromatic compounds from aqueous wastewater by concentrating them in the coacervate phase (18). These chemicals are common pollutants of great environmental concern originating from industrial effluents and gasoline tank leakage. Moreover, the coacervate solution, which contains a high concentration of surfactant, is recoverable because the volatile aromatic solubilizates can be removed by stripping, leaving the solute-free surfactant stream available for reuse. The objective of this research is to scale up the cloud point extraction technique in continuous operation in a multistage, differential extractor. To our knowledge, all previous studies of CPE have involved batch extractions. Even though high separation factors may be observed, it is not at all obvious that the extraction can be scaled up in a continuous, multistage unit without operational problems since the coacervate phase can be very viscous.

BACKGROUND

There is a phase separation of polyethoxylate nonionic surfactant solutions into two phases at a certain temperature known as the cloud point (1, 6-22). At the cloud point, the solution appears cloudy since the coacervate or micelle-rich phase is emulsified in the micellar-dilute phase. The coacervate phase can be very concentrated in surfactant, sometimes exceeding 50 wt %. The dilute aqueous phase contains a low surfactant concentration approximately 2 to 20 times the critical micelle concentration (CMC). The phase separation process is reversible and two phases can merge together to form a homogeneous phase on cooling (9, 14). The cloud point is generally defined at a surfactant concentration of 1 weight % (23). However, it is not highly concentration dependent (11, 21, 23, 24). At the surfactant concentration which exhibits the minimum cloud point, this temperature is known as the lower consolute temperature (LCT) (24). The clouding is reported to be due to an increase in dehydration of hydrated outer micellar layers, intermicellar attraction and micellar size when the temperature is increased (9, 14). Cloud points of nonionic surfactants depend on their structure. An increase in the degree of polymerization of ethylene oxide and decrease in hydrocarbon chain length of the hydrophobic moiety of polyethoxylated nonionic surfactants can elevate the cloud point (9, 22, 25, 26). An addition of polar compounds depresses the cloud point by decreasing the hydration of the polyoxyethylene chains due to the competition for the hydratable sites by the polar solubilizates (20). Added ionic surfactant can drastically increase the cloud point of the mixed micelles system by imposing an electrostatic repulsion between micelles which opposes the intermicellar attraction (27-29). An electrolyte can alter the cloud point due to the salting-in or the salting-out effect (21, 27-30).

Many studies of CPE have been done with low volatility organic solutes such as polycyclic aromatic hydrocarbons (PAHs) and biomaterials (1, 6-22). Despite their importance as pollutants in water, volatile organics have received little attention in CPE studies. We feel that this is largely due to the extreme care which must be taken to minimize leakage of solutes with high vapor pressures as detailed in our previous batch studies of trichloroethylene, dichloroethane, trichloroethane, tetrachloroethane, benzene, toluene, and ethylbenzene (12,13,18). A major advantage of CPE of volatile organic pollutants is the potential to regenerate the surfactant in the coacervate stream for reuse because these VOCs have high enough volatility to be separated from the concentrated surfactant solution by gas, steam or vacuum stripping (31-33).

Solute partition ratio is defined as the ratio of coacervate solute concentration to dilute phase solute concentration. Volatile organics do not tend to have as high of a partition ratio as higher molecular weight, less volatile organics. For example, at 30-50 °C, measured partition ratios of chloroethane range from 15 to 86 (13), trichloroethylene from 34 to 105 (12), benzene from 10 to 29 (18), toluene from 28 to 65 (18), ethylbenzene from 71 to 162 (18), compared to a range of 393 to 634 for tert-butylphenol (6). So, multiple stages will often be required to attain a required degree of separation for volatile organics. Large scale application of CPE requires a continuous steady-state operation for economical operation as with other liquid-liquid extraction unit operations. While physically separate extraction stages can be used, a column with multiple stages in a single unit is most efficient (34-36).

In continuous differential equipment, a density difference between the fluids being contacted makes a countercurrent operation possible. The denser phase enters at the top of the column and flows downward, whilst the lighter phase enters at the bottom and flows upwards. The cross-sectional area of the column must be large enough to avoid flooding. The height of the column is controlled by the rate of mass transfer and the amount of material required to be extracted. Due to a small density difference between the contacted liquids (the coacervate and the dilute phase), gravitational forces are insufficient to promote a good phase dispersion and turbulence mixing (34, 35). Hence, mechanical agitation is normally applied to improve the performance by increasing the interfacial area per unit volume and reducing the mass transfer resistance (37, 38). As shown in Fig. 1, a rotating agitator driven by a shaft is typically used since it can create a shear mixing zone axially throughout the column in a rotating disc contactor (RDC). The RDC has high efficiency per unit height, high throughput, high operational flexibility, ease of operation, and low cost (38). The RDC provides a good dispersion between phases because of the shear between rotor discs connected to a central rotating shaft.

Moreover, the stators attached to the inside of the wall of the column serves as baffles to reduce back mixing during the extraction.

EXPERIMENTAL

Materials

A polydisperse commercial branched t-octylphenolpolyethoxylate, $OP(OE)_7$, with an average of 7 moles of ethylene oxide per mole of octylphenol (trade name Triton X-114) from Dow Chemical Inc. (South Charleston, USA) was used as the nonionic surfactant in this study. Reagent grade toluene from J. T. Baker (Phillipsburg, USA) with a purity of 99.8 % and ethylbenzene from Fluka (Buchs, Switzerland) with a purity of 98 % were used. All chemicals were used as received. The water was distilled.

