การสกัดเตตระคลอโรเอทิลีนจากน้ำเสียโดยเทคนิคการแบ่งวัฏจักรของสารละลายลดแรงตึงผิว : การเพิ่มประสิทธิภาพด้วยการเติมตัวเชื่อมที่ชอบน้ำมันและสารลดแรงตึงผิวชนิดไม่มีประจุ

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TETRACHLOROETHYLENE REMOVAL FROM WASTEWATER USING A PHASE SEPARATION OF CATIONIC AND ANIONIC SURFACTANT MIXTURES: EFFICIENCY ENHANCEMENT BY LIPOPHILIC LINKERS AND NONIONIC SURFACTANTS ADDITION

Miss Suthida Khaolerk

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for the Degrees of Master of Science Program in Environmental Management
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Thesis Title	Tetrachlorothylene Removal from Wastewater using a Phase Separation of Cationic and Anionic Surfactant Mixtures: Efficiency Enhancement by Lipophilic Linkers and Nonionic Surfactants Addition
By	Miss Suthida Khaolerk
Field of Study	Environmental Management
Thesis Advisor	Punjaporn Weschayanwiwat, Ph.D.
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สุฐิดา ขาวฤกษ์ : การสกัดเตตระคลอโรเอทิลีนจากน้ำเสียโดยเทคนิคการแบ่งวัฏภาคของสารละลายลดแรงแรงตึงผิว: การเพิ่มประสิทธิภาพด้วยการเติมตัวเชื่อมที่ชอบน้ำมันและสารลดแรงตึงผิวชนิดไม่มีประจุ. (TETRACHLOROETHYLENE REMOVAL FROM WASTEWATER USING A PHASE SEPARATION OF CATIONIC AND ANIONIC SURFACTANT MIXTURES: EFFICIENCY ENHANCEMENT BY LIPOPHILIC LINKERS AND NONIONIC SURFACTANTS ADDITION) อ. ที่ปรึกษา: ดร. ปัญจพร เวชยันต์วิวัฒน์, อ.ที่ปรึกษาร่วม: ศ.ดร. จอห์น สเกมีฮอห์น 94 หน้า. ISBN 974-14-2542-2.

เตตระคลอโรเอทิลีนเป็นสารระเหยไฮโดรคาร์บอนที่ใช้เป็นตัวทำละลายพบได้บ่อยในอุตสาหกรรมที่มีการล้างไขออกจากแผ่นโลหะและอุตสาหกรรมการซักแห้ง สารเตตระคลอโรเอทิลีนที่เข้มข้มสูงสามารถพบในน้ำพื้นผิวและน้ำใต้ดิน การวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาวิธีการสกัดแบบใหม่เรียกว่าเทคนิคการแบ่งวัฏภาคของสารละลายของสารลดแรงแรงตึงผิว (ASTP) โดยการผสมระหว่างสารลดแรงแรงตึงผิวชนิดประจุบวกและสารลดแรงแรงตึงผิวชนิดประจุลบเพื่อทำให้สารเตตระคลอโรเอทิลีนถูกสกัดออกจากน้ำเสีย เทคนิคการแบ่งวัฏจักรของสารละลายลดแรงแรงตึงผิวมีลักษณะเฉพาะคือการที่สารละลายของสารลดแรงแรงตึงผิวผสมสามารถแบ่งออกเป็นสองวัฏภาค วัฏภาคหนึ่งประกอบไปด้วยไมเซลล์จำนวนมากซึ่งเกิดจากการรวมตัวกันของสารลดแรงแรงตึงผิวจำนวนมากและสารมลพิษที่ละลายอยู่ภายในก็มากเช่นกัน อีกวัฏภาคหนึ่งมีไมเซลล์จำนวนน้อยประกอบไปด้วยสารลดแรงแรงตึงผิวและสารมลพิษจำนวนน้อย ดังนั้นวัฏภาคนี้จึงเปรียบเสมือนน้ำที่ได้รับการบำบัดแล้ว การศึกษาขั้นแรกคือการเลือกระบบที่เหมาะสมสำหรับเทคนิคการแบ่งวัฏภาคของสารละลายของสารลดแรงแรงตึงผิว จากการทดลองเบื้องต้นพบว่าระบบที่เหมาะสมคือ การผสมของสารลดแรงตึงผิชนิดประจุบวก (DTAB) และประจุลบ (DOWFAX 8390) ที่อัตราโดยโมลที่ 2 : 1 การศึกษาผลของความเข้มข้นของสารละลายของลดแรงตึงผิวผสมกระทำที่ความเข้มข้นในช่วง 30 มิลลิโมลาร์ ถึง 110 มิลลิโมลาร์ พบว่าที่ความเข้มข้นของสารละลายของสารลดแรงตึงผิวผสม 70 มิลลิโมลาร์มีความเหมาะสมมากที่สุดโดยมีประสิทธิภาพในการสกัดสารเตตระคลอโรเอทิลีนออกจากน้ำเสียถึง 91.4 % หรือเพียง 8.6 พีพีเอ็มของสารเตตระคลอโรเอทิลีนเหลืออยู่ในวัฏภาคที่มีสารละลายลดแรงแรงตึงผิวจำนวนน้อยจากระดับความเข้มข้นเริ่มต้นของสารเตตระคลอโรเอทิลีนที่ 100 พีพีเอ็ม นอกจากนั้นยังพบว่าการเติมตัวเชื่อมที่ชอบน้ำมัน (แอลกอฮอล์ที่เป็นโซ่ตรง ออกทานอล โดเดกคานอล และเฮ็กซะเดกคานอล) และสารลดแรงตึงผิวชนิดไม่มีประจุ (TX-114 และ TX-100) สามารถเพิ่มประสิทธิภาพในการสกัด การเติมสารลดแรงตึงผิวชนิดไม่มีประจุในประมาณเพียง 2 มิลลิโมลาร์ สามารถเพิ่มประสิทธิภาพในการสกัดสารเตตระคลอโรเอทิลีนเป็น 96 % หรือประมาณ 4 พีพีเอ็มของสารเตตระคลอโรเอทิลีนเหลืออยู่ในวัฏภาคที่มีสารละลายลดแรงแรงตึงผิวจำนวนน้อย และพบว่าในการศึกษาผลการเติมแอลกอฮอล์ทั้งสามชนิด โดเดกคานอลแสดงประสิทธิภาพสูงสุดในการเพิ่มความสามารถในการสกัดสารเตตระคลอโรเอทิลีน โดยสามารถเพิ่มการสกัดสารเตตระคลอโรเอทิลีนได้ถึง 98 % ภายใต้การสกัดแบบขั้นตอนเดียวโดยการเติมโดเดกคานอลที่ความเข้มข้นเพียง 0.1 มิลลิโมลาร์เท่านั้น อย่างไรก็ตามพบว่าความเข้มข้นของสารลดแรงตึงผิวชนิดไม่มีประจุและแอลกอฮอล์ไม่มีนัยสำคัญต่อการเพิ่มประสิทธิภาพในการสกัดสารเตตระคลอโรเอทิลีน

สาขาวิชา....การจัดการสิ่งแวดล้อม..... ลายมือชื่อนิสิต Suthida Khaolerk

ปีการศึกษา....2549..... ลายมือชื่ออาจารย์ที่ปรึกษา

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม John Scamehorn

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KEY WORD: PHASE SEPARATION / CATIONIC AND ANIONIC SURFACTANTS / TETRACHLOROETHYLENE EXTRACTION / PRECONCENTRATION

SUTHIDA KHAOLERK: TETRACHLOROETHYLENE REMOVAL FROM WASTEWATER USING A PHASE SEPARATION OF CATIONIC AND ANIONIC SURFACTANT MIXTURES: EFFICIENCY ENHANCEMENT BY LIPOPHILIC LINKERS AND NONIONIC SURFACTANTS ADDITION. THESIS ADVISOR: PUNJAPORN WESCHAYANWIWAT, Ph.D., THESIS COADVISOR: PROF. JOHN F. SCAMEHORN, Ph.D., 94 pp. ISBN 974-14-2542-2.

Tetrachloroethylene (PCE) is a volatile chlorinated hydrocarbon commonly used as a solvent in metal degreasing and dry cleaning industries. A high concentration of PCE can be evidently found in the surface water and groundwater. This research aimed to investigate a novel separation technique called aqueous surfactant two-phase system (ASTP) using mixtures of cationic and anionic surfactants to preconcentrate and extract PCE from wastewater. The ASTP system has a unique characteristic where an aqueous surfactant solution can separate into two micellar phases. One is the surfactant-rich phase containing most of surfactant aggregates and solubilized pollutants; and the other is the surfactant-dilute phase which contains only small amount of surfactants and pollutants as treated water. The preliminary study on surfactant system selection reveals that the suitable cationic and anionic surfactants composition forming a stable ASTP system is DTAB:DOWFAX 8390 at molar ratio of 2:1. The total surfactant concentration was investigated in the range of 30 to 110 mM and found that the total surfactant concentration of 70 mM is the most suitable working condition in which the fraction of PCE removal is 91.4% or only 8.6 ppm of PCE remains in the surfactant-dilute phase from the original PCE concentration of 100 ppm. Moreover, an addition of lipophilic linkers (long straight chain alcohols; *n*-octanol, *n*-dodecanol, and *n*-hexadecanol) and nonionic surfactants (POE surfactants; TX-114 and TX-100) was found to enhance the PCE solubilization of this ASTP system. An addition of small amount of nonionic surfactant (2 mM) can greatly increase the fraction of PCE removal to about 96 % or only 4 ppm of PCE is left in the surfactant-dilute phase. Among three alcohols studied here, *n*-dodecanol shows the greatest ability to enhance the PCE solubilization, in which up to 98% of PCE is extracted within single stage with an addition of 0.1 mM dodecanol only. However, the concentrations of nonionic surfactants and alcohols added do not have significant effect onto the PCE removal efficiency.

Field of study..Environmental Management.... Student's signature.....Suthida Khaolerk

Academic year.....2006..... Advisor'ssignature.....

Co-advisor's signature....John Scamehorn

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ABBREVIATIONS

Abs	Absorbance
ADPODS	Alkyl Diphenyl Oxide Disulfonate
ASTP	Aqueous Surfactant Two-Phase System
CMCs	Critical Micelle Concentrations
C_t	Total Concentration
°C	Degree Centigrade
DNAPL	Dense Non-Aqueous Phase Liquid
DTAB	Dodecyltrimethylammonium Bromide
EO	Ethylene Oxide
EPA	Environmental Protection Agency
°F	Fahrenheit
FID	Flame Ionized Detector
GC	Gas Chromatograph
g/mL	Gram per milliliter
g/mol	Gram per mole
IARC	International Agency for Research on Cancer
M	Molar
MCL	Maximum Contaminant Level
mg/L	Milligram per Liter
mM	Millimole
mm Hg	Millimeters of Mercury
MW	Molecular Weight
nm	Nanometer
OSHA	Occupational Safety and Health Administration
PAH	Polycyclic Aromatic Hydrocarbons
PCE	Tetrachloroethylene or Perchloroethylene
POE	Poly Oxy Ethylene
ppm	Parts per Million
SMDNS	Sodium Mono- and Dimethyl-Naphthalene Sulfonate

TX-114	Octylphenol Polyethoxylate (EO = 7.5)
TX-100	Octylphenol Polyethoxylate (EO = 9.5)
USTs	Underground Storage Tanks
UV-VIS	UV-Visible Spectrophotometer
VOCs	Volatile Organic Compounds

CHAPTER I

INTRODUCTION

1.1 Introduction

Tetrachloroethylene (PCE) is a volatile chlorinated hydrocarbon commonly used as solvent in metal degreasing and dry cleaning industries. Like many chlorinated hydrocarbons, PCE is a central nervous system depressant, and inhaling its vapors (particularly in closed, poorly ventilated areas) can cause dizziness, headache, sleepiness, confusion, nausea, difficulty in speaking and walking, unconsciousness, and death (http://en.wikipedia.org/wiki/Tetrachloroethylene). Major environmental releases of PCE generate as air emissions due to its relatively low volatility. Although, air emission is a major release of PCE to the environment, PCE was evidently found loaded to the surface water and groundwater over a hundred thousand pounds (http://www.epa.gov/ OGWDW/dwh/t-voc/tetrachl.html). The maximum contaminant level (MCL) of PCE in drinking water recommended by U.S. EPA is 5 μg/L (Agency for Toxic Substances and Disease Registry). According to a stable structure of PCE, once it persists in the environment, it will cause vital effects to the environment, animals, and human health. Therefore, the wastewater containing PCE substances must be remediated using an appropriate technology.

This research aimed to investigate a novel separation technique called aqueous surfactant two-phase (ASTP) system using mixtures of cationic and anionic surfactants to preconcentrate and extract PCE from wastewater. The ASTP system has a unique feature that a phase separation of aqueous surfactant solution can be induced at specific surfactant compositions and concentrations forming two isotropic micellar phases (Zhao and Xiao, 1996; Kunanupap, 2004; and Krutlert, 2004). One phase is generally less in volume so called the surfactant-rich phase but contains most of surfactant aggregates with organic contaminants solubilized in an interior region. Another phase is dilute in surfactant micelles known as the surfactant-dilute phase, thus containing only small amount of contaminant as treated water. The ASTP technique does not merely remove the contaminants from wastewater but also preconcentrate the contaminants in the

concentrated form of the surfactant-rich phase, thus reducing the volume of the effluence for further treatment processes or final disposal.

The ASTP is a promising technique due to its high extraction efficiency, process stability and yielding less volume of the surfactant-rich phase (Kunanupap, 2004; and Krutlert, 2004). Moreover, the ASTP technique applies surfactants as an extractant, which has less toxicity and thus, more environmentally friendly as compared to other systems using toxic and flammable solvents as the extractant. Since PCE is a polar organic compound as compared to PAHs or straight chain hydrocarbons, i.e., *naphalene, n*-alkane, the solubilization of PCE into the surfactant aggregates is expected to be lower than that of non-polar organic compounds. Sabatini et al, 2003 found that the solubilization of chlorinated hydrocarbon can be enhanced by an addition of linkers in the microemulsion system. Therefore, it is expected that an analogous effect can be achieved in the system of cationic-anionic surfactant mixtures in such a way that the additives such as lipophilic linker and nonionic surfactants can enhance the solubilization of PCE into the surfactant aggregates. As a result, the preconcentration and extraction efficiency of PCE from wastewater can be increased in a greater extend. In this research, the effect of additives, lipophilic linkers (octanol, dodecanol, and hexadecanol) and nonionic surfactants (Triton X-100 and Triton X-114) have been investigated for PCE removal from wastewater. The obtained results have been compared to the ASTP system without additives.

The preliminary study on surfactant system selection reveals that the suitable cationic and anionic surfactants forming a stable phase separation are dodecyltrimethylammonium bromide (DTAB) and alkyl diphenyloxide disulfonate (ADPODS or DOWFAX 8390), respectively. The appropriate surfactant composition is 2:1 molar ratio of DTAB:DOWFAX 8390, in which there is no surfactant precipitation. The total surfactant concentration can be in the range of 30-110 mM.

1.2 Objectives

The main objective of this study was to apply the ASTP technique using mixtures of cationic and anionic surfactants to preconcentrate and extract PCE from wastewater. The sub objectives were:

1. To find out the suitable cationic-anionic surfactant total concentration to extract PCE from wastewater using the ASTP technique.
2. To determine the effect of additives, i.e. lipophilic linkers and nonionic surfactants on the extraction efficiency of PCE by altering the concentration and type of additives.
3. To determine the critical micelle concentrations (CMCs) of cationic-anionic surfactant solution in the presence and absence of additives.

1.3 Scope of the study

The ASTP systems formed by mixtures of cationic-anionic surfactants (DTAB:DOWFAX 8390) at various total surfactant concentration were used to remove PCE from wastewater. The effect of additives addition was also investigated in this research for PCE removal efficiency. Two additives were used which are polyoxyethylenated (POE) alkylphenol nonionic surfactant and long straight chain alcohols. The POE alkylphenol nonionic surfactant with varied ethylene oxide (EO) unit, namely Triton X-100 with EO of 9 units and Triton X-114 with EO of 7 units were used in order to investigate the effect of extended EO groups at the hydrophilic head portion. The effect of EO unit and its concentration on the PCE extraction efficiency were investigated. The second additive was lipophilic linkers, which were *n*-alcohols varied alkyl chain length C8, C12, and C16 (octanol, dodecanol, and hexadecanol). The extension of alcohols carbon chain length and its concentration onto the PCE removal was studied. The comparison on PCE removal efficiencies were revealed to find out whether the nonionic surfactant varied hydrophilic moiety or the lipophilic linker varied the hydrophobic moiety plays more roles on solubilization enhancement of PCE in the ASTP extraction system.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

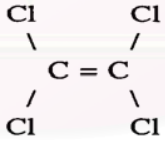
2.1 Tetrachloroethylene

2.1.1 Introduction

Tetrachloroethylene sometime called Perchloroethylene (PCE) is a commercially important chlorinated hydrocarbon solvent and chemical intermediate. PCE is widely used for dry-cleaning clothes, degreasing metal parts, and as an ingredient in the manufacturing of other chemicals such as typewriter correction fluid and shoe polish. Since PCE is able to dissolve many organic compounds, select inorganic compounds, and high-melting pitches and waxes, it can be used to clean and dry contaminated metal parts and other fabricated materials.

2.1.2 Identity, Physical and Chemical Properties

2.1.2.1 Identity

Chemical structure :	
Chemical formula :	C_2Cl_4
CAS number :	127-18-4
Common name :	Tetrachloroethylene
HSDB:	124 (#49 403 55)
Common synonyms :	Ethylene tetrachlororide, per, perc, perchlor, perchloroethylene, perk, PCE, (1,1,2,2)-tetrachloroethylene
Molecular weight :	165.83

2.1.2.2 Physical and Chemical Properties

PCE is an unsaturated aliphatic chlorinated hydrocarbon compound composed of the C=C double bonds with the presence of 4 chlorine atoms. PCE is a colorless liquid having less viscous but greater density than water. It is classified as a dense non aqueous phase liquid (DNAPL). It can dissolve slightly in the water. The principle physical and chemical properties of PCE are shown in Table 2.1.

Table 2.1 Some physical and chemical properties of PCE.

Physical state (at room temperature)	Liquid
Color	Colorless
Odor	Ethereal
Odor Threshold: Water Air	0.3 ppm 1.0 ppm
Melting/freezing point	-22.3 ºC
Boiling point	121.3 ºC
Density (@20 ºC)	1.6227 g/cm^3
Relative vapor density (air = 1)	5.7
Vapor pressure (@25 ºC)	18.5 mm Hg
Solubilities: (at room temperature) Water and Organic solvent(s)	150 mg/L Miscible with alcohol, ether, chloroform, benzene, hexane, and most of the fixed and volatile oils
Partition Coefficients: Log K_{ow} Log K_{oc}	3.40 2.2-2.7
Henry's law constant (@25 ºC)	1.8*10^{-2} atm-m^3/mol
Flashpoint	None
Flammability Limits	Nonflammable

2.1.3 The Effect of PCE in Environment

PCE is a volatile organic compound that is widely distributed in the environment. It is mainly released to the environment via industrial emissions. PCE enters to environment mostly by evaporating into the air. However, it can also get into water supplies and soil during disposal of sewage sludge or when there is leaking of underground storage tanks (USTs). PCE is quite persistence and can be present in the air for several months before it is broken down into other chemicals and transform to the soil and water by rain. PCE get through soils quite easily and can get into the underground drinking water supplies. If it gets into groundwater, it may stay there for several months without being broken down. Under some conditions, PCE may stick to the soil, present in surface water and contaminate into water sources, groundwater, and aquatic life.

2.1.4 Effects on Humans

The effects of PCE on human health depend greatly on how much PCE is exposed, and the length and frequency of exposure. Short-term exposure to high concentration of PCE can cause dizziness, headaches, sleepiness, confusion, and nausea. Only people working directly with PCE in closed, poorly ventilated areas are likely to be at risk for such an exposure. Contact with PCE in its liquid or vapor form can irritate the skin, eyes, nose and throat (http://www.cdphe.state.co.us/hm/drycleaner.pdf). Exposure to 100-200 ppm for 5-7 hours has produced headaches, drowsiness, dizziness and sleepiness. A 5-7 minutes exposure to 2000 ppm causes volunteers to feel as though they are going to collapse. A few deaths have been reported due to central nervous system depression and irregular heart beat (http://www.ccohs.ca/oshanswers/chemicals/chem_profiles/tetrachloroethylene/health_tetra.html).

Long-term exposure in animal studies conducted with amounts much higher than with people would be exposed to, show PCE can cause liver and kidney damage. In addition, the U.S. Department of Health and Human Services has determined that PCE may reasonably be anticipated to be a carcinogen or cancer-causing agent (http://www.cdphe.state.co.us/hm/drycleaner.pdf). Moreover, the International Agency

for Research on Cancer (IARC) has concluded that there are limited evidences for the carcinogenicity of PCE in humans. There are sufficient evidences for carcinogenicity in animals. The IARC classifies that PCE is probably carcinogenic to humans (Group2A) (http://www.ccohs.ca/oshanswers/chemicals/chem_profiles/tetrachloroethylene/health_tetra.html).

2.1.5 Regulation

According to the US EPA, recent federal regulations prohibit that any solid waste containing PCE must be listed as a hazardous waste unless the waste is shown not to endanger the health of humans or environment (EPA 1985b, 1988). The EPA maximum contaminant level for the amount of PCE that can be in drinking water is 0.005 milligrams PCE per liter of water (mg/L) (0.005 ppm). OSHA limits the amount of PCE that can be present in the environment is limited to 100 ppm for an 8-hour workday over a 40-hour workweek.

