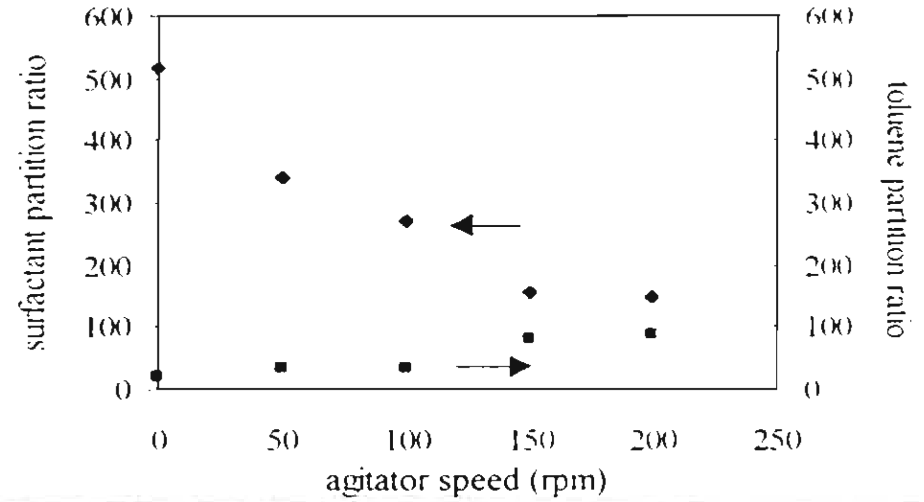

Figure 5. Surfactant and toluene partition ratio as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C).

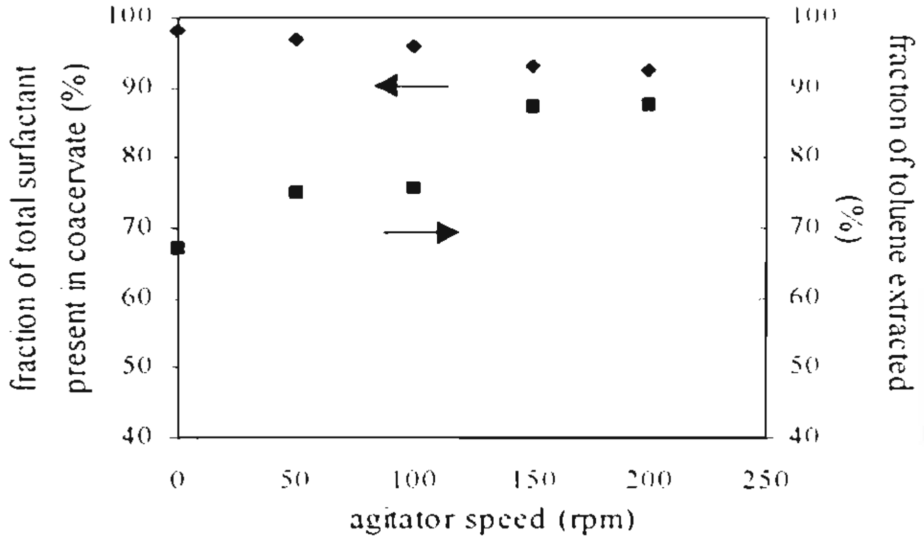

Figure 6. Fraction of total surfactant present in coacervate stream and fraction of toluene extracted in coacervate stream as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C).

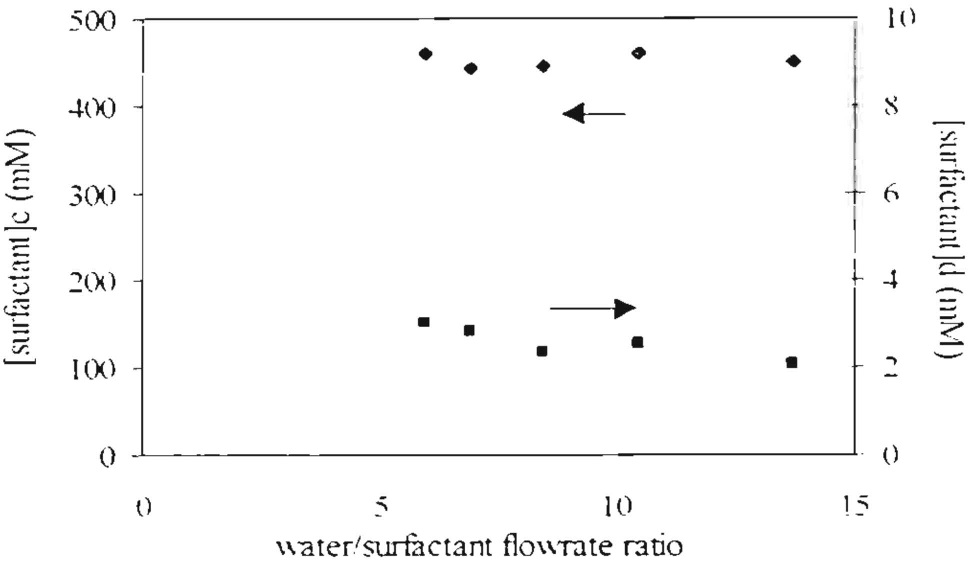

Figure 7. Surfactant concentration in coacervate stream (c) and dilute phase stream (d) as a function of wastewater/surfactant solution flowrate ratio (system: 100 ppm toluene, 300 mM surfactant solution, 150 rpm agitator speed, and 40 °C).

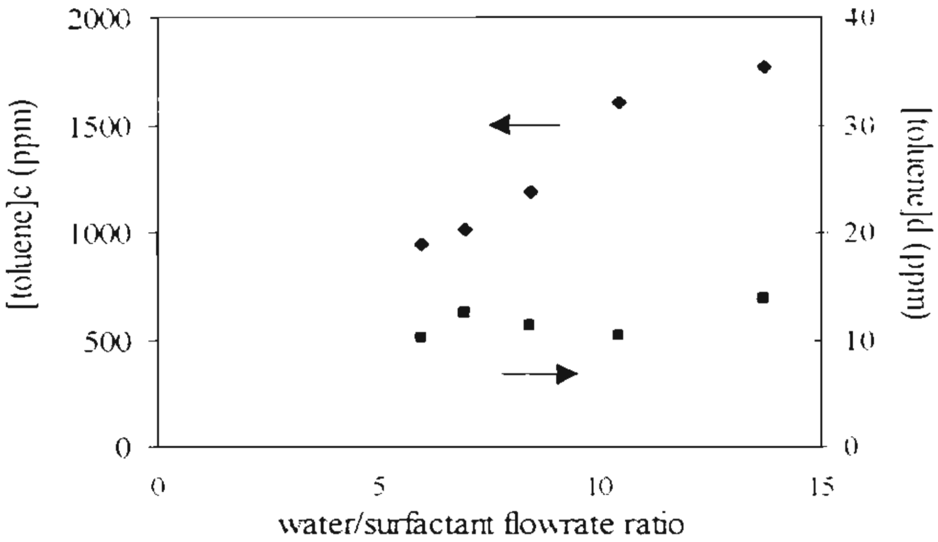

Figure 8. Toluene concentration in coacervate stream (c) and dilute phase stream (d) as a function of wastewater/surfactant solution flowrate ratio (system: 100 ppm toluene, 300 mM surfactant solution, 150 rpm agitator speed, and 40 °C).

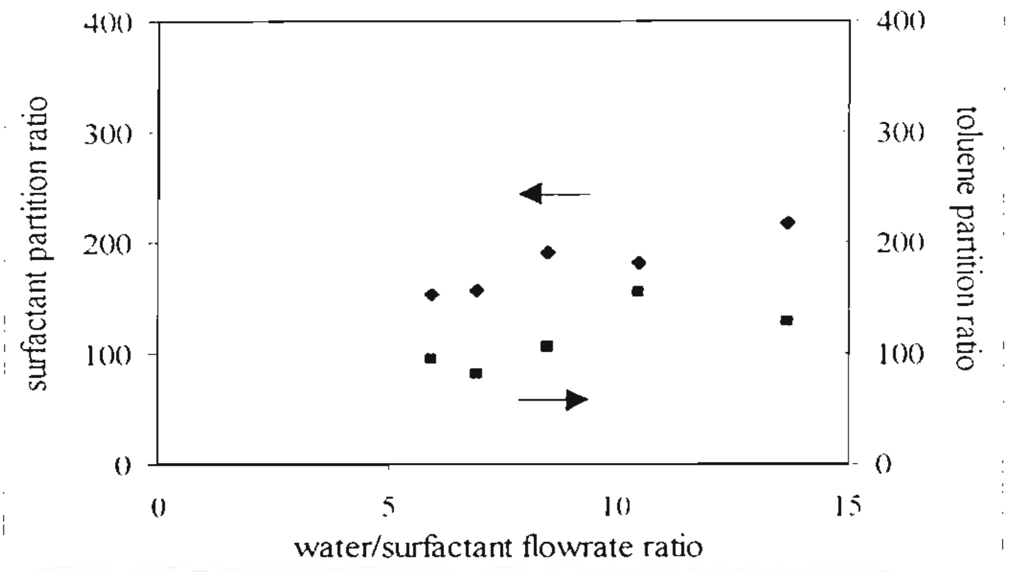

Figure 9. Surfactant and toluene partition ratio as a function of wastewater/surfactant solution flowrate ratio (system: 100 ppm toluene, 300 mM surfactant solution, 150 rpm agitator speed, and 40 °C).

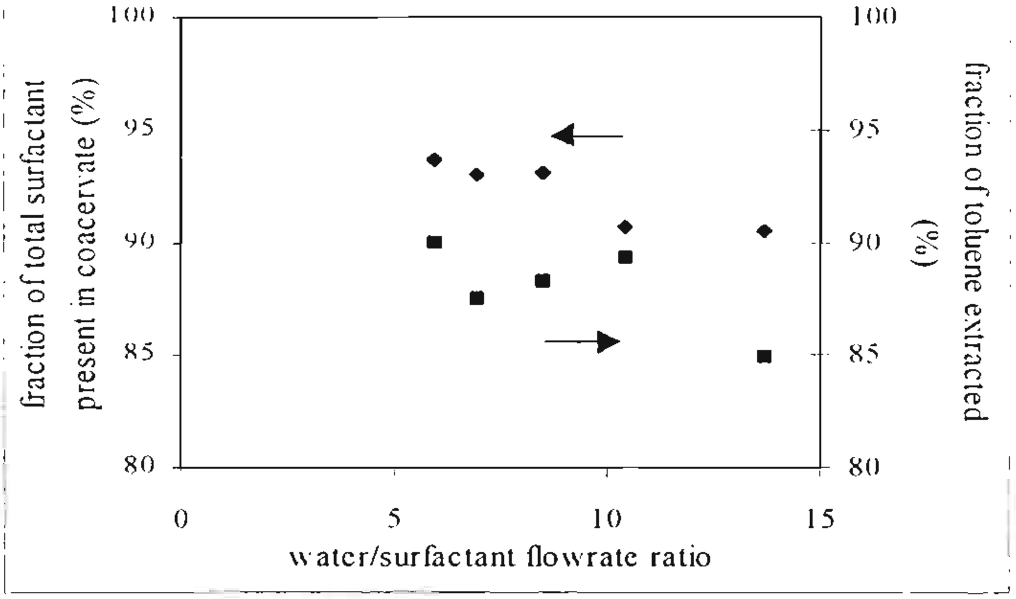

Figure 10. Fraction of total surfactant present in coacervate stream and fraction of toluene extracted in coacervate stream as a function of wastewater/surfactant solution flowrate ratio (system: 100 ppm toluene, 300 mM surfactant solution, 150 rpm agitator speed, and 40 °C).

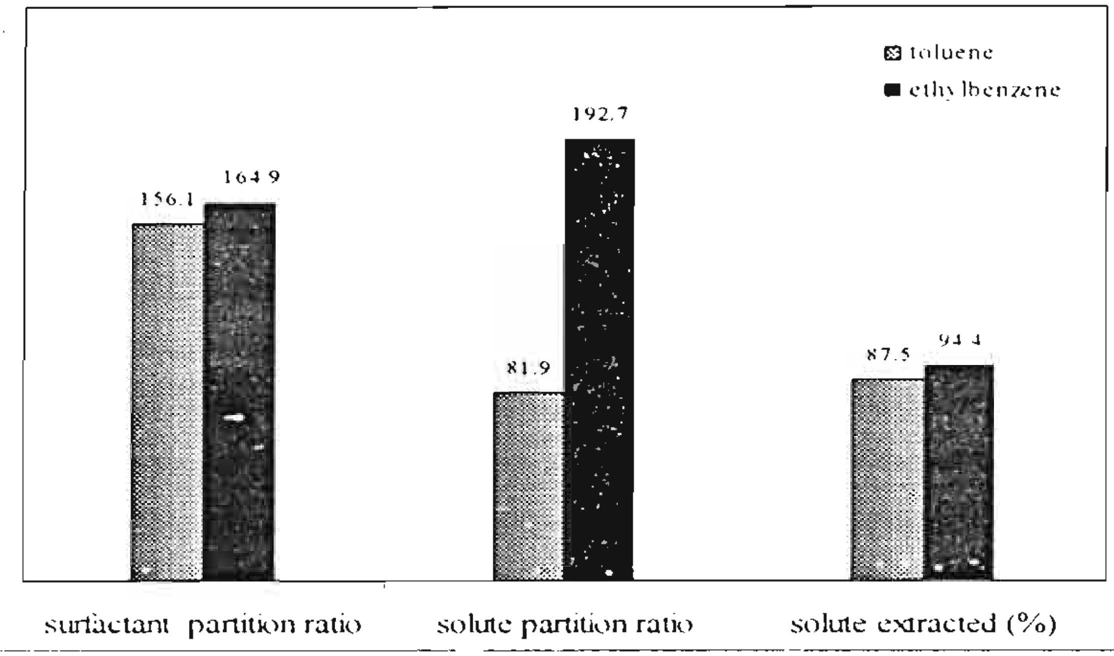

Figure 11. Comparison of surfactant and solute partition ratio and fraction of solute extracted in coacervate stream between toluene and ethylbenzene (system: 100 ppm solute, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C).

