



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 K_a 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 K_a and operating temperature is determined as shown in Fig. 11. A smooth increase in K_a is observed when the temperature is raised.

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.



REFERENCES

1. Bai, D.; Li, J.; Chen, S. B.; Chen, B. -H. A Novel Cloud-Point Extraction Process for Preconcentrating Selected Polycyclic Aromatic Hydrocarbons in Aqueous Solution. *Environ. Sci. Technol.* **2001**, *35*, 3936-3940.
2. Akita, S.; Takeuchi, H. Cloud-Point Extraction of Organic Compounds from Aqueous Solutions with Nonionic Surfactant. *Sep. Sci. Technol.* **1995**, *30*, 833-846.
3. Hinze, W. L.; Pramauro, E. A Critical Review of Surfactant-Mediated Phase Separations (Cloud-Point Extraction): Theory and Applications. *Crit. Rev. Anal. Chem.* **1993**, *24*, 133-177.
4. Akita, S.; Takeuchi, H. Equilibrium Distribution of Aromatic Compounds between Aqueous Solution and Coacervate of Nonionic Surfactants. *Sep. Sci. Technol.* **1996**, *31*, 401-412.
5. Ferrer, R.; Beltrán, J. L.; Guiteras, J. Use of Cloud Point Extraction Methodology for the Determination of PAHs Priority Pollutants in Water Samples by High-Performance Liquid Chromatography with Fluorescence Detection and Wavelength Programming. *Anal. Chim. Acta* **1996**, *330*, 199-206.
6. Quina, F. H.; Hinze, W. L. Surfactant-Mediated Cloud Point Extractions: An Environmentally Benign Alternative Separation Approach. *Ind. Eng. Chem. Res.* **1999**, *38*, 4150-4168.
7. Huddleston, J. G.; Willauer, H. D.; Griffin, S. T.; Rogers, R. D. Aqueous Polymeric Solutions as Environmentally Benign Liquid/Liquid Extraction Media. *Ind. Eng. Chem. Res.* **1999**, *38*, 2523-2539.
8. Gullickson, N. D.; Scamehorn, J. F.; Harwell, J. H. In *Surfactant-Based Separation Processes*; Scamehorn, J. F.; Harwell, J. H., Eds.; Marcel Dekker: New York, 1989; Chap. 6.
9. Kimchuwant, W.; Scamehorn, J. F.; Osuwan, S.; Harwell, J. H.; Haller, K. J. Use of a Micellar-Rich Coacervate Phase to Extract Trichloroethylene from Water. *Sep. Sci. Technol.* **2000**, *35*, 1991-2002.

10. Sakulwongyai, S.; Trakultamupatam, P.; Scamehorn, J. F.; Osuwan, S.; Christian, S. D. Use of a Surfactant Coacervate Phase to Extract Chlorinated Aliphatic Compounds from Water: Extraction of Chlorinated Ethanes and Quantitative Comparison to Solubilization in Micelles. *Langmuir* **2000**, *16*, 8226-8230.
11. 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.
12. Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd Ed.; Wiley: New York, 1989; Chap. 4.
13. Clint, J. H. *Surfactant Aggregation*; Blackie: Glasgow, 1992; Chap. 7.
14. Frankewish, R. P.; Hinze, W. L. Evaluation and Optimization of the Factors Affecting Nonionic Surfactant-Mediated Phase Separations. *Anal. Chem.* **1994**, *66*, 944-954.
15. Trakultamupatam, P.; Scamehorn, J. F.; Osuwan, S. Scaling Up Cloud Point Extraction of Aromatic Contaminants from Wastewater in A Continuous Rotating Disc Contactor: Part 1. Effect of Rotation Speed and Wastewater/Surfactant Flowrate Ratio. *Submitted to Separation Science and Technology*.
16. Domingo, X. *A Guide to the Surfactants World*; Edicions Proa: Barcelona, 1995; Chap. 8.
17. Komáromy-Hiller, G.; Calkins, N.; Wandruszka, R. V. Changes in Polarity and Aggregation Number upon Clouding of a Nonionic Detergent: Effect of Ionic Surfactants and Sodium Chloride. *Langmuir* **1996**, *12*, 916-920.
18. Kato, T.; Taguchi, N.; Terao, T.; Seimiya, T. Structure of Networks Formed in Concentrated Solutions of Nonionic Surfactant Studied by the Pulsed-Gradient Spin-Echo Method. *Langmuir* **1995**, *11*, 4661-4664.
19. Glatter, O.; Fritz, G; Lindner, H.; Brunner-Popela, J.; Mittelbach, R.; Strey, R.; Egelhaaf, S. U. Nonionic Micelles near the Critical Point: Micellar Growth and Attractive Interaction. *Langmuir* **2000**, *16*, 8692-8701.
20. Ganong, B. R.; Delmore, J. P. Phase Separation Temperatures of Mixtures of Triton X-114 and Triton X-45: Application to Protein Separation. *Anal. Biochem.* **1991**, *193*, 35-37.

