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โครงการ

การแยกสกัดสารอะโรเมติกส์ออกจากน้ำเสียโดยอาศัยการแยกวัฏภาคของสารลดแรงตึงผิวชนิดไม่มีประจุ

(Use of Coacervate Phase to Extract the Aromatic Solutes from Wastewater by Using A Nonionic Surfactant)

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การสกัดแบบขุ่นถูกนำมาใช้เพื่อแยกสกัดสารประกอบอะโรเมติกส์ออกจากน้ำเสียโดยศึกษาทั้งการสกัดแบบกะในหลอดทดลองและการสกัดแบบต่อเนื่องในเครื่องสกัดนำร่องแบบดิฟเฟอร์เรนเชียล เมื่อสารละลายของสารลดแรงตึงผิวชนิดไม่มีประจุมีอุณหภูมิสูงกว่าจุดขุ่นสารละลายจะแยกออกเป็นสองวัฏภาค ได้แก่ วัฏภาคที่มีไมเซลล์เป็นจำนวนมากหรือวัฏภาคโคแอคเซอร์เวท และวัฏภาคที่มีไมเซลล์เป็นจำนวนน้อย ตัวถูกละลายอินทรีย์ที่อยู่ในสารละลายจะละลายเข้าไปในไมเซลล์และมีความเข้มข้นสูงอยู่ในวัฏภาคโคแอคเซอร์เวท ทำให้วัฏภาคที่มีไมเซลล์เป็นจำนวนน้อยเปรียบเสมือนเป็นน้ำที่มีความบริสุทธิ์มากขึ้นเนื่องจากมีความเข้มข้นของตัวถูกละลายต่ำ ในการทดลองแบบกะสารละลายที่ประกอบด้วยสารลดแรงตึงผิวชนิดไม่มีประจุ ตัวถูกละลายอะโรเมติกส์ ทั้งที่มีการเติมเกลือและไม่มีการเติมเกลือถูกเตรียมในขวดเก็บตัวอย่างแล้วนำไปแช่ในอ่างควบคุมอุณหภูมิจนถึงสภาวะสมดุลจึงทำการวัดปริมาตรสัมพัทธ์ความเข้มข้นของสารลดแรงตึงผิวและตัวถูกละลายอะโรเมติกส์ในแต่ละวัฏภาค ผลการทดลองพบว่าอุณหภูมิ ความเข้มข้นของเกลือ และองศาการเติมหมู่อัลคิลของตัวถูกละลายอะโรเมติกส์จะช่วยเพิ่มอัตราส่วนการละลายของตัวถูกละลายอะโรเมติกส์ในวัฏภาคโคแอคเซอร์เวท ส่งผลให้ความเข้มข้นของตัวถูกละลายอะโรเมติกส์ในวัฏภาคโคแอคเซอร์เวทสูงขึ้น เครื่องสกัดแบบโรเทติ้งดิสก์คอนแทคเตอร์ถูกสร้างขึ้นในขนาดนำร่องเพื่อใช้ในการทดลองแบบต่อเนื่อง ในหอสกัดนี้น้ำเสียและสารละลายของสารลดแรงตึงผิวชนิดไม่มีประจุถูกป้อนเข้าหอสกัดแบบสวนทาง หลังจากนั้นทำการวิเคราะห์ความเข้มข้นของสารลดแรงตึงผิวและตัวถูกละลายอะโรเมติกส์ในแต่ละวัฏภาค จากผลการทดลองพบว่าเมื่ออุณหภูมิ ความเร็วรอบการกวน อัตราส่วนของอัตราการไหลของน้ำเสียต่อสารละลายของสารลดแรงตึงผิวและองศาการเติมหมู่อัลคิลของตัวถูกละลายอะโรเมติกส์เพิ่มขึ้นมีผลให้ความเข้มข้นของตัวถูกละลายในวัฏภาคโคแอคเซอร์เวทสูงขึ้น ค่าสัมประสิทธิ์รวมการถ่ายโอนมวลเชิงปริมาตร (Ka) และจำนวนหน่วยการถ่ายโอน (NTU) ในเครื่องสกัดแบบโรเทติ้งดิสก์คอนแทคเตอร์เพิ่มขึ้นเมื่อเพิ่มอุณหภูมิและความเร็วรอบของจานหมุน

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The cloud point extraction (CPE) of aromatic contaminants (benzene, toluene and ethylbenzene) from wastewater was studied as batch experiments in laboratory scale and continuous operation in a pilot scale differential extractor. When the temperature of the nonionic surfactant micellar solution is a greater than its cloud point, the solution will separate into two aqueous phases known as the micellar-rich phase or coacervate phase, and the micellar-dilute phase. The organic solutes contained in the solution tend to solubilize into the micelles and mostly concentrate into the coacervate phase, leaving the dilute phase with a low concentration of solutes as the purified water. In batch experiments, several vials containing nonionic surfactant, aromatic solute, and water with and without added electrolyte (NaCl) were placed in an isothermal water bath until equilibrium was reached. After phase separation occurred, the concentrations of nonionic surfactant and aromatic solute in both phases were analyzed. The results show that the solute concentrations in the coacervate phase increase as temperature, NaCl concentration and degree of alkylation of the aromatic solutes increase. In continuous operation, a pilot scale, rotating disc contactor (RDC) was fabricated. The polluted water and nonionic surfactant solution were fed to the column counter-currently. The phase separation occurred inside the column. The concentrations of nonionic surfactant and aromatic solutes in the coacervate stream and the micellar-dilute phase stream were analyzed. The concentrations of solutes in the coacervate phase increase as temperature, agitator speed, NaCl concentration, wastewater/surfactant solution flowrate ratio and degree of alkylation of the aromatic solutes increase. The overall volumetric mass transfer coefficient (Ka) and the number of transfer unit (NTU) in the RDC increase with increasing temperature and rotation speed of the rotor disc.

