APPLICATION OF THE SURFACTANT GRADIENT SYSTEM FOR OIL REMOVAL FROM SURFACES

Miss Salitta Pabute

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การประยุกต์ระบบเกรเดียนท์สารลดแรงตึงผิวเพื่อกำจัดคราบน้ำมันตกค้างบนพื้นผิว

นางสาว สลิตตา ปาบุตร

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สลิตตา ปาบุตร: การประยุกต์ระบบเกรเดียนท์สารลดแรงตึงผิวเพื่อกำจัดคราบน้ำมันตกค้างบนพื้นผิว (APPLICATION OF THE SURFACTANT GRADIENT SYSTEM FOR OIL REMOVAL FROM SURFACES) อ. ที่ปรึกษา: ดร. จันทรา ทองคำเภา, อ.ที่ปรึกษาร่วม: Prof. Dr. David A. Sabatini 99 หน้า ISBN 974-53-1703-9

การประยุกต์ระบบเกรเดียนท์สารลดแรงตึงผิวโดยใช้พื้นฐานความสัมพันธ์ระหว่างแรงตึงผิวและปริมาณสารที่ถูกกำจัด เพื่อเพิ่มการละลาย และลดการเคลื่อนที่ในแนวดิ่งของสารให้น้อยที่สุด งานวิจัยนี้มีวัตถุประสงค์เพื่อประยุกต์ระบบเกรเดียนท์สารลดแรงตึงผิวเพื่อกำจัดเตตระคลอโรเอทิลีนโดยเลือกระบบที่ปริมาณเกลือให้ค่าแรงตึงผิวที่เหมาะสมและศึกษาแบบต่อเนื่องในคอลัมน์ นอกจากนี้มีการประยุกต์ระบบนี้โดยปรับอุณหภูมิเพื่อกำจัดเดกเคนและเฮกซะเดกเคนจากพื้นผิวผ้าในกระบวนการซักผ้า จากการศึกษาพบว่าการปรับเปลี่ยนเกลือโดยใช้สารลดแรงตึงผิวผสมระหว่าง เอ ดี พี โอ ดี เอส และ เอ เอ็ม เอ สามารถเกิดระบบไมโครอิมัลชั่นที่เหมาะสมกับการกำจัดเตตระคลอโรเอทิลีนได้ ขณะที่อุณหภูมิที่เหมาะสมของระบบสารลดแรงตึงผิว $C_{12}EO_5$ เพื่อกำจัดเดกเคนและเฮกซะเดกเคนออกจากพื้นผิวผ้า คือ 30 และ 45 องศาเซลเซียส เมื่อศึกษาต่อในการศึกษาแบบต่อเนื่อง พบว่า ระบบเกรเดียนท์สารลดแรงตึงผิวสามารถกำจัดเตตระคลอโรเอทิลีนได้มากกว่า 99% และพบว่าการประยุกต์ระบบเกรเดียนท์เพื่อกำจัดเดกเคนและเฮกซะเดกเคนออกจากพื้นผิวผ้าโดยใช้การปรับอุณหภูมิให้ประสิทธิภาพการกำจัดสูงกว่าการกำจัดที่ไม่ใช้ระบบเกรเดียนท์ในน้ำมันชนิดเดกเคน มากกว่าในน้ำมันชนิดเฮกซะเดกเคน นอกจากนี้ การรวมกันของน้ำมันทั้งสองชนิดไม่ส่งผลต่อประสิทธิภาพการกำจัดน้ำมันออกจากผิวผ้า สรุปได้ว่าการประยุกต์ระบบเกรเดียนท์สามารถกำจัดเตตระคลอโรเอทิลีนได้โดยไม่เกิดการเคลื่อนที่ในแนวดิ่ง และการประยุกต์ระบบเกรเดียนท์โดยการปรับอุณหภูมิมีประสิทธิภาพในการกำจัดน้ำมันออกจากพื้นผิวผ้าโดยเฉพาะน้ำมันที่มีโครงสร้างสายสั้นในทั้งสองสภาวะ

สาขาวิชาการจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต……………………………….................

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ลายมือชื่ออาจารย์ที่ปรึกษาร่วม………………………...

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SALITTA PABUTE: APPLICATION OF THE SURFACTANT GRADIENT SYSTEM FOR OIL REMOVAL FROM SURFACES. THESIS ADVISOR: CHANTRA TONGCUMPOU, Ph.D. THESIS CO-ADVISOR: PROF. DAVID A. SABATINI, Ph.D. 99 PP. ISBN 974-53-1703-9

The gradient approach based on the relation between interfacial tension and oil removal was introduced to maximize the DNAPL solubilization while minimizing the potential for DNAPL vertical migration. The objective of this study was to apply the gradient system for PCE removal in a column with the selected surfactant system using electrolyte gradient. Moreover, this approach was carried out further in a washing study for decane and hexadecane removal from fabric substrate using temperature gradient. For this study, the result showed that the surfactant mixture of ADPODS and AMA were able to form microemulsion with PCE while optimum temperature to enhance decane and hexadecane removal from fabric with $C_{12}EO_5$ system are 30 and 45^{o}C, respectively. For further study, the PCE can be removed more than 99% using a surfactant gradient system. Moreover, the surfactant gradient application using temperature gradient shows the effectiveness of washing for decane removal more than washing for hexadecane removal. Furthermore, the combination of these two oils does not affect the oil removal efficiency. In conclusion, the application of surfactant gradient system has efficiency to remove PCE without mobilization and the surfactant gradient system by changing the temperature can effectively be used to remove oil from fabric surface especially in short chain alkane in both conditions.

Field of study: Environmental management	Student’s signature………………..
Academic year 2004	Advisor’s signature………………..
	Co-Advisor’s signature……………

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NOMENCLATURES

NAPLs = Nonaqueous phase liquids

DNAPLs = Dense nonaqueous phase liquids

LNAPLs = Light nonaqueous phase liquids

SEAR = Surfactant Enhance Aquifer Remediation

IFT = Interfacial Tension

CMC = Critical Micelle Concentration

HLB = Hydrophile-lipophile balance

$\gamma_{o/m}$ = Interfacial tension between the middle phase and excess oil

$\gamma_{w/m}$ = Interfacial tension between the middle phase and excess water

PIT = Phase Inversion Temperature

N.D. = indicates value not determined

N/A = indicates value cannot measured

C_{eq} = equilibrium concentration

$SP^{*\cdot}$ = solubilization parameter

ΔACN = range of alkane carbon number

d = a constant charateristic of the class of surfactant under consideration.

CHAPTER I

INTRODUCTION

1.1 Introduction

Subsurface contamination by chlorinated solvents and petroleum hydrocarbons is a growing environmental concern. Due to the leaking of chlorinated solvents and petroleum hydrocarbons, soil and groundwater become polluted. These contaminants are classified as nonaqueous phase liquids (NAPLs) because they are insoluble in water. NAPLs that have a lower density than that of water are called light nonaqueous phase liquids (LNAPLs) and those that are denser than water are termed dense nonaqueous phase liquids (DNAPLs). Conventional methods such as pump and treat remediation (water based flushing) have been commonly practiced to remediate NAPLs contamination. Bioremediation is another remediation method being introduced but it takes a long time to remediate completely and some of the chemicals resulting from this process may also be harmful (Russell, 1992). Pump and treat systems have proven ineffective and costly. Due to high interfacial tension and capillary force, oil droplets are trapped in porous media (Pennell et al., 1996). As a consequence, another method so called Surfactant Enhance Aquifer Remediation (SEAR) has been investigated and developed to enhance the extraction of residual oil saturation. SEAR can be used in three ways; (a) increasing contaminant mobility and solubility to improve pump and treat performance, (b) decreasing the mobility of contaminants to prevent their vertical migration, and (c) enhancing the rate of biodegradation of the contaminant in soil (Pennell et al., 1993 and 1996). Surfactants possess the ability to form micelles which increase the apparent solubility of the contaminant in water and reduce interfacial tension between water and NAPLs (Acosta et al., 2003; Sabatini et al., 2000; and Uchiyama et al., 2000). However, typical surfactant enhanced aquifer remediation, which is an effective method for the enhanced extraction of residual LNAPLs, may not be suitable for DNAPLs due to a problem of vertical migration. The potential for vertical migration of DNAPLs increases with decreasing interfacial tension (IFT) (Sabatini et al., 2000). The gradient approach is then introduced to maximize the DNAPLs solubilization while minimizing the potential for its mobilization. The gradient technique is based on the procedure in flushing surfactant solution at different salinity in order to provide different IFT between oil and the surfactant solution. From the change of IFT, the oil will be detached from subsurface and subsequently, be trapped in micelle (Childs et al., 2003). In this study, in order to verify the surfactant gradient approach for soil remediation in a column study, another substrate (e.g. fabric) was studied in comparison. The overall objective of this study was to apply the gradient approach for PCE removal from Ottawa sand in a column using a selected surfactant system with electrolyte gradient. Moreover, this approach was carried out further in a batch study for decane and hexadecane removal from fabric substrate. Temperature gradient was applied for the washing experiment.

1.2 Objectives

The main objective of this study was to remove oil from different surfaces using the gradient approach. The specific objectives were:

1. To apply the gradient approach for PCE removal in a column study with the selected surfactant system using an electrolyte gradient.
2. To apply the gradient approach for decane and hexadecane removal from fabric substrate in a batch study using the temperature gradient.

1.3 Hypotheses

1. A surfactant system with the electrolyte gradient can enhance the PCE solubilization and reduce the vertical migration.
2. A surfactant system applied with the temperature gradient can remove decane and hexadecane from fabric.

1.4 Scope of the study

This study was divided into two main parts; the phase behavior study, and the efficiency of gradient approach which included the column study, and the washing study. The phase behavior study aimed to select the best surfactant system for further use in the column and washing studies. PCE removal in a column study was investigated using an electrolyte gradient with the selected surfactant system. This latter experiment was applied the gradient approach for decane and hexadecane removal from fabric substrate in a batch study using the temperature gradient. Ottawa sand was used as medium in the column study, whereas blended polyester/cotton fabric was used as a substrate in the washing study.

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 Nonaqueous Phase Liquids (NAPLs)

Nonaqueous phase liquids (NAPLs) are immiscible hydrocarbons due to the physical and chemical property differences between water and liquid hydrocarbons. According to their densities, NAPLs can be divided into two classes; light nonaqueous phase liquids (LNAPLs) and dense nonaqueous phase liquids (DNAPLs).

2.1.1 Light Nonaqueous Phase Liquids (LNAPLs)

These are organic immiscible liquids with a density less than that of water, and typically include petroleum hydrocarbon compounds such as benzene, toluene, ethylene, xylene, decane, and hexadecane.

2.1.2.1 Sources

Petroleum hydrocarbons found in subsurface are contaminated from transport, distribution, and use of fuel and oil. Main sources of petroleum hydrocarbon contamination are underground or above ground storage tanks, tanker trucks, transfer terminals, pipelines, and refineries. Significant amounts of LNAPLs in subsurface media occur at locations with leaking underground storage tanks and around some petroleum refineries (Bedient et al., 1999, and National Research Council, 1997).

2.1.2.2 Fate and Transport

LNAPLs can be found in the subsurface in four phases: (1) sorbed to solids, (2) as NAPL, (3) dissolved in groundwater, and (4) as a vapor in unsaturated soil. The transport of contaminants through an aquifer depends on the presence of contaminants as nonaqueous phase liquids or in solution. Because of their lower density and low solubility, LNAPLs are typically found as NAPL phase or sorbed to solids. When LNAPLs leak into the subsurface, they accumulate in a soil layer above the water table. If the leaked hydrocarbons saturate the soil, free phase liquids are allowed to move and float to the top of the water table (National Research Council, 1997, and Sellers, 1998). A cross-section schematic of subsurface contamination by LNAPLs is shown as Figure 2.1.

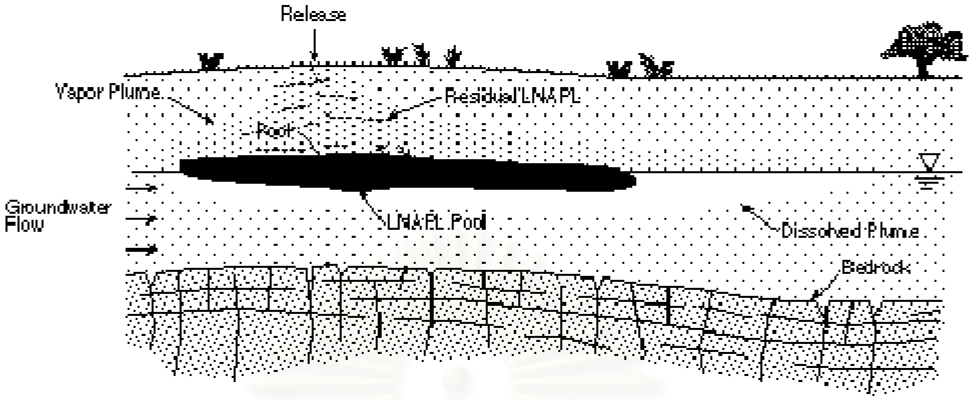


Figure 2.1 Subsurface contaminations by Light Nonaqueous Phase Liquids (United State Environmental Protection Agency, 2005).

2.1.2 Dense Nonaqueous Phase Liquids (DNAPLs)

DNAPLs are nonaqueous phase liquids with a density greater than that of water (e.g. chlorinated hydrocarbon).

2.1.2.1 Sources

There are a variety of industrial activities including chemical manufacturing, pesticide production garages, photographic shops, and dry cleaning which are associated with chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE). Chlorinated solvents can dissolve oily materials, have low flammability, and are stable both chemically and biologically. Due to these properties, they are used widely in industry as chemical carriers, solvents, paint removers, and cleaning solvents. Common uses of solvent in cleaning applications are in metal degreasing, circuit board cleaning and dry cleaning. Due to their wide use in industry, chlorinated solvents are the most common groundwater contaminants (Bedient et al. 1999, and National Research Council, 1997).