21. Gu, T.; Sjöblom, J. Surfactant Structure and Its Relation to the Krafft Point, Cloud Point and Micellization: Some Empirical Relationships. *Colloids Surf.* **1992**, *64*, 39-46.
22. Huibers, P. D. T.; Shah, D. O.; Katritzky, A. R. Predicting Surfactant Cloud Point from Molecular Structure. *J. Colloid Interface Sci.* **1997**, *193*, 132-136.
23. Koshy, L.; Saiyad, A. H.; Rakshit, A. K. The Effects of Various Foreign Substances on the Cloud Point of Triton X 100 and Triton X 114. *Colloid Polym. Sci.* **1996**, *274*, 582-587.
24. Gu, T.; Galera-Gómez, P. A. Clouding of Triton X-114: The Effect of Added Electrolytes on the Cloud Point of Triton X-114 in the Presence of Ionic Surfactants. *Colloids Surf.* **1995**, *104*, 307-312.
25. Marszall, L. Effect of Electrolytes on the Cloud Point of Ionic-Nonionic Surfactant Solutions. *Colloids Surf.* **1987**, *25*, 279-285.
26. Marszall, L. Cloud Point of Mixed Ionic-Nonionic Surfactant Solutions in the Presence of Electrolytes. *Langmuir* **1988**, *4*, 90-93.
27. Roberts, B. L. The Use of Micellar Solutions for Novel Separation Techniques. Ph.D. Dissertation, University of Oklahoma, 1993.
28. Choori, U. N.; Scamehorn, J. F.; O'Haver, J. H.; Harwell, J. H. Removal of Volatile Organic Compounds from Surfactant Solutions by Flash Vacuum Stripping in a Packed Column. *Ground Water Monit. Rem.* **1998**, *18*, 157-165.
29. Hasegawa, M. A.; Sabatini, D. A.; Harwell, J. H. Liquid-Liquid Extraction for Surfactant-Contaminant Separation and Surfactant Reuse. *J. Envir. Engr. Div. ASCE.* **1997**, *123*, 691-697.
30. Foust, A. S.; Wenzel, L. A.; Clump, C. W.; Maus, L.; Andersen, L. B. *Principles of Unit Operation*, 2nd Ed.; John Wiley & Sons: Singapore, 1980; Chap. 2.
31. Treybal, R. E. *Mass-transfer Operations*, 3rd Ed.; McGraw-Hill: New York, 1980; Chap. 10.
32. Tong, J.; Furusaki, S. Mean Drop Size and Size Distribution in Rotating Disc Contactor Used for Reversed Micellar Extraction of Proteins. *J. Chem. Eng. Jpn.* **1995**, *28*, 582-589.
33. Laddha, G. S.; Degaleesan, T. E. *Transport Phenomena in Liquid Extraction*, McGraw-Hill: New York, 1978; Chap. 12.

34. Laddha, G. S.; Degaleesan, T. E.; Kannappan, R. Hydrodynamics and Mass Transport in Rotary Disk Contactors. *Can. J. Chem. Eng.* **1978**, *56*, 137-150.
35. Strand, C. P.; Olney, R. B.; Ackerman, G. H. Fundamental Aspects of Rotating Disk Contactor Performance. *AIChE J.* **1962**, *8*, 252-261.
36. Zhang, S. H.; Ni, X. D.; Su, Y. F. Hydrodynamics, Axial Mixing and Mass Transfer in Rotating Disk Contactors. *Can. J. Chem. Eng.* **1981**, *59*, 573-583.
37. Kamath, M. S.; Subba Rau, M. G. Prediction of Operating Range of Rotor Speeds for Rotating Disc Contactors. *Can. J. Chem. Eng.* **1985**, *63*, 578-584.
38. King, C. J. *Separation Processes*, 2nd Ed.; McGraw-Hill, Inc.: Singapore, 1980; Chap. 6 and Chap. 14.