Keywords: cloud point, extraction, coacervate, and nonionic surfactant

TABLE OF CONTENTS

CHAPTER PAGE

LIST OF TABLES

LIST OF FIGURES

FIGURE **PAGE**

FIGURE | PAGE

FIGURE PAGE

FIGURE PAGE

Chapter IV

FIGURE PAGE

CHAPTER I

INTRODUCTION

1.1 Background

Environmental contamination due to wastewater discharges containing a trace amount of aromatic compounds can cause severe problems because of their toxicity either known or suspected carcinogens or mutagens (Bai *et al.*, 2001) Benzene, toluene, and ethylbenzene are common pollutants of great environmental concern originating from industrial effluents. A novel class of separation processes utilizing an environmentally friendly surface active agent is known as surfactant-based separations (Bai *et al.*, 2001; Scamehorn and Harwell, 1989). These techniques involve technologies such as surfactant enhanced oil recovery, foam fractionation, and froth flotation. These are increasingly used in process engineering (Scamehorn and Harwell, 2000). Cloud point extraction (CPE) is one of the surfactant-based separation technologies, which is effective in removal of organic compounds from polluted water (Bai *et al.*, 2001; Quina and Hinze, 1999; Huddleston *et al.*, 1999; Kimchuwanit *et al.*, 2000; Sakulwongyai *et al.*, 2000; Trakultamupatam *et al.*, 2002; Frankewish and Hinze, 1994; Hinze and Pramauro, 1993). This technique is economical and benign comparing to classical extraction methods, which are energy intensive and consume toxic organic solvents. Quina and Hinze (1999) provided a comprehensive review about CPE as an alternative separation approach. They reported that more than 94 % of polychlorinated biphenyls (PCBs), 88 % of polychlorinated dibenzofurans (PCDF), and 81 % of polycyclic aromatic hydrocarbons (PAHs) were extracted from wastewater by CPE in which Triton X-100, Brij-56, and Triton X-114 were utilized as nonionic surfactants, respectively.

An aqueous solution of nonionic surfactant undergoes a phase separation when it is at a temperature above its cloud point, attained either by heating or lowering the cloud point of the surfactant below the operating temperature (Bai *et al.*, 2001; Scamehorn and Harwell, 1989; Scamehorn and Harwell, 2000; Quina and Hinze, 1999, Huddleston *et al.*, 1999; Kimchuwanit *et al.*, 2000; Sakulwongyai *et al.*, 2000; Trakultamupatam *et al.*, 2002; Frankewish and Hinze, 1994; Hinze and Pramauro, 1993; Rosen, 1989). Two isotropic micellar phases are formed. One phase is generally less in volume and contains most of surfactant micelles and is known as a micellar-rich phase or coacervate phase. The other phase is an aqueous solution lean in surfactant micelles, known as a micellar-dilute phase. When nonionic surfactant is added to polluted water above the cloud point, the organic solutes contained in the solution will solubilize into surfactant micelles. After phase separation, the surfactant and pollutants are concentrated in the coacervate phase. The dilute phase, which contains a low concentration of organic pollutants, can be discharged to the environment as the effluent water. If a single stage results in insufficient purification, multiple stages can be used as with other traditional liquid-liquid extraction units.

Although many researchers have showed that the cloud point extraction is a promising technique to remove the organic contaminants from the wastewater, few works have dealt with the volatile organic compounds (VOCs) (Huddleston *et al.*, 1999). It is probably due to the experimental difficulty of making accurate measurements on these systems since leakage of these species is difficult to overcome. However, it is economically worthwhile to study the removal of these pollutants from water since the surfactant recovery is conceivable. These solutes have high volatility enough to be released from the coacervate phase by vacuum stripping, leaving the solute-free coacervate phase for reuse. In the other circumstances, when the organic solutes are non-volatile organic compounds, the coacervate phase, which contains a high solute concentration in small volume, can be disposed or incinerated.

For economic prospective, it is necessary to study the CPE in continuous operation on multistage extractor for large scale application. The principles of CPE and traditional liquid-liquid extractions are similar, except that two contacted phases in CPE can be completely miscible. The phase separation of CPE occurs because of the cloud point phenomenon of the nonionic surfactant solution at temperature beyond the cloud point. But the phase separations in the common liquid-liquid extraction systems occur by the immiscibility of two contacted liquids.

1.2 Objectives

The objectives of this research were to study the CPE of volatile aromatic solutes: benzene, toluene, and ethylbenzene from wastewater as batch experiments in a laboratory scale. The factors affecting the extraction were studied as follows: operating temperature, total surfactant concentration, added electrolyte concentration, and degree of alkylation of aromatic solutes. For large scale application, CPE requires a continuous, steady-state operation as with other liquid-liquid extraction units. Hence, the CPE was subsequently scaled up to continuous operation in a multistage, differential extractor. A standard size of rotating disc contactor was fabricated as a pilot scale apparatus. The effects of rotation speed of rotor disc, wastewater/surfactant flowrate ratio, operating temperature, added electrolyte concentration, and degree of alkylation of aromatic solutes on the extraction were studied. In addition, the number of transfer unit, the height of transfer unit, and the overall volumetric mass transfer coefficient were determined. Moreover, a comparison between results obtained from batch and continuous operation was present.

Prior to this work, a preliminary study on the CPE was studied in the systems containing di-, tri-, and tetrachloroethane as the organic solutes in laboratory scale at equilibrium condition in order to understand the extraction process in principles as outlined in the following section. This work was presented as a part of published paper in Langmuir as shown in the appendix.