Apparatus: Rotating disk contactor (RDC)

Figure. 1 shows a schematic diagram of the cloud point extraction pilot plant. A cylindrical column made of Pyrex glass with 29.2 mm ID has an acrylic water jacket with 49.2 mm ID, through which temperature controlled water can be circulated. The extractor column has a mixing zone in the middle and a settling or empty zone at either end of the column. In order to increase the residence time of the raffinate (micellar dilute phase) and the extract phase (coacervate phase) before leaving the column, the diameter of the settling zone (100 mm ID) needs to be substantially larger than that of the mixing zone (29.2 mm ID). The heights of the settling zone and mixing zone are 150 mm and 700 mm, respectively. In the mixing zone, there are 32 horizontal rotor discs of 17.52 mm in diameter and 1 mm in thickness mounted on a speed adjustable, vertical shaft at the center of the column. In addition, there are 33 annular stator rings with an outer and inner diameter of 29.2 mm and 20.44 mm, respectively and 1 mm in thickness. The opening of the stator rings is larger than the rotor disc diameter. The compartment spacing between stators is 22 mm. The rotor discs, stators and shaft are made of 316 stainless steel.

Procedures

In general, the phase, which has a lower flowrate and/or possesses a higher viscosity, is chosen to be the dispersed phase. In this work, the coacervate or surfactant solution (solvent) has been selected to be the dispersed phase. As a result, wastewater (feed) is the continuous phase. Based on the density difference, the heavy surfactant solution is fed into the top of the column while the light wastewater is fed into the bottom of the extractor. The interface is controlled to be at the bottom of the column. After the unit was assembled and checked for leaks, the continuous phase was fed into the column until the level was above the top agitator, followed by the dispersed phase to completely fill the column as indicated by some overflow occurring from the top of the column. While filling the column, the water jacket was filled with temperature-controlled circulating water under conditions which maintained column temperature at 40 °C.

The contaminated feed water and the surfactant solvent solution were fed into the extractor counter-currently at defined flowrates regulated by rotameters. When the system reached steady state, as indicated by no change in the surfactant and solute concentration in the dilute phase with time, samples were collected from the effluent dilute phase and the coacervate phase (see Fig. 1) to determine the concentration of nonionic surfactant and aromatic solute. In addition, the flowrate of the dilute phase stream was determined by measuring the volume of the dilute phase collected over a measured time interval whilst the flowrate of the coacervate phase stream is obtained from an overall material balance.

The concentrations of $OP(EO)_7$ and aromatic solutes were measured by using a CE 2000 series UV-spectrophotometer (Cecil Instrument Limited, Cambridge, England) at 224 nm and a gas chromatograph with a flame ionization detector (Perkin Elmer, Inc., Shelton, USA), respectively. Because of the high volatility of aromatic solutes, static headspace sampling was used as the sample injection technique which eliminated interference of the high molecular weight nonionic surfactant. The gas chromatograph conditions were: column: Supelcowax 10; carrier: ultra-pure nitrogen with the flowrate of 20 mL/min; oven temperature: 100 °C isothermal; injector temperature: 150 °C; detector temperature: 250 °C. The external standard quantitative calibrations were obtained for the analysis of surfactant and aromatic solutes in both phases. Closure of the material balance is taken as evidence that leakage of the volatile solute is negligible.

The RDC operating conditions and variables were as follows: column temperature: 40 °C; concentration of surfactant: 300 mM; concentration of aromatic pollutant in wastewater: 100 ppm; agitator speed: 0 to 200 rpm; wastewater/surfactant solution flowrate ratio (feed/solvent flowrate ratio): 5.97 to 13.70; solutes: toluene and ethylbenzene.

RESULTS AND DISCUSSION

Steady state time analysis

A determination of the time to attain steady state in the RDC is determined by measuring the concentration of solute in the effluent dilute phase as a function of time. The concentration of the solute in the wastewater feed stream and the position of the interface were determined to be constant throughout the experiment.

Phenol was used as the solute in the determination of time to attain steady state for convenience because it has similar molecular structure and size but lower volatility than the target solutes (toluene and ethylbenzene) used in this study; hence, less concern about loss of solute into the head-space. The effect of wastewater/surfactant flowrate ratio on the steady state time is shown in Fig. 2. The inlet phenol concentration was held constant at 500 ppm in every experiment. The wastewater/surfactant solution flowrate ratio was varied from 6.9 to 13.9 to cover the entire wastewater/surfactant ratio range used in subsequent experiments. As the flowrate ratio increases, the system reaches steady state faster but the concentration of phenol in the dilute phase is higher, which indicates poorer extraction efficiency. At the lowest wastewater/surfactant flowrate ratio studied here, the system takes 3.5 hours to reach steady state. Therefore, 4 hours of operation was allowed for all runs to ensure steady state is attained.

Effect of agitator speed in CPE of toluene

The rotation speed of the rotor disc does not show a significant effect on the surfactant concentration in the coacervate solution, but it causes a substantial increase in the surfactant concentration in the dilute phase as shown in Fig. 3. At higher agitator speed, the coacervate phase is beaten up into tiny drops, which can entrain to the top of the column with the dilute phase as indicated by a higher surfactant concentration in the dilute phase. Beyond a speed of 200 rpm, flooding is approached because the coacervate drops are too fine to flow downward and settle down against the dilute phase stream, which flows upward. The flooding condition corresponds to the appearance of a cloudy surfactant solution at a certain location in the mixing zone. Below that particular position, there is no appearance of the coacervate droplets.

When the agitation speed increases, the dispersed drop size is smaller, resulting in a higher interfacial area and longer residence time of droplets in the mixing zone (37-39). Tong et al. (38) studied the effect of agitator speed in a RDC in the reversed micellar extraction of lysozyme. They reported that 70 to 90 % of lysozyme was extracted and extraction efficiency depended on agitator speed. Fig. 4 shows an increase in toluene concentration in the coacervate solution with increased rotation speed of the rotor disc. The toluene concentration in the dilute phase decreased from 29.2 ppm with no rotating agitator to 12.9 ppm at an agitator speed of 200 rpm. With no agitation, the static rotors and stators serve as baffles to break up the coacervate droplets along the column. The average coacervate drop size with no agitation is visually larger than that obtained when mechanical agitation is applied.