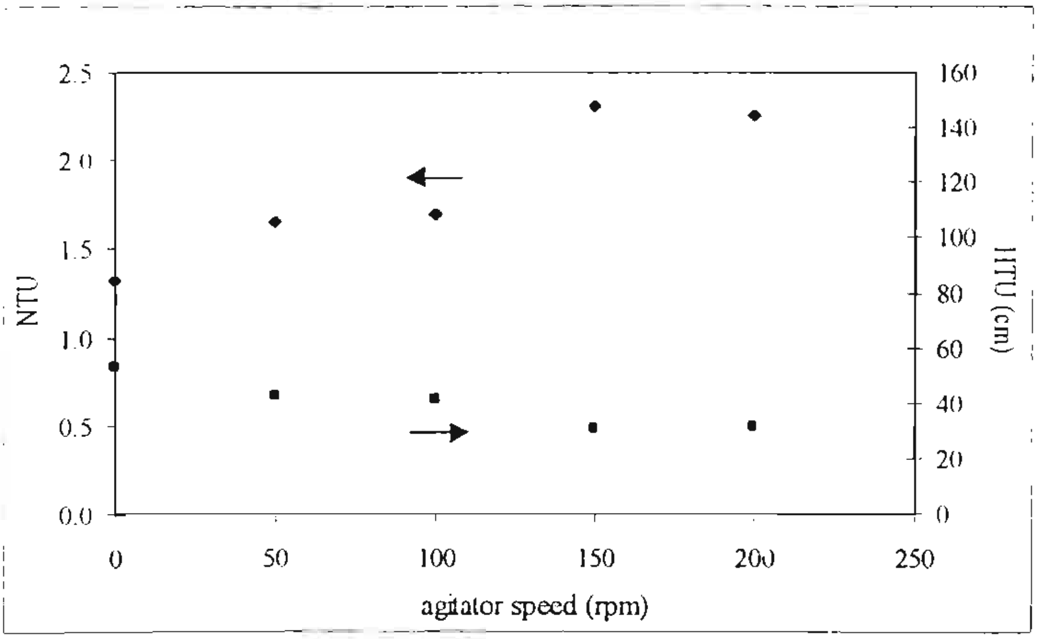

Figure 12. Number of transfer unit (NTU) and height of transfer unit (HTU) as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C).

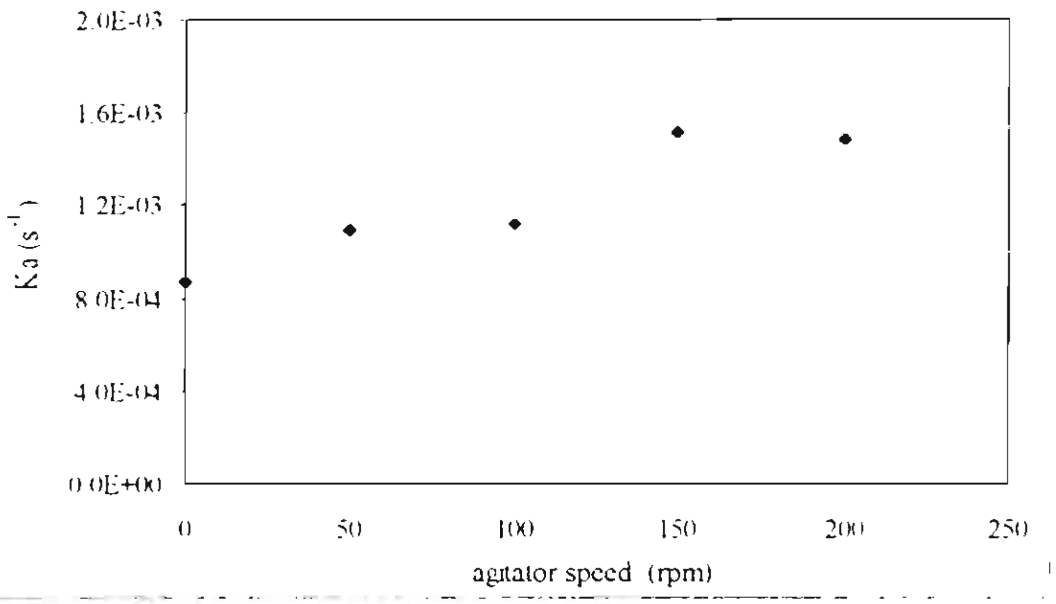

Figure 13. Overall volumetric mass transfer coefficient (Ka) as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C).

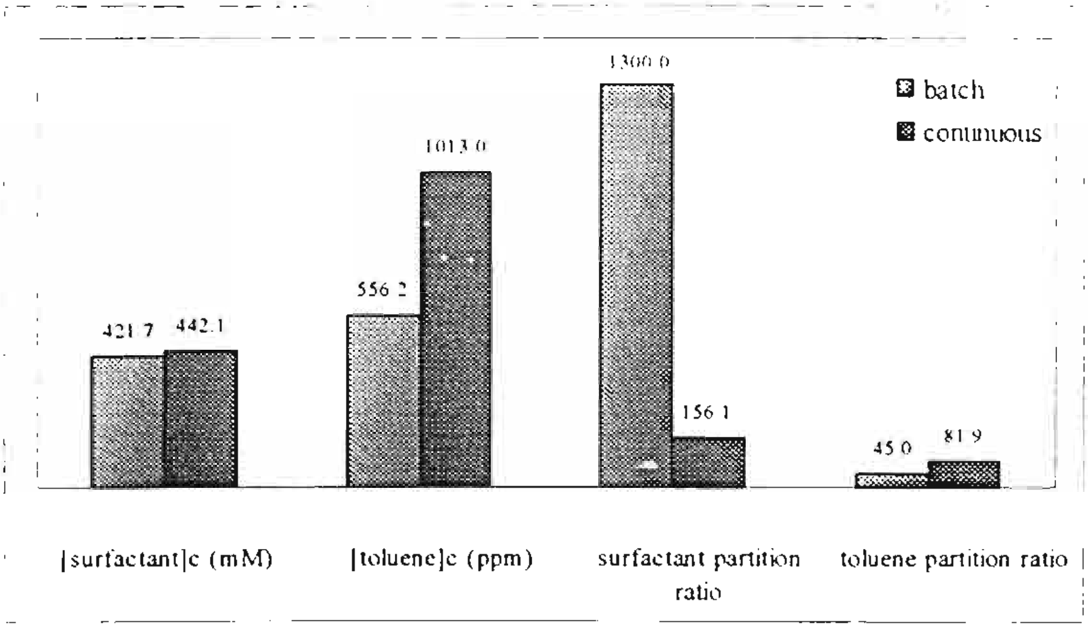

Figure 14. Comparison of surfactant and toluene concentration in coacervate stream (c) and partition ratio between a single stage equilibrium, batch and multistage continuous operation (system: batch; 3.75 wt % surfactant, 100 ppm toluene, and 40 °C. continuous; 2.03 wt % surfactant, 100 ppm toluene,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

CHAPTER IV

SCALING UP CLOUD POINT EXTRACTION OF AROMATIC CONTAMINANTS FROM WASTEWATER IN A CONTINUOUS ROTATING DISC CONTACTOR: PART 2. EFFECT OF OPERATING TEMPERATURE AND ADDED ELECTROLYTE

ABSTRACT

When a nonionic surfactant solution is heated above the cloud point, a phase separation occurs. Two isotropic phases are formed: a micellar-rich or coacervate phase and a micellar-dilute phase. The organic contaminant dissolved in the wastewater tends to solubilize into the micelles and concentrate in the coacervate phase resulting in a low concentration of contaminant in the dilute phase. This cloud point extraction was scaled up from batch to continuous operation in a multistage rotating disc contactor to remove toluene from wastewater. The t-octylphenolpolyethoxylate was utilized as a nonionic surfactant. The surfactant partition ratio, toluene partition ratio and the concentration of surfactant and toluene in the coacervate phase increase with increasing temperature. The addition of NaCl shows corresponding results to an increase in operating temperature. The overall volumetric mass transfer coefficient and the number of transfer unit increase and the height of transfer unit decreases when temperature is raised.

INTRODUCTION

A cloud point extraction (CPE) has been successfully demonstrated to remove and preconcentrate the organic pollutants from an aqueous wastewater with high separation factors in batch experiments for decades (1-11). It occurs when an aqueous solution of nonionic surfactant is heated above a certain temperature known as the cloud point. The solution separates into two isotropic phases: a micellar-rich or coacervate phase and a micellar-dilute phase. (1-14). The coacervate phase is a viscous phase, which is generally denser than the dilute phase and can be very concentrated in surfactant, sometimes exceeding 50 wt %. The surfactant concentration in the dilute phase is much more dilute than the coacervate: approximately 2-20 times the critical micellar concentration (CMC). The pollutants dissolved in the wastewater will solubilize into the surfactant micelles and concentrate in the coacervate phase leading to a low concentration of organic pollutants presence in the dilute phase (8-11). If a single stage extraction results in insufficient purification, multiple stages can be used as with traditional liquid-liquid extraction as investigated in this paper. The dilute phase, which contains a low concentration of organic pollutants, can be discharged to the environment as the effluent water. If the volatile organic solute is removed from the coacervate phase by vacuum stripping, the solute-free coacervate stream is available for reuse. When the organic solutes are non-volatile organic compounds or in low-volume applications where regeneration of the coacervate is not worthwhile, the coacervate phase, which contains a high solute concentration in small volume, can be disposed or incinerated. From our previous work, we have shown in batch experiments that CPE is a promising technique to remove aromatic compounds (benzene, toluene, and ethylbenzene) from aqueous wastewater by concentrating them in the coacervate phase (9-11). These chemicals are common pollutants of great environmental concern originating from industrial effluents and gasoline tank leakage. The objective of this work is to scale up the cloud point extraction technique to remove volatile aromatic contaminants from wastewater continuously in a differential rotating disc contactor (RDC). The effects of column operating temperature and added electrolyte on the CPE of toluene will be studied here.

BACKGROUND

A phase separation of the nonionic surfactant solution can be induced by a change in temperature or salt concentration. This phase separation is reversible on cooling. Two phases can merge together forming a homogenous micellar solution (3, 6). The lowest temperature at which this phenomenon takes place is the lower critical temperature or lower consolute temperature (LCT) at the critical surfactant concentration (13). At other surfactant concentrations, this temperature is referred as the cloud point. The cloud point is not highly concentration dependent and generally defined at 1 wt % of surfactant concentration (16). When the nonionic surfactant aqueous solution approaches the cloud point, the dehydration of the hydrophilic head groups on the exterior layer of the nonionic surfactant micelles is promoted as indicated by a gradual decrease in polarity of the environment around a fluorescent probe (17). At the cloud point, there is a sharp decrease in polarity indicating that a less polar coacervate phase is forming. When temperature increases, the micelles grow with higher aggregation number to form larger entities (17, 18). Glatter et al. (19) reported that a sphere-to-rod micelle shape transition for n-alkyl polyglycol ether (CiEj) occurs as temperature increases.

The cloud point can be altered by varying the nonionic surfactant structure. An increase in the degree of polymerization of ethylene oxide and a decrease in the hydrocarbon chain length of the hydrophobic moiety of the nonionic surfactant can elevate the cloud point (3, 12, 13, 20-22). At constant degree of polymerization of ethylene oxide, the cloud point can be reduced by a branching of the hydrophobic group and a decrease in molecular weight of the surfactant. Polar compounds such as benzene and phenol, which solubilize in the outer regions of the micelle, depress the cloud point probably due to a decrease in the number of hydratable sites of polyoxyethylene chains (12). In addition, the cloud point can be influenced by the addition of electrolyte due to the salting-in and the salting-out effect depending on the type of ions. The ions that are water structure formers, i.e. SO_4^{2-}, OH^-, F^-, and Cl^-, depress the cloud point by reducing the availability of free water molecules to hydrate the polyethylene oxide head groups. Meanwhile, the water structure breaker ions, i.e. I and SCN^-, raise the cloud point by enhancing the number of free water molecules available to interact with the polyethylene oxide head group (1, 12, 23, 24). In a mixed system of nonionic and ionic surfactant, the cloud point is raised due to an increase in electrostatic repulsion between micelles which opposed the intermicellar attraction (17, 25, 26).

A single stage CPE has been shown to be a promising technique to remove the organic pollutants and biomaterial from an aqueous stream in equilibrium batch experiments (1-11). However, the CPE of volatile organic solutes has received limited attention, even though they are common pollutants of great environmental concern. The unpopularity of volatile organics for study is probably due to a difficulty in minimizing leakage of solutes with high vapor pressures as detailed in our previous batch studies of trichloroethylene, dichloroethane, trichloroethane, tetrachloroethane, benzene, toluene, and ethylbenzene (9-11). A major advantage of CPE of volatile organic pollutants is, surfactant regeneration of the coacervate stream for reuse is feasible by gas, steam or vacuum stripping since these organics have high volatility (27-29).

For economical operation, a continuous multistage extractor in steady state operation is desirable. The denser phase enters at the top of the column and flows downward, whilst the lighter phase enters at the bottom of the column and flows upward. Due to a small density difference between the coacervate and dilute phase, an external energy for mixing and separation is applied by mechanical agitation to make the counter-current extraction possible (30). The cross-sectional area of the column must be large enough to avoid flooding (31). Since the concentrations of both liquids differentially change along the column, the height of tower is expressed in term of transfer units instead of steps or stages. As shown in Fig. 1, a rotating disc contactor (RDC) is applied to CPE due to its high efficiency per unit height, high throughput, high operational flexibility and ease of operation (32). A shear force generated by rotor discs provides a good phase dispersion. Unlike some type of extractors, a phase dispersion is induced by blade or impeller which may cause foam formation, resulting in a lower extraction efficiency since pressure drops across the column are increased. Moreover, the stators attached to the internal wall of the column behave as baffles to reduce back mixing between stages. The severe back mixing may reduce the concentration driving force. Thus, the mass transfer rate is decreased (33).