1.3 Preliminary Study on the CPE of Chlorinated Hydrocarbon

1.3.1 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 (Scamehorn and Harwell, 1989; Frankewish and Hinze, 1994; Hinze and Pramauro, 1993; Rosen, 1989). The concentration of surfactant in the dilute phase can be very low but is generally above the critical micelle concentration. 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 as shown in Fig. 1. 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 (1986) showed that the nonideality of mixed aggregate formation between anionic and nonionic surfactants is very similar in coacervate and in micelles. This liquid/coacervate extraction (sometimes referred to as cloud point extraction) is a specific example of aqueous biphasic extractions (Roger and Eiteman, 1995). This technique shows great potential for removing toxic solutes from polluted water. The present study focuses on chlorinated hydrocarbons, a major class of pollutants, and quantifies the effect of the degree of chlorination of the solute.

1.3.2 Experimental

Octylphenoxypoly (ethyleneoxy) ethanol with an average of 7 moles of ethylene oxide per mole of octylphenol [$OP(EO)_7$] from Rhodia was the nonionic surfactant 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. 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 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.

The cloud points were visually determined as the temperature at which a 50 mM surfactant solution became turbid at a heating rate of 1°C/minute.

1.3.3 Results and Discussion

1.3.3.1 Effect of temperature on coacervate extraction

The cloud point of the 50 mM $OP(EO)_7$ system is shown in Table 1 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.

Table 2 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.

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* Partition ratio of substance is defined as the ratio of coacervate substance concentration to dilute phase substance concentration.

1.3.3.2 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 2. The large increase in the partition ratio 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 (Nawakowska *et al.*, 1989). However, the degree of chlorination of the solute affects the partition ratio of the surfactant also as seen in Table 2, complicating the interpretation of data. For example, in a cloud point (or coacervate) extraction of a series of chlorinated phenols, Frankewich and Hinze 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- (Frankewish and Hinze, 1994).

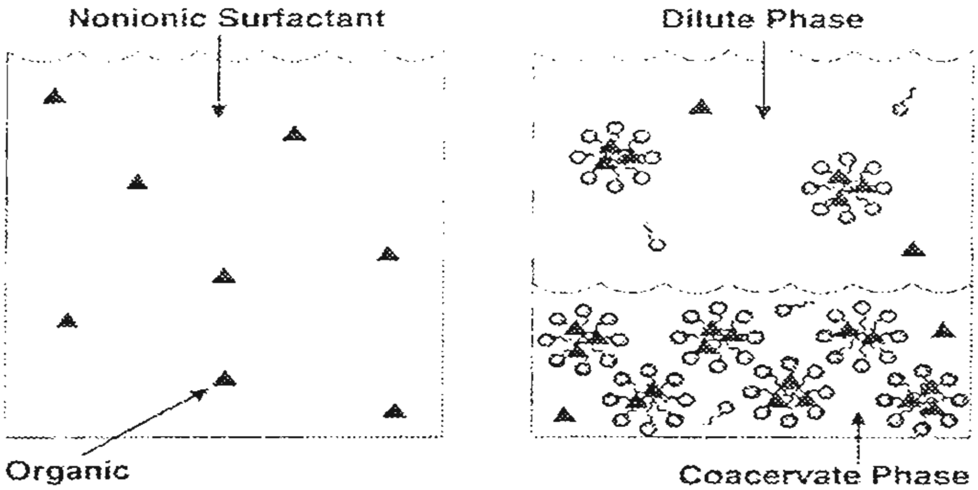

Figure 1 Schematic of liquid-coacervate extraction.

Table 1 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 2 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	18.9
	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

CHAPTER II

REMOVAL OF VOLATILE AROMATIC CONTAMINANTS FROM WASTEWATER BY CLOUD POINT EXTRACTION

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.

INTRODUCTION

A novel class of separation processes utilizing a surface active agent are known as surfactant-based separations (1, 2). These are increasingly used 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 a solvent in the extraction process, have to be recovered. Since, these aromatic solutes have high enough 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. Also, it is quite difficult experimentally to study the types of systems used here due to loss of solute by volatilization, so 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). One is rich in surfactant micelles called a micellar-rich phase or coacervate phase. The other phase is lean in surfactant micelles, which has the concentration of surfactant approximately 2 to 20 times the critical micelle concentration (CMC), called a dilute phase. The phase separation is reversible so, both phases can merge together 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 weight % (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 cloud point extraction 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 a fatty acid, an aliphatic alcohol and phenol generally lower 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 raise 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 the temperature higher than the cloud point They stated that the existence of the new phase is controlled by nucleation phenomenon. Turro et al. (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 the 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 micelle-like 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 cloud point extraction 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 t-octylphenolpolyethoxylate, $OP(OE)_7$, 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 Asia 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 (22mL) to neglect vapor volume. The rubber septa coated with polytetrafluoroethylene (PTFE) were used to seal these vials to make sure that no leakage was occurring. The vials were placed in an isothermal water bath and the phase separation immediately occurred because of the density difference between two phases. When 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 phase and dilute phase 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, 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 with no interference of the 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; 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 mM, but solute concentrations are in ppm because wastewater pollutant concentrations are often designated in these weight-base 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, for our base case of 70 mM 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 extraction of benzene