Although an increase in agitation enhances the extraction efficiency, there is a limitation. Beyond a certain point, an excessive agitation may inhibit the process (37, 39). The partition ratio of surfactant and toluene are shown in Fig. 5. where the fraction of total surfactant present and fraction of toluene extracted in the coacervate phase are shown in Fig. 6. The partition ratio is the ratio of solute or surfactant concentration in the coacervate phase to that of in the dilute phase. A higher partition ratio indicates a better separation. Fig. 5 illustrates an increase in toluene partition ratio as the agitator speed is raised. On the other hand, the surfactant partition ratio decreases when the agitator speed is increased due to the entrainment of the coacervate drops. At an agitator speed of 150 rpm, the toluene partition ratio as high as 81.9 is observed and 87.5 % of toluene are extracted into the coacervate solution as seen in Fig. 6. There is no significant further change in extractor performance as the agitator speed further increases from 150 rpm to 200 rpm. Beyond a speed of 200 rpm, flooding occurs. Although there is the entrainment of coacervate droplets, more than 92 % of the surfactant resides in the effluent coacervate solution at every agitator speed studied here.

Effect of wastewater/surfactant flowrate ratio on the CPE of toluene

The surfactant concentrations in the coacervate and the dilute phase are not much affected by the wastewater/surfactant flowrate ratio as shown in Fig 7. Therefore, the flowrate of the extracted coacervate phase decreases with increasing wastewater/surfactant flowrate ratio as required from material balance considerations. This result corresponds to that obtained from batch experiments in previous work when the total surfactant concentration was varied (12, 18). A higher toluene concentration in the coacervate solution is observed when the flowrate ratio increases (or the flowrate of surfactant solution decreases) due to a longer residence time of the coacervate drops in the extraction column. However, the concentration of toluene in the dilute phase is not significantly affected by the wastewater/surfactant flowrate ratio as demonstrated in Fig. 8. An increase in flowrate ratio does not have a substantial effect on the toluene and surfactant partition ratios and the fraction of toluene and surfactant retaining in the coacervate solution as illustrated in Fig. 9 and Fig. 10, respectively. As an illustration of the effectiveness of this separation in the RDC, at a wastewater/surfactant flowrate ratio of 5.79, the surfactant and toluene partition ratio are 153.1 and 93.8, respectively. In addition, the fraction of toluene extracted in the coacervate solution is 90.0 % and 93.6 % of surfactant presents in the coacervate solution.

Effect of solute structure in CPE

A comparison of solute partition ratio, surfactant partition ratio, and the fraction of solute extracted in the coacervate solution between toluene and ethylbenzene are shown in Fig. 11. Ethylbenzene can depress the cloud point of the system more than toluene as shown in a previous paper (18), resulting in the operating temperature being more above the cloud point and the surfactant partition ratio being higher for the ethylbenzene system. The solute partition ratio and the fractional extraction of ethylbenzene are higher than that of toluene. In addition to the cloud point depression effect, this is due to ethylbenzene having lower water solubility than toluene; hence it tends to solubilize to a greater degree into the micelles in the coacervate phase. These same trends were also observed in equilibrium batch experiments. At 40 °C, the ethylbenzene partition ratio is 192.7

and 94.4 % of ethylbenzene is extracted in the coacervate solution compared to a toluene partition ratio of 81.9 and 87.5 % of toluene extracted in the coacervate solution.

Determination of number of transfer unit (NTU), height of transfer unit (HTU) and the overall volumetric mass transfer coefficient (Ka)

The HTU is the column height required to attain the separation which is equivalent to one equilibrium batch extraction and the NTU is the number of these single stage, batch extraction equivalents in the experimental column used. The HTU is particularly important in the design of industrial scale extraction columns. Based on the design of differential extractors in the literature, the graphical method can be used to determine the NTU by constructing the equilibrium line and the operating line on a plot between the mass fraction of toluene in the coacervate phase (X_{tou}) and the mass fraction of toluene in the dilute phase (Y_{tou}). The slope of the equilibrium line is a partition ratio obtained from batch experiments at equilibrium, whereas the slope of the operating line is the ratio of mass flowrate of the coacervate phase to mass flowrate of the dilute phase at the relevant position in the extractor (35). In our case, we assume that the mass flowrates of both phases are constant since the volumes of the separated phases are governed by the operating temperature, which is held constant throughout the column. Therefore, the operating line is a straight line with a constant slope. The NTU can be evaluated by either drawing a step line between those two lines as in the McCabe-Thiele method or by a numerical method (34, 35). Since the total active height of the extraction column is a product of NTU and HTU, the HTU is calculated. A smaller HTU (or higher NTU) shows a higher Ka or better extraction efficiency. Fig. 12 shows that NTU increases as the agitator speed increases, from 1.3 transfer units with no agitation to the 2.3 transfer units at a rotating disc speed of 150 rpm. As a result, the HTU decreases when the agitator speed is raised, from 53.1 cm. per transfer unit at no agitation to 30.5 cm. per transfer unit at an agitator speed of 150 rpm. When the agitator speed is increased, the interfacial area of the coacervate drops increases as droplet diameter decreases, leading to a higher Ka as illustrated in Fig. 13. The Ka obtained in this study (in the range of 10^{-4} to10^{-3} s^{-1}) is on the same order as that reported by Tong et al. in the reversed micellar extraction of proteins (in the range of 10^{-3} to10^{-2} s^{-1})(38).

Comparison of extraction performance between batch and continuous operation

The surfactant and toluene concentration in the coacervate solution, as well as the partition ratio obtained from a batch equilibrium single stage and from continuous operation, are shown in Fig. 14. The surfactant concentration in the coacervate solution from both operations are nearly the same. However, the surfactant partition ratio obtained from the extractor is notably less than that obtained from the batch experiment due to the entrainment of coacervate drops with the dilute phase, resulting in a higher surfactant concentration in the dilute phase and a lower in surfactant partition ratio. The concentration of toluene in the coacervate solution obtained from the continuous extractor is twofold higher than that obtained from the batch experiment since it is a multistage extraction compared to a single stage extraction in the batch operation; the NTU can be as high as 2.3 or the equivalent of 2.3 batch extractors in the continuous column. Obviously, the column height can be adjusted in designing a commercial unit to permit as many equivalent stages as needed.