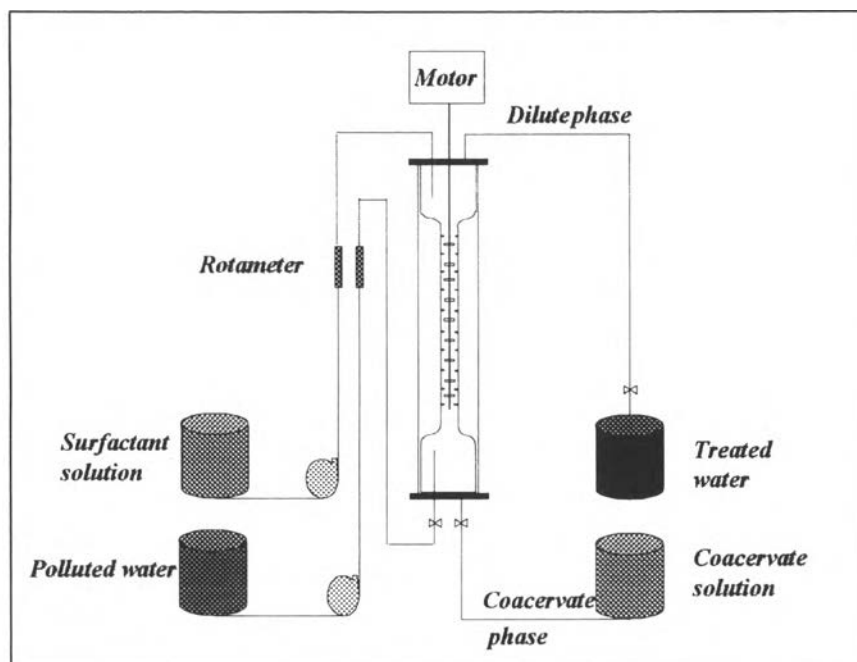


Figure 1. A schematic diagram of the cloud point extraction pilot plant.

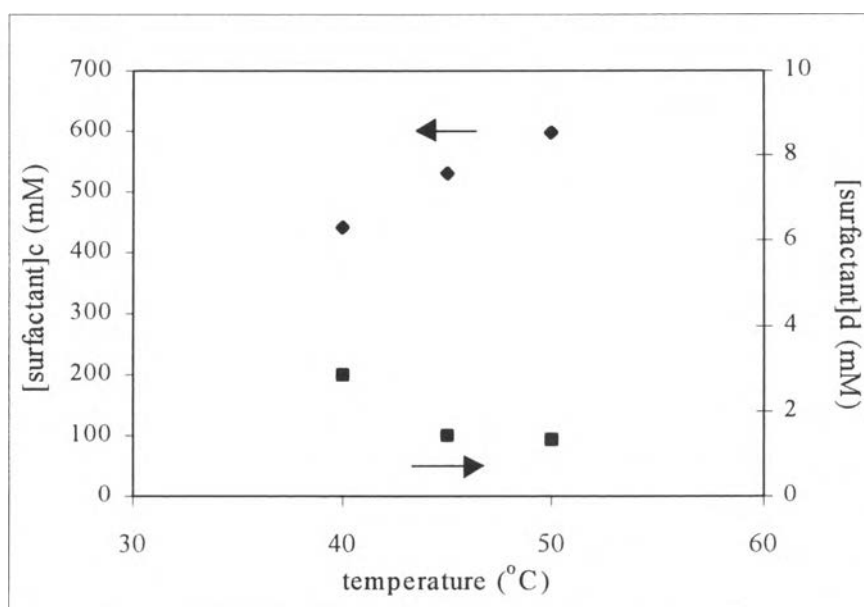


Figure 2. Surfactant concentration in coacervate stream (c) and dilute phase stream (d) as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 150 rpm agitator speed).