Although the cloud point temperature is surfactant concentration dependent, under the conditions used here (30 to 110 mM), 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. Fig 1 indicates 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 of in the dilute phase (surfactant partition ratio) also remains constant as illustrated in Fig.3. In addition, the benzene partition ratio, which is the ratio of benzene concentration in the coacervate phase to that of 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 cloud point extraction of polycyclic aromatic hydrocarbons (PAHs) studied by Sirimanne et al. follows the same trend (17). From Fig. 5, at the lowest temperature studied here (30 °C), at the total surfactant concentration of 110 mM, 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 be less water soluble. The dehydration of the hydrophilic polyethoxylate groups in the surfactant increase the inter-surfactant attraction and hence, inter-micellar attraction which makes the coacervate more concentrated and with lower volume as temperature is increased above the cloud point. As the temperature increases, both surfactant and benzene partition ratio substantially increase as shown in Fig. 3 and Fig. 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 operating 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 substantially affect the fraction of benzene extracted into the coacervate phase as shown in Fig. 5. Although the concentration of benzene in the coacervate phase substantially increases as the temperature is raised, the fractional coacervate volume decreases. Therefore these opposing effects results 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 on 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 operating temperature. It has been reported that the lowering of the cloud point is directly related 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 mM 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 increases substantially 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 in 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

Effect of degree of alkylation of aromatic solutes on cloud point extraction

A series of VOC aromatic solutes in which the degree of alkylation is varied (benzene, toluene, and ethylbenzene) was studied. A higher degree of alkylation of the solutes within a homologous series results in a greater partition ratio for ethylbenzene, toluene, and benzene as shown in Fig. 7. This is in agreement with the solubilization study of organic solutes in aqueous solutions of nonionic surfactant Where 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 here (50 °C) and the total surfactant concentration of 70 mM , 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 cloud point extractions were carried out in batch experiment on a laboratory scale (4, 8-19). In order for this technology to become commercialized, scale-up to continuous, multi-stage units will be necessary. Also, recovery and reuse of the surfactant from the coacervate is crucial for economical operation; hence, the emphasis on volatile solutes here is because they 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 the stickiness and viscous nature of the coacervate phase. Efficient thermodynamic extraction behavior (high partition ratio) is not a sufficient criteria 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. Fig. 8 shows the integrated flow diagram of the multistage cloud point extraction 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 mechanically mixed 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 is lighter, will rise up to the top of the extractor as a raffinate phase which will hopefully be clean enough 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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Table 1. Cloud points of 70 mM $OP(EO)_7$ system.

System \ Solute concentration	0 ppm	100 ppm
Benzene	22 ° C	17 ° C
Toluene	22 ° C	14 ° C
Ethylbenzene	22 ° C	11 ° C

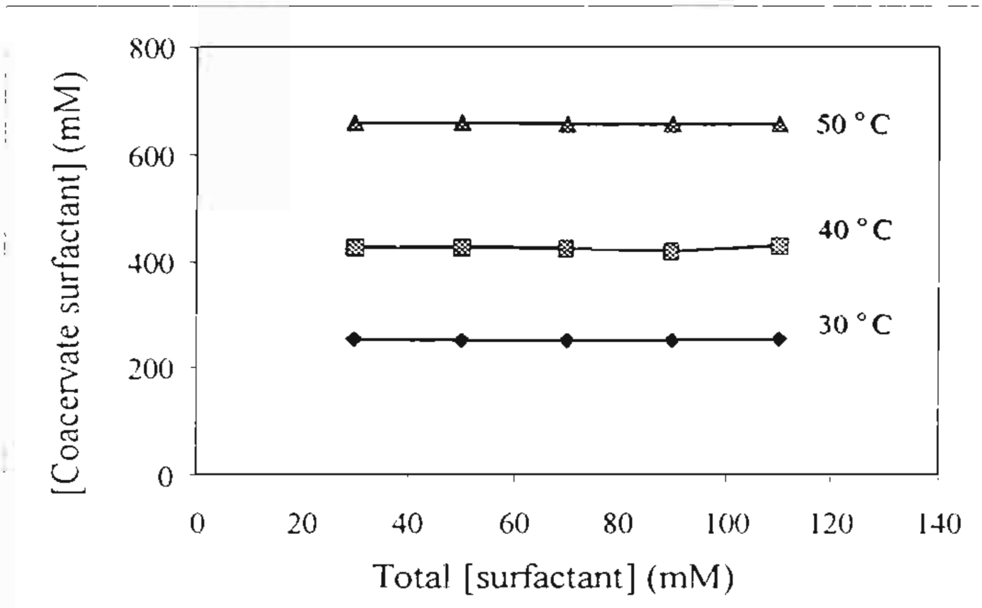

Figure 1. Surfactant concentration in coacervate phase as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte).

