การนำสารลดแรงตึงผิวกลับมาใช้ใหม่โดยการสกัดด้วยตัวทำละลายและการสกัดแบบรีเวอร์สไมเซลล์

นางสาวกุลธิดา ไกรสรเจริญ

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SURFACTANT RECOVERY BY LIQUID-LIQUID EXTRACTION AND REVERSE MICELLAR EXTRACTION

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กุลธิดา ไกรสรเจริญ : การนำสารลดแรงตึงผิวกลับมาใช้ใหม่โดยการสกัดด้วยตัวทำละลายและการสกัดแบบรีเวอร์สไมเซลล์. (SURFACTANT RECOVERY BY LIQUID-LIQUID EXTRACTION AND REVERSE MICELLAR EXTRACTION) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ปัญจพร เวชขันต์วิวัฒน์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: เดวิด เอ ซาบาตินี, 128 หน้า.

การศึกษานี้มีวัตถุประสงค์เพื่อกำจัดสารเตตระคลอโรเอทิลีนหรือสารพีซีอี และนำสารลดแรงตึงผิวกลับมาใช้ใหม่โดยใช้การสกัดสองวิธี ได้แก่ การสกัดด้วยตัวทำละลายที่เป็นของเหลวและการสกัดแบบรีเวอร์สไมเซลล์ร่วมกับกระบวนการกรองแบบอัลทราฟิลเทรชัน สารลดแรงตึงผิวถูกใช้อย่างแพร่หลายเพื่อบำบัดพื้นที่ปนเปื้อน อย่างไรก็ดีสารลดแรงตึงผิวควรผ่านกระบวนการทำให้บริสุทธิ์ก่อนนำกลับมาใช้ใหม่ โดยสารลดแรงตึงผิวที่ใช้ในการศึกษานี้ได้จำลองให้เสมือนเป็นสารละลายของสารลดแรงตึงผิวที่สูบกลับขึ้นมาจากพื้นดินหลังการบำบัดพื้นที่ปนเปื้อน ประกอบไปด้วยเอเอ็มเอเข้มข้น 4 เปอร์เซนต์โดยน้ำหนัก (สารลดแรงตึงผิวชนิดประจุลบ), โซเดียมคลอไรด์ 3 เปอร์เซนต์โดยน้ำหนัก และสารพีซีอีเข้มข้น 10,000 มิลลิกรัมต่อลิตร การสกัดด้วยตัวทำละลายที่เป็นของเหลว โดยใช้ตัวทำละลายที่มีค่าความไม่มีขั้วเมื่อเทียบกับอัลเคนทั่วไป (อีเอซีเอ็น) แตกต่างกันห้าชนิดถูกนำมาศึกษา เพื่อดูผลการกระจายตัวของสารพีซีอีและการสกัดสารพีซีอีออกจากสารละลายตั้งต้น ส่วนวิธีสกัดแบบรีเวอร์สไมเซลล์เป็นวิธีการสกัดภายใต้สภาวะวินเซอร์ไทด์ทูไมโครอีมัลชัน โดยระหว่างกระบวนการสกัด ไมเซลล์แตกตัวและเข้าไปละลายอยู่ในตัวทำละลายเกิดเป็นรีเวอร์สไมเซลล์ ทั้งนี้สารพีซีอีจะกระจายตัวเข้าไปอยู่ในตัวทำละลายด้วย จากผลการทดลองพบว่าค่าอีเอซีเอ็นของตัวทำละลายและอัตราส่วนของสารลดแรงตึงผิวต่อตัวทำละลายเป็นปัจจัยสำคัญต่อประสิทธิภาพในการสกัดด้วยตัวทำละลายที่เป็นของเหลว นอกจากนี้ปัจจัยอื่นๆ เช่น โครงสร้างโมเลกุลและหมู่ฟังก์ชันของตัวทำละลายก็มีอิทธิพลต่อการกระจายตัวและการสกัดของสารพีซีอีโดยวิธีสกัดด้วยตัวทำละลายที่เป็นของเหลวเช่นกัน สำหรับการสกัดแบบรีเวอร์สไมเซลล์พบว่าผลของอัตราส่วนของสารลดแรงตึงผิวต่อตัวทำละลาย (อยู่ในช่วง 40:1-5:1) ไม่มีนัยสำคัญต่อผลการสกัดสารลดแรงตึงผิว (84.9-86.9%) และผลการสกัดสารพีซีอี (96.7-98.4%) นอกจากนี้กระบวนการกรองแบบอัลทราฟิลเทรชันยังถูกใช้ร่วมกับการสกัดแบบรีเวอร์สไมเซลล์เพื่อเพิ่มความเข้มข้นของสารลดแรงตึงผิว (รีเวอร์สไมเซลล์) ให้อยู่ในส่วนสารคงค้างหรือส่วนรีเทนเทต ขณะที่สารพีซีอีและตัวทำละลายสามารถผ่านตัวกรองออกไปได้เป็นส่วนเพอมีเอท

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KUNTIDA KRISORNCHAROEN: SURFACTANT RECOVERY BY LIQUID-LIQUID EXTRACTION AND REVERSE MICELLAR EXTRACTION. THESIS PRINCIPAL ADVISOR: PUNJAPORN WESCHAYANWIWAT, THESIS COADVISOR: DAVID A. SABATINI, 128 pp.

This study aimed to investigate two extraction techniques namely liquid-liquid extraction (LLE) and reverse micellar extraction coupled with ultrafiltration process for tetrachloroethylene (PCE) removal and surfactant recovery purposes. Using surfactant solution to remediate NAPLs gains more attractions. Nevertheless, prior reusing surfactant, a decontamination of surfactant solutions is recommended. In this study, we imitated the surfactant solution similar to one pumped out of the contaminated site, which contains 4%AMA (anionic surfactant), 3%NaCl and 10,000 ppm solubilized PCE. The conventional LLE using five extracting solvents varying the equivalent alkane carbon number (EACN) was investigated to determine the partitioning of PCE from surfactant solution into solvent phase and the %PCE removal. The reverse micellar extraction is another extraction technique based on Winsor type II microemulsion formation, where the micelles break up, migrate into the solvent phase and re-aggregate to form reverse micelles. The released PCE during the micelles break up also partitions into the solvent phase. The result showed that the EACN of extracting solvent and the surfactant solution:solvent volumetric ratio were crucial parameters governing the extraction efficiency of LLE. In addition, other parameters such as molecular structure and functional groups of solvent also have an influence on the PCE partitioning and PCE removal in LLE technique. For reverse micellar extraction, the surfactant solution:solvent volumetric ratio (ranged from 40:1 to 5:1) used in this study did not show significant effects on the surfactant removal (84.9-86.9%) and PCE removal (96.7-98.4%). Furthermore, an ultrafiltration process was used as an additional downstream process after reverse micellar extraction to concentrate the surfactant reverse micelles in the retentate, while passing PCE and solvent as the permeate stream.

Field of study:.Environmental Management.. Student's signature: Kuntida Krisorncharoen
Academic year:.....2007......................... Principal Advisor's signature:..........
Co-advisor's signature:..................

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List of Abbreviations

ACN	alkane carbon number
Aerosol-MA or AMA	sodium dihexyl sulfosuccinate
c	concentration
CFC-113	trichloro-1,2,2-trifluoroethane
CMC	critical micelle concentration
CPC	cetyl pyridinium cloride
CPE	cloud point extraction
DCM	dichloromethane
DNAPLs	dense nonaqueous phase liquids
EACN	equivalent alkane carbon number
FID	flame ionized detector
HLB	hydrophile-lipophile balance
$HLB_{mixture}$	hydrophile-lipophile balance of surfactant mixture
GC	gas chromatography
GC-FID	gas chromatography with flame ionized detector
IFT	interfacial tension
kDa	kilo dalton
K_{ow}	Octanol-water coefficient
LLE	liquid-liquid extraction
Ln(s*)	logarithm of the optimum electrolyte concentration
MEUF	micellar enhanced ultrafiltration
MF	microfiltration
mg/L	milligrams per liter
µg/L	micrograms per liter
MW	molecular weight
MWCO	molecular weight cutoff
NAPLs	non-aqueous phase liquids
PCBs	polychlorinated biphenyls
PCE	tetrachloroethylene
ppm	part per million

psi	pascal per square inch
SEAR	surfactant-enhanced aquifer remediation
S^*	optimum salinity
SLLEM	liquid-liquid extraction model
Span-20	sorbitan monolaurate
TCA	trichloroethane
TCE	trichloroethylene
TOC	total organic carbon analyzer
TPH	total petroleum hydrocarbon
UF	ultrafiltration
VOCs	volatile organic compounds
Winsor Type I microemulsion	oil-in-water microemulsion with excess oil
Winsor Type II microemulsion	water-in-oil microemulsion excess aqueous phase
Winsor Type III microemulsion	middle-phase microemulsion with excess aqueous and oil phases
WOR	water/oil volume ratio
X_{A}	weight fraction of surfactant (A)

CHAPTER I

INTRODUCTION

Tetrachloroethylene is a volatile chlorinated hydrocarbon widely used as a solvent in the chemical industries, a dry-cleaning fluid in the textile industries, and a metal-degreasing agent in electroplating industries. Other names for tetrachloroethylene are perchloroethylene (PCE), perc, and tetrachloroethene. PCE is a central nervous system depressant, and inhaling its vapors can cause headache, sleepiness, dizziness, confusion, nausea, difficulty in speaking and walking, and death (http://en.wikipedia.org/wiki/Tetrachloroethylene). PCE is a common soil contaminant. Such contamination most often results from spillage, overfilling, sewer leakage, and an illegal disposal. Although the major environmental releases of PCE generate as air emissions due to its relatively low volatility, the high mobility and density of PCE cause it sinking below the water table. Thus, the clean-up activities tend to be more problematic as compared to clean-up of oil spills. PCE was evidently found loaded to the surface water and groundwater over a hundred thousand pounds (EPA, 1998). 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). Because of the high toxicity and the presence of PCE in the environment, PCE contaminated groundwater and soil need to be remediated using the appropriate technology.

Surfactant-enhanced aquifer remediation (SEAR) is a promising technology using a surfactant solution to remedy the subsurface contaminated by non-aqueous phase liquid (NAPL). To minimize surfactant losses by surfactant sorption to subsurface media, anionic surfactants are often considered for SEAR (Dwarakanath et al., 1999). Since surfactant costs are significant in large-scale implementation of SEAR, the decontamination and reuse of surfactant solutions are desirable (Cheng and Sabatini, 2001).

The hydrophobic interior core of surfactant micelles can promote the solubilization of NAPLs in the micelles leading to desorption of these compounds from soil media. The bulk solution containing solubilized contaminants in surfactant micelles can then be treated to separate surfactants and contaminants (Lee et al., 2001). Recovery of surfactant solution is very important in the development of the surfactant-based remediation. In addition, a reduced volume of wastewater, recycled of used surfactant solutions will reduce the chemical costs for the treatment of hydrophobic organic contaminated soils and groundwater (Lee et al., 2001). This research aimed to compare two environmentally friendly separation techniques called the liquid-liquid extraction and the reverse micellar extraction. Both techniques were investigated to determine their efficiency by means of surfactant recovery and PCE removal.

Liquid-liquid extraction is an alternative for separating organics from groundwater (King et al., 1984; Hiler and Cameon, 1985). It has been widely utilized for industrial applications. Hewes et al., 1974 (Hasegawa et al., 1997) stated that it also has a potential to efficiently remove a wide variety of environmental and groundwater contaminants. The principle of liquid-liquid extraction of contaminant from micellar surfactant solution is based on the competitive partitioning of contaminant molecules among solvent phase, micellar pseudo-phase, and water. To be effective for contaminant removal, the solubilization of extracting solvents in the surfactant solution should be minimized, as this can significantly reduce the partitioning of contaminant into the solvent phase (Cheng, M.S. thesis, 2000).

The solvent extraction using reversed micelles is promising for dye removal from water in terms of its simplicity and efficiency of the process. The recovery of solvent and reuse of dye after its removal is related to the economic viability of the process (Pandit and Basu, 2004). A form of reversed micellar extraction has been applied in the biotechnology field for a recovery of proteins and other bio-products that are highly water-soluble (Kinugasa et al., 1998; Rabie et al., 1996). Electrolytes are typically added in such extractions to decrease the hydrophile-lipophile balance (HLB) of the surfactant system and thus, facilitate the formation of Winsor type II microemulsion systems. The reversed micelles contain inner cores for solubilized water, which are encapsulated by surfactant molecules and shielded from the organic solvent. This water uptake decreases with increasing counterion concentration (Kinugasa et al., 1998; Rabie et al., 1996). The reversed micelles are water-in-oil microemulsion droplets stabilized by surfactants in apolar solvents, and have been widely studied to extract proteins in liquid–liquid extraction process (Luisi et al., 1988; Dekker et al., 1989; Lye et al., 1994; Krei et al., 1992). This method has been widely noticed for its energy-saving feature and the possibility of sequential operations. Many enzymes have been successfully extracted by reversed micelles without losing too much bioactivity.

Lipe et al. (1996) demonstrated that ultrafiltration (UF) could be effectively used for surfactant-contaminant separation purpose since the most of the surfactants in fact do not pass through the membrane. They used 10,000 molecular weight cutoff (MWCO) membrane to retain micelles while monomers passed through the permeate. They achieved in excess of 90% surfactant retention (in some cases >95%) while maintaining water-normalized fluxes of 90%. While the UF process effectively retained surfactant micelles, monomeric concentrations would pass through the permeate. If economics dictate, smaller UFs (e.g., 500±1000 MWCO) can recover monomers for reuse (Sabatini et al., 1995).

The main advantages of utilizing membranes in the industries include low energy consumption, safety, no addition of chemicals, elimination of wastewater treatment, simple operation and easy change of scale (Ochoa et al., 2001). The recovery and recycling of surfactants from treated effluent aqueous solutions not only reduces or eliminates the discharge of contaminated water into the environment but also reduces the overall cost of industrial processes. The separation and recovery of these surfactants from wastewater is important as they can be a costly component of the solution since the loss of the original surfactant and the subsequent need for the addition of more becomes expensive (Dahanayake and Ventura, 2001).

The use of reverse micellar extraction coupled with an ultrafiltration (UF) technique for the separation of micromolecules (PCE) dissolved in the fluid solvents was described in a current study. It was expected that this integrated technology can separate solutes (PCE) from the reverse micellar solution, where the solutes and solvent were allowed to pass through the membrane as the permeate while the macromolecule (surfactant) retained in the ultrafiltration unit as the retentate.

1.1 Objectives of this study

The main objective of this study was to recover surfactant for reuse by removing tetrachloroethylene (PCE) from surfactant solution using two extracting techniques. The specific objectives are as follows:

1. To remove solubilized PCE from surfactant aqueous solution by using two techniques: liquid-liquid extraction and reverse micellar extraction.
2. To study the effect of solvent type and surfactant solution:solvent volumetric ratio on the PCE removal efficiency on each technique.
3. To apply a stirred cell UF unit to separate surfactant from PCE after the reverse micellar extraction.

1.2 Hypotheses

Liquid-liquid extraction and reverse micellar extraction techniques can be used to separate solubilized PCE from surfactant aqueous solution for surfactant recovery purposes; and the solvent type and surfactant solution:solvent volumetric ratio have effects on PCE removal efficiency.

1.3 Scope of study

The research was divided into four phases as follows

Phase 1: Preliminary study

Surfactant system screening for maximize the solubility of PCE at supersolubilization condition using sodium dihexyl sulfosuccinate (AEROSOL MA-80-I or in short as AMA) as an anionic surfactant was determined by salinity scan with NaCl. The phase transition was investigated and the interfacial tension (IFT) between PCE/surfactant solutions was measured. The concentration of solubilized PCE at supersolubilization condition was determined.

Phase 2: Liquid-liquid extraction study

Five extracting solvents were used including palm oil, sunflower oil, dodecane, octadecane and squalane. The surfactant solution containing certain amount of solubilized PCE obtained from preliminary study was used to imitate the flushed surfactant solution from SEAR technique. The surfactant solution:solvent volumetric ratio was varied in the system that used palm oil as an extracting solvent to determine the PCE partitioning between two phases and the PCE removal from surfactant aqueous solution to solvent phase was investigated. The best surfactant solution:solvent volumetric ratio was applied to other extracting oils and the results were compared.

Phase 3: Reverse micellar extraction study

3.1 The surfactant aqueous solution obtained from preliminary study in the absence of PCE was used to form the Winsor Type II microemulsion with 2 oils (palm oil and dodecane) by salinity scan with NaCl. The surfactants in the system were adjusted either on concentration or composition (if the second surfactant needed to be added to decrease the HLB of the system). The volumetric ratio of surfactant solution:oil was fixed in this study. The appropriate surfactant(s)-oil-NaCl system was evaluated regarding to the least amount of surfactant(s) and oil remained in the aqueous phase.

3.2 The selected surfactant(s)-oil-NaCl system obtained from 3.1 was applied with different volumetric ratios of surfactant solution:oil. The appropriate volumetric ratio of surfactant solution:oil was determined.

3.3 The selected surfactant(s)-oil-NaCl system with appropriate volumetric ratio of surfactant solution:oil obtained from 3.2 was studied in the presence of 10,000 PCE concentration. The migration of surfactant(s) and PCE to oil phase was investigated via the remained concentration of surfactant(s), and PCE in aqueous solution.

Phase 4: Ultrafiltration process for surfactant recovery after reverse micellar extraction

The solution of oil obtained from 3.3 was subjected to a batch stirred cell ultrafiltration (UF) unit. The effect of applied pressure on the UF cell was investigated via the removal of PCE from original reverse micellar surfactant solution to the permeate solution passed through the membrane. In overall, the comparison on the percentage of PCE removal efficiency between the liquid-liquid extraction and the reverse micellar extraction followed by UF process was revealed.

CHAPTER II

THEORECTICAL BACKGROUND AND LITERATURE REVIEW

2.1 Tetrachloroethylene

Chlorinated hydrocarbons are ubiquitous ground water contaminants due to their widespread use as organic solvents and cleaners/degreasers. The immiscibility of chlorinated organics with ground water causes them to exist as nonaqueous phase liquids (NAPLs); this results in their occurrence in the subsurface as residual and free phases. Having a density greater than water, they are often referred to as dense nonaqueous phase liquids (DNAPLs). Water solubilities of these chlorinated hydrocarbons are frequently several orders of magnitude above their drinking water standards, yet low enough to limit dissolution during pump-and-treat remediation (Palmer and Fish, 1992).

Tetrachloroethylene is also known as PCE, perchloroethylene, tetrachloroethene, perc, percelene, and perchlor. PCE is a man-made substance widely used for dry cleaning fabrics and textiles and for metal-degreasing operations. It is also used as a starting material (building block) for the production of other man-made chemicals (EPA, 2006). Although PCE is a liquid at room temperature, some of the liquid can be expected to evaporate into the air producing an ether-like odor; evaporation increases as temperature increases. Due to PCE is a nonflammable, colorless liquid that belongs to a class of chemicals known as volatile organic compounds (VOCs) meaning that PCE easily evaporates into air. PCE moves easily through soil and ends up contaminating to groundwater. PCE does not mix very well with water but over time may dissolve in sufficient amounts to become a health concern. PCE is denser than water and tends to sink to the bottom of aquifers (EPA, 2006). PCE may stay in groundwater 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.

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 (modified from www.en.wikipedia.org/wiki/tetrachloroethylene). The effects of PCE on human health greatly depend on how much PCE is exposed, and the length and frequency of exposure. Contact with PCE in its liquid or vapor form can irritate the skin, eyes, nose and throat (Boer, 2002). Exposure to 100-200 ppm for 5-7 minutes causes volunteers to feel as though they are going collapse. The 5-7 hours has produced drowsiness, headache, and sleepiness. A few deaths have been reported due to central nervous system depression and irregular heart beat (Canada's National Occupational Health and Safety Resource, 1999). 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, 1988). The EPA maximum contaminant level for the amount of PCE that can be in drinking water is 0.005 mg/L (0.005 ppm). Occupational Health and Safety Administration (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.

In Thailand, there are insufficient data for some VOCs compounds due to a limitation in data availability. Since some chemicals share similar harmonized code, thus import-export data of individual compound cannot be distinguished. As for dichloromethane (DCM) and tetrachloroethylene (PCE), there have neither import-export data nor production data available. In 2001-2006, PCE are consumed in a smaller amount (1,000-1,400 tons per year) compared to trichloroethylene, TCE (4,900-7,700 tons per year) and DCM (8,200-10,900 tons per year) as shown in Figure 2.1. These might be caused by their high toxicity and banning of this chemical or replacing to other chemical as results of international agreement such as those ozone depleting substances under the Montreal Protocol in 1991 (Sarawut, 2006). Consequently, the reduction of PCE production to be a raw material in trichloro-1,2,2-trifluoroethane (CFC-113) and trichloroethane (TCA) synthesis occurs. Thus, after the reduction of PCE application in 1991, TCE was used as the substitute building block for CFC-113 instead of PCE. Figure 2.2 showed the PCE consumption in 2007 was used mainly in industrial process as the intermediate compound in metal degreasing process and as solvent in dry-cleaning products in textile industry.

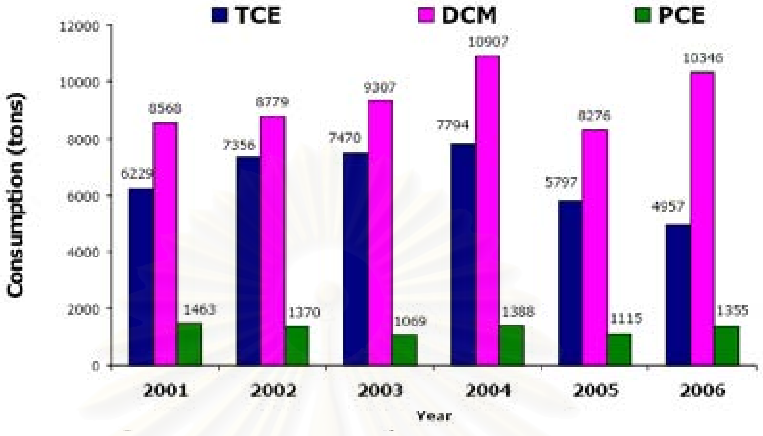
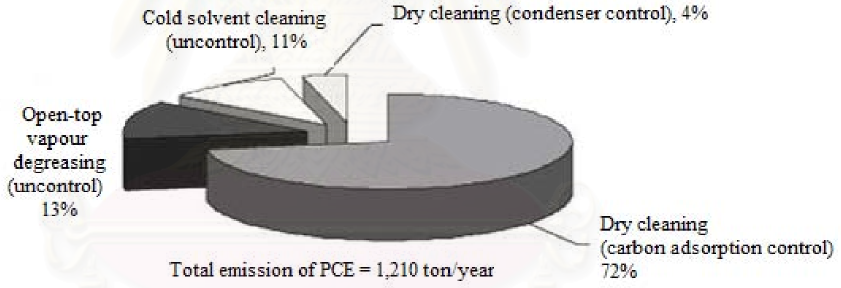


Figure 2.1 Trends of volatile organic compounds (VOCs) consumption in Thailand (Pollution Control Department, Thailand, 2008)



Note: Estimation based on preliminary survey and questionnaires, 2007

Figure 2.2 Estimated emission of PCE in 2007, Thailand (Pollution Control Department, Thailand, 2008)

For the treatment of used PCE and TCE in Thailand, the PCE and TCE were collected in plastic containers with other waste waited for the conventional treatment processes. The remediation of chlorinated ethylene contaminated in soil and groundwater could be physical, biological and chemical processes. There are some possible techniques applied in PCE remediation (ERTC, 2001):

For PCE contaminated in soil

(1) Thermal desorption is applied with the temperature in the range of 100-600 ˚C to evaporate PCE and TCE out of the soil. Then, the contaminated air with PCE or TCE have to be further treated.

(2) Solvent extraction (or soil washing) is the technique widely used by mixing the solvent or surfactant with the contaminated soil and the solvent would be further treated in waste water treatment.

(3) Soil vapor extraction is commonly used with the chlorinated ethylene volatile compounds. This technique is suitable for the unsaturated zone and with high porosity of soil.

(4) Stabilization and solidification are the processes that change the waste into cement to reduce the toxicity of waste.

For PCE contaminated in groundwater

Generally, pump and treat is used in ground water remediation by pumping out the contaminated water above ground and further treated with the suitable processes.

(1) Activated carbon adsorption is applied with the volatile organic compounds by using the activated carbon for the direct adsorption of the contaminated water.

(2) Air sparging is *in situ* remedial technology that reduces concentrations of volatile constituents in petroleum products that are adsorbed to soils and dissolved in groundwater. This technology involves the injection of contaminant-free air into the subsurface saturated zone, enabling a phase transfer of hydrocarbons from a dissolved state to a vapor phase. The air is then vented through the unsaturated zone

(3) Bioremediation is involved with the microorganisms (bacteria, fungi, etc.) application to degrade contaminant. This technique is better than physical and chemical process where further treatment does not require. This technique can be applied in both anaerobic and aerobic condition.

Moreover, from the study of Environmental Resources Training Center, Thailand (ERTC) in 1999, there was high amount of TCE contaminated in soil and ground water in the industrial estate at Lampoon province. The concentration of TCE (968.85 ppm) was higher than the standard of ground water to make drinking water in Japan (0.03 ppm) (Department of Environmental Quality Promotion, 2002). Consequently, TCE which is one of chlorinated aliphatic hydrocarbon, is a major chemical caused a contamination to ground water in Thailand than PCE. However, there is no formal report of PCE contaminated in ground water and soils.

Traditional pump-and-treat methods have proven to be ineffective for remediating NAPL source zones due to the low aqueous solubility of most NAPLs, lack of technologies to characterize the subsurface, and heterogeneities associated with formation properties and NAPL entrapment (Mackay and Cherry, 1989; Palmer and Fish, 1992; MacDonald and Kavanaugh, 1994).

To improve the performance of pump-and-treat systems, surfactant flushing has been proposed as a mean to enhance the recovery of NAPLs. Surfactant enhanced aquifer remediation (SEAR) is based on the ability of surfactants to increase the aqueous solubility of and displace NAPLs from porous media. At concentration exceeding the critical micelle concentration (CMC), surfactant molecules aggregate to form micelles that are able to solubilize organic contaminants. Displacement of NAPLs as free product may also occur if the interfacial tension between the organic liquid and the aqueous phase is reduced to such an extent that viscous and buoyancy forces exceed capillary forces acting on the NAPL. Although the latter recovery process is extremely efficient, displacement of free product may lead to uncontrolled downward migration of DNAPLs and contamination of pristine regions of an aquifer. For these reasons, SEAR treatment of DNAPL source zones has focused on surfactants that function primarily as solubilizing agents (Taylor et al., 2001).

A surfactant flushing system consists of a network of injection and extraction wells designed to hydraulically sweep the targeted volume of aquifer that is contaminated with DNAPL as shown in Figure 2.3. A surfactant fluid, having properties appropriate for the DNAPL and geosystem under consideration, is injected into the vadose zone or saturated zone and transported through the DNAPL zone. The injected solution interacts with the contaminants by lowering the interfacial tension between DNAPLs in the aqueous phase (mobilization), enhancing DNAPL solubility (solubilization), or altering other physical properties, as it is flushed through the zone of contamination. In situations where the DNAPL is the wetting phase in the aquifer (i.e., in direct contact with the media), the surfactant will reduce the interfacial tension between the DNAPL and the rock (or soil) matrix and make the system water-wet (the fluid that preferentially wets the mineral grain surface in a multiphase system is the wetting fluid). The mixture of the injected surfactant fluid, contaminant and the groundwater are then captured through extraction wells. Once brought to the surface, the groundwater with the mixture of surfactant and contaminant are either treated or discharged (ITRC, 2003).