EXPERIMENTAL

Materials

The reagent grade toluene from J. T. Baker (Phillipsburg, USA) with purity of 99.8 % and NaCl from AJAX chemical (Auburn, Australia) with purity of 99.9 % were used. 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) purchased from the Dow Chemical Inc. (Charleston, USA) was used as the nonionic surfactant. 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 unit. 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 the 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 in 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 at desired temperature.

The contaminated feed water and the surfactant solvent solutions were fed into the extractor counter-currently at defined flowrates regulated by the 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 extract phase and the raffinate phase 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: operating temperatures: 40 to 50 °C; concentration of surfactant solution: 300 mM; concentration of aromatic pollutant in wastewater: 100 ppm; concentrations of NaCl: 0 to 0.6 M; agitator speed: 150 rpm; wastewater/surfactant solution flowrate ratio (feed/solvent flowrate ratio): 6.9/1 and solute: toluene.

RESULTS AND DISCUSSION

Most studies of liquid-liquid extraction in the RDC have been focused on the hydrodynamics and mass transport aspects. There are many attempts to improve the extraction performance by considering the effect of rotation of the rotor disc on the dispersed phase drop size, characteristic velocity of drops, etc. (34-37). However, an adjustment of temperature and the addition of foreign substances do not generally have a dramatic effect on the extraction efficiency in these customary systems. In contrast, in CPE, the extraction efficiency can be highly dependent on operating temperature and electrolyte addition.

Effect of temperature on cloud point extraction of toluene

When temperature increases, the system is further away from the cloud point leading the nonionic surfactant to be less water soluble. The dehydration of the hydrophilic polyethoxylate groups of the surfactant enhances the intermicellar attraction, which makes the coacervate more concentrated and with lower volume as temperature is raised above the cloud point. The surfactant concentration in the coacervate phase increases substantially while that in the dilute phase declines with increasing temperature as shown in Fig. 2. The flowrate of the coacervate phase decreases when temperature is raised as required from material balance considerations. The micellar size and aggregation number of the nonionic surfactant micelles increase with increasing temperature especially beyond the cloud point (17-19). The increased surfactant concentration in the coacervate with increasing temperature results in a higher toluene concentration in the coacervate phase as shown in Fig. 3. In addition, the concentration of toluene in the dilute phase, which is an effluent stream, decreases to 7.7 ppm at 50 °C. The ratio of toluene or surfactant concentration in the coacervate phase to that in the dilute phase is the partition ratio. Fig. 4 shows a substantial increase in surfactant and toluene partition ratio (about threefold and twofold, respectively) as temperature increases 10 °C from 40 °C to 50 °C. The concentration of toluene in the coacervate is 159 times as concentrated as in the dilute phase stream while the concentration of surfactant in the coacervate is 454 times as concentrated as in the dilute phase stream at 50 °C These results correspond to the previous results carried out in batch experiments (9-11) However, the surfactant partition ratio obtained from the extractor is less than that obtained from a single stage batch experiments For example, the surfactant partition ratio in the continuous RDC is 156 compared to approximately 1300 in batch experiment at 40 °C (11) This is due to an entrainment of fine coacervate droplets to the top of the column with the dilute phase, resulting in a higher surfactant concentration in the dilute phase and a lower surfactant partition ratio However, as much as 93 % of surfactant and 87.5 % of toluene are extracted in the coacervate stream at the lowest temperature studied here as demonstrated in Fig. 5. The fraction of total surfactant present in the coacervate and fraction of toluene extracted in the coacervate slightly increase with increasing temperature.

It is very beneficial to increase the temperature since it results in a higher surfactant and toluene partition ratio and a lower toluene concentration in the dilute phase. Also, the coacervate volumetric flowrate decreases when temperature is raised, which causes the treatment of the coacervate downstream for surfactant recovery to be more economical. Nevertheless, there are theoretical limitations on the operating temperature of CPE. Upon increasing temperature, the upper critical temperature can be reached, above which the phase separation does not take place (13). Upon decreasing temperature, the coacervate droplets cannot flow downward and settle down at the bottom of the column since a density difference between the coacervate and the dilute phase is too small to accomplish a countercurrent operation in an agitated extractor. Flooding occurs corresponding to the appearance of a cloudy surfactant solution at a certain location in the mixing zone. Below that position, there is no existence of the coacervate droplets. This particular problem occurs only in the agitated extractor at operating temperature below 40 °C. In batch experiments, the CPE showed a good phase separation even at 30 °C because the separated phases were not disturbed while separating and settling as detailed in the previous paper (11). This is dissimilar to RDC where the separated phases are dispersed and coalesced along the column.

Effect of added electrolyte on the CPE of toluene

The addition of NaCl to the micellar solution of Triton X-114 can reduce the cloud point due to the salting-out effect (9, 11, 12, 24). The cloud point depression is greater as the NaCl concentration increases (23). Hence, an increase in electrolyte concentration is analogous to increasing operating temperature at constant solution composition. The effect of electrolyte concentration on the surfactant and toluene concentration in the coacervate phase and the dilute phase are shown in Figs. 6 and 7. The results show that the concentrations of surfactant and toluene in the coacervate phase increase with increasing electrolyte concentration, while these concentrations in the dilute phase decrease, which correspond to the effect of increasing operating temperature. The addition of NaCl does not only depress the cloud point of the system but also reduce the solubility of the nonionic surfactant in the dilute phase. A decrease in surfactant concentration in the dilute phase causes a substantial increase in surfactant partition ratio from 156 without added electrolyte to 704 with the addition of 0.6 M NaCl at 40 °C as shown in Fig. 8. Likewise, the toluene partition ratio increases several fold from 82 without added electrolyte to 282 with the addition of 0.6 M NaCl. This salinity is approximately equivalent to more than 20 °C temperature increase in the effect on the toluene partition ratio. The fraction of surfactant and toluene presenting in the coacervate stream are enhanced by an increase in NaCl concentration as shown in Fig. 9. As high as 95 % of toluene is extracted in the coacervate at 40 °C with 0.6 M NaCl addition. Since an increase in operating temperature is energy intensive, the addition of electrolyte is an alternative to achieve a greater extraction efficiency. The other method is to adjust the nonionic surfactant structure to lower the cloud point to substantially below the operating temperature.

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

A measure of the difficulty of separation is usually studied by means of the HTU which dictates the height of an extraction column required to achieve a given separation. Moreover, a mass transfer between two contacted liquids is determined by a specific rate of transport of mass across the interface or the mass transfer. The general graphical approach has proven extremely useful for the analysis of multistage separation. The NTU can be evaluated by either drawing a step line between the equilibrium line and the operating line as in McCabe-Thiele method or numerical method (30, 38). The method to construct these lines was described in the previous work (15). Since the total active height of column is a product of NTU and HTU, the HTU is then calculated. A smaller HTU (or higher NTU) shows a higher Ka or better extraction efficiency.

When temperature increases, a transfer of toluene to the coacervate droplets is enhanced as indicated by a higher toluene partition ratio and toluene concentration in the coacervate phase. The NTU increases from 2.3 transfer units to 2.75 transfer units attaining better extraction efficiency as operating temperature increases 10 °C from 40 to 50 °C as shown in Fig. 10. In turn, the HTU decreases 5 cm. from 30.4 to 25.4 cm. The relationship between Ka and operating temperature is determined as shown in Fig. 11. A smooth increase in Ka is observed when the temperature is raised.

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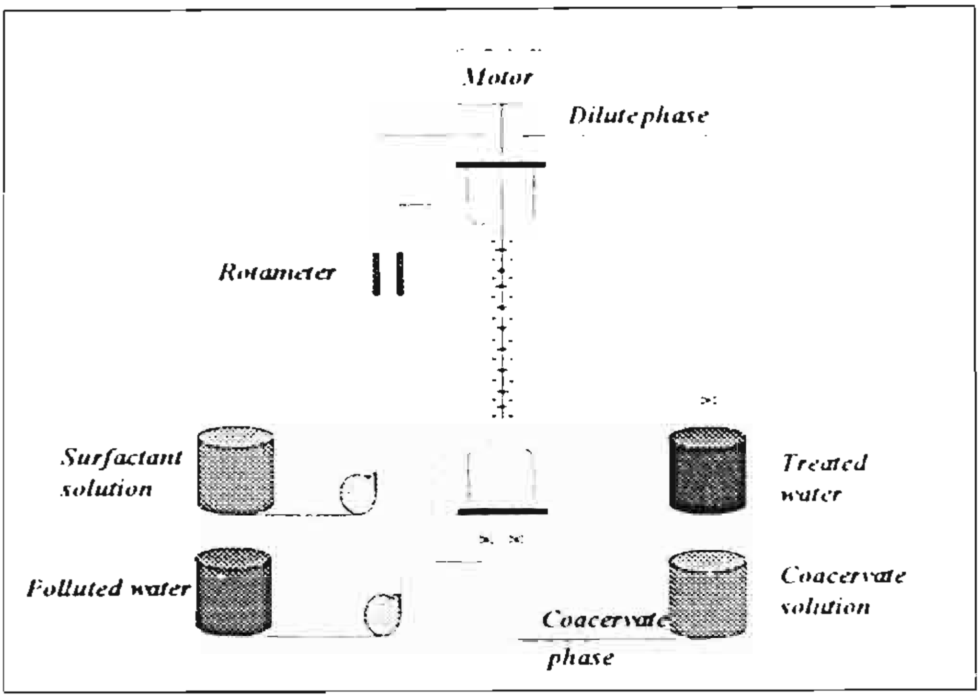

Figure 1. A schematic diagram of the cloud point extraction pilot plant

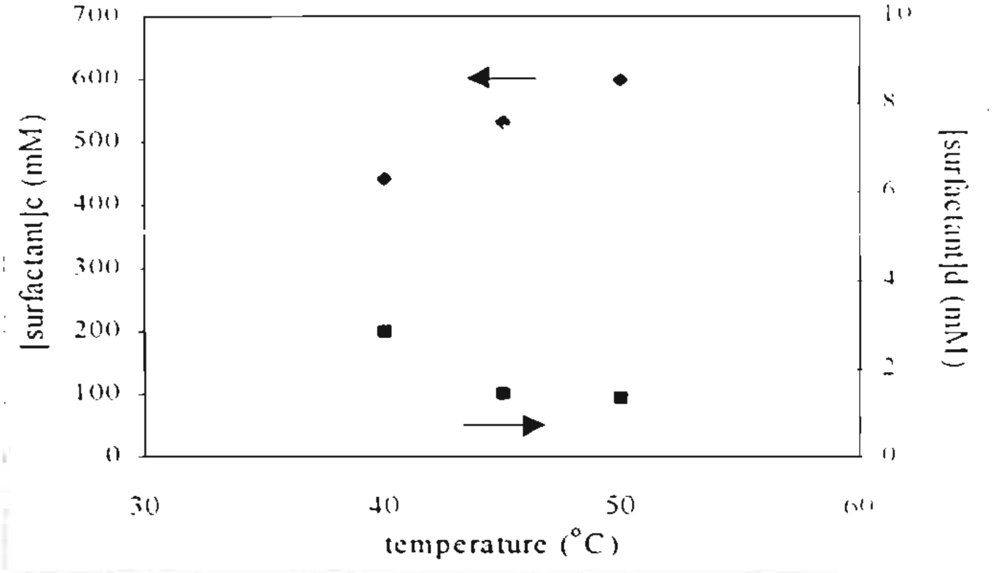

Figure 2. Surfactant concentration in coacervate stream (c) and dilute phase stream (d) as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 150 rpm agitator speed).

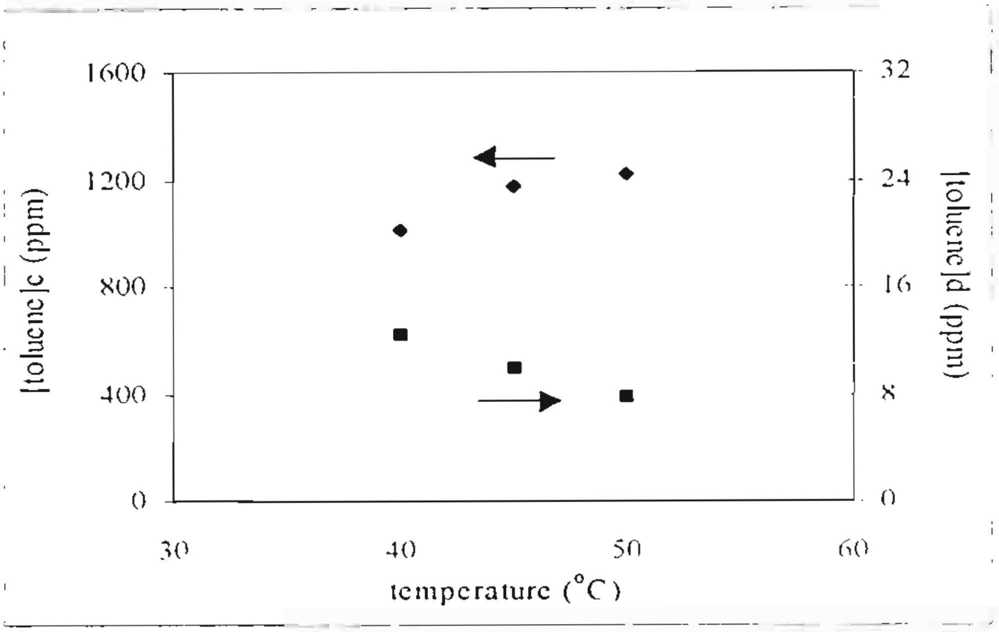

Figure 3. Toluene concentration in coacervate stream (c) and dilute phase stream (d) as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 150 rpm agitator speed).