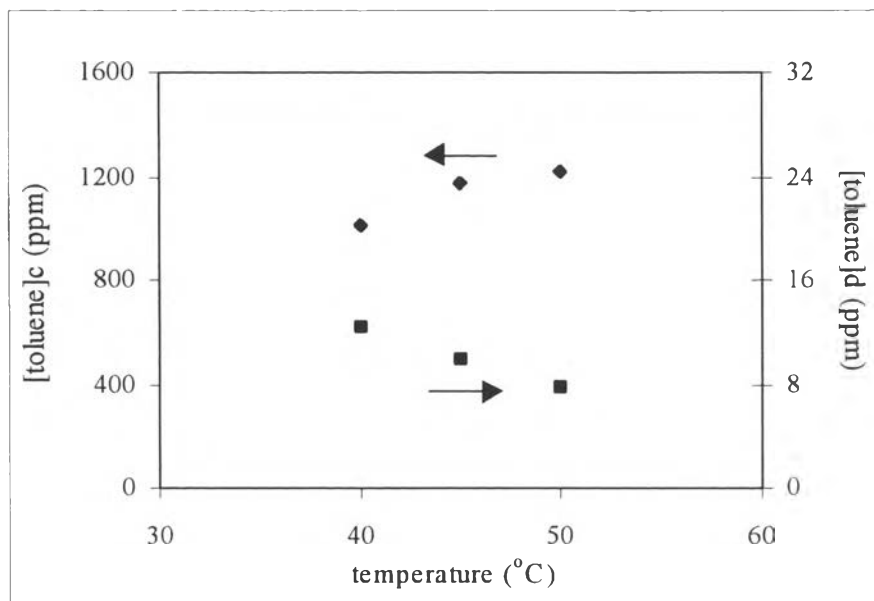


Figure 3. Toluene concentration in coacervate stream (c) and dilute phase stream (d) as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 150 rpm agitator speed).

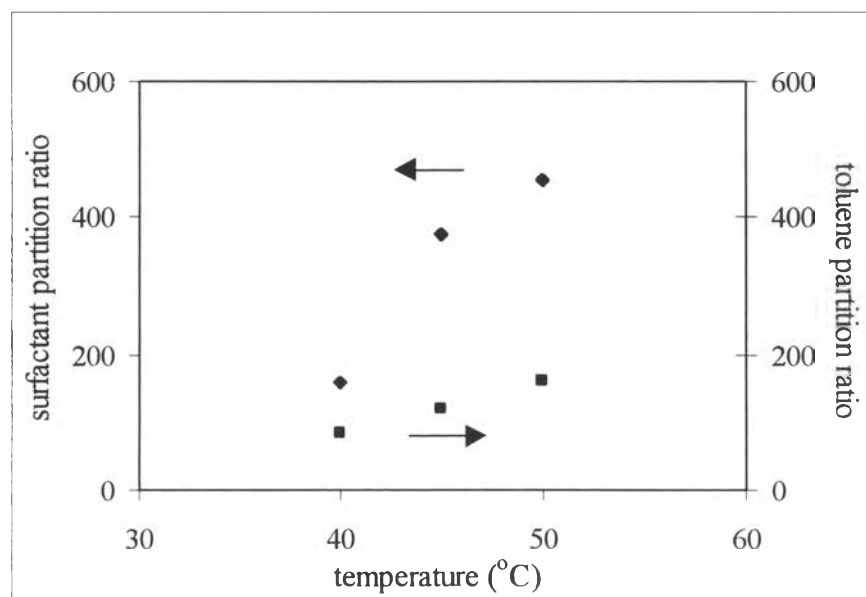


Figure 4. Surfactant and toluene partition ratio as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 150 rpm agitator speed).