2.1.2.2 Fate and Transport

DNAPLs can enter the environment through use, leak, or disposal of neat liquids or through the disposal of wash and rinse water containing residual solvents. The dispersion and transportation of chlorinated solvents depend on the form of compounds. If they are released in dissolved form, hydrogeological processes will govern the chlorinated solvent migration. On the other hand, chlorinated solvents released in a neat liquid form will migrate downward through the soil under gravity. DNAPLs move across the water table and further into the saturated zone of the groundwater aquifer due to their much greater density relative to water. There are many problems arising from the release of chlorinated solvents to groundwater including gas phase solvent in the vadose zone, sorbed solvent and residual DNAPL both above and below the water table, and dissolve phase contamination occurring in both the shallow and deep levels of the aquifer (Bedient et al. 1999; and Charbeneau, 2000). Figure 2.2 illustrates the DNAPLs contamination in the subsurface.

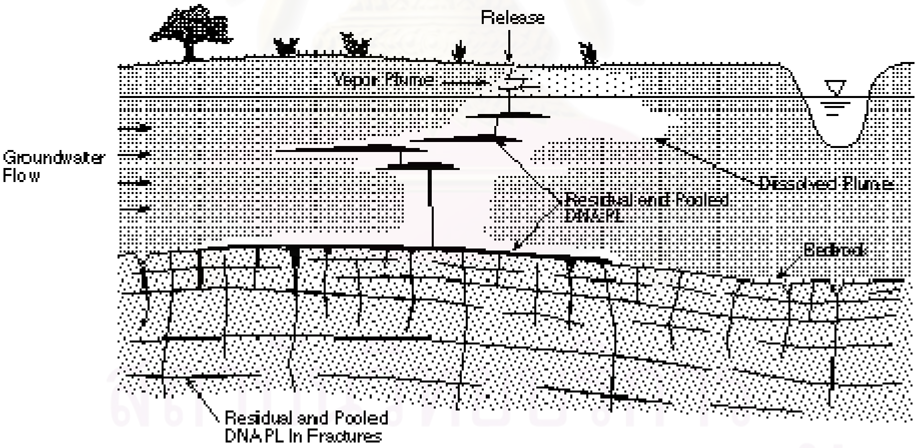


Figure 2.2 Subsurface contaminations by Dense Nonaqueous Phase Liquids (United State Environmental Protection Agency, 2005).

The maximum saturation level at which a NAPL comprises discontinuous blobs and ganglia in soil pores and fractures is explained by the term residual saturation. At residual saturation, NAPL is trapped in pore spaces by capillary forces while at saturation levels or saturated zone, the NAPL becomes a continuous mass and can flow through the soil as a separated phase. As a result, the separated phase of NAPLs flows through soil or rock causing as a long term source of dissolved contamination in groundwater. In the unsaturated zone, residual NAPL will dissolve in water infiltrating from the surface, whereas residual NAPL in the saturated zone will dissolve in flowing groundwater (Sellers, 1998).

NAPLs cause special problems in the characterization and remediation of hazardous waste sites DNAPLs in particular are a more severe problem than LNAPLs. In groundwater LNAPLs do not migrate vertically as DNAPLs thus they are easier to detect and remove (Sellers, 1998). As it is currently very difficult or impossible to remove all residual NAPLs trapped in substrate pores, NAPLs removal technologies need to be improved (Bedient et al. 1999).

2.2 Tetrachloroethylene

Tetrachloroethylene (C_2Cl_4) is one of the chlorinated hydrocarbons and is widely used for dry cleaning and metal degreasing. The other names for tetrachloroethylene are perchloroethylene, PCE, perc, perclene, and perchlor (Agency for Toxic Substances and Disease Registry, 2003a). Human are at risk of exposure to PCE because of its widespread use and distribution in the environment (Agency for Toxic Substances and Disease Registry, 2003a, and 2003b). PCE can affect humans by inhalation and when passing through skin causing skin irritation, burns, and the drying and cracking of the skin. PCE may also damage the liver, kidneys and central nervous system (New Jersey Department of Health and Senior Services, 2003). The International Agency for Research on Cancer (IARC) has found that PCE is probably carcinogenic to humans. In addition, very high levels of PCE exposure can be toxic to unborn pups of pregnant rats and mice. The maximum contaminant level of PCE in drinking water recommended by U.S. EPA is 0.005 ppm (Agency for Toxic Substances and Disease Registry, 2003a).

2.3 Decane

Decane is a petroleum hydrocarbon and a component of gasoline, jet fuel, kerosene and petroleum solvents used in the rubber industry, paper industry. Moreover, it is a constituent of polyolefin manufacturing wastes. The International Agency for Research on Cancer (IARC) has not evaluated the carcinogenicity of this chemical. However, it causes severe skin, eye, and respiratory tract irritation while prolonged exposure can cause narcotic effects and can affect the central nervous system. Moreover, it may react violently with strong oxidizing agents such as peroxides, nitrates and perchlorates increasing the risk of fire and explosion. For long term health effects, continued skin contact may cause dermatitis and hair loss. Decane has also been found to enhance the carcinogenicity of known carcinogens and has demonstrated tumor promoting activity when tested dermally in mice (Canadian Centre for Occupational Health & Safety, 2004, and Pohanish, 2004).

2.4 Hexadecane

Hexadecane is one of the petroleum hydrocarbons. Another name of hexadecane is cetane. Hexadecane is harmful or fatal if swallowed or inhaled. Inhalation of vapor may be irritating to the mucous membrane and the upper respiratory tract. Direct aspiration into the lung may cause chemical pneumonitis and lung damage. Moreover, it causes severe skin and eye irritation and prolonged exposure can have narcotic effects. In addition, it is incompatible with oxidizing agents (Mallinckrodt Baker, Inc., 2004c).

2.5 Surfactants

Surfactants, surface active agents, are molecules that have an amphiphilic nature because they comprise oil-like (non-polar or hydrophobic) and water-like (polar or hydrophilic) moieties. As a result, when surfactants are placed in a water-oil system, hydrophobic moieties will accumulate in a non-polar phase (oil phase) while hydrophilic moieties will accumulate in a polar phase (water phase). In this case, both moieties of surfactants are in a preferred phase and the free energy of the system is minimized (Rosen, 2004). The interfacial free energy per unit area represents the amount of work required to expand the interface often used in the term interfacial tension (Holmberg et al., 2003).

The hydrophobic part of surfactant may be branched or linear and is normally a hydrocarbon. At one end of the alkyl chain, the polar head group is usually attached. As a result, the degree of chain branching, the position of the polar head group and the length of the chain are important parameters for defining the physicochemical properties of the surfactant (Holmberg et al., 2003). Due to the hydrophilic group, surfactants can be classified as anionic, cationic, nonionic and zwitterionic (Holmberg et al., 2003, Rosen, 2004).

2.5.1 Anionic Surfactants

The surface active portion of the molecule is a negatively charged. Carboxylate, sulfate, sulfonate and phosphate are the polar groups of anionic surfactants. Anionic surfactants are the largest surfactant class. They are favorable because of their low cost of manufacture. They are used in most detergent formulations. Moreover, the alkyl chain in the C12-C18 range serves as the best detergency. They are generally incompatible with cationics.

2.5.2 Cationic Surfactants

The surface active charge of the molecule is a positively charged. The polar head groups found in cationic surfactants are both amine and quaternary ammonia based products. Cationic surfactants are the third largest surfactant class. They are also incompatible with anionic surfactants. Their main uses are related to in situ surface modification because they adsorb strongly to most surfaces.

2.5.3 Nonionic Surfactants

The surface active charge of the molecule is no ionic charged. A polyether consisting of oxyethylene units made by the polymerization of ethylene oxide are usually the polar groups of nonionic surfactants. They are the second largest surfactant class and are normally compatible with all other types of surfactants. The physicochemical properties of ethoxylated compounds are very temperature sensitive because their solubility increases with temperature. In contrast, ionic surfactants are less water soluble and more hydrophobic, at high temperature.

2.5.4 Zwitterionic Surfactants

The surface active charge of the molecule contains both negatively and positively charged. The positive charge is almost invariably ammonia, while a carboxylate group is the most common form of the negative charge. Due to their high price, they are the smallest surfactant class. This surfactant type is compatible with all other classes of surfactants. They are well suited for use in shampoos and other personal care products because of their very low eye and skin irritation.

The surfactant molecules or surfactant monomers have ability to self-assemble into dynamic aggregates known as micelles. Micelle formation occurs with increasing surfactant concentrations until critical micelle concentration (CMC). Micelles are highly soluble in water because of their polar exterior, while their non-polar interior provides a hydrophobic sink for organic compounds, thus increasing its organic compound solubility. Contaminant solubility and extraction efficiently is maximized when the surfactant concentration is above the CMC. On the other hand, minimal effect on enhanced contaminant solubility is produced when adding surfactant concentrations near or only slightly above the CMC (Sabatini et al., 1995 and 2000).

2.6 Solubilization

One important phenomenon for surfactant solution is solubilization. Solubilization explains the spontaneous dissolving of a substance by changing interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material. Solubilization produces the ultralow interfacial tension required for oil mobilization in enhanced oil recovery. The location that solubilization occurs depends on the nature of the solubilizate and the type of interaction between the solubilizate and surfactant Solubilization can occur at different sites in the micelle as follows;

a. On the surface of the micelle or at the micelle-solvent interface

b. Between the hydrophilic head group

c. In the palisade layer of the micelle between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups

d. More deeply in the palisade layer
e. In the inner core of the micelle

Surfactants are used to reduce IFT between the oil and water phase and to increase oil solubilization within the surfactant micelles as an emulsion (Rosen, 2004).

There are many factors affecting solubilization;

1) Structure of Surfactants

Any factors causing an increase in either the diameter of the micelle or its aggregation number can be expected to produce an increase in the solubilization capacity. For example, an increase of chain length of hydrophobic part causes an increase in the solubilization capacity of hydrocarbon.

2) Structure of Solubilizate

For aliphatic compounds, the solubilization capacity is decreased with an increase in chain length. An increase in molecular size of aromatic hydrocarbons leads to a decrease in the solubilization capacity.

While for polar solubilizates, the more polarity, the more solubilized. Polar compounds are solubilized close to the micelle water interface; they should be solubilized to a greater extent than non polar solubilizates that are located in the inner core.

3) Effect of Electrolyte

The addition of a neutral electrolyte to an ionic surfactant solution decreases the repulsion between similarly charged ionic surfactant head groups, thereby decreasing the CMC and increasing the aggregation number. As a result, hydrocarbon solubilization in micelle is increased.

4) Effect of Temperature

For ionic surfactants, an increase in solubilization for both polar and non polar solubilizates is a result of increasing temperature. Thermal agitation increases the space available for solubilization in the micelle. For nonionic surfactants, aliphatic compound solubilization increases with temperature. In the same manner, polar solubilizates, their solubilization increase with temperature. This is because an increase in temperature results to dehydration and a tighter coiling of the polyoxyethylene chains, subsequently decrease the space available in the palisade layer.

2.7 Microemulsions

Microemulsions are thermodynamically stable with homogeneous mixtures of oil, water and surfactant and small aggregates (~10-100 nm). However, the addition of salt or a second surfactant, or a cosurfactant, such as a medium chain alcohol is often required to lead the formation of microemulsion. This system can be divided into three types, which are known as Winsor Type I, III and II microemulsion (Rosen, 2004).

The phase transition of microemulsion is related to hydrophile-lipophile balance (HLB). HLB is a parameter that shows the partitioning of surfactants between oil and water phases relative to surfactant hydrophilicity. The transition of microemulsions and decreasing of HLB for ionic surfactants is induced by increasing salinity, while for nonionic surfactants the transition occurs by raising the temperature of the system (Holmberg et al., 2003). Figure 2.3 shows the relationship between the type of microemulsion and interfacial tension. On the left hand side, Winsor Type I microemulsion is shown. The interfacial tension between oil and water decreases with increasing salinity for ionic surfactant systems and with increasing temperature for nonionic surfactant systems making oil solubilized in micelles. It shows oil in water microemulsion (o/w) equilibrating with an excess oil phase. The middle phase or Winsor Type III microemulsion is formed when the microemulsion structure becomes bicontinuous in equilibrium with excess water and excess oil phases. With continual decreases in salinity or temperature, the interfacial tension between the middle phase and excess oil ($\gamma_{o/m}$) equals the interfacial tension between the middle phase and excess water ($\gamma_{w/m}$) and is known as the lowest interfacial tension or the optimum salinity and phase inversion temperature or PIT. If the salinity or temperature is increased further, the interfacial tension between oil and water will increase, making water solubilized in reverse micells. This is called Winsor type II microemulsion (Rosen, 2004). With these properties of low IFT and high solubilization, microemulsions are considered as an effective mean to enhance oil remediation (Holmberg et al., 2003).

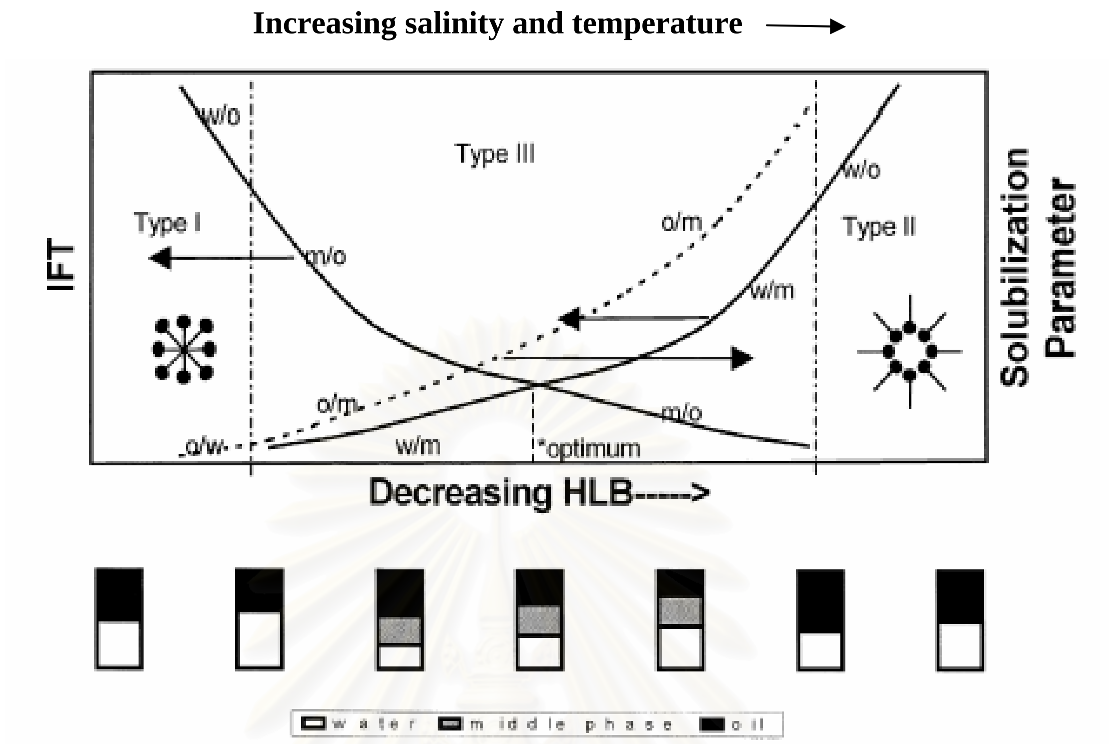


Figure 2.3 Relationship between microemulsion system and interfacial tension of salinity and temperature scan and HLB value (Sabatini et al., 2000).