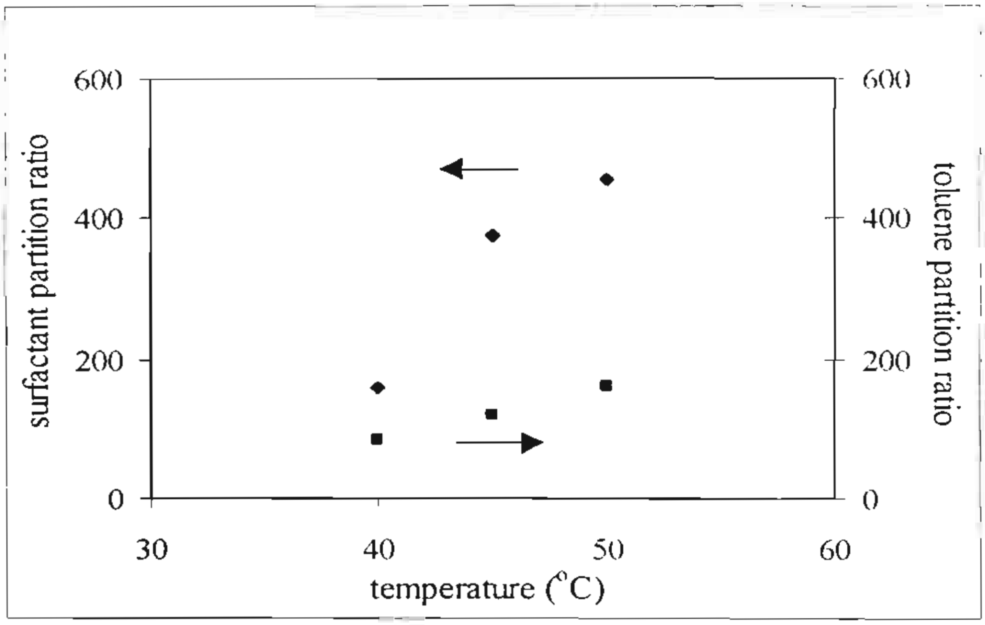

Figure 4. Surfactant and toluene partition ratio as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 150 rpm agitator speed).

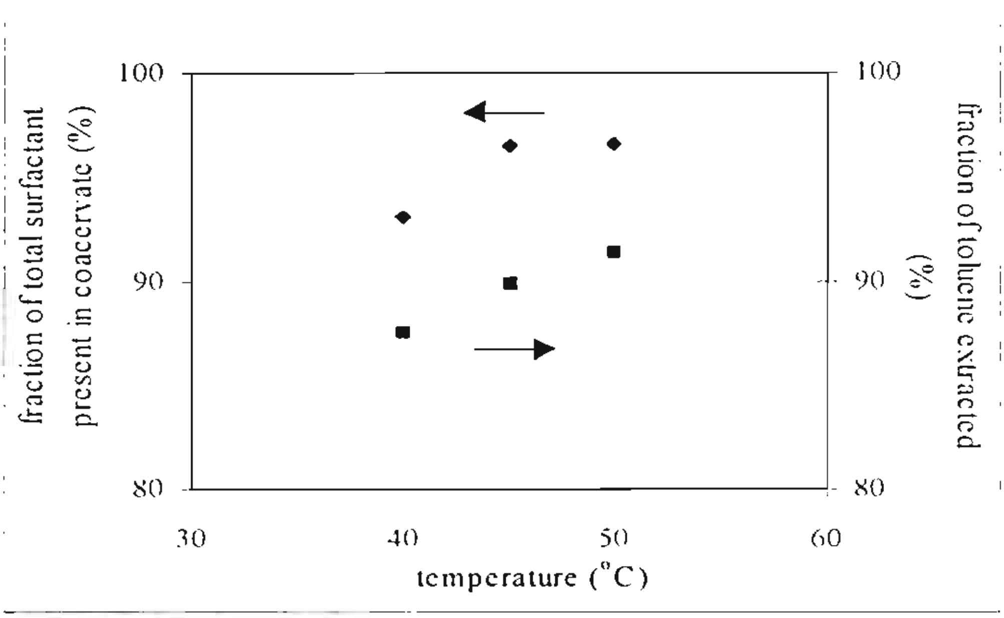

Figure 5. Fraction of total surfactant present in coacervate stream and fraction of toluene extracted in coacervate stream as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 150 rpm agitation speed).

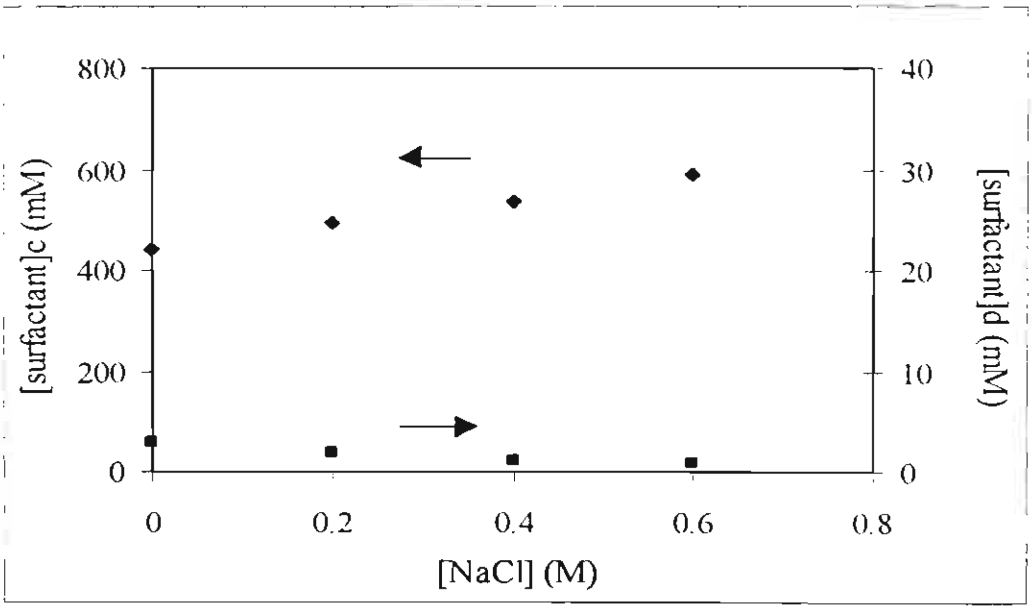

Figure 6. Surfactant concentration in coacervate stream (c) and dilute phase stream (d) as a function of NaCl concentration (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C).

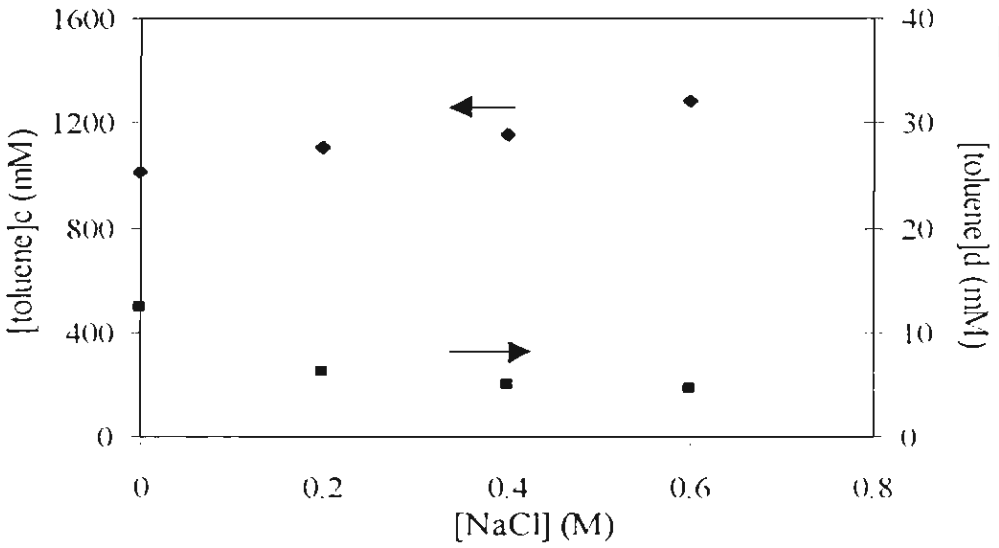

Figure 7. Toluene concentration in coacervate stream (c) and dilute phase stream (d) as a function of NaCl concentration (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C).

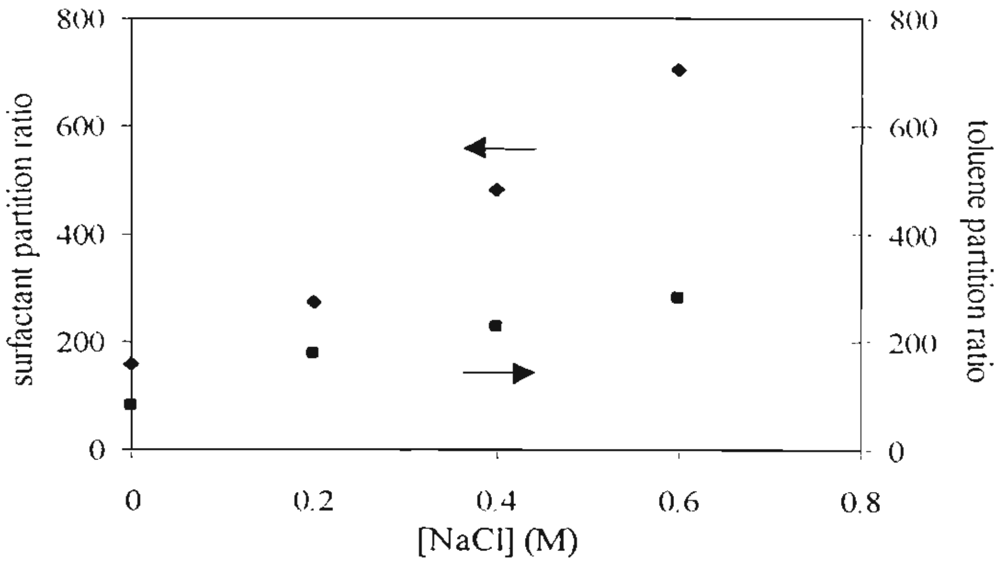

Figure 8. Surfactant and toluene partition ratio as a function of NaCl concentration (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C).

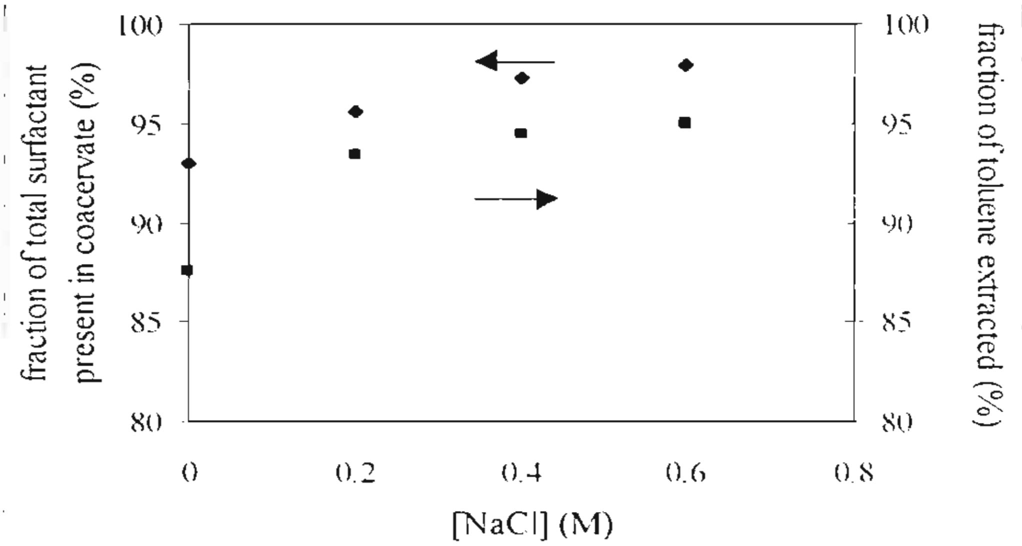

Figure 9. Fraction of total surfactant present in coacervate stream and fraction of toluene extracted in coacervate stream as a function of NaCl concentration (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitation speed, and 40 °C)

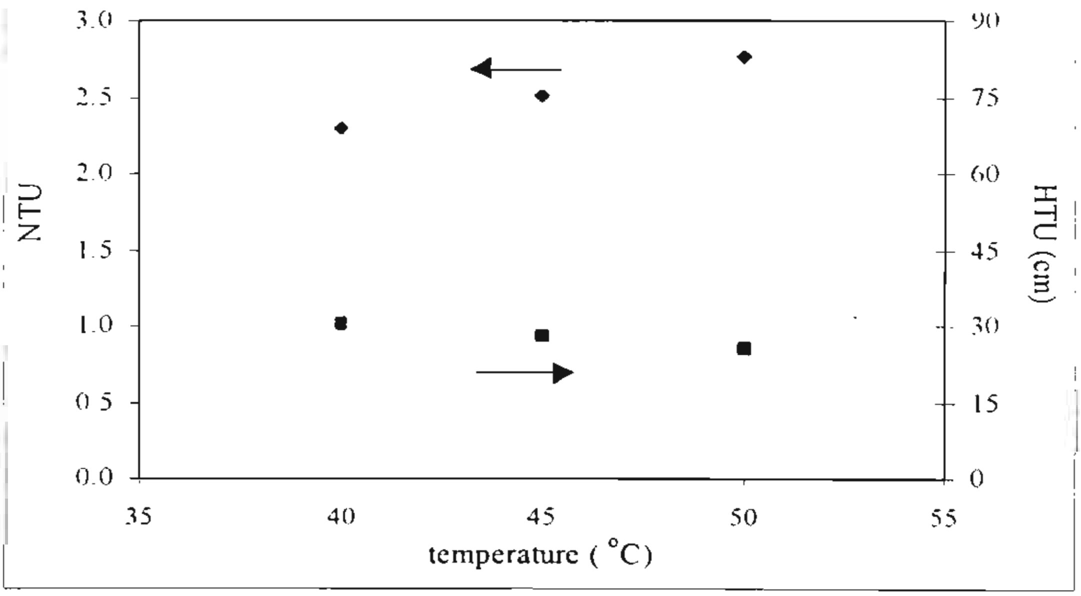

Figure 10. Number of transfer unit (NTU) and height of transfer unit (HTU) as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C).