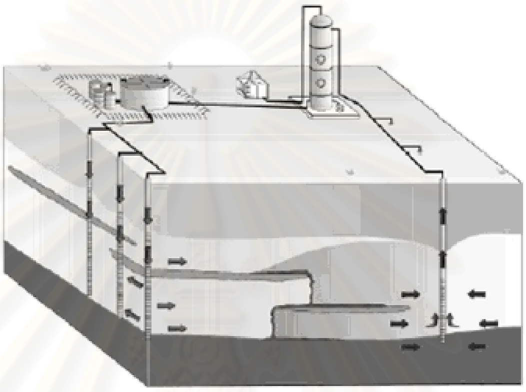


Figure 2.3 Conceptual design of a surfactant flushing system (IRTC, 2003)

2.2 Surfactant

2.2.1 Introduction

The term “surfactant” is a truncation of surface active agent. The surfactant under several names such as detergents, coagulants, dispersants, emulsifiers, de-emulsifiers, foaming agents and defoamers is one of the most widely used class of chemicals in industries. They are used in various products such as pharmaceuticals, detergents, drilling muds and flotation agents. Of late, surfactants have applied in such high-technology areas such as electronic printing, magnetic recording, biotechnology, microelectronics and viral research (Rosen, 2004). Surfactants are molecules that consist of hydrophilic and hydrophobic moieties referred to as heads and tails, respectively as shown in Figure 2.4. The hydrophobic group is usually a long-chain hydrocarbon residue, and less often a halogenated or oxygenated hydrocarbon or siloxane chain; the hydrophilic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants are classified as anionic, cationic, zwitterionic, and nonionic (Rosen, 2004).

Anionic surfactants are molecules possessed a negatively charged in the hydrophobic portion such as sulfonate, carboxylate, sulfate and phosphate which are the polar group found in this type. The most commonly used surfactants are including alkylbenzene sulfonates (detergents), soaps (fatty acid), lauryl sulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent), lignosulfonates (dispersants), etc. They are the largest volume used in the commercial and household product, account for about 50% of the world production.

In contrast to anionic surfactant, cationic surfactants are molecule possessed a positively charge in the hydrophilic portion such as a quaternary ammonium salt, with one or several long chain of the alkyl group. They are often coming from natural fatty acids. Due to the positive charge on the head group giving the strong substantively on negatively charged fibers such as cotton and hair, they are used as fabric and hair conditioners. In general, this surfactant is more expensive than anionic because of the high pressure hydrogenation reaction used during synthesis.

Nonionic surfactants are surfactant without charges in their hydrophilic part of molecule. They typically have a polymeric group or an uncharged hydrophilic group like poly(ethylene oxide) as the head group. A large proportion of nonionic surfactant used in industries has their hydrophilic portion as monoglyceride of long-chain fatty acid or polyethylene glycol chain, obtained by the polycondensation of ethylene oxide. Hence, they are called polyethoxylated nonionic surfactant.

Zwitterionic surfactant has both of positive and negative charges on the head group. This group is milder on the skin particular on eyes than anionic surfactants. They are used in toiletries and baby shampoos. Amphoteric surfactants have their head group which charges depending on pH. For example, they have got positive charge at low pH but they become negative charge at high pH. Because amphoteric are generally zwitterionic surfactant at some pH. Zwitterionic surfactants are often amphoteric. Then, the terms “zwitterionic” and “amphoteric” are used as synonyms. Both of surfactants are generally expensive. Then, their applications are limited such using in cosmetics (Rosen, 1989; Holmberg, 1998; Rosen, 2004; Scamehorn et al., 2004).

The hydrophilic portion of surfactant is attracted to water while them hydrophobic portion of the surfactant is repelled by water. The nature of surfactants causes them to accumulate at interfaces, thereby altering the properties of these interfaces. For example, surfactant monomers adsorb at the gas-liquid interface with the hydrophilic heads extending into the liquid phase and the hydrophobic tails extending into the gaseous phase (Adamson, 1990; Rosen, 1978).

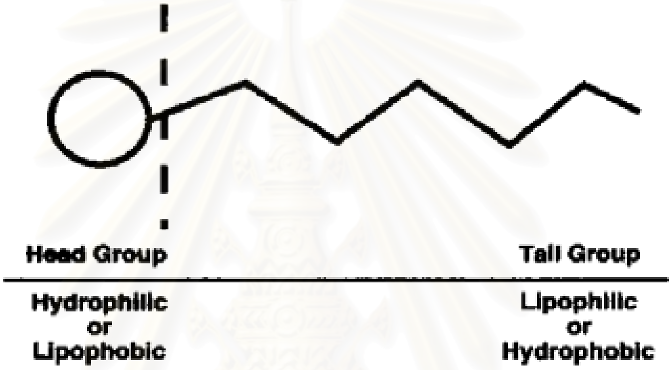


Figure 2.4 General representation of surfactant molecule (Scamehorn et al., 2004)

2.2.2 Geometrical aspects of the aggregation

The structure of aggregates formed from surfactant molecules varied widely. Possibilities include spherical, rod-like micelles, bilayers and inverted structure etc. (Figure 2.5). The aggregation structures of surfactant in aqueous solution depend on the chemical structure of surfactant and solution condition such as concentration, temperature, pH and ionic strength. These structures can transform from one to another when solution are changed (Aswal, 2003).

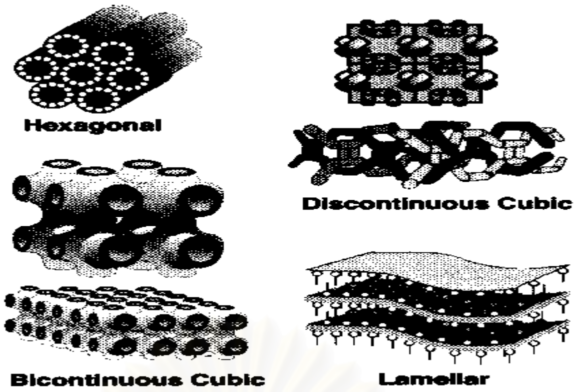


Figure 2.5 Types of surfactant liquid crystals (Scamehorn et al., 2004)

2.2.2.1 Micelles

(i) Spherical Micelles

Spherical micelles with an interior composed of the hydrocarbon chains and a surface of the polar head groups facing with water. Spherical micelles are characterized by a low surfactant number (critical packing parameter) and a strongly positive spontaneous curvature. The hydrocarbon core has a radius close to the length of the extended alkyl chain (Holmberg et al., 2003).

(ii) Rod-like or Cylindrical Micelles

Cylindrical micelles with an interior composed of the hydrocarbon chains and a surface of the polar head groups facing water. The cross-section of the hydrocarbon core is similar to that of spherical micelles. The micelle length is highly variable so these micelles are polydisperse (Holmberg et al., 2003).

(iii) Vesicles or Liposome

Vesicles are built from bilayers similar to those of the lamellar phase and are characterized by two distinct water compartments, with one forming the core and one the external medium. Vesicles may have different shapes and there are also reversed-type vesicles (Holmberg et al., 2003).

(iv) Lamellar Micelles

Surfactant bilayers which build up lamellar liquid crystals have for surfactant-water systems a hydrocarbon core with a thickness of *ca.* 80% of the length of two extended alkyl chains (Holmberg et al., 2003).

(v) Reversed Micelles

Reversed or inverted micelles have a water core surrounded by the surfactant polar head groups. The alkyl chains together with a non-polar solvent make up the continuous medium. Like ‘normal’ micelles, they can grow into cylinders (Holmberg et al., 2003)

2.2.3 Solubilization by Solutions of Surfactant: Micellar Catalysis

Solubilization may be defined as the spontaneous dissolving of a substance (solid, liquid, or gas) by reversible interaction with the micelles of the surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material. Although both solvent-soluble and solvent-insoluble materials may be dissolved by the solubilization mechanism, the importance of phenomenon from the practical point of view is that it makes possible the dissolving of substances in solvent in which they are normally insoluble (Rosen, 2004).

Adsorption of surfactants at the gas-liquid interface can significantly alter the physical properties of the aqueous interface. On saturating the interface, and above a critical surfactant concentration, the molecules align together in globular, quite often spherical, colloids with the hydrophilic portion on the exterior and the hydrophobic portion on the interior. The resulting formation is called a micelle. The center core of the micelle has properties of a pseudo oil phases; the properties of micelles are thus frequently described in terms of an oil-drop model (Hasegawa et al., 1997).

The addition of small amounts of neutral electrolyte to solutions of ionic surfactants appear to increase the extent of solubilization of hydrocarbons that are solubilized in the inner core of micelle and to decrease that of polar compounds that are solubilizaed in the outer portion of the palisade layer (Klevens, 1950). The effect of neutral electrolyte addition on the ionic surfactant solution is to decrease the repulsion between the similarly charged ionic surfactant head groups, thereby decreasing the CMC and increasing the aggregation number and volume of the micelles. The increase in aggregation number of the micelles presumably results in an increase in hydrocarbon solubilization in the inner core of micelle. The decrease in mutual repulsion of the ionic head groups causes closure packing of the surfactant molecules in the palisade layer and a resulting decrease in the volume available there for solubilization of polar compounds (Rosen, 2004).

At electrolyte concentrations below a critical value, anionic surfactants typically display Winsor Type I (oil-in-water microemulsion in equilibrium with excess oil) phase behavior and NAPL aqueous solubility increases with increasing electrolyte concentration. However, above a critical electrolyte concentration, the Type I system may convert to a Winsor Type III with the formation of a separate middle-phase microemulsion in equilibrium with excess aqueous and oil phases. At a second higher critical electrolyte concentration, the system may convert to a Winsor Type II system (water-in-oil microemulsion in equilibrium with an excess aqueous phase) in which surfactant partitions into the NAPL phase resulting in a negligible increase in aqueous NAPL solubility (Field et al., 2000).

2.3 Phase transition

A systematic approach to selecting and optimizing surfactants for microemulsion formation would be to study the classical Winsor type phase behavior of the systems (Baran et al., 2001). At low salinity, Winsor type I (oil-in-water, O/W) microemulsions are formed. As the salinity is increased, both the extent of solubilization and the opacity of the microemulsion increase. At certain salinity, there is a transition to a Winsor type III (middle-phase) system, which begins with the middle phase having a water/oil volume ratio (WOR) near infinity. Formation of middle phase microemulsion requires matching the hydrophile lipophile balance (HLB) of the surfactant system with that of the oil (Child et al., 2006). It is widely recognized that the IFT between the microemulsion-oil and microemulsion-water both reach a minimum in the middle phase microemulsion region. As the salinity is increased, the system gradually passes through the optimum state, where the middle-phase WOR=1, and ultimately, to a system where the middle-phase WOR approaches 0. Further increases in the salinity generate Winsor type II (water-in-oil, W/O) systems with decreasing opacity and water solubilized in oil. For optimum system composition, the salinity required is called the optimum salinity, $S*$. The solubilization parameter is a measure of the surfactant's solubilizing power and is defined as the volume of water (or oil) solubilized per unit weight of surfactant plus cosurfactant (if any). The optimum solubilization parameter occurs when equal volumes of oil and water are solubilized and simultaneously the I/III and III/II interfacial tensions are equal. A generic diagram of such a system is shown in Figure 2.6.

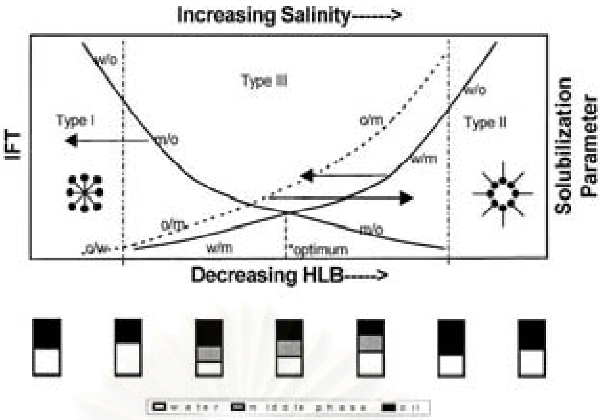


Figure 2.6 Illustration of phase behavior and interfacial tension (IFT) as the scanning variable is altered for an anionic surfactant: oil is o; w is water; m is middle phase (Child et al., 2006)

2.4 Supersolubilization system

The oil–water interfacial tension (IFT) decreases with increasing electrolyte concentration, and an empirical correlation between contaminant solubilization capacity and IFT had been proposed. Salinity scans are typically conducted to find the optimum electrolyte addition to maximize the contaminant solubilization. Ionic surfactant solutions with electrolyte concentrations that are close to the Winsor type I–III transition boundary have ultralow IFTs (0.001–1 dyne/cm) without forming Winsor type III microemulsion. Such systems have extremely high contaminant solubilization capacities compared to solutions at lower electrolyte concentrations, and are thus called ‘supersolubilization’ systems (Cheng and Sabatini, 2001).

The supersolubilization concept takes advantage of the fact that as one scans from a Type I to a Type III system, the IFT continually decreases and the solubility enhancement continually increases as suggested by the Chun Huh relationship (Huh, 1979), and discussed in Pope and Wade (1995). By operating near the Type I-Type III boundary, it is possible to maximize the solubility enhancement while minimizing the vertical migration potential (Sabatini et al., 2000). They also introduced the gradient concept, which sequentially adjusts the surfactant formulation to reduce the IFT and increase the solubilization potential as the system becomes increasingly tolerant of a more aggressive surfactant system. In other words, as the solubilization progresses, the reduced oil saturation (due to the amount of oil removed) allows the system to be adjusted to a lower IFT without mobilization but with increasing solubilization capacity.

2.5 Application of surfactant for NAPLs remediation

Cationic, anionic and nonionic surfactant can be used for soil washing or flushing. They are useful in displacing DNAPL by reducing interfacial tension between DNAPL and groundwater. It is these capillary forces that restrict the mobility of DNAPL (Falatko, 1991). The mobilized contaminant can then be recovered in extraction wells. Surfactants can be used in mixtures or with additives such as alcohol and/or salts such as sodium chloride. Polymers or foams can also be added to control the mobility of the contaminants. The surfactants must be recovered and reused to make the process become more economical.

Petroleum users have traditionally been the major users, as in enhanced oil recovery applications. In this application, surfactants increase the solubility of petroleum components (Falatko, 1991) or lower IFT to enhance mobility of petroleum. They have also been used for mineral flotation as well as the pharmaceutical industries. Typical desirable properties include solubility enhancement, surface tension reduction, the critical micelle concentrations (Falatko, 1991), wettability and foaming capacity.

Surfactants are able to improve the mass transfer of hydrophobic pollutants from solids (Tiehm, 1994). The unique amphiphilic structures and properties of surfactants are able to be applied in many areas. Therefore, surfactants are widely used for solubilization and mobilization purposes in agricultural and industrial areas. In recent years, SEAR has been employed to remove PCE from contaminated groundwater (Child et al., 2004). Results from several laboratory studies on the use of surfactants for washing hydrophobic contaminants from soils have shown that this enhanced washing method has a good potential (Fountain et al., 1991; Abdul and Ang, 1994). Results compared from many papers showed the percentage of PCE removal (Kao et al., 2003) between 33-85% and total petroleum hydrocarbon (TPH) recoveries between 60-90% (Lee et al., 2002). Laboratory studies of surfactant washing of contaminated soils have shown some promise. Abdul et al. (1990) studied a variety of surfactants in an attempt to wash automatic transmission fluid from a sandy soil. They concluded from batch and column washing studies that certain surfactant solutions had the potential to effectively remove nonaqueous phase liquids from soil. Soil column studies conducted by Pennell et al. (1994) showed that a solution of the surfactant polyoxyethylene-20 sorbitan monooleate could considerably enhance the recovery of residual dodecane. However, mixed results have been obtained in various pilot studies. Abdul and Ang (1994) used a nonionic ethoxylated alcohol to remediate a site contaminated with polychlorinated biphenyls (PCBs) and oils quite successfully.

SEAR techniques for removing PCE from soil and groundwater are now receiving a lot of attention (Lee et al., 1998). Moreover, surfactants can help the extraction of organic contaminants from an aquifer by reducing IFT between DNAPLs and groundwater, and by increasing the solubility of the contaminants. A surfactant molecule contains a hydrophilic head and a hydrophobic tail. The hydrophilic head is a polar moiety, which has an affinity for water and the other polar substances, while the hydrophobic tail is nonpolar moiety (Edwards et al., 1991). The tail, usually a long hydrocarbon, acts to reduce solubility in water while the hydrophilic head has opposite effect (Li and Chen, 2003). Surfactants enhance the remediation of PCE-contaminated sites by increasing the PCE’s aqueous phase concentration via micelle/emulsion formation.

In 2000, Uchiyama et al. had studied the chlorinated hydrocarbon contaminated in subsurface by using SEAR technique. The aqueous contaminant solubility in water is increased by the presence of surfactant micelles, which form above the surfactant’s critical micelle concentration (CMC), promote contaminant displacement, where the capillary forces entrapping the contaminant are overcome by the ultralow IFT achieved by optimal surfactant formulations enabling the removal of more contaminant with less water flushing through the contaminated area.

Many papers published on the study of remediation dealing with issues of PCE by vapor extraction methods or bioremediation (Chai and Miura, 2004; Kao et al., 2003). A pump-and-treat method was frequently evaluated by many researchers (Mackay et al., 2000) and it was used as a conventional remedial method for contaminated water. Especially, the pump-and-treat method is a treatment technology to remediate groundwater contaminated by organic materials. Treatment methods (air stripping, steam stripping, activation by carbon filtration, etc.) are differently applied according to target compounds or field configurations (Mackay et al., 1989; Oostrom et al., 1999; Nadim et al., 2000). Moreover DNAPLs are difficult to remediate from aquifers because these compounds tend to remain in a separate phase (Marta et al., 2003). The pump-and-treat method is limited by parameters such as water flow rates, the organic material's composition, mass transfer rates, and the surface area available for mass transfer of constituents (Fountain et al., 1991; Geller and Hunt, 1993; Lee et al., 2002).

Based on Childs et al. (2004) conducted the criteria used for screening surfactants in the batch studies because every site and contaminant mixture has unique characteristics, the surfactant system must be customized to achieve the maximum removal at the lowest cost (environmental and monetary), includes: (A) low microemulsion density to avoid vertical migration; (B) fast coalescence to prevent the formation of metastable macroemulsions in the subsurface; (C) low microemulsion viscosity to prevent PCE displacement and high head loss through the media; (D) high solubilization capacity to reduce the number of pore volumes needed to achieve the remediation goals; (E) high PCE-microemulsion IFT to eliminate downward PCE migration; and (F) temperature independent phase behavior, this means that the properties described above do not become undesirable at low temperature (7 ˚C). An additional screening parameter is compatibility between the surfactant and soil, including low surfactant adsorption. In general, a suitable surfactant for these purposes should have high coalescence rates, clear (neat) microemulsion phases, a high solubilization capacity, no precipitation, and a liquid crystal or gel formation at subsurface conditions and should be environmentally acceptable (Uchiyama et al., 2000).

Numerous field studies evaluating surfactant-enhanced removal of DNAPLs have been formulated using sodium dihexyl sulfosuccinate (Aerosol-MA or AMA) as the surfactant (Londergan et al., 2001). These field studies have produced DNAPL removals ranging from 70% to as high as 98%. The main reasons chosen AMA as surfactant are its compatibility with most soil media, its low potential to form gel or metastable phases, and its very fast solubilization rate (Mayer et al., 1992; Dwarakanath and Pope, 2000). Despite these desirable properties, AMA-based formulations may reduce the IFT too much and produce mobilized DNAPL that may ‘‘sink’’ in the subsurface (Pennell et al., 1996), potentially into regions not previously contaminated.

2.6 Surfactant Recovery

Separation of surfactant solution from the contaminants for recycle is a crucial step in the development of the surfactant-assisted remediation technique. Besides reducing the volume of waste stream, recycling of used surfactant solutions will reduce chemical costs. Surfactant-based remediation is not economically feasible without a means for surfactant recovering and recycling (Abdul and Ang, 1994). Surfactant separation and potential reuse is imperative for the economical and thus successful full implementation of this technology required surfactant recovery and reuse (i.e., decontamination of the surfactant stream for reinjection) (Krebs et al., 1995; Sabatini et al., 1998).

Surfactant recovery costs were estimated to be less than 10% of the annual surfactant replacement costs. In a subsequent economic analysis, Krebs et al. (1996) demonstrated that for 1/4 acre sites with residual saturations of 5% or less, the cost of solubilization remediation was only 40% of the cost of pump-and treat. Thus, these economic studies illustrate that surfactant-enhanced remediation is economically viable, and that surfactant decontamination and reinjection is critical to the technology’s success. Sabatini et al. (1998) suggested two different separation steps necessary for surfactant regeneration and reuse were contaminant removal from the surfactant stream (surfactant-contaminant separation) and concentration of the surfactant stream for reinjection (surfactant-water separation). The surfactant-contaminant separation renews the solubility enhancement potential of the surfactant stream while minimizing contaminant levels reinjected into the aquifer. Since surfactant-water separation will be necessary to reconcentrate the surfactant stream.

There is currently no practical way of recycling used surfactant solutions although several researchers have proposed various methods such as vacuum steam strip organic extraction, micellar enhanced ultrafiltration (MEUF) and air stripping (Cusack and Glatz, 1996; Lipe et al., 1996; Kandori and Schechter, 1990).

Hasegawa et al. (1997) showed that air stripping and liquid-liquid extraction could effectively regenerate surfactant systems laden with volatile and nonvolatile compounds, respectively, and that ultrafiltration (UF) could be used for surfactant reconcentration. These concepts have been reinforced and the technology proven through numerous field demonstrations, including the following: Traverse City, MI (Knox et al., 1997; Sabatini et al., 1997), three studies at Hill Air Force Base, UT (Knox et al., 1997), and a study at Tinker Air Force Base, OK (Sabatini et al., 1998).

Lipe et al. (1996) demonstrated that UF can be effectively used for the contaminant-surfactant separation purpose. They used 10,000 molecular weight cutoff (MWCO) membrane to retain micelles while monomers passed through the permeate. They achieved in excess of 90% surfactant retention (in some cases > 95%) while maintaining water-normalized fluxes of 90%. While the UF process effectively retained surfactant micelles but monomeric concentrations passed through membrane. If economics dictate, smaller UFs (e.g., 500-1,000 MWCO) could recover monomers for reuse. Vane et al. (2001) stated that the University of Oklahoma was tasked to apply MEUF technique was used for reconcentrate surfactant after the contaminant had been removed.

According to Gannon et al. (1989); Clarke et al. (1991); Lee et al. (2001), these studies showed that solvent extraction methods may help recycle anionic surfactant solutions used for remediation of contaminated soil and thereby will help reduce costs of remediation. The recovered surfactant solution could be reused to improve the economic viability of in-situ surfactant washing of contaminated sites. The effectiveness of the solvent extraction technique is directly related to the structure of the surfactant and nature of contaminant.

A surfactant recovery process was also constructed by teams from the EPA and the University of Oklahoma at Norman (OU). The process included decontamination of the effluent (a mixture of groundwater, DNAPL, and surfactant) by a membrane technology called pervaporation, followed by surfactant recovery using MEUF. This was the first field demonstration of surfactant injection, extraction, separation, and reinjection in the United States. The recovered surfactant was acceptable for reinjection under North Carolina regulatory requirements of 95% contaminant removal (Strbak, 2000).

Hasegawa et al. (1997) used liquid–liquid extraction to separate the surfactant–contaminant mixtures by pumping the mixture through a liquid–liquid extraction column where the pollutant was partitioned from the micellar phase (the surfactant–contaminant mixtures) into an organic solvent phase (e.g. squalane). Although the removal efficiencies of the more hydrophobic compounds such as naphthalene and phenanthrene by liquid–liquid extraction are surfactant concentration dependent, their performances were significantly better than those of air stripping.

Air stripping is an attractive separation process for surfactant-contaminant separation of high volatility contaminants. Surfactants can alter the performance of air strippers in several ways. First, conventional packed tower air strippers will typically produce significant foam with surfactant solutions which can impair the performance of the air stripper. Second surfactant-enhanced contaminant solubilization reduces the apparent contaminant volatility and thus efficiency of air stripping. Surfactant-induced foam formation can reduce the efficiency of the stripping process. Several methods can be used to mitigate the foaming potential. The air to water ratio can be decreased in an attempt to avoid high foam formation in the column. However, lowering the air to water ratio will decrease the efficiency of the system, thereby increasing the required tower height (Lipe et al., 1996). Antifoams can be used to mitigate the problem without lowering the air flow rates but other implications of using an antifoam must be considered.

The use of hollow fiber columns can thus mitigate the foaming problem without sacrificing efficiency and without requiring the use of antifoams. When using hollow fibers back pressure regulation may be necessary to prevent weeping of the surfactant solution across the membrane (Lipe et al., 1996). Surfactants will also impact air stripping in a second way. Surfactant-enhanced solubilization results from contaminant partitioning into the surfactant phase. During air stripping the aqueous-phase contaminant now competitively partitions into surfactant and air phases, thereby reducing the overall air phase partitioning (Lipe et al., 1996).

Hollow fiber membranes can also be critical to the success of liquid-liquid extraction for removing nonvolatile contaminants from surfactants. Hasegawa et al. (1997) conducted their liquid-liquid extraction studies in hollow fiber units to eliminate emulsion problems. They also developed a surfactant liquid-liquid extraction model (SLLEM) which accounts for the competitive partitioning of the contaminant between surfactant and oil phases. The excellent agreement between naphthalene experimental data and model predictions provides confidence in the model, especially since the predictions were made independent of the column data. Using the modified design equations will allow proper design of the liquid-liquid extraction units to achieve treatment goals. Thus, once again hollow fiber systems are attractive because of their ability to eliminate a major operating problem in this case emulsification (Sabatini et al., 1998).

The cloud point extraction (CPE) method, sometimes also called micellar or micelle-mediated, liquid-coacervate extraction is based upon this unique phase separation behavior exhibited by aqueous solution of certain neutral (non-ionic and zwitterionic) surfactant micelles. Consequently, any desired analyte that solubilized by or bound to the micellar aggregate entity can be separated and extracted (and preconcentrated) into the small volume element of the surfactant-rich phase as a conventional liquid-liquid extraction step (Quina and Hinze, 1999). CPE offers many advantages over traditional liquid–liquid extraction, for example, CPE is an aqueous-based extraction system that avoids using a large amount of toxic and flammable organic solvents as conventional solvent-extraction technique. In addition, CPE can lead to higher recovery efficiency and preconcentration factor because the presence of surfactant can minimize losses of analytes due to their adsorption onto the container and the surfactant-rich is generally small in volume (Li and Chen, 2003). Moreover, this technique serves in terms of experimental convenience, lower cost and accrues with respect to sample/analyte storage and analyte detection (Quina and Hinze, 1999).

2.7 Equivalent Alkane Carbon Number (EACN)

Having stated that NAPL EACN (hydrophobicity) is critical to designing successful surfactant systems, a method is needed to determine the EACN of hydrophobic NAPLs. The EACN concept was introduced by Wade and Schecter and co-workers in the 1970s for understanding and correlating surfactants for enhanced oil recovery (Salager et al., 1979; Bourrel and Schecter, 1988) and later found to be of great value in understanding and evaluating surfactant enhanced subsurface remediation (Baran et al., 1994). The ACN of a linear alkane is simply its carbon number. For example, the ACNs of n-octane and n-decane are 8 and 10, respectively. Given the EACN of an unknown oil, and using known parameters for a given surfactant, it is possible to estimate the optimal salinity for making a middle phase microemulsion with this system (Bourrel and Schecter 1988), as discussed below. Phase behavior experiments have been conducted for anionic surfactants and linear alkanes by varying the electrolyte concentration. The logarithm of the optimum electrolyte concentration, (Ln(s*)), was found to be an increasing linear function of the alkane ACN. The optimum salinities for linear alkane mixtures were determined for the same anionic surfactant and electrolyte. Analysis of Ln(s*) versus linear-alkane-ACN showed the ACN of the mixture to be a mole fraction average of the individual linear-alkane-ACNs. For example, the optimum salinity for and EACN of the mixture of n-octane and n-decane (an equal molar mixture of n-octane and n-decane) is the same as the optimum salinity for and ACN of n-nonane. Later studies showed the EACNs of chlorocarbons and their mixtures to follow these same mixing rules (Baran et al., 1994). Many chlorocarbon compounds have negative EACNs. For example the EACNs of TCE and DCB are –3.81 and –4.89, respectively (Dwarakanath et al., 1999).