This study has demonstrated that scaling up CPE to a continuous extraction unit is straightforward and the normal type of design parameters to design a commercial column to attain any desired degree of separation (HTU or Ka) can be obtained from a pilot scale extraction column. Some small entrainment of coacervate into the dilute phase is the only factor observed which decreases performance of the RDC compared to predictions from equilibrium stage operations as long as flooding conditions are avoided.

ACKNOWLEDGMENTS

Financial support for this work was provided by The Thailand Research Fund under The Royal Golden Jubilee Ph.D. Program and The Basic Research Grant. In addition, support was received from the industrial sponsors of the Institute for Applied Surfactant Research including Akzo Nobel Chemicals Inc, Albemarle Corporation, Amway Corporation, Clorox Company, Colgate-Palmolive, Dial Corporation, Dow Chemical Company, DowElanco, E. I. DuPont de Nemours & Co., Halliburton Services Corp., Henkel Corporation, Huntsman Corporation, ICI Americas Inc., Kerr-McGee Corporation, Lever Brothers, Lubrizol Corporation, Nikko Chemicals, Phillips Petroleum Company, Pilot Chemical Company, Procter & Gamble Company, Reckitt Benckiser North America, Schlumberger Technology Corp., Shell Chemical Company, Sun Chemical Corporation, Unilever Inc. and Witco Corporation. John Scamehorn holds the Asahi Glass Chair in Chemical Engineering at the University of Oklahoma.

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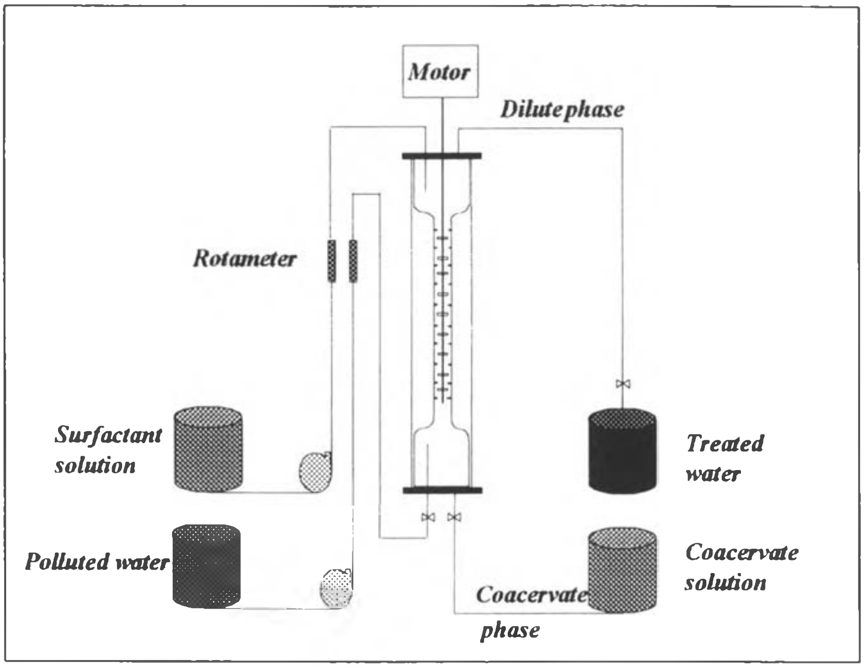

Figure 1. A schematic diagram of the cloud point extraction pilot plant.

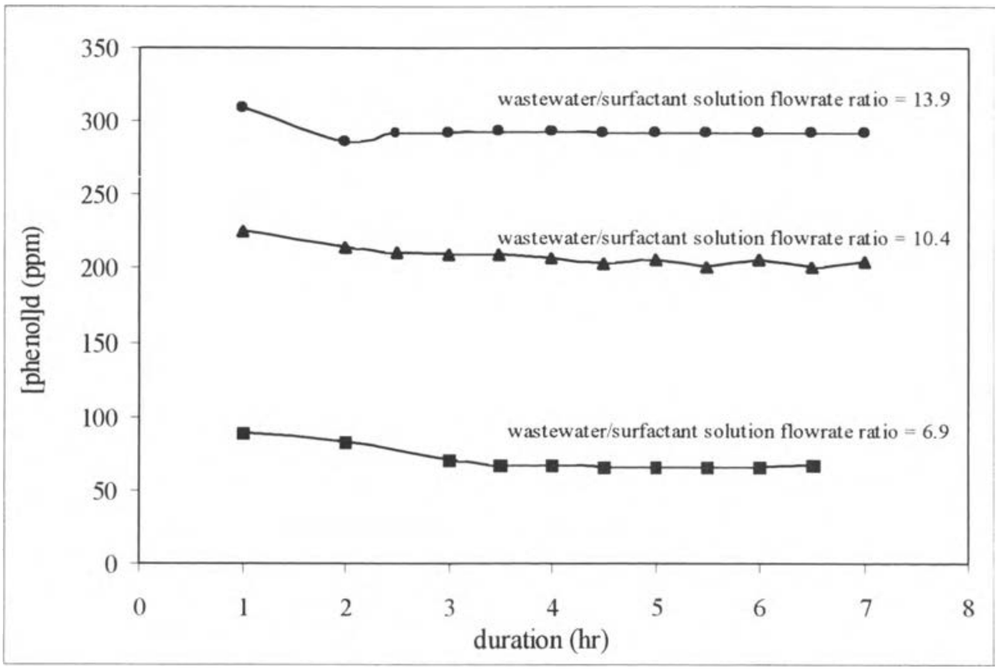

Figure 2. Phenol concentration in dilute phase stream (d) as a function of operating time (system: 500 ppm phenol, 300 mM surfactant solution, 150 rpm agitator speed, and 40 °C).