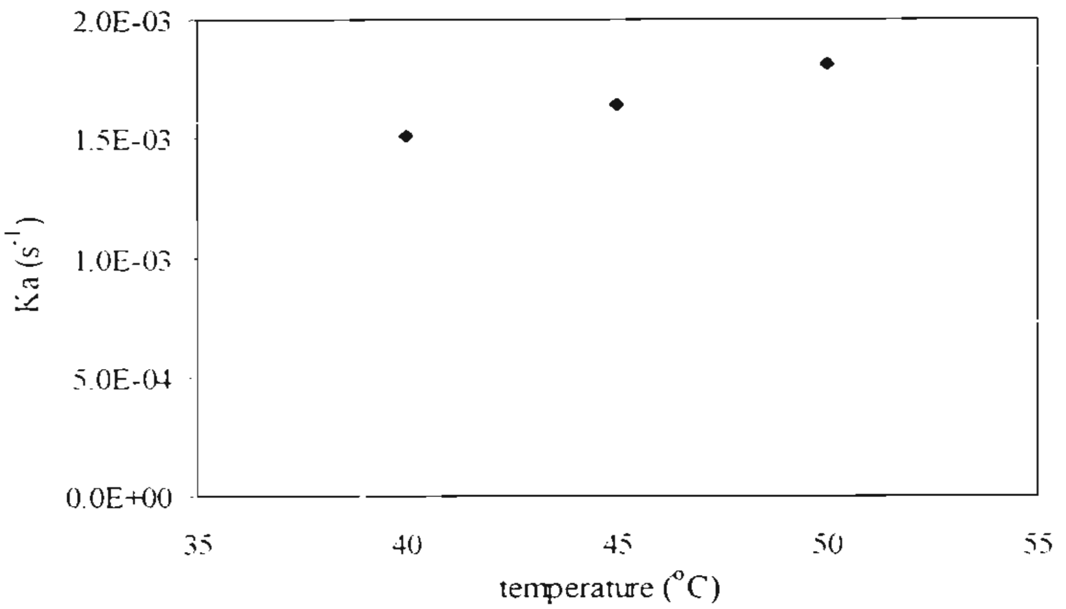

Figure 11. Overall volumetric mass transfer coefficient (Ka) as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C).

Output จากโครงการวิจัยที่ได้รับทุนจาก สกว.

1. ผลงานตีพิมพ์ในสารสารวิชาการนานาชาติ :

Trakultamupatam, P.; Scamehorn, J. F.; Osuwan, S. Removal of Volatile Aromatic Contaminants from Wastewater by Cloud Point Extraction. *Sep. Sci. Technol.* **2002**, *37*, 1291-1305.

2. การนำเสนอผลงานวิจัย :

2.1 Punjaporn Trakultamupatam, John F. Scamehorn, and Somchai Osuwan. *Cloud Point Extraction of Benzene from Wastewater by Using Nonionic Surfactant.* AIChE 2000 Annual Meeting. Los Angeles, USA, November 12-17, 2000.

2.2 Punjaporn Trakultamupatam, Somchai Osuwan, and John F. Scamehorn. *Removal of Aromatic Contaminants from Wastewater by Cloud Point Extraction.* Proceedings of Regional Symposium on Chemical Engineering 2000. Singapore, December 11-13, 2000.

2.3 Punjaporn Trakultamupatam, John F. Scamehorn, and Somchai Osuwan. *Removal of Aromatic Contaminants from Wastewater by Cloud Point Extraction.* ACS 220th National Meeting. Washington, DC, USA, August 20-24, 2000.

2.4 Punjaporn Trakultamupatam, John F. Scamehorn, and Somchai Osuwan. *Scaling-up Cloud Point Extraction of Aromatic Contaminants from Wastewater.* AOCS 93rd Annual Meeting. Montreal, Canada, May 5-8, 2002.

2.5 Punjaporn Trakultamupatam, John F. Scamehorn, and Somchai Osuwan. *Removal of Aromatic Contaminants from Wastewater by A Continuous Cloud Point Extraction.* 85th The Canadian Society for Chemistry Vancouver, Canada, June 1-5, 2002.

CHAPTER V

CONCLUSIONS

CONCLUSIONS

This work demonstrates for the first time that the cloud point extraction (CPE) can be scaled up from batch experiments in laboratory scale to continuous operation in a pilot scale, multistage, differential extractor. In batch experiments, the CPE of volatile aromatic solutes: benzene; toluene; and ethylbenzene, from polluted water were carried out at equilibrium condition in laboratory scale. It was found that an increase in operating temperature, added electrolyte (NaCl) concentration and degree of alkylation of aromatic solutes can enhance the solute concentration in the coacervate phase and solute partition ratio with less coacervate volume. The partition ratio of benzene, toluene, and ethylbenzene are 29.4, 65.1, and 162.4 while 77.9, 89.1, and 94.8 % of these solutes are extracted in the coacervate phase at 50 °C, respectively.

The CPE was subsequently scaled up to operate continuously in a multistage, differential rotating disc contactor. Toluene and ethylbenzene were used as the aromatic solutes. The solute concentration in the coacervate phase and the solute partition ratio increase as operating temperature, rotation speed of rotor disc, added electrolyte concentration, wastewater/surfactant solution flowrate ratio and degree of alkylation of the aromatic solutes increase. With the addition of 0.6 M NaCl, 95.0 % of toluene was extracted in the coacervate phase and as high as 282 of toluene partition ratio was obtained even at the lowest operating temperature studied here, which was 40 °C. The number of transfer unit (NTU) was found to be equal to 2.75, which is equivalent to 2.75 batch extractors in the continuous column. The overall volumetric mass transfer coefficient (Ka) and the NTU in the RDC increase with increasing operating temperature and rotation speed of the rotor disc. However, the surfactant partition ratio obtained from continuous operation was substantially high compared to that obtained from batch experiment.

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Appendix A

Use of a Surfactant Coacervate Phase to Extract Chlorinated Aliphatic Compounds from Water: Extraction of Chlorinated Ethanes and Quantitative Comparison to Solubilization in Micelles

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Abstract

At temperatures above the cloud point, aqueous solutions of nonionic surfactants separate into a coacervate phase and a dilute phase. The distribution of di-, tri-, and tetra- chloroethanes between these phases was shown to increasingly favor the coacervate phase as the hydrophobicity (degree of chlorination) of the solute increases. The solute solubilization equilibrium constant was shown to be very similar for solubilization into coacervate surfactant aggregates compared to micellar solubilization per aggregated surfactant molecule for octylphenol polyethoxylate surfactants and to increase with increasing temperature and increasing solute hydrophobicity. As temperature increases above the cloud point, the partition ratio increases primarily because the concentration of surfactant in the coacervate increases, secondly because the solubilization equilibrium constant in the coacervate surfactant aggregate increases, and thirdly because the concentration of micellized surfactant (and solubilization therein) in the dilute phase decreases.

This work is dedicated to the memory of Sherril D. Christian who died on March 17, 2000

Introduction

As the temperature of an aqueous solution of nonionic surfactant is increased, a temperature may be reached where the solution turns cloudy; this temperature is referred to as the cloud point. Above the cloud point, the solution may separate into a micellar concentrated or coacervate phase, and a dilute phase.[1-4] The concentration of surfactant in the dilute phase can be very low but is generally above the critical micelle concentration (CMC). When an organic solute is originally present in an aqueous solution and nonionic surfactant is added to the water, at temperatures above the cloud point, the organic solute will tend to partition into the coacervate phase. This liquid/coacervate extraction (sometimes referred to as cloud point extraction) is a specific example of aqueous biphasic extractions.[5] This technique shows great potential for removing toxic solutes from polluted water. In a previous related study[6], the removal of trichloroethylene from water was investigated in detail. The present study focuses on chlorinated hydrocarbons, a major class of pollutants, and quantifies the effect of the degree of chlorination of the solute.

The vast majority of surfactant is present in the coacervate phase in some kind of aggregated form of the concentrated micellar solution. For example, Yoesting and Scamehorn[6] showed that the nonideality of mixed aggregate formation between anionic and nonionic surfactants is very similar in coacervate and in micelles. In this study, incorporation of the organic solute into the coacervate surfactant aggregates is quantitatively compared to solubilization into micelles composed of a surfactant of similar structure.

Experimental Section

Materials. Octylphenoxypoly(ethyleneoxy)ethanol with an average of 7 moles [$OP(EO)_7$: trade name Igepal CA-620], and 9 moles [$OP(EO)_9$: trade name Igepal CA-630] of ethylene oxide per mole of octylphenol from Rhodia were the nonionic surfactants used as received in this study. Reagent grade 1,2-dichloroethane and 1,1,1,2-tetrachloroethane from Fluka Chemika-Biochemika, and 1,1,1-trichloroethane, from J.T. Baker Inc. were used as received. The water was deionized and distilled.

Methods. In order to measure the distribution of solutes between dilute and coacervate phases, several identical 100-mL separatory funnels containing aqueous solutions with 50 mM $OP(EO)_7$ and an 1.0 mM of organic solute were placed in an isothermal water bath until equilibrium was reached, generally after about 2 days. After phase separation had occurred, the fractional volume of each phase was measured. The $OP(EO)_7$ and organic solute concentrations were measured[7] by using CE 2000 series UV spectrometer at 224 nm. and gas chromatography with a flame ionization detector, respectively, in both the coacervate and dilute phases.

In order to measure the micellar solubilization equilibrium constant, ordinary 5-mL equilibrium dialysis cells and transparent regenerated cellulose membranes (6000 Dalton molecular weight cutoff) were obtained from Fisher Scientific and used without modification in a technique called semi-equilibrium dialysis[8-10] which can be used to measure solubilization of an organic solute into micelles. When these experiments were performed, aqueous solution of 50 mM $OP(EO)_6$ plus 1.0 mM of organic solute was loaded in one compartment of the cell, and pure water was added to the other side. The cells were kept in a desiccator that was submerged in a thermostated bath until "semi-equilibrium" was reached, approximately 24 hours. The surfactant and solute concentrations were measured in both the retentate and permeate sides as described above.

The CMC values were obtained from the change in slope of surface tension vs. log (surfactant concentration) plot. Surface tension was measured by DuNouy ring tensiometry using a Cahn DCA-322 dynamic contact angle analyzer. The cloud points were visually determined as the temperature at which a 50 mM surfactant solution became turbid at a heating rate of 1^0C/minute.

Theory

Solubilization in Micelles. In aqueous surfactant solution, solubilization, that is the ability to dissolve the organic solutes in micelles, is an important property of surfactants.[2,11] Solubilization studies in the laboratory have provided accurate vapor pressure results for volatile hydrocarbons in anionic and cationic micelles.[12-16] Numerous solubilization data have also been obtained for polar organic solutes by using the semi-equilibrium dialysis (SED) method[8-10,17-20] In SED experiments (Figure 1), ordinary equilibrium dialysis cells are used with membranes permeable to small molecules (such as the organic solute and surfactant monomers) but impermeable to the surfactant micelles. Initially, the retentate side of the cell contains the surfactant solution with the solute and the permeate side contains only water The slow migration of surfactant through the membrane (over a period of 16-24 h) occurs simultaneously with the migration of the unsolubilized organic solute, which ordinarily diffuses rapidly enough to reach equilibrium with the solutions on both sides of the membrane. After equilibration, the solute concentration on the permeate side is almost equal to the unsolubilized solute concentration on the retentate side of the membrane.

The ability of micelles to solubilize solutes in the retentate is described by a solubilization equilibrium constant (K) defined by:

$$K_m = X_{m,ret} / C_u = [O]_{mic,ret} / (C_u ([\text{Surfactant}]_{mic,ret} + [O]_{mic,ret})) \qquad (1)$$

where $X_{m,ret}$ is the mole fraction of solute in micelles in the retentate, C_u is the concentration of unsolubilized or monomeric organic solute, $[O]_{mic,ret}$ is the retentate concentration of organic solute associated with surfactant micelles and $[\text{Surfactant}]_{mic,ret}$ denotes retentate concentration of surfactant in micellar form. A small correction needs to be made to account for formation of a few micelles (with solubilization therein) in the permeate[8,10,17-20] and eq. 1 applies to the permeate as well:

$$K_m = X_{m,per} / C_u = [O]_{mic,per} / (C_u ([\text{Surfactant}]_{mic,per} + [O]_{mic,per})) \qquad (2)$$

where $X_{m,per}$ is the mole fraction of solute in micelles in the permeate, C_u is the concentration of unsolubilized or monomeric organic solute, $[O]_{mic,per}$ is the permeate concentration of organic solute associated with surfactant micelles and $[\text{Surfactant}]_{mic,per}$ denotes permeate concentration of surfactant in micellar form.