2.8 Liquid-Liquid Extraction

Liquid-liquid extraction, sometimes referred to as solvent extraction, is basically alternative to air stripping organics from ground water (King et al., 1984; Hiler and Cameon, 1985). Liquid-liquid extraction has been widely utilized for industrial applications. It also has the potential to efficiently remove a wide variety of environmental groundwater contaminants (Hewes et al., 1974). The principles behind liquid-liquid extraction are similar to air stripping, with the exception that in liquid-liquid extraction, the contaminant partitions into a solvent instead of air. The driving force behind solvent extraction is the equilibrium distribution coefficient (K_d) for the contaminant-aqueous-solvent solution (Barbari and King, 1982; Zander et al., 1989). Furthermore, the distribution of a solute depends on its preference for one or the other liquid, which is closely related to its solubility in each one of them. Thus, the general subject of solubilities is highly relevant to solvent extraction (Marcus, 2004).

Liquid-liquid extraction may be highly effective for removal of hydrophobic, nonvolatile contaminants that cannot be economically removed using air stripping (Hewes et al., 1974). Another advantage of this process is the ability to select an ideal extraction solvent. Since each solvent will have a different affinity for each contaminant, it may be possible to determine the optimum solvent for a given contaminant (King et al., 1984). By obtaining an optimum solvent, the efficiency of the extraction column can be maximized. Also, the driving force for liquid-liquid extraction is typically several orders of magnitude greater than that of air stripping (Hasagawa et al., 1997). This allows the flow of extracting solvent to be reduced significantly without significant loss of extraction efficiency, potentially resulting in reduced operating and solvent costs.

A disadvantage of solvent extraction is the potential for contamination of the aqueous stream by the extracting solvent (extractant). Since this process is designed to maximize mass transfer of a contaminant into the solvent, the potential for the solvent to partition into the aqueous phase is also high. However, this problem can be minimized by selecting a nontoxic, low solubility solvent (Hasegawa et al., 1997). Also, removing the contaminant from the solvent can be an expensive process (Hutter and Vandegrift, 1992). In particular, distillation, a likely candidate for solvent regenerating, is expensive.

Although water is almost always one of the liquids in the liquid-liquid extraction process, the choice of organic solvent is quite wide. A good extraction solvent needs four essential features: (1) it has to be practically immiscible with water; (2) it has to have a different density to water; (3) it needs good stability and volatility so that it can easily be removed from the organic compound by evaporation; (4) the solute you want to extract has to dissolve easily in it. Ideally an extraction solvent should also be nontoxic and nonflammable, but these two criteria are less easy to meet. Commonly used extraction solvents include diethyl ether (the most common extraction solvent of all), ethyl acetate and hydrocarbons, such as light petroleum, hexane or toluene. Another group comprises chlorinated solvents, such as dichloromethane (DCM) and chloroform, with DCM being the preferred solvent because of its lower toxicity. However, chlorinated solvents do have a greater tendency to form emulsions than non chlorinated solvents. Emulsions are suspensions of small droplets of one immiscible liquid in another.

2.9 Reverse Micellar Extraction

The hydrophile-lipophile balance (HLB) is a parameter that characterizes surfactants in terms of their abilities to produce optimum emulsions with a given oil. As the surfactant HLB decreases, the microemulsion system transitions in the order of Winsor type I–III–II (Shiau et al., 1994). While an ionic surfactant is assigned a single HLB value, electrolyte addition alters its effective HLB value. As the contaminant becomes more hydrophobic, surfactant systems with lower HLB values are required to form the optimum microemulsions. Such surfactant systems will form Winsor type II (water-in-oil) microemulsions upon contacting solvents that are much less hydrophobic than the contaminant. A form of reverse micellar extraction has been applied in the biotechnology field for recovery of proteins and other bio-products that are highly water-soluble (Rabie et al., 1996). Electrolytes are typically added in such extractions to decrease the surfactant system HLB and thus facilitate the formation of Winsor type II systems. The reversed micelles contain inner cores of water, which are encapsulated by surfactant molecules and shielded from the organic solvent. This water uptake decreases with increasing counterion concentration (Cheng and Sabatini, 2001). Theoretical HLB value for a given mixture of surfactants is given by equation 1 (ICI, 1992):

$$\mathrm{HLB}_{\mathrm{mixture}} = (\mathrm{HLB}_{\mathrm{A}})(X_{\mathrm{A}}) + (\mathrm{HLB}_{\mathrm{B}})(X_{\mathrm{B}}) \qquad (1)$$

Where X_A and X_B are the weight fraction of every surfactant present in the mixture

Cheng and Sabatini (2001) evaluated reverse micellar extraction as an alternative of liquid-liquid extraction. They demonstrated the feasibility of using this extraction strategy to decontaminant a high ACN contaminant (tetradecane, ACN=14) laden surfactant solution. A Winsor type II microemulsion will form when a low HLB surfactant system is in contact with a hydrophilic solvent. Micelles break up and migrate into such a solvent and re-aggregate into reversed micelles, and the micellar-solubilized contaminant is released during the micelle breakup. The contaminant molecules will also be extracted into the solvent phase, promoted by both the disappearance of micelles and the high affinity of the solvent phase for the contaminant. A small amount of water with dissolved electrolyte will be accumulated in the reversed micelle interiors, and the contaminant concentration in the water will be its water solubility.

Reverse micellar extraction is a useful for separating biomolecules and shows a close similarity with liquid-liquid extraction since both are diphase processes which consist in partitioning a targeted solute between an aqueous feed phase and an organic phase and then operating the back transfer to a second aqueous stripping phase (Rodrigues et al., 1999).

Moreover the reverse micellar extraction is used in biotechnology field for concentrating highly water-soluble species, the reverse micellar extraction used for decontamination extracts the hydrophobic contaminant into the solvent phase instead of the reversed micelle cores. The residual aqueous contaminant concentration depends upon its water solubility, and is affected by co-solvation effects and salting out effects from the solubilized solvent and residual electrolyte in aqueous phase. Therefore, the aqueous solution will be decontaminated of both contaminant and surfactant after a reverse-micellar extraction, while electrolyte and solubilized solvent will be left in the aqueous phase (Cheng and Sabatini, 2001).

Dekker et al. (1986) studied on recovery of α-amylase from aqueous phase to transport to another by using reversed micelles of the cationic surfactant, trioctylmethylammonium chloride to solubilize α-amylase in isooctane. A continuous forward and back extraction of the enzyme was performed in two mixer-settler units, with the reverse micellar phase circulating between the two units. During the forward extraction the conditions (pH, ionic strength) favored the transfer of α-amylase from the aqueous phase towards the reverse micellar phase. The reverse micellar phase containing the α-amylase was subsequently extracted with a second aqueous phase, which favored the transfer of the enzyme towards the aqueous phase. In this way, the concentration of active α-amylase in the second aqueous phase was eight times greater than that of the original solution. The forward and back extraction could be described in terms of the data on the distribution coefficients and the mass transfer rate constants.

Some proteins can be solubilized in these polar cores and thus in the hostile organic solvent without denaturation (Pessoa and Vitolo, 1998). At the early stages of downstream processing, reversed micelles can be used in lieu of solvents for protein separation and purification (Regalado et al., 1996). Reverse micellar extraction is an efficient and selective process that works continuously, saves energy and can be easily scaled up (Pessoa and Vitolo, 1998; Chang and Chen, 1997). Besides, it can be used to recover peptides, intra- and extracellular proteins, nucleic acids, organic acids, antibiotics and steroids (Kilikian et al., 2000).

The revere micellar extraction also is somehow similar to cloud point extraction (CPE) used for separation or concentration of hydrophobic species (Cheng and Sabatini, 2001). A hydrophilic solvent is used to promote the formation of a Winsor type II microemulsion system in reverse micellar extraction, while raising the temperature is used to induce the coacervation of non-ionic surfactant solution in cloud point extraction. With the formation of a Winsor type II microemulsion system in reverse micellar extraction, almost all surfactant molecules migrate into the solvent phase to form reversed micelles and the contaminant concentration in the aqueous phase does not exist beyond its water solubility (solubilized solvent and residual electrolyte may also affect the aqueous contaminant concentration). In cloud point extraction, the surfactant concentration is still several times its CMC in the dilute phase, which can enhance the solubilization of the hydrophobic species. Organic compounds partitioning into the solvent phase are independent of the reversed micelles existing in it in reverse micellar extraction, while the distribution of surfactant micelles between the coacervate phase and the dilute phase determines that of the organic species in cloud point extraction. Also, coacervation is a characteristic of non-ionic surfactants only (a zwitterionic surfactant has been reported by Saitoh and Hinze, 1991), while the reverse micellar extraction depends only on matching the solvent with the surfactant solution HLB, and is thus applicable to all types of surfactant systems.

2.10 Ultrafiltration

Ultrafiltration (UF) membranes contain pores in the range 1-100 nm. Thus, large pore UF membranes have pore sizes similar to small pore microfiltration (MF) membranes (Singh et al., 2008). UF is a relatively low pressure membrane process which used as a water treatment. UF has rapidly increased in the last decade due to stricter regulations for water quality, decreased cost, improved membrane materials and modules, simplicity of installation and improved reliability when compared with conventional treatment process such as sedimentation and rapid sand filtration. The applications of UF can be analyzed from two different points of view. In some cases, the aim of the process is to recover or concentrate some valuable substances from a solution common in chemical and pharmaceutical industries (Molina et al., 2006). Another application related to this is the concentration of wastewater stream for further treatment where a higher concentration is required, as seen in some advanced oxidation processes. The second principle application comprises the removal of undesirable products such as particles, colloids, high molecular weight materials, bacteria and viruses (Cho et al., 2000) from an effluent stream in order to obtain more purified water. It has been applied either to remove organic and inorganic solutes of environmental concern from aqueous wastes, as well as peculiar preconcentration step in some analytical determinations. The separation procedure is based on the association of solutes to added micellar aggregates, successively removed from the bulk solution through an UF membrane. The membrane pore-size has to be small enough to block the aggregates (and their guest solutes) in the retentate, and large enough to allow acceptable flux rates in the system (Pramauro and Prevot, 1995).

MF and UF have been suggested as a means of recovery of surfactants with critical micelle concentration (CMC). If the surfactant concentration is low, that is, monomer concentration, (c < CMC) then nanofiltration (NF) has been suggested as an effective removal process (Kowalska, 2008).

Micellar enhanced ultrafiltration (MEUF) may be a viable alternative technique which is effective and economical for removing organic matters and metal ions from wastewater. In MEUF, surfactant is added into the aqueous stream containing organic matters or metal ions. When the surfactant concentration in the aqueous stream is above its CMC, surfactant monomers will assemble and aggregate to form micelles. Micelle can solubilize organic matters into its hydrophobic core or adsorb counter metal ions on its surface. Then the aqueous stream is ultrafiltered by a proper UF membrane whose pore size is smaller than the micelle size. In consequence, micelles and solubilized organic matters as well as adsorbed metal ions are rejected into the retentate stream and the permeate stream is produced where only small quantity of free organic matters or metal ions and surfactant monomers are present. The concentrations of surfactant and organic matters or metal ions in the retentate stream are much higher than those in the feed stream and the volume of the retentate stream is much less than that of the feed stream. Therefore, the further treatment of the retentate stream, i.e. the separation and recovery of surfactants and organic matters or metal ions, is easy and economical. Generally, in MEUF complete surfactant retention is assumed, because surfactant concentrations are enough high to form large micells. If the surfactant concentration is below the CMC, what usually occurs in real waste effluents, small surfactant monomers appear in the treated solutions (Nowak et al., 2008).

Purkait et al. (2005) concluded from the experimental results of MEUF studies of separation different aromatic alcohols using cetyl pyridinium chloride, cationic surfactant (CPC) solution, they stated that the solute retention is independent of the cross flow rate and transmembrane pressure drop but the permeate flux increases with pressure drop and cross flowrate.

Associated problems, such as the leakage of monomeric surfactant molecules, the interactions of the surfactants with the membranes, ion exclusion effects or possible recycling of the micellar phase, should be considered in developing a MEUF method (Scamehorn and Harwell, 2000).

CHAPTER III

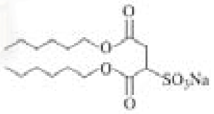
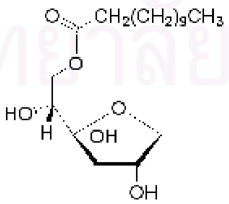
METHODOLOGY

3.1 Materials

3.1.1 Surfactants

Sodium dihexyl sulfosuccinate (AEROSOL MA-80-I or in short as AMA) was used as an anionic surfactant purchased from Fluka Co., Ltd. (Singapore) with 80% active, mixture of sodium dihexyl sulfosuccinate and 5% isopropanol. The nonionic surfactant used in this experiment was sorbitan monolaurate (trade name of Span-20 with 100% active) supported from The East Asiatic (Thailand) Public Company Limited. Their properties were listed in Table 3.1.

Table 3.1 Physical and chemical properties of surfactants

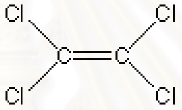
Surfactant	MW (g/mol)	Chemical Structure	HLB
Sodium dihexyl sulfosuccinate (AMA), $C_{16}H_{29}O_7NaS$	388		16.15 (1)
Sorbitan monolaurate (Span-20), $C_{18}H_{34}O_6$	346		8.6 (2)

(1) calculated from Davies method
(2) http://www.dispersion.com/pages/newsletter/articles/Newsletter15a.pdf

3.1.2 Pollutants

Tetrachloroethylene or PCE (EACN=2.9) with 95% purity was utilized in this study purchased from Aldrich Company (United States). The physical and chemical properties were shown in Table 3.2.

Table 3.2 Physical and chemical properties of PCE

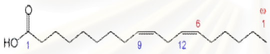
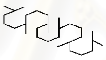
PCE	**MW (g/mol)**	**Chemical Structure**	**Log K_{ow}**	**Water solubility (g/100 mL)**
Tetrachloroethylene (C_2Cl_4)	165.8		3.40 (1)	0.015 (2)

(1) http://www.epa.gov/chemfact/s_perchl.txt, (2) http://en.wikipedia.org/wiki/Tetrachloroethylene

3.1.3 Extracting Solvents

Five extracting oils with different EACNs were used in this study as follows: 1) dodecane ($C_{12}H_{26}$, ACN=12) purchased from Aldrich Company (United States), 2) palm oil ($C_{16}H_{32}O_2$, EACN=13) purchased from Lamsoon (Thailand), 3) sunflower oil ($C_{18}H_{32}O_2$, EACN=18) purchased from Healthymate (Thailand), 4) octadecane ($C_{18}H_{38}$, ACN=18) purchased from Aldrich Company (United States), and 5) squalane ($C_{30}H_{62}$, ACN=30) purchased from Aldrich Company (United States). All extracting oils have purity higher than 99% and were used as received. Their physical and chemical properties were shown in Table 3.3.

Table 3.3 Physical and chemical properties of extracting solvents

Chemical name	**Chemical structure**	**Chemical formula**	**MW (g/mol)**	**Density**
Dodecane (ACN=12)		$C_{12}H_{26}$	170.34 g/mol	0.75 g/cm^3 at 25°C
Palmitic acid (palm oil) (EACN=13)		$C_{16}H_{32}O_2$	256.42 g/mol	0.85 g/cm^3 at 62°C
Linoleic acid (sunflower oil) (EACN=18)		$C_{18}H_{32}O_2$	280.45 g/mol	0.90 g/cm^3 at 62°C
Octadecane (ACN=18)		$C_{18}H_{38}$	254.50 g/mol	0.78 - 0.79 g/cm^3 at 25°C
Squalane (ACN=30)		$C_{30}H_{62}$	422.82 g/mol	0.81 - 0.82 g/cm^3 at 25°C

[Source from http://en.wikipedia.org/wiki/Dodecane;
http://en.wikipedia.org/wiki/Palmitic_acid; http://en.wikipedia.org/wiki/Linoleic_acid;
http://www.chemexper.com/chemicals/supplier/cas/111-01-3.html;
http://www.chemexper.com/chemicals/supplier/cas/593-45-3.html]

3.1.4 Electrolyte

Analytical grade NaCl with 99% purity was used as an electrolyte for microemulsion phase scanning. It was purchased from Lab-Scan Ltd. (Ireland).

3.2 Methodology

3.2.1 The phase behavior study

The phase behavior studies were conducted in 12 mL centrifuge tubes with teflon screw caps where equal volumes of aqueous surfactant solution and PCE was added into the tube. The concentration of AMA was held constant at 4 wt% and a salinity scan was conducted using NaCl. Prior added with PCE, the constant surfactant solution (4%AMA) with varied wt% NaCl were blended properly and set for the 10-15 minutes for precipitation investigate. The surfactant solution mixed with electrolyte needed to be clear solution without precipitation of salt. Then, only the surfactant solution added with NaCl performing clear solution were further mixed gently with PCE. The mixture of PCE and surfactant with added NaCl samples were homogenized again for 5 minutes and were equilibrated in the room controlled temperature at 25˚C for 5 days. The phase transition of Winsor type I-III-II microemulsion was observed visually and confirmed by interfacial tension measurement (IFT). The NaCl concentration that caused the Winsor type I (oil in water) microemulsion that closed at the boundary between Winsor type I-III microemulsion or so called the "supersolubilization condition" was determined. In addition, the concentration of solubilized PCE at supersolubilization condition in the surfactant aqueous phase was analyzed by gas chromatography (GC) equipped with headspace autosampler, where a flame ionized detector (FID) was used as a detector. The schematic diagram for phase behavior study was shown in Figure 3.2.1.

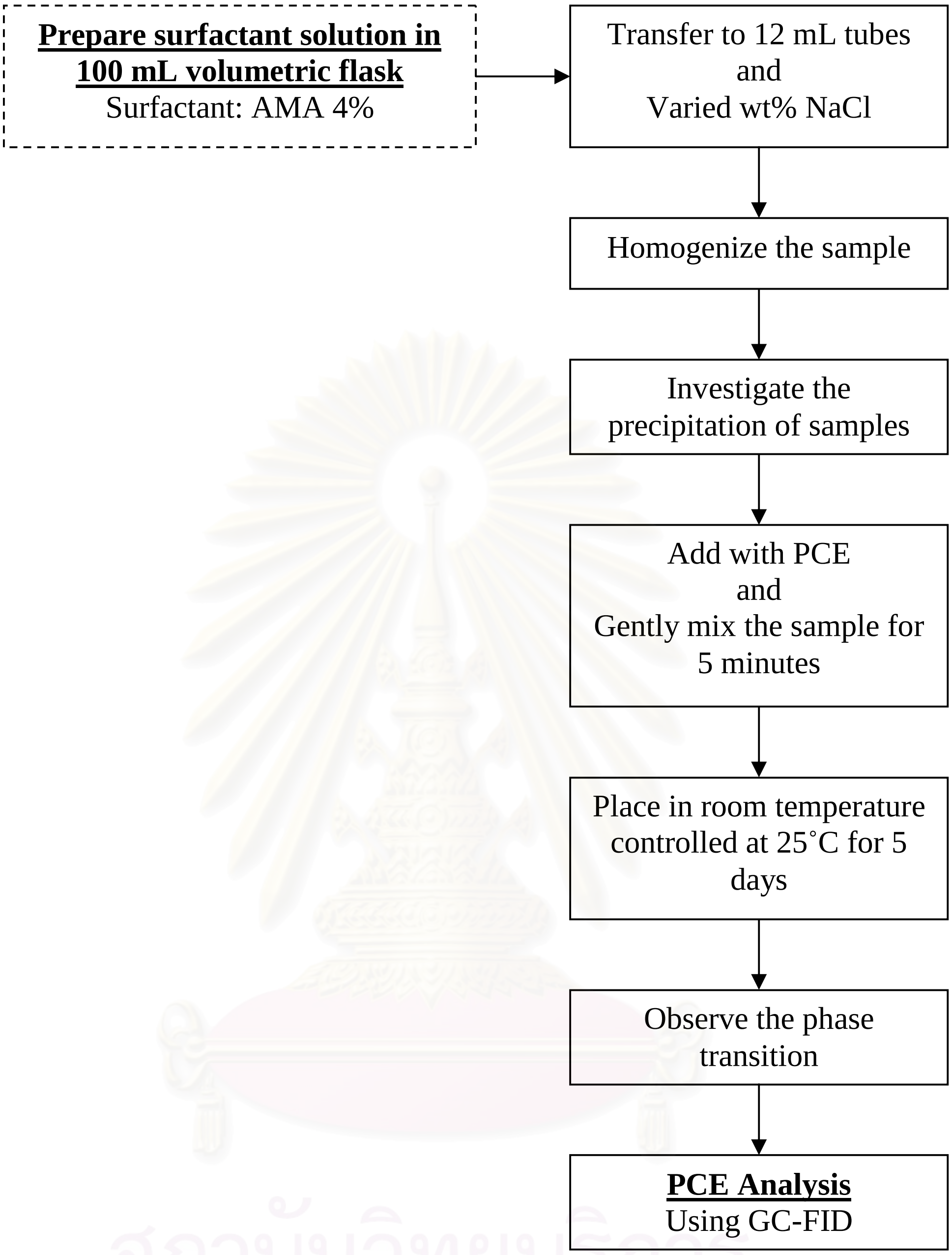


Figure 3.2.1 The schematic diagram for phase behavior study in liquid -liquid extraction

3.2.2 Liquid-liquid extraction study

3.2.2.1 Equilibruim time determination

The surfactant solution with certain amount of solubilized PCE at the supersolubilization condition as obtained from phase behavior study was prepared. The equilibrating time was determined using one oil (palm oil) at specific surfactant solution:solvent volumetric ratio of 5:1. The concentration of PCE in both phases were analyzed by GC-FID. The time at which the concentrations of PCE in both phases remain constant defined as the equilibrium time. The schematic diagram for equilibrium time determination was shown in Figure 3.2.2.

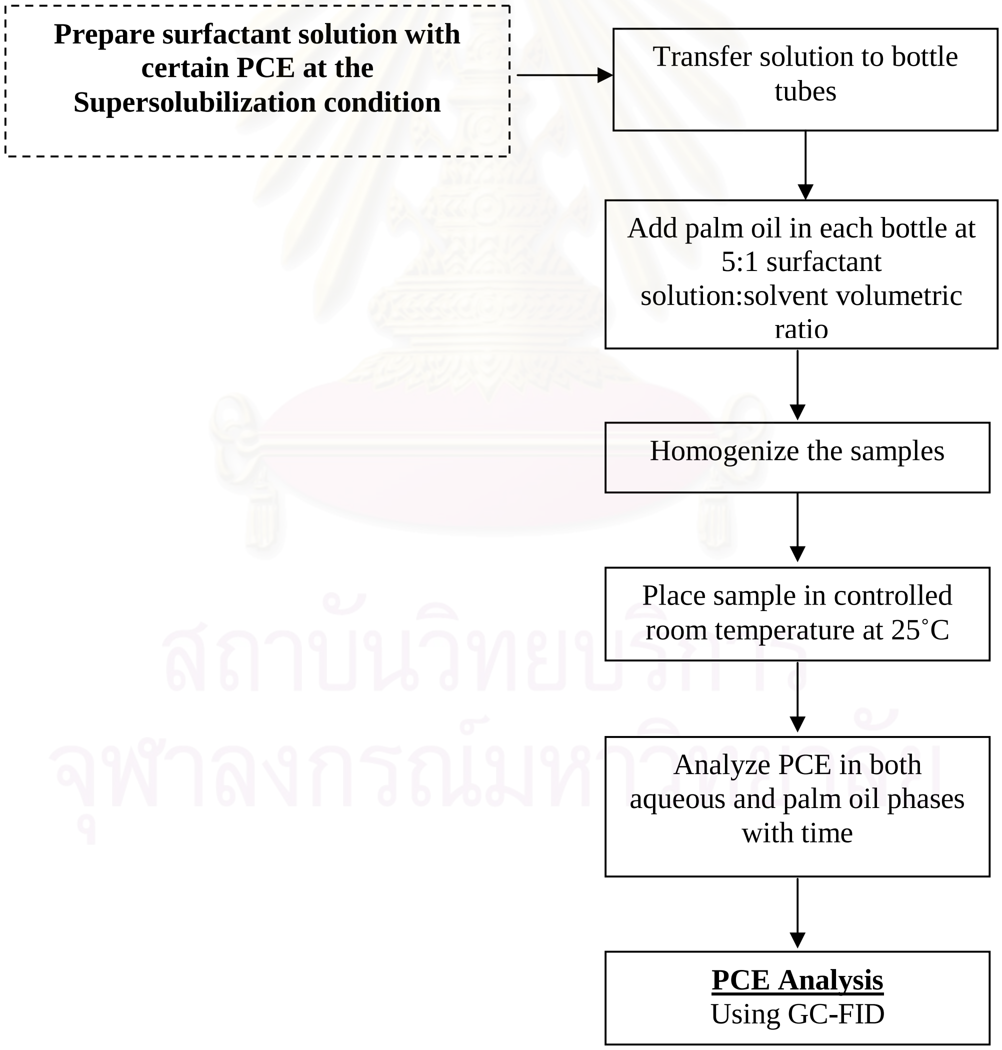


Figure 3.2.2 The schematic diagram for equilibrium time determination in liquid-liquid extraction

3.2.2.2 Effect of surfactant aqueous solution:solvent volumetric ratio

Palm oil was used as only extracting solvent in this experiment to determine the optimal surfactant aqueous solution:solvent volumetric ratio for liquid-liquid extraction technique. The surfactant solution was blended with pure solvent (palm oil) at volumetric ratios of 1:1, 5:1, 10:1, and 20:1 in the test tubes in such a way to minimize the headspace volume in order to avoid the loss of PCE into air phase. All procedures were the same as previously mentioned and the equilibrium partitioning of palm oil between two phases occurred. The concentration of PCE in aqueous and palm oil phases were analyzed using GC-FID and mass balance of PCE with the closer of material balance of PCE between phases of 10% were carried out to assure the reliability of experiment. As a consequence, the relationship between the PCE removal and surfactant aqueous solution:solvent volumetric ratio was investigated. Consequently, the optimal volumetric ratio of surfactant aqueous solution:solvent was further applied to study of the effect of EACNs of extracting solvent in liquid-liquid extraction of PCE from surfactant aqueous solution. The schematic diagram for effect of surfactant aqueous solution:solvent volumetric ratio study was shown in Figure 3.2.3.