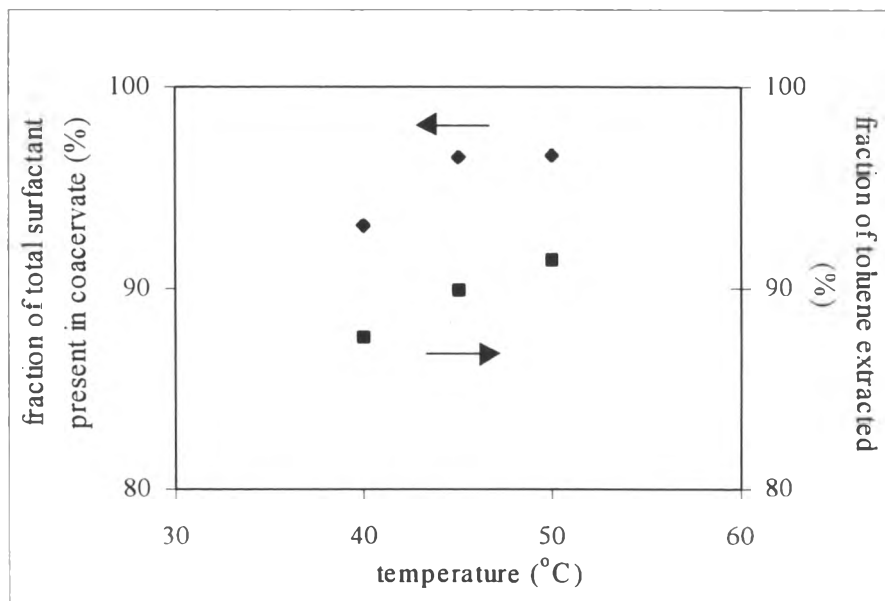


Figure 5. Fraction of total surfactant present in coacervate stream and fraction of toluene extracted in coacervate stream as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 150 rpm agitation speed).

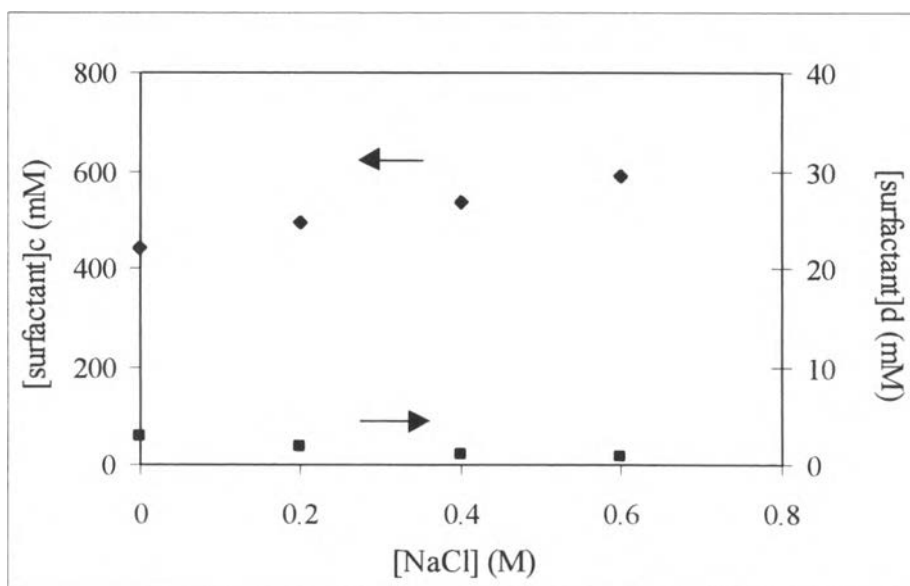


Figure 6. Surfactant concentration in coacervate stream (c) and dilute phase stream (d) as a function of NaCl concentration (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C).

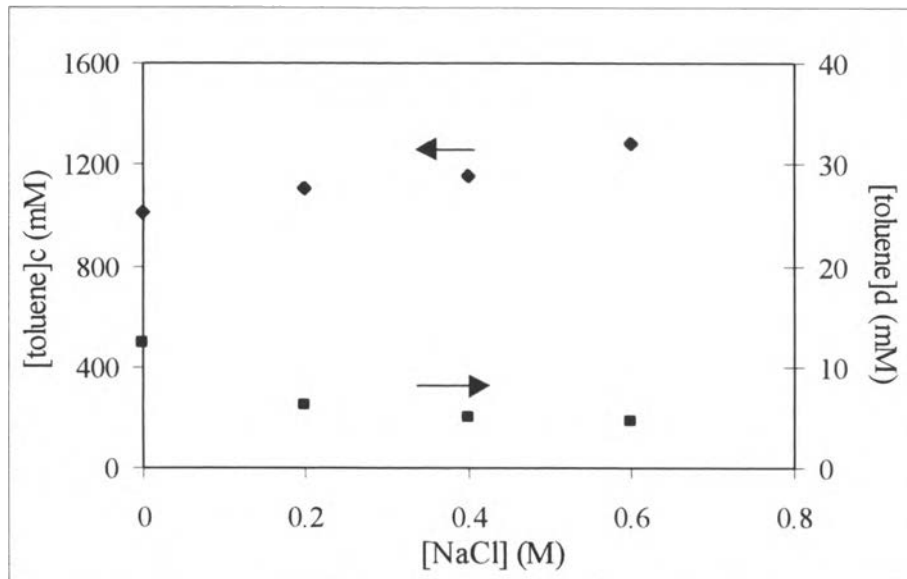


Figure 7. Toluene concentration in coacervate stream (c) and dilute phase stream (d) as a function of NaCl concentration (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C).