It is assumed that C_u is the same in permeate and retentate (activity coefficient of unsolubilized solute is the same), as well as the value of K_m. The total concentration of organic solute and surfactant in the two compartments can be related to C_u and to the concentration of surfactant monomer (CMC) by material balances:

$$[O]_{ret} = C_u + [O]_{mic,ret} \tag{3}$$

$$[O]_{per} = C_u + [O]_{mic,per} \tag{4}$$

$$[\text{Surfactant}]_{ret} = \text{CMC} + [\text{Surfactant}]_{mic,ret} \tag{5}$$

$$[\text{Surfactant}]_{per} = \text{CMC} + [\text{Surfactant}]_{mic,per} \tag{6}$$

where $[O]_{ret}$ and $[O]_{per}$ refer to the total solute concentration in retentate and permeate, respectively; and $[\text{Surfactant}]_{ret}$ and $[\text{Surfactant}]_{per}$ refer to the total surfactant concentration in retentate and permeate, respectively.

While the monomeric surfactant concentration (equals critical micelle concentration or CMC) is mildly dependent on the presence of solubilizate,[2] at the low solute concentrations used here, the CMC is assumed to be that of the pure surfactant.

Combining these equations yields:

$$K_m = ([O]_{ret} - C_u) / (C_u([\text{Surfactant}]_{ret} - \text{CMC} + [O]_{ret} - C_u)) \tag{7}$$

$$K_m = ([O]_{per} - C_u) / (C_u([\text{Surfactant}]_{per} - \text{CMC} + [O]_{per} - C_u)) \tag{8}$$

Simultaneous solution of eqs. 7 and 8 for K_m and C_u permits calculation of solubilization equilibrium constants directly from measurable parameters in SED experiments.

Extraction into Coacervate. Aqueous solutions of most nonionic surfactant micelles become turbid after heating to a temperature known as the cloud point. Above this temperature, the solution separates into two phases as shown in Figure 2: one, generally small in volume, composed of a concentrated micellar solution (referred to as the micellar-rich or coacervate phase) and the other, the bulk aqueous solution (aqueous or dilute phase) in which the surfactant concentration is generally on the order of 2 to 20 times the CMC as shown in Figure 2.

The overall distribution coefficient or partition ratio (solute concentration ratio in coacervate to that in dilute phase) is normally reported in studies of coacervate extraction. This only requires straightforward measurement of total concentration in coacervate and dilute phases. In addition in this study, we wish to directly compare the tendency of the solute to "solubilize" into the surfactant aggregate in the coacervate to that tendency in micelles.

This comparison requires definition of a coacervate solubilization equilibrium constant (K_c) exactly analogous to K_m for micelles:

$$K_c = X_c / C_u \tag{9}$$

where X_c is the mole fraction of solute in the coacervate aggregate and C_u is the concentration of unsolubilized solute. From the definition of X_c and correcting for surfactant and solute not in aggregated form:

$$K_c = ([O]_c - C_u) / C_u ([\text{Surfactant}]_c - \text{CMC} + [O]_c - C_u) \tag{10}$$

where $[O]_c$ and $[\text{Surfactant}]_c$ are the total solute and surfactant concentrations in the coacervate phase.

In order to apply eq. 10, the value of C_u is assumed to be the same in dilute and coacervate phases (i.e., unassociated solute activity coefficients are assumed to be the same in the two phases when the system reaches equilibrium). The surfactant monomer concentration (CMC) is assumed to be the same in dilute and coacervate phases also, so surfactant concentration in aggregated form in the coacervate is equal to total coacervate surfactant concentration minus the CMC (this correction is very small so the validity of this approximation is of little concern). Since micelles are present in the dilute phase, the micellar solubilized solute concentration must be subtracted from the measured total solute concentration in the dilute phase to obtain C_u. The value of K_m obtained from SED experiments for $OP(EO)_9$ is assumed to be the same as that for OP(EO)$_7$ in the dilute phase, both at the same temperature. Simultaneous solution of eqs 1, 3, and 5 to describe micellization in the dilute phase and eq 10 permits calculation of K_c from measurable parameters and K_m. For solutes and surfactants of the type used here, K_m can depend on solute concentration [10,21], this was not accounted for here since this would be a small correction at the very low solute mole fractions in micelles under these conditions.

Results and Discussion

Effect of Temperature on Coacervate Extraction. The CMC of OP(EO)$_7$ and OP(EO)$_9$ with no organic solutes at the various temperatures is shown in Table 1. The CMC decreases as the temperature and the number of EO groups increase. The cloud point of the 50 mM OP(EO)$_7$ system (same concentration as used in coacervate extraction experiments) is shown in Table 2 at several solute concentrations. The cloud point is only mildly dependent on the presence of the solute at the low solute concentrations used. The cloud point depression is greater as the degree of chlorination of the solute increases. Note that the CMC can be measured even above the cloud point since the clouding does not occur until a surfactant concentration at least several times the CMC is attained.

Table 3 shows the concentrations in coacervate and dilute phases, fractional distributions of components in phases, and partition ratio of solute and surfactant. Up to 99 % of OP(EO)$_7$, 79 % of 1,2-dichloroethane, 84 % of 1,1,1-trichloroethane, and 87 % of 1,1,1,2-tetrachloroethane are removed in the coacervate phase. As the temperature increases, the separation improves; the fractional volume of the coacervate decreases, partition ratio increases, and fraction of solute in coacervate increases. The reason is when the temperature of the system increases, the system is further from the lower consolute solution temperature (which is approximately the cloud point), resulting in increasing dissimilarity between the coacervate phase and dilute phase, causing a decrease in the coacervate phase volume. The concentration of the surfactant and the chloroethanes in the coacervate phase increases with increasing temperature while these concentrations in the dilute phase are not much affected.

Effect of Organic Solute Structure on Coacervate Extraction. The 1,1,1-trichloroethane and 1,1,1,2-tetrachloroethane both partition more effectively into the coacervate phase than 1,2-dichloroethane as seen in Table 3. The large increase in the distribution coefficient with an increase in solute hydrophobicity is probably mainly due to the decrease in the water solubility of the hydrocarbon compounds with increasing degree of chlorination.[22] However, the degree of chlorination of the solute affects the partition ratio of the surfactant also as seen in Table 3, complicating the interpretation of data. For example, in a cloud point (or coacervate) extraction of a series of chlorinated phenols, Frankewich and Hinze[4] observed an increase in the fraction of solute in the coacervate from mono- to di- to tri- chlorination, a decrease for the tetra-, and a large increase for the penta-.

Comparison of Solute Solubilization between Coacervate and Micelles. In order to compare solubilization in coacervate and micelles, a surfactant with a higher cloud point was used for micelle solubilization studies (7 vs. 9 ethylene oxides in hydrophilic group). The solubilization of the chlorinated hydrocarbons is predominately in the core of the micelle and changing the hydrophilic group length slightly is expected to have very little effect on K_m.[23] Table 4 shows the SED data and calculated value of K_m. Table 5 shows the comparison between K_m and K_c. The solute coacervate solubilization equilibrium constant is an average of 13 % higher than the micelle solubilization equilibrium constant, which indicates that they are nearly the same within experimental precision for the octylphenol polyethoxylate surfactants studied. This supports the view that the surfactant aggregates in the coacervate are micelle-like in structure. The coacervate has been proposed to contain wormlike micelles from measurements of the nonionic surfactant self-diffusion coefficient. An entangled wormlike micelles network is formed at low temperatures and gradually changes to a multiconnect cross-links network when temperature is increased.[24] Whatever the exact structure, the aggregate structure probably consists of the surfactant hydrocarbon chains intertwining, removing themselves from aqueous solution, and hydrophilic groups covering the surface of this hydrophobic region.[7]

If the correction due to micelles in the permeate (and solubilization therein) were ignored, the error in the value of K_m would be about 7 %. If the correction due to micelles in the dilute phase (and solubilization therein) were ignored, the error in the value of K_c would be about 5 %. In other words, about 93 % of the solute in the permeate in SED experiments and about 95 % of the solute in the dilute phase in equilibrium with coacervate is unsolubilized, so ignoring the existence of micelles does not lead to gross errors. This is the first time this has been analyzed for the coacervate system, so it is important to have shown that the micelles in the dilute phase do not substantially reduce the efficiency of the separation, at least for volatile chlorinated alkanes.

Interpretation of Temperature Effects. It is interesting to note that the partition ratio increases much more rapidly with temperature than the value of K_c. For example, the ratio of partition ratios at 50 °C to 30 °C are 3.43, 2.66, and 2.65 for the di, tri, and tetrachloroethanes, respectively and equivalent ratios of K_c are 1.62, 1.21, and 1.22 for these same compounds. As temperature increases above the cloud point, the partition ratio increases primarily because the concentration of surfactant in the coacervate increases, secondly because the solubilization equilibrium constant in the coacervate surfactant aggregate increases, and thirdly because the concentration of micellized surfactant (and solubilization therein) in the dilute phase decreases. As an example calculation, of the increase in the partition ratio from 30 °C to 50 °C for the tetrachloroethane, 75 % is due to the increase in coacervate surfactant concentration, 16 % is due to the increase in the coacervate solubilization constant, and 9 % is due to the reduction in the concentration of surfactant in micelles in the dilute phase.

Acknowledgments

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Table 1 CMC of Surfactants with No Organic Solutes.

Temperature (°C)	CMC (mM)	
	$OP(EO)_7$	$OP(EO)_9$
30	0.092	0.083
40	0.086	0.076
50	0.075	0.066

Table 2 Cloud Points of 50 mM $OP(EO)_7$ System.

Solute Concentration (mM)	0	1.0
1,2-dichloroethane	22 °C	19 °C
1,1,1-trichloroethane	22 °C	16 °C
1,1,1,2-tetrachloroethane	22 °C	15 °C

Table 3 Liquid-Coacervate Extraction Data : Initial [OP(EO)$_7$] = 50 mM, Initial [solute] = 1.0 mM.

System	Temperature (°C)	Fractional coacervate volume	[OP(EO)$_7$] (mM)		[Solute] (mM)		Fraction in Coacervate		Partition Ratio = [in coacervate]/ [in dilute phase]	
			Dilute	Coacervate	Dilute	Coacervate	OP(EO)$_7$	Solute	OP(EO)$_7$	Solute
OP(EO)$_7$/ dichloroethane	30	0.12	1.13	393	0.28	4.05	0.98	0.66	348	14.5
	40	0.08	1.05	560	0.29	7.47	0.98	0.69	533	25.8
	50	0.06	0.74	777	0.25	12.46	0.99	0.79	1050	49.8
OP(EO)$_7$/ trichloroethane	30	0.12	0.98	409	0.23	7.06	0.98	0.81	417	30.7
	40	0.08	0.72	603	0.18	8.81	0.99	0.81	838	48.9
	50	0.06	0.59	816	0.11	9.00	0.99	0.84	1383	81.8
OP(EO)$_7$/ tetra chloroethane	30	0.13	0.76	422	0.22	7.14	0.99	0.83	555	32.5
	40	0.08	0.52	633	0.17	9.26	0.99	0.83	1217	54.5
	50	0.07	0.49	846	0.15	12.90	0.99	0.87	1727	86.0

Table 4 Semiequilibrium Dialysis Data for Micellar Solubilization of 50 mM $OP(EO)_9$ and 1.0 mM Organic Solute Initial Retentate Concentrations.

Organic Solute	Temperature (° C)	Initial		Permeate		Retentate		Km (L/mol)
		$[OP(EO)_9]$ (mM)	[Solute] (mM)	$[OP(EO)_9]$ (mM)	[Solute] (mM)	$[OP(EO)_9]$ (mM)	[Solute] (mM)	
Dichloroethane	30	50	1.0	1.13	0.28	48.9	0.72	33.7
	40	50	1.0	1.05	0.25	49.0	0.75	43.0
	50	50	1.0	0.74	0.20	49.3	0.80	63.6
Trichloroethane	30	50	1.0	1.98	0.19	48.0	0.81	80.9
	40	50	1.0	0.72	0.17	49.3	0.83	83.1
	50	50	1.0	0.59	0.14	49.4	0.86	109.8
Tetrachloroethane	30	50	1.0	0.76	0.17	49.2	0.83	83.7
	40	50	1.0	0.52	0.16	49.5	0.84	89.1
	50	50	1.0	0.49	0.15	49.5	0.86	99.3

Table 5 Summary of Partitioning and Solubilization Parameters for the Solute

System	Temperature (°C)	K_m (L/mol)	K_c (L/mol)	Partition Ratio of Solute	Fractional Coacervate Volume	$[OP(EO)_9]$ in Dilute Phase/CMC
$OP(EO)_n$/ Dichloroethane	30	33.7	44.5	14.5	0.12	12.3
	40	43.0	53.4	25.8	0.08	12.2
	50	63.6	72.2	49.8	0.06	9.9
$OP(EO)_n$/ Trichloroethane	30	80.9	94.1	30.7	0.12	10.7
	40	83.1	94.4	48.9	0.08	8.4
	50	109.8	114.2	81.8	0.06	7.9
$OP(EO)_n$/ tetra-chloroethane	30	83.7	92.0	32.5	0.13	8.3
	40	89.1	96.7	54.5	0.08	6.0
	50	99.3	111.9	86.0	0.07	6.5

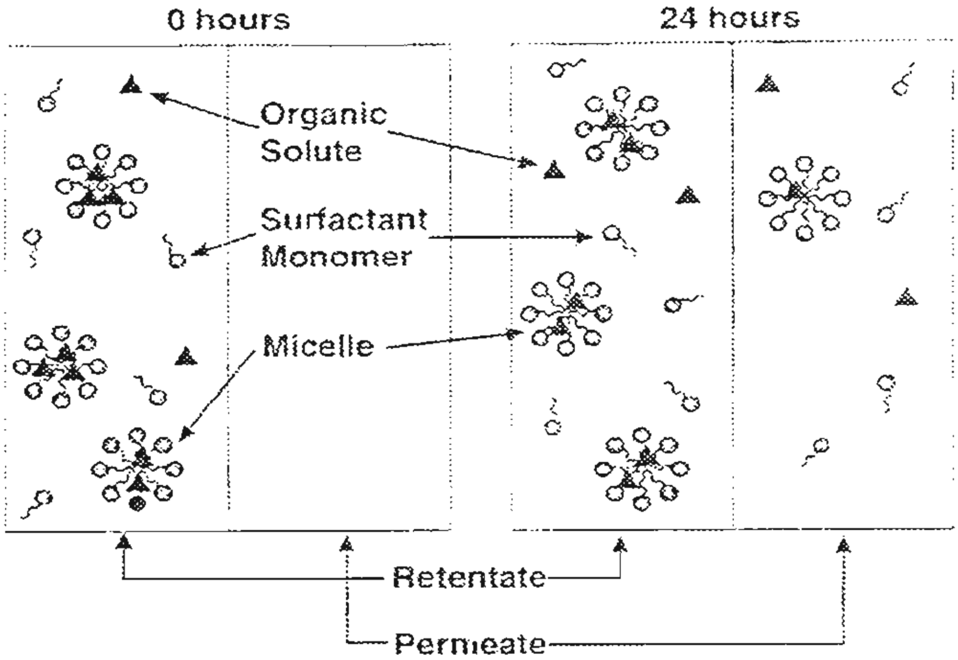

Figure 1 Schematic of semiequilibrium dialysis.