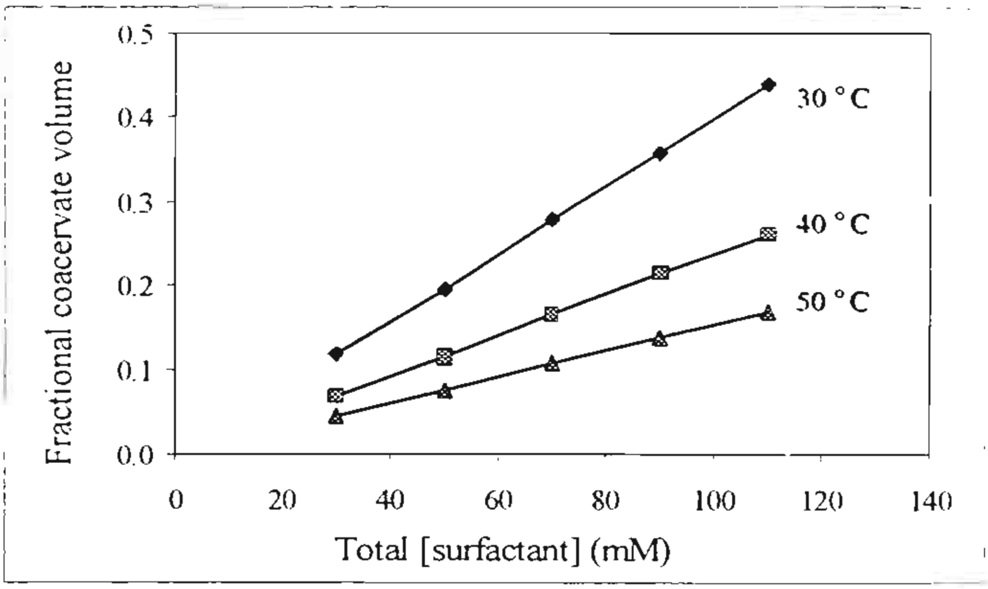

Figure 2. Fractional coacervate volume as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte).

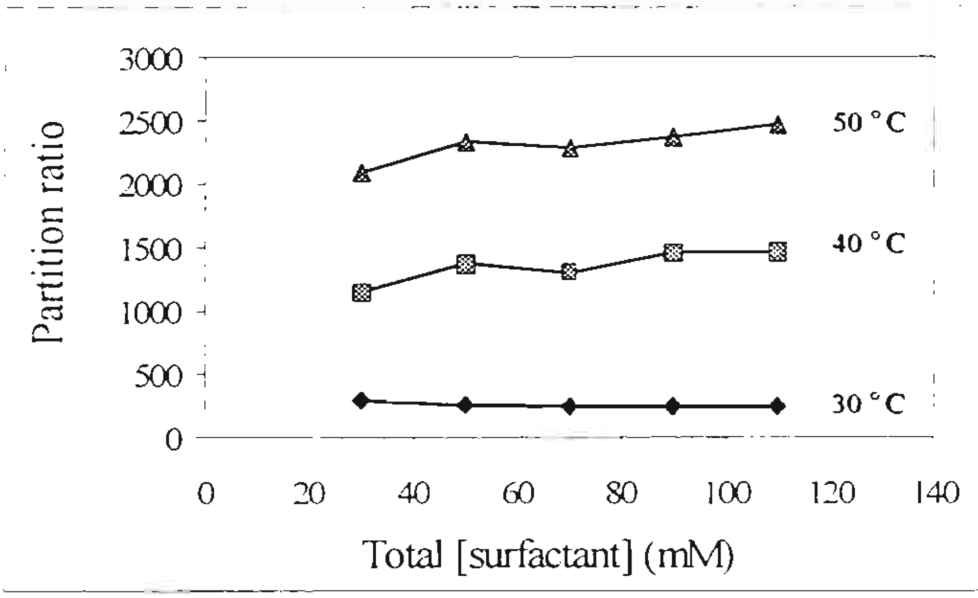

Figure 3. Surfactant partition ratio as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte).

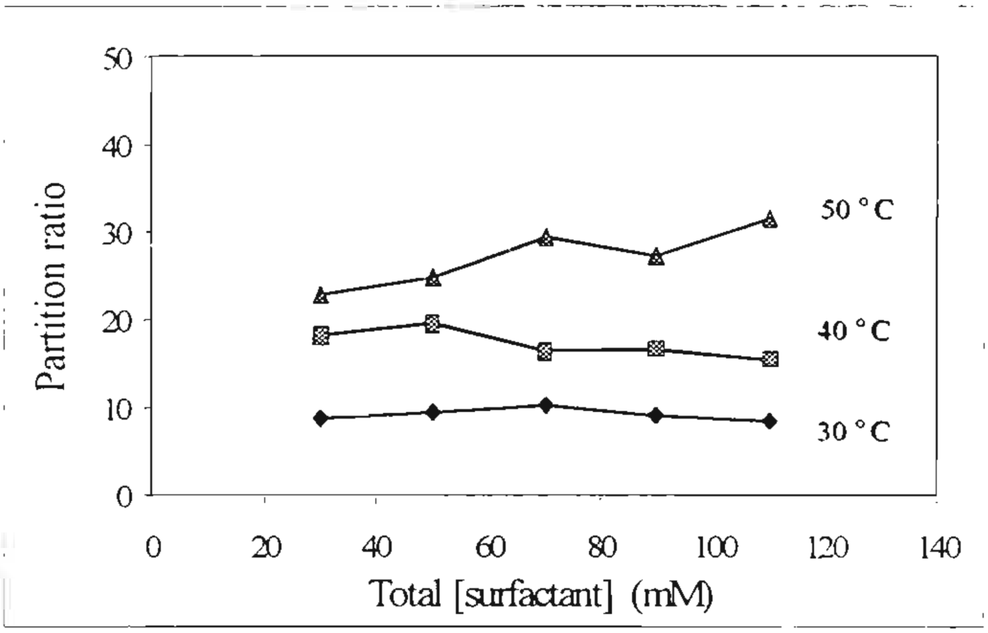

Figure 4. Benzene partition ratio as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte).