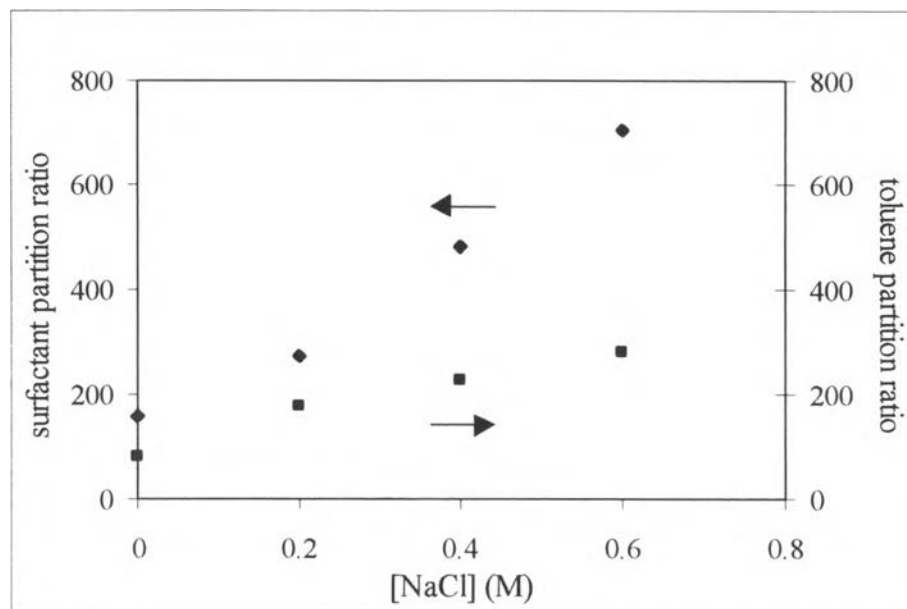


Figure 8. Surfactant and toluene partition ratio as a function of NaCl concentration (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C).

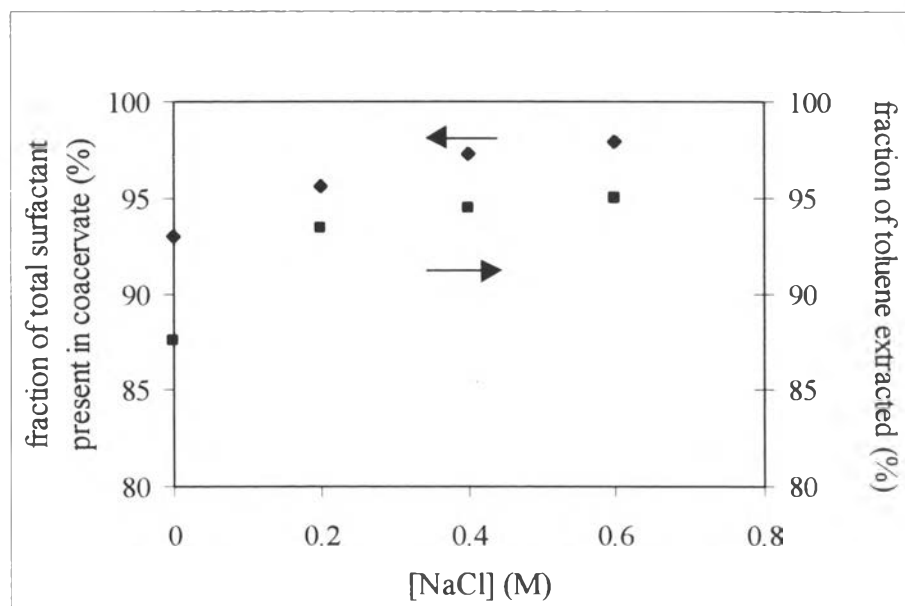


Figure 9. Fraction of total surfactant present in coacervate stream and fraction of toluene extracted in coacervate stream as a function of NaCl concentration (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitation speed, and 40 °C).