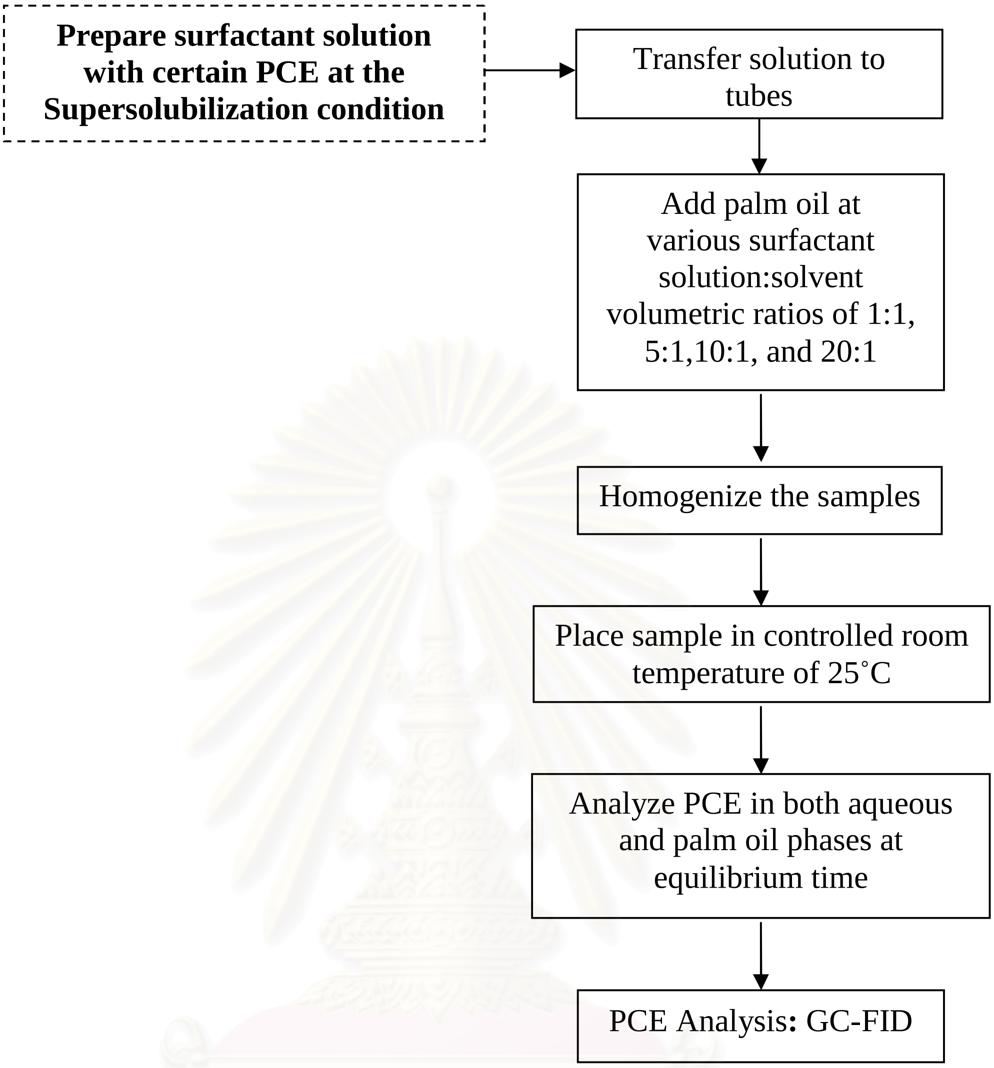


Figure 3.2.3 The schematic diagram for surfactant aqueous solution:solvent volumetric ratio determination in liquid-liquid extraction

3.2.2.3 Effect of EACNs of extracting solvents

Five extracting solvents at various EACNs were used including dodecane (ACN=12), palm oil (EACN=13), sunflower oil (EACN=18), octadecane (ACN=18) and squalane (ACN=30). The experiment was done as the same procedure as described previously in 3.2.2.2 to avoid the headspace lost of PCE except EACNs of extracting solvents was varied and the volumetric ratio of surfactant aqueous solution:solvent was held constant. The PCE partitioning between phases and the PCE removal from surfactant aqueous solution to solvent phase could be revealed.

The schematic diagram for effect of EACNs of extracting solvents was shown in Figure 3.2.4.

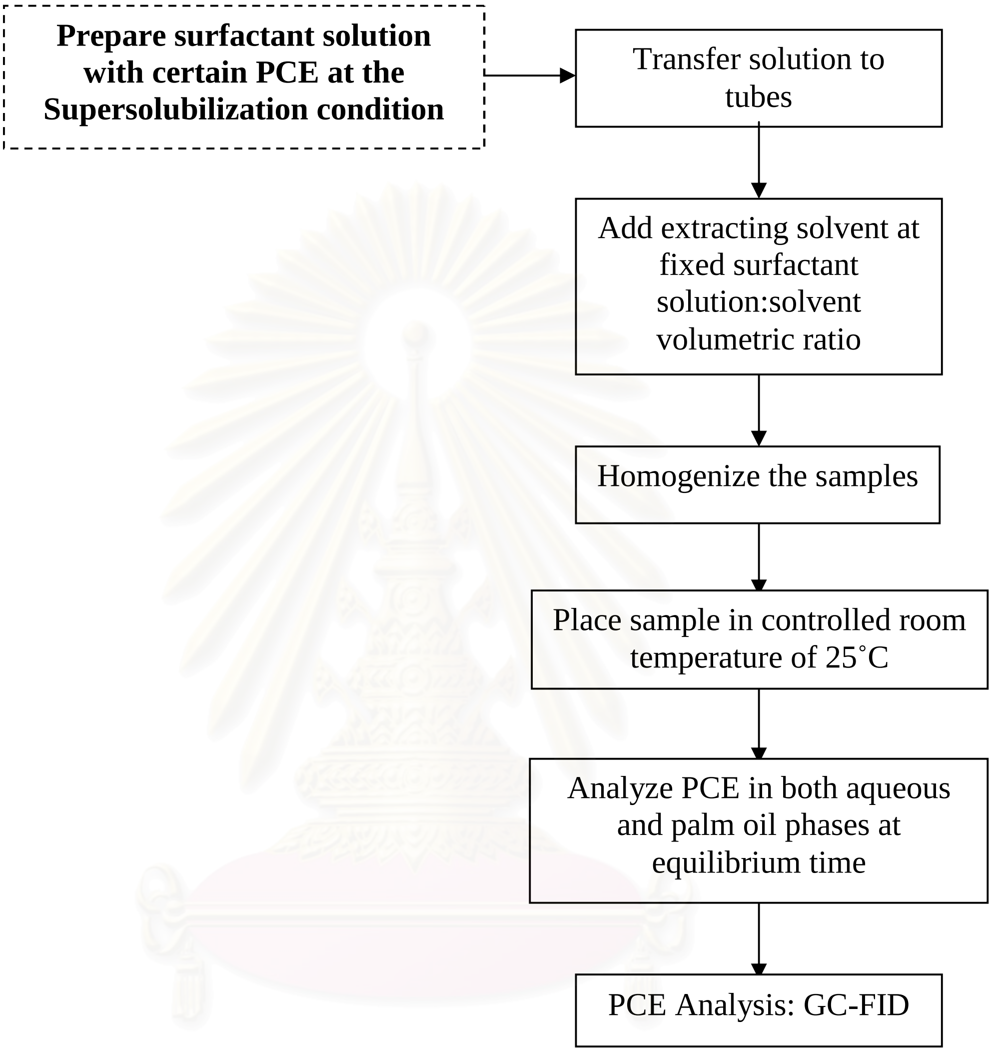


Figure 3.2.4 The schematic diagram for effect of EACNs of extracting solvents determination in liquid-liquid extraction

3.2.3 Reverse micellar extraction study

3.2.3.1 Phase behavior study

The reverse micellar extraction was studied using 2 oils (palm oil and dodecane). The surfactant aqueous solution obtained from preliminary study in the presence of PCE at fixed volumetric ratio of surfactant solution:solvent was used to form the Winsor Type II microemulsion by salinity scan with NaCl. If Winsor type II condition could not be formed solely by AMA, the second surfactant needed to be added to help reducing the HLB of the system. The total amounts of surfactant(s) along with the extracting oil presenting in the aqueous phase were analyzed using Total Organic Carbon Analyzer (TOC). The suitable NaCl that can form microemulsion type II with least amount of surfactant(s) and oil in the aqueous phase was selected. The schematic diagram for Winsor type II microemulsion determination was shown in Figure 3.2.5.

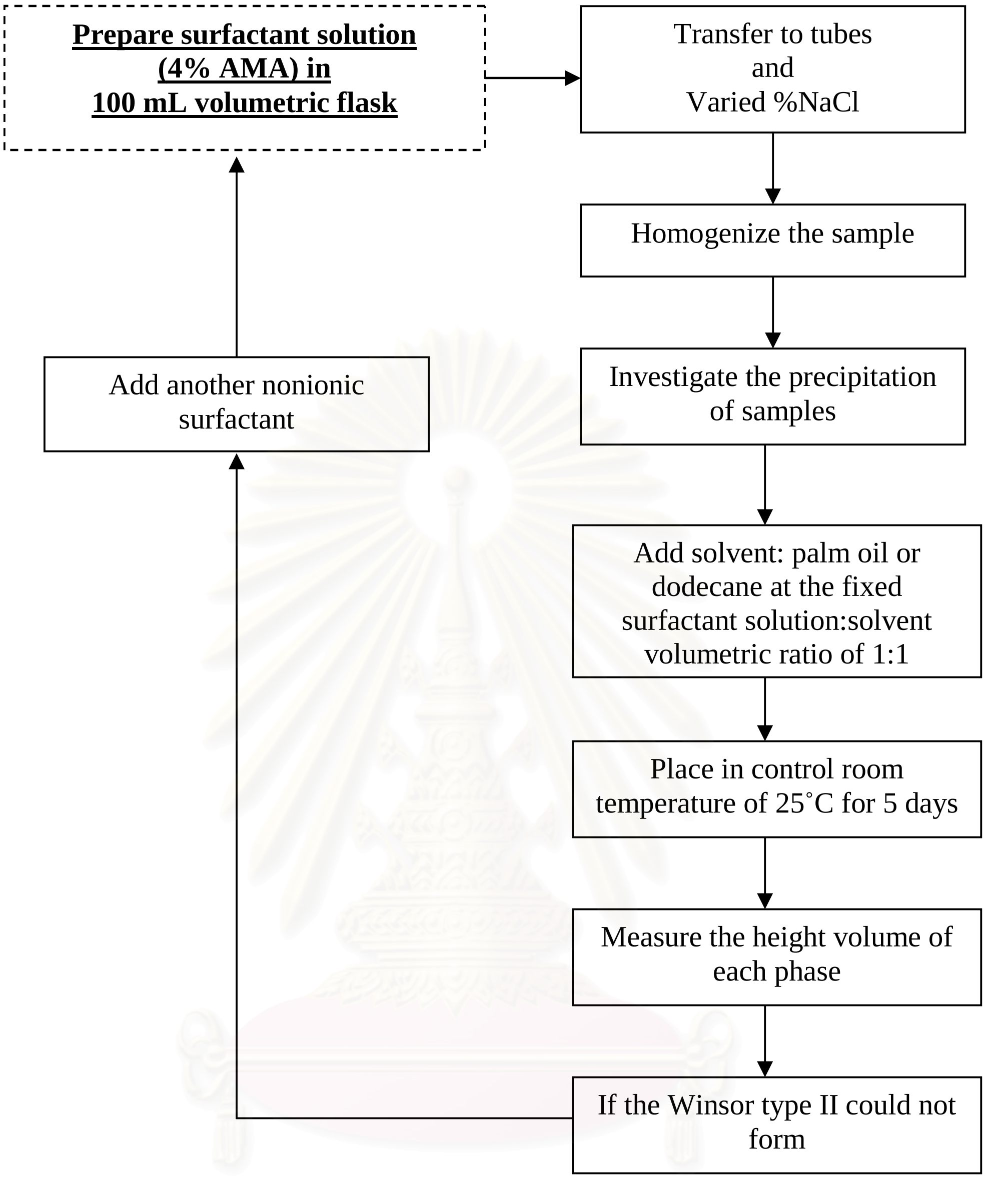


Figure 3.2.5 The schematic diagram for Winsor type II microemulsion formation determination in reverse micellar extraction

3.2.3.2 Effect of surfactant aqueous solution:solvent volumetric ratio

The effect of volumetric ratios of surfactant solution:extracting oil was studied at 4 ratios including 5:1, 10:1, 20:1, and 40:1; and applied to the above surfactant(s)-oil-NaCl system obtained from the phase behavior study. The appropriate volumetric ratio of surfactant solution:extracting oil was determined by considering that Winsor type II microemulsion system that has the least amount of surfactant(s) and oil in the aqueous phase. The surfactant(s)-oil-NaCl system with appropriate volumetric ratio of surfactant solution:extracting oil was studied in the presence of 10,000 ppm PCE concentration. The concentration of remaining surfactant(s) and PCE in aqueous solution was determined by TOC analyzer and GC-FID, respectively. The schematic diagram for effect of surfactant aqueous solution:solvent volumetric ratio determination was shown in Figure 3.2.6.

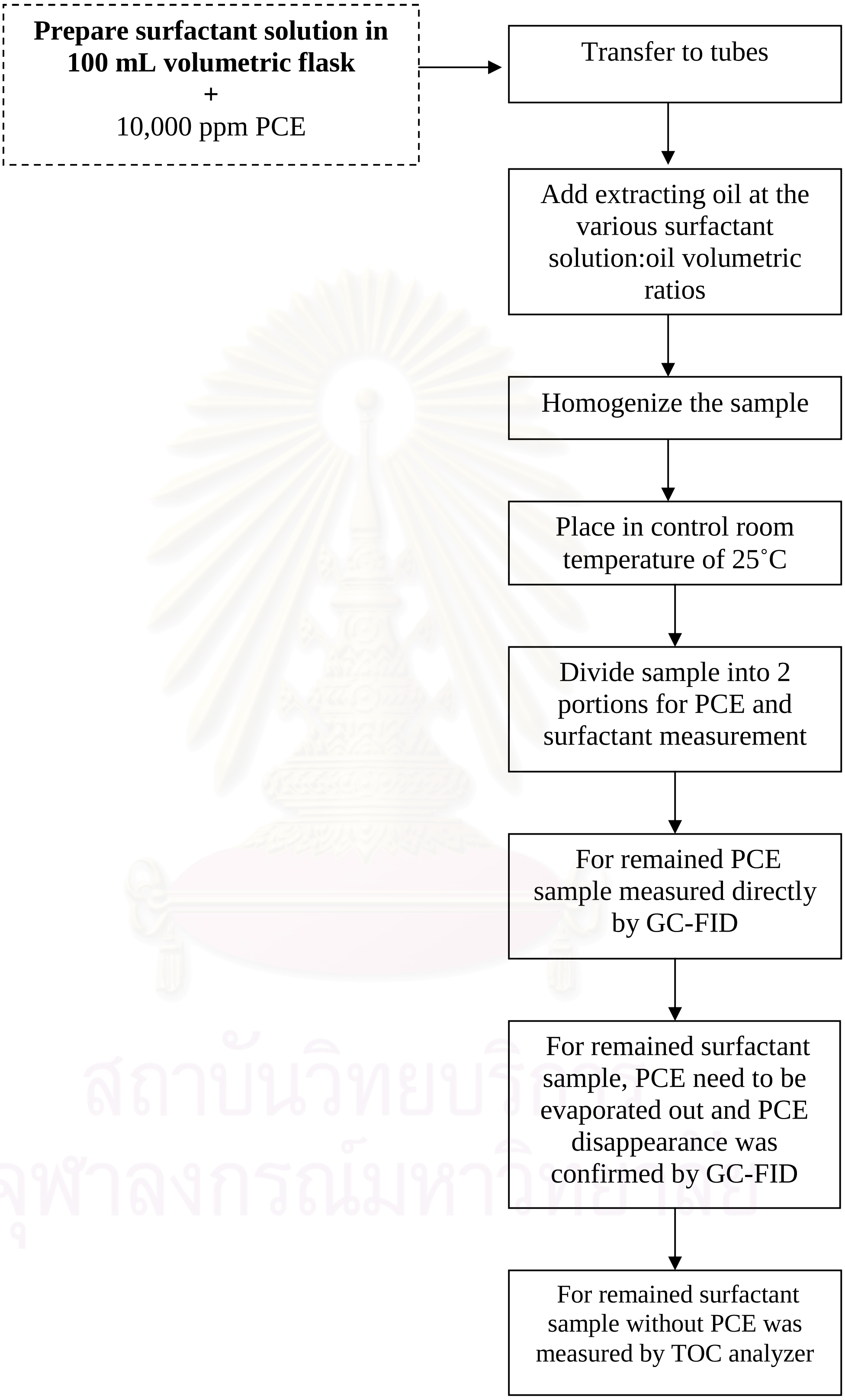


Figure 3.2.6 The schematic diagram for effect of volumetric ratios of surfactant solution:extracting oil in reverse micellar extraction

3.2.4 Ultrafiltration process

The oil solution at the same compositions as obtained from phase 3.2.3 was prepared for 100 mL and pour into a 350 mL-stirred cell ultrafiltration (UF) unit (Amicon Stirred Cell Ultrafiltration Cell, Model 8400). The 50,000 ppm PCE was added in the mixed surfactant with the best surfactant:oil volumetric ratio obtained from 3.2.3.2. The regenerate cellulose membrane with 5,000 Dalton cutoff was used to block the passage of surfactant reverse micelles in the retentate stream while allowing only PCE, extracting solvent, and some of surfactant monomers to migrate into the permeate stream. A schematic diagram of reverse micellar enhance ultrafiltration process was shown in Figure 3.2.7. The effect of applied N_2 gas pressure on the UF cell was studied. The UF process was terminated when the volume of retentate stream decrease to 25 mL or retentate:permeate volumetric ratio of 1:3 (or 25 mL:75 mL). The concentration of PCE in the permeate stream and retentate were analyzed and the percentage of PCE removal could then be evaluated.

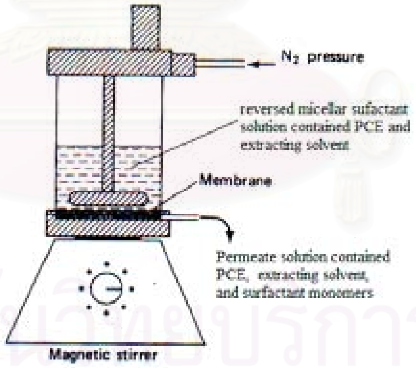


Figure 3.2.7 The schematic diagram of stirred cell ultrafilter

3.2.4.1 The ultrafilter operation

The experiment was set up following a protocol from the UF stirred cell manufacturer as follows:

1. Regenerate cellulose membrane was placed in the holder, shiny side up; then place O-ring on top of membrane. Gently push O-ring down so that it contacted and seated membrane evenly in bottom of holder. Handle membrane by its edges to avoid scratching or contaminating surface.

2. Fit membrane holder into cell body, aligning tabs on sides of holder with slots in base of cell body.

3. Invert cell body and membrane holder; screw base firmly into bottom of cell body. A definite “stop” will be felt when base and body are fully engaged. Top of membrane holder will be flush with bottom of slots in cell body.

4. Push filtrate exit tubing onto exit spout of membrane support.

5. Place stirrer assembly into cell body. When properly installed, arms of stirrer assembly will rest on small ridge inside top of cell body.

6. Introduce oil solution sample contained PCE into cell.

7. With a twisting motion, push cap down onto cell body, orienting gas inlet port on cap opposite filtrate exit port on holder. If cap assembly does not slide easily, lubricate O-ring lightly with petroleum jelly.

8. Set pressure-relief valve to horizontal (open) position.

9. Slide cell into retaining stand, fitting ring on cell base into hole in stand. Flatten edges on bottom flange of cap ensures that cell is inserted properly and prevents rotation of cell once inside stand. Place cell on magnetic stirring table.

10. Turn pressure-relief valve to vertical (closed) position.

11. Attach gas pressure line. Nitrogen gas is recommended for pressurizing cell. Use of compressed air can cause large pH shifts due to dissolution of carbon dioxide. With sensitive solutions, oxidation can also occur, leading to other potential problems.

12. Hold cell steady on the stirring table and pressurize according to instructions in membrane package. Generally 55 psi (3.7 kg/cm^2) is optimal, maximal 70 psi (4.7 kg/cm^2) nitrogen gas pressure. Cap assembly moves upward, forming a secure lock with retaining stand once system is pressurized.

13. Turn on stirring table and adjust stirring rate

14. The ultrafilter was operated until obtained the desired volumetric ratio of permeate:retentate. Collect permeate solution.

15. When finished, turn off nitrogen pressure source and stirring table.

16. Vent pressure inside cell by slowly turning pressure-relief knob to horizontal position. Push cap down, then slide cell out from retaining stand. Note: overly rapid depressurization can cause the membrane to buckle up and rupture.

17. Using a twisting motion, remove cell cap and the magnetic stirrer assembly. Always remove the cell top with the pressure-relief valve set to the horizontal (open) position. Removal in vertical (closed) position can create a partial vacuum which can rupture the membrane.

18. Pour out and collect retentate solution.

19. Disassemble cell, then wash all components with a mild detergent/water solution, then rinse thoroughly.

3.3 Analysis of PCE and surfactant concentration

3.3.1 Analysis of PCE

The concentration of PCE was measured by gas chromatography (GC) with a flame ionize detector (FID). The external standard quantitative calibrations were conducted for the analysis of PCE in both aqueous surfactant solution and extracting solvent phases (palm oil, dodecane, sunflower oil, octadecane, and squalane). Closure of the material balances of PCE was taken as evidences to ascertain the reliability of experiments.

A GC (Perkin Elmer, Model Clarus 500GC) with headspace autosampler was used for PCE analysis. A capillary column HP-5 (5% phenyl methyl siloxane, 30.0 m x 320 µm x 0.25 µm nominal) was used in the analysis. The oven temperature was programmed as follows: hold 140 ˚C, 4 minutes; ramp rate 40 ˚C min^{-1} to 250 ˚C, hold 1 minute. The injection volume was 10-20 µL and injection mode were a split-less type or split type depend on capacity of partitioning of PCE in sample where an injection port was maintained at 200 ˚C. Heluim (He) and Nitrogen (N_2) were used as carrier gases at a flow rate of 0.45 mL/min and individual flow of Nitrogen 20 mL/min.

The condition of gas chromatography and headspace autosampler was as follows:

- Instrument Brand : Perkin Elmer
- Model : Clarus 500GC
- Column : HP-5 with 30 m x 0.32 mmID, 0.25 µm film thickness
- Oven temperature : 140 - 250 ˚C
- Injector temperature : 200 ˚C
- Detector temperature : 250 ˚C

The experimental condition for headspace autosampler was as follows:

- Instrument Brand : Perkin Elmer
- Model : Turbomatrix 40
- Thermostatting times : 30 minutes
- Oven temperature : 80 ˚C
- Needle temperature : 100 ˚C
- Transfer line temperature : 90 ˚C
- GC cycle time : 10.0 minutes
- Injection time : 0.04 minutes
- Withdrawal time : 0.2 minutes

3.3.2 Analysis of surfactant

The concentration of AMA and span-20 could be indirectly evaluated by Total Organic Carbon Analyzer (Shimadzu Scientific Instruments, Inc., Model TOC-VCPH) equipped with autosampler (Shimadzu Scientific Instruments, Inc., Model ASI-V). The surfactant concentration was measured as the total organic carbon of surfactant(s) in that solution and calculated in to concentration unit. It should be noted that the TOC amount cannot be used to distinguish the exact concentration of each surfactant component in the solution since it represents the concentration as a whole. The summary of overall study was shown by a diagram in Figure 3.2.8.

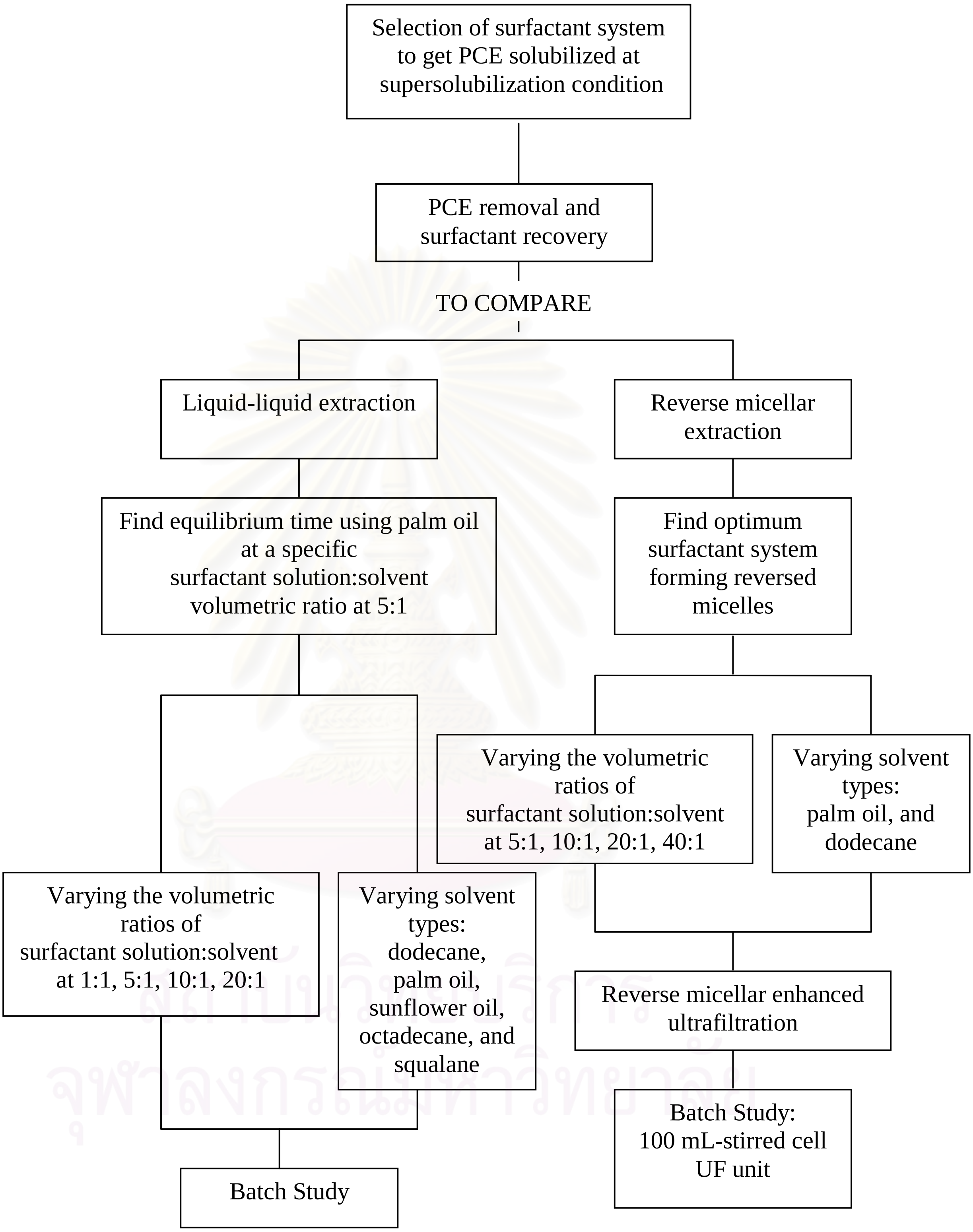


Figure 3.2.8 The summarized diagram for the overall study

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Phase behavior study

The aims of phase behavior study were to determine the supersolubilization condition of PCE in Winsor type I surfactant microemulsion solution and to investigate the maximum PCE concentration in that surfactant solution for further used to represent the effluent surfactant solution flushed out of the PCE contaminated area. The phase behavior study was studied by gently mixing PCE with Aerosol-MA or AMA at the volume ratio of 1:1 by varied NaCl concentration. The solutions were allowed to equilibrate at room temperature of 25˚C for at least 12 hours prior to observe the phase transition. The volume of each phase was carefully recorded by measuring the phase height within 0.01 cm scale.

According to the visual observation of the phase transition between Microemulsion Winsor type I-III-II, the 4%AMA/3%NaCl system was found to exhibit the Winsor type I microemulsion (oil in water) closed to a boundary of Winsor type I/III prior to form the middle phase microemulsion at 4%NaCl. Figure 4.1 showed a phase transition from Winsor type I to type III by scanning with NaCl to decrease the HLB of the surfactant solution containing 4%AMA. By solution appearance, it was found that the one before the type I-III transition showed the milky-like surfactant solution, which is generally used to identify that the surfactant system is at the supersolubilization region where the solubilization of solute in the surfactant micelles is maximum. This surfactant solution was corresponded to work done by Child et al. (2006), which also used AMA as the surfactant in field demonstration for surfactant-enhanced solubilization of DNAPL at Dover Air Force Base, Delaware.

The addition of NaCl to solutions of ionic surfactants tends to extend of solubilization of PCE that is likely to solubilize in the inner core of micelle. Due to the fact that an electrolyte addition in the ionic surfactant solution can decrease the repulsion between the similar charged ionic surfactant head groups, thereby decrease the CMC and increase the aggregation number and volume of the micelles. The increase in aggregation number of the micelles presumably results in an increase in PCE solubilization in the inner core of micelle. The decrease in mutual repulsion of the ionic head groups on the other hands causes a closure packing of the surfactant molecules at the palisade layer and results in a decrease in the volume available for polar compounds solubilization (Rosen, 2004).

However, in this study, the NaCl concentration that can cause the supersolubilization condition was required. Too high NaCl concentration can greatly reduce the HLB of the surfactant system until the Winsor type III or middle phase microemulsion is formed. Although the middle phase microemulsion can give the maximum solubilization and lowest IFT, it is not applicable to be used if the solution was designed to flush the subsurface soil. The most suitable NaCl concentration was found to be 3% wt. Thus, the 4%AMA/3%NaCl system was further used to evaluate the maximum PCE solubilization.