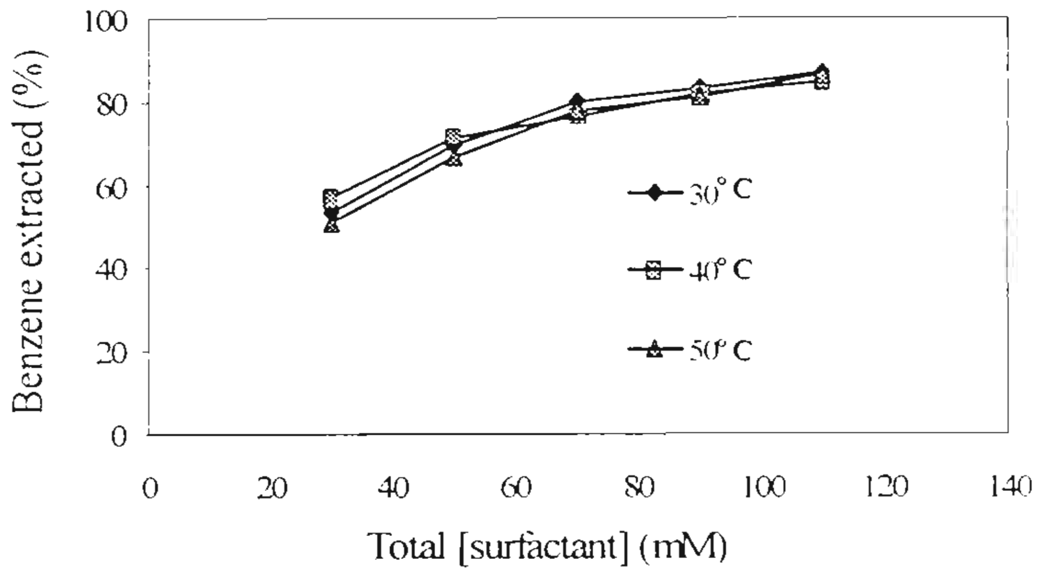

Figure 5. Percentage of benzene extracted in coacervate phase as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte)

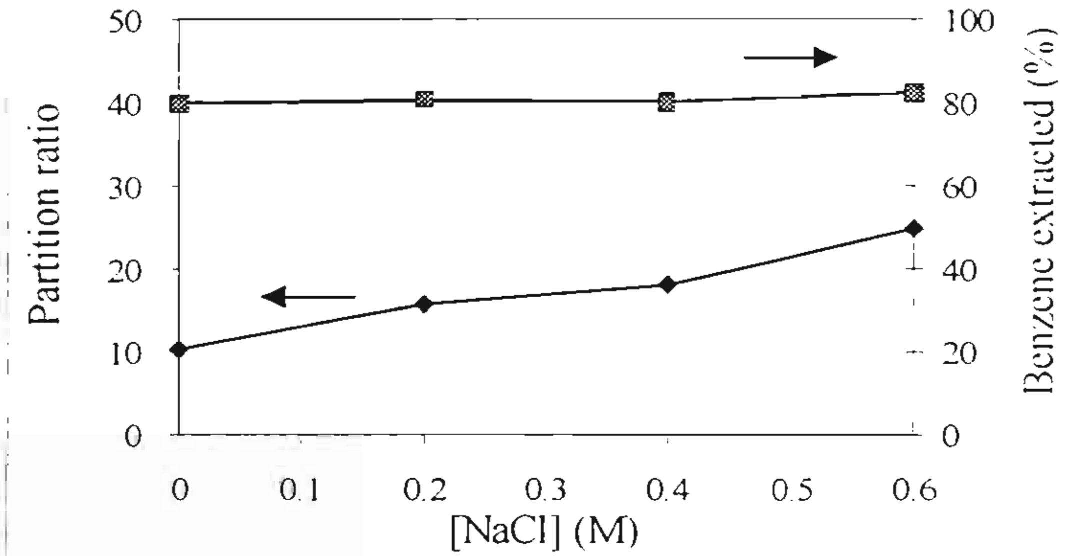

Figure 6. Benzene partition ratio and percentage of benzene extracted in coacervate phase as a function of NaCl concentration (system: 100 ppm benzene, 70 mM surfactant, and 30 °C).

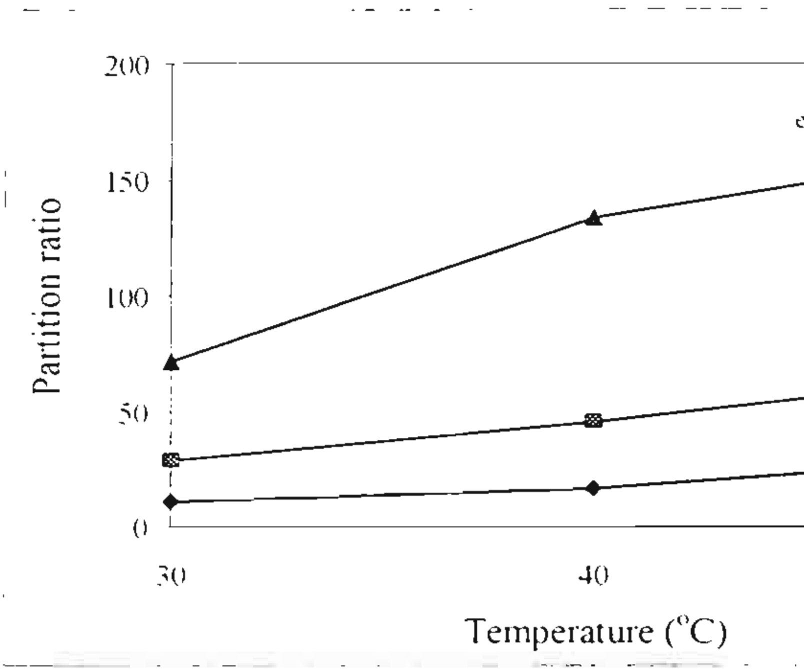

Figure 7. Partition ratio of several aromatic solutes as a function of temperature (system: 100 ppm aromatic solutes, 70 mM surfactant without added electrolyte).