2.2 Surfactant

2.2.1 Characteristic of surfactants

Surfactant (surface active agent) is a substance that improves contact between surfaces of two substances. Especially, when present at low concentration in a system, surfactant has a property of adsorbing onto the surface or interface of the system (Rosen 1989). Surfactants generally reduce the surface tension between two immiscible phases by decreasing the dissimilarity between two phases, which surfactant itself acts as a linkage between two phases leading to a decline of surface tension. Surfactants are amphiphilic molecules comprising of two opposite characteristics (polar and non polar) in the same molecule. Therefore, a surfactant molecule has both hydrophilic (water-like) and hydrophobic (oil-like) characteristics. Thus, surfactants can dissolve in both water or oil solution and also have an ability to solubilize either water or oil to form a homogeneously solution.

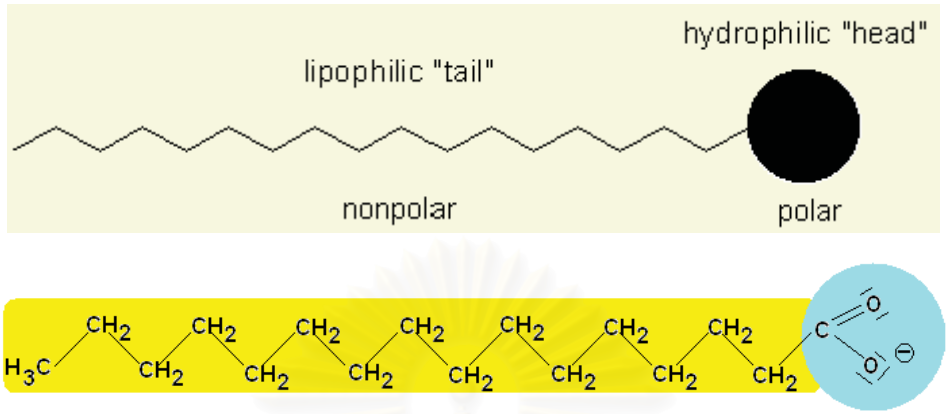


Figure 2.1 Surfactant molecules (monomer)

Two unique properties of surfactants are its ability to adsorp at interfaces and self-assemble into clusters. For adsorption phenomenon, surfactant monomers are usually found at the interface between two immiscible liquid phases or a liquid phase and an air phase. This molecular property leads to the macroscopic properties of wetting, foaming, detergency and emulsion formation. Self-assembly is a tendency for surfactant molecules to organize themselves into extended structures in water. This includes the formation of micelles, bilayers and liquid crystals.

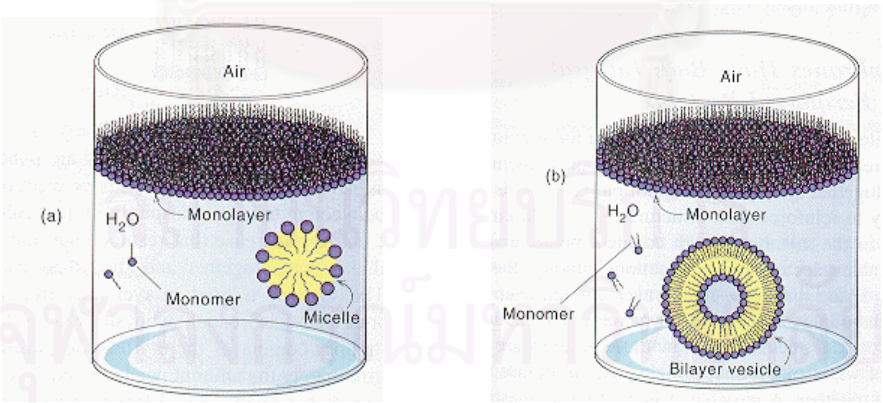


Figure 2.2 Formation of (a) micelle and (b) bilayer structure in aqueous solution

2.2.2 Types of surfactants

Types of surfactants are based on the charge of their hydrophilic head group (Rosen, 1989; http://encyclopedia.thefreedictionary.com/surfactant), which can be classified into 4 types as shown below:

- **Anionic:** Surfactants bear negative charge at the hydrophilic head. Anionic surfactants are the most widely used surfactant. Since they are more specialized and commonly used as detergents (laundry and dishwashing) and household cleaners. Examples of anionic surfactants are alkyl benzenesulfonates, alkyl sulfonates and alkyl phosphates.

- **Cationic:** Surfactants bear positive charge at the hydrophilic head. Cationic surfactants are generally used less in frequency but one group, the ethoxylated fatty amines. Cationic surfactants are widely used in fabric softener, laundry detergents, and some household cleaners.

- **Nonionic:** Surfactants that contain no ionic charge at the hydrophilic head. Nonionic surfactants are the second popular used next to anionic surfactants, which can be accounted to be about 45% as they are less costly than other types of surfactants. The predominant use of these surfactants is in foods and drinks, pharmaceuticals and skin-care products. Examples of nonionic surfactants are alcohol ethoxylates and alkylphenol ethoxylates.

- **Zwitterionic:** Surfactants that carry both positive and negative charges depended on the pH. Zwitterionic surfactants are very expensive and considered to be specialty surfactants as

their use is fairly limited such as in skin-care products. Examples of zwitterionic surfactants are ammonium carboxylate, ammonium sulfate and amine oxide.

2.2.3 Micelle formation

The unique property of surfactants is micelle formation, which will occur when surface-active molecules forming colloidal-sized clusters in the solution. The concentration of surfactant when this phenomenon occurs is called the critical micelle concentration (CMC) as shown below:

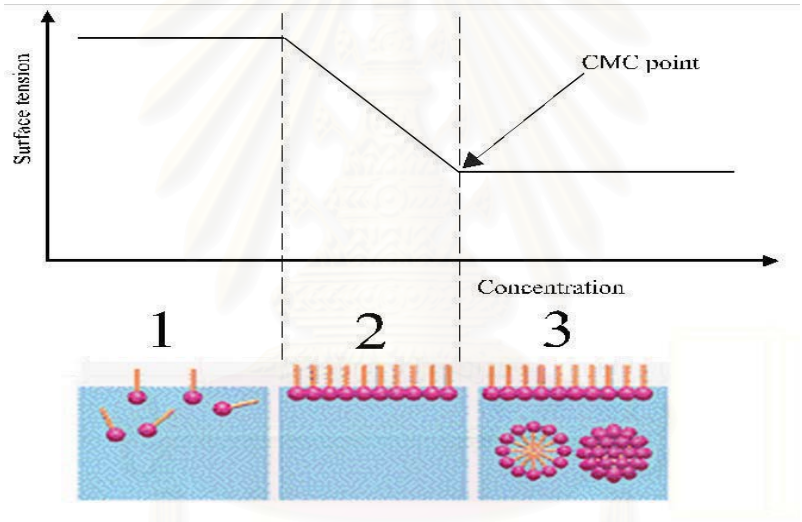


Figure 2.3 Micelle formation

From Figure 2.3, the micelle formation phenomenon starts when the surfactant molecules (monomers) are dissolved in water at low concentration. Then the hydrophobic groups (tail moiety) distort the structure of water and reorient themselves until the hydrophobic tails direct away from water. After the interface is filled with surfactant monomers, an increase in surfactant concentration in the solution will result in an aggregation of surfactant monomers into clusters called micelles. In the clusters, the hydrophobic tails will be oriented toward the interior of the cluster and the hydrophilic head will be directed toward water (Rosen, 1989).

Moreover, CMC value can be observed by various parameters as shown in the Figure 2.4. Surface tension, osmotic pressure, light scattering, solubilization, turbidity, conductivity and self-diffusion can be used to determine the CMC. However, surface tension is the most common physical property used to investigate the CMC.

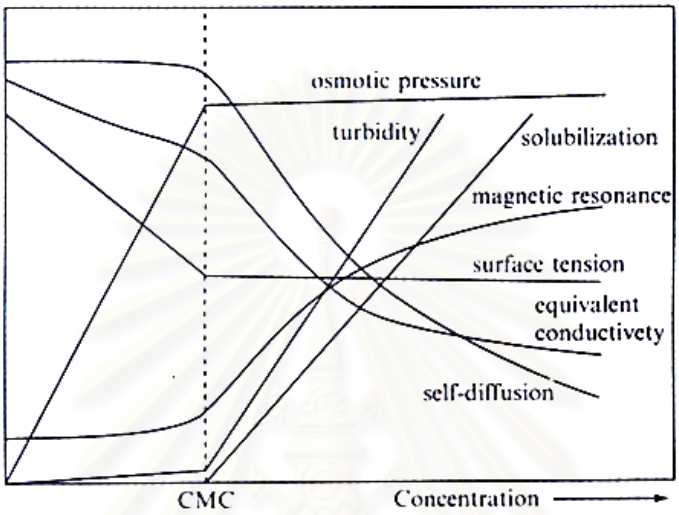


Figure 2.4 Determination of CMC

It is generally accepted that the rapid change in the concentration curve is due to the formation of aggregates of micelles in the solution. Considering micelles in aqueous solution, their tails form a core that is like an oil droplet, and their heads form an outer shell that maintains favorable contact with water. However, when surfactants assemble in oil, the aggregate is referred to as a reverse micelle as shown in Figure 2.5. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil.

(a) Normal Micelle **(b) Reverse Micelle**

Figure 2.5 Formation of Micelle (a) Normal micelle (b) Reverse micelle

The form of micelle structure depends on the molecular architecture of amphiphilic compounds, solution composition, and temperature. The structure of surfactants can be in various forms as shown in the Figure 2.6.

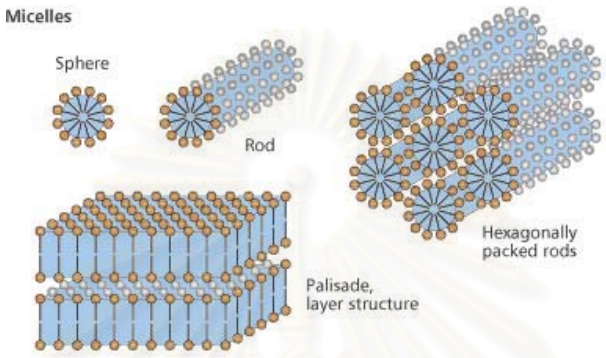
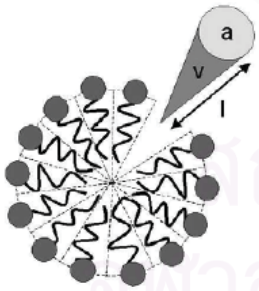


Figure 2.6 The aggregation structures of surfactants

Structure of micelle is characterized by the area (a_0) occupied by the hydrophilic group in the core, the length (l_c) of the hydrophilic group in the core and the volume (V_H) occupied by the hydrophilic groups in the micellar core, being combined in the so-called packing parameter (Φ). The packing parameter is calculated by $\mathbf{V_H / l_c a_0}$ (Rosen, 1989; Nagarajan, 2001).



Value of $V_H / l_c a_0$	Structure of micelle
0 - 1/3	Spherical micelle
1/3 - $^1/_2$	Wormlike micelle
$^1/_2$- 1	Bilayer, vesicles
> 1	Reverse micelles

2.2.4 Factors affect to the CMC

Factors affecting the value of the CMC in aqueous media are (I) structure of the surfactant (II) electrolyte (III) organic additives (IV) temperature.

(I) Structure of the surfactant

Hydrophobic group:

- The greater the hydrophilicity, the lower the CMC up to number of carbon equal to 16. The further increase in number of carbons exceeds 18, there is no change in the CMC value.
- For nonionic and zwitterionic surfactants, the decrease in CMC with increase in the hydrophilic group is larger, an increase of 2 methylene groups can decrease the CMC to one-tenth of its previous value.
- An introduction of bulky hydrophobic group may result in an increase in the CMC due to the difficulty of incorporate the bulky hydrophobic group in the interior of a spherical or cylindrical micelle.

Hydrophilic group:

- At the same hydrophilic length, the ionic surfactant has higher CMC than that of zwitterionic and nonionic surfactants due to an electrostatic repulsion force between the hydrophilic head groups.
- For POE nonionic surfactant, the greater the number of ethylene oxide unit, the higher the CMC.
- The mixture of oppositely charge ionic surfactants can greatly decline the CMC.

(II) Electrolyte

- The effect of electrolyte to change the CMC is more pronounced for ionic surfactant than zwitterionic and nonionic surfactants.
- The addition of electrolyte generally decreases the CMC of ionic surfactant due to the electrostatic repulsion are screened out.
- The change in the CMC of the nonionic and zwitterionic surfactants is mainly due to the salting in and salting out effects on the hydrophilic group of the surfactant molecule.

(III) Organic additives

- The effect of organic additives depends on the role of organic additives on the micelle whether it incorporates into the micelle or it modifies the solvent-surfactant interactions.

Class I Materials:

- First types of materials that can affect the CMC of aqueous solutions are such as alcohols and amides. The members of this class change the CMC at low concentration in the bulk phase.
- This type of material reduces the CMC as the shorter-chain lengths of the members are probably adsorbed mainly in the outer portion of the micelle close to the water-micelle (interface).
- While the longer-chain members are probably adsorbed mainly in the outer portion of the core, between the surfactant molecules.
- The straight chain compound can decrease CMC more than branched one.
- In addition, the increase in chain length tends to have a greater effect on CMC reduction that the shorter chain until it reaches a maximum chain length where the hydrophobic chain length of additives is approximately equal to that of surfactant.

Class II Materials:

- Members of this class include urea, formamide, guanidinium salts, N-methylacetamide, short-chain alcohols, water-soluble esters, dioxane ethylene glycol. The members of this class change the CMC, at concentration in the bulk phase much higher that that of Class I material.
- The CMC is changed by modifying the interaction of water with the surfactant molecule or with the micelle, e.g. structure of the water, solubility parameters.
- Urea, formamide, guanidinium salts will increase the CMC of surfactants in aqueous solution, especially, polyoxyethylenated nonionics. This may increase the degree of hydration of the hydrophilic group, thus opposing the micellization resulted in an increase in the CMC.

(IV) Temperature

- The effect of temperature on the CMC of surfactants in aqueous medium is complex. As the value appearing first to decrease with temperature to some minimum and then to increase with further increase in temperature.
- An increase in temperature will decline the hydration of hydrophilic head favoring the micellization. Moreover, temperature increases can also causes disruption of the structured water surrounding the hydrophobic group that may disfavor micellization.

2.2.5 Solubilization

Solubilization is one of the most important properties of surfactants, which is related directly to the micelle formation. Solubilization is an ability to dissolve the water-insoluble hydrophobic molecules (solubilizates) in micelle core which has the oil-like environment (Rosen, 2004). Solubilization is important in many areas such as separation technology, oil recovery enhancement, pharmaceutical application, etc. The significance of this phenomenon is the ability to enhance the solubility of solvent-insoluble material without using organic or cosolvents. At first, the solubility of solute is very slight, but after the surfactant concentration reaches to CMC, the solubility will increase linearly with the surfactant concentration.

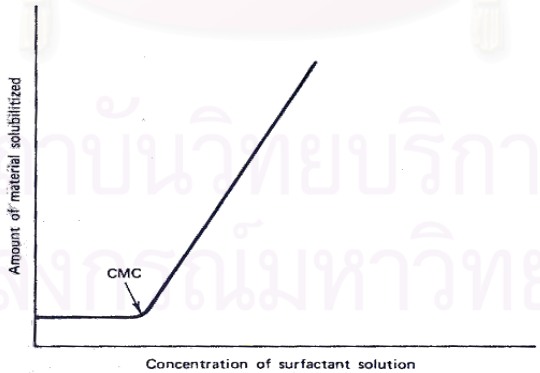


Figure 2.7 Amount of material solubilized with surfactant concentration

2.2.6 Cationic-Anionic surfactant mixtures

Surfactant mixtures are commonly utilized in many surfactant formulations and practical applications because mixtures often exhibit synergistic effect and provide more favorable or desirable properties than the constituent single surfactants (Rosen, M.J., Phenomena in Mixed Surfactant Systems; Scamehorn, J. F., Ed.; ACS Symposium Series 311; American Chemical Society: Washington, DC, 1986). In general, cationic and anionic surfactants are inharmonious because their mixtures often form water insoluble complexes known as precipitates.

The cationic or anionic surfactant alone can be greatly soluble in water due to their ionic charges, while the nonionic surfactant can be soluble in water due to its relatively large hydrophilic head groups (Mehreteab, 1999). However, there are some surfactant compositions that the mixtures of cationic and anionic surfactant can be formed appropriately without forming precipitates, i.e., when the hydrophobic tail group of surfactants are branched and/or contain a bulky substituent such as benzene group; and either one surfactant or both has a large hydrophilic group. In addition, when cationic-anionic surfactants are mixed and their charges are neutralized, it possesses a similar characteristic to the nonionic surfactants. So, it is thought of as the pseudononionic surfactant. The properties of this complex are not only combined from its parent molecule, but also generate some new properties, for instance, a possession of the cloud point phenomenon, which is a unique feature of nonionic and zwitterionic surfactants, high surface activity, and reduction of CMC (Mehreteab, 1999; Minardi, Schulz and Vuan, 2002). The CMC of cationic-anionic surfactant mixtures is much lower than that of anionic or cationic surfactant alone (Xiao et al., 2000).

2.2.7 Aqueous Surfactants Two Phase (ASTP) System

ASTP system is a new surfactant-based separation technique in which a phase separation of aqueous surfactant solution can be induced at specific surfactant compositions and concentrations forming two isotropic micellar phases with a clear interfacial boundary between them. One phase is a surfactant-rich containing most of

surfactant aggregates. The other phase is a surfactant-dilute phase where minority of surfactant aggregates present there. The ASTP of cationic-anionic surfactant mixture is different from the phase separation of single nonionic or zwitterionic surfactant in such a way that the phase separation is induced by changing the surfactant compositions and concentrations not an altering of temperature.

This novel ASTP system has many unique characteristics, for instance, the ASTP system can be obtained at low temperature, while the phase separation of nonionic surfactants take place only above a critical temperature known as cloud point. Thus, the ASTP for partitioning application can be achieved at desired temperature (Xiao et al., 2000). It is worthwhile to note that this benefit is importance for partitioning of biomaterials, i.e. protein, because the conventional ASTP may be effective at high operating temperature causing a protein to denature. Moreover, his studied show that ASTP system is labile and adjustable. Phase behavior, volume ratio and settling time strongly influenced by total concentration and molar ratio of mixed surfactants. Also, it is critical for the partitioning of VOCs due to the fact that the VOCs tend to vaporize if operated at high temperature. Another environmental application of ASTP system has been proposed by Krutlert et al., (2005). They showed that the ability of ASTP system formed by the mixture of cationic-anionic surfactants exhibits the synergistic effect as result of a great reduction in CMC value of the mixtures as compared to the individual ionic surfactant. While the work of Kunanuparp et al., (2005) studied the phase separation of mixture of cationic-anionic surfactants (DTAB and DOWFAX) and its competency to extract benzene from wastewater. Their work evidenced that the main parameters governing the phase separation and benzene extraction efficiency are surfactant composition and concentration, while the effect of operating temperature and pH are less pronounced.

2.3 Effect of additives

2.3.1 Nonionic surfactant

Nonionic surfactants are surfactant molecules without charges in the hydrophilic portion. Nonionic surfactants are useful in the formation of emulsions as the aqueous solutions of nonionic surfactants show complex phase behavior including liquid-liquid phase separation at high temperature (Sharma et al., 2002). Nonionic surfactants exhibit clouding behavior when their aqueous solutions are heated to a certain temperature (cloud point), which is a characteristic of the molecular architecture of nonionic surfactant. It is widely used as solubilizers, emulsifier and detergents in many industrial processes. It has been shown that the nonionic surfactants can increase the surface concentration of soluble organics on non-reactive surfaces such as soil and sediment particle in water (Loraine, 2000).

The addition of nonionic surfactants onto the ionic surfactant system can enhance the solubilization of various solubilizates due to a decline in an electrostatic repulsion between ionic surfactant head groups (Loraine, 2000). However, there is no investigation on the effect of nonionic surfactant addition onto the solubilization of system containing the mixture of cationic and anionic surfactants. Acosta et al., (2004) showed that an increase in the interaction between the surfactant and the aqueous phase can enhance solubilization of chlorinated hydrocarbon such as PCE or TCE in microemulsion system. They used hydrophilic linker such as SMDNS to extend the interaction between surfactant and aqueous solution because the hydrophilic linkers have short hydrophobe and a strong hydrophile. Thus, it is capable to adsorb or segregate nears the surfactant/water interface. Their further investigation confirmed their previous theory such that the hydrophilic linker molecules partially coadsorb with the surfactants at hydrophilic region and certainly expand the interfacial area but do not interact substantially with the oil phase (Acosta et al., 2004). Although the hydrophilic linker is not a nonionic surfactant since it has very short hydrophobic portion as compared to the nonionic surfactant, they are similar in such a way that both of them are strong

hydrophiles and can greatly interact with aqueous phase but do not contain charges on their hydrophilic portions.

2.3.2 Lipophilic linkers

The concept of lipophilic linkers was first introduced by Graciaa et al. (Graciaa et al., 1993). The lipophilic linker by its name meaning oil-loving is a molecule that oriented along the surfactant tails and facilitates the oil molecules to dissolve into the oil phase. Thus, lipophilic linker can be classified as a link between oil molecules and the surfactant tails, for example, it can improve the interaction between surfactant and alkane oil leading to enhance the solubilization capacity of surfactants (Uchiyama et al., 2000). They are two kinds of linker; lipophilic and hydrophilic linkers. These linker molecules enhance the interaction between the surfactant and oil phase (lipophilic linkers) or between the surfactant and water phase (hydrophilic linkers). Lipophilic linker and hydrophilic linker themselves can increase the solubilization capacity but the combination of them would work best. The lipophilic linker can increase the surfactant-oil interaction and hence increase oil solubilization capacity. However, the solubilization enhancement reaches a plateau at certain lipophilic linker concentration. The hydrophilic linker was thereby introduced since it can coabsorb with the surfactant and increase the surfactant-water interaction although its interaction with oil phase is poor due to their short hydrophobic tail (Sabatini et al., 2003).