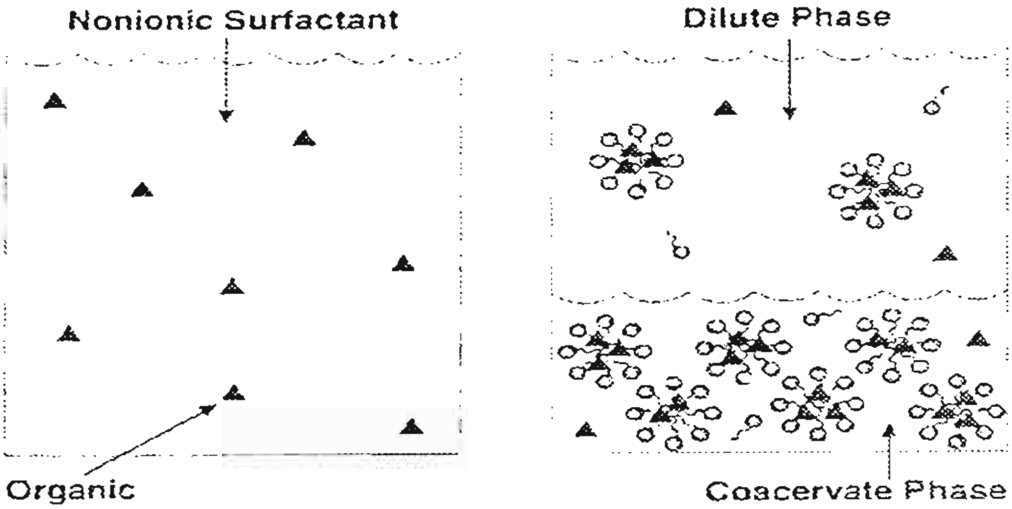

Figure 2 Schematic of liquid-coacervate extraction.

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REMOVAL OF VOLATILE AROMATIC CONTAMINANTS FROM WASTEWATER BY CLOUD POINT EXTRACTION

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ABSTRACT

Removal of the aromatic contaminants benzene, toluene, and ethylbenzene from wastewater was investigated using cloud point extraction (CPE). A nonionic surfactant, *t*-octylphenolpolyethoxylate, was utilized as the separating agent. When the nonionic surfactant solution is heated above the cloud point temperature, phase separation is induced. The micellar-rich phase or coacervate phase and the micellar-dilute phase are formed. The aromatic contaminants tend to solubilize into the micelles and concentrate in the coacervate phase. The concentration of the solutes in the coacervate increases as temperature, added electrolyte concentration, and degree of alkylation of the aromatic solutes increase.

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INTRODUCTION

A novel class of separation processes utilizing a surface-active agent are known as surfactant-based separations (1,2). These are used increasingly in process engineering (3). Processes such as froth flotation and micellar-enhanced ultrafiltration can be effective in environmental clean up (1,4). One surfactant-based separation of interest is cloud point extraction (CPE), which has been shown to be an effective technique to remove dissolved organic contaminants from water. This research focuses on cleaning up wastewater containing volatile aromatic pollutants benzene, toluene, and ethylbenzene, which can originate from gasoline tank leakage.

From an economic perspective, the surfactants, which serve as solvents in the extraction processes, have to be recovered. Since, these aromatic solutes have high volatility, they can be released from the surfactant solution by vacuum stripping, leaving a solute-free surfactant stream available for reuse (5–7). There have been literature studies of less volatile compounds using CPE such as phenolics (8–10). While these compounds can show excellent separation efficiency, there is no demonstrated efficient way to separate the solute from surfactant for surfactant reuse. In addition, as it is quite difficult to study experimentally the types of systems used here due to loss of solute by volatilization, previous investigations have tended to avoid these contaminants despite their importance.

BACKGROUND

Cloud point extraction is a separation technology using the benign polyethoxylate nonionic surfactant as a separating agent (8–19). It has been shown to be an alternative to traditional liquid–liquid extraction because of efficiency, cost effectiveness, and environmental friendliness without any usage of toxic and flammable organic solvents (11,16). This CPE is a specific example of aqueous biphasic extractions (20). When the aqueous nonionic surfactant solution is at a temperature higher than a certain temperature known as cloud point, phase separation is induced, forming two isotropic aqueous phases (8–19,21,22). The phase rich in surfactant micelles is called micellar-rich phase or coacervate phase. The other phase, which is lean in surfactant micelles and has the concentration of surfactant approximately 2–20 times the critical micelle concentration (CMC), is called dilute phase. As the phase separation is reversible, both phases can merge into a single phase upon cooling (11). Dissolved organic solutes will tend to solubilize in surfactant aggregates like micelles and thus concentrate in the coacervate phase, which contains surfactant in concentrated form. The cloud point temperature is sometimes defined at a surfactant concentration of 1 wt% (23), but is not highly concentration dependent (13,22–24). The minimum cloud point occurs at the lower consolute temperature or lower critical temperature (LCT) at the critical surfactant concentration (22).

To accomplish the phase separation, the temperature of the nonionic surfactant solution must be above the cloud point. The total surfactant concentration must be above the surfactant concentration existing in the dilute phase above the cloud point. Either the solution can be heated or the cloud point of nonionic surfactant reduced below the operating temperature. The CPE can be a low-energy separation process since a surfactant can be chosen with a cloud point below the wastewater operating temperature. Lowering the degree of polymerization of ethylene oxide or lengthening the hydrocarbon chain of the hydrophobic moiety of the nonionic surfactant can depress the cloud point (11,25,26). The addition of polar organic solutes, such as fatty acids, aliphatic alcohols, and phenol, generally lowers the cloud point (27). Added electrolyte can affect the cloud point with some anions, such as chloride, sulfate, and carbonate, depressing the cloud point due to the salting-out effect (24,28). On the other hand, some ions, such as thiocyanate, iodides, and nitrates increase the cloud point due to the salting-in effect (29). Adding anionic surfactant increases the cloud point (24,30,31). The effect of electrolytes on the cloud point of a pure nonionic surfactant and a mixed ionic–nonionic surfactant system has been discussed in the literature (24,30,32).

Studies of both the microstructure and macroscopic thermodynamic properties of the coacervate have given insight into its nature. Hoffmann et al. (33) studied the kinetics of aqueous nonionic surfactant solutions at the cloud point and found the formation of a new phase at a temperature higher than the cloud point. They stated that the existence of the new phase is controlled by nucleation phenomenon. Turro and Kuo (34) proved the presence of micelles in that phase by using three types of fluorescence probes as the indicator. Kato et al. (35,36) studied the microstructure of nonionic surfactant in semidilute solutions of nonionic surfactant including a system at a temperature higher than the cloud point via various techniques. They proposed that below the cloud point, the micelles form entangled networks. When temperature increases, the extent of cross-linking increases, forming the multiconnected network as determined by the self-diffusion technique (36). The comparison between the solubilization of organic solute into surfactant aggregates in a coacervate phase and the solubilization into surfactant micelles showed that the thermodynamic solubilization equilibrium constant for each of the aggregates is similar for similar surfactants and solutes (15). The nonideality of mixing of anionic and nonionic surfactants in the coacervate aggregates was shown to be similar to that in micelles existing below the cloud point (31). The last two studies support the hypothesis that the surfactant aggregates in the coacervate are micellelike in structure in that they have a hydrophobic region and a hydrophilic region where head groups interact in a similar fashion as normal micelles.

Many researchers have studied the CPE of organic contaminants, but few works have dealt with the volatile organic compounds (VOCs) of great environmental concern (16). We believe that this is due to the experimental difficulty of making accurate measurements on these systems since leakage of these species is difficult to overcome. It is economically worthwhile to study removal of these pollutants from water because these solutes have high vapor pressures, permitting them to be stripped off from the coacervate phase, leaving this phase solute-free for reuse.

EXPERIMENTAL

Materials

A polydisperse commercial, $OP(OE)_7$, with an average of 7 moles of ethylene oxide per mole of octylphenol (trade name Igepal CA-620) contributed by Rhodia (Cranbury, USA) was used as the nonionic surfactant in this study. Reagent grade benzene from Labscan Co. Ltd. (Bangkok, Thailand) with purity of 99.7%, toluene from J. T. Baker (Phillipsburg, USA) with purity of 99.8%, ethylbenzene from Fluka (Buchs, Switzerland) with purity of 98%, and NaCl from AJAX chemical (Auburn, Australia) with purity of 99.9% were purchased. All chemicals were used as received. The water was distilled and deionized.

Methods

A solution, containing nonionic surfactant, aromatic solute, and water with and without added electrolyte, was transferred into several identical vials. To prevent headspace loss, the solution must occupy almost all of the vial volume (22 mL) to neglect vapor volume. The rubber septa coated with polytetrafluoroethylene (PTFE) were used to seal these vials to make sure that no leakage occurred. The vials were placed in an isothermal water bath and the phase separation occurred immediately because of the density difference between the two phases. When the equilibrium was reached, which is defined as the condition where no further change in coacervate volume is observed, the relative phase volumes of each phase were measured by the solution height. The concentrations of nonionic surfactant and aromatic solute in both coacervate and dilute phases were measured.

The concentrations of $OP(EO)_7$ and aromatic solutes were measured by using a CE 2000 series UV-spectrophotometer (Cecil Instrument Limited, Cambridge, UK) at 224 nm and a gas chromatography 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 with no interference of a high molecular weight nonionic surfactant. The conditions used for determination of the aromatic solute concentrations were as follows: column, Supelcowax 10; carrier, ultra-pure nitrogen with the flow rate of 20 mL/min; oven temperature, 100°C isothermal; injector temperature, 150°C; and 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.

RESULTS AND DISCUSSION

In the reported data, surfactant concentrations are reported in m*M*, but solute concentrations are in ppm because wastewater pollutant concentrations are often designated in these weight-based units. There was no significant effect on the extraction due to changes in an initial concentration of organic solute (trichloroethylene) at low solute/surfactant molar ratio, as shown by Kimchuwanit et al. (14). To illustrate the relative magnitude of these concentrations, at our base case of 70 m*M* surfactant and 100 ppm solute initial concentrations. The solute/surfactant molar ratio is 0.0183 for benzene, 0.0155 for toluene, and 0.0135 for ethylbenzene.

Effect of Total Surfactant Concentration on Cloud Point Temperature of Benzene

Although the CPE is surfactant concentration dependent, under the conditions used here (30–110 m*M*), the cloud points of $OP(EO)_7$ are fairly constant at 22°C. The addition of 100 ppm benzene can lower the cloud point by 5°C, as shown in Table 1. Figure 1 shows that as the total surfactant concentration increases, the surfactant concentration in the coacervate phase remains essentially unchanged. The fractional coacervate volume increases with total surfactant concentration, as required from material balance considerations, as shown in Fig. 2. The ratio of surfactant concentration in the coacervate phase to that in the dilute phase (surfactant partition ratio) also remains constant as shown in Fig. 3. In addition, the benzene partition ratio, which is the ratio of benzene concentration in the coacervate phase to that in the dilute phase, is not much affected by increasing total surfactant concentration as shown in Fig. 4. There is a higher concentration of micelles in the coacervate phase, leading to a higher micellar solubilization capacity for aromatic solutes. Hence, the percentage of benzene extracted increases. The CPE of polycyclic aromatic hydrocarbons (PAHs), studied by Sirimanne et al., follows the

Table 1. Cloud Points (°C) of 70 mM *t*-Octylphenolpolyethoxylate System

	Solute Concentration (ppm)	
System	0	100
Benzene	22	17
Toluene	22	14
Ethylbenzene	22	11

same trend (17). From Fig. 5, at the lowest temperature studied here (30 C), at the total surfactant concentration of 110 m*M*, 86% of the benzene is extracted into the coacervate phase in a single stage.

Effect of Temperature on Cloud Point Extraction of Benzene

As temperature increases, the system is further away from the cloud point causing the nonionic surfactant micelles to be less water soluble. The dehydration of the hydrophilic polyethoxylate groups in the surfactant increases the inter-surfactant attraction and hence, inter-micellar attraction, which makes the coacervate more concentrated and with lower volume as the temperature is

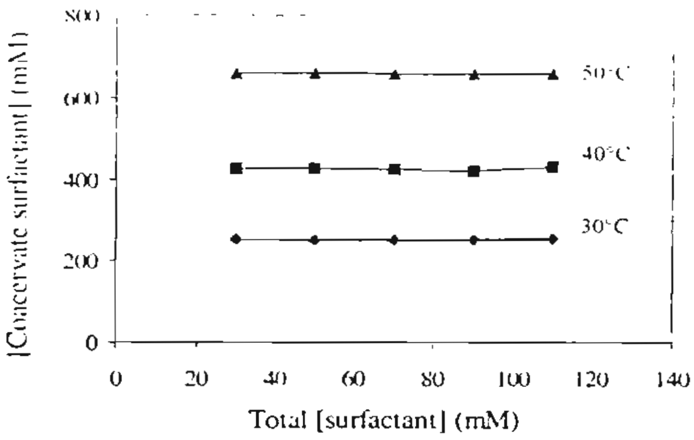

Figure 1. Surfactant concentration in coacervate phase as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte).