The known PCE concentrations ranging from 5,000 to 20,000 ppm were prepared in a series of identical surfactant solutions. The results showed this surfactant system could maximize the PCE solubilization up to 10,000 ppm without forming an excess phase of PCE. In addition, the concentration of solubilized PCE at this supersolubilization condition was found to be about 12,000 ppm measured by Gas chromatography (GC). Consequently, this 4%AMA/3%NaCl system was used to represent the supersolubilization system for PCE and PCE at concentration of 10,000 ppm was applied throughout the experiment as a base PCE concentration.

Figure 4.1 The phase transition of microemulsion solution by scanning with NaCl in the system containing 4%AMA

4.2 Effect of EACN of solvent on liquid-liquid extraction

4.2.1 Equilibrium time determination

The surfactant solution at supersolubilization region containing 4%AMA/3%NaCl with the solubilized PCE concentration of 10,000 ppm was used to represent the contaminated surfactant solution. To find the equilibrium time, the volumetric ratio of surfactant aqueous solution:solvent (palm oil) was fixed at 5:1. The experiment was set in the controlled room temperature of 25°C. The equilibrium time was determined by plotting PCE concentration in palm oil with respect to time and the time that PCE concentration reaching a plateau was determined as the equilibrium time for this liquid-liquid extraction process. The analysis of PCE in palm oil was done using GC equipped with headspace autosampler. The plot between PCE concentration in palm oil and time was shown in Figure 4.2. The result showed that the concentration of PCE remained almost constant after at 4 days (96 hours). Thus, 4 days was defined as the equilibrium time for the liquid-liquid extraction and applied in the next experiments to study the effects of surfactant solution:solvent volumetric ratio and the EACNs of extracting solvent.

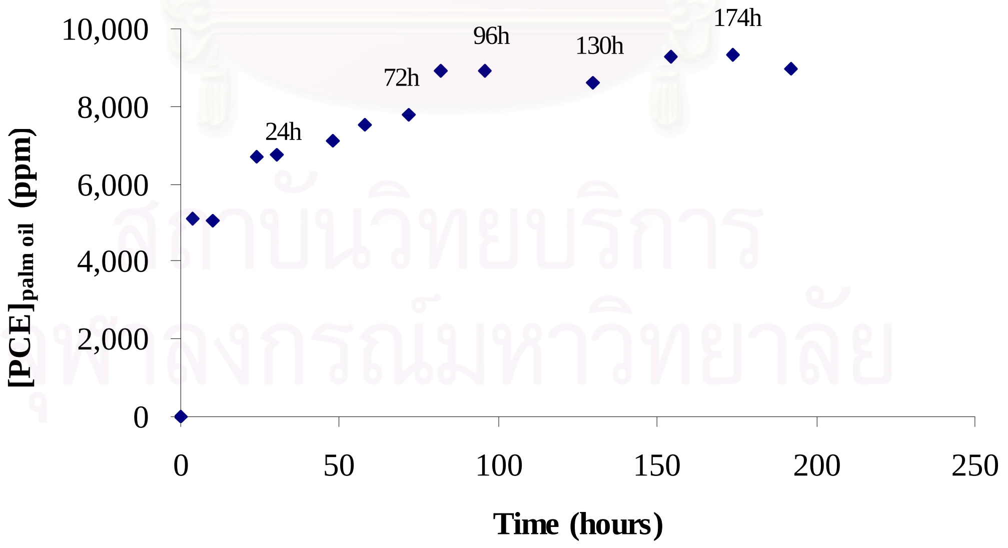


Figure 4.2 The concentration of PCE in palm oil phase at various time using the volumetric ratio of surfactant solution:solvent of 5:1

4.2.2 Effect of surfactant solution:solvent volumetric ratio

Palm oil was used to determine the optimal surfactant aqueous solution:solvent volumetric ratio. The concentration of PCE in both phases was analyzed and the material balance of PCE was carried out to assure the reliability of the data. The deviation of mass of PCE in material balance was less than 10%. The distribution of PCE between phases (PCE concentration in solvent phase divided by PCE concentration in surfactant aqueous phase) and %PCE removal from surfactant aqueous phase to extracting oil phase at different surfactant aqueous solution:solvent volumetric ratio were shown in Table 4.1.

Table 4.1 The effect of the surfactant solution: solvent volumetric ratios in liquid-liquid extraction on % PCE removal and distribution coefficient of PCE by using palm oil as extracting solvent

Surfactant solution: solvent volumetric ratios	**$[PCE]_{initial}$(1) (ppm)**	**$[PCE]_{aqueous}$(2) (ppm)**	**$[PCE]_{solvent}$(3) (ppm)**	**%PCE Removal(4)**	**$\frac{[PCE]_{solvent}}{[PCE]_{aqueous}}$**
1:1	9,782	1,662	7,667	83.0	4.6
5:1	9,964	3,653	26,288	63.3	7.2
10:1	9,959	4,571	64,674	54.1	14.1
20:1	9,986	6,478	67,686	35.0	10.4

(1) $[PCE]_{initial}$ was concentration of initial PCE in 4%AMA/3%NaCl solution
(2) $[PCE]_{aqueous}$ was concentration of PCE in aqueous phase
(3) $[PCE]_{solvent}$ was concentration of PCE in solvent phase
(4) %PCE removal was calculated from a subtraction between mass of $PCE_{initial}$ and $PCE_{aqueous}$ and divided by mass of $PCE_{initial}$ x 100

The results showed that PCE can partition from surfactant aqueous phase to extracting oil phase followed a rule of thumb “like dissolve like” but the partitioning ability depends greatly on the surfactant aqueous solution:solvent volumetric ratio used. The distribution coefficient of PCE was found to increase with increasing surfactant aqueous solution:solvent volumetric ratio. On another word, it increases with decreasing the volume of extracting oil used as illustrated in Figure 4.3. Due to the fact that the concentration of solute can be high if the volume of solution is low. In this case, a decrease in volume of extracting oil used caused a reduction in the %PCE removal, meanwhile increasing the concentration of PCE in the oil phase resulting in a greater PCE distribution coefficient. As the reduction of volume of extracting oil reached a certain point, the distribution coefficient cannot be improved since the volume of extracting oil is inadequate to induce the PCE partitioning into the oil phase. From this study, at the surfactant solution:palm oil volumetric ratio greater than 10:1, PCE could not partition into palm oil because a maximum capacity of palm oil for PCE partitioning was reached as illustrated by a plateau PCE amount in palm oil phase in Figure 4.3. In this study, the volume of palm oil was fixed, while the volume of surfactant solution used was varied. Thus, an initial mass of PCE in surfactant solution increases with increasing surfactant solution:palm oil ratio resulting in a higher PCE amount in palm oil phase due to PCE partitioning. However, it was found that at volumetric ratio of surfactant:palm oil over 10:1, the amount of PCE in palm oil phase reached a plateau since no more PCE from surfactant aqueous solution can partition into palm oil phase. Thus, the partitioning of PCE in palm oil phase was limited when the inadequate volume of palm oil was used. The remaining PCE concentration in aqueous surfactant solution increases with increasing ratio (or less volume of solvent used) resulting in a lower percentage of PCE removal. The lower the volume of extracting solvent used to extract the same amount of solubilized PCE, the lower the degree of PCE removal from aqueous into solvent phase. This finding was in good agreement with Elbashir et al. (2002) who investigated the effect of critical parameters in solvent extraction for recycling used lubricating oils, i.e., type of solvent, solvent to oil ratio, and extraction temperature. They found that an increasing in solvent:oil volumetric ratio (increase amount of solvent used) can increases the solubility of oil in the solvent phase, resulting in a greater extraction efficiency.

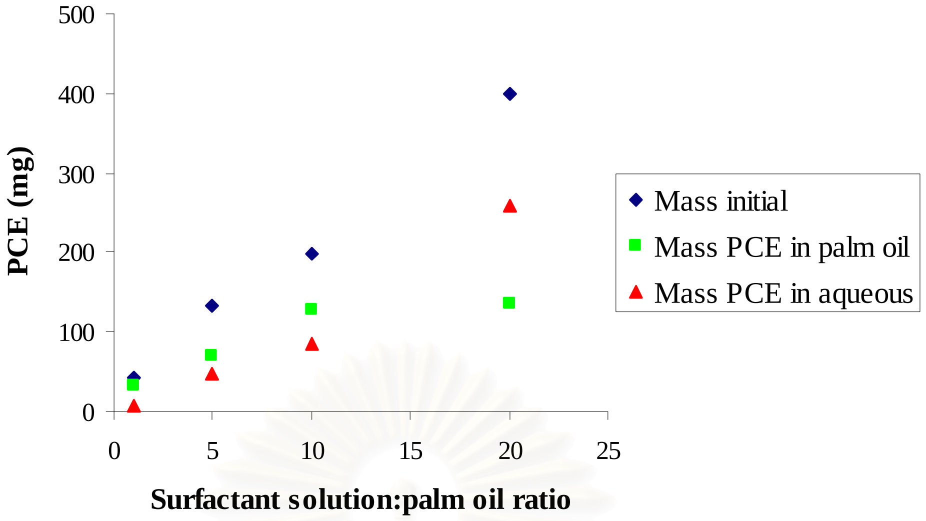


Figure 4.3 The co-plot between mass of PCE in palm oil and aqueous phase at various surfactant solution:palm oil ratios

From this study, the ratio of 10:1 was selected to be an optimal surfactant aqueous solution:solvent volumetric ratio using 3 main criteria including (1) the %PCE removal from aqueous surfactant solution to extracting solvent, (2) the used volume of extracting solvent and (3) the distribution coefficient of PCE ($[PCE]_{solvent}/[PCE]_{aqueous}$). At the 10:1 ratio, although the %PCE removal from surfactant aqueous solution into the extracting solvent (palm oil) phase was not the highest (54.1%) but the highest PCE distribution coefficient of 14.1 was achieved at this ratio. The greatest PCE removal of 83.0% was found at volumetric ratio of 1:1, which is about 30% higher than one obtained at 10:1 ratio. However, the 1:1 ratio used the volume of extracting oil 3 times greater that of 10:1 and yielded an obvious lower distribution coefficient. Consequently, the volumetric ratio of surfactant aqueous solution:solvent at 10:1 was further used to study of the effect of EACNs of extracting solvent in liquid-liquid extraction of PCE from surfactant aqueous solution.

4.2.3 Effect of EACNs of extracting solvents

Two groups of selected extracting solvents used in this study were vegetable oil (non-alkanes) and alkanes at varied EACN values. In this study, the term EACN was used for the non-alkane solvents, while the term ACN was used for alkane solvents. Five extracting oils were used namely dodecane (ACN=12), palm oil (EACN=13), sunflower oil (EACN=18), octadecane (ACN=18), and squalane (ACN=30). The aim of this study was to investigate the effect of EACN of extracting solvent and its functional group on the liquid-liquid extraction efficiency. Table 4.2 illustrated the distribution coefficient of PCE and %PCE removal obtained from different extracting solvents. The results showed that alkane showed a greater extraction performance than the vegetable oil although having the similar EACN values as can be seen by a comparison between dodecane and palm oil (EACN of 12-13); and octadecane and sunflower oil (EACN of 18). This can be explained by the fact that even the extracting oils have the same EACN, the function groups of solvent are different which influent the affinity of solvent to PCE. The vegetable oils are classified as fatty acids containing carboxyl groups as the main functional group. Thus, the affinity of PCE to partition into these polar oils is less than that of straight chain hydrocarbon or *n*-alkane. Cox and Rydberg (2004) stated that solutes have differing solubilities in different solvents due to variations in strength of the interaction of solute molecules with those solvents. Thus, in a system of two immiscible or only partially miscible solvents, different solutes become unevenly distributed between two solvent phases, and this is a basis for solvent extraction technique.

Table 4.2 The effect of the EACNs of extracting solvents in liquid-liquid extraction on %PCE removal and distribution coefficient of PCE with constant surfactant aqueous solution:solvent volumetric ratio of 10:1

Extracting solvents	**EACNs**	**$[PCE]_{initial}$(1) (ppm)**	**$[PCE]_{aqueous}$(2) (ppm)**	**$[PCE]_{solvent}$(3) (ppm)**	**%PCE Removal(4)**	**$\frac{[PCE]_{solvent}}{[PCE]_{aqueous}}$**
Dodecane	12	11,263	4,397	50,978	84.3	49.4
Palm oil	13	9,959	4,571	64,674	54.1	14.1
Sunflower oil	18	10,039	3,254	58,778	67.6	18.1
Octadecane	18	8,949	941	81,079	89.5	86.2
Squalane	30	10,263	3,805	50,978	57.2	11.6

(1) $[PCE]_{initial}$ was concentration of initial PCE in 4%AMA/3%NaCl solution
(2) $[PCE]_{aqueous}$ was concentration of PCE in aqueous phase
(3) $[PCE]_{solvent}$ was concentration of PCE in solvent phase
(4) %PCE removal was calculated from a subtraction between mass of $PCE_{initial}$ and $PCE_{aqueous}$ and divided by mass of $PCE_{initial}$ x 100

By comparing the same group of solvent such as group of vegetable oils and group of alkanes, the results showed that the EACNs of extracting solvent has a great effect on the extraction ability. The extracting oil with greater EACN value tended to give the higher %PCE removal and distribution coefficient of PCE as displayed in Table 4.2. For series of alkane, the partitioning of PCE into octadecane (ACN=18) was two times higher than that of into dodecane (ACN=12). For series of vegetable oil, the partitioning of PCE into sunflower oil (EACN=18) slightly higher than that of into palm oil (EACN=13). The significant improvement of the PCE distribution coefficient by EACN was found in the system of alkanes but a slight improvement was also evidenced in the system of vegetable oils.

However, the result was not in agreement with squalane (straight chain hydrocarbon with ACN=30) which was the extracting solvent having the highest ACN used in this study. It was possible that squalane has too high degree of hydrophobicity or in another word, too nonpolar for PCE to dissolve. Since PCE has low EACN value (EACN=2.9) and log K_{ow} of 3.40, PCE was relatively non-polar compound if compared with water but quite polar if compared with squalane

(ACN=30), resulting in a less favorable in PCE partitioning into squalane solution. This finding also confirms the like dissolve like phenomenon. In addition, it corresponds well with work done by Burns (2006). His study aimed to separate a polymer namely perfluorinated polyether (PFPE) into two groups at different molecular-weight using liquid-liquid extraction technique. Two types of solvent varying the polarity were applied. One was alcohol or cyclic ether, which was considered as high polarity solvent. The other solvent was fluorinated solvent which was considered as a low polarity solvent. He found that the high polarity alcohol or cyclic ether solvent can extract the lower molecular weight PFPE, while the low polarity fluorinated solvent has more preferential to extract the PFPE at higher molecular weight (Burns, 2006).

For vegetable oil, the trend of PCE partitioning coefficient was similar to that of alkanes in such a way that the higher the EACN of vegetable oil, the higher affinity of PCE partitioned into the solvent phase. Nevertheless, it should be addressed that a prediction on the liquid-liquid extraction efficiency based on EACN may be acceptable if the applied solvents are in the same homologous series but cautions should be made if the differences of physical and chemical properties between solute and solvent are obvious. However, EACN solely cannot be used if solvents applied are not in the same homologous series. Thus, other physical-chemical properties of compounds, i.e., functional groups, water solubility, log K_{ow}, etc. should be considered. In addition, besides the extraction performance, other factors determining the suitability of compounds to be used as the extracting solvent should also be incorporated such as cost, availability, and toxicity of the solvents.

It should be noted that in this liquid-liquid extraction, most of surfactant and electrolyte remained in the aqueous solution, only PCE partitioned out of surfactant micellar aqueous solution and moved into the extracting solvent phase due to affinity between PCE and extracting oil or “like dissolve like” rule of thumb as discussed in the section 4.2.2. So most of surfactant, NaCl and some of PCE were remained in the aqueous solution because the hydrophile-lipophile balance (HLB) surfactant system with this extracting solvent was not low enough to force the transition from Winsor microemulsion type I into type II or reversed micelle where surfactant can move into the extracting solvent phase. Since the surfactant aqueous solution was prepared at the supersolubilization condition (4%AMA/3%NaCl), no surfactant migration from aqueous phase to solvent phase was assumed based on theory. Moreover, the analysis of the surfactant concentration in aqueous solution used in the liquid-liquid extraction study via total organic carbon analyzer showed an insignificant change in TOC amount prior and after liquid-liquid extraction at that NaCl concentration. Consequently, most surfactant still be in the aqueous phase while PCE removed from aqueous phase to solvent phase depended on the affinity of PCE with that applying solvent.

Moreover, from the criteria for extracting solvent selection, the one that has high EACN is preferable since it tends to be less soluble with water phase or soluble with their allowance solubility, thus the loss of solvent into aqueous phase can be reduced. From the observation of liquid-liquid extraction with various EACN and functional group of extracting solvent, there were little volume phase changes as noticed from a constant the interfacial boundary level between aqueous surfactant solution-extracting solvent as marked. Some losses of extracting solvent into aqueous solution were found only vegetable oils (palm oil and sunflower oil) as a result of the polarity of carboxyl group (-COOH) present in the molecule. There were some small droplets of vegetable oil attached at the inner side of glass bottle. However, this evidence was not found when using *n*-alkanes as the extracting solvents. So the presence of carboxyl group in the vegetables oil also reduced the extraction efficiency in terms of a lower in %PCE removal and distribution coefficient plus the loss of extracting oil as compared to the alkane as shown in Table 4.2. Due to very less amount of extracting oil was in aqueous solution and the very less amount of AMA surfactant was in extracting solvent, this study then neglected to investigate that the partitioning of surfactant and oil between two phases.

4.3 Effect of EACN of solvent on reverse micellar extraction

4.3.1 The reverse micellar extraction with palm oil

Palm oil (EACN=13) was used as the extracting solvent to form the Winsor type II microemulsion for reversed micellar extraction, which aimed to extract PCE and surfactant from aqueous solution into the extracting solvent (palm oil) phase prior using an ultrafiltration unit to separate reverse micelles from PCE and solvent. Palm oil was used as the extracting solvent because of its non toxicity, cheap price, and environmentally friendly. Moreover working with palm oil as the extracting solvent in the area of microemulsion was challenging since very limited studies were done on palm oil due to its complexity in structure. So this step aimed to investigate the surfactant systems that can form the Winsor type II microemulsion with palm oil. Not only the efficiency of PCE removal from solution to extracting oil, other criteria considered for reverse micellar extraction included (1) the used volume of extracting solvent, and (2) the toxicity of extracting solvent.

As a result from the phase behavior study in section 4.1, the 4%AMA/ 3%NaCl performed the Winsor type I microemulsion with palm oil, so to force this surfactant solution from Winsor microemulsion type I to type II, the suitable extracting solvent type, second surfactant addition (if needed) and concentration of NaCl were investigated to depress the hydrophile-lipophile balance (HLB) of system for reverse micelle formation. From the rule thumb of Winsor type II microemulsion, the surfactants with low HLB, more lipid loving, tend to make a water in oil microemulsion (type II microemulsion) while those with high HLB are more hydrophilic and tend to make an oil in water microemulsion (type I microemulsion). The HLB value of each surfactant can be determined by considering the characteristics of the surfactant. In the formation of a stable emulsion, it is advisable to have a blend of two or more nonionic surfactants rather than a single surfactant molecule. If more than one surfactant is used to form miroemulsion, the HLB value of the blend can be calculated as the sum of the weight fraction of each individual HLB of surfactant (ICI, 1992).

However, this 4%AMA/3%NaCl system could not form microemulsion type II with palm oil although the NaCl and $CaCl_2$ were added for decreasing HLB of the system. The phase transition shifted from Winsor type I to type III microemulsion or middle phase upon increasing salt concentration. The precipitation of salt in surfactant aqueous solution was observed if an excessive electrolyte concentration was used. In addition, the phase separation between surfactant and water can be observed in some cases because of the density of components in the system was altered resulted from the salt added. Thus, the HLB of AMA used in this system was too high to form Winsor type II microemulsion with palm oil since AMA is normally soluble with water with high degree of hydrophilicity. In many cases, a mixed surfactant system will produce better emulsification than a single surfactant (Perkins, 1998).

Sorbitan monolaurate (Span-20 with HLB = 8.6) is a nonionic surfactant widely applied in pharmacology, cosmetics, and food industries (Zadymova et al., 2002). Span-20 had been used to reduce the HLB of surfactant system because they were safe and admitted to be used as food additive by the current European Regulations (EC Regulation, 2004). This study selected this nonionic surfactant to mix with AMA for HLB reduction and to gear the surfactant property from water soluble toward oil soluble (Perkins, 1998).

The phase behavior study was studied using AMA as a based surfactant and varied Span-20 and NaCl concentration with added PCE at constant volumetric ratio of surfactant aqueous solution:palm oil at 1:1. The formed phases between surfactant mixtures and palm oil were allowed to equilibrate at room temperature of 25˚C for at least 12 hours prior observing the phase transition. It was found that both the 2%AMA/1%Span-20/20%NaCl and 1%AMA/1%Span-20/ 20%NaCl prepared at the surfactant solution:solvent volumetric ratio of 1:1 were able to form the Winsor type II microemulsion as observed by an obvious increase in volume of palm oil phase because some water and surfactant mixture partitioned into palm oil phase as exhibited in Figure 4.4. Therefore, reducing %AMA with added certain amount of Span-20 and electrolyte (NaCl) can adjust the HLB of surfactant system, until the micelles break up and reagregate into reversed micelle (Sabatini and Cheng, 2001).

This formation of Winsor type II microemulsion was confirmed using TOC analyzer to assure the removal of surfactant from aqueous to oil phase. Due to some limitations on surfactant analysis, the actual concentration of AMA and Span-20 in palm oil could not be determined in this study. Thus, the removal of surfactant mixture (both 2%AMA/1%Span-20 and 1%AMA/1%Span-20) from aqueous to oil phase was indirectly determined by subtraction between initial TOC amount of surfactants and the remained TOC amount of surfactants in aqueous solution after Winsor type II microemulsion formation. One assumption applied here was the amount of palm oil solubilized into aqueous phase was small and negligible. Thus, the TOC amount measured in the aqueous phase was solely from the surfactants presented in that solution.

It was also expected that most of electrolyte added was in the aqueous solution because that phase became clearer than the original surfactant mixture solution prior contacting with palm oil. On the other hand, the palm oil solution was a little bit more turbid and viscous. Since more than 80% surfactant partitioned into palm oil phase, a larger volume of palm oil phase was observed as shown in Figure 4.4.

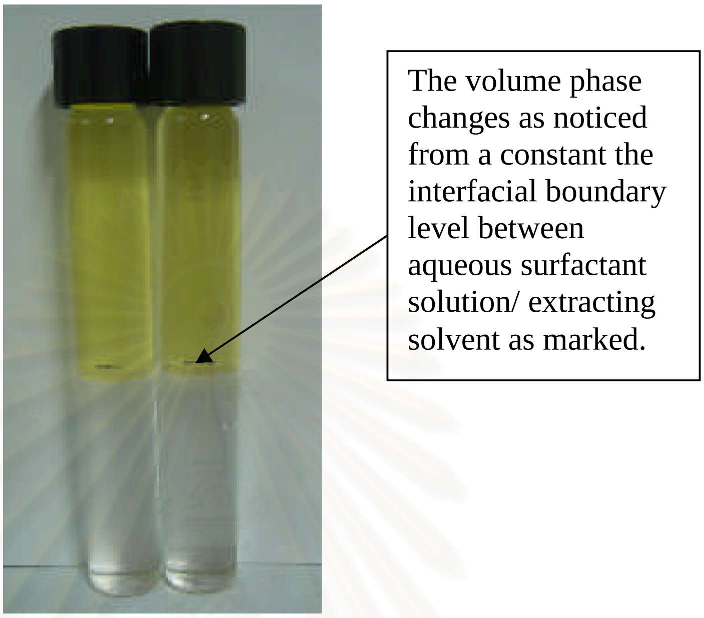

The volume phase changes as noticed from a constant the interfacial boundary level between aqueous surfactant solution/ extracting solvent as marked.

Figure 4.4 The microemulsion type II with palm oil by using 2%AMA/ 1%Span-20/20%NaCl in the absence of PCE in both tubes

The results from TOC measurement on the remained surfactant mixture in aqueous solution with the presence of PCE were reported in term of %surfactant removal as shown in the Table 4.3. When the account for the remained surfactants concentration in aqueous solution, the sample with added PCE was be evaporated to reduce the carbon interference from PCE compounds, so the amount of the TOC of PCE was be neglected from that action. To confirm the disappearance of PCE, the sample was analyzed by GC-HS expected for at least to none amount of PCE concentration prior surfactant account by TOC analyzer. Since TOC counts all components that contains carbon, in this case are AMA and Span-20. The percentages of PCE and surfactant removal were calculated by comparing the initial amount and the remained amount of PCE and surfactants after Winsor type II microemulsion formation. From these surfactant mixtures, more than 80% of surfactant removed from aqueous solution into palm oil phase which corresponded well with the study of Cheng and Sabatini (2001). They reported that almost complete surfactant (Alfoterra 145-4PO sulfate) and contaminant (tetradecane) removal were achieved with the formation of Winsor type II system. However, for a too hydrophobic solvent (e.g. 1-dodecanol), an ideal Winsor type II system might not form with the surfactant system to completely remove the surfactant and contaminant.

Hence, this reverse micellar extraction with vegetable oil demonstrated an exciting potential for SEAR application since a waste stream can be decontaminated; and surfactant can be separated and reused.

Table 4.3 The percentage of surfactant removal in reverse micellar extraction with palm oil (EACN=13) using 2 surfactant systems at constant surfactant aqueous solution:solvent volumetric ratio of 1:1 in the absence of PCE

Surfactant systems	**HLB of system**	**$TOC_{initial}$ (1) (mg/L)**	**$TOC_{remained}$ (2) (mg/L)**	**%Surfactant Removal (3)**
2%AMA/ 1%Span-20/ 20%NaCl	13.63 (a)	15,585	1,693	89.1
1%AMA/ 1%Span-20/ 20%NaCl	12.38 (b)	9,363	1,572	83.2

(a), (b) were the HLB of surfactants mixture calculated by the summation of each weight fraction of surfactant (ICI, 1992)

(1) $TOC_{initial}$ was total organic carbon of surfactant at initial surfactant

(2) $TOC_{remained}$ was total organic carbon of remained surfactant in aqueous solution

(3) %Surfactant removal was calculated by the subtraction of $TOC_{initial}$ with $TOC_{remained}$ and divided by $TOC_{initial}$ x 100

There was insignificant difference of %surfactant removal in both surfactant systems because the HLB of surfactant mixtures were not much different and similar phase behavior could occur within the optimal HLB range for particular oil. As previously mentioned in section 4.3.1 about the criteria for reverse micelles formation, although both surfactant formulas could form reverse micelles with similar degree of surfactant removal but focus was paid into the 2%AMA/1%Span-20/ 20%NaCl system. Because of the higher surfactant removal and the reduced step of the surfactant preparation to be closed to the flushed surfactant solution from groundwater (original surfactant solution), which was the 4%AMA/3%NaCl/PCE, the surfactant solution system containing 2%AMA/1%Span-20/20%NaCl/PCE was selected as an optimum surfactant formulation for Winsor type II microemulsion formation with palm oil.

Although, a large amount of NaCl needed to add to induce the Winsor type II microemulsion resulted in a high salinity in water phase exceeded the standard for discharge to the environment, the precipitation or evaporation processes, which are relatively easy and consume less energy, were suggested to mitigate this problem. Some surfactants remained in the aqueous solution after electrolyte removal could be possible reused to flush the soil with some surfactants make up.