2.8 Application of Surfactants for Oil Removal

Surfactant enhanced aquifer remediation (SEAR) is a technique that uses surfactants to remediate subsurface contamination; such as those by chlorinated solvents and petroleum hydrocarbons. This enhancement is due to a reduction of IFT and a maximizing of oil solubilization. The SEAR can be used in three ways; (a) increasing contaminant mobility and solubility to improve pump and treat performance, (b) decreasing the mobility of contaminants to prevent its vertical migration, and (c) to speed the rate of biodegradation of the contaminant in soil (Pennell et al., 1993 and 1996). Surfactant enhanced aquifer remediation is categorized into two systems; solubilization and mobilization. Solubilization occurs from contaminant partitioning into the oil-like core of the surfactant micelles. Mobilization is the displacement of oil from trapped residual oil resulting from a reduction of interfacial tension between NAPLs and water phases (Bedient et al., 1999). There have been many research studies on oil removal using surfactants.

Pennell et al. (1994) studied the ability of surfactant solution to remediate PCE entrapped in an Ottawa sand column. 90% and 97% of residual PCE was removed from 20-30 and 40-120 mesh Ottawa sand when a 4% solution of polyoxyethylene (POE) was injected into the column. In another experiment, the addition of sodium sulfosuccinate was shown to remove >99% of the residual PCE from a 40-270 mesh Ottawa sand column. Moreover, 80% of the PCE was mobilized as a separate phase after flushing with <100 mL of these surfactant solutions. They concluded that PCE mobilization lead to extend the area of NAPL contamination into fine textured media or uncontaminated area.

Dwaraknath et al. (1999) studied the remediation of soil columns contaminated by NAPLs with an anionic surfactant. Tetrachloethylene (PCE), trichloroethylene (TCE) and jet fuel were studied as contaminants in the subsurface. The surfactant system was first screened by phase behavior experiments and only the best one was selected for use in the column study. The results showed that up to 99.9% of the contaminants were removed as a result of surfactant flooding of the soil columns.

Shiau et al. (2000) studied the removal of a chlorinated solvent from a soil column using food grade surfactants. Noninoic sorbitan polyethoxylate monosterate was used for the solubilization experiments and bis-2-ethylhexyl sodium sulfosuccinate and sodium mono- and dimethyl naphthalene sulfonate were used in the mobilization experiments. Surfactant enhanced mobilization was more efficient than solubilization for removing PCE. They concluded that the performance of surfactant flushing depended on many factors including the type of microemulsion, temperature and type of contaminant.

2.9 Application of Surfactant Gradient System

Even though the SEAR technique effectively reduce interfacial tension between oil and water phase, the use of this system must also consider vertical migration of DNAPLs and the system must be controlled to achieve maximum removal at lowest cost (Acosta et al., 2002; and Uchiyama et al., 2000).

Sabatini et al. (2000) identified that solubility enhancement, interfacial tension, viscosity and density of selected surfactant systems were important variables affecting remediation. Thus a surfactant gradient system was introduced to increase the solubilization potential while minimizing the mobilization of trapped oil.

The gradient approach based on the concept of maximizing contaminant solubility while minimizing contaminant mobility by adjusting the surfactant formulation (Sabatini et al., 2000). As a consequence, the problem of mobilization of DNAPLs can be reduced. This means that surfactant systems can be formulated to obtain maximum solubilization of oil in a surfactant solution without a middle phase formation. This phenomenon is believed to be occurred in the supersolubilization region. The supersolubilization region is a system operated near a type I/type III microemulsion boundary (Childs et al., 2004).

In 2004, Childs et al. developed a surfactant gradient approach to enhance DNAPLs remediation. They used an electrolyte gradient to maximize the PCE solubilization while minimizing the potential for PCE mobilization. Column experiments were studied with selected surfactant systems from the phase behavior study. The additional gradient step with initial IFT above 1 mN/m can dramatically reduce the amount of PCE that mobilize. They suggested that this approach can be effectively used to improve the efficiency of surfactant enhanced DNAPL remediation.

In addition, Tongcumpou et al. (2003) studied the comparison of IFT between the supersolubilization region and Winsor type III microemulsion for detergency application. They found that the supersolubilization region provides oil solubilization and water/oil IFT which are almost as good as the optimum condition in a middle phase system.

2.10 Application of Surfactants for Detergency

The removal of oil from different substrates such as fabric by microemulsion formation involves interfacial interaction as well as other mechanisms. In the soil remediation process, solubilization or mobilization are the important mechanisms, while in fabric detergency, roll-up, emulsification, and solubilization play important roles for oily soil removal. Roll-up mechanism is related to surfactant and fabric interaction. When the contact angle is more than 90^o, oily soil can be released effectively. This usually occurs for oily soil removal from polar fabric such as cotton. On the other hand, the contact angle is less than 90^o and the interfacial tension reduction is so small when oily soil is removed polyester or other non polar fabric substrates. This situation is known as the snap-off mechanism, or emulsification-solubilization. However, with either roll-up or snap-off mechanisms in the detergency process or solubilization in soil remediation, interfacial tension is the key parameter involved (Holmberg, 2003).

There are many research studies on the effect of temperature or phase inversion temperature (PIT) on phase behavior and detergency experiments. Thompson (1994) studied the detergency of oil from fabric by the washing process. Nonionic surfactant; n-dodecyl pentaethylene glycol ($C_{12}EO_5$), anionic surfactant; sodium hexadecyl o-xylene sulfonate and a mixture of sodium dodecyl sulfate/$C_{12}EO_3$ were used to remove hexadecane, triolein, squalene and decane from fabric. Interfacial tension was found to be varied with temperature change. As a result, oil removal from fabric using $C_{12}EO_5$ was shown to be temperature dependent.

The effect of temperature on the phase behavior of ionic-nonionic microemulsion was studied by Aramaki, Ozawa and Kunieda (1997). They studied the microemulsion system formed in salt/sodium dodecyl sulfate/polyoxyethylene dodecyl ether ($C_{12}EO_2$ or $C_{12}EO_3$)/decane over a wide range of temperature. The results show that the declination of hydrophilicity of nonionic surfactants occurred with increasing temperature. Moreover, the $C_{12}EO_3$ system was a temperature insensitive microemulsion system.

In 1998, Goel studied the detergency of oily soil from blended polyester/cotton fabrics using alcohol ethoxylate surfactant with PIT. Hexadecane was used as an oily soil. He found that maximal detergency occurred as a function of washing temperature at approximately 35, 62 and 80^{o}C for $C_{12}EO_4$, $C_{12}EO_5$ and $C_{12}EO_{6,}$ respectively. Moreover, the addition of sodium carbonate caused a decrease in the optimum detergency temperature while the addition of an anionic surfactant increased the optimum detergency temperature of $C_{12}EO_5$.

For this present study, the systems of mixed surfactants from the previous by Childs and his coworkers (2004) were investigated further for surfactant gradient in the column study while in the system of Thompson (1994) were selected for temperature study to remove different oils.

CHAPTER III

METHODOLOGY

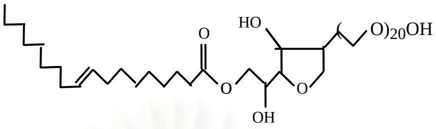
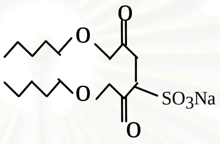
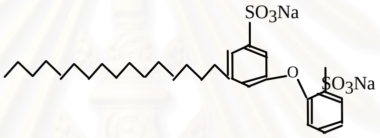
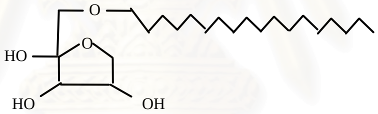
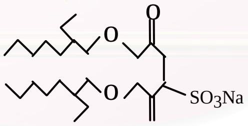
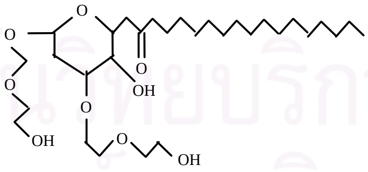
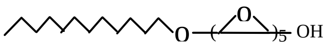
3.1 Materials

3.1.1 Surfactants

Surfactants used in this research were polyoxyethylene sorbitan monooleate (Polysorbate 80), sodium dihexyl sulfosuccinate (AMA), C16 monoalkylated diphenyloxide disulfonate (ADPODS), sorbitan monooleate (Span 80), Bis (2-ethylhexly) sulfosuccinic acid sodium salt (AOT), polyoxyethylene sorbitan monostearate (Polysorbate 60) and n-dodecyl pentaethylene glycol ($C_{12}EO_5$).

Polyoxyethylene sorbitan monooleate (Polysorbate 80), a nonionic surfactant with 100 % activity was purchased from APS Finechem (LABCHEM). Sodium dihexyl sulfosuccinate (AMA), an anionic surfactant with 80% activity was obtained from Cytec. C16 monoalkylated diphenyloxide disulfonate (ADPODS) in 36 % solution, a commercial grade anionic surfactant was obtained from Dow Chemical Co., known as Dowfax 8390 as the tradename. Sorbitan monooleate (Span 80), an anionic surfactant with 100 % activity was obtained from ICI Uniquema Co. Bis (2-ethylhexly) sulfosuccinic acid sodium salt (AOT), an anionic surfactant with 100 % activity was purchased from Fluka. Polyoxyethylene sorbitan monostearate (Polysorbate 60), a nonionic surfactant with 100 % activity was purchased from East Asiatic (Thailand) Co. Ltd. n-dodecylpentaethylene glycol ($C_{12}EO_5$), an nonionic surfactant with 100 % activity was purchased from Huntsman. Properties and selected characterization of these surfactants are shown in Table 3.1.

Table 3.1 Properties and selected characterization of surfactants.

Chemical name	Chemical structure	Type	MW	HLB
Polyoxyethylene sorbitan monooleate (Polysorbate 80)		Nonionic	1300	15.0
Sodium dihexyl sulfosuccinate (AMA)		Anionic	388	-
C16 monoalkylated diphenyloxide disulfonate (ADPODS)		Anionic	642	44.4
Sorbitan monooleate (Span 80)		Anionic	428.6	4.3
Bis (2-ethylhexly) sulfosuccinic acid sodium salt (AOT)		Anionic	444	10.2
polyoxyethylene sorbitan monostearate (Polysorbate 60)		Nonionic	1311.7	14.9
n-dodecyl pentaethylene glycol ($C_{12}EO_5$)		Nonionic	417	10.6

3.1.2 Oils

The NAPLs used in this study were tetrachloroethylene (PCE) as a DNAPL in the column study while hexadecane and decane were used as LNAPLs in the washing study. Tetrachloroethylene, an analytical grade chemical with 99 % purity was purchased from Labscan Asia Co. Ltd. Hexadecane and decane with 99 % purity were purchased from Fluka. Table 3.2 shows the physical and chemical properties of these studied oils.

Table 3.2 Physical and Chemical Properties of Tetrachloroethylene, Decane and Hexadecane (Mallinckrodt Baker, Inc., 2004a, 2004b, 2004c).

Properties	**Tetrachloroethylene**	**Decane**	**Hexadecane**
Chemical Formulation	C_2Cl_4	$CH_3(CH_2)_8CH_3$	$CH_3(CH_2)_{14}CH_3$
Molecular Weight	165.83	142.29	226.45
Appearance	Clear, Colorless liquid	Clear, Colorless liquid	Clear, Colorless liquid
Odor	Ethereal odor	Gasoline-like odor	No
Solubility	150 ppm	Insoluble in water	Insoluble in water
Density (at 20^{o}C)	1.62	0.730	0.773
Boiling Point	121^{o}C	174^{o}C	287^{o}C
Melting Point	-19^{o}C	-30^{o}C	18^{o}C
Vapor Pressure (mmHg)	18 (at 25^{o}C)	1.4 (at 25^{o}C)	1 (at 105.3^{o}C)

3.1.3 Electrolytes

The electrolytes used in this research were sodium chloride and calcium chloride. Sodium chloride (NaCl), analytical grade with 99 % purity, was purchased from Carlo ERBA reagent Co. Ltd. Calcium chloride ($CaCl_2$), analytical grade with 99 % purity, was purchased from UNIVAR.

3.1.4 Substrates

The substrates for the experiment in the column study and batch study were 20-30 mesh Ottawa sand and blended polyester/cotton fabrics, respectively. 20-30 mesh Ottawa sand, nonporous silica sand, was purchased from Fisher Scientific. Pennell (1993) reported the specific surface area of this sand that are 0.1 m^2/g. Fabrics used for the washing study, a standard unsoiled polyester/ cotton blend (65/35), were purchased from Test Fabrics Co. (Middlesex, NJ, USA).

3.1.5 Water

Ultra pure water was used throughout this research for preparing aqueous surfactant solutions and other chemical solutions. It was also used as rinse water and for cleaning glassware.

3.1.6 Dyed Oil

Oil red O (solvent Red 27, CI No. 26125) was purchased from Aldrich Chemical Company, Inc. It was used for preparing dyed oil solution to be applied on fabric samples.

3.1.7 Other Chemicals

Dichloromethane, analytical reagent grade with 99% purity, was used for diluting dyed oil before being applied on fabrics. It was purchased from Labscan Asia Co. Ltd. 2-propanol, analytical grade with 99 % purity, was used to extract the oil from fabric for determining the amount of oil removal from fabrics after washing. It was purchased from Labscan Asia Co. Ltd.

All chemicals were used as received without further purification.

3.2 Methodology

This study was divided into three parts: the phase behavior study, the column study, and the washing study. Figure 3.1 shows the experimental procedure diagram.