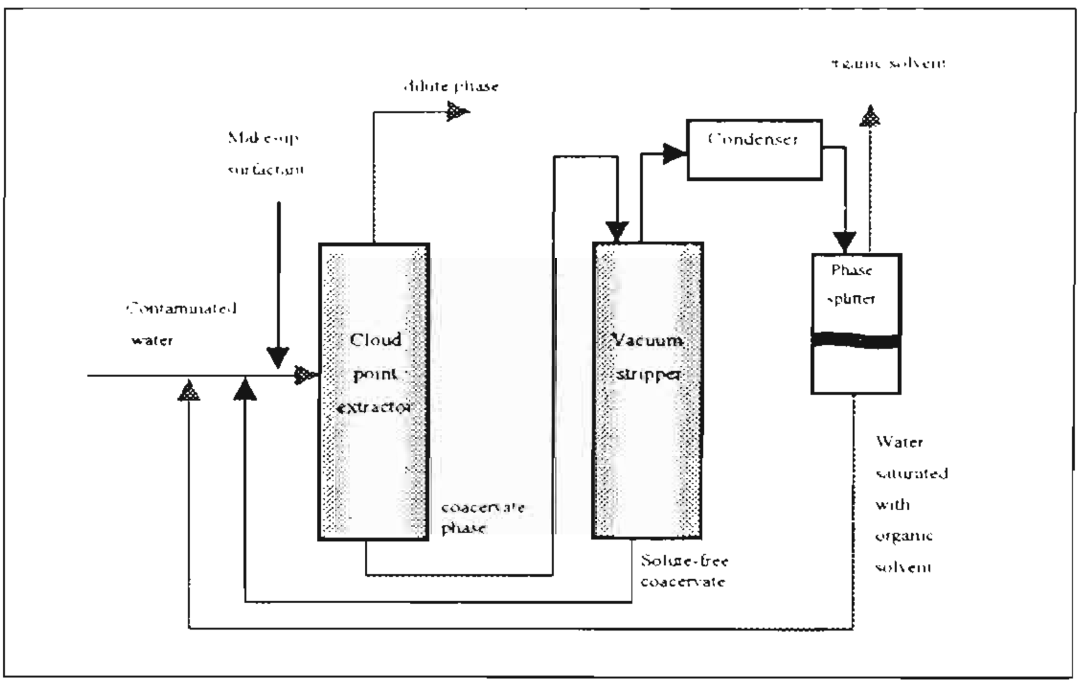

Figure 8. Schematic of integrated process including a multistage cloud point extractor and vacuum stripper.

CHAPTER III

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

ABSTRACT

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

INTRODUCTION

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

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

BACKGROUND

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

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

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

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

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

EXPERIMENTAL

Materials

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

Apparatus: Rotating disk contactor (RDC)

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

Procedures

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

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

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

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

RESULTS AND DISCUSSION

Steady state time analysis

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

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

Effect of agitator speed in CPE of toluene

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

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

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

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

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

Effect of solute structure in CPE

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

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

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

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

Comparison of extraction performance between batch and continuous operation

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

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

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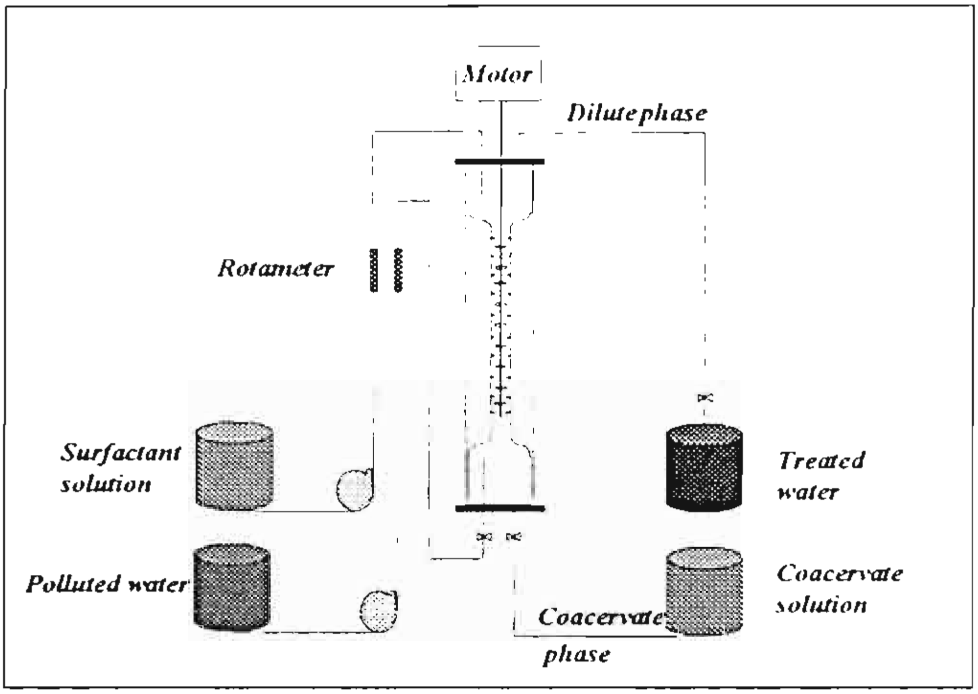

Figure 1. A schematic diagram of the cloud point extraction pilot plant.