4.3.2 The reverse micellar extraction with dodecane

Dodecane was used as another extracting solvent in order to compared with palm oil surfactant removal by using AMA and Span-20 as the main surfactants. Dodecane is an alkane molecule consisted of 12 carbon atoms thus, having ACN of 12 similar to that of palm oil, which has EACN of 13. It was found that 4%AMA could not form the Winsor type II microemulsion with dodecane, because the HLB of surfactant system was too high, which was similar to results obtained when formed with palm oil as shown in section 4.3.1. Since the 2%AMA/1%Span-20/20%NaCl without PCE was used as suitable surfactant solution to form Winsor type II microemulsion with palm oil, so this surfactant system was used to investigate the Winsor type II microemulsion formation with dodecane. The same experimental procedure on phase behavior study was done using salinity scan to depress the HLB of surfactant system in the absence of PCE. It was found that similar surfactant formulas can form Winsor type II microemulsion with dedecane. The TOC measurement was carried out to investigate the TOC amount of remained surfactant in aqueous solution as compared to ones in original surfactant solution, as a consequence, the percentage of surfactant removal from aqueous to dodecane phase was calculated as illustrated in Table 4.4.

However, it was observed that the Winsor type II microemulsion with dodecane required less salt concentration to form where only 9%NaCl was needed as compared to 20%NaCl needed if forming with palm oil. Therefore, surfactants were more favorably to dissolve in dodecane than in palm oil thus, required less salt to decrease the HLB of the system. Comparison only %surfactant removal in both extracting solvent; palm oil and dodecane, palm oil was more promising because it provided higher %surfactant removal, being nontoxic, cheap and available in the market even utilizing higher salt concentration.

Table 4.4 The percentage of surfactant removal in reverse micellar extraction with dodecane (ACN=12) using 3 surfactant systems at constant surfactant aqueous solution:solvent volumetric ratio of 1:1 in the absence of PCE

Surfactant systems	**HLB of system**	**$TOC_{initial}$ (1) (mg/L)**	**$TOC_{remained}$ (2) (mg/L)**	**%Surfactant Removal (3)**
2%AMA/ 2%Span-20/ 9%NaCl	12.38 (a)	21,532	3,127	85.5
2%AMA/ 2%Span-20/ 10%NaCl	12.38 (a)	21,532	2,856	86.7
2%AMA/ 2%Span-20/ 15%NaCl	12.38 (a)	21,532	2,459	88.6

(a) HLB of surfactant mixture calculated by the summation of each weight fraction of surfactants (ICI, 1992)

(1) $TOC_{initial}$ was total organic carbon of surfactant at initial surfactant

(2) $TOC_{remained}$ was total organic carbon of remained surfactant in aqueous solution

(3) %Surfactant removal was calculated by the subtraction of $TOC_{initial}$ with $TOC_{remained}$ and divided by $TOC_{initial}$ x 100

4.3.3 Effect of surfactant aqueous solution:solvent volumetric ratio

In previous study, palm oil was found to be a more suitable extracting solvent to form Winsor type II microemulsion than dodecane. Thus, the system of 2%AMA/1%Span-20/20%NaCl with palm oil was used to study the effect of surfactant solution:solvent volumetric ratio in the present of the solubilized PCE. It has been well known that the amount of solvent used is an important operating variable in industrial process since it does not reflect only efficiency of process, but also the cost of operation (Chen et al., 2007). This section aimed to study the effect of surfactant solution:solvent volumetric ratio on the percentages of PCE and surfactant removal from aqueous into palm oil phase and to investigate the best ratio suited for this reverse micellar extraction. The surfactant solution:palm oil volumetric ratio was varied as follows: 5:1, 10:1, 20:1, and 40:1. The remained PCE and surfactant in aqueous solution was investigated by GC-HS and TOC analyzer, respectively with the same manner stated in the upper section 4.3.1. The actual PCE and surfactants concentrations in palm oil phase were not directly determined due to some obligations as previously discussed. From the results, as shown in Figure 4.5, there was no significant effect of surfactant solution:solvent volumetric ratio on the percentage of PCE and surfactant removal from aqueous phase into the solvent phase (palm oil) where upto 85% of surfactants and 96% of PCE can migrate to oil phase. However, PCE and surfactant tended to behave in a similar fashion except PCE shows a little bit favorable to dissolve into oil phase rather than surfactants as shown by a slightly higher %PCE removal.

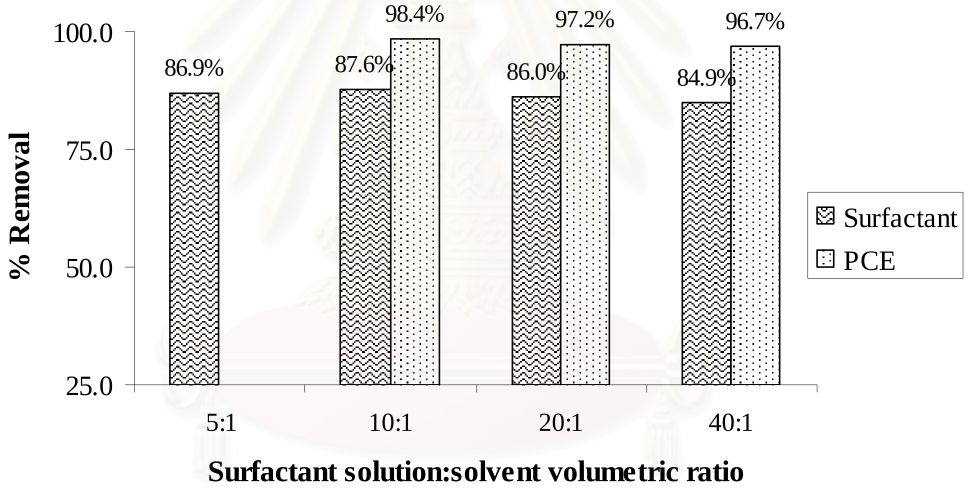


Figure 4.5 Effect of surfactant solution:solvent volumetric ratio on % surfactant and PCE removal in reverse micellar extraction using palm oil

Due to an almost independence of surfactant solution:solvent volumetric ratio, the reverse micellar extraction was proven to be very attractive extraction technique since high extraction efficiency can be achieved and remain although least volume of extracting solvent was used, unlike the liquid-liquid extraction where the volume ratio of surfactant solution and extracting oil was one of the main parameter governing the degree of extraction. This result was well agreed with Cheng and Sabatini (2001), since they stated that one advantage of reverse micellar extraction over typical solvent extraction was that almost complete surfactant and contaminant removal achieved with formation of an ideal Winsor type II microemulsion with the less of solvent used. Therefore, the surfactant solution:solvent volumetric ratio of 40:1 was selected to further study in ultrafiltration process to separate surfactant reverse micelles from PCE and palm oil.

Also, this reverse micellar extraction better performed than in cloud point extraction (Cheng and Sabatini, 2001) because the surfactant concentration in the dilute phase is several times higher than its CMC, which could enhance the solubilization of hydrophobic species in that phase. Moreover, coacervation was a characteristic of non-ionic surfactants only, while the reverse micellar extraction depends only on a matching between solvent and surfactant solution with proper HLB. It is thus applicable to all types of surfactant systems (Saitoh and Hinze, 1991; Lee et al., 2001). In addition, Pessoa and Vitolo (1998); Kilikian et al. (2000) studied the application of reverse micelle extraction, they found that this promising method showed an efficient and selective process that works continuously, saves energy and could be easily scaled up. Besides, it could be used to recover peptides, intra- and extracellular proteins, nucleic acids, organic acids, antibiotics and steroids.

4.4 Ultrafiltration

The palm oil stream at the same compositions obtained from the optimal surfactant formula shown in the section 4.3.1, which comprised of 2%AMA/ 1%Span-20/PCE and the selected surfactant solution:palm oil volumetric ratio of 40:1 was prepared for 100 mL. The solution contained reversed surfactant micelles and PCE soluble in palm oil. This 100 mL palm oil stream was poured into a 350 mL-stirred cell UF unit (Amicon Stirred Cell Ultrafiltration Cell, Model 8400) as the initial solution prior applying N_2 gas to separate surfactant from solvent and PCE by size exclusion. The hydrophilic regenerated cellulose membrane (Amicon Inc., USA) was used in the experiment with 5,000 kDa molecular weight cut off (MWCO). This ultrafiltration membrane is 76 mm external diameter and the effective surface area of the membrane was 45.3 cm^2.

The main reason to select the ultrafiltration process in this study was to recover most of surfactant reversed micelles in the retentate stream while passing PCE along with palm oil in the permeate stream by the size exclusion via the pore size of membrane. There are many advantages of UF overcome other techniques (e.g. reverse osmosis, distillation, etc.) such as ease operation, low energy consumption, less complexity and proven to be effective separation technique. Moreover a significant difference between the surfactant aggregates size and PCE made the UF technique applicable. Therefore, it is desirable to develop a low-energy separation processes that may be of general use in the environmental remediation aspect as well as in the treatment of industrial waste streams.

All ultrafiltration experiments were conducted in a 350-mL Amicon cell at room temperature of 32±2˚C placed on a magnetic stirrer adjusted the speed to 400 rpm to minimize foam formation and to homogenize the oil solution. This condition was adapted from Overdevest et al. (2000). Only PCE, solvent and some surfactant monomer passed from the membrane and was collected as the permeate stream as driven by pressurized N_2 gas. A majority of surfactant in form of reversed micelles still retained in the retentate stream. The main purpose was to investigate the effect of pressurized N_2 gas applied to the UF batch stirred cell on the percentage of PCE removal from the original surfactants solution to the permeate stream. The other parameters such as initial PCE concentration feed, the stirring speed of 400 rpm, membranes material, and the size of membrane (regenerated cellulose with the 5,000 MWCO pore size) were held constant. In addition, other parameters, for instances, transmembrane pressure, temperature, and type of membrane were not investigated in this study.

4.4.1 Preliminary work for the UF stirred cell set up

Firstly, the maximum concentration of partitioned PCE in palm oil solution containing 2%AMA/1%Span-20 after Winsor type II microemulsion formation at the selected surfactant solution:palm oil ratio of 40:1 was determined. From the result of surfactants and PCE removal in section 4.3.3, this palm oil solution was consisted of more than 85% of partitioned surfactant (the mixture of AMA and Span-20 of 2:1 by weight in the assumed proportion the same as a prepared ratio), and more than 96% of PCE partitioned into palm oil during the micelles break up. Thus, from the material balance of PCE in the system, the PCE concentration in palm oil after reverse micellar extraction was high as 400,000 ppm (or 96% of total PCE are now in the palm oil phase) and this solution was prepared and used as the feed solution for the stirred cell UF unit.

Nevertheless, it was found that the palm oil solution with 400,000 ppm PCE and 2%AMA/1%Span-20 could not be filtered through the membrane even applied at the maximum allowance pressure of 70 psi. The microstructure analysis was not conducted here but a speculation was that the presence of high concentration of PCE (400,000 ppm PCE) and the 2%AMA/1%Span-20 in palm oil may swell the palm oil molecules thus, that expanded molecules were rejected from the membrane passage. This solution may be filtered if a membrane with larger pore size was applied. Then lower concentration of PCE was tried if it was applicable to be used in this UF study.

From the variation of initial concentration of PCE, the presence of 50,000 ppm of PCE with the same composition of AMA and Span-20 could be filtered through the membrane pore. Thus the 50,000 ppm PCE was mixed with surfactants in palm oil and further used as a feed palm oil solution. A schematic diagram of ultrafiltration process was shown in Figure 4.6.

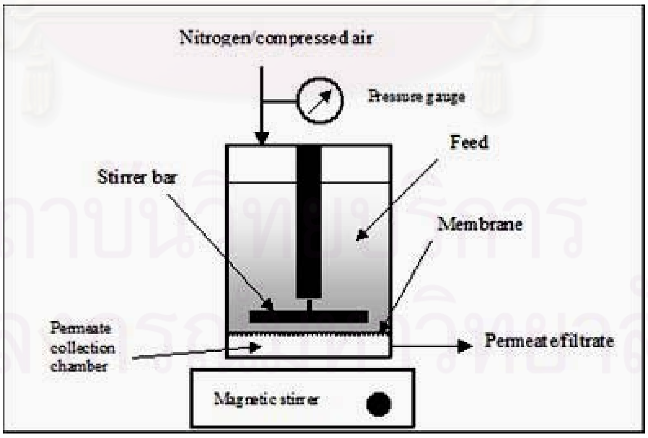


Figure 4.6 Schematic of stirred cell ultrafiltration (Singh et al., 2008)

4.4.2 Effect of applied pressure on PCE removal

The main purpose of this study was to concentrate surfactant reversed micelles into the retentate stream while passing PCE and palm oil into the permeate stream. A number of limitations and assumptions were applied here as follows: 1) the concentrations of surfactants in both streams (retentate and permeate) were not directly measured based on the concept that only surfactant monomer can pass through the membrane while the reverse micelles cannot, thus almost all surfactants retained in the retentate solution 2) the possibility of surfactant recovery was investigated based on how PCE removes from the retentate stream, thus the percentage of PCE removal from retentate implied the level of surfactant decontamination, 3) the ultrafiltration process was terminated when the volume of retentate was ¼ of original feed palm oil solution. The concentration of PCE in both the permeate stream and retentate were collected and analyzed by using GC and the percentage of PCE removal at that condition was evaluated. Because of the volatility of PCE as the contaminant used in this study, the short operational time of separation process was crucial.

The applied pressure of N_2 gas were varied at 30, 40, 50, and 60 psi in the UF cell. The percentage of PCE removal was evaluated as shown in the Table 4.5. Moreover, the material balance of PCE where the deviation of PCE mass less than ±12% was approved.

Table 4.5 The percentage of PCE removal at various applied pressures

Pressure (psi)	**Termination time (minute)**	**[PCE]$_{initial}$(1) (ppm)**	**[PCE]$_{permeate}$(2) (ppm)**	**[PCE]$_{retentate}$(3) (ppm)**	**% PCE Removal (4)**
30	32.5	73,655	62,799	71,002	76.0
40	26.1	63,230	64,322	57,126	77.6
50	19.2	72,573	72,787	66,276	77.2
60	25.2	70,157	63,051	68,472	75.7

(1) [PCE]$_{initial}$ was the initial PCE concentration in 2%AMA/1%span-20 in palm oil with the surfactant solution:solvent volumetric ratio of 40:1
(2) [PCE]$_{permeate}$ was PCE concentration in permeate stream
(3) [PCE]$_{retentate}$ was the remained PCE concentration in retentate stream
(4) %PCE removal was calculated from a subtraction between mass of PCE$_{initial}$ and PCE$_{aqueous}$ and divided by mass of PCE$_{initial}$ x 100

There was no significant change in %PCE removal upon altering applied pressure as illustrated in Table 4.5. Since more than 75% of PCE could separate from retentate into permeate phase for all applied pressures, while only 25% of PCE still remained in the retentate stream. Although the highest pressure utilized in this study (60 psi) which closed to the maximum allowable pressure for this Amicon stirred cell (70 psi), the performance of this separation process was the same as the lowest applied pressure (30 psi). This result was similarly to ones obtained by Molina et al. (2006). They found that the degree of separation of organic polymer from wastewater water by UF process was insensitive to pressure if applied at the relatively low pressures (1, 2 and 3 bar or 14.5, 29.0, and 43.5 psi, respectively). In addition, Nowak et al. (2006) found that no distinct relationship was observed between SDS (anionic surfactant) retention coefficient and applied pressure. A slight decrease in separation efficiency with increasing pressure difference was observed for the 10,000 and 30,000 MWCO membrane series, whereas for some of the 5,000

MWCO membrane series (PES5, PS5, and PA5), the opposite result was noticed. Therefore, the UF process was proven to be an effective way to retain reversed micelles in the retentate stream. However, the presence of PCE in the retentate was still high of about 25% of the initial PCE. To increase the potential of surfactant recovery or to lower the PCE concentration in the retentate, some possible suggestions are as follows: 1) the other extracting oil with high affinity to PCE might be possible to apply in this reverse micellar extraction to enhance the PCE removal in the ultrafiltration step. With solvent with higher affinity with PCE, PCE tends to dissolve strongly in that solvent. Thus, both PCE and solvent can be filtered through the porous membrane together. Therefore, if we decrease the volume of retentate left in the UF unit (by increasing the filtering time and passing more permeate stream), the remained PCE in the retentate was expected to be lower since the volume of solvent left in the retentate solution is less. Nevertheless, it should be noted that the new solvent has to be proven first that it is able to form reversed micelle or Winsor type II microemulsion with this surfactant system 2%AMA/1%Span-20/20%NaCl. 2) the multi-stage ultrafiltration process might also be a good choice for increasing extraction efficiency as usually done in the traditional water treatment if the level of decontamination is above that can be treated by conventional filtration alone (IRC, 2007). This invention comprised of feeding the contaminated solution to the first ultrafiltration stage where the feed is contacted with an ultrafiltration membrane thereby producing the first permeate and retentate. Then feeding this first permeate to the second ultrafiltration stage where the first permeate is contacted with an ultrafiltration membrane which is the same as the ultrafiltration membrane in the first ultrafiltration stage to recover the second permeate and retentate. The second permeate can be sent to subsequent ultrafiltration stages utilizing the same membrane with permeate from each such stage being used. Retentate from the different stages can be recycled to the feed of the previous upstage ultrafiltration stage or can be combined with the retentate streams from the various ultrafiltration stages (Feimer, and Desjardine, 1993).

4.5 Comparison between Liquid-Liquid Extraction and Reverse Micellar Extraction

The comparison of two extraction techniques which were liquid-liquid extraction and reverse micellar extraction on PCE removal from aqueous solution to solvent phase was investigated. The advantages and disadvantages of each extraction technique were determined. Furthermore, other parameters such as the complexity of technique, the cost effective, time consuming, the convenient of operation, the environmental friendliness of solvent used, the make up of new surfactant, and the need of downstream process were also included in the determination.

From the result of PCE removal of both techniques with the specific conditions were displayed in the Table 4.6. Using palm oil as an extracting solvent at the same surfactant solution:palm oil volumetric ratio ranged from 20:1-10:1, the reverse micellar extraction obviously showed the higher extraction efficiency, where 97.2-98.4% PCE removal was obtained as compared to 35.0-54.1% by liquid-liquid extraction. By considering at the same surfactant solution:palm oil volumetric ratio of 10:1 and same extracting solvent (palm oil), the %PCE removal by reverse micellar extraction (98.4%) was twice better than that by liquid-liquid extraction (54.1%).

However, the high efficiency of 83.0% PCE removal can also be achieved by the liquid-liquid extraction except the fact that a high surfactant solution:palm oil volumetric ratio of 1:1 was required. Thus, a lot of palm oil was spent reflecting the high solvent cost and the large volume of solvent (palm oil) contaminated by PCE was produced and needed to be further clean to remove PCE from the solvent.

Table 4.6 The percentage of PCE removal by liquid-liquid extraction and reverse micellar extraction

Extraction Technique	**Solvent Type**	**Surfactant solution:solvent volumetric ratio**	**% PCE Removal**
Liquid-Liquid Extraction	Palm oil (EACN 13)	1:1	83.0*
		5:1	63.3*
		10:1	54.1*
		20:1	35.0*
	Dodecane (ACN 12)	10:1	84.3*
	Sunflower oil (EACN 18)		67.6*
	Octadecane (ACN 18)		89.5*
	Squalane (ACN 30)		57.2*
Reverse Micellar Extraction	Palm oil (EACN 13)	10:1	98.4**
		20:1	97.2**
		40:1	96.7**

* calculated from the actual PCE concentration in aqueous and solvent phases
** calculated from the different between the initial and the remained PCE in aqueous solution

Moreover, the PCE removal by reverse micellar extraction using palm oil at the surfactant solution:solvent volumetric ratio of 40:1 was as high as 96.7%, which was better than that of the conventional liquid-liquid extraction with octadecane (the best extracting solvent in liquid-liquid extraction), where only 89.5% was achieved even at the surfactant solution:solvent volumetric ratio of 10:1 or used extracting solvent 4 times greater than in reverse micellar extraction. It means even the best performance of liquid-liquid extraction (at the best solvent: octadecane) still gave a lower percentage of PCE extraction. Thus, the extraction efficiency of the liquid-liquid extraction can be increase by selecting a suitable type of solvent to have a high affinity to PCE but caution on toxicity of solvents needed to be concerned.

Interestingly, the percentage of PCE removal by reverse micellar extraction was not effected from the surfactant solution:palm oil volumetric ratio, which PCE removal from aqueous into palm oil phase was more than 96% for all surfactant solution:palm oil volumetric ratio studied here (10:1, 20:1 and 40:1) Therefore, the highlighted advantage of reverse micellar extraction was the high extraction efficiency even at the rather less extracting solvent used (Cheng and Sabatini, 2001).

The operation time was another factor to determine the efficiency of extraction process. The shorter time is preferred. In this study, the equilibrium PCE partitioning occurred around 4 days for the liquid-liquid extraction and 1 day for the reverse micellar extraction. Thus, the reverse micellar extraction required much shorter time since the microemulsion occurs spontaneously. Hence, from this study, the reverse micellar extraction was a promising technique as shown by these advantages: the high %PCE removal, the environmentally safety of solvent used, required less volume of solvent, less time consuming, and the less volume of produced solvent phase that contaminated by PCE.

However, the complexity of surfactant preparation of Winsor type II microemulsion for reverse micellar extraction technique was a disadvantage along with a fact that an additional separation step is needed for surfactant separation from solvent and PCE. So, high cost may result from the complexity of that surfactant preparation and the downstream separation process. The difficulty in surfactant system preparation included 1) the addition of second surfactant, in this case, a nonionic surfactant (Span-20) for HLB adjustment, 2) the dilution process was needed since the original surfactant solution (4%AMA) could not form microemulsion with palm oil (dilute to 2%AMA would work well), 3) the electrolyte (NaCl) was essential to add to induce the microemulsion phase transition to Winsor type II microemulsion.

The additional separation process of PCE from surfactant (both exist together in solvent phase) was needed to fulfill the surfactant recovery purpose since without the decontamination of PCE from solvent, the surfactant was not ready to reuse. Unlike the liquid-liquid extraction, PCE partition out of surfactant aqueous solution to solvent phase, the surfactant was simultaneously decontaminated and ready to be used. The ultrafiltration stirred cell with small pore size (5,000 Da MWCO) regenerate cellulose membrane was used as the downstream surfactant purification step followed with reverse micellar extraction. The reversed micelles surfactant was retained in the stirred cell because the aggregate size is larger than the membrane pores opening, while PCE, palm oil (solvent) and monomer of surfactant could permeate through the pores as the permeate stream. The ultrafilter was general used in the separation purpose with low energy consumption and ease of operation (Scamehorn and Harwell, 2001).

Although PCE could separate from surfactant reversed micelles by the ultrafiltration unit to fulfill the surfactant recovery purpose, the generated PCE waste in palm oil collected as the permeate stream was still a problem. The decontamination process of PCE from palm oil was needed to solve the PCE contaminated waste and the palm oil without PCE could be reused again. The decontamination of PCE from permeate stream could be done by decreased pressure distillation or vacuum stripping process that widely applied for the volatile organic compound decontamination.

In summary, a trade-off process should be done by considering all involved advantages and disadvantages for extraction technique selection. Table 4.7 summarized the liquid-liquid extraction and the reverse micellar extraction.

Table 4.7 The comparison on various important parameters between two extraction techniques

Parameter	**Extraction Technique**	
	Liquid-liquid extraction	**Reverse micellar extraction**
%PCE removal	low	high
Amount of used solvent	high	low
Time consuming	long	short
The complexity	easy	complex
Downstream process for surfactant recovery	no	yes

Since Winsor type II microemulsion can be formed with some specific solvents and the optimal HLB surfactant system by the affinity between solvent and surfactant. Consequently, the application of reverse micellar extraction with the mixed contaminants could be possible. If the real contaminated site containing the mixed pollutants, the Winsor type I microemulsion has to be applied first to solubilized mixed pollutants into the surfactant micelles, where the main mechanism for solubilization of mixed pollutants is still the like dissolve like. The next step for surfactant recovery can be later on carried out by forcing the mixed pollutants and surfactant to move from aqueous phase into the solvent phase by forming the Winsor type II microemulsion. The HLB of surfactant and solvent has to be optimized to cause this transition from Winsor type I to type II. The free energy reduction during the phase transition causes the micelle to breakup, the mixed pollutants releases and partition into the solvent phase due to its affinity to that solvent. The surfactant also moves into the extracting solvent phase. However, in the environmental aspect, only one technique could not be solved the complex environmental problem but the integrated solutions should be applied to mitigate the problem.

Since the DNAPL normally sink at the bottom of aquifer by its high density, the SEAR technique was applied and various degree of clean-up was achieved depended on many factors. The physical and chemical properties of the contaminant (e.g., hydrophobicity, density, viscosity, and interfacial tension with water and solid matrix) are the primary factors that dictate the choice of surfactant solution used. Site conditions (e.g., heterogeneity of soil, hydraulic properties of an aquifer, groundwater geochemistry, and soil mineralogy) also affect the choice of surfactant applied as well as the solution delivery technique to reach the target DNAPL zone in subsurface.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research demonstrated the surfactant recovery by two techniques, which were a conventional liquid-liquid extraction; and a reverse micellar extraction coupled with ultrafiltration process. An aqueous surfactant solution contained 4%AMA/3%NaCl with solubilized 10,000 ppm PCE was imitated as the pumped solution from contaminated subsurface. This aqueous surfactant was used as the initial solution prior extracted by solvent in liquid-liquid extraction and reverse micellar extraction. The investigated parameters of liquid-liquid extraction included the EACNs and functional group of solvent and the surfactant solution:solvent volumetric ratio, which were expected to affect the percentage of PCE removal and the PCE partitioning coefficient.

From the results of liquid-liquid extraction study, the EACN of extracting solvent and the surfactant solution:solvent ratio were crucial parameters governing the removal of PCE from surfactant aqueous phase to solvent phase followed the rule thumb of ‘like dissolve like’. So the high EACN value of extracting solvent in the same homologous series showed the great potential for PCE removal in the following order; for alkanes; octadecane (ACN 18 with PCE removal of 89.5%) > dodecane (ACN 12 with PCE removal of 84.3%) > squalane (ACN 30 with PCE removal of 57.2%); for vegetable oils; sunflower (EACN 18 with PCE removal of 67.7%) > palm oil (EACN 13 with PCE removal of 54.1%). In overall, these results were in good agreement with the hydrophobicity of the extracting solvents, except for the fact that too high EACN value such as squalane (ACN 30) resulted in the less partitioning of PCE from aqueous surfactant solution because of it was too hydrophobic for hydrophilic molecule like PCE to dissolve. Final remark was EACN of solvents being a considerably good indication to predict the degree of liquid-liquid extraction only if the solvents are in the same homologous series and the affinity between solute and solvent are relatively strong. Otherwise, EACN alone cannot be used and other factors should be incorporated such as function group of extracting solvent.

On the other hand, the surfactant solution:solvent (palm oil) volumetric ratio also had an effect on the PCE removal and PCE partitioning. An increasing in the amount of solvent used can increase the extraction efficiency. While the reduction of volume of extracting oil reached a certain point, where the partitioning coefficient could not be improved since the volume of extracting oil was inadequate to induce the PCE partitioning into the oil phase. From this study, at the surfactant solution:palm oil volumetric ratio greater than 10:1, PCE could not partition into palm oil because a maximum capacity of palm oil for PCE partitioning was reached.

From the results of the reverse micellar extraction, palm oil (EACN 13) and dodecane (ACN 12) were used as the extracting solvents and the comparison on %surfactant removal was investigated. The based surfactant solution system (4%AMA/3%NaCl) could not form Winsor type II microemulsion with either palm oil or dodecane because of too high HLB of AMA. The Span-20 (nonionic surfactant) was used as the second surfactant to decrease the HLB of the system. From the result of phase behavior study, both 2%AMA/1%Span-20/20%NaCl and 1%AMA/1%Span-20/20%NaCl could form Winsor type II microemulsion with palm oil and yielded a high surfactant removal of 89.1% and 83.2%, respectively. In addition, 2%AMA/2%Span-20/9-15%NaCl could form Winsor type II microemulsion with dodecane and gave the surfactant removal of 85.5 - 88.6%.