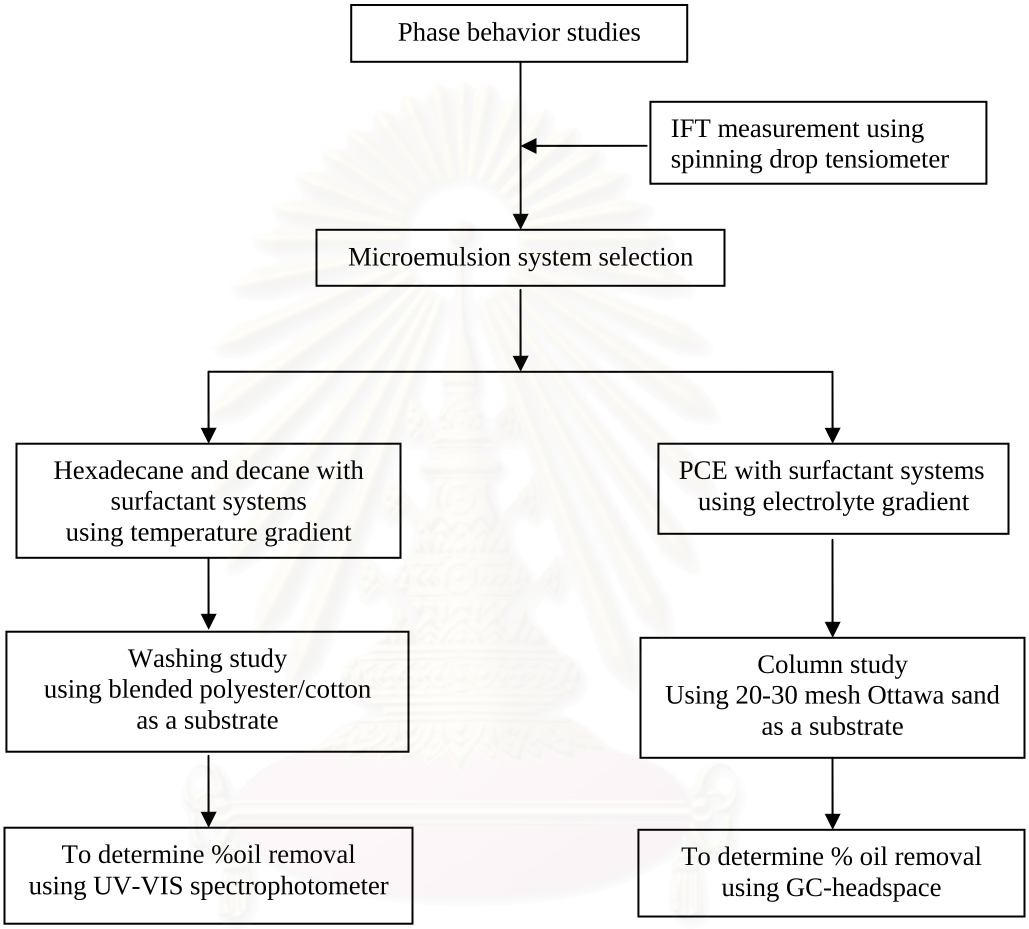


Figure 3.1 Experimental procedure diagram.

3.2.1 Phase Behavior Study

Several mixed surfactant systems were studied for salinity scan with PCE and temperature scan with decane and hexadecane. The surfactant systems studied in this part shows in Table 3.3

Table 3.3 Surfactant systems studied in phase behavior study.

No	System of surfactants	Salinity		Temperature (^oC)	Oil		
		wt% NaCl	wt% $CaCl_2$		Decane	Hexadecane	PCE
1	5 wt% ADPODS, 3 wt% AMA	0-9	0	25			x
2	5 wr% ADPODS, 3 wt% AMA	0	0-9	25			x
3	5 wt% ADPODS, 3 wt% AMA	3	0-9	25			x
4	2.5 wt% polysorbate 80, 2.5 wt% AMA	0	0-7	25			x
5	2.5 wt% IPA, 5 wt% AMA	0	0-1	25			x
6	3 wt% AOT	0-20	0	15-40	x	x	
7	4 wt% AOT	0-20	0	15-40	x	x	
8	5 wt% AOT	0-20	0	15-40	x	x	
9	3 wt% Polysorbate 80	0-20	0	15-40	x	x	
10	4 wt% Polysorbate 80	0-20	0	15-40	x	x	
11	5 wt%Polysorbate 80	0-20	0	15-40	x	x	
12	2 wt% ADPODS, 4 wt% AOT	0-20	0	25	x	x	
13	2 wt% ADPODS, 4 wt% AOT	5.0, 8.5	0	15-40	x	x	
14	5 wt% Polysorbate 60	0-1.0	0	25-60	x	x	
15	5 wt% Polysorbate 60	0	0-1.0	25-60	x	x	
16	4 wt% Polysorbate 60, 0.5 wt% AOT	0-1.0	0	25-60	x	x	
17	4 wt% Polysorbate 60, 0.5 wt% AOT	0	0-1.0	25-60	x	x	
18	3 wt% Polysorbate 60, 0.5 wt% AOT	0-1.0	0	25-60	x	x	
19	5 wt% Polysorbate 60, 0.5 wt% AOT	0	0-1.0	25-60	x	x	
20	5 wt% AOT, 5 wt% Span 80, 1.5 wt% ADPODS	2.0	0	15-40	x	x	
21	2 wt% AOT, 3 wt% Span 80, 1.5 wt% ADPODS	2.0	0	30	x	x	
22	0.125 wt% $C_{12}EO_5$	0.585	0	25-60	x	x	

The phase study was carried out at a ratio of oil to surfactant solution equal to one to one. First, an aqueous surfactant solution was added to flat-bottom-screw cap-tubes and followed by oil. The tubes were shaken and left for reaching equilibrium conditions at desired temperature in an incubator. Once the volume of each phase remained constant the system had reached equilibrium. The volume of each phases of microemulsion was measured. The interfacial tension (IFT) between each phase was measured for the desired systems by a spinning drop tensiometer (Dataphysics, Model SVT20).

3.2.2 Column Study

Column studies were used for determining the performance of the surfactant gradient approach using salinity scan for PCE removal from Ottawa sand.

3.2.2.1 Surfactant Sorption Study

Surfactant sorption was studied using a 22 mL headspace vial with Teflon septa. Approximately 2 g of Ottawa sand was placed into each vial and then the selected surfactant solution from phase behavior study was added until no headspace existed in the vial (~20 mL). The samples were shaken at room temperature for seven days. The concentration of surfactant in aqueous phase was determined by absorbance at 241 nm using a UV/VIS spectrophotometer (Thermo Electron Corporation, Model Helios Alpha).

3.2.2.2 Soil Column Preparation

Preparation for soil column was adapted from Pennell (1994) and Childs et al. (2004). Column apparatus consisted of a chromatography column with 2.5 cm ID KONTES equipped with an adjustable flow adapter. The column was packed with 20-30 mesh Ottawa sand. The pore volume of the column was determined as the volume of water used to pack the column. The water was prepared in a separated container. The initial volume of water was measured. A small amount of water was poured into the column followed by a certain amount of sand until the sand level was a little lower than that of water. After that, the water and sand were gradually added into the column by this manner until the desired level of sand was reached. The volume of water in the container was measured over again after packing the column. The difference of volume before and after packing indicates the pore volume of the column since the water replaces the space of air originally presented in the column. Approximately 40 pore volume of de-aired water was pump downward into the column using a peristaltic pump (Watson-Marlow, Model 323S/D) at a flow rate of 0.30 mL/min (9.73 cm/hr). After that, 20 pore volumes of de-aired water containing 0.01 M $Ca(NO_3)_2$ was also pumped at a flow rate of 0.30 mL/min through the column in a downward direction. Residual PCE saturations were established by pumping PCE into the packed column in an up flow mode and then free phase PCE was displaced with water in a downward direction at a flow rate of 0.30 mL/min. Ten pore volumes of de-aired water were pumped into the contaminated column at a flow rate of 0.30 mL/min and the volume of displaced free phase PCE was measured. The volume of entrapped PCE was calculated as in equation (1).

$$A = x - (y + z) \tag{1}$$

A: Volume of residual PCE in column (mL)

x: Volume of PCE before the contamination procedure (total PCE introduced to the column) (mL)

y: Volume of PCE after the contamination procedure (exiting column during PCE flooding) (mL)

z: Volume of the free phase of PCE leaving the column during water flushing (mL)

3.2.2.3 PCE Removal from Soil Column

The surfactant solution with different salinities selected from phase behavior study was pumped through the column in a down flow mode at a flow rate of 0.3 mL/min (9.73 cm/hr). For flushing with surfactant gradient, each of three steps was flushed for 1.5 pore volume while the last steps were flushed for 5.5 pore volume. For flushing without surfactant gradient, a surfactant solution was flushed for 10 pore volume at the same salinity. The column effluents were collected in 0.20 pore volume increments of 5 mL by fraction collector (Amersham Bioscience, Model Frac 100). The characteristics of effluents were observed to determine the PCE solubilization and the PCE free phase as PCE mobilization. Micellarly solubilized PCE was diluted with a solution of 10 wt% ADPODS to a concentration in the linear region of detection in the gas chromatography. The diluted solutions were used to determine the PCE concentrations by gas chromatography (Perkin Elmer, Model Clarus 500 GC) with an Electron Capture Detector (ECD); column DB-5 with 30 m x 0.32 mm ID, 0.25 µm film thickness; carrier gas: helium at 65 mL/min; oven temperature: 150^{o}C for 9 min; injector temperature: 250^{o}C; and detector temperature: 300^{o}C. The static headspace sampling technique was applied using a headspace autosampler (Perkin Elmer, Model Turbometrix 40). The volume of PCE free phase was measured and then the mass of PCE mobilization was calculated.

3.2.3 Washing Study

To investigate the gradient approach for a surfactant system that response to temperature change, batch washing studies in the washing process were conducted for temperature gradient. The following steps were carried out to determine the performance of this approach.

3.2.3.1 Oily Soiled Fabric Preparation

Prior to soiling oil into fabric, the fabric was pre-washed to eliminate residual agents that may affect the washing results. The pre-wash method was done according to the ASTM standard guide D4265-98 (Annual Book of ASTM standards, 2000). Hexadecane and decane were dyed by an oil soluble Oil-Red-O dye following the standard method (Goel, 1998). First, 0.1 g of the oil-soluble dye was added to 100 mL of oil. The dyed oil was stirred and filtered until clear. For the soiling procedure, 10 mL of the dyed oil was diluted by dichloromethane to 100 mL. The dyed oil was poured onto a large piece of fabric folded in a glass bottle until the fabric was submerged and then left for one minute. Then, the soiled fabric was unfolded and placed on a flat plate in a ventilated hood to dry at room temperature overnight. The dried soiled fabric was cut into 3 x 4 inch swatches and all swatches were used in the same batch of experiment. The soiling procedure was prepared separately for each type of oil.

3.2.3.2 Washing Procedures

Washing studies were conducted by using a Terg-O-Tometer (Copley, Model DIS 8000). The machine contains of six vessels in the water bath for temperature controlling. The agitators are attached and submerge in each vessel. The Terg-O-Tometer is an equipment that simulates the top loading washing machine.

The selected surfactant formulation obtained from phase behavior study was used as a washing solution. The washing studies were performed by adding 1000 mL washing solution to three vessels. Four soiled swatches were put into one vessel for replication of decane soiled and four hexadecane swatches were put into another vessel. For mixed soiled washing, two decane soiled swatches and two hexadecane soiled swatches were added in the same vessel. For water washing, 1000 mL water was added to other three vessels. Soil swatches were also added as the same in surfactant washing. There were five washing batches for five temperatures; 30°C, 35°C, 40°C, 45°C and gradient temperature from 30°C to 45°C. The washing duration using in all washing studies was determined by conducting the gradient washing first and this washing duration was used in other washing studies without gradient system. The rinsing time was 3 min for the first step and 2 min for the second step as in the detergency study (Tongcumpou et al., 2003). Temperatures of both the washing solution and the water as rinsing water were the same.

3.2.3.3 Oil Removal Measurement

Oil removal was determined by measuring the different amount of stained oil on fabric before and after washing. The quantities of the stained oil were extracted from the fabric by submerging a swatch in 2-propanol overnight at room temperature. The extracted solution was measured by absorbance at 520 nm using a UV/VIS Spectrophotometer (Thermo Electron Corporation, Model Helios Alpha). This method represented that the dye and the oil loading on the fabric which was removed by surfactant solution at the same proportion (Goel, 1998). The %oil removal was calculated by the following equation (2):

$$\%\text{ oil removal} = ((A-B)/A) \times 100 \qquad (2)$$

A: Concentration of oil loading on fabric before wash (ppm)

B: Concentration of oil loading on fabric after wash (ppm)

3.2.3.4 Dynamic Interfacial Tension Measurement

In washing experiments, the washing solution to oil ratio was much higher than the 1:1 ratio used in the phase behavior study. Therefore, the dynamic IFT was studied because the equilibrium phase behavior in the washing experiment may be different from the results from 1:1 oil/ water ratio in the phase behavior study (Tongcumpou, 2003). The dynamic interfacial tension was measured using a spinning drop tensiometer (Dataphysics, Model SVT20). The ratio of oil and water volume was 0.01: 2 and the spinning speed was 3000 rpm.

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Phase Behavior with Salinity Scan

All preliminary study of the mixed system with the studied oils in salinity scan system as mentioned in Chapter 2 are showed in Appendix A., Due to the desirable phase transition of surfactant systems, only two systems that found to be able to formed microemulsion with PCE were selected for further study in phase behavior i.e. the system of mixed surfactants 5 wt% ADPODS, 3 wt% AMA, and 3 wt% NaCl and the system of mixed surfactants polysorbate and 2.5%wt AMA . The $CaCl_2$ scan was conducted for these two systems. The IFT between oil and microemulsion phase at equilibrium were measured for both systems. Table 4.1 and 4.2 shows the results of phase transition and IFT values. The first surfactant system, 5 wt% ADPODS, 3 wt% AMA, and 3 wt% NaCl was scanned with $CaCl_2$ in the range of 0-9.0 wt%. The results showed that at this range of $CaCl_2$ concentration, only microemulsion Type I was formed. The interfacial tension between PCE and surfactant solution gradually decreased as the concentration of $CaCl_2$ increases. However, in the whole range of salinity, the IFT values were in the same magnitude (as shown in Table 4.1). For the system of 2.5 wt% Polysorbate 80 and 2.5 wt% AMA, the transition of microemulsion from Type I to Type III and to Type II were observed with $CaCl_2$ scan in the range of 0-7.0 wt% (as shown in Table 4.2). While the IFT value was found one magnitude lower in the microemulsion Type III as compared to in the microemulsion Type I. Figure 4.1 and 4.2 demonstrate the relationship between interfacial tension and salinity concentration of a system of 5 wt% ADPODS and 3 wt% AMA and a system of 2.5 wt% Polysorbate 80 and 2.5 wt% AMA, respectively.