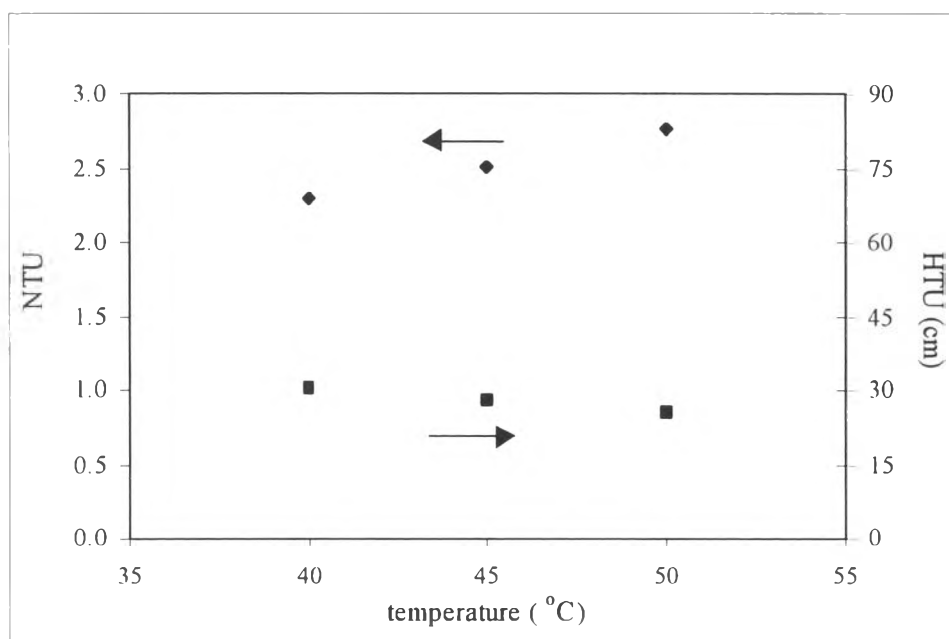


Figure 10. Number of transfer unit (NTU) and height of transfer unit (HTU) as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C).

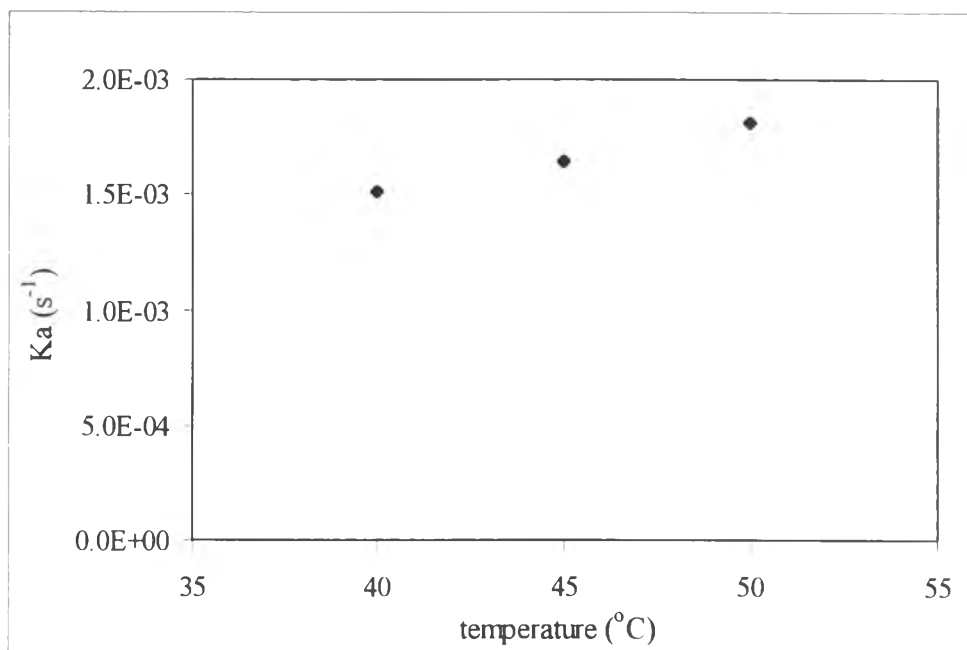


Figure 11. Overall volumetric mass transfer coefficient (K_a) as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 $^{\circ}\text{C}$).