However, it was observed that the Winsor type II microemulsion with dodecane required less salt concentration where only 9%NaCl was needed as compared to 20%NaCl needed if forming with palm oil. Therefore, surfactants were more favorably to dissolve in dodecane than in the palm oil thus, required less salt to decrease the HLB of the system. Comparison only %surfactant removal in both extracting solvent; palm oil and dodecane, palm oil was more promising because it provided higher %surfactant removal, being non-toxic, cheap and available in the market even it requires a higher salt concentration.

The effect of surfactant solution:solvent volumetric ratio (ranged from 5:1, 10:1, 20:1, and 40:1) was determined by means of the percentages of PCE and surfactant removal from aqueous into palm oil phase to find out the best surfactant solution:solvent volumetric ratio suited for this reverse micellar extraction with palm oil. From the study, there was no significant effect of surfactant solution:solvent volumetric ratio on the percentages of PCE and surfactant removal from aqueous phase into palm oil, where upto 85% of surfactants and 96% of PCE can migrate to oil phase. However, PCE and surfactant tended to behave in a similar fashion except PCE shows a little bit favorable to dissolve into oil phase rather than surfactants as shown by a slightly higher %PCE removal.

Ultrafiltration process was applied to concentrate reverse micelles into the retentate while passing PCE and palm oil into the permeate stream. A majority of surfactants in form of reverse micelles still retained in the retentate stream, where it was expected to be reused as an ultimate goal of this study. The effect of pressurized N_2 gas applied to the UF batch stirred cell on the percentage of PCE removal from the original surfactants solution to the permeate stream was investigated. The result showed that there was no significant change in %PCE removal upon altering applied pressure 30, 40, 50, and 60 psi. More than 75% of PCE could separate from retentate into permeate phase for all applied pressures, while only 25% of PCE still remained in the retentate stream. Therefore, the UF process was proven to be an effective way to retain reverse micelles in the retentate stream. However, the PCE concentration in the retentate was still high of about 25% of the initial PCE amount. Some further investigations may be carried out to improve the quality of retentate solution to have a higher purity than that obtained from this study.

The comparison on technique efficiency between liquid-liquid extraction and reverse micellar extraction was also investigated. The highlighted advantages of reverse micellar extraction were the high extraction efficiency even using small volume of the extracting solvent, thus receiving less volume of PCE waste production. Furthermore, the environmentally friendly solvent (palm oil) was successfully to be applied here with less consuming time.

However, the complexity of surfactant preparation of Winsor type II microemulsion for reverse micellar extraction technique was a disadvantage along with a fact that an additional separation step was needed for surfactant separation from solvent and PCE. The additional separation process of PCE from surfactant, which was in this case the UF unit, was needed to fulfill the surfactant recovery purpose since without the decontamination of PCE from solvent, the surfactant was not ready to be reused. So, high operational cost may result from the complexity of that surfactant preparation and the downstream separation process.

Unlike the liquid-liquid extraction, PCE partition from surfactant aqueous solution to solvent phase, the surfactant was simultaneously decontaminated and ready to be used. Thus, the extraction efficiency of the liquid-liquid extraction can be increased by selecting a suitable type of solvent to have a high affinity to PCE but caution on toxicity of solvents needed to be concerned. In summary, a trade-off decision process should be done by considering all involved advantages and disadvantages for extraction technique selection.

In term of environmental and economic concerns, it is important to recover the surfactant from the waste solutions for reuse. The recovery and recycling of surfactants from treated aqueous solutions not only reduces or eliminates the discharge of contaminated water into the environment but also reduces the overall cost of industrial processes. The separation and recovery of these surfactants from the waste streams is of particular importance in aqueous solutions containing surfactants as they can be a costly component of those solutions. Moreover in some cases, surfactant can have poisonous effects to aquatic livings if they present in sufficient quantities. It has been reported that some surfactants destroy the external mucus layers that protect the fish from bacteria and parasites. In addition, they can cause severe damage to the gills (Lenntech Water treatment & air purification, 1998).

5.2 Recommendations

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

1. This liquid-liquid extraction or reverse micellar extraction at an optimal extracting solvent and the surfactant solution:solvent volumetric ratio should be scaled up to investigate the feasibility study for PCE removal and surfactant recovery.

2. Due to an advantage of the reverse micellar extraction that required very little volume of extracting oil, it should be applied to extract and preconcentrate other kind of hazardous substances of environmental concerns.

3. For further applications of the reverse micellar extraction, another parameters such as temperature, additive addition such as electrolyte and alcohol should be investigated.

4. A wider range of vegetable oils, which are the environmentally friendly solvent, should be explored both for the liquid-liquid extraction and the reverse micellar extraction since they showed a potential to be used as the extracting solvent in this study.

5. The other common surfactant solutions (such as AOT, Dowfax, SDS and Tween, etc.) should be investigated to find out the possibility to formulate the Winsor type II microemulsion with vegetable oil for surfactant recovery purposes.

6. A multi-stage ultrafilter may be used after the reverse micellar extraction to separate surfactant reversed micelles from PCE and palm oil to obtain higher separation efficiency.

7. The used extracting solvent should be decontaminated in order to be reused again by a suitable process such as a distillation to separate the extracting solvent, the contaminant and surfactant based on the their boiling point difference.

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APPENDICES

APPENDIX A

Terms Notification

To investigate the extraction performance, these following terms are introduced.

(i) Percentage of PCE removal

$$\%\text{PCE removal} = \frac{(\text{mass of PCE}_{initial} - \text{mass of PCE}_{remained})}{\text{mass of PCE}_{initial}} \text{ x } 100$$

where mass PCE$_{initial}$ is the initial PCE mass in aqueous surfactant solution

mass PCE$_{remained}$ is the remained PCE mass in surfactant phase

(ii) PCE Partition Ratio

$$\text{PCE partition ratio} = \frac{[\text{PCE}]_{oil}}{[\text{PCE}]_{aqueous}}$$

where [PCE]$_{oil}$ is the concentration of PCE in extracting solvent phase

[PCE]$_{aqueous}$ is the concentration of PCE in surfactant aqueous phase

(iii) Percentage of surfactant removal

$$\%\text{Surfactant removal} = \frac{\text{mass of surfactant}_{initial} - \text{mass of surafctant}_{remained})}{\text{mass of surfactant}_{initial}} \text{ x } 100$$

where mass of surfactant$_{initial}$ is the initial surfactant mass in aqueous surfactant solution

mass of surfactant$_{remained}$ is the remained surfactant mass in aqueous phase

APPENDIX B

1. HLB Calculation (Davies' method)

Davies (1957) suggested a method based on calculating a value based on the chemical groups of the molecule. The advantage of this method is that it takes into account the effect of strongly and less strongly hydrophilic groups. The equation for HLB calculation is shown as following:

$$\mathbf{HLB = 7 + \sum(n_h * X_h) + \sum(n_l * X_l)} \qquad \textbf{(a)}$$

Where n is the amount of group, X is the HLB value, subscript h and l mean hydrophilic and lipophilic, respectively.

Table B-1 HLB value of hydrophilic group for Davies calculation

Hydrophilic Group	HLB
RCOOK (potassium salt of acid)	21.2
RCOONa (sodium salt of acid)	19.1
RCOOH (acid)	2.1
RSO_4Na (sodium salt of sulfate)	38.7
RSO_3H (sulfonic acid)	11.0
R(NR')R" (tertiary amine)	9.4
ROR' (ether)	1.3
ROH (alcohol)	1.9
R(CO)OR' (ester)	2.4
RCH_2R' (methylene link)	-0.475
SoOH (sorbitan ring alcohol)	0.5
RCH_2CH_2OR' (ethoxy link)	0.33
SoO(CO)R (sorbitan ring ester)	6.8

Lange,K.R. Surfactants: A Practical Handbook; HanserGardner Publications: Cincinnati, OH, 1999.

Table B-2 HLB value of lipophilic group for Davies calculation

Lipophilic Group	**HLB**
RCH_3 (methyl group)	-0.475
RCH=(CH)R' (ethylene link)	-0.475
R(CR')R" (branch in chain)	-0.475
$RCH_2CH(CH_3)OR'$ (propoxy link)	-0.15

Lange,K.R. Surfactants: A Practical Handbook; HanserGardner Publications: Cincinnati, OH, 1999.

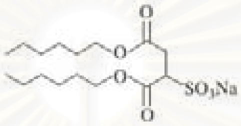


Figure B-1 The chemical structure of AMA

From the chemical structure of AMA, all HLB values of both hydrophilic and lipophilic group of AMA are calculated as equation (a)

$$HLB_{AMA} = 7 + 12*-0.475 + 2*2.4 + 2*-0.475 + 11$$
$$= 16.15$$

2. Total HLB of the mixture of surfactant

Theoretical HLB value for a given mixture of surfactants is given by equation (b) (ICI, 1992):

$$\mathbf{HLB_{mixture} = (HLB_{A})(\mathit{X}_{A}) + (HLB_{B})(\mathit{X}_{B})} \qquad \textbf{(b)}$$

Where X_A, and X_B are the weight fraction of every surfactant present in the mixture

Table B-3 HLB value of surfactant used in reverse micellar extraction

Solvent type	**Surfactant solution**	**HLB**	
		Calculation	**HLB value**
Reverse micellar extraction with palm oil	2%AMA + 1%Span-20	2/3(16.15) [a] + 1/3(8.6) [b]	13.63
	1%AMA + 1%Span-20	1/2(16.15) [a] + 1/2(8.6) [b]	12.38
Reverse micellar extraction with dodecane	2%AMA + 2%Span-20	2/4(16.15) [a] + 2/4(8.6) [b]	12.38

[a] HLB of AMA = 16.15 (calculated by Davies' method)

[b] HLB of Sapn-20 = 8.6 (http://www.dispersion.com/pages/newsletter/articles/Newsletter15a.pdf)

APPENDIX C

Table C-1 All surfactant formula formed Winsor type II microemulsion with the surfactant solution:dodecane volumetric ratio of 1:1 (in the absence of PCE)

Surfactant System	**$TOC_{initial}$ (1) (mg/L)**	**$TOC_{remained}$ (2) (mg/L)**	**%Surfactant removal (3)**
2%AMA + 1%AOT + 1%Span-20 + 9%NaCl	18,020	3,744	79.2
2%AMA + 2%Span-20 + 9%NaCl	23,658	3,375	85.7
2%AMA + 20%NaCl + 0.3%linker dodecanol	16,658	1,898	88.6
3%AMA + 20%NaCl + 0.3%linker Dodecanol	16,658	1,898	88.6
4%AMA + 25%NaCl + 0.3%linker Dodecanol	17,598	3,009	82.9
4%AMA + 25%NaCl	17,988	1,810	89.9

(1) $TOC_{initial}$ was total organic carbon of surfactant at initial surfactant

(2) TOC_{remain} was total organic carbon of remained surfactant in aqueous solution

(3) %Surfactant removal was calculated by the subtraction of $TOC_{initial}$ with $TOC_{remained}$ and divided by $TOC_{initial}$ x 100

Table C-2 (1) The preliminary study of various surfactant formula formed with the surfactant solution:palm oil volumetric ratio of 1:1 (in the absence of PCE)

Surfactant System	**$TOC_{initial}$ [1] (mg/L)**	**$TOC_{remained}$ [2] (mg/L)**	**%Surfactant removal [3]**	**Description**
4%AMA + 1%AOT +3%NaCl	23,740	25,380	-6.9	No surfactant removal
4%AMA + 2%AOT + 3%NaCl	28,420	29,675	-4.4	No surfactant removal
4%AMA + 3%AOT + 3%NaCl	34,048	33,138	2.7	No surfactant removal
4%AMA + 2%AOT + 2%NaCl	33,583	29,535	12.1	Insignificant surfactant removal
4%AMA + 2%AOT + 3%NaCl	34,535	28,658	17.0	Insignificant surfactant removal
4%AMA + 2%AOT + 4%NaCl	29,053	29,473	-1.4	No surfactant removal
4%AMA + 2%AOT + 5%NaCl	31,575	31,670	-0.3	No surfactant removal
4%AMA + 1%AOT +1%NaCl	23,533	25,615	-8.8	No surfactant removal
4%AMA + 1%AOT + 2%NaCl	23,533	24,945	-6.0	No surfactant removal
4%AMA + 1%AOT + 3%NaCl	23,533	24,278	-3.2	No surfactant removal
4%AMA + 1%AOT + 4%NaCl	23,533	25,038	-6.4	No surfactant removal
4%AMA + 1%AOT + 5%NaCl	23,533	24,803	-5.4	No surfactant removal
2%AMA + 2%AOT + 1%NaCl	19,783	16,623	16.0	Insignificant surfactant removal

(1) $TOC_{initial}$ was total organic carbon of surfactant at initial surfactant

(2) $TOC_{remained}$ was total organic carbon of remained surfactant in aqueous solution

(3) %Surfactant removal was calculated by the subtraction of $TOC_{initial}$ with $TOC_{remained}$ and divided by $TOC_{initial}$ x 100

Table C-2 (2) The preliminary study of various surfactant formula formed with the surfactant solution:palm oil volumetric ratio of 1:1 (in the absence of PCE)

Surfactant System	**TOC$_{initial}$ $^{(1)}$ (mg/L)**	**TOC$_{remained}$ $^{(2)}$ (mg/L)**	**%Surfactant removal $^{(3)}$**	**Description**
2%AMA + 2%AOT + 4%NaCl	19,783	18,848	4.7	No surfactant removal
2%AMA + 2%AOT + 3%NaCl	19,783	18,998	4.0	No surfactant removal
2%AMA + 1%AOT + 1%NaCl	17,078	16,278	4.7	No surfactant removal
2%AMA + 1% AOT + 2%NaCl	17,078	15,653	8.3	No surfactant removal
2%AMA + 1% AOT + 3%NaCl	17,078	16,230	5.0	No surfactant removal
2%AMA + 1%AOT + 4%NaCl	17,078	15,893	6.9	No surfactant removal
2%AMA+1%AOT + 5%NaCl	17,078	14,718	13.8	Insignificant surfactant removal
4%AMA+ 0.5%Span-20 + 3%NaCl	23,065	23,370	-1.3	No surfactant removal
4%AMA+ 1%Span-20 + 3%NaCl	26,608	27,548	-3.5	No surfactant removal
4%AMA+ 1.5%Span-20 + 3%NaCl	30,075	30,505	-1.4	No surfactant removal
4%AMA+ 2%Span-20 + 3%NaCl	31,960	32,590	-1.9	No surfactant removal
4%AMA+ 2.5%Span-20 + 3%NaCl	37,453	34,630	7.5	Insignificant surfactant removal
4%AMA+ 3%Span-20 + 3%NaCl	39,720	37,138	6.5	Insignificant surfactant removal

(1) TOC$_{initial}$ was total organic carbon of surfactant at initial surfactant

(2) TOC$_{remained}$ was total organic carbon of remained surfactant in aqueous solution

(3) %Surfactant removal was calculated by the subtraction of TOC$_{initial}$ with TOC$_{remained}$ and divided by TOC$_{initial}$ x 100

Table C-2 (3) The preliminary study of various surfactant formula formed with the surfactant solution:palm oil volumetric ratio of 1:1 (in the absence of PCE)

Surfactant System	**$TOC_{initial}$ (1) (mg/L)**	**$TOC_{remained}$(2) (mg/L)**	**%Surfactant removal (3)**	**Description**
1%AMA+ 1%Span-20 +2%NaCl	10,675	9,485	11.1	Insignificant surfactant removal
1%AMA+ 1%Span-20 +3%NaCl	10,675	7,123	33.2	Significant surfactant removal
1%AMA+ 1%Span-20 +4%NaCl	10,675	3,843	64.0	Significant surfactant removal
1%AMA+ 1%Span-20 +5%NaCl	-	-	-	Phase separation
1%AMA+ 1%Span-20 +6%NaCl	-	-	-	Phase separation
1%AMA+ 1%Span-20 +7%NaCl	-	-	-	Phase separation
1%AMA+ 1%Span-20 +8%NaCl	-	-	-	Phase separation
1%AMA+ 1%Span-20 +9%NaCl	-	-	-	Phase separation
1%AMA+ 1%Span-20 +10%NaCl	-	-	-	Phase separation
2%AMA+ 2%Span-20 +2%NaCl	-	-	-	Phase separation
2%AMA+ 2%Span-20 +3%NaCl	-	-	-	Phase separation
2%AMA+ 2%Span-20 +4%NaCl	-	-	-	Phase separation

(1) $TOC_{initial}$ was total organic carbon of surfactant at initial surfactant

(2) $TOC_{remained}$ was total organic carbon of remained surfactant in aqueous solution

(3) %Surfactant removal was calculated by the subtraction of $TOC_{initial}$ with $TOC_{remained}$ and divided by $TOC_{initial}$ x 100

Table C-(4) The preliminary study of various surfactant formula formed with the surfactant solution:palm oil volumetric ratio of 1:1 (in the absence of PCE)

Surfactant System	**$TOC_{initial}$ [(1)] (mg/L)**	**$TOC_{remained}$[(2)] (mg/L)**	**%Surfactant removal [(3)]**	**Description**
2%AMA+ 2%Span-20 +5%NaCl	-	-	-	Phase separation
2%AMA+ 2%Span-20 +6%NaCl	-	-	-	Phase separation
2%AMA+ 2%Span-20 +7%NaCl	-	-	-	Phase separation
2%AMA+ 2%Span-20 +8%NaCl	-	-	-	Phase separation
2%AMA+ 2%Span-20 +10%NaCl	-	-	-	Phase separation
3%AMA+ 3%Span-20 +1%NaCl	33,613	27,303	18.8	Insignificant surfactant removal
3%AMA+ 3%Span-20 +2%NaCl	33,613	28,125	16.3	Insignificant surfactant removal
3%AMA+ 3%Span-20 +3%NaCl	33,613	29,5955	11.9	Insignificant surfactant removal
3%AMA+ 3%Span-20 +5%NaCl	-	-	-	Phase separation
2%AMA + 2%Tergitol + 0.25%Dowfax + 5%NaCl	23,935	21,870	8.6	Insignificant surfactant removal
2%AMA + 1%Tergitol + 1%AOT + 5%NaCl	20,385	18,823	7.7	Insignificant surfactant removal
1%AMA + 2%Tergitol + 5%NaCl	15,663	14,935	4.6	Insignificant surfactant removal
1%AMA + 2%Tergitol + 0.5%Dowfax + 8%NaCl	21,190	20,333	4.0	Insignificant surfactant removal

(1) $TOC_{initial}$ was total organic carbon of surfactant at initial surfactant

(2) $TOC_{remained}$ was total organic carbon of remained surfactant in aqueous solution

(3) %Surfactant removal was calculated by the subtraction of $TOC_{initial}$ with $TOC_{remained}$ and divided by $TOC_{initial}$ x 100

Table C-(5) The preliminary study of various surfactant formula formed with the surfactant solution:palm oil volumetric ratio of 1:1 (in the absence of PCE)

Surfactant System	**$\text{TOC}_{\text{initial}}$ (1) (mg/L)**	**$\text{TOC}_{\text{remained}}$(2) (mg/L)**	**%Surfactant removal (3)**	**Description**
4%AMA + 2%Tergitol + 1%Dowfax + 5%NaCl	37,370	38,368	-2.7	Insignificant surfactant removal
4%AMA + 0.5%Span-20 + 5%NaCl	22,580	24,625	-9.1	Insignificant surfactant removal
0.5%AMA + 0.5%AOT + 1%Span-20 + 8%NaCl	-	-	-	Phase separation
0.5%AMA + 0.5%AOT + 1%Span-20 + 9%NaCl	-	-	-	Phase separation
0.5%AMA + 0.5%AOT + 1%Span-20 + 10%NaCl	-	-	-	Phase separation
0.5%AMA + 0.5%AOT + 1%Span-20 + 20%NaCl	-	-	-	Phase separation
1%AMA + 1%AOT + 13%NaCl	-	-	-	Phase separation
1%AMA + 1%AOT + 15%NaCl	-	-	-	Phase separation
1%AMA + 1%AOT + 20%NaCl	-	-	-	Phase separation
0.9%AMA + 0.1%AOT + 12%NaCl	-	-	-	Phase separation

(1) $\text{TOC}_{\text{initial}}$ was total organic carbon of surfactant at initial surfactant

(2) $\text{TOC}_{\text{remained}}$ was total organic carbon of remained surfactant in aqueous solution

(3) %Surfactant removal was calculated by the subtraction of $\text{TOC}_{\text{initial}}$ with $\text{TOC}_{\text{remained}}$ and divided by $\text{TOC}_{\text{initial}}$ x 100

Table C-(6) The preliminary study of various surfactant formula formed with the surfactant solution:palm oil volumetric ratio of 1:1 (in the presence of PCE)

Surfactant System	**TOC$_{initial}$ $^{(1)}$ (mg/L)**	**TOC$_{remained}$$^{(2)}$ (mg/L)**	**%Surfactant removal $^{(3)}$**	**Description**
0.8%AMA + 0.2%AOT + 1%Span-20+ 12%NaCl	-	-	-	Phase separation
0.8%AMA + 0.2%AOT + 1%Span-20+ 15%NaCl	-	-	-	Phase separation
0.8%AMA + 0.2%AOT + 1%Span-20+ 20%NaCl	-	-	-	Phase separation
1%AMA + 1%Span-20+ 13%NaCl	-	-	-	Phase separation
1%AMA + 1%Span-20+ 15%NaCl	9,363	1,924	79.5	Type II microemulsion
1%AMA + 1%Span-20+ 20%NaCl	9,363	1,572	83.2	Type II microemulsion
2%AMA + 1%Span-20+ 15%NaCl	15,585	1,845	88.2	Type II microemulsion
2%AMA + 1%Span-20+ 20%NaCl	15,585	1,693	89.14	Type II microemulsion
3%AMA + 1%Span-20+ 20%NaCl	-	-	-	Phase separation
4%AMA + 1%Span-20+ 20%NaCl	-	-	-	Phase separation

$^{(1)}$ TOC$_{initial}$ was total organic carbon of surfactant at initial surfactant

$^{(2)}$ TOC$_{remained}$ was total organic carbon of remained surfactant in aqueous solution

$^{(3)}$ %Surfactant removal was calculated by the subtraction of TOC$_{initial}$ with TOC$_{remained}$ and divided by TOC$_{initial}$ x 100

APPENDIX D

Table D-1 Standard curve of PCE in 4%AMA and 3%NaCl (for palm oil as extracting solvent)

GC condition: 140˚C hold 5 minutes, splitless mode (sampling size volume of 20µL)

PCE concentration (ppm)	Peak area (1)	Peak area (2)	Peak area (avg)	STDEV	%RSD
2,000	83,895	74,413	79,154	6,704.95	8.5
4,000	160,290	152,337	156,314	5,623.44	3.6
6,000	242,115	226,693	234,404	10.904.82	4.7

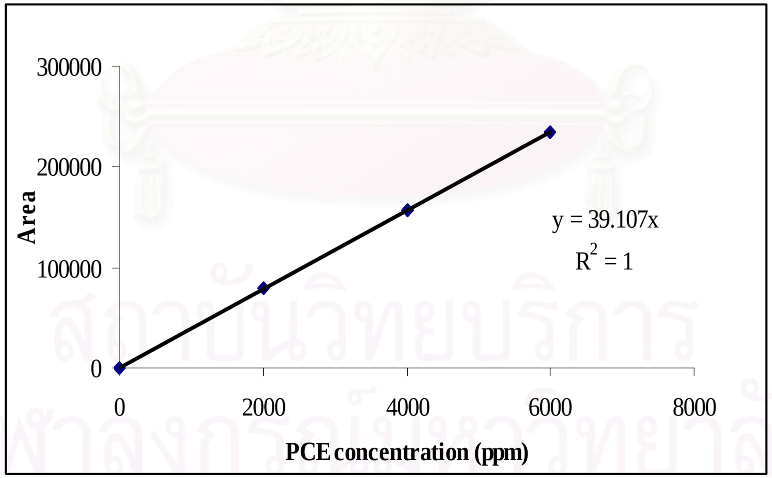


Table D-2 Standard curve of PCE in palm oil (for palm oil as extracting solvent)

GC condition: 140˚C hold 5 minutes, splitless mode (sampling size volume = 20µL)

PCE concentration (ppm)	Peak area (1)	Peak area (2)	Peak area (avg)	STDEV	%RSD
10,000	297,984	305,612	301,798	5,393.74	1.8
15,000	445,164	460,616	452,890	10,926.04	2.4
20,000	595,076	608,438	601,757	9,448.11	1.6

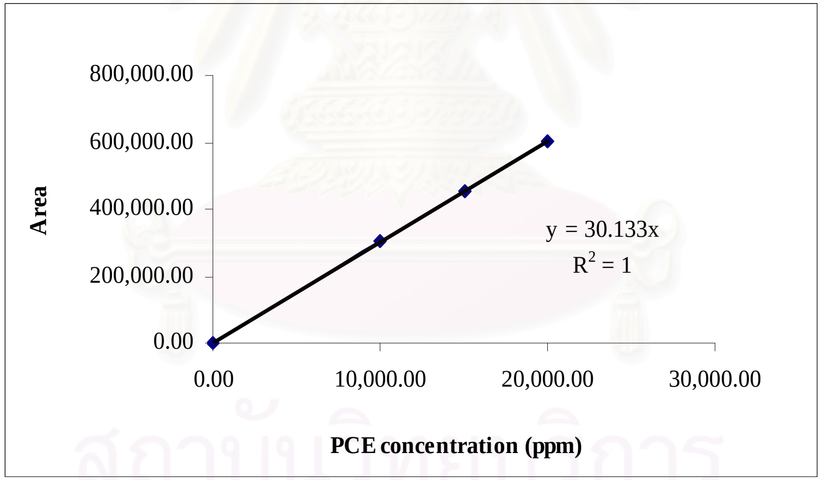


Table D-3 Standard curve of PCE in 4%AMA and 3%NaCl (for sunflower oil as extracting solvent)

GC condition: 140˚C hold 5 minutes, splitless mode (sampling size volume = 20µL)

PCE concentration (ppm)	**Peak area (1)**	**Peak area (2)**	**Peak area (avg)**	**STDEV**	**%RSD**
2,000	83,895	74,413	79,154	6,704.95	8.5
4,000	160,290	152,337	156,314	5,623.44	3.6
6,000	242,115	226,693	234,404	10.904.82	4.7

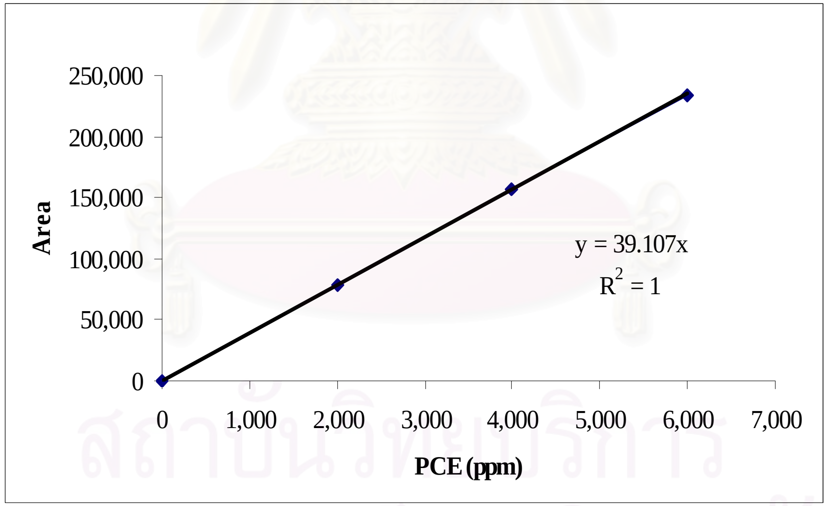


Table D-4 Standard curve of PCE in sunflower oil (for sunflower oil as extracting solvent)

GC condition: 140˚C hold 5 minutes, splitless mode (sampling size volume = 20µL)

PCE concentration (ppm)	Peak area (1)	Peak area (2)	Peak area (avg)	STDEV	%RSD
10,000	319,895	306,800	313,348	9,259.61	2.9
15,000	460,792	467,247	464,019	4,563.90	0.9
20,000	606,933	604,137	605,535	1,976.99	0.3