Accordeing to Childs et al. (2004), the starting IFT values of less than 1 mN/m was observed to be able to produce mobilization thus the system of 5 wt% ADPODS, 3 wt% AMA, and 3 wt% NaCl was selected for column study in this present work. Moreover, it was found that the initial IFT at above 1 mN/m for the initial gradient step in column study was high enough to prevent mobilization of DNAPL.

Table 4.1 Interfacial tension of PCE system with 5 wt% ADPODS/ 3 wt% AMA/ 3 wt% NaCl at different $CaCl_2$ concentration.

PCE microemulsion (Winsor type I)						
No.	**wt% ADPODS**	**wt% AMA**	**wt% NaCl**	**wt%$CaCl_2$**	**Winsor type**	**IFT (mN/m)**
1	5.0	3.0	0.0	0.0	I	5.897
2	5.0	3.0	3.0	0.0	I	0.846
3	5.0	3.0	3.0	1.0	I	0.521
4	5.0	3.0	3.0	2.0	I	0.612
5	5.0	3.0	3.0	3.0	I	0.460
6	5.0	3.0	3.0	4.0	I	0.400
7	5.0	3.0	3.0	5.0	I	0.393
8	5.0	3.0	3.0	6.0	I	0.332
9	5.0	3.0	3.0	7.0	I	0.310
10	5.0	3.0	3.0	8.0	I	0.368
11	5.0	3.0	3.0	9.0	I	0.235

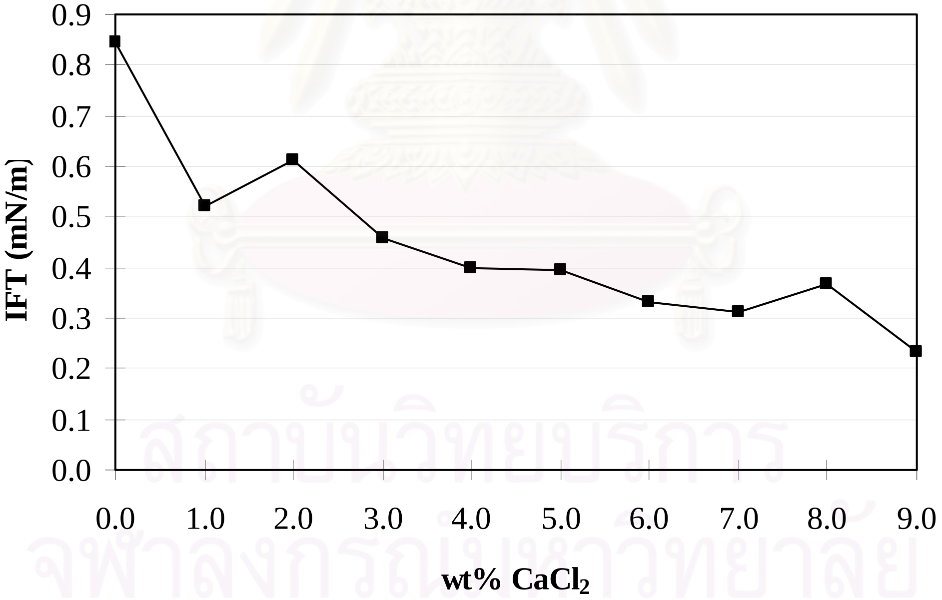


Figure 4.1 Relationship between interfacial tension and salinity concentration of PCE system with 5 wt% ADPODS/ 3 wt% AMA/ 3 wt% NaCl at different $CaCl_2$ concentration.

Table 4.2 Interfacial tension of PCE system with 2.5 wt% Polysorbate 80/ 2.5 wt% AMA at different $CaCl_2$ concentration.

PCE microemulsion (Winsor type I-III-II)					
No.	**wt% Polysorbate 80**	**wt% AMA**	**wt% $CaCl_2$**	**Winsor type**	**IFT (mN/m)**
1	2.5	2.5	0.0	I	N.D.*
2	2.5	2.5	0.5	I	0.102
3	2.5	2.5	1.0	III	0.056
4	2.5	2.5	1.5	III	0.065
5	2.5	2.5	2.0	III	0.035
6	2.5	2.5	2.5	III	N/A**
7	2.5	2.5	3.0	III	N/A**
8	2.5	2.5	3.5	III	N.D.*
9	2.5	2.5	4.0	III	N.D.*
10	2.5	2.5	4.5	III	N.D.*
11	2.5	2.5	5.0	III	N.D.*
12	2.5	2.5	5.5	II	N.D.*
13	2.5	2.5	6.0	II	N.D.*
14	2.5	2.5	6.5	II	N.D.*
15	2.5	2.5	7.0	II	N.D.*

N.D.* indicates value not determined

N/A** indicates value cannot be measured

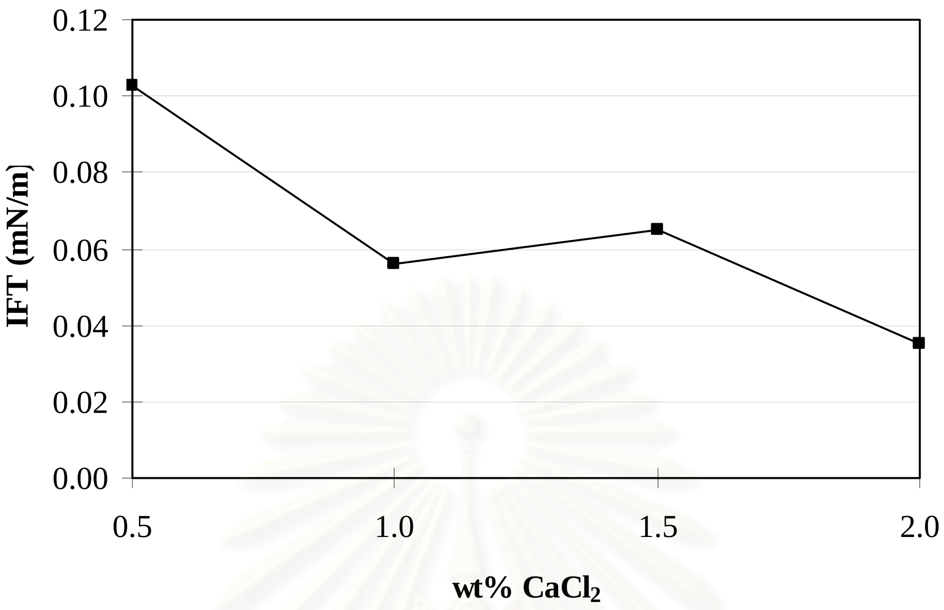


Figure 4.2 Relationship between interfacial tension and salinity concentration of PCE system with 2.5 wt% Polysorbate 80/ 2.5 wt% AMA at different $CaCl_2$ concentrations.

From these results in Figure 4.2, phase transition occurs with increasing salinity. A Winsor type I microemulsion become a Winsor type III microemulsion because the system change to be more lypophilic or hydrophilic. The phase transition of microemulsion and IFT decreasing are related to hydrophile-lipophile balance (HLB) of the system (Holmberg, 2003). HLB is a parameter that shows partitioning of surfactant between oil and water phases relative to surfactant hydrophobicity. With decreasing HLB the surfactant moves from the water phase to the oil phase as the surfactant system becomes more hydrophobic. Adding salt can promote the formation of middle phase microemulsion because salt can reduce the repulsive force between the ionic charges of surfactants at their head group. As a result, the CMC decreases while the aggregation number increases. So the transition of microemulsion and decreasing of HLB for ionic surfactants is induced by increasing salinity (Holmberg, 2003, Rosen, 2004).

The structure of surfactants was also concerned as the effect of type of surfactants on microemulsion system. For ADPODS, it is more hydrophilic and prefers to solubilize in a water phase rather than in an oil phase because of their two hydrophilic head groups. While AMA is twin-tailed ester sulfonates. These twin tails are hydrophobic. Moreover, AMA is well behaved because it has additional branching in each tail consisting of two methyl branches. The main reason of using AMA for DNAPL removal is its compatibility with most soil media (Childs et.al, 2004). In addition, it promotes solubilization rate very fast. Despite these desirable properties, AMA would produce mobilized DNAPLs that may sink in the subsurface, potentially into unpreviously contamination regions. In contrast, Polysorbate 80 is a nonionic surfactant that has HLB of 15. Nonionic surfactants are not as sensitive to salinity as compared with ionic surfactants; however, they are more sensitive with temperature.

According to the solubilization properties of these three surfactants, a mixture of 5 wt% ADPODS, and 3 wt% AMA is more hydrophilic surfactant system than a system of mixed of 2.5 wt% Polysorbate 80 and 2.5 wt% AMA. This is the reason that why at 9 wt% $CaCl_2$ for the first system, microemulsion type I still exists while in the latter system, only at 1 wt% $CaCl_2$, the transition of microemulsion from Type I to III and to type II can be observed.

Dwarakanath et al. (1999) illustrated that use of anionic surfactants was preferable to nonionic surfactants for surfactant flushing since the ionic system is temperature insensitive and controlling temperature during soil flushing is cost-prohibitive. In addition, the salinity can be adjusted continuously and inexpensively. Thus, anionic surfactant flushing is a very practical system. This is a significant advantage of using anionic surfactants over nonionic surfactants. In addition, for the mixed surfactant system, another advantage is the system often temperature insentitive (Childs, et al., 2004)

4.2 Phase Behavior with Temperature Scan

To apply gradient approach for nonionic surfactant, phase behavior studies were conducted for a different surfactant system as in Appendix A. For this study, a solution of 0.125 wt% $C_{12}EO_5$ with 0.585 wt% NaCl was selected to form microemulsion with decane and hexadecane. It has been known that the transition of microemulsion and HLB decreasing for nonionic surfactants occurs by raising the temperature of the system. The

IFT reaches its minimum value at the phase inversion temperature (PIT) (Holmberg, 2003). However, for some systems, solubilization is rather low, and phase transition may not be visually observed. Thus, IFT value was measured to investigate whether microemulsion system transformation occurred. The experimental results from phase behavior study are shown in Appendix A.

Temperature scan in the range from 25-60 °C for the system of $C_{12}EO_5$ and decane and hexadecane is shown in Figure 4.3. It was found that the IFT value between $C_{12}EO_5$ and decane system decreased from 0.576 mN/m at 25°C to minimum IFT at 0.240 mN/m at 30°C, and then it gradually increased to 0.350 mN/m at 55°C and finally it jumped to 0.767 mN/m at 60°C. In the same manner, for $C_{12}EO_5$ and hexadecane system, the IFT value decreased from 1.458 mN/m at 25°C and dramatically decreased to the minimum IFT at 0.271 mN/m at 45°C and slightly increased to 0.635 mN/m at 60°C. Therefore, the PIT of decane and hexadecane are found at 30°C and 45°C, respectively.

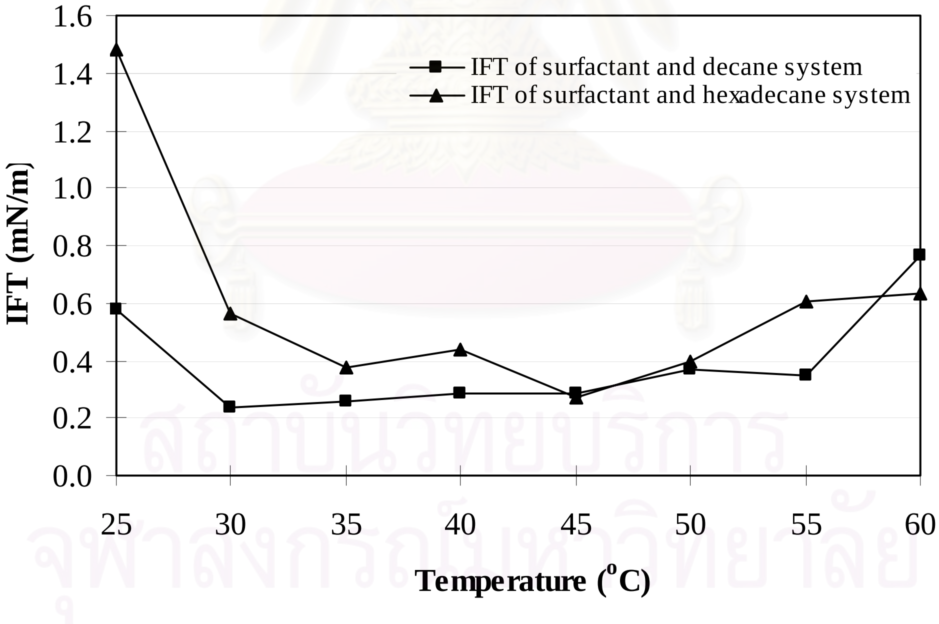


Figure 4.3 Comparison between effect of temperature changing on interfacial tension of decane and hexadecane systems with 0.125 wt% $C_{12}EO_5$/ 0.585 wt% NaCl.

Aramaki, Ozawa and Kunieda (1997) studied the effect of temperature on the phase behavior of ionic-nonionic microemulsion. The microemulsion system formed in salt/sodium dodecyl sulfate/polyoxyethylene dodecyl ether ($C_{12}EO_2$ or $C_{12}EO_3$)/decane over a wide range of temperature. The results showed that the hydrophilicity of nonionic surfactant decreased with increasing temperature. Moreover, the $C_{12}EO_3$ system was a temperature insensitive microemulsion system since their hydrophobicity.

Thompson (1994) showed that nonionic surfactants are highly temperature sensitive. From his study, he found the PIT of $C_{12}EO_5$/decane system is 35^{o}C while $C_{12}EO_5$/hexadecane system has PIT at 50^{o}C. In the current study the PIT for these two oils is slightly higher but similar in magnitude.