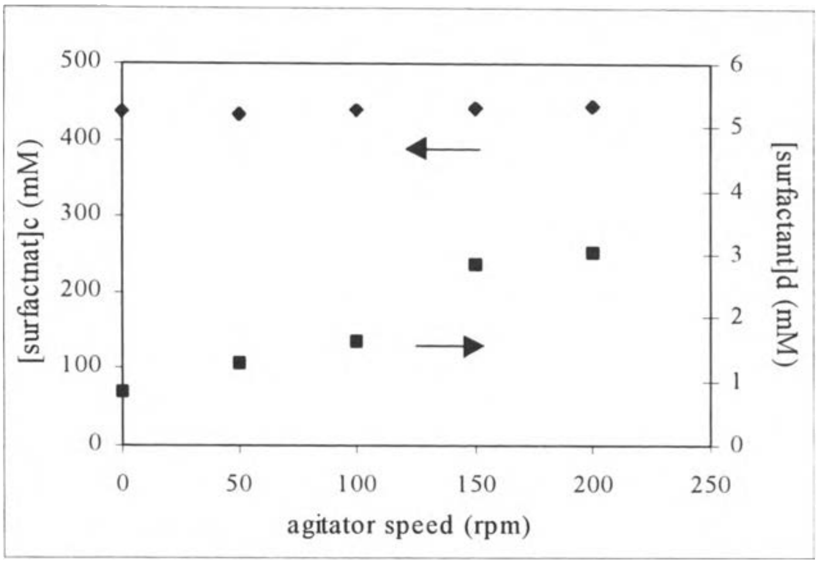

Figure 3. Surfactant concentration in coacervate stream (c) and dilute phase stream (d) as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C).

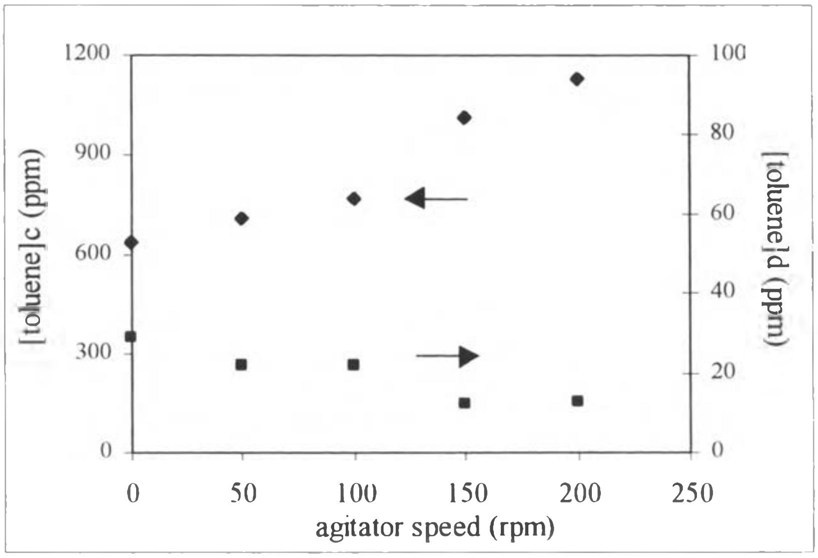

Figure 4. Toluene concentration in coacervate stream (c) and dilute phase stream (d) as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C).

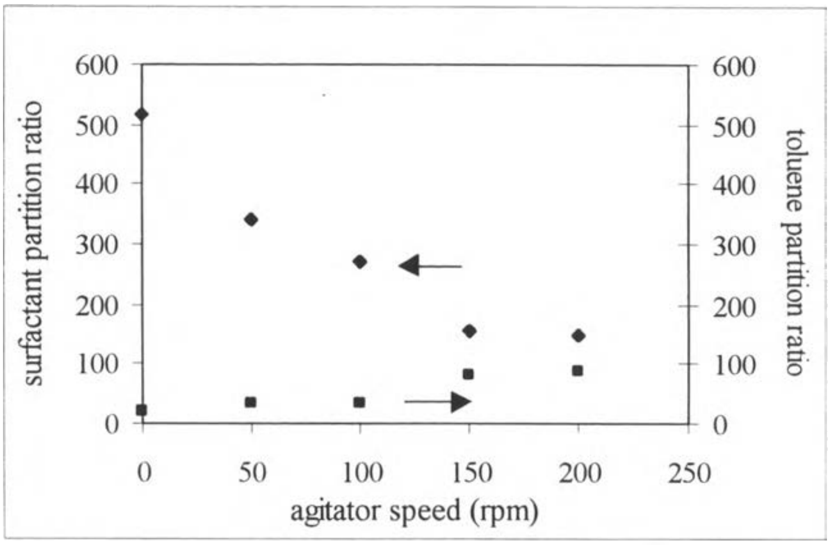

Figure 5. Surfactant and toluene partition ratio as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C).

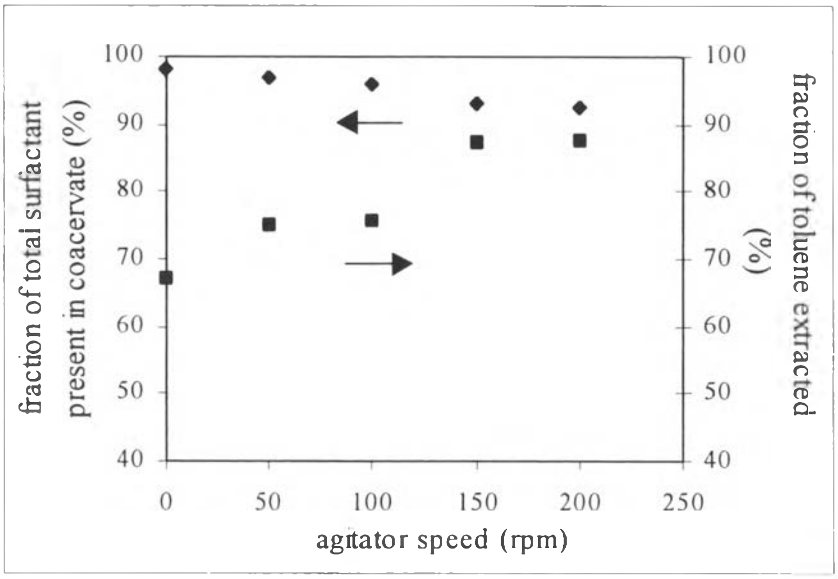

Figure 6. Fraction of total surfactant present in coacervate stream and fraction of toluene extracted in coacervate stream as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C).