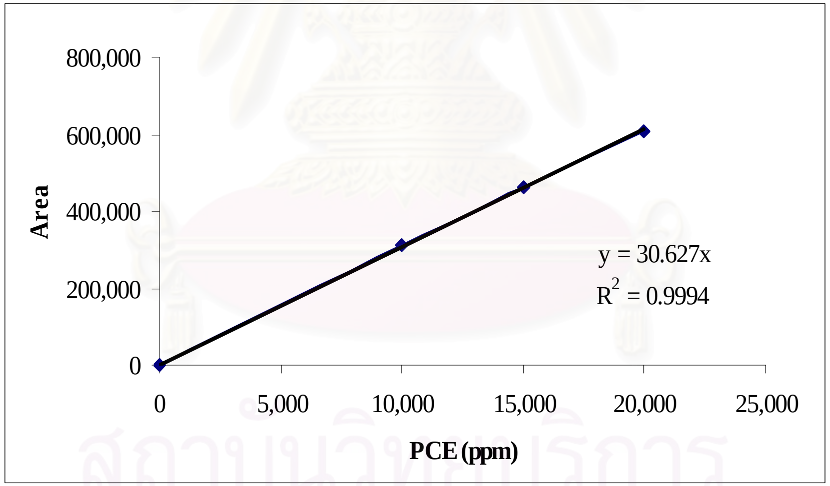


Table D-5 Standard curve of PCE in 4%AMA and 3%NaCl (for octadecane as extracting solvent)

GC condition: 140˚C hold 5 minutes, split ratio mode: 100:1 (sampling size volume = 20µL)

PCE concentration (ppm)	Peak area (1)	Peak area (2)	Peak area (avg)	STDEV	%RSD
1,000	26,985	27,607	27,296	439.73	1.6
2,000	59,492	57,622	58,557	1,322.77	2.3
3,000	84,651	81,781	84,331	6,173.33	7.3
4,000	107,046	99,609	103,328	5,258.38	5.1

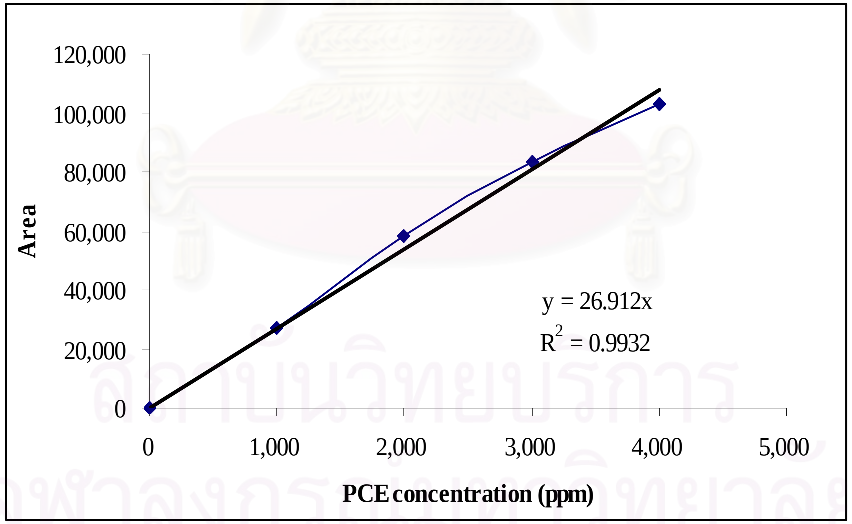


Table D-6 Standard curve of PCE in octadecane (for octadecane as extracting solvent)

GC condition: 140˚C hold 5 minutes, split ratio mode: 100:1 (sampling size volume = 20µL)

PCE concentration (ppm)	Peak area (1)	Peak area (2)	Peak area (avg)	STDEV	%RSD
20,000	392,081	391,366	391,724	505.40	0.1
40,000	841,866	852,644	847,255	7,620.86	0.9
60,000	1,271,864	1,280,989	1,276,426	6,452.17	0.5

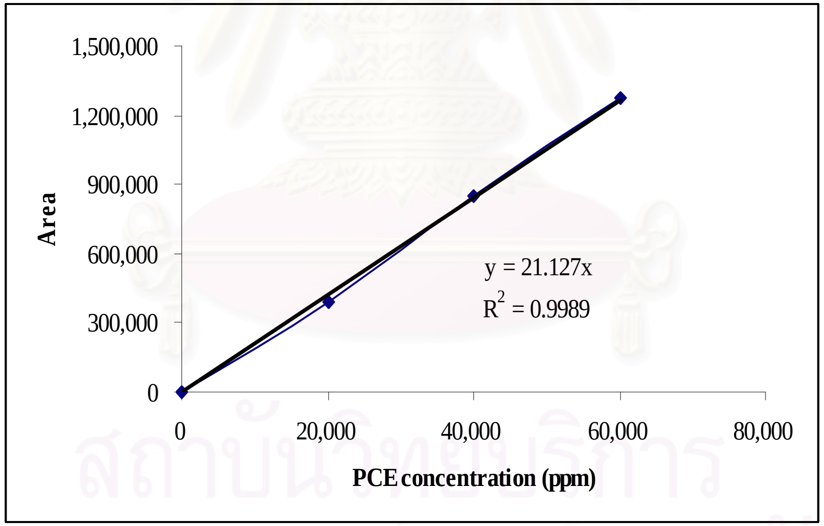


Table D-7 Standard curve of PCE in squalane (for squalane as extracting solvent)

GC condition: 140˚C hold 5 minutes, split ratio mode of 100:1 (sampling size volume = 20µL)

PCE concentration (ppm)	Peak area (1)	Peak area (2)	Peak area (avg)	STDEV	%RSD
20,000	534,631	527,711	531,171	4,892.86	0.9
40,000	1,054,509	1,004,893	1,029,701	35,083.75	3.4
60,000	1,445,023	1,475,163	1,460,093	21,311.82	1.5

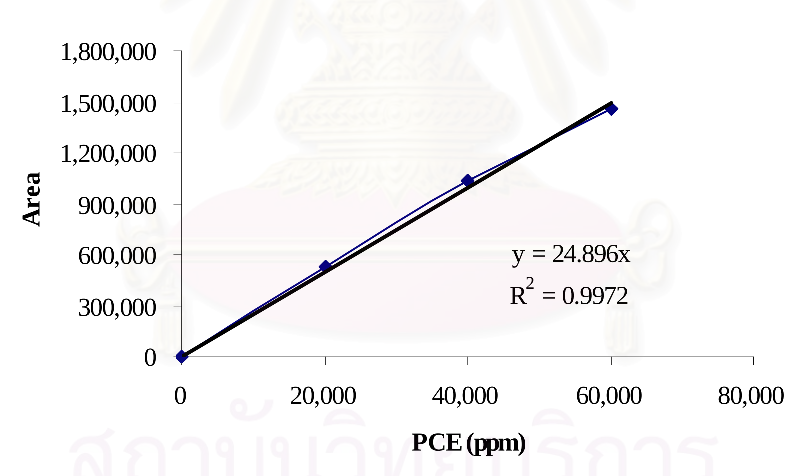


Table D-8 Standard curve of PCE in dodecane (for dodecane as extracting solvent)

GC condition: 140˚C hold 5 minutes, split ratio mode of 100:1 (sampling size volume = 20 µL)

PCE concentration (ppm)	Peak area (1)	Peak area (2)	Peak area (3)	Peak area (avg)	STDEV	%RSD
20,000	395,669	395,264	409,032	399,989	7,834.70	2.0
40,000	863,719	867,235	830,789	865,477	46,306.19	0.3
60,000	1,361,041	1,369,398	1,241,153	1,340,414	28,966.85	2.1

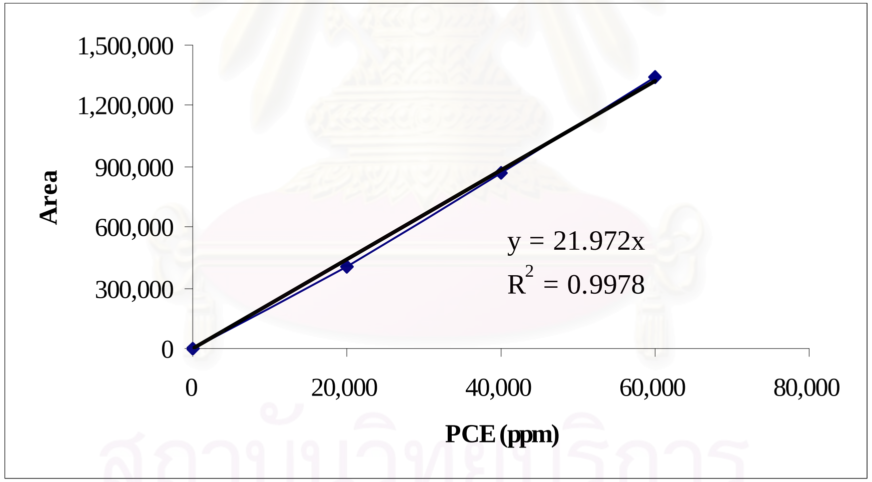


Table D-9 Standard curve of PCE in water (for palm oil as extracting solvent in reverse micellar extraction)

GC condition: 140˚C hold 5 minutes, splitless mode (sampling size volume = 20 µL)

PCE concentration (ppm)	Peak area (1)	Peak area (2)	Peak area (3)	Peak area (avg)	STDEV	%RSD
40	1,309	1,218	1,335	1,287	61.49	4.8
60	1,868	1,929	2,206	2,001	180.06	9.0
100	3,812	3,638	3,665	3,705	93.68	2.5

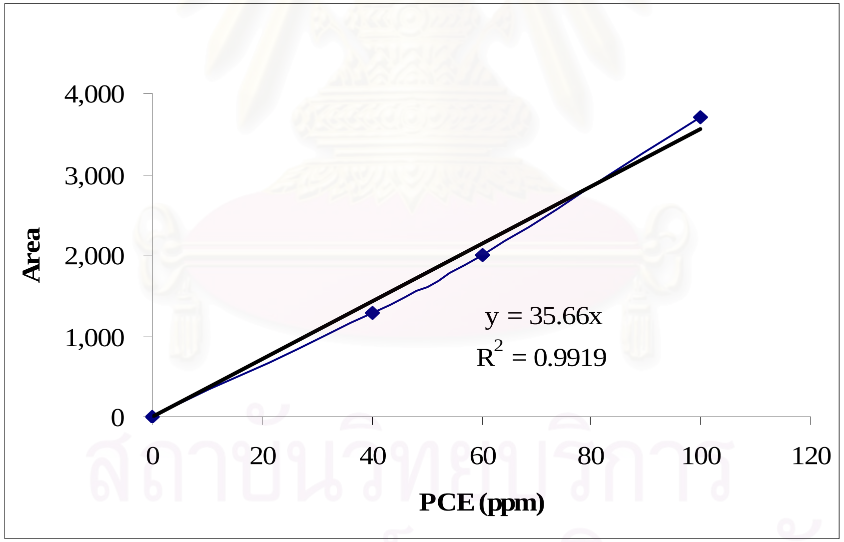


Table D-10 Standard curve of PCE in palm oil (for palm oil as extracting solvent Ratio 20:1 in reverse micellar extraction)

GC condition: 140˚C hold 5 minutes, split mode ratio of 400:1 (sampling size volume = 20 µL)

PCE concentration (ppm)	**Peak area (1)**	**Peak area (2)**	**Peak area (3)**	**Peak area (avg)**	**STDEV**	**%RSD**
20,000	360,562	352,634	351,565	354,920	4,915.0	1.4
50,000	794,910	464,748	-	794,909	-	-
100,000	1,308,844	1,406,676	1,078,226	1,357,760	69,177.7	5.1

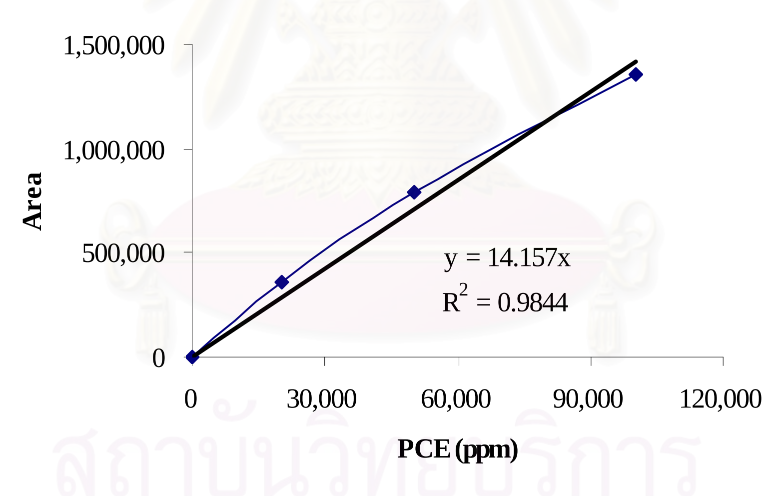
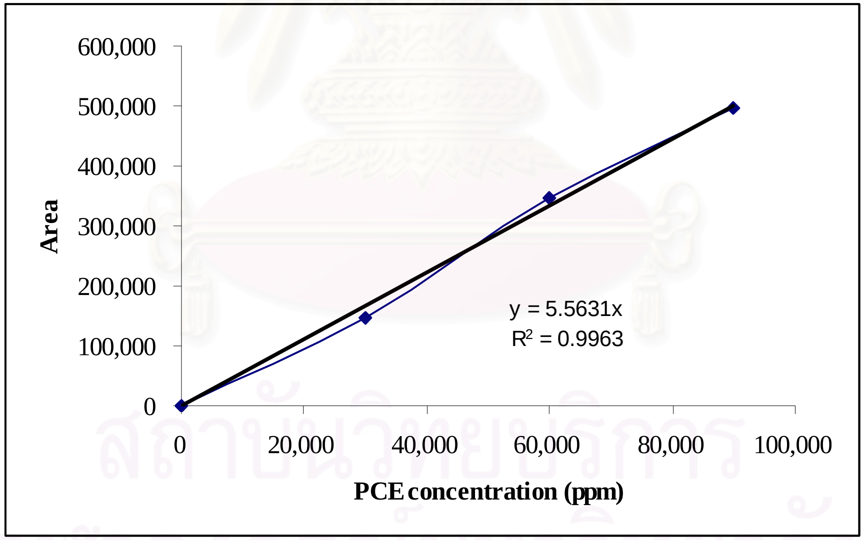


Table D-11 Standard curve of PCE in palm oil (Reverse micllar extraction Ratio 40:1, Ultrafiltration)

GC condition: 140˚C hold 5 minutes, split ratio mode of 400:1 (sampling size volume = 10 µL)

PCE concentration (ppm)	Peak area (1)	Peak area (2)	Peak area (3)	Peak area (avg)	STDEV	%RSD
30,000	118,333	118,293	148,125	148,125	27.8	0.02
60,000	341,567	346,646	353,322	347,179	5895.2	1.7
90,000	475,189	492,506	503,499	498,003	14,272.5	2.9



APPENDIX E

Table E-1 The %PCE removal by liquid-liquid extraction at the surfactant solution:palm oil at volumetric ratio ranged from 20:1-1:1

Surfactant solution: solvent ratio	**PCE**											
	PCE at initial				**PCE in surfactant aqueous solution**				**PCE in solvent (palm oil)**			
	peak area of PCE			**[PCE](1) (ppm)**	**peak area of PCE**			**[PCE](2) (ppm)**	**peak area of PCE**			**[PCE](3) (ppm)**
	1	**2**	**average**		**1**	**2**	**average**		**1**	**2**	**average**	
1:1	363,956	384,173	374,064	9,783	65,189	64,873	65,030	1,663	216,864	245,425	231,055	7,668
5:1	408,468	368,058	388,263	9,964	139,401	141,642	140,522	3,593	845,361	796,524	820,943	27,244
10:1	2,200,334	2,005,365	2,102,849	9,960	964,522	973,863	969,193	4,572	4,096,921	4,118,199	4,107,560	64,675
20:1	2,267,327	1,961,527	2,114,427	9,986	1,437,362	1,309,291	1,373,327	6,478	4,424,422	4,173,198	4,298,810	67,686

(1) [PCE] was the concentration of initial PCE in 4%AMA/3%NaCl solution

(2) [PCE] was the concentration of remained PCE in surfactant aqueous solution

(3) [PCE] was the concentration of partitioned PCE in palm oil

Table E-2 Summary of the percentage PCE removal by liquid-liquid extraction at the surfactant solution:palm oil volumetric ratio ranged from 20:1-1:1

Surfactant solution:Palm oil Ratio	**$[PCE]_{initial}$(1) (ppm)**	**$[PCE]_{remained}$(2) (ppm)**	**$[PCE]_{oil}$(3) (ppm)**	**% PCE removal(4)**	**$\frac{[PCE]_{oil}}{[PCE]_{remained}}$**	**% Mass balance(5)**
1:1	9,783	1,663	7,668	83.0	4.6	95.4
5:1	9,964	3,654	26,288	63.3	7.2	90.2
10:1	9,960	4,572	64,675	54.1	14.1	108.1
20:1	9,987	6,478	67,686	35.0	10.4	101.25

(1) $[PCE]_{initial}$ was concentration of the initial PCE in 4%AMA/3%NaCl solution

(2) $[PCE]_{remained}$ was concentration of the remained PCE in surfactant aqueous solution

(3) $[PCE]_{oil}$ was concentration of the partitioned PCE in extracting solvent (palm oil)

(4) %PCE removal was calculated from a subtraction between mass of $PCE_{initial}$ and $PCE_{remained}$ and divided by mass of $PCE_{initial}$ x 100

(5) % Mass balance of PCE was calculated from the subtraction of mass of $PCE_{initial}$ with (mass of $PCE_{remained}$ + mass of PCE_{oil}) and divided by mass of $PCE_{initial}$ x 100

Table E-3 The PCE distribution in liquid-liquid extraction with different solvent types at the surfactant solution:solvent volumetric ratio of 10:1

Solvent Type	PCE											
	PCE at initial				PCE in aqueous surfactant solution				PCE in solvent			
	peak area of PCE			[PCE](1) (ppm)	peak area of PCE			[PCE](2) (ppm)	peak area of PCE			[PCE](3) (ppm)
	1	2	average		1	2	average		1	2	average	
Palm oil	2,200,334	2,005,365	2,102,849	9,959.55	964,522	973,863	969,193	4,571.67	4,096,921	4,118,199	4,107,560	64,674.79
Dodecane	334,349	340,361	334,109	11,207	55,358	56,348	55,853	1,758.56	1,957,031	1,920,198	1,908,786	86,873.57
Sunflower oil	384,073	404,234	394,154	10,039.43	122,496	132,019	127,258	3,254	1,839,400	1,760,995	1,800,197	58,778.13
Octadecane	204,873	220,328	212,600	8,949.93	25,317	24,079	25,324.76	941.02	1,647,262	1,750,530	1,712,963	81,079.37
Squalane	289,043	280,743	283,315	10,263.75	124,563	121,864	122,309	3,805.87	1,287,668	1,308,068	1,293,697	50,978.24

(1) [PCE] was the concentration of initial PCE in 4%AMA/3%NaCl solution
(2) [PCE] was the concentration of remained PCE in surfactant aqueous solution
(3) [PCE] was the concentration of partitioned PCE in solvent

Table E-4 The summary of PCE removal by liquid-liquid extraction at the optimal surfactant solution:solvent volumetric ratio of 10:1

Solvent type	**$[PCE]_{initial}$(1) (ppm)**	**$[PCE]_{remained}$(2) (ppm)**	**$[PCE]_{oil}$(3) (ppm)**	**% PCE removal(4)**	**$\frac{[PCE]_{oil}}{[PCE]_{remained}}$**	**% Mass balance(5)**
Palm oil	9,959.6	4,571.7	64,674.8	54.1	14.1	108.1
Dodecane	11,263.7	1,758.6	86,873.6	57.2	49.4	93.6
Sunflower oil	10,039.4	3,254.1	58,778.1	67.6	18.1	91.0
Octadecane	8,949.9	941.0	81,079.4	89.5	86.2	101.5
Squalane	10,263.8	3,805.9	50,978.2	57.2	11.6	92.8

(1) $[PCE]_{initial}$ was concentration of the initial PCE in 4%AMA/3%NaCl solution

(2) $[PCE]_{remained}$ was concentration of the remained PCE in surfactant aqueous solution

(3) $[PCE]_{oil}$ was concentration of the partitioned PCE in extracting palm oil

(4) %PCE removal was calculated from a subtraction between mass of $PCE_{initial}$ and $PCE_{remained}$ and divided by mass of $PCE_{initial}$ x 100

(5) % Mass balance of PCE was calculated from the subtraction of mass of $PCE_{initial}$ with (mass of $PCE_{remained}$ + mass of PCE_{oil}) and divided by mass of $PCE_{initial}$ x 100

APPENDIX F

Table F-1 The % PCE removal by reverse micellar extraction with palm oil at the surfactant solution:solvent volumetric ratio of 20:1 to 10:1

Surfactant solution: palm oil ratio	**$[\mathrm{PCE}]_{\mathrm{initial}}$(1) (ppm)**	**PCE remaining in aqueous surfactant solution**				**$[\mathrm{PCE}]_{\mathrm{remained}}$(2) (ppm)**	**% PCE removal (3)**
		peak area of PCE					
		1	**2**	**3**	**average**		
10:1	9,909.5	4,953	5,009	5,332	5,097.9	142.9	98.6
		6,094	5,962	5,779	6,053.5	169.8	98.3
		4,384	5,193	4,513	4,617.2	129.5	98.7
20:1		8,466	8,312	8,757	8,511.7	236.7	97.6
		9328	9635	9,402	9,660.4	270.9	97.3
		8,367	8,573	7,873	8,270.9	228.9	97.7

(1) $[\mathrm{PCE}]_{\mathrm{initial}}$ was concentration of the initial PCE in 2%AMA/1%Span-20/20%NaCl solution

(2) $[\mathrm{PCE}]_{\mathrm{remained}}$ was concentration of the remained PCE in surfactant aqueous solution

(3) %PCE removal was calculated from a subtraction between mass of $\mathrm{PCE}_{\mathrm{initial}}$ and $\mathrm{PCE}_{\mathrm{remained}}$ and divided by mass of $\mathrm{PCE}_{\mathrm{initial}}$ x 100

Table F-2 The % PCE removal by reverse micellar extraction with palm oil at the surfactant solution:solvent volumetric ratio of 40:1

Surfactant solution: palm oil ratio	**$[PCE]_{initial}$(1) (ppm)**	**PCE remained in aqueous surfactant solution**				**$[PCE]_{remained}$(2) (ppm)**	**%PCE removal (3)**
		peak area of PCE					
		1	2	3	average		
40:1	9,909.5	15,336	14,904	14,968	15,069.3	415.2	95.8
		12,687	11,464	12,475	12,209.3	350.4	96.5
		11,147	13,206	-	12,176.3	341.5	96.6
		14,604	14,970	13,744	14,439.2	404.9	95.9

(1) $[PCE]_{initial}$ was concentration of the initial PCE in 2%AMA/1%Span-20/20%NaCl solution

(2) $[PCE]_{remained}$ was concentration of the remained PCE in surfactant aqueous solution

(3) %PCE removal was calculated from a subtraction between mass of $PCE_{initial}$ and $PCE_{remained}$ and divided by mass of $PCE_{initial}$ x 100

Table F-3 The % surfactant removal (only in term of TOC of surfactant) by reverse micellar extraction with palm oil at various surfactant solution:solvent volumetric ratio from 5:1 to 40:1

Surfactant solution: palm oil ratio	**TOC$_{initial}$(1) (ppm)**	**TOC$_{remained}$ (2) (ppm)**				**%Surfactant removal(3)**
		1	**2**	**3**	**average**	
5:1	12,146.9	1,467	1,561	1,548	1,525.0	87.4
		1,691	1,684	1,656	1,676.7	86.2
		1,774	1,570	1,425	1,589.3	86.9
10:1		1,522	1,647	1,588	1,585.3	86.9
		1,429	1,407	1,442	1,425.8	88.3
20:1		1,619	1,862	1,676	1,718.8	85.8
		1,711	1,802	1,731	1,747.7	85.6
40:1		1,736	1,773	1,631	1,713.0	85.9
		1,715	1,922	1,791	1,809.2	85.1

(1) TOC$_{initial}$ was total organic carbon of the initial surfactant solution (2%AMA/1%Span-20/20%NaCl)

(2) TOC$_{remained}$ was total organic carbon of the remained surfactant in aqueous solution

(3) %Surfactant removal was calculated by the subtraction of TOC$_{initial}$ with TOC$_{remained}$ and divided by TOC$_{initial}$ x 100

APPENDIX G

Table G-1 PCE concentration in permeate and retentate stream at varied applied pressure in UF

Applied pressure (N_2) (psi)	**PCE**														
	PCE at initial					**PCE in permeate stream**					**PCE in retentate stream**				
	peak area of PCE				**[PCE]$^{(1)}$ (ppm)**	**peak area of PCE**				**[PCE]$^{(2)}$ (ppm)**	**peak area of PCE**				**[PCE]$^{(3)}$ (ppm)**
	1	**2**	**3**	**average**		**1**	**2**	**3**	**average**		**1**	**2**	**3**	**average**	
30	433,091	456,956	475,905	455,318	81,846	368,308	381,769	-	375,905	67,415	389,312	479,891	178,510	434,602	78,122
	429,043	390,460	11,068	409,751	73,655	353,000	345,714	-	349,357	62,799	391,585	380,774	412,619	394,993	71,002
40	318,951	310,040	-	318,951	56,532	235,266	296,311	-	296,311	53,263	286,814	158,435	-	286,814	51,556
	386,569	411,557	368,935	389,020	69,928	395,356	430,662	432,041	419,353	75,381	427,779	354,143	343,432	348,787	62,969
50	393,916	413,548	307,974	403,732	72,573	405,127	409,201	400,448	404,925	72,787	28,944	368,701	135,400	368,701	66,276
60	411,732	418,457	-	415,095	74,615	359,599	343,830	390,561	364,663	65,550	417,834	408,708	469,028	431,857	77,628
	353,164	391,164	351,457	365,493	65,699	278,347	314,867	417,351	296,607	53,316	333,630	329,659	-	331,645	59,615

(1) $[PCE]_{initial}$ was the concentration of initial PCE in palm oil with reverse micelle surfactant (2%AMA/1%Span-20)

(2) $[PCE]_{permeate}$ was the PCE in permeate stream

(3) $[PCE]_{retentate}$ was the PCE remained in retentate stream

Table G-2 Summary of PCE removal by ultrafiltration effected by applied pressure

* The PCE with the same composition of surfactant (AMA+span) in palm oil with the surfactant solution:palm oil volumetric ratio of 40:1 was used as the based feed solution to UF.

** All feed palm oil samples were terminated until the retentate:permeate volumetric ratio was 1:3 (or 25mL:75 mL)

Pressure (psi)	**Termination time (min)**	**$[PCE]_{initial}$ (1) (ppm)**	**$[PCE]_{permeate}$ (2) (ppm)**	**$[PCE]_{retentate}$ (3) (ppm)**	**%PCE removal (4)**	**%Mass balance**
30	46.5	81,846	67,415.4	78,122.3	76.1	85.6
	32.5	73,655	62,799.1	71,002.4	75.9	88.0
40	26.1	56,532	53,263.7	51,556.5	77.5	92.2
	29.2	69,928	75,381.3	62,696.7	77.6	103.3
50	19.2	72,573	72,787.76	66,276.20	77.2	98.1
60	25.2	74,615	65,550.5	77,628.8	74.0	91.9
	25.1	65,699	53,316.96	59,615.2	77.3	91.8

(1) $[PCE]_{initial}$ was the concentration of initial PCE in palm oil with reverse micelle surfactant (2%AMA/1%Span-20)

(2) $[PCE]_{permeate}$ was the PCE in permeate stream

(3) $[PCE]_{retentate}$ was the PCE remained in retentate stream

(4) %PCE removal was calculated from a subtraction between mass of $PCE_{initial}$ and $PCE_{remained}$ and divided by mass of $PCE_{initial}$ x 100

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Proceeding:

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