The hydrophobic interactions of nonionic surfactants can be varied by changing the number of ethylene oxide unit. The solubilization of oils at optimum increases with the length of surfactant lipophile as the ethylene oxide number is increased correspondingly. Moreover, increasing the molecular weight of pure n-alkanes generally decrease the solubilization (Bourrel and Schechter, 1988). Furthermore, the high solubilization of oil is obtained when the three phase region is narrow. The width of three phase region defined as the range of alkane of carbon number. A correlation between the width of three phase region and interfacial tension can be explained as the nearer the two critical endpoint of temperature are positioned to one another, the smaller will be the interfacial tension at optimum. For different n-alkanes, the minimum interfacial tension and the depth of the minimum in the same condition are always different. At optimum condition, the interfacial tension of more hydrophobic chain length of oil is often greater than the less hydrophobic chain length (Bourrel and Schechter, 1988).

The different PIT for the same surfactant system with the two studied oils can be explained by the fact that more hydrophobic oils have higher PIT values. At 30^{o}C, for the system of $C_{12}EO_5$, the IFT values between the surfactant solution and the oil were 0.240 and 0.566 mN/m for decane and hexadecane, respectively. While at 45^{o}C for the same system, the IFT values were 0.2855 and 0.271 mN/m for decane and hexadecane, respectively. From the fact that the hydrophobicity of decane is less than that of hexadecane, the PIT of decane appears at 30^{o}C while the PIT of hexadecane appears at

45^{o}C and the width of middle phase region of hexadecane is narrower than the width of decane phase transition.

Thus, it is expected that the differences PIT of decane and hexadecane can be applied for temperature gradient approach. To evaluate the concept, the removal of these two types of oils, decane and hexadecane from fabric was conducted in washing experiment by using temperature gradient process.

4.3 Dynamic Interfacial tension

In the real washing process, surfactant solution to oil ratio was much higher than unity as used in the phase behavior study. This may effect the phase transition and IFT values. According to Tongcumpou et al. (2003), the measurement of dynamic IFT was introduced to simulate the real situation. Therefore, dynamic IFT were also measured for this experiment. The dynamic IFT for the system of 0.125 wt% $C_{12}EO_5$ with decane and hexadecane were measured at different temperature range from 25^{o}C to 60^{o}C. The experimental data shows in Appendix D.

Surprisingly, the PIT when minimum IFT occurred for both decane and hexadecane were found at higher temperature as compared to the results from the phase study. The PIT for decane moved from 30^{o}C to 45^{o}C while for hexadecane PIT moved from 45^{o}C to 55^{o}C. The results are as shown in figure 4.4 and 4.5 for decane and hexadecane, respectively.

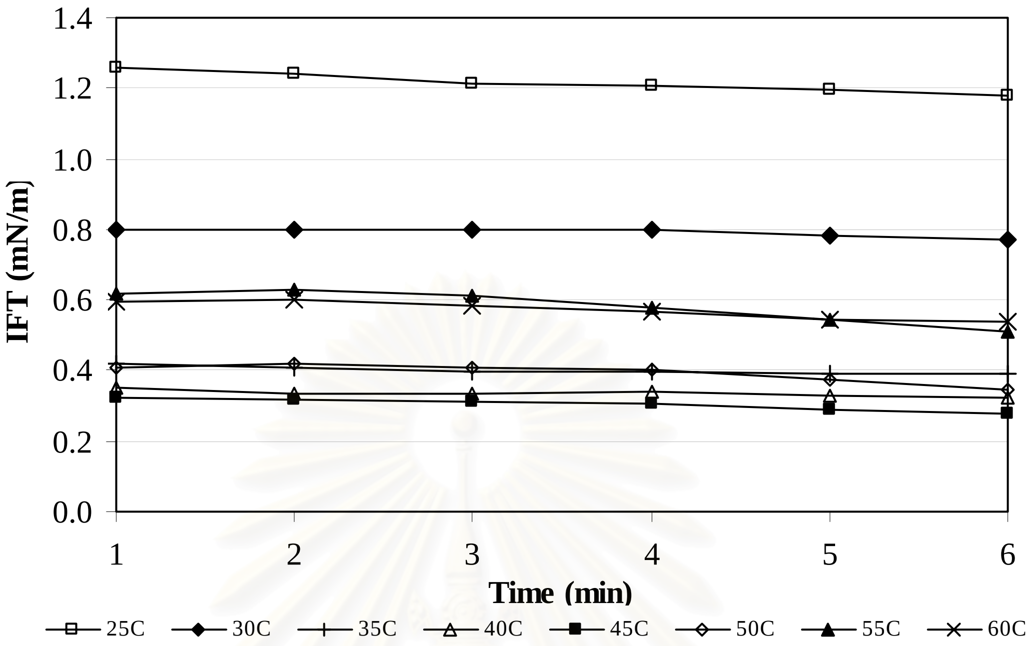


Figure 4.4 Dynamic interfacial tension of decane system with 0.125 wt% $C_{12}EO_5$/ 0.585 wt% NaCl.

However, the IFT values for both systems found to be changed only in the same magnitude. The temperature for washing experiment was selected from the PIT of the phase study ranging from 30°C to 45°C since the higher PIT from dynamic IFT experiment would effect the fabric substrate and oil removal.

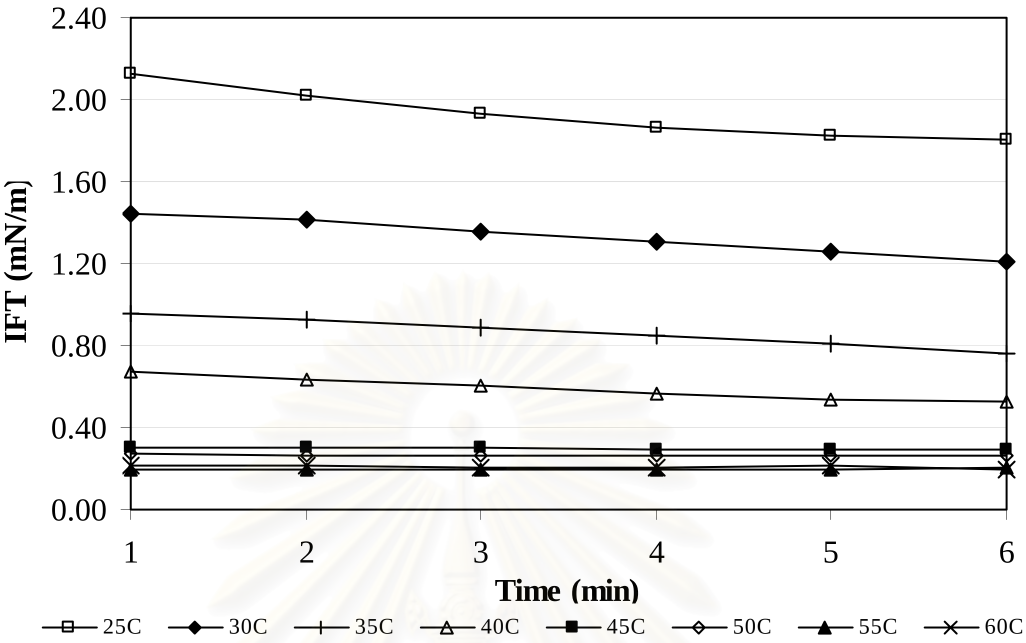


Figure 4.5 Dynamic interfacial tension of hexadecane system with 0.125 wt% $C_{12}EO_5$/ 0.585 wt% NaCl.

4.4 Surfactant Gradient Approach in Column Study

4.4.1 Surfactant Sorption

The adsorption of ADPODS was found to be negligible on Ottawa sand as shown in Table 4.3. All experimental results of surfactant sorption study shows in Appendix B.

Table 4.3 Adsorption Data of ADPODS on Ottawa Sand.

Initial Concentration (ppm)	Blank (ppm)	Average Ceq (ppm)	Average Adsorption Concentration (ppm)
0	0.00	0.00	0.00
10000	10030.86	9969.14	61.73
20000	20064.21	20032.10	32.10
30000	30016.05	29983.95	32.10
40000	40085.80	40051.48	34.32
50000	50082.82	50069.01	13.80

As a result, surfactants used in this study shows negligible adsorption on Ottawa sand because of their anionic characteristic and the negative surface of the Ottawa sand, and also because the sand contains no measurable organic carbon. Thus, surfactants solubilized PCE without effect of adsorption on Ottawa sand and interference from organic carbon was unable to observe.

Ottawa sand is nonporous silica sand containing little if any organic materials and has been found to exhibit no detectable sorption of TCE (Pennell et.al, 1993). Moreover, little or none of the surfactant will sorb to the Ottawa sand due to its anionic character (Mayer, 1999).

4.4.2 Column Study

The best system chosen from phase behavior study in this study was 5 wt% ADPODS/ 3 wt% AMA/ NaCl/ $CaCl_2$ because they have desirable PCE microemulsion IFT that would prevent vertical mobilization of PCE as mentioned earlier. The experimental data for the column study is shown in Appendix B.

Figure 4.6 shows the results of surfactant flushing through the experimental column that has a higher IFT (5.897 mN/m) at the initial stage (1.5 pore volumes) or absent of added salinity. After that the second stage was flushing of the surfactant system with a lower IFT (0.846 mN/m) in another 1.5 pore volumes. Then the third stage was flushing with a lower IFT (0.460 mN/m) for 1.5 pore volumes and followed by the last stage with an IFT of 0.332 mN/m for 5.5 pore volumes. The PCE solubilization was slightly increased when until the surfactant flushing reached 4 pore volumes and gradually decreased until the PCE concentration was zero at the 6.2 pore volumes. While flushing surfactant, the mobilization could not be observed as a free phase. Despite this fact, the PCE in column was removed close to 100% of the PCE within 10 pore volumes. Figure 4.7 shows the comparison between PCE solubilization and the cumulative PCE mass eluted from the column; it was observed that the PCE is gradually removed out of the column with gradually decrease IFT using the surfactant gradient system.

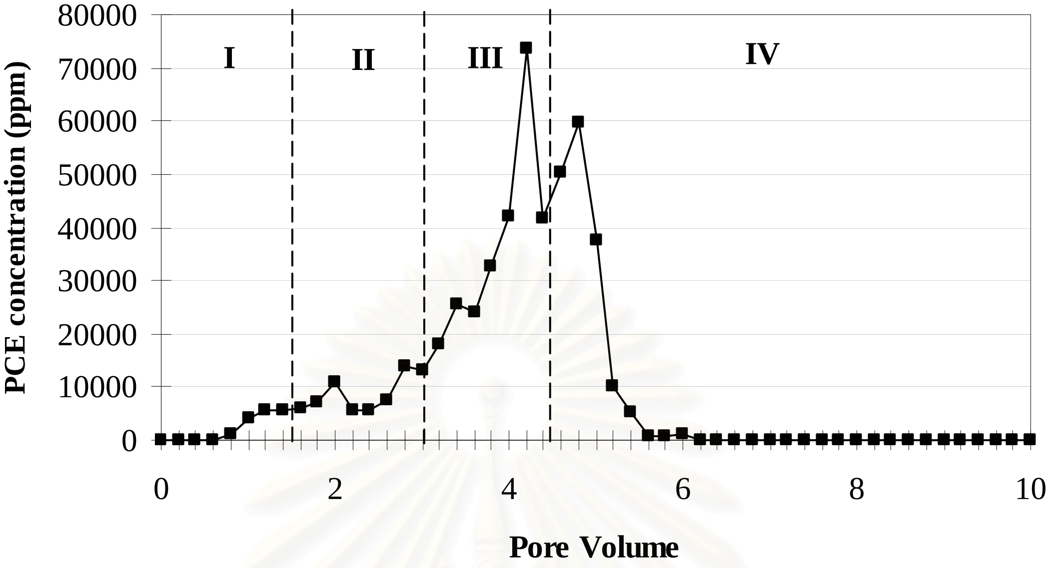


Figure 4.6 Column experiment results for the system of 5 wt% ADPODS/ 3 wt% AMA/ NaCl flushing at different $CaCl_2$ concentration: I- the first stage of flushing (IFT =5.897 mN/m); II- the second stage of flushing (IFT (0.846 mN/m); III- the third stage of flushing (IFT 0.332 mN/m); IV- the last stage of flushing (IFT 0.460 mN/m).

Childs et.al. (2004) found that the starting surfactant flushing with IFT less that 1 mN/m also produces PCE mobilization. Furthermore, an initial IFT above 1 mN/m should be added to reduce the vertical migration potential of PCE to design a gradient system. In this work, the initial IFT above 1mN/m is also added in the system to reduce the potential of PCE mobilization. Thus, the result from this study shows the PCE removal with high solubilization while the mobilization of PCE as a free phase is not observed.

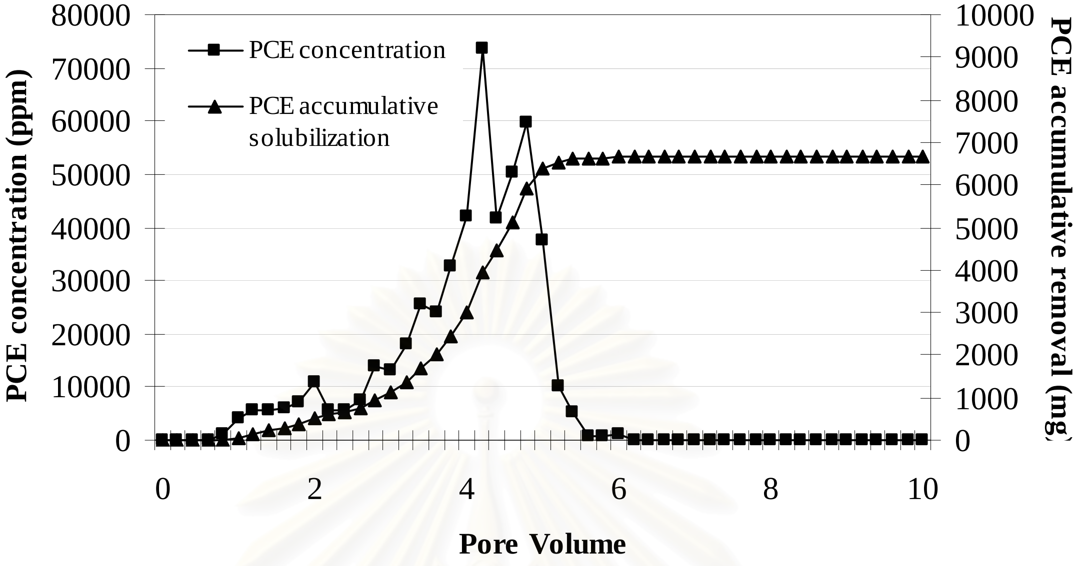


Figure 4.7 Comparison between PCE solubilization and PCE accumulative solubilization for the system of 5 wt% ADPODS/ 3 wt% AMA/ NaCl/ $CaCl_2$ flushing.