The combination of lipophilic and hydrophilic linkers (Dodecanol and SMDNS) was studied and the results revealed that the combined linkers can enhance the solubilization of chlorinated hydrocarbons as compared to the lipophilic linker alone (Acosta et al., 2004). This formulation technique shows potential advantage in reducing surfactant costs and remedial times, as well as allowing the use of more environmentally friendly additives when designing surfactant-enhanced remediation systems (Acosta et al., 2002).

As reported by Gracia et al, the long chain alcohols with more than 9 carbons in its tails were used as lipophilic linker. The result showed that the interaction of alcohol

molecules at the oil/water interface varied with the length of the alcohol. They concluded that alcohols with carbons less than 4 show a co-solvent effect resulting in a decline of interaction between surfactants. The alcohols with chain length in the range 3-7 can be considered as co-surfactants. The defining alcohols as cosurfactants arrived from alcohol's function that even medium-chain alcohols dissolve preferentially into the surfactant monolayer rather than being adsorbed at the interfacial layer (Garti et al., 1995). The alcohols with chain length of 8 or higher, they behave as lipophilic linkers by adsorbing at the palisade layer of the surfactant micelle by orienting the hydroxyl group towards the micelle-water interface while alkyl chain orients toward the hydrophobic region. Though, the role of long chain alcohols in surfactant formations was still unclear (Sabatini et al., 2003). So far the research from Tan and O' Haver (2004) proved that the lipophilic linkers (long chain alcohols; *n*-octanol, *n*-decanol, and *n*-dedecanol) have ability to be the effective additives. Since these alcohols capable to enhance the adsolubilization of styrene in the admicelles of nonionic surfactant onto precipitated silica. However, Garti et al., (1995) studied about water solubilization and chain length compatibility in nonionic microemulsions. Interestingly, their work reveals that the water solubilization capacity of a system can increase, decrease, or show a maximum, depending upon the structure and chain length of the alcohol used and the concentration of surfactant and alcohol at the interface.

Finally, in this research we applied to use the condition from the research work of Kunanuparp et al., (2005) whose studied the phase separation of mixture of cationic-anionic surfactants (DTAB and DOWFAX) and its competency to extract benzene from wastewater. We opted to use the suitable condition from their work including a condition of cationic and anionic surfactants forming a stable phase separation of dodecyltrimethylammonium bromide (DTAB) and alkyl diphenyloxide disulfonate (ADPODS or DOWFAX 8390) at an appropriate surfactant composition of 2:1 of DTAB:DOWFAX 8390 molar ratio at controlled temperature of 30 °C.

CHAPTER III

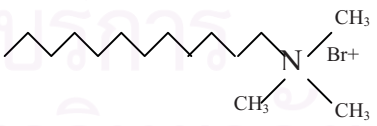
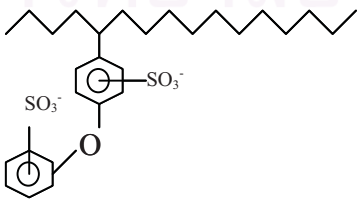
METHODOLOGY

3.1 Materials

3.1.1 Surfactants

Three surfactants were used in this study. Dodecyltrimethylammonium bromide (DTAB) was used as a cationic surfactant purchased from Nanjing Robiot Co., Ltd. (China) with 99% purity. Alkyl diphenyl oxide disulfonate (ADPODS or trade name DOWFAX 8390) was used as an anionic surfactant contributed by DOW chemical Co., Ltd. (USA) with 35% active. Octyl phenol polyethoxylate with ethylene oxide of 7.5 and 9.5 units as trade name of Triton X-114 and Triton X-100 were used as nonionic surfactant additives purchased from DOW chemical Co., Ltd. (USA) with 100% active. The properties of cationic and anionic surfactants were listed in Table 3.1, the properties of nonionic surfactants and alcohols were listed in Table 3.2 and Table 3.3, respectively.

Table 3.1 Physical and chemical properties of surfactants

Chemical Name	Type	Charge	Chemical Formula	Chemical Structure	MW (g/mol)
Dodecyltrimethyl Ammonium Bromide (DTAB)	Cationic	+1	$C_{15}H_{34}BrN$		308.35
Alkyl Diphenyloxide Disulfonate (DOWFAX 8390)	Anionic	-2	$C_{16}H_{33}C_{12}H_7O(SO_3Na_2)$		642

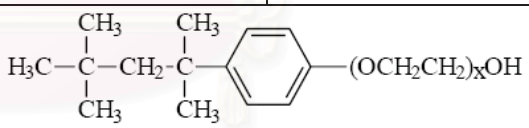
3.1.2 Organic contaminant

The organic contaminant concerned in this research was Tetrachloroethylene or Perchloroethylene (PCE) with 99 % purity purchased from Labscan Asia Co. Ltd. (Thailand).

3.1.3 Additives

Octylphenol polyethoxylate nonionic surfactant with varied EO unit, namely Triton X-100 with EO of 9.5 units and Triton X-114 with EO of 7.5 units) were used as additives purchased from DOW chemical Co., Ltd. with 100% active as previously mentioned. The second additive was long straight chain alcohols varied alkyl chain length from C8 to C12 and C16 (octanol, dodecanol, and hexadecanol) purchased from Merck Ltd. with 99% purity (Germany), Fluka Chemika (Switzerland) with 99.5% purity, and Fluka Chemika (Germany) with 99% purity, respectively.

Table 3.2 Physical and chemical properties of nonionic surfactants

Description	TX-114	TX-100
Molecular structure		
Molecular weight	537	625
Form	Liquid	Liquid
Average EO Units (x)	7-8	9-10
Active Ingredient, %	100%	100%
Color, APHA	100	100
Specific Gravity, 25°/25°C (g/ml)	1.054	1.065
Density (lb/gal)	8.8	8.9
Viscosity, Brookfield [1], at 25°C, cP	260	240
Pour Point [3], °F	15	45
Cloud Point, 1% aqueous solution, °C	22	65
HLB Value (calculated) [4]	12.4	13.5
Surface Area [5], Angstrom^2	50	48-54
Critical Micelle Concentration (CMC)	0.2 mM	0.24 mM
Aggregation Number	--	140

(1) Spindle #2 at 12 rpm (2) Spindle #2 at 30 rpm (3) ASTM D 97-57 (4) HLB (Hydrophile-Lipophile Balance values range from 0 (completely lipophilic or oil-loving) to 20 (completely hydrophilic or water-loving) and are calculated by dividing the weight percent of ethylene in the surfactant by 5. (5) Surface area is the area per molecule in square Angstroms.
[Source: http://www.mpbio.com/product_info.php?cPath=491_1_12&products_id=807423]

Table 3.3 Physical and chemical properties of alcohols

Descriptions	Octanol	Dodecanol	Hexadecanol
Chemical Structure			
Molecular Formula	$C_8H_{18}O$	$C_{12}H_{26}O$	$C_{16}H_{34}O$
Molecular Weight	130.22	186.33	242.45
Color/Form	Colorless liquid	Colorless liquid	Solid white crystals
Odor	Fresh, orange-rose odor	Fatty odor	Odorless
Taste	Oily, sweet	Fatty, waxy flavor	Bland, Mild taste
Boiling Point	194-195 °C	259 °C @ 760 mm Hg	334 °C @ 760 mm Hg
Melting Point	-16 > -17 °C	24 °C	49.3 °C
Specific Gravity	0.827	0.8309	0.8187
Octanol/Water partition Coefficient	Log Kow = 3.00	Log Kow = 5.13	Log Kow = 6.65
Water Solubility	540 mg/L@ 25 °C	4 mg/L @ 25 °C	$1.34*10^{-5}$ g/L @ 25 °C
Surface Tension	27.53 mN/m	29.493 mN/m	28.449 mN/m
Vapor Density	4.5 (Air=1)	6.43 (Air=1)	8.360 (Air =1)
Vapor Pressure	$7.94*10^{-2}$ mm Hg	$8.48*10^{-4}$ mm Hg	$3.06*10^{-6}$ mm Hg
Viscosity	10.6 cP @ 15 °C	18.8 cP @ 20 °C	53 cP @ 75 °C

[Source; http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB]

3.2 Methodology

3.2.1 CMC Determination in the Presence and Absence of Additive

The CMC determination was conducted by measuring a surface tension of a series of surfactant solution at different concentration at ambient temperature. The CMC values can be identified as a surfactant concentration in which there is a dramatic change in the plot between surface tension versus logarithm of surfactant

concentration. Firstly, the CMC value of mixture of DTAB and DOWFAX at molar ratio of 2: 1 without additives was investigated. Secondly, the CMC determination for mixture of DTAB and DOWFAX at molar ratio of 2: 1 in the presence of individual nonionic surfactant as additive was studied. The molar ratio of TX-100 to original surfactant mixture of DTAB and DOWFAX was 1:35 (adapted from actual operating condition used for PCE extraction in which the surfactant concentration of DTAB and DOWFAX mixture was 70 mM and the lowest nonionic surfactant concentration was 2 mM) were investigated. The same procedure was applied for TX-114. Lastly, the CMC values of mixture of DTAB and DOWFAX at molar ratio of 2: 1 in the presence of individual alcohols were investigated where the molar ratio of alcohol to original surfactant mixture of DTAB and DOWFAX was 1:700 (adapted from actual operating condition used for PCE extraction in which the surfactant concentration of DTAB and DOWFAX mixture was 70 mM and the lowest alcohol concentration was 0.1 mM). The same procedure was applied for octonol, dodecanol, and hexadecanol.

3.2.2 Preparation of ASTP System for PCE Removal

The ASTP systems were prepared by mixing a cationic and an anionic surfactant at molar ratio of DTAB and DOWFAX of 2:1 with 100 ppm of PCE into 100 mL volumetric flask with distilled water to make surfactant aqueous solutions at total surfactant concentration varied from 30, 50, 70, 90, and 110 mM, The molar ratio of DTAB and DOWFAX of 2:1 was adopted from the previous works as the most appropriate surfactant composition since it is believed that this cationic-anionic surfactant composition is a neutral condition (charges balanced) and a surfactant mixture behaves as pseudo-nonionic surfactant in which the aggregates flocculate forming the surfactant-rich phase at highest surfactant concentration (Kunanupap 2004; Krutlert, 2004). Prior adding 100 ppm of PCE, the sample must be mixed properly by magnetic stirrer for 10-15 minutes. After PCE addition, the solution was homogenized again for another 10-15 minutes and the sample were transferred into several identical 22 mL vials sealed with rubber septa to prevent the leakage of PCE. It should be noted that the overhead volume must be minimized to avoid the

headspace lost of PCE. The samples were equilibrated in the water bath at controlled temperature of 30 ºC for 5 days. The equilibrium condition was approached when there was no change in either phase height or concentration of surfactants in both phases. The volume of each phase was carefully measured by the height of the separated phases. Each phase (top and bottom) were collected separately for surfactant and PCE concentration analysis using UV-spectrophotometer and gas chromatography with a flame ionized detector (FID), respectively. The following parameters were investigate from the prepared ASTP systems after phase separation including the fraction surfactant-rich phase volume, the partitioning of surfactant and PCE into the surfactant-rich phase as compared to the surfactant-dilute phase (known as the surfactant and PCE partition ratio, respectively), the fraction of PCE extracted into the surfactant-rich phase (known as the PCE removal efficiency). The schematic diagram for sample preparation of ASTP systems was shown in Figure 3.2.2.1.

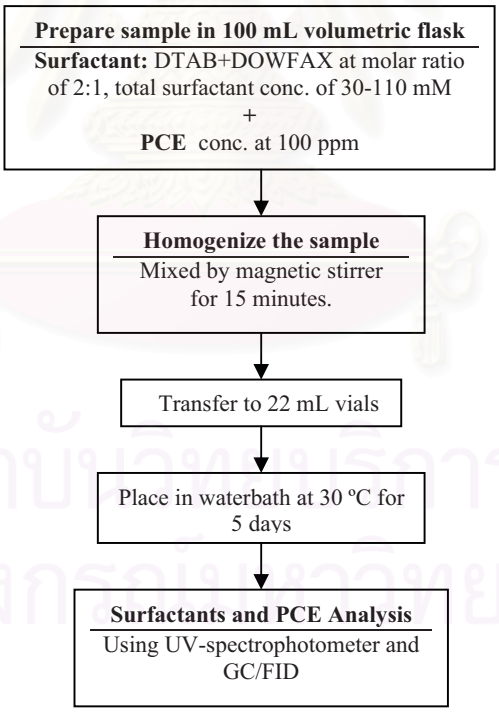


Figure 3.2.2.1 The schematic diagram for sample preparation of ASTP systems

3.2.3 Effect of Additives on PCE Removal

3.2.3.1 Effects of Nonionic Surfactants

In this study, the effect of nonionic surfactants addition as additives was investigated using the same experimental procedure as previously mentioned. Each type of nonionic surfactant was added into the sample at a time at varied concentrations. The concentration of nonionic surfactant in the separated phases was not measured. However, it should be noted that there was a slight interference of Triton X-100 and Triton X-114 at wavelength of 240 nm which was the wavelength used to measure the concentration of DOWFAX. To overcome this problem, both surfactant-rich and surfactant-dilute phases were diluted into a suitable condition where the concentration of nonionic surfactant was very low and become negligible but the concentration of DOWFAX was still in the measurable range. This dilution technique was applicable in this study because the molar ratio of DOWFAX to nonionic surfactant was considerably high.

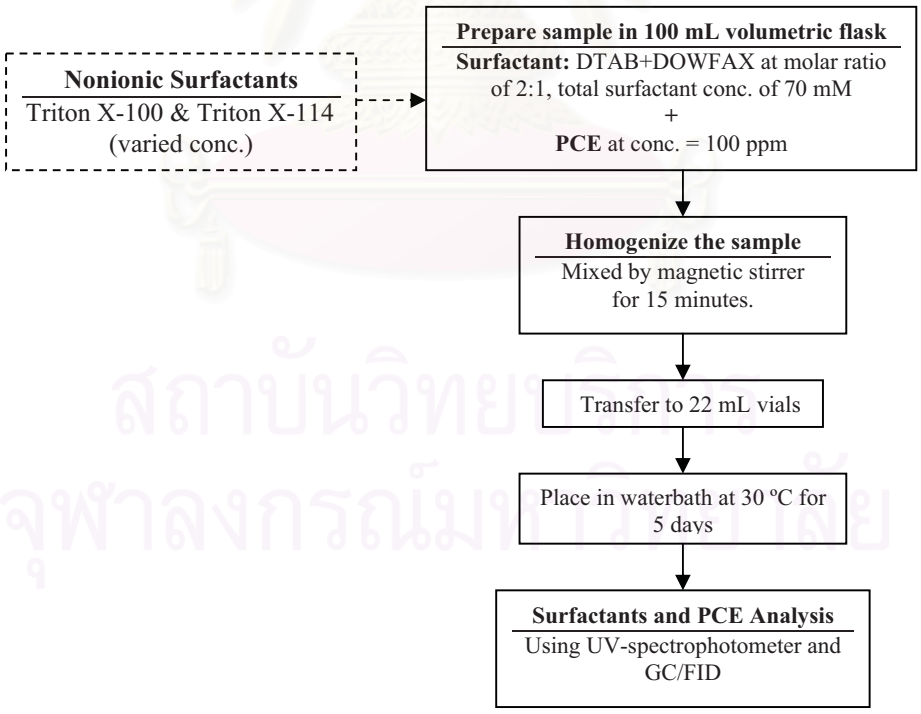


Figure 3.2.2.2 The schematic diagram for sample preparation of ASTP systems with the presence of nonionic surfactants

3.2.3.2 Effects of Lipophilic Linkers

The same procedure was applied to prepare the ASTP system to extract PCE from synthesis wastewater. The most suitable total surfactant concentration obtained from previous experiments (70 mM) was then applied to this study. In addition, the effect of long chain alcohol addition as an additive was investigated at various concentrations. Octanol, dodecanol, and hexadecanol were added into the solutions each at a time. The concentration of alcohol in the separated phases was not measured.

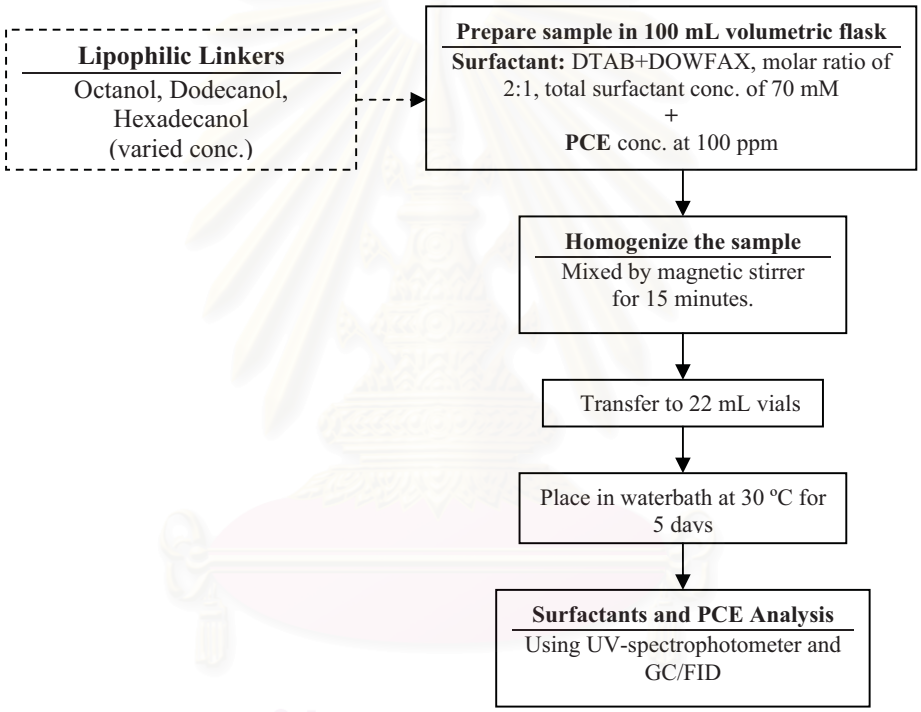


Figure 3.2.2.3 The schematic diagram for sample preparation of ASTP systems with the presence of lipophilic linkers

3.3 Investigated Parameters

3.3.1 Determination of fractional surfactant-rich phase volume

$$\text{Fractional surfactant-rich phase volume} = \frac{[V]_{rich}}{[V]_{total}}$$

where $[V]_{rich}$ -- volume of the surfactant-rich phase

$[V]_{total}$ -- total volume of the solution

3.3.2 Determination of surfactant partition ratio

$$\text{Surfactant partition ratio} = \frac{[S]_{rich}}{[S]_{dilute}}$$

where $[S]_{rich}$ -- concentration of surfactant in the surfactant-rich phase

$[S]_{dilute}$ -- concentration of surfactant in the surfactant-dilute phase

3.3.3 Determination of PCE partition ratio

$$\text{PCE partition ratio} = \frac{[PCE]_{rich}}{[PCE]_{dilute}}$$

where $[PCE]_{rich}$ -- concentration of PCE in the surfactant-rich phase

$[PCE]_{dilute}$ -- concentration of PCE in the surfactant-dilute phase

3.3.4 Determination of PCE removal efficiency

$$\% \text{ PCE removal} = \left(\frac{[(Fr_R) * (PCE)_R]}{[(Fr_R) * (PCE)_R] + [(1-Fr_R) * (PCE)_D]} \right) * 100$$

where (Fr_R) -- fractional surfactant-rich phase volume

$(PCE)_R$ -- concentration of PCE in the surfactant-rich phase

$(PCE)_D$ -- concentration of PCE in the surfactant-dilute phase

3.3.5 Determination of mass balance for PCE

$$[(Fr_R) * (PCE)_R] + [(1-Fr_R) * (PCE)_D] = (PCE)_{Initial}$$

where (Fr_R) -- fractional surfactant-rich phase volume

$(PCE)_R$ -- concentration of PCE in the surfactant-rich phase

$(PCE)_D$ -- concentration of PCE in the surfactant-dilute phase

$(PCE)_{Initial}$ -- initial concentration of PCE in sample

3.3.6 Determination of mass balance for total surfactant concentration

$$[(Fr_R) * (Surf)_R] + [(1-Fr_R) * (Surf)_D] = (Surf)_{Initial}$$

where (Fr_R) -- fractional surfactant-rich phase volume

$(Surf)_R$ -- concentration of surfactant in the surfactant-rich phase

$(Surf)_D$ -- concentration of surfactant in the surfactant-dilute phase

$(Surf)_{Initial}$ -- initial concentration of surfactant in sample

3.4 Analytical instruments and methods

The concentration of DOWFAX was determined using UV-Visible spectrophotometer at wavelength of 240 nm. The concentration of DOWFAX was used to estimate the concentration of DTAB since the surfactant aggregates in the separated phases still exhibit at surfactant composition as originally prepared (in this studies was 2:1 molar ration of DTAB:DOWFAX). Therefore, the total surfactant concentration of each phase was determined. The PCE concentration was measured using gas chromatography equipped with a flame ionized detector (FID). The static headspace sampling technique using headspace autosampler was applied due to a high volatility of PCE. The condition of gas chromatography and headspace autosampler were as follows: brand: Perkin Elmer; model: Clarus 500GC; column: Elite-wax with 30 m × 0.32 mm ID, 0.25 μm film thickness; oven temperature: 140 °C; injector temperature: 200 °C; and detector temperature: 200 °C. The experimental conditions for headspace autosampler were as follows: brand: Perkin Elmer; model: Turbomatrix 40; thermostatting time: 15 min; oven temperature: 80 °C; needle temperature: 100 °C; transfer line temperature: 90 °C; GC cycle time: 5 min; pressurization time: 1 min; injection time: 0.04 min; and withdrawal time: 0.2 min.