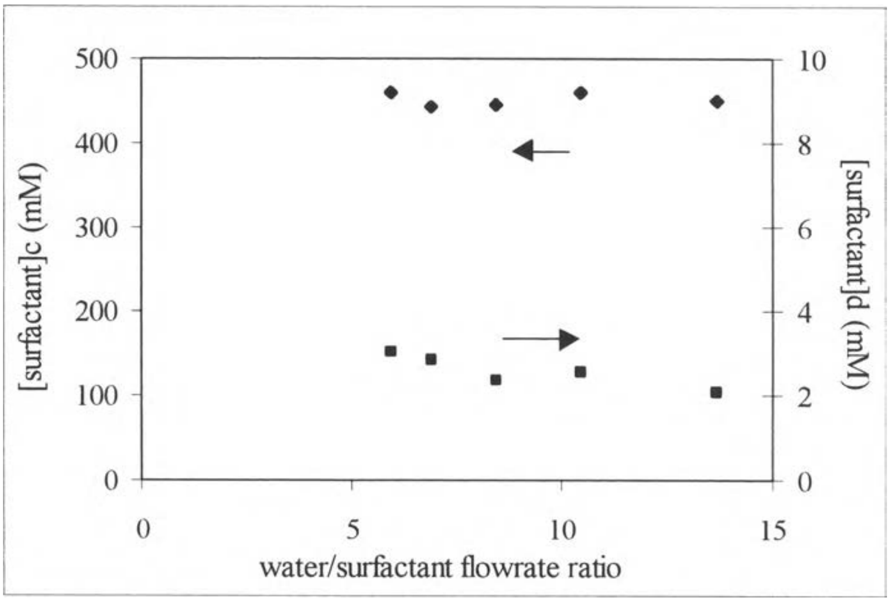

Figure 7. Surfactant concentration in coacervate stream (c) and dilute phase stream (d) as a function of wastewater/surfactant solution flowrate ratio (system: 100 ppm toluene, 300 mM surfactant solution, 150 rpm agitator speed, and 40 °C).

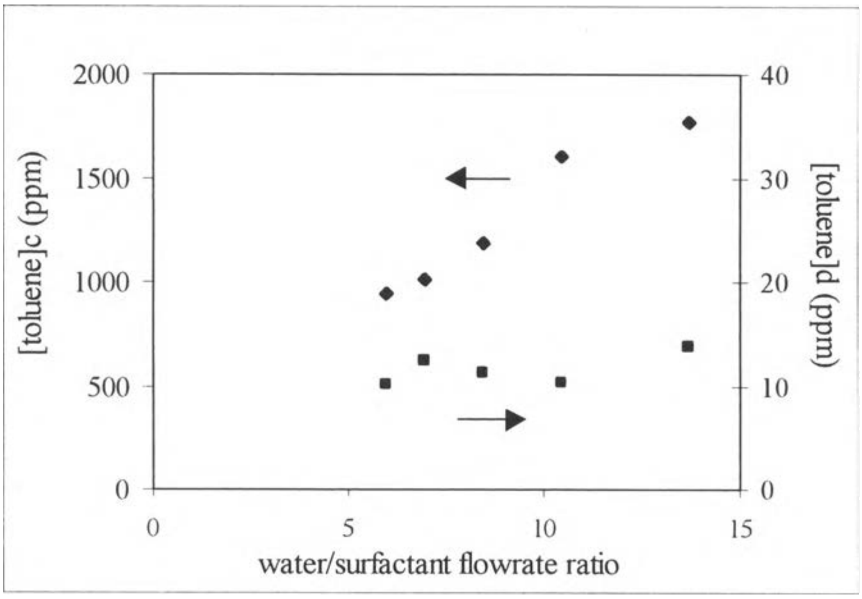

Figure 8. Toluene concentration in coacervate stream (c) and dilute phase stream (d) as a function of wastewater/surfactant solution flowrate ratio (system: 100 ppm toluene, 300 mM surfactant solution, 150 rpm agitator speed, and 40 °C).