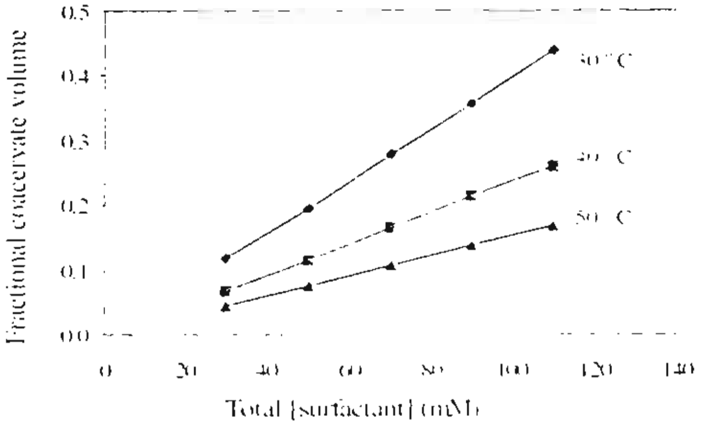

Figure 2. Fractional coacervate volume as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte).

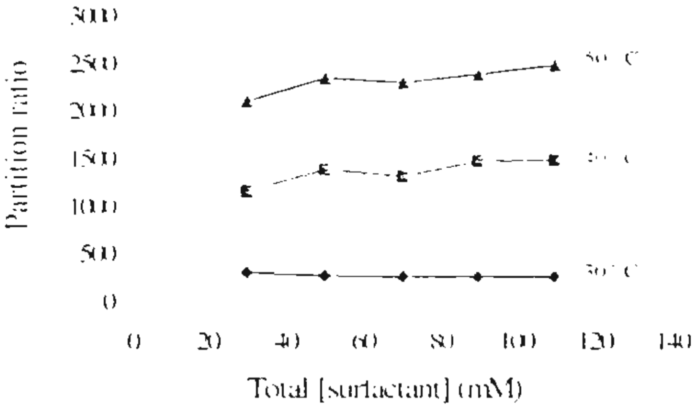

Figure 3. Surfactant partition ratio as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte).

increased above the cloud point. As the temperature increases, both surfactant and benzene partition ratio increase substantially, as shown in Figs. 3 and 4, respectively. At 50°C, a surfactant partition ratio exceeding 2000 and a benzene partition ratio exceeding 30 are observed. It is very beneficial to increase the temperature because it gives a very high surfactant partition ratio, which makes surfactant recovery more economical. Nevertheless, there are limitations on increasing temperature. The upper critical temperature can be reached, above which the phase separation does not occur (22). Since raising the operating

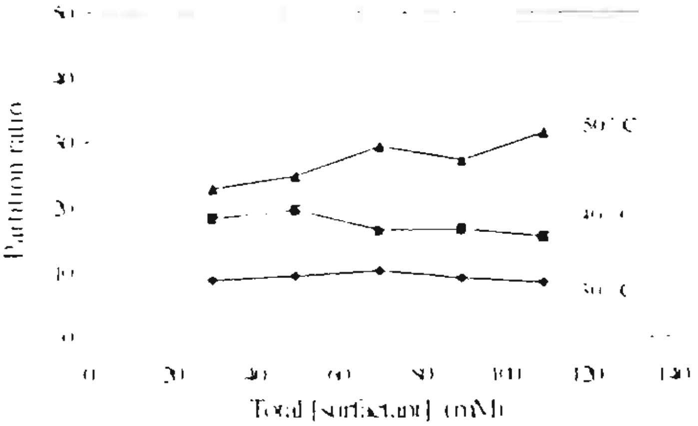

Figure 4. Benzene partition ratio as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte)

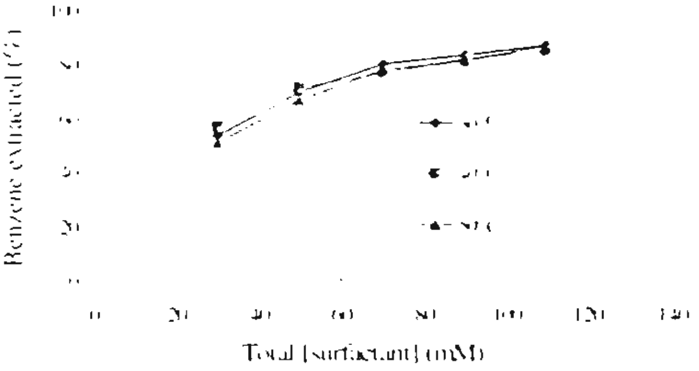

Figure 5. Percentage of benzene extracted in coacervate phase as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte)

temperature is energy intensive, the alternative of adjusting surfactant structure and other solution conditions so the cloud point is substantially below the operating temperature is desirable. However, an increase in temperature does not affect the fraction of benzene extracted into the coacervate phase substantially, as shown in Fig. 5. Although the concentration of benzene in the coacervate phase increases substantially as the temperature is raised, the fractional coacervate volume decreases. Therefore, these opposing effects result in the fraction of benzene extracted remaining nearly unchanged. However, higher temperature definitely has advantages in that it results in a lower solute concentration in the dilute phase and a higher solute concentration in the coacervate and a resulting lower coacervate phase volume with reduced processing costs downstream in treatment of the coacervate for surfactant recovery.

Effect of Added Electrolyte on Cloud Point Extraction of Benzene

The addition of NaCl to the micellar solution of $OP(EO)_7$ can depress the cloud point due to the salting-out effect (14,24,31). Therefore, it is analogous to an increase in the operating temperature. It has been reported that the lowering of the cloud point is related directly to an increase in added electrolyte concentration. The effect of electrolyte concentration on benzene partition ratio and fraction of benzene extracted at a total surfactant concentration of 70 m*M* and 30°C is shown in Fig. 6. The result demonstrates that the fractional coacervate volume decreases slightly with increasing salt concentration. The benzene partition ratio substantially increases with increasing NaCl concentration. This added electrolyte effect agrees with previous studies by several groups (12,14). An increase in NaCl concentration up to 0.6 *M* at 30°C can increase the benzene partition ratio a few fold. This salinity effect is approximately equivalent to the effect of a 20°C (from 30 to 50°C) temperature increase while increasing the benzene partition ratio. Nevertheless, the fraction of benzene extracted is not much affected by increasing the NaCl concentration, which is similar to the result shown in Fig. 5, where an increase in operating temperature has little effect on fraction of benzene extracted into the coacervate phase.

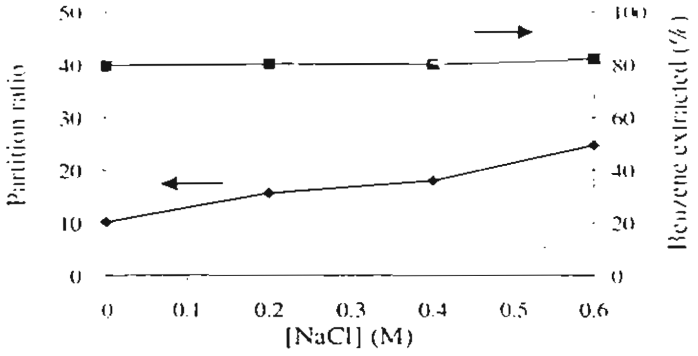

Figure 6. Benzene partition ratio and percentage of benzene extracted in coacervate phase as a function of NaCl concentration (system: 100 ppm benzene, 70 m*M* surfactant, and 30°C).

Effect of Degree of Alkylation of Aromatic Solutes on Cloud Point Extraction

A series of VOC aromatic solutes with varying degrees of alkylation (benzene, toluene, and ethylbenzene) was studied. A higher degree of alkylation of the solutes within a homologous series results in a greater partition ratio, as shown for ethylbenzene, toluene, and benzene in Fig. 7. This is in agreement with the solubilization study of organic solutes in aqueous solutions of nonionic surfactant. The higher the degree of alkylation (or lower the water solubility) of a homologous series of solutes, the higher the solubilization constant generally is (37). A secondary effect is that the addition of ethylbenzene can depress the cloud point of the system more than the other two solutes, as shown in Table 1. Thus, it gives the highest temperature difference between cloud point and operating temperature, which is analogous to increasing the temperature. The same trend with water solubility has been observed in systems where degree of chlorination was varied except at high degrees of chlorination where anomalies are sometimes seen (10,15). In addition, the fraction of aromatic solutes extracted into the coacervate phase depends on the degree of alkylation of the solutes. At the highest operating temperature studied (50 C) and the total surfactant concentration of 70 m*M*, up to 95, 89, and 78% of ethylbenzene, toluene, and benzene are extracted within a single stage, respectively.

Scale-Up of Cloud Point Extraction

Essentially all reported CPEs were carried out in a batch experiment on a laboratory scale (4,8–19). In order for this technology to become commercia-

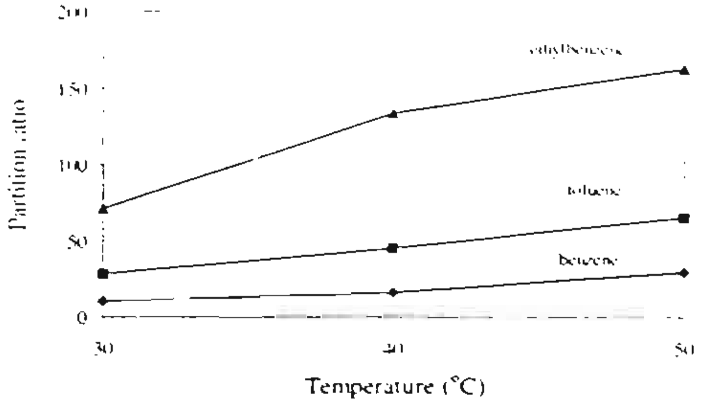

Figure 7. Partition ratio of several aromatic solutes as a function of temperature (system: 100 ppm aromatic solutes, 70 m*M* surfactant without added electrolyte).

lized, scale-up to continuous, multi-stage units will be necessary. In addition, recovery and reuse of the surfactant from the coacervate is crucial for economical operation; hence, the emphasis here is on volatile solutes, which can be stripped away. These two engineering problems are far from trivial; the viscous coacervate phase may cause plugging of extractors or strippers and efficient liquid–liquid contact may be difficult to attain in an extractor due to stickiness and viscous nature of the coacervate phase. Efficient thermodynamic extraction behavior (high partition ratio) is not a sufficient criterion for an efficient integrated separation scheme.

The principles of CPE are analogous to that of a conventional liquid–liquid extraction, except that the solvent can be completely miscible with the feed solution. Figure 8 shows the integrated flow diagram of the multistage CPE process including a surfactant recovery unit. The contaminated feed water and a concentrated surfactant solution are fed to a temperature-controlled extractor where two streams are mixed mechanically at the temperature above the cloud point. As a result, phase separation takes place. The heavy coacervate phase, which contains the majority of the solutes, settles down at the bottom of the extractor as an extract phase due to a density difference. The dilute phase, which

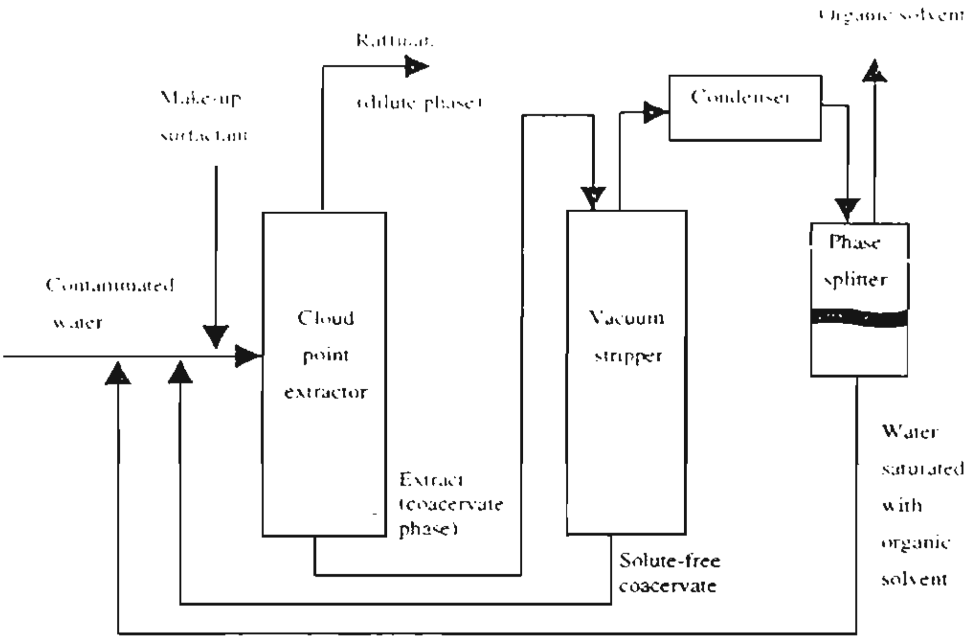

Figure 8. Schematic of integrated process including a multistage cloud point extractor and vacuum stripper.

is lighter, will rise up to the top of the extractor as a raffinate phase, which will be clean enough hopefully to be returned to the environment. Moreover, a vacuum stripper can strip the aromatic solutes, which have high volatility, from the coacervate phase, so that this resulting surfactant-rich phase can be recycled for reuse. Current work includes design, construction, and operation of a continuous, steady-state, multistage trayed liquid–liquid extractor and a continuous, steady-state, packed-column vacuum stripper for scale-up of this process.

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