The external standard quantitative calibrations were conducted to analyze the surfactant and PCE concentrations in both phases. The material balances of surfactant and PCE were carried out to assure the reliability of the experiments in which the error percentage was controlled to be less than 10 % for both surfactant and PCE.

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 The CMC Determination in the Presence and Absence of Additive

The CMC values can be determined by measuring a surface tension of a series of surfactant solution at different concentration. The surface tensions were plotted as a function of logarithm of surfactant concentration. At low surfactant concentration, the surface tension decreases linearly with the surfactant concentration until a certain concentration in which the surface tensions remain constant upon increasing the surfactant concentration. The dramatic change in the plot indicates the CMC. From previous study, a mixture of cationic and anionic surfactants shows synergism by decreasing the CMC value to be much lower than individual surfactant (Kunanupap, 2004). Therefore, in this research the CMC values were determined to study the effect of additives. From the results, there is insignificant different of the CMC values in the absence or presence of additive. Without additive, the CMC value of mixture of DTAB and DOWFAX at molar ratio of 2: 1 is 0.016 mM. Upon the addition of 0.1 mM of octanol, dodecanol, and hexadecanol (molar ratio of surfactant to alcohol is 700), the CMC values are 0.010 mM, 0.016 mM, and 0.014 mM, respectively as shown in Table 4.1.1. The same observation was found upon the addition of nonionic surfactants as additives. Both additions of TX-100 and TX-114 at 2 mM (molar ratio of cationic/anionic surfactant to nonionic surfactant is 35) give the same CMC value of 0.014 mM. From these results, the addition of long chain alcohol and POE nonionic surfactant do not have significant effect to the CMC value.

Table 4.1.1 The CMC values of DTAB:DOWFAX at molar ratio of 2: 1 in the absence and presence of additive

Additive	CMC (mM)
No additive	0.016
Octanol	0.010
Dodecanol	0.016
Hexadecanol	0.014
TX-100	0.014
TX-114	0.014

4.2 Effect of Total Surfactant Concentration on PCE Removal by ASTP System

The total surfactant concentration was varied in the range of 30 mM to 110 mM at fixed surfactant composition at 2:1 molar ratio of DTAB:DOWFAX to extract PCE from wastewater at 30 ^{o}C. From Figure 4.2.1-4.2.4, the fractional surfactant-rich phase volume proportionally increases upon an increase in surfactant concentration as required by material balance. The surfactant concentration in the surfactant-rich phase slightly increases while that of in the surfactant-dilute phase increase two folds as the total surfactant concentration increases resulting in a decline of surfactant partition ratio with surfactant concentration. However, upon an increase in total surfactant total concentration, the concentration of PCE in the surfactant-rich decreases attributed to an increase in volume of the surfactant-rich phase while that of in the dilute phase shows the minimum PCE concentration at total surfactant concentration of 70 mM. The concentration of PCE remains in the surfactant-dilute phase is about 8.6 ppm or 91.4 % of PCE can be extracted by this ASTP system within single stage without any additives. At the total surfactant concentrations greater than 70 mM, the PCE concentration in the surfactant dilute-phase increases probably due to a significant increase of surfactant concentration in the surfactant-dilute phase, thus the amount of PCE associated with

surfactant aggregate is also large resulting in high PCE concentration. On the other hands, at low total surfactant concentration of 30 mM, the concentration of PCE remains in the surfactant-dilute phase is high and the percentage of PCE removal is rather low. This can be explained that the amount of surfactant aggregates at the total surfactant concentration of 30 mM is probably not sufficient to solubilize PCE.

In addition, the PCE partition ratio slightly declines as the total surfactant concentration increases from 30 to 70 mM and greatly decline if the total surfactant concentration further increases to 90 and 110 mM. Consequently, the total surfactant concentration of 70 mM was chosen as the most suitable concentration to extend the study onto the effect of additive for PCE removal since it gives the lowest PCE concentration remained in the surfactant-dilute phase and the highest percentage of PCE removal even though the PCE partition ratio is slightly lower than at the total surfactant concentration of 30 and 50 mM.

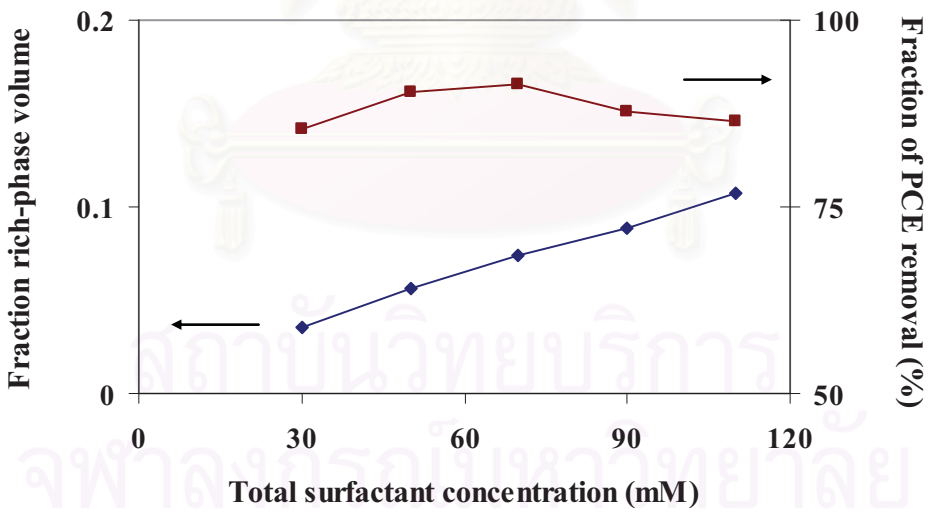


Figure 4.2.1 Effect of total surfactant concentration on the fractional rich-phase volume and the fraction of PCE removal

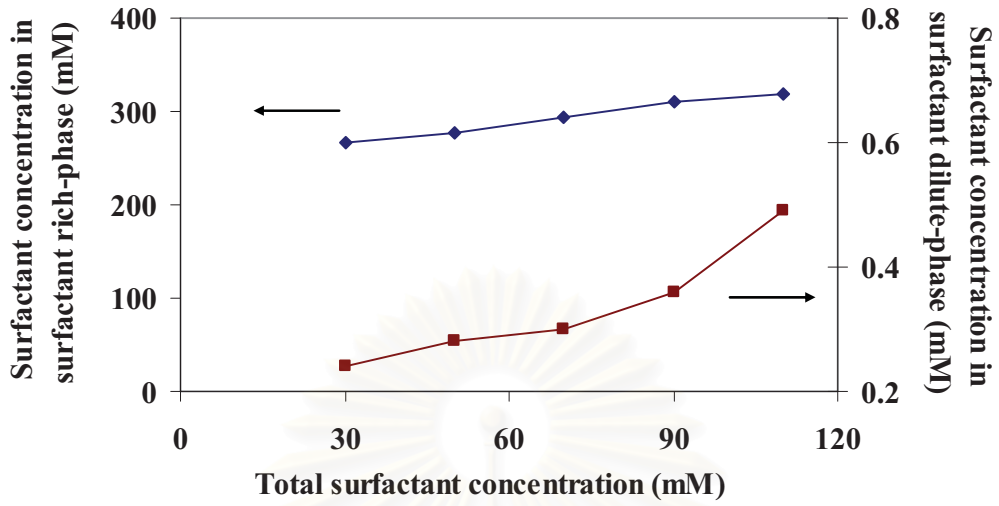


Figure 4.2.2 Effect of total surfactant concentration on the surfactant concentration in the surfactant-rich and in the surfactant-dilute phase

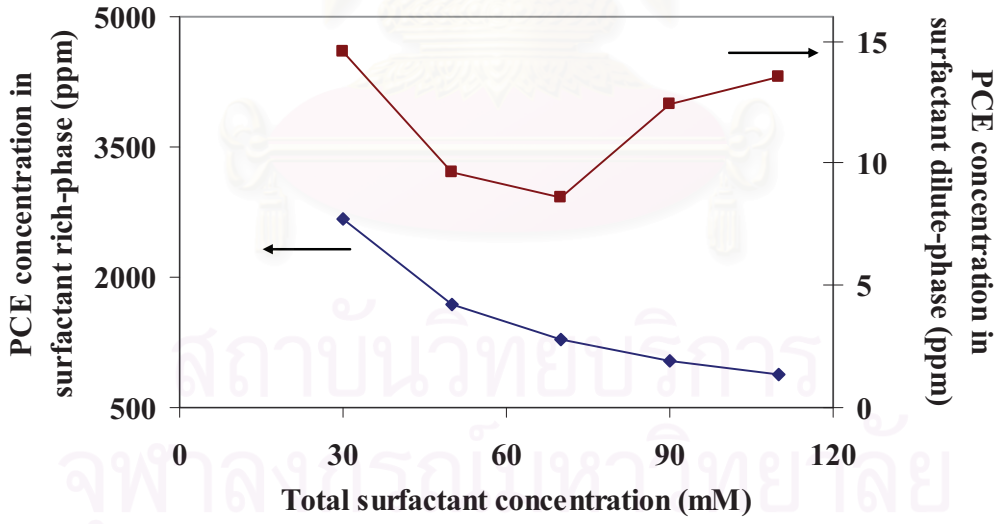


Figure 4.2.3 Effect of total surfactant concentration on the PCE concentration in the surfactant-rich and in the surfactant-dilute phase

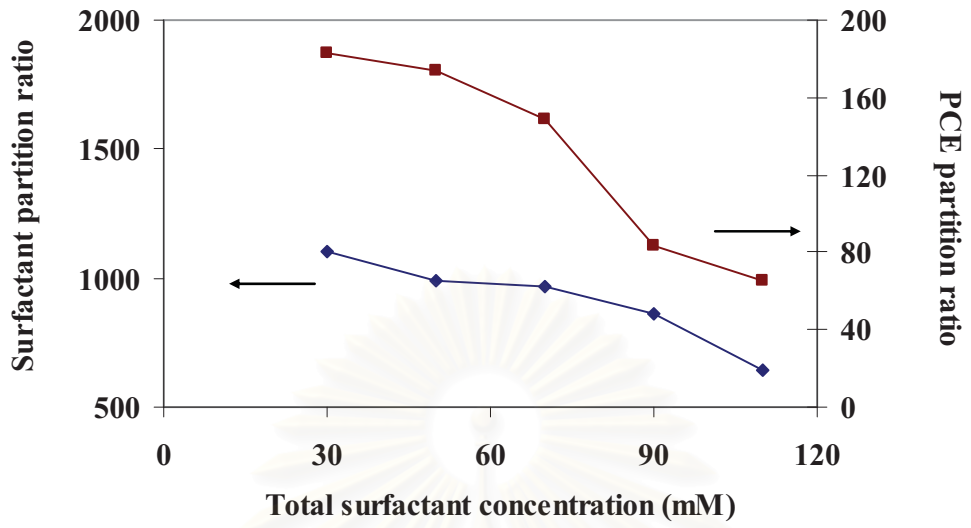


Figure 4.2.4 Effect of total surfactant concentration on surfactant partition ratio and PCE partition ratio

4.3 Effect of Additives on PCE Removal by ASTP System

4.3.1 Effect of Nonionic Surfactants

In this research, TX-100 (EO = 9.5 units) and TX-114 (EO = 7.5 units) were used as nonionic surfactants to study the effect of hydrophilic head of nonionic surfactant onto the PCE removal using ASTP system of DTAB:DOWFAX. The concentration of TX-100 and TX-114 were varied at 2 mM, 10 mM, and 20 mM. The appearance of solutions after phase separation was shown below.

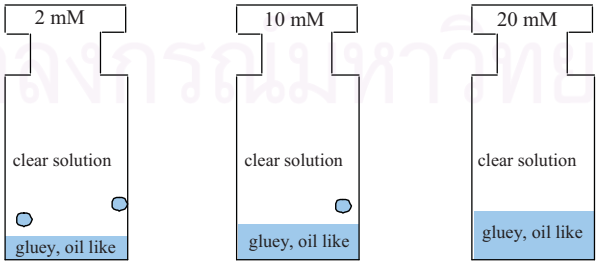


Figure 4.3.1.1 Phase behavior of systems upon the addition of TX-100 at various concentrations

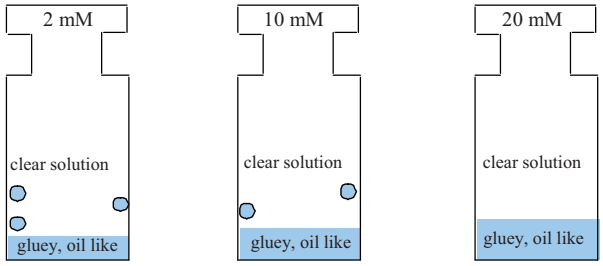


Figure 4.3.1.2 Phase behavior of systems upon the addition of TX-114 at various concentrations

From Figure 4.3.1.1 and 4.3.1.2, it was found that the surfactant-dilute phase appears to be very clear especially, at nonionic surfactant concentration of 20 mM. The addition of nonionic surfactant does not obligate or change the phase separation phenomenon. The PCE removal efficiency upon addition of nonionic surfactants was illustrated in Figure 4.3.1.3 - 4.3.1.10. However, it should be noted that in this experiment, the determination of PCE concentration in the surfactant rich-phase was indirectly evaluated by calculation based on the PCE mass balance principle. However, the PCE concentration in the surfactant dilute-phase was directly measured as well as the volume of each separated phase. The measuring results were used to calculate the PCE concentration in the surfactant rich-phase. The calculation method for PCE mass balance was shown in chapter 3.

It was found that the results obtained from both nonionic surfactants are in the same fashion. When the concentration of nonionic surfactant increases, the fractional surfactant rich-phase volume increases as accounted for the amount of surfactant added. Upon the addition of nonionic surfactants at concentration of 20 mM (total surfactant concentration in the system is 90mM), the fractional surfactant rich-phase volume are 0.19 and 0.12 for TX-100 addition and for TX-114 addition, respectively as compared to about 0.089 at the same total surfactant concentration of 90 mM in the absence of nonionic surfactant additive. Therefore, the presence of nonionic surfactant can swollen the surfactant-rich phase causing a great reduction in surfactant concentration in the surfactant-rich phase. Moreover, it can be observed that TX-100 can greater swollen the surfactant-rich phase than TX-114 which is probably due to a longer hydrophilic head

group promoting more steric hindrance that avoid a close arrangement of surfactant aggregates.

The concentration of surfactant in the surfactant-dilute phase was found to be reduced by half if the nonionic surfactant was added at high concentration such as at 10 and 20 mM for both nonionic surfactants. As a consequence, the surfactant partition ratio tends to increase upon the addition of nonionic surfactants except for the addition of TX-100 at concentration of 20 mM where the concentration of surfactant in the surfactant-rich phase is very low due to a large fractional surfactant-rich phase volume as mentioned previously. Since the concentration of surfactant in the surfactant-dilute phase is low upon the addition of nonionic surfactants, the concentration of PCE in the surfactant-dilute phase is undoubtedly low in which the concentration of PCE remaining in the surfactant-dilute phase was in the range of 3 to 5 ppm as compared to 8.6 ppm without additive. The concentration of PCE in the surfactant-dilute phase and the fraction of PCE removal are nonionic surfactant concentration independent. However, in the view point of PCE partition ratio which reflects the preconcentration ability of the system, the results showed that the high PCE partition ratio is achieved at low nonionic surfactant concentration due to high PCE concentration in the surfactant-rich phase and low fractional surfactant-rich phase volume. Therefore, the small amount of POE nonionic surfactants addition can improve the extraction efficiency of ASTP system for PCE removal. This can be seen clearly in table 4.3.3 and in figure 4.3.2.9 where the summary of the fraction of PCE removal with absence and presence of nonionic surfactants at various concentrations were described.

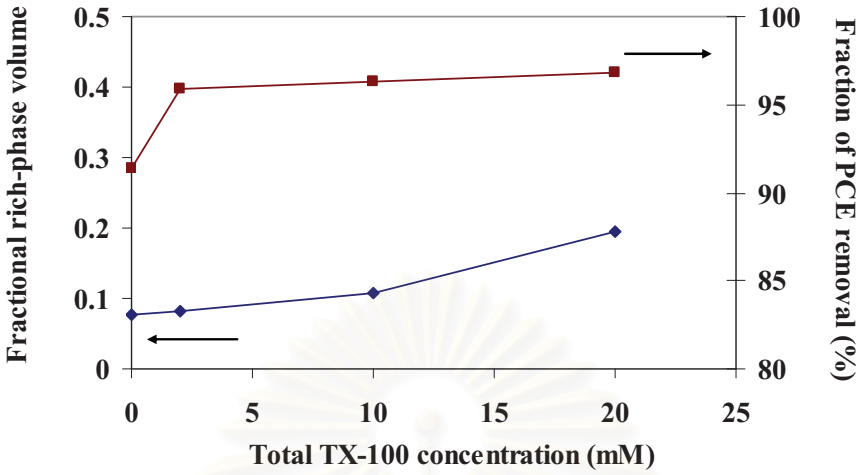


Figure 4.3.1.3 Effect of total TX-100 concentration on the fractional rich-phase volume and the fraction of PCE removal (system: 2:1 molar ratio of DTAB:DOWFAX at 70 mM)

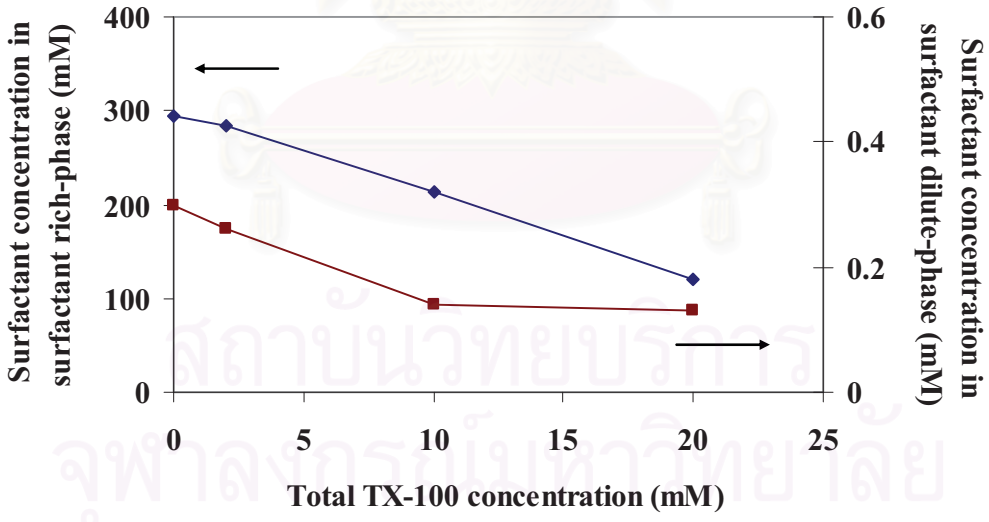


Figure 4.3.1.4 Effect of total TX-100 concentration on the surfactant concentration in the surfactant-rich and in the surfactant-dilute phase (system: 2:1 molar ratio of DTAB:DOWFAX at 70 mM)

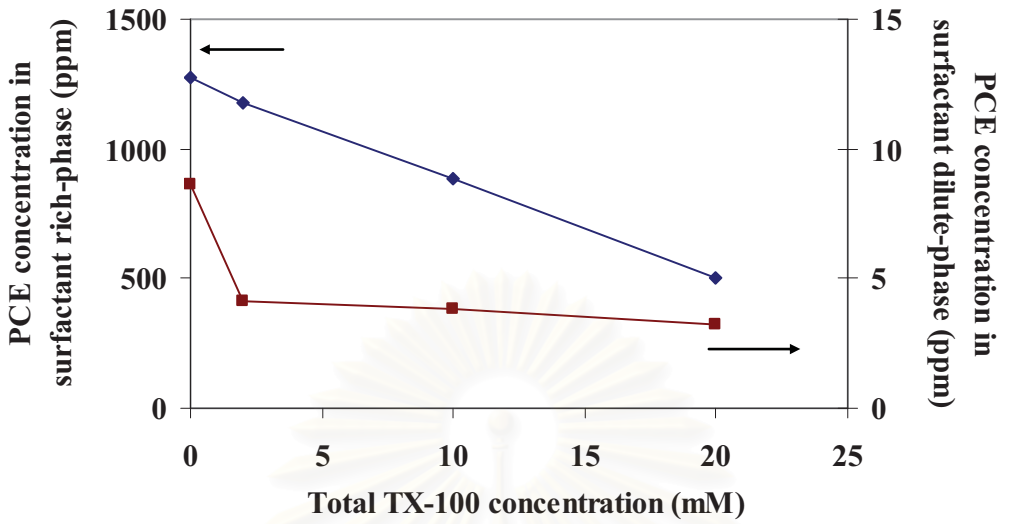


Figure 4.3.1.5 Effect of TX-100 concentration on the PCE concentration in the surfactant-rich and in the surfactant-dilute phase (system: 2:1 molar ratio of DTAB:DOWFAX at 70 mM)