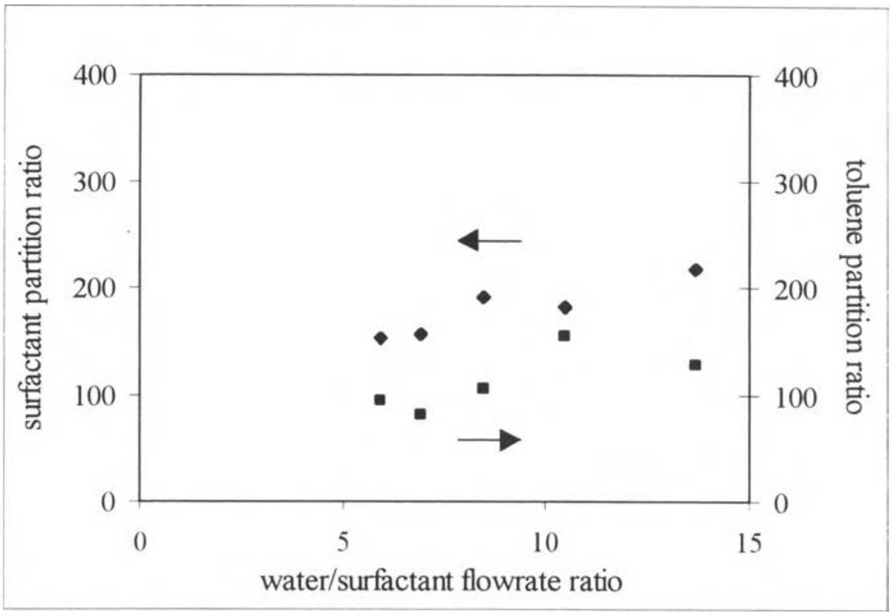

Figure 9. Surfactant and toluene partition ratio as a function of wastewater/surfactant solution flowrate ratio (system: 100 ppm toluene, 300 mM surfactant solution, 150 rpm agitator speed, and 40 °C).

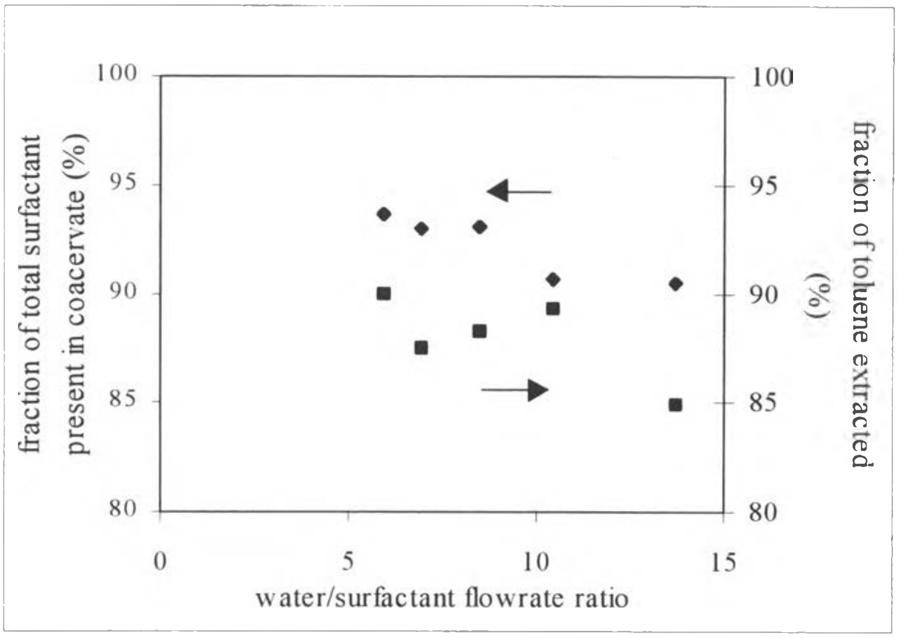

Figure 10. Fraction of total surfactant present in coacervate stream and fraction of toluene extracted in coacervate stream as a function of wastewater/surfactant solution flowrate ratio (system: 100 ppm toluene, 300 mM surfactant solution, 150 rpm agitator speed, and 40 °C).

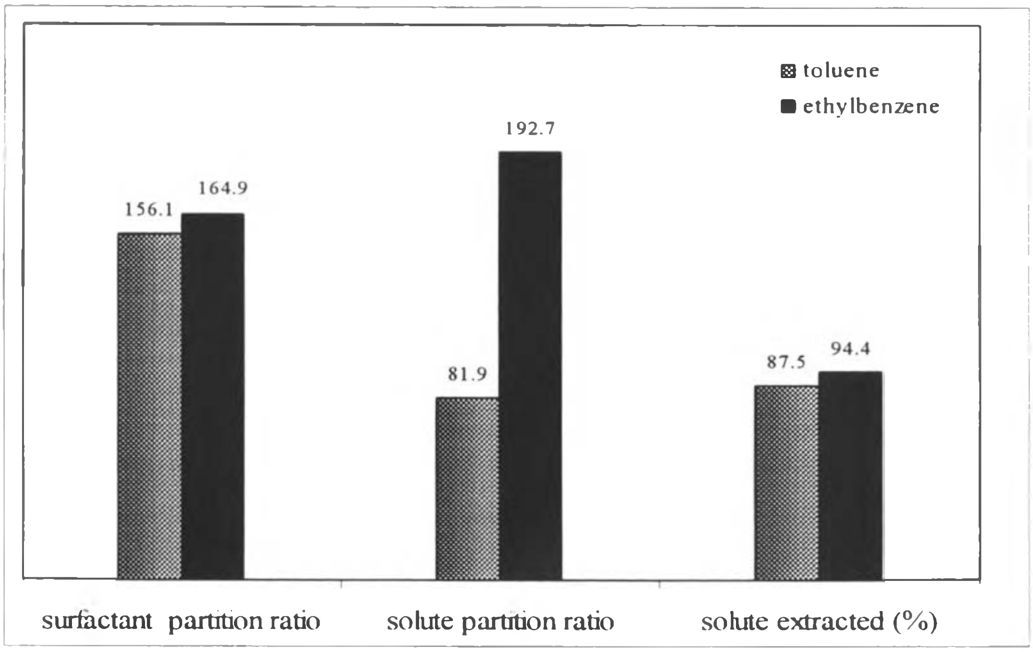

Figure 11. Comparison of surfactant and solute partition ratio and fraction of solute extracted in coacervate stream between toluene and ethylbenzene (system: 100 ppm solute, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C).