Surfactant flushing without gradient system can either cause PCE mobilization that would migrate vertically in deep zone of groundwater to be the new contamination source, if the IFT is too low, or can render the flushing system much less efficient, if the IFT is too high. Thus the surfactant flushing system without gradient was studied in comparison.

The system of 5 wt% ADPODS/ 3 wt% AMA/ 3 wt% NaCl/ 3 wt% $CaCl_2$, which giving a lowest IFT (0.332 mN/m) was used as a solely surfactant flushing system in the column study. The result of surfactant flushing without the gradient concept shows in Figure 4.8. The experimental data is shown in Appendix B. Moreover in Figure 4.9, the comparison between PCE solubilization, PCE accumulation and PCE mobilization shows that the main process to remove PCE out of the column using this surfactant system is mobilization process.

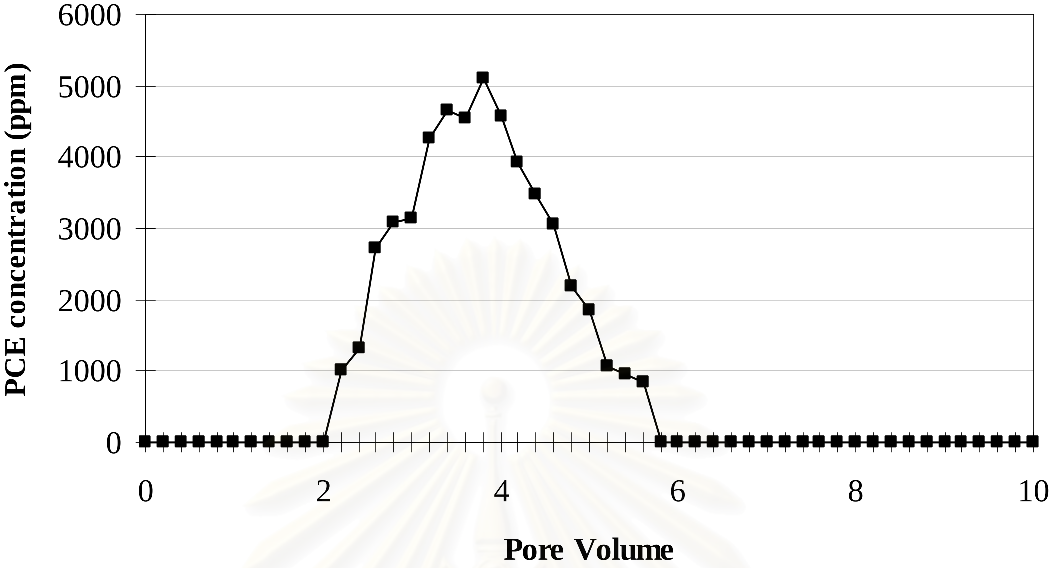


Figure 4.8 Column experiment results for the system of 5 wt% ADPODS/ 3 wt% AMA/ 3 wt% NaCl/ 6 wt% $CaCl_2$ flushing.

As Pennell et.al.(1994) showed that PCE mobilization occurred when flushing PCE from Ottawa sand with one surfactant system (without surfactant gradient concept). As a result, DNAPLs vertical migration was concerned because mobilization could extend the contamination area to uncontaminated zones.

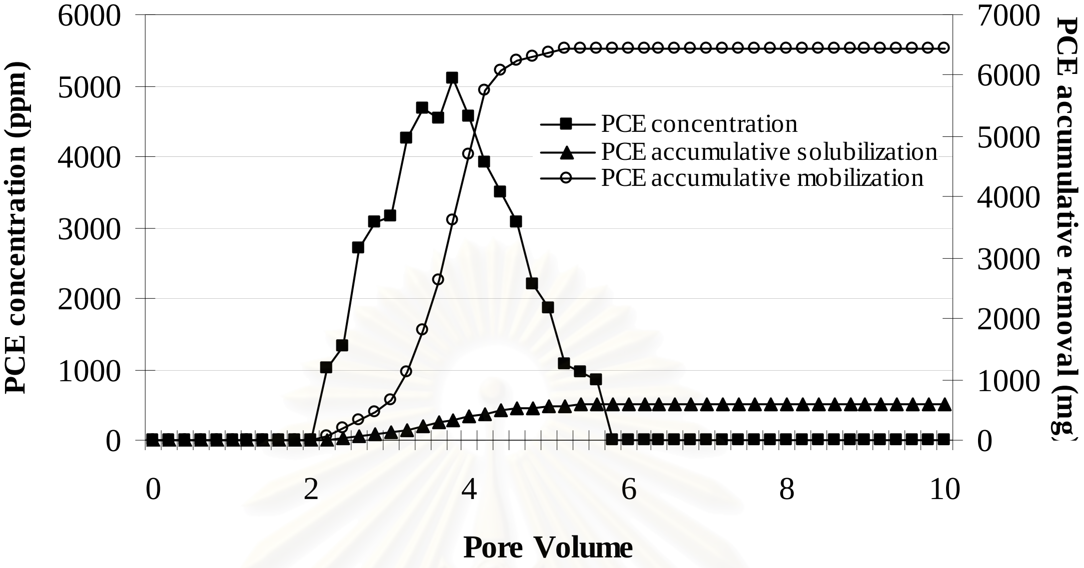


Figure 4.9 Comparison between PCE solubilization, PCE accumulative solubilization and PCE accumulative mobilization for the system of 5 wt% ADPODS/ 3 wt% AMA/ NaCl/ $CaCl_2$ flushing.

Table 4.4 shows the condition of surfactant flushing and the results of flushing with and without surfactant gradient systems. The PCE mobilization was not detected as a free phase for the surfactant flushing with gradient system while there are obviously PCE free phase that was the PCE mobilization. For surfactant flushing with gradient system, 6.7 g of PCE was added into the column. PCE was solubilized for 6.648 g. This results show that PCE was removed by solubilization mechanism for 99.22% while PCE mobilization was unable to be observed. In comparison, PCE of 7 g was added into the column for surfactant flushing without gradient system. PCE was solubilized only for 0.506 g while PCE mobilization was observed for 6.427 g. It means that PCE was removed by solubilization just only 0.8% and mainly removed by mobilization mechanism (>90% of residual PCE).

Table 4.4 Conditions of Surfactant flushing with and without gradient system.

No.	Added PCE (g)	Solubilized PCE (g)	Mobilized PCE (g)	Surfactant system	wt% NaCl	wt% $CaCl_2$	IFT (mN/m)	Pore volume
1	6.7	6.648	0	5 wt% ADPODS, 3 wt% AMA	0	0	5.897	0-1.5
					3	0	0.846	1.5-3.0
					3	3	0.460	3.0-4.5
					3	6	0.332	4.5-5.5
2	7	0.506	6.427	5 wt% ADPODS, 3 wt% AMA	3	6	0.332	0-10

From this study, a gradient system flushing PCE from Ottawa sand column show the effectiveness of gradient system compared to the surfactant flushing without the gradient system.

4.5 Surfactant Gradient Approach in Washing Study

In 1998, Goel studied on the detergency of oily soil from blended polyester/cotton fabrics using alcohol ethoxylate surfactant with phase inversion temperature (PIT). Hexadecane was used as an oily soil. The study revealed that maximal detergency occurred as a function of washing temperature at approximately 35, 62 and 80^{o}C for $C_{12}EO_4$, $C_{12}EO_5$ and $C_{12}EO_6$, respectively. Moreover, the addition of sodium carbonate caused decrease in the optimum detergency temperature while the addition of anionic surfactant increased the optimum detergency temperature of $C_{12}EO_5$.

In this study, the polyester/cotton blend fabric is used as a soiled with decane and hexadecane because their moderate hydrophilic/ hydrophobic characteristic. The washing experiment was divided into two main type of washing conditions. Surfactant washing with only one oil contaminated soiled was the first studied condition that using the 0.125 wt% $C_{12}EO_5$/ 0.585 wt% NaCl washing. To investigate the efficiency temperature gradient to remove different oil contaminant in the same batch of washing the surfactant washing with two swatches of each stained oils; decane and hexadecane was conducted. Water washing without surfactant was a reference condition to compare if there ar other factor affected on detergency performance. The washing study results are shown in Appendix C.

The temperature values used in this study part were selected from the phase behavior study. The minimum IFT of 0.125 wt% $C_{12}EO_5$/ 0.585 wt% NaCl system with decane is at the temperature of 30°C while the minimum IFT of the same surfactant system with hexadecane is at 45°C. As a result, the temperature washing of 30°C, 35°C, 40°C, and 45°C were studied to compare the gradient washing temperature from 30°C to 45°C. The washing time was 130 min same as the one used in the temperature gradient washing batch. Other conditions were controlled to be the same as in the temperature gradient washing.

Figure 4.10 illustrates the results from two washing conditions: surfactant washing with decane-only contaminated soiled and surfactant washing with hexadecane-only contaminated soiled. For decane-only contaminated soiled washing, it shows that the gradient temperature washing gives the highest oil removal from fabric of 92.08% while 86.23% decane removal from fabric is obtained from washing at the temperature of 30°C where the minimum IFT is observed in the phase study. According to these results, the temperature gradient from 30°C to 45°C produces a higher decane removal while also having promise for also removing hexadecane more effectively than at 30°C. The results from hexadecane-only contaminated soiled washing show the gradient temperature washing gives %oil removal from fabric of 85.65% while 89.27% hexadecane removal from fabric is obtained from washing at the temperature of 45°C where the minimum IFT is observed in the phase study. At the same time, the hexadecane removal for the gradient system is far superior to what it would have been if the optimum decane temperature of 30°C was used. The hexadecane removal at the temperature gradient condition is less effective than the removal at temperature that has minimum IFT. The gradient temperature is performed from 30°C and increase continually to 45°C while IFT between hexadecane and water is slightly decreased. In contrast, the temperature of 45°C presents the minimum IFT, so this condition making dramatically decrease in IFT to the minimum value and surfactant can contact with surfactants at this temperature for long time compared with the temperature gradient condition.

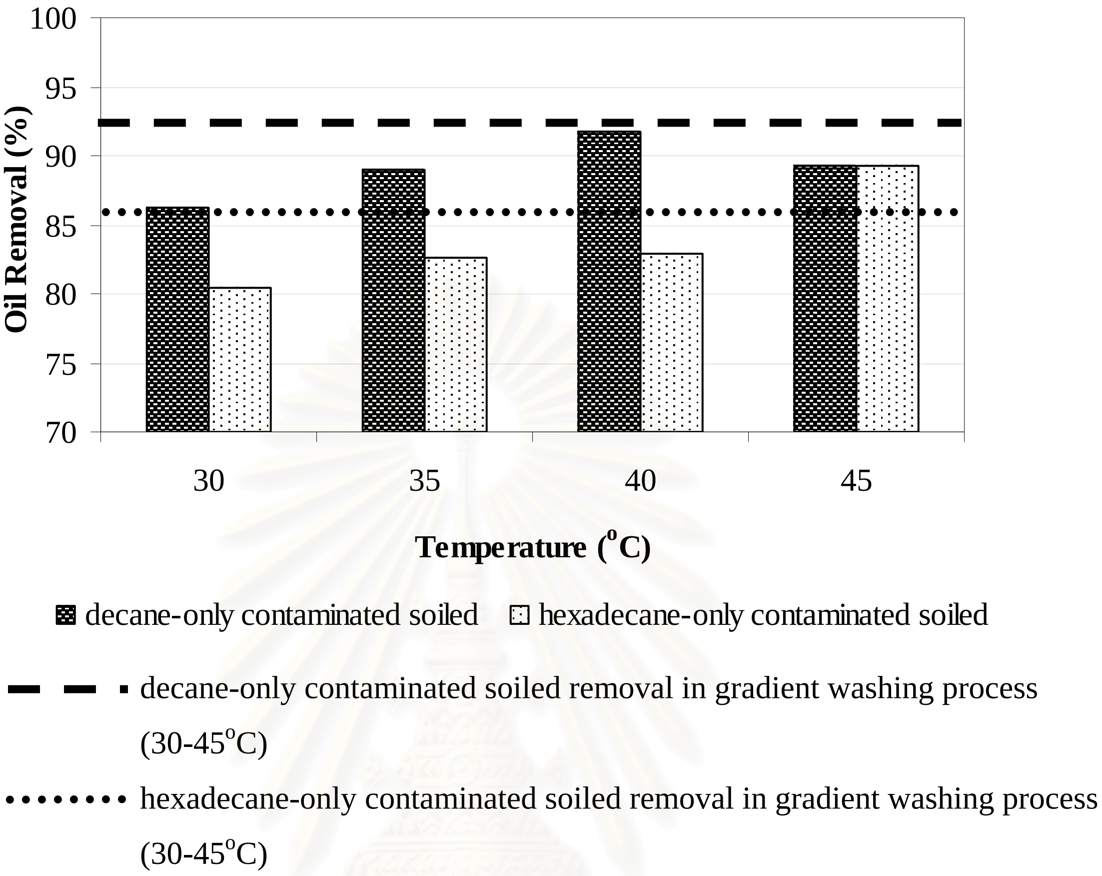


Figure 4.10 Surfactant washing with decane-only contaminated soiled and surfactant washing with hexadecane-only contaminated soiled at different temperatures.

Figure 4.11 shows the surfactant washing decane mixed with hexadecane soiled. For %decane removal, it also shows that the gradient temperature washing gives highest oil removal from fabric of 91.78% while 85.64% decane removal from fabric is obtained from washing at the temperature of 30°C where the minimum IFT is observed in the phase study. For amount of decane removal from fabric, hexadecane fabric does not affect on decane removal efficiency. The percentage of decane removal from fabric at temperature gradient condition is still higher than the percentage of decane removal at 30°C. Thus, the mixing of decane with hexadecane in the same condition does not affect on the removal efficiency.