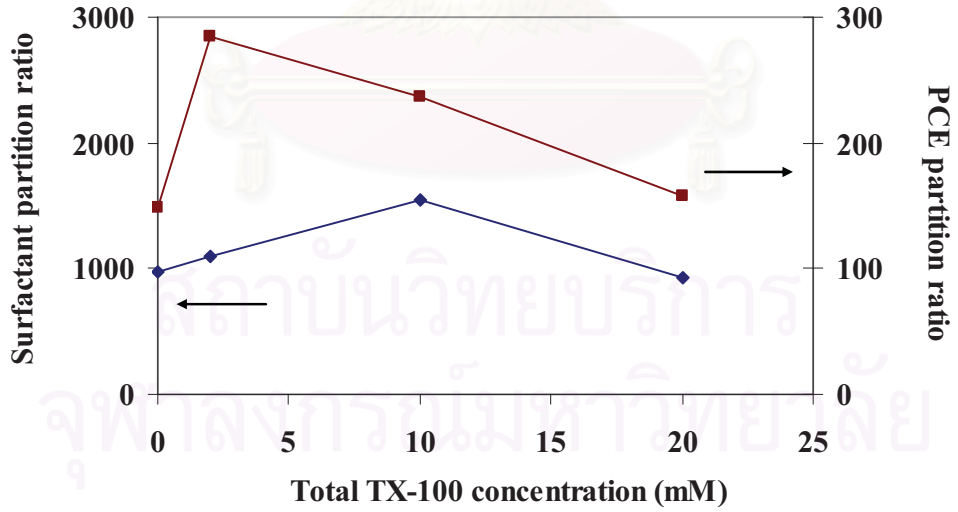


Figure 4.3.1.6 Effect of TX-100 concentration on surfactant partition ratio and PCE partition ratio (system: 2:1 molar ratio of DTAB:DOWFAX at 70 mM)

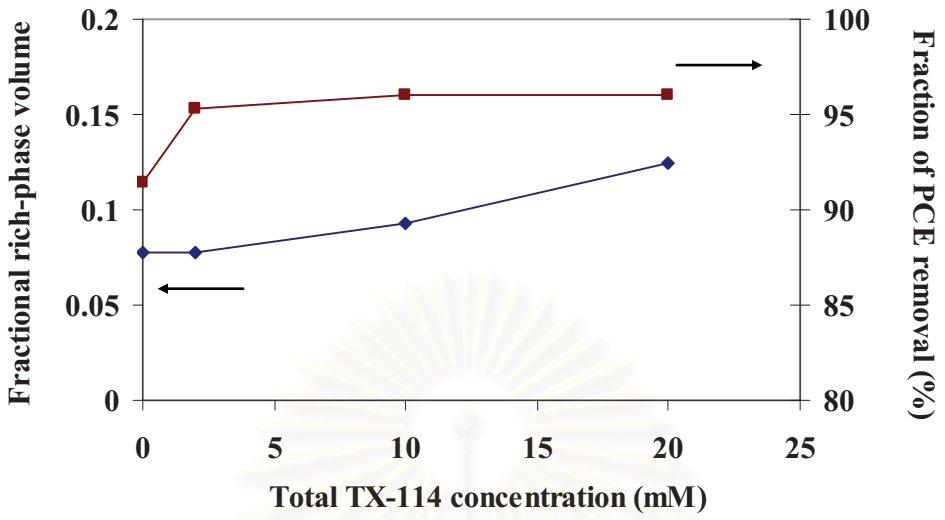


Figure 4.3.1.7 Effect of total TX-114 concentration on the fractional rich-phase volume and the fraction of PCE removal (system: 2:1 molar ratio of DTAB:DOWFAX at 70 mM)

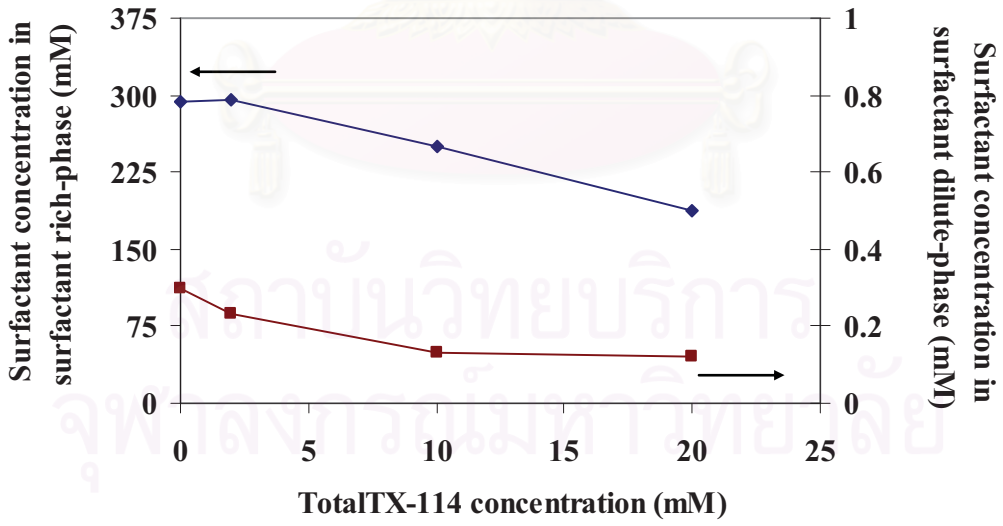


Figure 4.3.1.8 Effect of total TX-114 concentration on the surfactant concentration in the surfactant-rich and in the surfactant-dilute phase (system: 2:1 molar ratio of DTAB:DOWFAX at 70 mM)

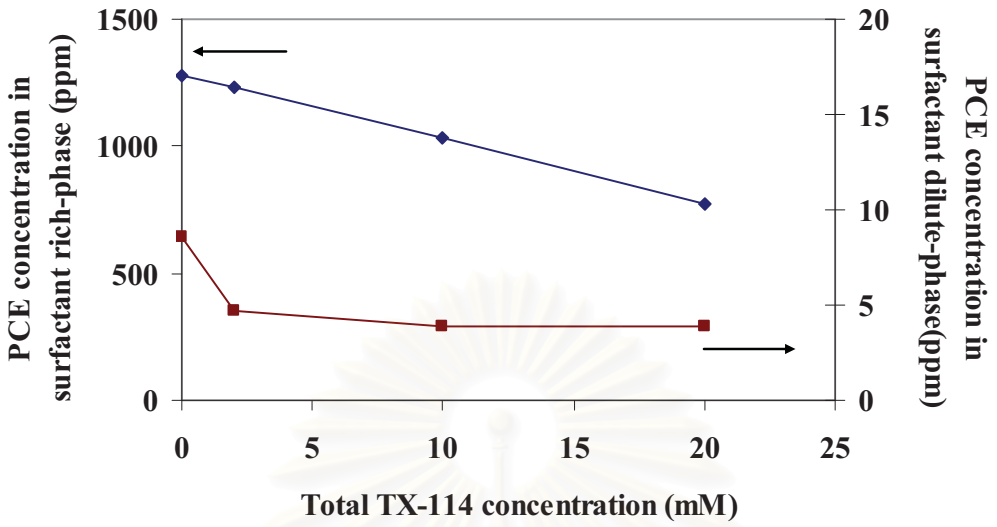


Figure 4.3.1.9 Effect of TX-114 concentration on the PCE concentration in the surfactant-rich and in the surfactant-dilute phase (system: 2:1 molar ratio of DTAB:DOWFAX at 70 mM)

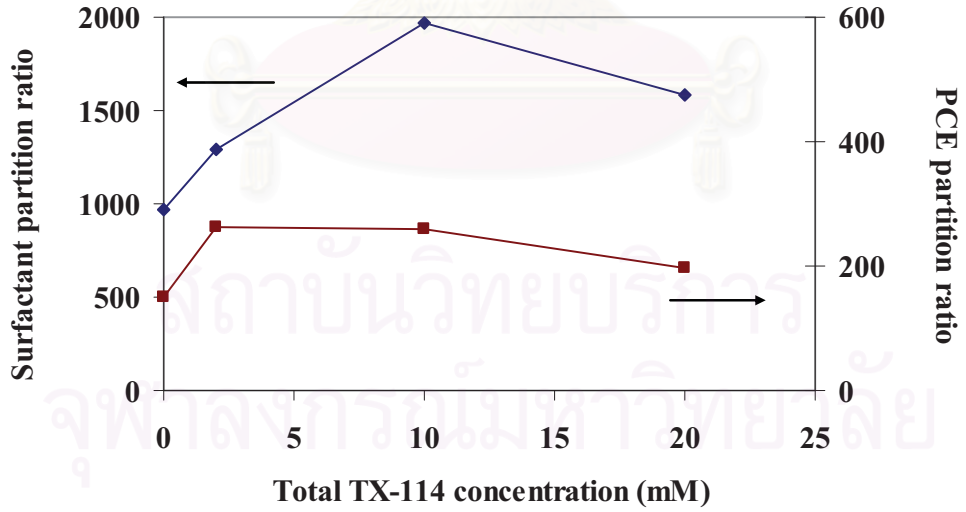


Figure 4.3.1.10 Effect of TX-114 concentration on surfactant partition ratio and PCE partition ratio (system: 2:1 molar ratio of DTAB:DOWFAX at 70 mM)

A more precise experiment was designed to investigate the effect of nonionic surfactant addition on solubilization ability of surfactant aggregates by preparing a solution at total surfactant concentration of 70 mM inclusive of 2 mM TX-100 nonionic surfactant (mixture of DTAB:DOWFAX at 68 mM plus TX-100 at 2 mM). The comparison of results between this new prepared system and existing system in the absence of nonionic surfactant addition, both having the same total surfactant concentration of 70 mM to eliminate the effect of total concentration on the extraction ability, was shown in Table 4.3.1. It was found that there is no significant difference in surfactant concentration in both separated phases as well as the fractional surfactant-rich phase volume but the PCE concentration left in the surfactant-dilute phase in the presence of 2 mM of nonionic surfactant is more than 2 folds lower than that of in the absence of nonionic surfactant (3.6 ppm versus 8.6 ppm). Also, the PCE partition ratio upon the addition of nonionic surfactant is more than 2 times greater than in the absence of additive. Therefore, the nonionic surfactants are promising additives. Upon the presence of TX-100 at only 2 mM, the fraction of PCE removal is raised by 5%. This may be caused by an interaction of nonionic surfactant with cationic-anionic surfactant, thus induce a synergistic effect which can enhance the solubilization of PCE into the surfactant aggregate resulting in less PCE presented in the surfactant-dilute phase.

Table 4.3.1 The concentration of PCE in the surfactant-dilute phase and % PCE removal in the presence and absence of nonionic surfactant at total surfactant concentration of 70 mM

Concentration of DTAB:DOWFAX (mM)	**Concentration of TX-100 (mM)**	**Total surfactant concentration (mM)**	**[PCE] in the surfactant-dilute phase (mM)**	**% PCE removal**
70	0	70	8.6	91.4
68	2	70	3.6	96.4

A similar synergism was found in adsolubilization study (Tan and O'Haver, 2003), they claimed that nonionic surfactant alone has low adsolubilization capacity. But the adsolubilization capacity increases greatly in mixed ionic-nonionic surfactant admicelles. As reviewed in Tan and O'Haver's paper, Esumi et al. proposed that the difference in surfactant structures exhibits a different adsolubilization behavior and the adsolubilization capacity is proportional to alkyl chain length of surfactant. In addition, the addition of hydrophilic linkers, sodium mono- and dimethyl-naphthalene sulfonate (SMDNS), to enhance the PCE solubilization in microemulsion system was studied (Sabatini et al., 2003). They reported that the presence of hydrophilic linkers can create the opened spaces between the surfactant tails, which facilitate the movement of the surfactant tails and thereby increase the solubilization capacity of PCE. Although the nonionic surfactant is not classified as hydrophilic linker since its molecular structure is composed of long chain hydrocarbon in both surfactant head and tail groups, the addition of POE nonionic surfactant to the ASTP system formed by a mixture of cationic and anionic surfactants at least alters the characteristics of surfactant aggregates at the hydrophilic portion due to a presence of polar polyethylene oxide group. Therefore, with the association of nonionic surfactant into the mixed cationic-anionic surfactant aggregates, it is believed that the spaces between two adjacent surfactant molecules are enlarged (or the curvature of surfactant aggregates decreases), thus PCE molecules can easily diffuse to solubilize perhaps at the hydrophobic region near the palisade layer. As a consequence, PCE solubilization is enhanced.

4.3.2 Effect of Lipophilic Linkers

In this research, alcohols including octanol, dodecanol, and hexadecanol were used as lipophilic linker to systematically vary the hydrophobicity of the linkers. Firstly, the octanol concentration was varied to investigate the suitable working range as shown in the Figure 4.3.2.1.

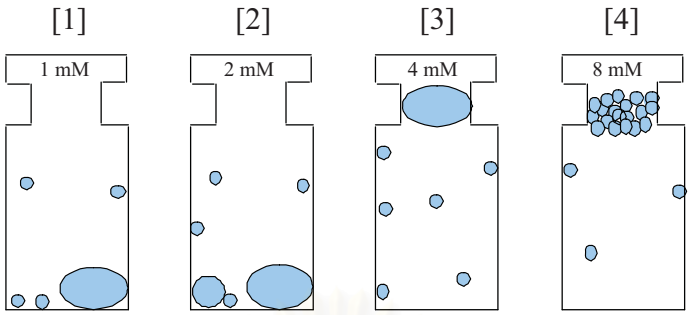


Figure 4.3.2.1 Preliminary investigation to determine suitable octanol concentration
(● -- droplet of surfactant-rich phase)

It can be seen that at octanol concentration exceed 2 mM as shown in [2], the appearance of the system changes in such a way that the excess octanol phase floats on top of the solution. Therefore, the concentrations of octanol, dodecanol, and hexadecanol were varied in the range of 0.1 mM to 2 mM. Figure 4.3.2.2 to 4.3.2.4 show the solution behavior as regarded to different type of alcohol as additive.

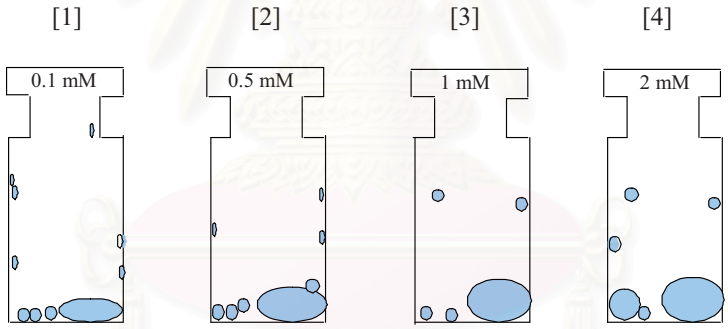


Figure 4.3.2.2 Determination of suitable octanol concentration
(● -- droplet of surfactant-rich phase)

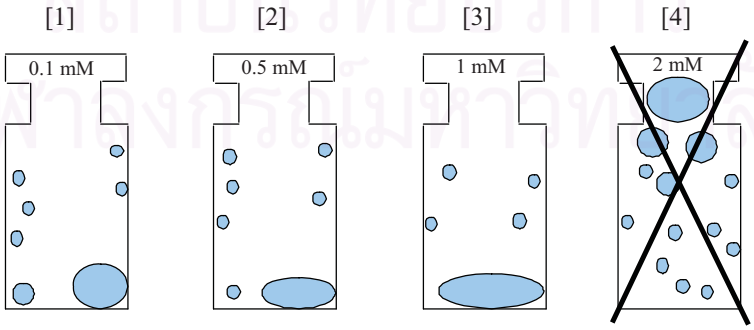


Figure 4.3.2.3 Determination of suitable dodecanol concentration
(● -- droplet of surfactant-rich phase)

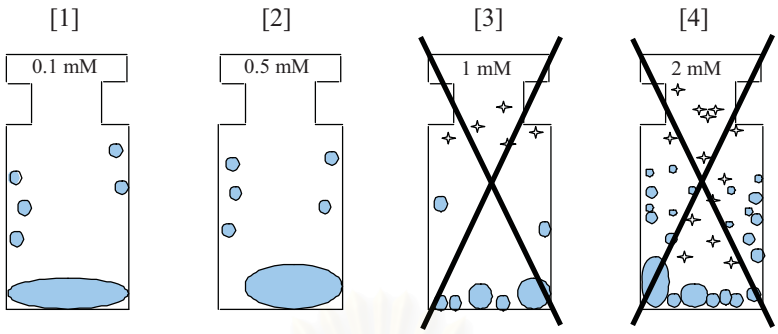


Figure 4.3.2.4 Determination of suitable hexadecanol concentration
(● -- droplet of surfactant-rich phase)
(✧ -- undissolved powder of hexadecanol)

It was found that at longer alcohol chain length, the less concentration was applicable as the additive for these experiments, which was resulted from the lower water solubility of alcohol with longer carbon chain length. Thus, the suitable working concentration was 0.1-2 mM for octanol, 0.1-1 mM for dodecanol and 0.1-0.5 mM for hexadecanol.

The addition of octanol as an additive at various concentrations into ASTP system formed by mixture of DTAB:DOWFAX at molar ratio of 2:1, 70 mM, 30 ^{o}C for PCE removal was illustrated as shown in Figure 4.3.2.5 to 4.3.2.8.

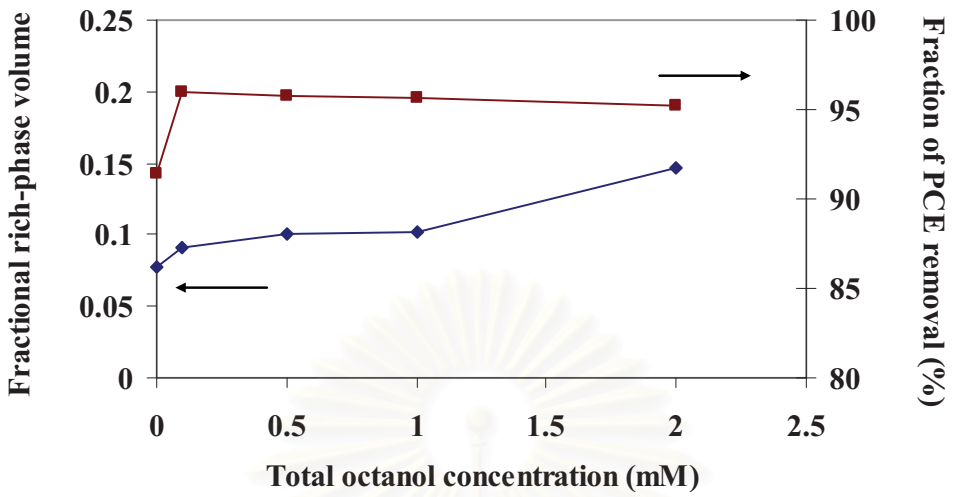


Figure 4.3.2.5 Effect of octanol concentration on the fractional rich-phase volume and the fraction of PCE removal (system: 2:1 molar ratio of DTAB:DOWFAX at 70 mM)

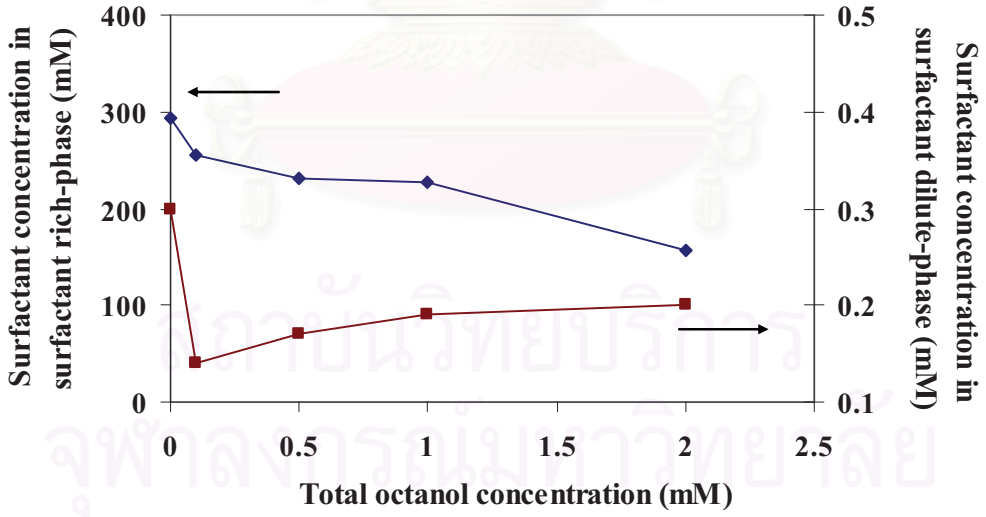


Figure 4.3.2.6 Effect of octanol concentration on the surfactant concentration in the surfactant-rich and in the surfactant-dilute phase (system: 2:1 molar ratio of DTAB:DOWFAX at 70 mM)

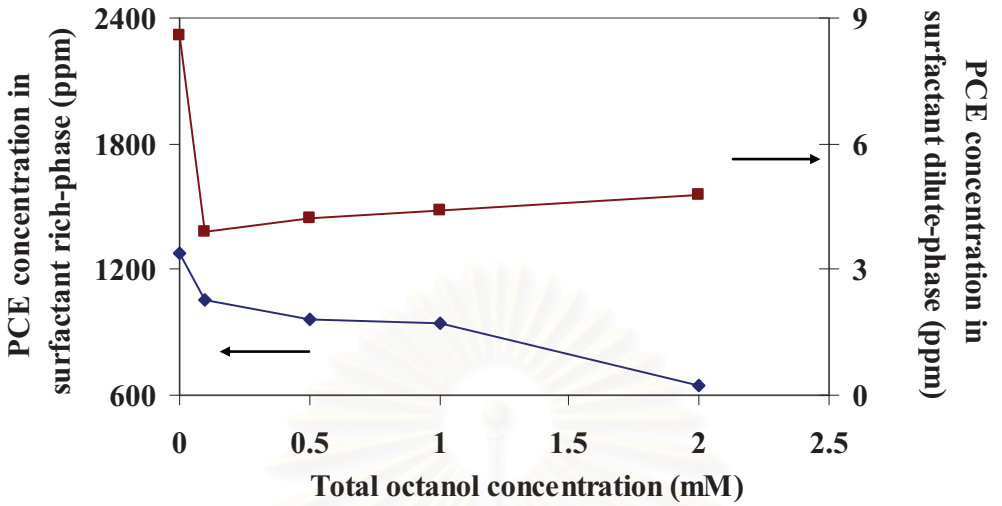


Figure 4.3.2.7 Effect of octanol concentration on the PCE concentration in the surfactant-rich and in the surfactant-dilute phase (system: 2:1 molar ratio of DTAB:DOWFAX at 70 mM)

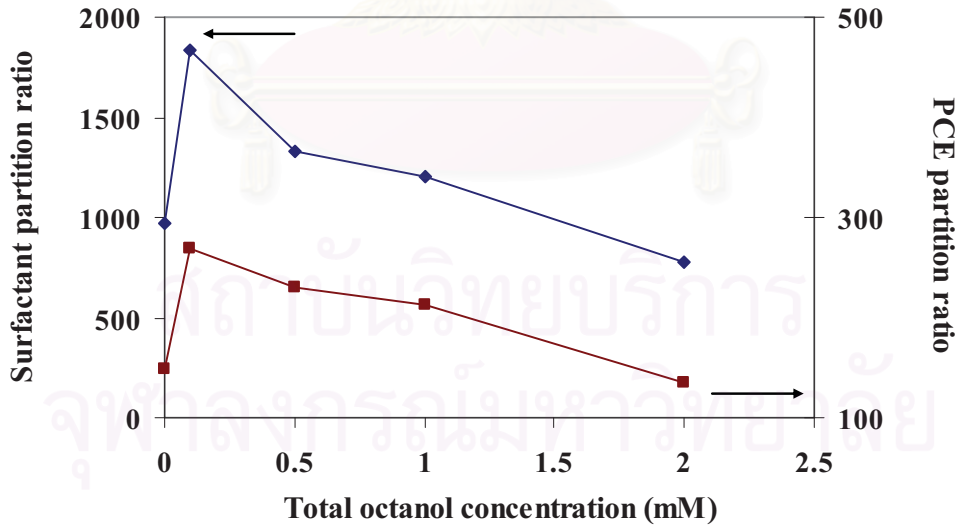


Figure 4.3.2.8 Effect of octanol concentration on surfactant partition ratio and PCE partition ratio (system: 2:1 molar ratio of DTAB:DOWFAX at 70 mM)

The effect of octanol addition was described in Figure 4.3.2.5 to 4.3.2.8. The same trends of results were obtained for the effect of dodecanol and hexadecanol as summarized in Table 4.3.2. It should be noted that the interface between the surfactant-rich and the surfactant-dilute phase is not as smooth as mirror-like as usually get from other systems. Therefore, there was a difficulty in measuring volume of each phase resulted in an imprecise fraction surfactant-rich phase volume. Therefore, we preferred to calculate the fractional surfactant-rich phase volume based on a surfactant mass balance principle, in which the concentrations of surfactant in both phases were carefully analyzed and the fractional surfactant-rich phase volume can be evaluated eventually. The PCE concentration in the surfactant rich-phase was indirectly determined using the PCE mass balance principle due to a difficulty to collect the sample accurately. However, the actual PCE concentration in the surfactant-dilute phase was carefully analyzed. The calculation method for PCE mass balance was illustrated in chapter 3.