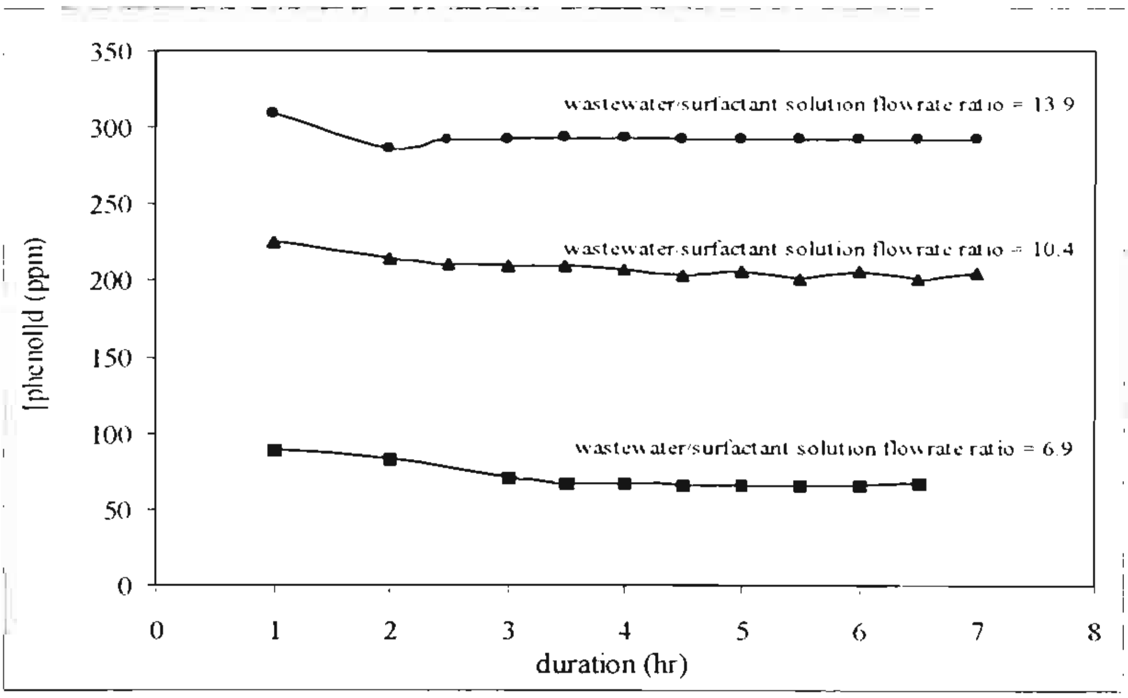

Figure 2. Phenol concentration in dilute phase stream (d) as a function of operating time (system: 500 ppm phenol, 300 mM surfactant solution, 150 rpm agitator speed, and 40 °C).

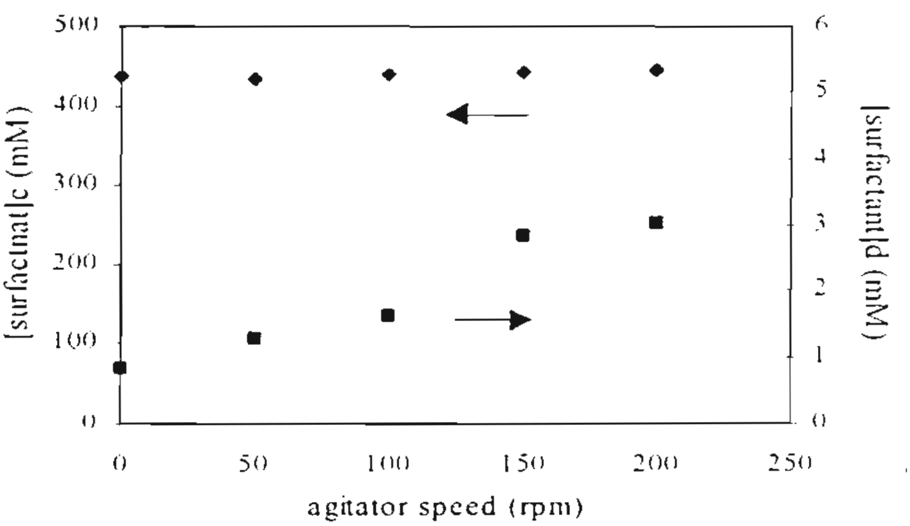

Figure 3. Surfactant concentration in coacervate stream (c) and dilute phase stream (d) as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C).

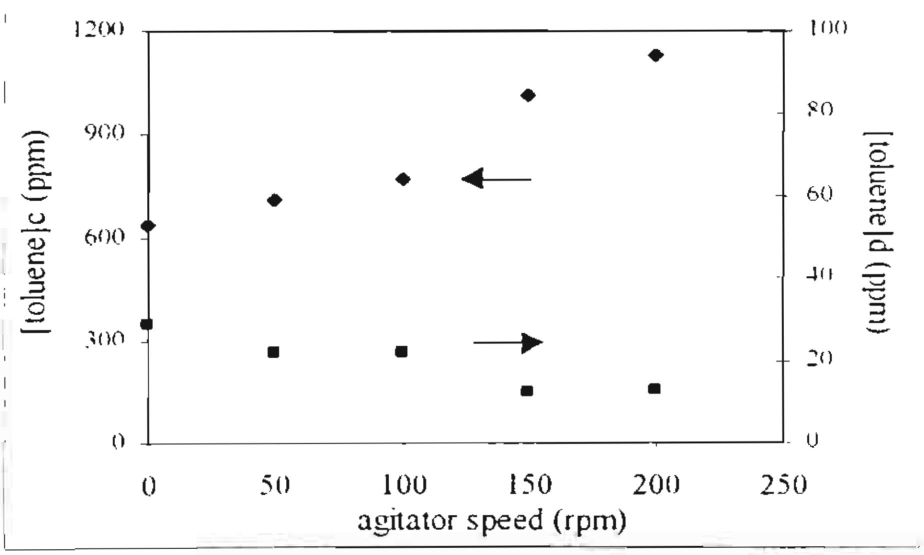

Figure 4. Toluene concentration in coacervate stream (c) and dilute phase stream (d) as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C).