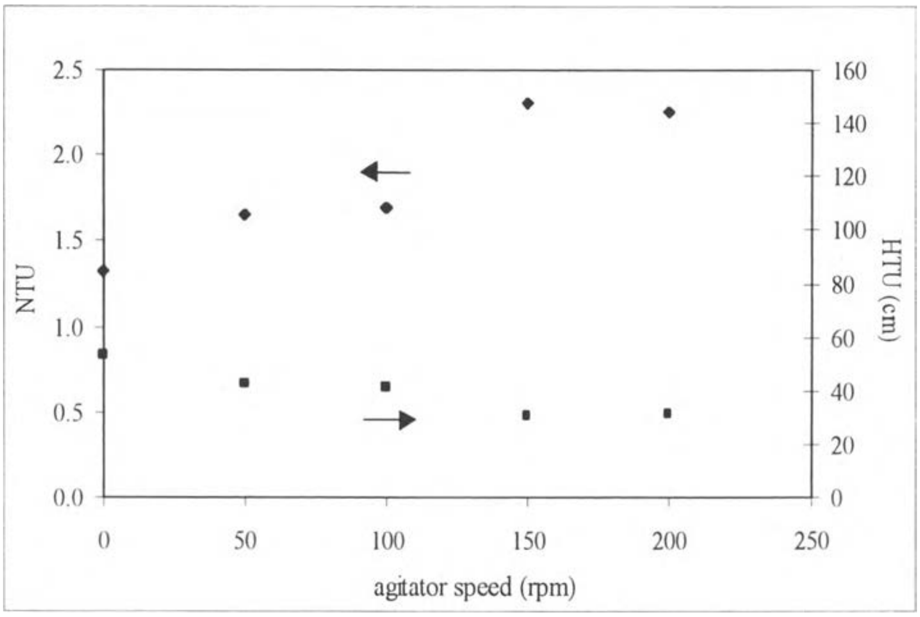

Figure 12. Number of transfer unit (NTU) and height of transfer unit (HTU) as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C).

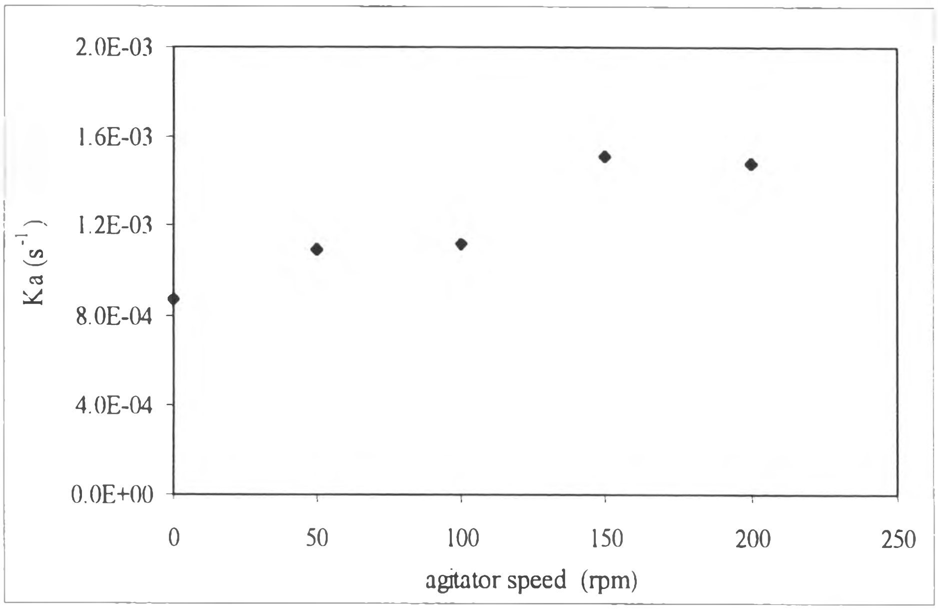

Figure 13. Overall volumetric mass transfer coefficient (Ka) as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C).

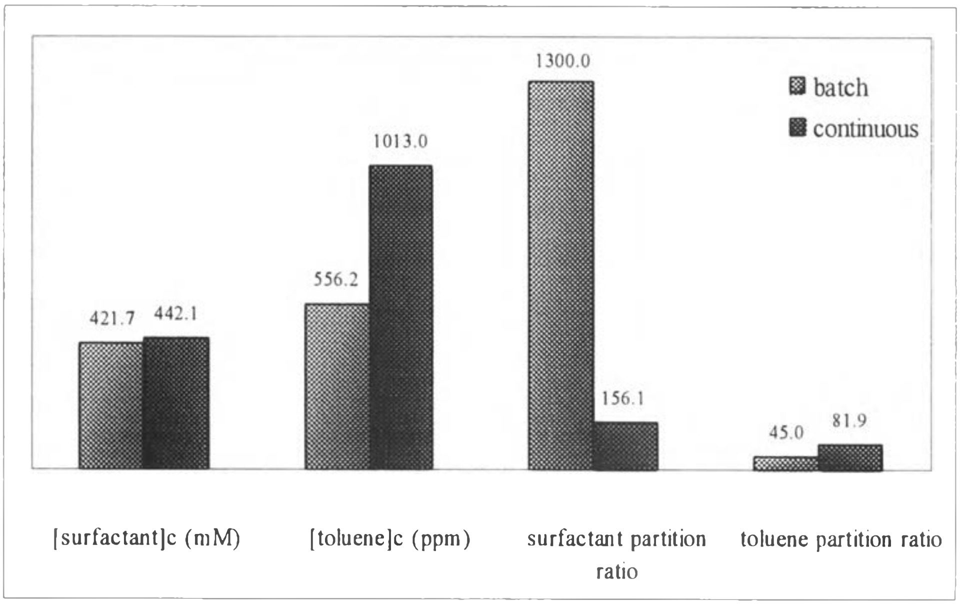

Figure 14. Comparison of surfactant and toluene concentration in coacervate stream (c) and partition ratio between a single stage equilibrium, batch and multistage. continuous operation (system: batch; 3.75 wt % surfactant, 100 ppm toluene, and 40 °C. continuous; 2.03 wt % surfactant, 100 ppm toluene, 6.9/1 wastewater/surfactant flowrate ratio, 150 rpm agitator speed, and 40 °C).