Upon an increase in octanol concentration, the surfactant and PCE concentrations in the surfactant rich-phase decline probably due to an increase in the fractional surfactant-rich phase volume. However, it can be seen that the concentration of surfactant in the surfactant-dilute phase obviously drops, thus the concentration of PCE in this phase declines correspondingly upon the addition of octanol. The lower the concentration of alcohols, the greater competency is achieved in term of the remaining PCE and surfactant concentrations in the surfactant-dilute phase, the PCE and surfactant partition ratios, as well as the fraction of PCE extracted into the surfactant-rich phase as shown in Table 4.3.2. This can probably be explained by 2 reasons which are the competition between PCE and alcohols at high concentration and the more rigidity of surfactant tails upon the addition of alcohols that hinders the solubilization. When lipophilic linker dissolves in a surfactant aqueous solution, it will solubilize into the surfactant aggregates where its hydroxyl group orients toward the hydrophilic portion and its long hydrocarbon chain penetrate into the hydrophobic core region (Tan and O'Haver, 2004; Graciaa et al., 1993). Therefore, too much addition of long chain alcohol can thereby reduce the available space for PCE solubilization and also promote a rigidity of the surfactant membrane (Sabatini et al., 2003). The tightness interaction between lipophilic linkers and the surfactant tails results in a difficulty of PCE to get through to

the solubilization sites at the hydrophobic core region. However, it is believed that an addition of alcohol at low concentration can enhance the solubilization capacity of surfactant aggregates due to a packing of alcohol chain along with surfactant tails causing an inner core of surfactant aggregates having more degree of hydrophobicity. Moreover, the summary of the fraction of PCE removal for all alcohols addition were described in table 4.3.3 and in figure 4.3.2.9 for better consideration. At the concentrations of additives at 0.1 mM, the fraction of PCE removal in the presence of octanol is 96 %, in the presence of dodecanol is 98.3 %, and in the presence of hexadecanol is 95.5 %, respectively. Hence, we can conclude that the addition of alcohols at low concentration can enhance the solubilization of chlorinated compound to some extent. The length of added alcohol affects the efficiency of the system. It was found that dodecanol shows greatest efficiency where the there is no difference between octonol and hexadecanol which does not comply with the conclusion drawn by Tan and O'Haver. They found that an increase in solubilization capacity is proportional to the linker tail length (Tan and O'Haver, 2004). As reviewed in Tan and O'Haver's paper, Salager et al. concluded that the best lipophilic linker for microemulsion formulation should have a tail length which is intermediate between the length of the oil and the length of surfactant. Moreover, Graciaa et al. also proposed that the solubilization enhancement is proportional to the concentration of alcohol and the number of carbons in the alcohols molecules (Graciaa et al., 1993).

Table 4.3.2 Summary of data obtained from ASTP system of DTAB and DOWFAX on PCE removal

Total surfactant concentration (mM)	Additives (mM)	DOWFAX						PCE			
		Rich phase		Dilute phase		Fractional rich volume	Surfactant Partition ratio	Rich phase	Dilute phase	PCE Partition ratio	Fraction of PCE removal (%)
		Volume (ml)	Conc. (mM)	Volume (ml)	Conc. (mM)			Conc. (ppm)	Conc. (ppm)		
30	-	0.75	265.8	20.75	0.24	0.035	1104.8	2679.3	14.6	183.37	85.4
50	-	1.21	276.7	20.29	0.28	0.056	991	1679.3	9.6	174.11	90.4
70	-	1.6	293.3	19.9	0.3	0.074	967.7	1278.3	8.6	148.65	91.4
90	-	1.93	310.8	19.57	0.36	0.089	864.9	1035.7	12.4	83.89	87.7
110	-	2.3	319.2	19.2	0.49	0.107	646.4	879.5	13.5	65.01	86.5
70	-	1.6	293.3	19.9	0.3	0.074	967.7	1278.3	8.6	148.65	91.4
68	2 mM (TX-100)	1.77	281.7	19.73	0.28	0.082	1008.9	1177.8	3.6	369.87	96.4
70	2 mM (TX-100)	1.75	283.3	19.75	0.26	0.081	1105.6	1315.6	4.1	284.85	95.9
	TX-100										
70	2	1.75	283.3	19.75	0.26	0.081	1105.6	1177.8	4.1	284.85	95.9
70	10	2.33	213.3	19.17	0.14	0.108	1551.5	886.9	3.8	236.43	96.3
70	20	4.17	120	17.33	0.13	0.194	929	499.6	3.2	157.19	96.8
	TX-114										
70	2	1.67	295.8	19.83	0.23	0.078	1290.9	1228.9	4.7	260.95	95.3
70	10	2	250	19.5	0.13	0.093	1967.2	1032.5	3.9	260.83	96
70	20	2.67	186.7	18.83	0.12	0.124	1585.8	774.5	3.9	197.25	96
	Octanol										
70	0.1	1.95	255.8	19.55	0.14	0.091	1832.8	1059.1	3.9	268.7	96
70	0.5	2.15	231.7	19.35	0.17	0.1	1334.9	958	4.2	229.9	95.8
70	1	2.18	227.5	19.31	0.19	0.102	1200	940.6	4.4	212.7	95.6
70	2	3.17	156.7	18.32	0.2	0.147	779.3	649.4	4.8	135.9	95.2
	Dodecanol										
70	0.1	2.23	224.2	19.27	0.06	0.104	3415.8	946.5	1.7	545.8	98.3
70	0.5	2.37	210.8	19.13	0.13	0.11	1619.2	873.9	3.8	231	96.2
70	1	2.44	203.3	19.06	0.25	0.114	820.2	817.7	7.1	115.7	92.9
	Hexadecanol										
70	0.1	2.83	175.8	18.66	0.16	0.132	1125.3	725.5	4.5	151.1	95.5
70	0.5	2.96	168.3	19.83	0.17	0.138	979.4	688.8	5.1	143.5	94.9

Table 4.3.3 Summary of the fraction of PCE removal obtained from ASTP system of DTAB and DOWFAX with total surfactant concentration of 70 mM at 2:1 molar ratio of DTAB:DOWFAX, 30 °C in the absence and presence of additive

Type of Additive	Additive Concentration (mM)	Fraction of PCE removal (%)
No additive	-	91.4
TX-100	2	95.9
	10	96.3
	20	96.8
TX-114	2	95.3
	10	96.0
	20	96.0
Octanol	0.1	96.0
	0.5	95.8
	1	95.6
	2	95.2
Dodecanol	0.1	98.3
	0.5	96.2
	1	92.9
Hexadecanol	0.1	95.5
	0.5	94.9

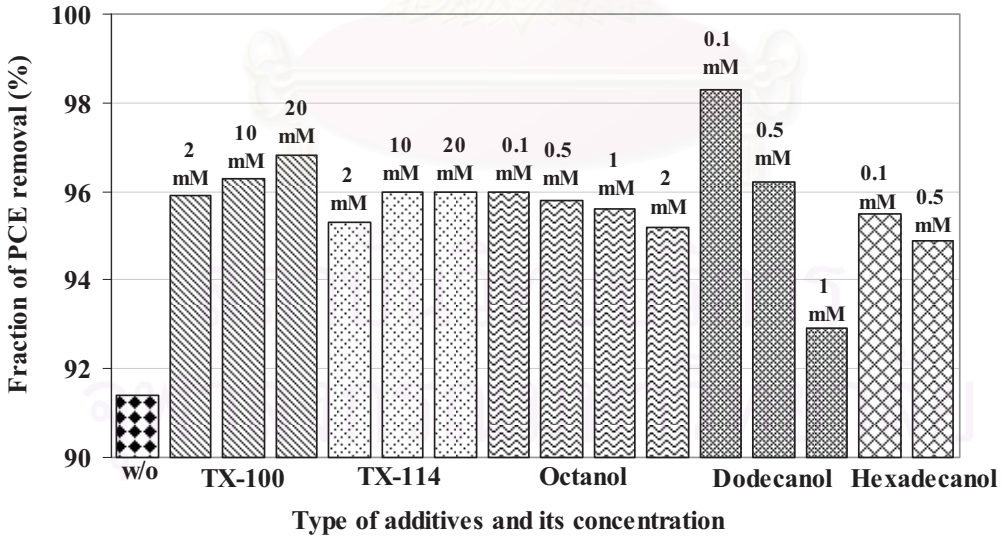


Figure 4.3.2.9 The fraction of PCE removal on the absence and presence of additive at various concentrations (system: 2:1 molar ratio of DTAB:DOWFAX at 70 mM)

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research aimed to investigate the efficiency enhancement by lipophilic linkers and nonionic surfactants addition into an aqueous surfactant two-phase system (ASTP) using mixtures of cationic and anionic surfactants to preconcentrate and extract PCE from wastewater. The base surfactant system was a mixture of DTAB:DOWFAX at 2:1 molar ratio. The CMC determination was determined in the absence and presence of additives. The results revealed that the CMC of DTAB:DOWFAX at 2:1 molar ratio is 0.016 mM. However, the addition of additive does not show pronounced effect onto the CMC values. The total surfactant concentration was investigated in the range of 30-110 mM. The PCE concentration remaining in the surfactant-dilute phase was only 8.6 ppm at the total surfactant concentration of 70 mM or 91.4 % of PCE can be extracted by this ASTP system without any additives from the original PCE concentration of 100 ppm. In addition, the surfactant and PCE can be preconcentrated into the surfactant-rich phase in a small volume. The partition ratios of surfactant and PCE are as high as 967.7, and 148.65, respectively.

In this study, the nonionic surfactants used were Triton X-114 with EO of 7.5 units and Triton X-100 with EO of 9.5 units. From the result, we can conclude that the different of 2 EO units has insignificant effect to the PCE removal efficiency. However, the addition of both nonionic surfactants at the lowest nonionic surfactant concentration studied here (2 mM) is capable to enhance the PCE removal efficiency by 5%. In addition, the results showed that the lipophilic linkers (long straight chain alcohol) are excellent additives. The addition of alcohols at very low concentration (molar ratio of surfactant to alcohol is 700 or alcohol concentration of 0.1 mM) can dramatically enhance the PCE solubilization especially *n*-dodecanol that shows the greatest ability to extract up to 98% of PCE into the surfactant-rich phase within single stage, followed by *n*-octanol and *n*-hexadecanol, where the fractions of PCE removal are 96% and 95.5%,

respectively. Finally, it is worthwhile to note that both nonionic surfactants and lipophilic linkers can enhance the PCE solubilization to the greater extent but the solubilization enhancement is independent to the additive concentration. Therefore, a further increase in concentration of nonionic surfactants and alcohols does not provide advantages to the system.

5.2 Recommendations

Based on the results from this research, the recommendations for further studies are suggested as follows.

1. The ASTP system formed by a mixture of cationic-anionic surfactants should be scaled up to investigate the system feasibility whether this technique can be operated in a continuous mode instead of a single extraction stage in a small lab scale. In addition, the study of additives addition should also be considered in the continuous system.

2. This ASTP system with the addition of additives may be applied to extract and preconcentrate other kinds of hazardous materials of environmental concerns.

3. Future research should explore a wider range of molecules that can serve as hydrophilic linker and lipophilic linker according to the needs of the specific application.

4. The combination of hydrophilic linker and lipophilic linkers should be further studied to investigate whether the combination of linkers can cause the synergistic effects onto the solubilization.

5. The ASTP technique should be applied as one method for soil remediation, e.g. soil washing. The contaminated soil can be cleaned up by this system.

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APPENDICES

APPENDIX A

Table A-1 Phase behavior of cationic-anionic surfactant system

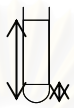
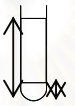
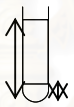
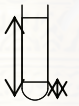
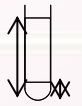
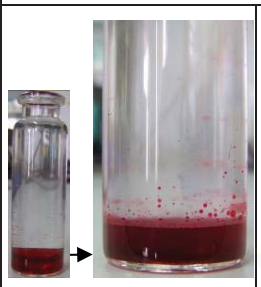
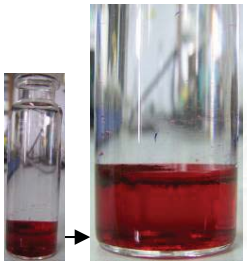
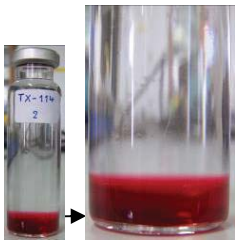
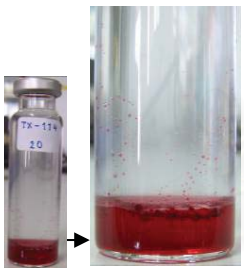
System	Total surfactant conc. (mM)	Molar ratio	Phase appearance		Interfacial boundary
DTAB:DOWFAX	30	2:1	 6.45 cm 0.23 cm	upper: clear solution lower: clear solution, oil-like, not much gluey	clear interface, unstable
DTAB:DOWFAX	50	2:1	 6.45 cm 0.38 cm	upper: clear solution lower: clear solution, gluey-like	clear interface, unstable
DTAB:DOWFAX	70	2:1	 6.45 cm 0.5 cm	upper: clear solution lower: clear solution, highly gluey- like	clear interface, stable
DTAB:DOWFAX	90	2:1	 6.45 c 0.61 cm	upper: blur solution with dispersed droplet lower: clear solution, highly gluey- like	clear interface, stable
DTAB:DOWFAX	110	2:1	 6.45 cm 0.73 cm	upper: blur solution with dispersed droplet lower: clear solution, highly gluey- like	clear interface, stable

Table A-2 Phase separation data of DTAB:DOWFAX at total surfactant concentration of 70 mM at 2:1 molar ratio, 30 °C with the presence of TX-100 at various concentration

Additives concentration (mM)	Phase appearance		Interfacial boundary	DOWFAX				
				Rich Phase		Dilute Phase		Surfactant Partition Ratio
				Volume (ml)	Conc (mM)	Volume (ml)	Conc (mM)	
2		upper: clear solution, no dispersed droplet lower:, highly gluey-like	clear separation, stable	1.75	283.3	19.75	0.26	1105.6
10		upper: clear solution, no dispersed droplet lower:, highly gluey-like	clear separation, stable	2.33	213.3	19.17	0.14	1551.5
20		upper: clear solution, no dispersed droplet lower: highly gluey-like	clear separation, stable	4.17	120	17.33	0.13	929

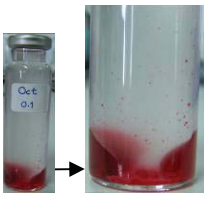
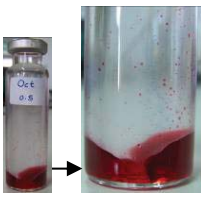
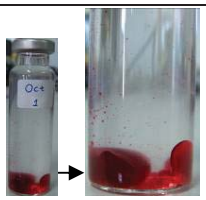
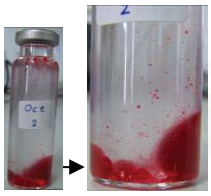
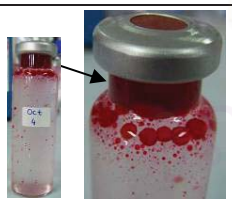
*The samples were added with red dye to form a color to show the interface

Table A-3 Phase separation data of DTAB:DOWFAX at total surfactant concentration of 70 mM at 2:1 molar ratio, 30 °C with the presence of TX-114 at various concentration

Additives concentration (mM)	Phase appearance		Interfacial boundary	DOWFAX				
				Rich Phase		Dilute Phase		Surfactant Partition Ratio
				Volume (ml)	Conc (mM)	Volume (ml)	Conc (mM)	
2		upper: clear solution, no dispersed droplet lower:, highly gluey-like	clear separation, stable	1.67	295.8	19.83	0.23	1290.9
10		upper: clear solution, no dispersed droplet lower:, highly gluey-like	clear separation, stable	2	250	19.5	0.13	1967.2
20		upper: clear solution, no dispersed droplet lower: highly gluey-like	clear separation, stable	2.67	186.7	18.83	0.12	1585.8

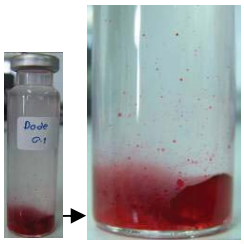
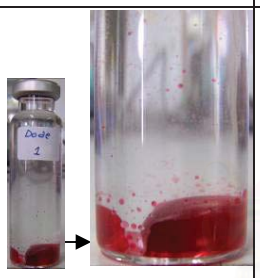
*The samples were added with red dye to form a color to show the interface

Table A-4 Phase separation data of DTAB:DOWFAX at total surfactant concentration of 70 mM at 2:1 molar ratio, 30 °C with the presence of octanol at various concentration

Additives concentration (mM)	Phase appearance		Interfacial boundary	DOWFAX				
				Rich Phase		Dilute Phase		Surfactant Partition Ratio
				Volume (ml)	Conc (mM)	Volume (ml)	Conc (mM)	
0.1		upper: blur solution, no dispersed droplet lower:, oil-like	unclear phase separation, unstable	1.95	0.1	19.55	0.14	1832.8
0.5		upper: blur solution, no dispersed droplet lower:, oil-like	unclear phase separation, unstable	2.15	0.5	19.35	0.17	1334.9
1		upper: blur solution, no dispersed droplet lower: gluey-like	unclear phase separation, unstable	2.18	1	19.31	0.19	1200
2		upper: blur solution with dispersed droplet lower: clear solution, highly gluey- like	unclear phase separation, unstable	3.17	2	18.32	0.2	779.3
4		upper: highly gluey-like lower: blur solution, with a lot of droplet suspend in the solution	No Phase Separation					
8		upper: highly gluey-like lower: blur solution, with a lot of droplet suspend in the solution	No Phase Separation					

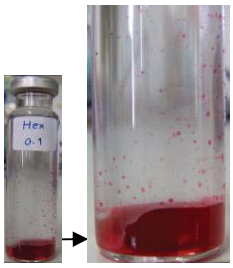
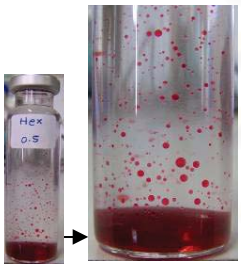
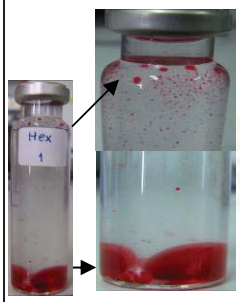
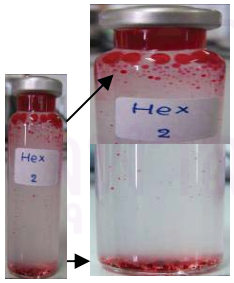
*The samples were added with red dye to form a color to show the interface

Table A-5 Phase separation data of DTAB:DOWFAX at total surfactant concentration of 70 mM at 2:1 molar ratio, 30 °C with the presence of dodecanol at various concentration

Additives concentration (mM)	Phase appearance		Interfacial boundary	DOWFAX				
				Rich Phase		Dilute Phase		Surfactant Partition Ratio
				Volume (ml)	Conc (mM)	Volume (ml)	Conc (mM)	
0.1		upper: blur solution, no dispersed droplet lower:, gluey-like	unclear phase separation, unstable	2.23	224.2	19.27	0.06	3415.8
0.5		upper: blur solution, no dispersed droplet lower:, gluey-like	unclear phase separation, unstable	2.37	210.8	19.13	0.13	1619.2
1		upper: blur solution, no dispersed droplet lower: highly gluey-like	unclear phase separation, unstable	2.44	203.3	19.06	0.25	820.2
2		upper: : highly gluey-like lower: blur solution, with a lot of droplet suspend in the solution	No Phase Separation					

*The samples were added with red dye to form a color to show the interface

Table A-6 Phase separation data of DTAB:DOWFAX at total surfactant concentration of 70 mM at 2:1 molar ratio, 30 °C with the presence of hexadecanol at various concentration

Additives concentration (mM)	Phase appearance		Interfacial boundary	DOWFAX				
				Rich Phase		Dilute Phase		Surfactant Partition Ratio
				Volume (ml)	Conc (mM)	Volume (ml)	Conc (mM)	
0.1		upper: blur solution, few dispersed droplet lower:, oil-like, hole-like	unclear phase separation, unstable	2.83	175.8	18.66	0.16	1125.3
0.5		upper: blur solution, less dispersed droplet in upper area, but increase in the middle lower:, oil-like, highly gluey-like	unclear phase separation, unstable	2.96	168.3	19.83	0.17	979.4
1		upper: blur solution, a lot of dispersed droplet lower: gluey-like, many oil droplet	Unclear phase separation, highly saturated hexadecanol suspends in the solution					
2		upper: : highly gluey-like, a lot of oil droplet lower: cloud solution, with a lot of droplet suspend at the bottom	No Phase Separation					

*The samples were added with red dye to form a color to show the interface

APPENDIX B

Table B Determination of surface tension and surfactant concentration data for different types of additive with condition of DTAB:DOWFAX at 2:1 molar ratio, 30 °C

Concentration and type of additive	Surface Tension (mN/m)														
	5 (mM)	2 (mM)	1 (mM)	0.5 (mM)	0.1 (mM)	0.08 (mM)	0.04 (mM)	0.01 (mM)	0.008 (mM)	0.006 (mM)	0.004 (mM)	0.002 (mM)	0.001 (mM)	0.0005 (mM)	CMC (mM)
No additive	30.243	30.316	30.681	30.896	31.327	31.544	31.629	33.697	35.846	37.917	39.666	44.476	48.793	53.744	0.016
TX-100*	30.797	30.941	31.082	31.306	31.792	31.845	32.213	33.455	34.969	35.899	38.344	42.255	45.975	51.106	0.014
TX-114*	30.383	30.176	30.458	30.538	31.045	31.064	31.793	32.746	34.576	35.821	38.214	41.732	45.629	50.915	0.014
Octanol**	30.298	30.166	30.172	30.63	30.85	31.239	31.52	31.213	33.816	34.873	38.124	45.582	50.007	57.203	0.010
Dodecanol**	29.649	30.186	30.367	30.516	30.786	31.168	31.431	34.336	34.86	36.329	38.422	42.86	47.278	52.494	0.016
Hexadecanol**	30.457	30.619	30.65	30.821	31.146	31.404	31.922	33.935	34.946	36.377	38.52	43.307	47.921	53.357	0.014

* Molar ratio of cationic/anionic surfactant to nonionic surfactant is 35

** Molar ratio of surfactant to alcohol is 700

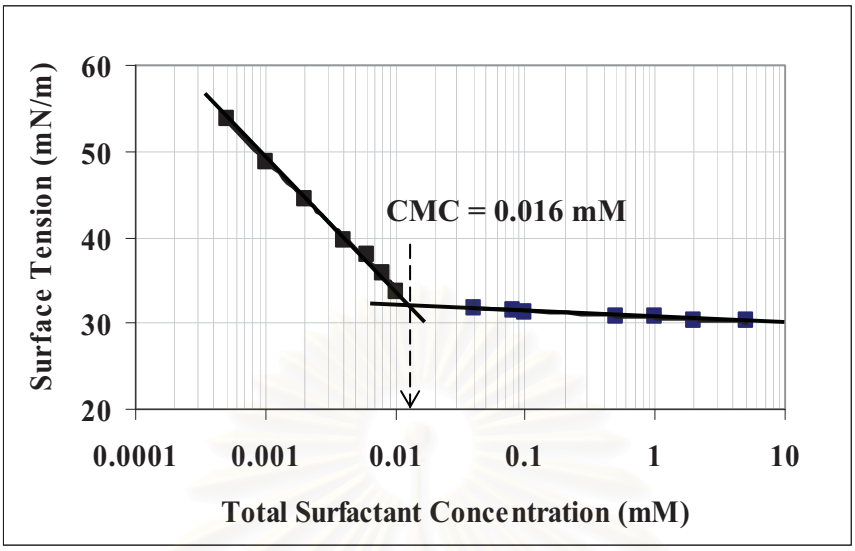


Figure B-1 The CMC value of DTAB and DOWFAX at 2:1 molar ratio in an absence of additive

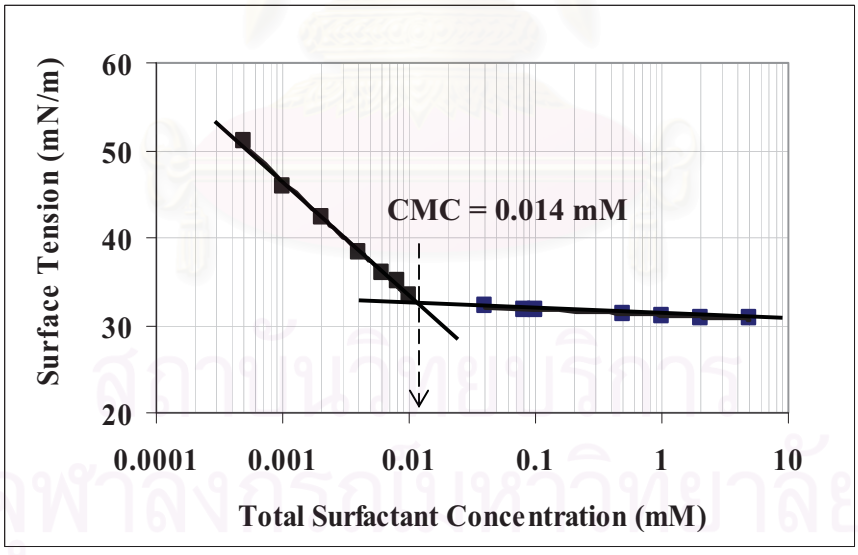


Figure B-2 The CMC value of DTAB and DOWFAX at 2:1 molar ratio in the presence of 2 mM TX-100

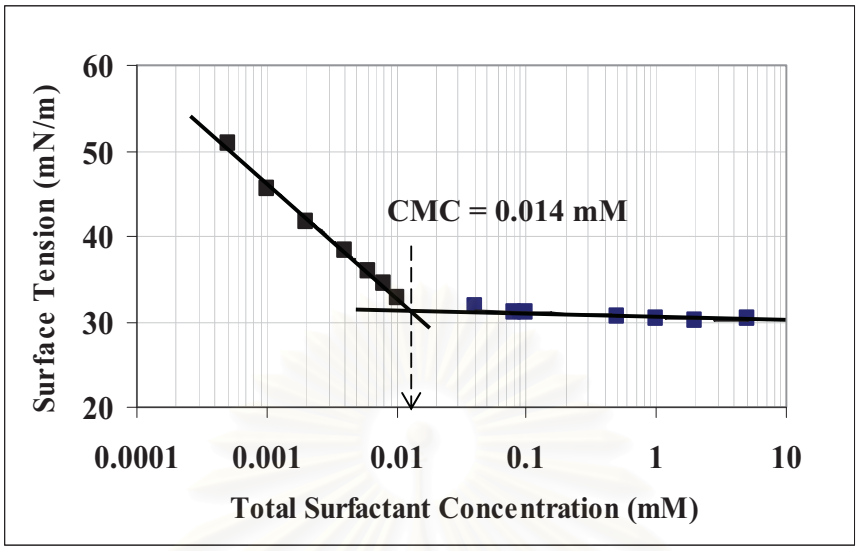


Figure B-3 The CMC value of DTAB and DOWFAX at 2:1 molar ratio in the presence of 2 mM TX-114

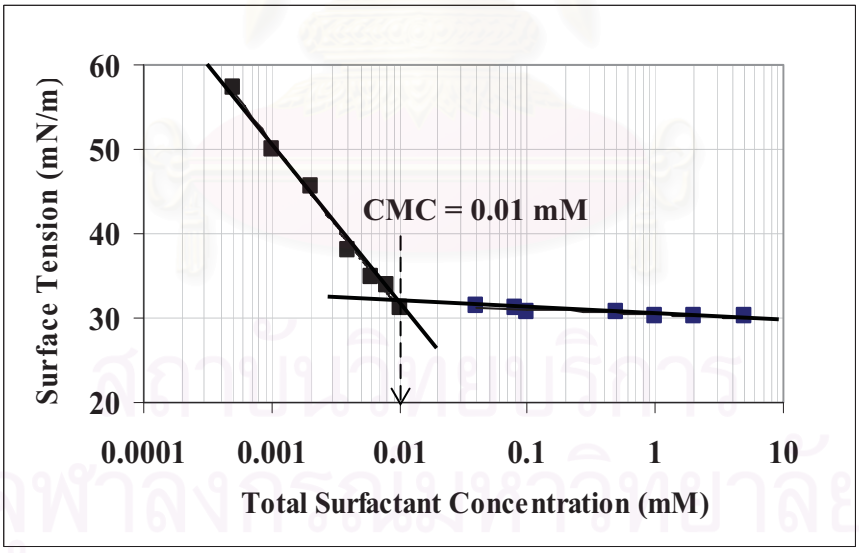


Figure B-4 The CMC value of DTAB and DOWFAX at 2:1 molar ratio in the presence of 0.1 mM octanol

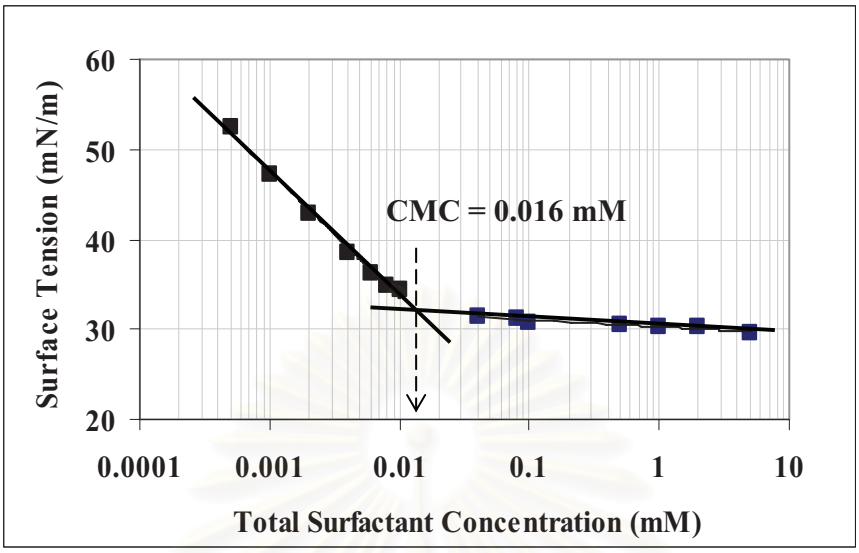


Figure B-5 The CMC value of DTAB and DOWFAX at 2:1 molar ratio in the presence of 0.1 mM dodecanol

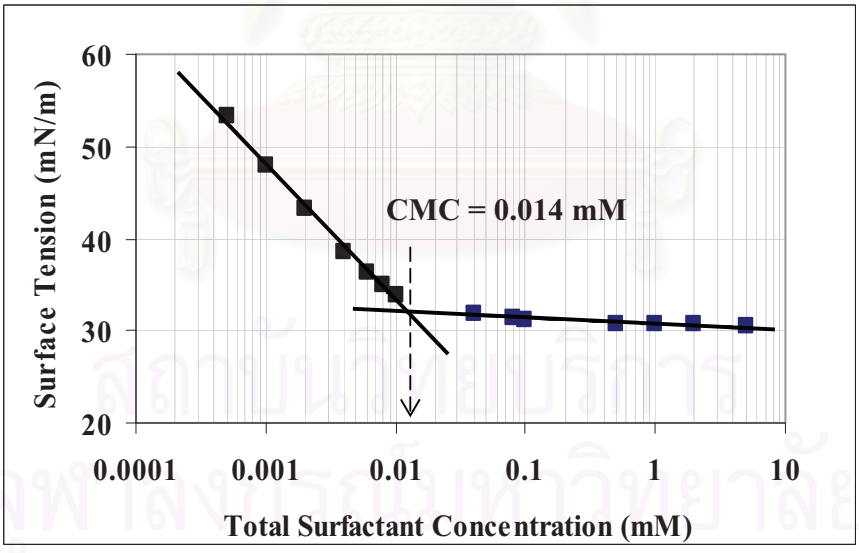


Figure B-6 The CMC value of DTAB and DOWFAX at 2:1 molar ratio in the presence of 0.1 mM hexadecanol

APPENDIX C

Table C-1 Determination of DOWFAX and PCE concentration in each phase at total surfactant concentration of 30 mM, DTAB:DOWFAX molar ratio of 2:1, 30 °C in the absence of additive

	DOWFAX Concentration (mM)					PCE Concentration (ppm)			
	Rich Phase[1]		Dilute Phase[2]			Rich Phase		Dilute Phase	
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	Area (uV.s)	Conc. (ppm)
1	0.515	0.079	0.389	0.06	1	359265.7	2911.86	16746.37	14.96
2	0.538	0.082	0.369	0.057	2	324590.5	2630.82	16341.48	14.59
3	0.517	0.079	0.368	0.056	3	302154.4	2448.97	16400.22	14.65
4	0.517	0.079	0.371	0.057	4	372636.1	3020.23	15972.71	14.27
5	0.543	0.083	0.39	0.06	5	292154.4	2367.92	16507.12	14.75
6	0.518	0.079	0.372	0.057	6	332636.1	2696.03	16168.39	14.44
Avg	0.523	0.079	0.375	0.057	Avg	330573	2679.3	16356	14.61
SD	0.0103	0.0015	0.0097	0.0015	SD	31357	254.15	268.14	0.24
%RSD	1.98	1.88	2.59	2.59	%RSD	9.48	9.48	1.64	1.64

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table C-2 Determination of DOWFAX and PCE concentration in each phase at total surfactant concentration of 50 mM, DTAB:DOWFAX molar ratio of 2:1, 30 °C in the absence of additive

	DOWFAX Concentration (mM)					PCE Concentration (ppm)			
	Rich Phase[1]		Dilute Phase[2]			Rich Phase		Dilute Phase	
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	Area (uV.s)	Conc. (ppm)
1	0.558	0.087	0.431	0.067	1	196193.2	1590.15	10925.57	9.76
2	0.533	0.083	0.443	0.069	2	217672	1764.24	10834.44	9.68
3	0.528	0.082	0.425	0.066	3	198685.4	1610.35	10413.52	9.30
4	0.528	0.082	0.427	0.066	4	210319.5	1704.65	10833.09	9.68
5	0.542	0.084	0.427	0.066	5	211153.5	1711.41	10632.55	9.49
6	0.535	0.083	0.445	0.069	6	209108.3	1694.83	11138.34	9.95
Avg	0.534	0.083	0.432	0.067	Avg	207189	1679.3	10796	9.64
SD	0.0058	0.0008	0.0090	0.0014	SD	8152.5	66.08	248.94	0.22
%RSD	1.08	0.98	2.09	2.11	%RSD	3.93	3.93	2.31	2.31

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table C-3 Determination of DOWFAX and PCE concentration in each phase at total surfactant concentration of 70 mM, DTAB:DOWFAX molar ratio of 2:1, 30 °C in the absence of additive

	DOWFAX Concentration (mM)					PCE Concentration (ppm)			
	Rich Phase[1]		Dilute Phase[2]			Rich Phase		Dilute Phase	
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	Area (uV.s)	Conc. (ppm)
1	0.573	0.089	0.471	0.073	1	164523.5	1333.47	9939.89	8.88
2	0.56	0.087	0.473	0.073	2	157939.4	1280.11	9627.61	8.60
3	0.565	0.088	0.471	0.073	3	152095.8	1232.74	9523.16	8.51
4	0.547	0.085	0.445	0.069	4	149996.7	1215.73	9521.31	8.51
5	0.573	0.089	0.469	0.073	5	156196	1265.97	9427.43	8.42
6	0.568	0.088	0.464	0.072	6	165530.1	1341.63	9716.69	8.68
Avg	0.566	0.088	0.468	0.073	Avg	157714	1278.28	9626.02	8.59
SD	0.0054	0.0008	0.0033	0.0005	SD	6339.35	51.38	183.15	0.16
%RSD	0.96	0.93	0.70	0.69	%RSD	4.02	4.02	1.90	1.90

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table C-4 Determination of DOWFAX and PCE concentration in each phase at total surfactant concentration of 90 mM, DTAB:DOWFAX molar ratio of 2:1, 30 °C in the absence of additive

	DOWFAX Concentration (mM)					PCE Concentration (ppm)			
	Rich Phase[1]		Dilute Phase[2]			Rich Phase		Dilute Phase	
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	Area (uV.s)	Conc. (ppm)
1	0.617	0.096	0.553	0.086	1	134370.4	1089.08	13620.3	12.17
2	0.598	0.093	0.566	0.088	2	138077.6	1119.12	14066.03	12.56
3	0.585	0.091	0.548	0.085	3	112648.4	913.02	13438.61	12.01
4	0.605	0.094	0.546	0.085	4	130098.5	1054.45	13846.22	12.37
5	0.612	0.095	0.553	0.086	5	129567	1050.15	13683.59	12.22
6	0.587	0.091	0.565	0.088	6	121955.9	988.46	14260.35	12.74
Avg	0.601	0.093	0.555	0.086	Avg	127786	1035.71	13819.2	12.34
SD	0.0107	0.0017	0.0077	0.0013	SD	9175.28	74.37	303.01	0.27
%RSD	1.77	1.83	1.39	1.46	%RSD	7.18	7.18	2.19	2.19

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table C-5 Determination of DOWFAX and PCE concentration in each phase at total surfactant concentration of 110 mM, DTAB:DOWFAX molar ratio of 2:1, 30 °C in the absence of additive

	DOWFAX Concentration (mM)					PCE Concentration (ppm)			
	Rich Phase[1]		Dilute Phase[2]			Rich Phase		Dilute Phase	
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	Area (uV.s)	Conc. (ppm)
1	0.612	0.095	0.381	0.059	1	104519.8	847.14	14573.67	13.02
2	0.617	0.096	0.394	0.061	2	104099.8	843.73	15385.76	13.74
3	0.604	0.094	0.374	0.058	3	114234.2	925.87	15784.67	14.10
4	0.617	0.096	0.376	0.058	4	113471.6	919.69	14834.49	13.25
5	0.621	0.097	0.381	0.059	5	111895.5	906.92	14655.08	13.09
6	0.618	0.096	0.392	0.061	6	102830	833.44	15627.91	13.96
Avg	0.616	0.0957	0.382	0.059	Avg	108509	879.47	15143.6	13.53
SD	0.0027	0.0005	0.0068	0.0013	SD	5224.55	42.34	522.15	0.46
%RSD	0.44	0.52	1.77	2.12	%RSD	4.81	4.81	3.45	3.45

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

APPENDIX D

Table D-1 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 2 mM TX-100

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.542	0.084	0.391	0.061	1	4378.09	3.91	6	5419.9	4.84
2	0.545	0.085	0.387	0.06	2	4043.20	3.61	7	5156.77	4.61
3	0.545	0.085	0.393	0.061	3	5490.94	4.91	8	4761.76	4.25
4	0.54	0.084	0.402	0.063	4	4478.00	4.00	9	4160.61	3.72
5	0.548	0.086	0.395	0.062	5	4482.12	4.00	10	4189.14	3.74
6	0.552	0.086	0.395	0.062				Avg	4628.29	4.13
Avg	0.545	0.085	0.3935	0.0615				SD	453.85	0.41
SD	0.0024	0.0008	0.005	0.0006				%RSD	9.81	9.81
%RSD	0.45	0.96	1.27	0.94						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table D-2 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 10 mM TX-100

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.418	0.065	0.232	0.036	1	3950.29	3.53	6	4884.83	4.36
2	0.413	0.064	0.219	0.034	2	4099.37	3.66	7	4053.6	3.62
3	0.399	0.061	0.215	0.033	3	4330.52	3.87	8	4396.65	3.93
4	0.415	0.064	0.201	0.031	4	3826.92	3.42	9	4304.09	3.84
5	0.406	0.063	0.215	0.033	5	4377.77	3.91	10	4207.52	3.76
6	0.417	0.065	0.21	0.032				Avg	4199.55	3.75
Avg	0.408	0.064	0.215	0.033				SD	196.01	0.17
SD	0.0073	0.0014	0.0037	0.0008				%RSD	4.67	4.67
%RSD	1.78	2.21	1.72	2.47						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table D-3 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 20 mM TX-100

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.257	0.04	0.202	0.031	1	3566.11	3.19	6	3598.63	3.21
2	0.246	0.038	0.202	0.031	2	3673.52	3.28	7	3548.87	3.17
3	0.233	0.036	0.204	0.031	3	3453.68	3.08	8	3502.72	3.13
4	0.232	0.036	0.201	0.031	4	3571.09	3.19	9	3332.66	2.98
5	0.214	0.033	0.201	0.031	5	3765.41	3.36	10	3544.64	3.17
6	0.22	0.034	0.201	0.031				Avg	3557.41	3.18
Avg	0.233	0.036	0.2015	0.031				SD	64.84	0.06
SD	0.0106	0.0016	0.0006	0				%RSD	1.82	1.82
%RSD	4.56	4.54	0.29	0						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table D-4 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 2 mM TX-114

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.565	0.089	0.354	0.056	1	5059.91	4.52	6	5411.54	4.83
2	0.537	0.085	0.357	0.056	2	5099.65	4.56	7	5420.27	4.84
3	0.550	0.087	0.341	0.054	3	5408.78	4.83	8	4824.81	4.31
4	0.569	0.09	0.347	0.055	4	5190.53	4.64	9	5588.96	4.99
5	0.562	0.089	0.322	0.051	5	5099.88	4.56	10	5486.32	4.90
6	0.581	0.092	0.35	0.055				Avg	5272.11	4.71
Avg	0.554	0.089	0.342	0.055				SD	176.09	0.16
SD	0.0141	0.0022	0.0147	0.0022				%RSD	3.34	3.34
%RSD	2.54	2.49	4.31	3.93						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table D-5 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 10 mM TX-114

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.486	0.075	0.244	0.038	1	4912.46	4.39	6	4652.9	4.16
2	0.491	0.076	0.183	0.029	2	4675.60	4.18	7	4408.14	3.94
3	0.488	0.076	0.192	0.03	3	4313.25	3.85	8	4221.43	3.77
4	0.476	0.074	0.203	0.032	4	4256.22	3.80	9	4307.19	3.85
5	0.483	0.075	0.197	0.031	5	4433.59	3.96	10	4399.75	3.93
6	0.474	0.074	0.185	0.029				Avg	4430.83	3.96
Avg	0.484	0.075	0.194	0.029				SD	155.98	0.14
SD	0.0066	0.0009	0.0085	0.0013				%RSD	3.52	3.52
%RSD	1.35	1.28	4.37	4.23						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table D-6 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 20 mM TX-114

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.34	0.053	0.17	0.026	1	4446.47	3.97	6	4503.68	4.02
2	0.353	0.055	0.184	0.029	2	4137.42	3.69	7	4505.13	4.02
3	0.359	0.056	0.189	0.029	3	4508.72	4.03	8	4375.84	3.91
4	0.358	0.056	0.18	0.028	4	4191.62	3.74	9	4496.05	4.02
5	0.362	0.057	0.173	0.027	5	4253.15	3.79	10	4390.43	3.92
6	0.388	0.061	0.219	0.034				Avg	4395.29	3.93
Avg	0.358	0.056	0.182	0.028				SD	118.73	0.11
SD	0.0037	0.0008	0.0067	0.0009				%RSD	2.70	2.70
%RSD	1.04	1.46	3.72	3.38						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

APPENDIX E

Table E-1 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 0.1 mM octanol

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.486	0.076	0.212	0.033	1	3818.74	3.41	6	4534.94	4.05
2	0.503	0.078	0.219	0.034	2	4248.61	3.79	7	4703.5	4.20
3	0.482	0.075	0.221	0.034	3	4599.32	4.11	8	4773.25	4.26
4	0.467	0.073	0.214	0.033	4	3536.24	3.16	9	4753.37	4.25
5	0.498	0.078	0.214	0.033	5	4040.73	3.61	10	4595.22	4.10
6	0.499	0.078	0.222	0.034				Avg	4411.80	3.94
Avg	0.491	0.0767	0.218	0.033				SD	338.44	0.30
SD	0.0085	0.0015	0.0043	0.0006				%RSD	7.67	7.67
%RSD	1.74	1.95	1.99	1.72						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table E-2 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 0.5 mM octanol

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.455	0.071	0.269	0.042	1	4549.05	4.06	6	4979.35	4.45
2	0.451	0.07	0.265	0.041	2	4150.76	3.71	7	4396.05	3.93
3	0.451	0.07	0.262	0.041	3	4668.32	4.17	8	4748.93	4.24
4	0.445	0.069	0.265	0.041	4	4857.06	4.34	9	4587.3	4.09
5	0.443	0.069	0.273	0.043	5	4693.02	4.19	10	4823.38	4.31
6	0.439	0.068	0.278	0.043				Avg	4665.38	4.17
Avg	0.447	0.069	0.268	0.042				SD	151.95	0.13
SD	0.0041	0.0006	0.0038	0.0009				%RSD	3.26	3.26
%RSD	0.92	0.83	1.43	2.29						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table E-3 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 1 mM octanol

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.451	0.07	0.292	0.045	1	4899.98	4.38	6	5084.47	4.54
2	0.444	0.069	0.284	0.044	2	4694.01	4.19	7	5134.74	4.59
3	0.434	0.068	0.297	0.046	3	4952.05	4.42	8	4966.36	4.44
4	0.433	0.067	0.291	0.045	4	5165.89	4.61	9	4804.07	4.29
5	0.442	0.069	0.302	0.047	5	5061.78	4.52	10	4479.21	4.00
6	0.413	0.064	0.297	0.046				Avg	4949.68	4.42
Avg	0.438	0.068	0.294	0.045				SD	148.47	0.13
SD	0.0056	0.0009	0.0032	0.0006				%RSD	2.99	2.99
%RSD	1.27	1.40	1.09	1.28						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table E-4 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 2 mM octanol

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.304	0.047	0.312	0.049	1	5392.11	4.82	6	5251.32	4.69
2	0.298	0.046	0.309	0.048	2	5645.58	5.04	7	5456.79	4.87
3	0.31	0.048	0.321	0.05	3	5833.07	5.21	8	5597.1	5.00
4	0.311	0.048	0.31	0.048	4	4961.7	4.43	9	5106.49	4.56
5	0.304	0.047	0.31	0.048	5	5102.48	4.56	10	5237.65	4.68
6	0.291	0.045	0.294	0.046				Avg	5348.69	4.78
Avg	0.304	0.047	0.310	0.048				SD	208.57	0.19
SD	0.0049	0.0008	0.0013	0.0005				%RSD	3.89	3.89
%RSD	1.61	1.74	0.40	1.04						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table E-5 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 0.1 mM dodecanol

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.427	0.067	0.099	0.015	1	1936.75	1.73	6	1922.59	1.72
2	0.431	0.067	0.105	0.016	2	1893.28	1.69	7	1834.2	1.64
3	0.433	0.067	0.105	0.016	3	2012.39	1.79	8	2099.37	1.87
4	0.436	0.068	0.112	0.017	4	1838.26	1.64	9	1496.82	1.34
5	0.441	0.068	0.097	0.015	5	2242.76	2.00	10	1994.6	1.78
6	0.426	0.066	0.103	0.016				Avg	1941.43	1.73
Avg	0.432	0.067	0.103	0.0157				SD	90.75	0.08
SD	0.0038	0.0005	0.0028	0.0005				%RSD	4.67	4.67
%RSD	0.87	0.74	2.75	3.17						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table E-6 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 0.5 mM dodecanol

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.406	0.063	0.204	0.031	**1**	4101.59	3.66	**6**	4314.44	3.85
2	0.411	0.064	0.219	0.033	**2**	4195.57	3.75	**7**	4110.68	3.67
3	0.407	0.063	0.211	0.032	**3**	4353.52	3.88	**8**	4026.12	3.59
4	0.412	0.064	0.201	0.031	**4**	4102.04	3.66	**9**	3692.36	3.29
5	0.402	0.062	0.201	0.031	**5**	4676.27	4.18	**10**	4803.95	4.29
6	0.406	0.063	0.202	0.031				**Avg**	4235.03	3.78
Avg	0.407	0.063	0.204	0.031				**SD**	210.85	0.19
SD	0.0024	0.0005	0.0045	0.0005				**%RSD**	4.98	4.98
%RSD	0.58	0.79	2.20	1.6						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table E-7 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 1 mM dodecanol

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.398	0.061	0.381	0.059	1	8905.5	7.95	6	7412.36	6.62
2	0.416	0.064	0.378	0.059	2	7961.47	7.11	7	7537.67	6.73
3	0.407	0.062	0.371	0.058	3	7449.39	6.65	8	8469.65	7.57
4	0.394	0.06	0.387	0.06	4	8257.61	7.38	9	7298.47	6.52
5	0.399	0.061	0.387	0.06	5	9071.39	8.10	10	8418.66	7.52
6	0.393	0.06	0.395	0.062				Avg	7911.51	7.07
Avg	0.399	0.061	0.383	0.059				SD	585.55	0.52
SD	0.0054	0.0008	0.0045	0.0006				%RSD	7.40	7.40
%RSD	1.36	1.34	1.17	0.97						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table E-8 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 0.1 mM hexadecanol

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.342	0.053	0.237	0.037	1	7065.88	6.31	6	5437.51	4.86
2	0.347	0.054	0.226	0.035	2	5493.92	4.91	7	4483.09	4.00
3	0.351	0.055	0.252	0.039	3	4659.79	4.16	8	4970.69	4.44
4	0.332	0.051	0.237	0.037	4	4280.30	3.82	9	5245.59	4.69
5	0.341	0.053	0.253	0.039	5	5179.47	4.63	10	4822.49	4.31
6	0.315	0.049	0.239	0.037				Avg	5036.57	4.49
Avg	0.341	0.053	0.241	0.037				SD	364.99	0.33
SD	0.0062	0.0013	0.0072	0.0010				%RSD	7.25	7.25
%RSD	1.83	2.38	2.99	2.67						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table E-9 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 0.5 mM hexadecanol

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.334	0.051	0.265	0.041	1	5704.02	5.09	6	5944.71	5.31
2	0.327	0.05	0.263	0.041	2	5540.97	4.95	7	5639.12	5.04
3	0.336	0.052	0.271	0.042	3	5869.58	5.24	8	5364.44	4.79
4	0.329	0.05	0.274	0.043	4	5988.21	5.35	9	5744.04	5.13
5	0.328	0.05	0.266	0.041	5	6901.27	6.16	10	5620.85	5.02
6	0.334	0.051	0.266	0.041				Avg	5756.44	5.14
Avg	0.331	0.050	0.267	0.041				SD	161.88	0.14
SD	0.0032	0.0006	0.0027	0.0005				%RSD	2.81	2.81
%RSD	0.97	1.14	1.01	1.21						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

APPENDIX F

Table F-1 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 68 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 2 mM TX-100

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase[1]		Dilute Phase[2]			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.549	0.084	0.438	0.067	1	3248.28	2.90	6	4198.28	3.75
2	0.549	0.084	0.433	0.066	2	3817.42	3.41	7	4305.92	3.85
3	0.553	0.085	0.431	0.066	3	4452.90	3.98	8	3627.65	3.24
4	0.550	0.084	0.438	0.067	4	3453.09	3.08	9	4662.50	4.16
5	0.562	0.086	0.445	0.068	5	3856.91	3.44	10	4324.76	3.86
6	0.557	0.085	0.443	0.068				Avg	4004.62	3.58
Avg	0.552	0.084	0.438	0.067				SD	365.45	0.33
SD	0.0036	0.0006	0.0041	0.0008				%RSD	9.13	9.13
%RSD	0.65	0.68	0.93	1.22						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

Table F-2 Determination of DOWFAX concentration in each phase and PCE concentration in dilute phase (PCE concentration in rich phase was indirectly calculated using mass balance principle showed in chapter 3). Total surfactant concentration of 70 mM, DTAB and DOWFAX at molar ratio of 2:1, 30 °C in the presence of 2 mM TX-100

	DOWFAX Concentration (mM)					PCE Concentration (ppm)				
	Rich Phase(1)		Dilute Phase(2)			Dilute Phase				
No. of Sample	Abs @ 240 nm	Conc. (mM)	Abs @ 240 nm	Conc. (mM)	No. of Sample	Area (uV.s)	Conc. (ppm)	No. of Sample	Area (uV.s)	Conc. (ppm)
1	0.549	0.084	0.399	0.061	1	4378.09	3.91	6	5419.90	4.84
2	0.549	0.084	0.392	0.06	2	4043.20	3.61	7	5156.77	4.61
3	0.549	0.084	0.392	0.06	3	5490.94	4.90	8	4761.76	4.25
4	0.574	0.088	0.425	0.065	4	4478.00	4.00	9	4160.61	3.72
5	0.464	0.086	0.412	0.063	5	4482.12	4.00	10	4189.14	3.74
6	0.463	0.086	0.408	0.062				Avg	4628.29	4.13
Avg	0.506	0.085	0.402	0.061				SD	453.85	0.40
SD	0.0494	0.0012	0.0090	0.0013				%RSD	9.81	9.81
%RSD	9.75	1.36	2.23	2.09						

(1) The samples were diluted for 10,000 times from its original concentration in surfactant rich-phase

(2) The samples were diluted for 12.5 times from its original concentration in surfactant dilute-phase

APPENDIX G

Table G-1 Determination of calibration curve of DOWFAX concentration measuring at wavelength (λ) of 240 nm

DOWFAX Concentration (mM)	UV-VIS Absorbance
0	0
0.05	0.325
0.07	0.453
0.09	0.587
0.1	0.628
0.13	0.859
0.17	1.072

* The samples were diluted for 100 times from its original concentration

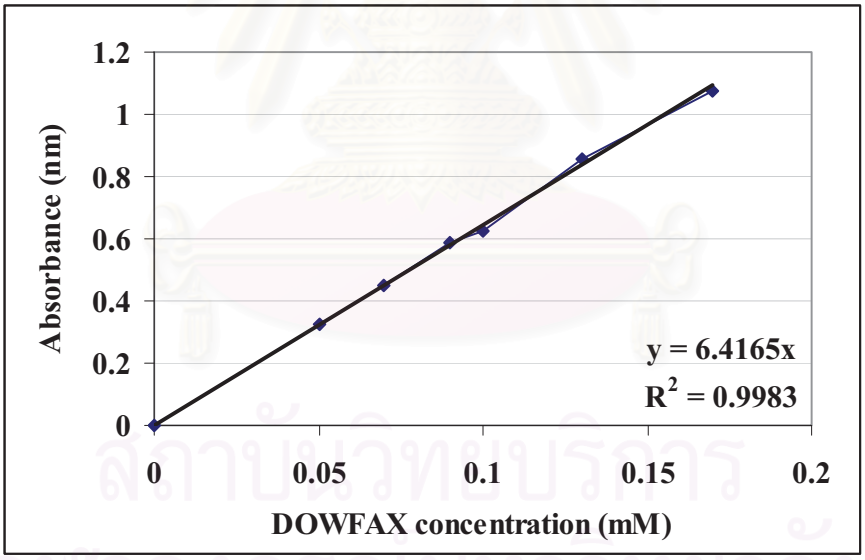


Figure G-1 Relationship between DOWFAX concentration (mM) and absorbance measured using UV-Visible spectrophotometer

Table G-2 Determination of calibration curve of PCE concentration in surfactant dilute-phase

PCE concentration (ppm)	Area (uV.s)	Average Area (uV.s)	SD	%RSD
5	5004.26	5063.018	84.17	1.66
	5034.06			
	5187.85			
	5025.9			
10	10993.97	10909.89	91.98	0.84
	10815.42			
	10846.78			
	10983.39			
15	16851.61	16800.69	107.32	0.64
	16878.8			
	16642.54			
	16829.8			
20	22117.28	22655.00	563.88	2.49
	23086.51			
	22221.85			
	23194.36			

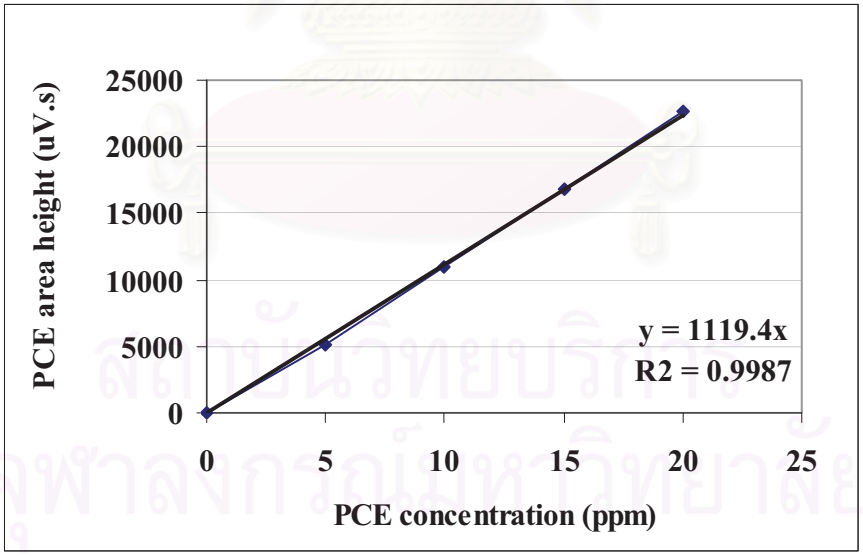


Figure G-2 Relationship between PCE concentration (ppm) and area height (uV.s) at thermostat time of 15 min measured using gas chromatography equipped with a flame ionized detector (FID)

Table G-3 Determination of calibration curve of PCE concentration in surfactant rich-phase

PCE concentration (ppm)	Area (uV.s)	Average Area (uV.s)	SD	%RSD
500	67373.75	66207.11	2029.92	3.07
	63250.86			
	67676.34			
	66527.47			
1000	127400.8	122966.4	4786.539	3.89
	120386.3			
	117528.6			
	126549.9			
1500	194816.5	185688.3	6153.348	3.31
	183918.4			
	182185.4			
	181833			
2000	252126.6	245374.0	8214.55	3.35
	242622.1			
	251777.8			
	234969.3			

* The samples were prepared at total surfactant concentration of 858 mM, DTAB:DOWFAX molar ratio of 2:1

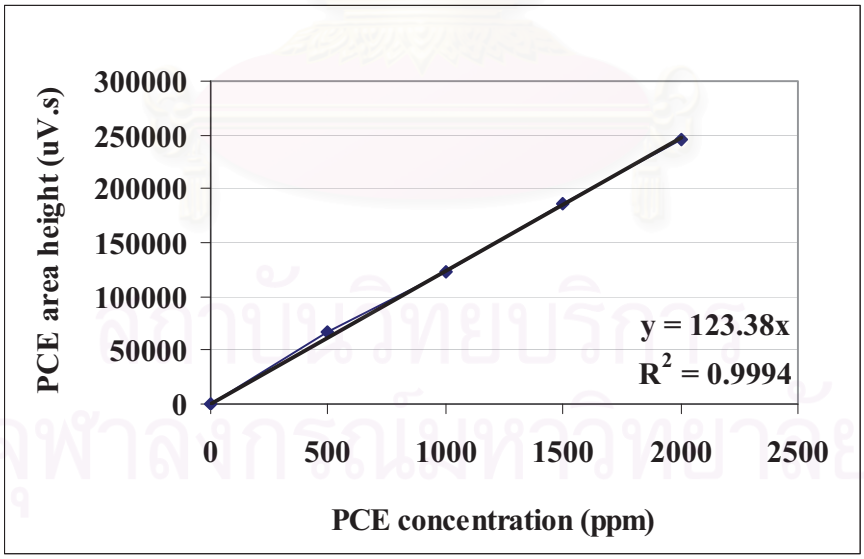


Figure G-3 Relationship between PCE concentration (ppm) and area height (uV.s) at thermostat time of 15 min measured using gas chromatography equipped with a flame ionized detector (FID)

APPENDIX H

Table H Determination of an interference of nonionic surfactants (TX-100 and TX-114) onto the wavelength of DOWFAX (240 nm) at nonionic surfactants concentration of 1 wt% at various wavelength

	Sample	Absorbance									
		λ = 225 nm	λ = 240 nm	λ = 270 nm	λ = 300 nm	λ = 330 nm	λ = 400 nm	λ = 450 nm	λ = 500 nm	λ = 600 nm	λ = 700 nm
Original Samples	TX-100 (1wt%)	3.121	3.031	2.778	0.097	0.01	0.001	0	-0.001	-0.001	-0.001
	TX-114 (1wt%)	3.126	3.453	2.754	0.351	0.284	0.236	0.218	0.206	0.19	0.181
	DOWFAX (1wt%)	3.701	3.475	3.012	1.08	0.014	-0.001	-0.002	-0.002	-0.002	-0.002
	TX-100 + DOWFAX	3.495	3.355	2.963	1.056	0.009	-0.007	-0.007	-0.007	-0.007	-0.006
	TX-114 + DOWFAX	3.419	3.296	2.954	1.087	0.018	-0.005	-0.005	-0.005	-0.005	-0.004
Samples with Dilution of 200 times	TX-100 (1wt%)	0.78	0.045	0.078	-0.008	-0.008	-0.006	-0.005	-0.005	-0.004	-0.004
	TX-114 (1wt%)	0.908	0.067	0.099	-0.003	-0.003	-0.003	-0.002	-0.002	-0.001	-0.001
	DOWFAX (1wt%)	0.707	0.776	0.136	0.005	-0.002	-0.002	-0.001	-0.001	-0.001	-0.001
	TX-100 + DOWFAX	1.624	0.862	0.246	0.011	0.003	0.002	0.002	0.002	0.001	0.001
	TX-114 + DOWFAX	1.584	0.85	0.231	-0.002	-0.009	-0.007	-0.005	-0.006	-0.005	-0.004
Samples with Dilution of 500 times	TX-100 + DOWFAX	0.643	0.363	0.100	0.008	0.004	0.003	0.003	0.003	0.002	0.002
	TX-114 + DOWFAX	0.648	0.343	0.089	-0.006	-0.007	-0.006	-0.005	-0.005	-0.004	-0.004

- Nonionic surfactants (TX) of 1 wt% ≈ 16 mM and DOWFAX of 1 wt% ≈ 15.6 mM

BIOGRAPHY

Miss Suthida Khaolerk was born on May 28, 1982 in Bangkok, Thailand. She graduated in Bachelor of Environmental Management from Sirindhorn International Institute of Technology (SIIT), Thammasat University in April 2004. After she graduated she continued her Master Degree study in the International Postgraduate Programs in Environmental Management, Inter-Department of Environmental Management, Chulalongkorn University in May 2004.