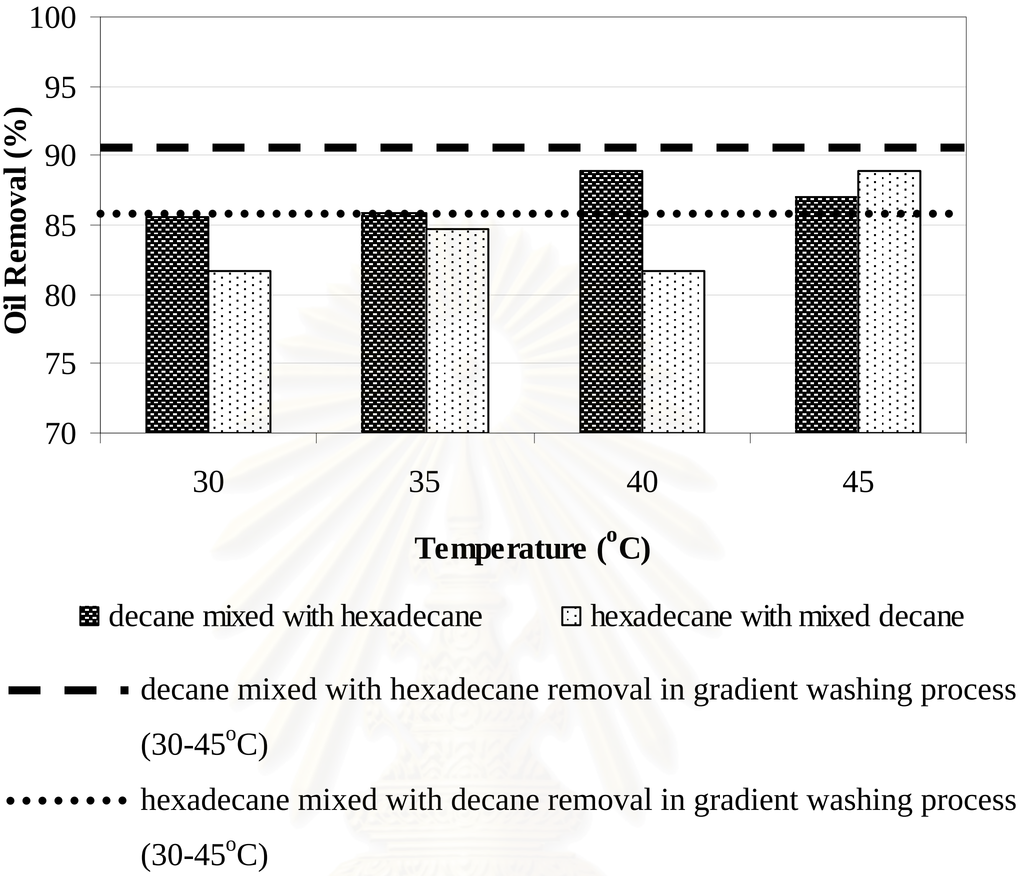


Figure 4.11 Surfactant washing soiled with mixed decane / hexadecane oil at different temperature.

Figure 4.12 shows the comparison between decane-only soiled washing and decane mixed hexadecane soiled washing conditions. The temperature gradient shows the highest effectiveness of washing for decane removal in both conditions; decane-only soiled and mixed decane soiled with hexadecane soiled, more than washing at 30^{o}C providing the minimum IFT value of decane system.

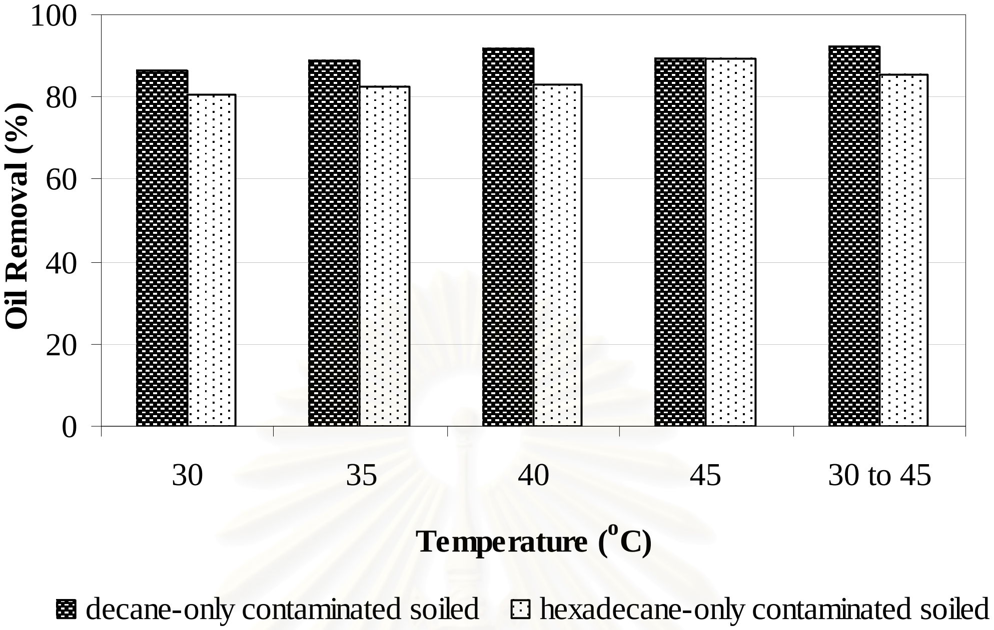


Figure 4.12 Comparison between decane-only soiled washing and decane mixed with hexadecane soiled washing conditions.

Figure 4.13 shows the comparison between hexadecane-only soiled washing and hexadecane mixed decane soiled washing conditions. In the same manner, removal of hexadecane from soiled was not affected by the decane soiled. Hexadecane removal when mixed with decane fabric shows the similar result with surfactant washing with hexadecane contaminated soiled. The combination of decane fabric does not affect on hexadecane removal. In comparison, surfactant washing mixed hexadecane contaminated soiled with decane contaminated soiled results show that the gradient temperature washing gives %oil removal from fabric of 85.64% while 88.87% hexadecane removal from fabric was obtained from washing at the temperature of 45^{o}C where the minimum IFT was observed in the phase study.

Conclusively, the combination of two different oils in the same batch of washing did not affect each types of oil removal performance significantly. Both oils were removed from fabric as similar as the one in the washing batch that contained only one stained oil on four swatches. However, for the case of hexadecane the temperature gradient condition was found slightly less efficiency as compared to the washing batch at

45°C. This may be because in the process of temperature gradient, the duration time for the temperature gradient washing bath at 45°C is much less that the batch at constant temperature 45°C. Thus, the condition of minimum IFT that allowed surfactant and oil coalescent each other was shorter. Consequently, hexadecane removal was found lower for the temperature gradient experiment.

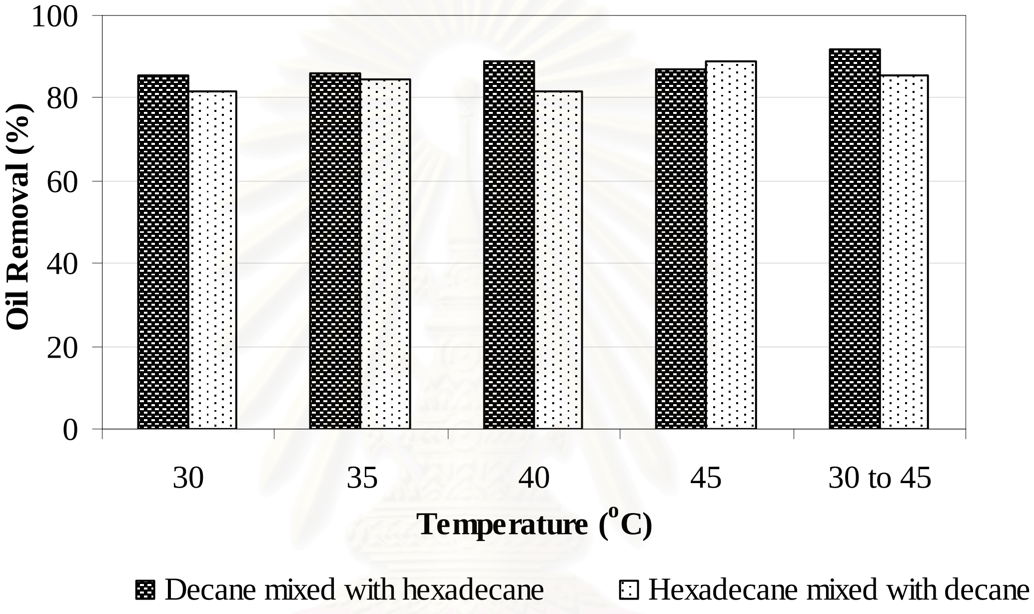


Figure 4.13 Comparison between hexadecane-only soiled washing and hexadecane mixed decane soiled washing conditions.

Moreover, the pure stained and the mixing of two stained; decane and hexadecane washing result at the same temperature gradient condition are compared shown in Figure 4.14. This results show that there is not significant different between washing with pure stained and mix stained. Thus, the temperature gradient approach can be applied to remove both of these two oils at the same time of washing effectively.

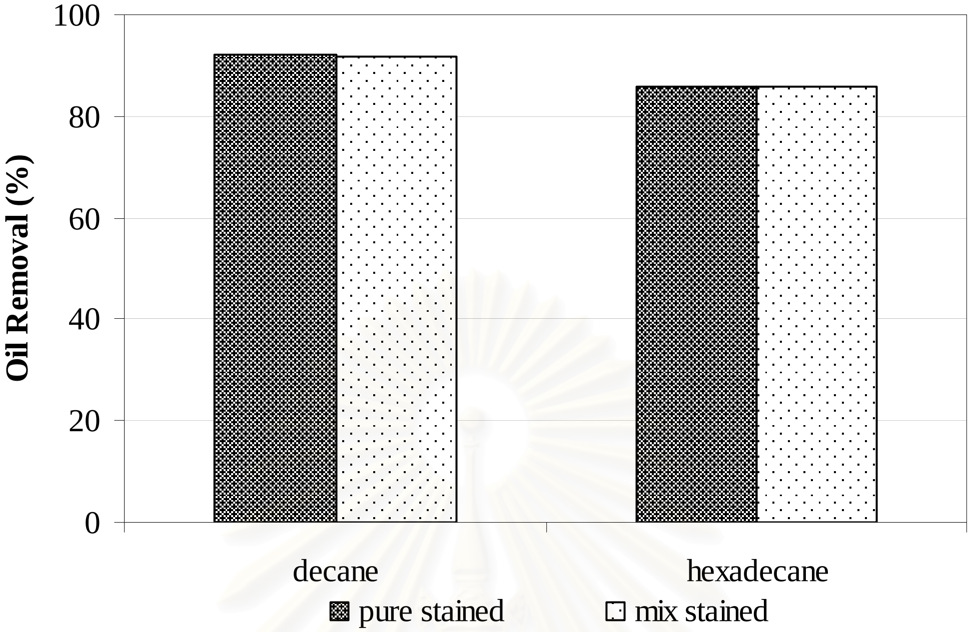


Figure 4.14 Comparison % oil removals from temperature gradient washing experiment between pure stained washing and mixed stained washing condition of decane and hexadecane.

The result from this study indicates that the temperature gradient system can effectively use to remove oil from fabric especially in short chain alkane type because the solubilization obtained from short chain alkane removal are greater than alkane removal in the same surfactant system are shown as follows:

$$SP^{*}\cdot\Delta ACN = d \qquad (1)$$

SP* = solubilization parameter
ΔACN = the range of alkane carbon number
d = a constant charateristic of the class of surfactant

A constant charateristic of the class of surfactant under consideration is defined as d. For example, alkylbenzene sulfonates, α-olefin sulfonate, and ethoxylated oleyl sulfonates has the d value of 5.5, 24.7, and 40.3, respectively. SP* is defined as solubilization parameter that shows the efficiency of oil solubilization in the surfactant system.

In conclusion, the surfactant gradient system by changing the temperature using in nonionic surfactant system is effectively used to remove oil from fabric surface especially in short chain alkane in both conditions; a condition with only short chain alkane and a condition with mixing with long chain alkane.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study was to remove oil from different surfaces using the surfactant gradient approach. The specific application was to apply the gradient approach for PCE removal in a column study with the selected surfactant system by using an electrolyte gradient and to apply the gradient approach for decane and hexadecane removal from fabric substrate in a batch study by using the temperature gradient.

From the phase behavior results, the 5 wt% ADPODS/ 3 wt% AMA/ NaCl/$CaCl_2$ system was selected for column studies of PCE removal from Ottawa sand because of the IFT values that would maximize solubilization while preventing vertical mobilization. The phase behavior of a system of 0.125 wt% $C_{12}EO_5$ and 0.585 wt% NaCl were used in washing experiment. The PIT values of these two types of oils, decane and hexadecane that were 30^{o}C and 45^{o}C, respectively. The efficiency of temperature gradient for surfactant gradient approach was studied to remove these two oils from polyester/cotton blend fabrics.

The result from the column study shows the PCE removal with the gradient system had more effectiveness than the PCE removal without PCE mobilization which corresponds to the previous works. As a result, the gradient system can be used to remove PCE and prevent vertical migration effectively.

In washing study, the surfactant gradient system can be effectively used to remove decane from fabrics both of using pure oil fabric and mixed with hexadecane fabric condition in washing experiments. In conclusion, the surfactant gradient system by changing the temperature using in nonionic surfactant is effectively used to remove oil from fabric surface especially in short chain alkane removal.

5.2 Recommendations

Since the experimental result confirmed the efficiency of application of surfactant gradient system for DNAPLs removal, The study on surfactant gradient systems should be extended to other solid surface that simulate the real soil. In addition, different surfactant systems may be investigated to find the optimum condition for some DNAPL contamination.

This approach would be worked to remove many types of oil with the similar structure contaminated in the same site. The combination of surfactant gradient approach may be introduced to soil washing process. Moreover, this surfactant gradient by varying the temperature can be studied further in soil washing study to remove the mixing oils contamination. However, the surfactant gradient system using temperature gradient should be concerned energy consumption for changing temperature.

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APPENDICES

Appendix A Experimental Data of Phase Behavior Study.

Table A-1 Phase Behavior Study Results for Different Surfactant System.

No	Surfactant system	Salinity scan		Temperature scan (°C)	Oil			Results	NOTE
		wt% NaCl	wt% $CaCl_2$		Hexadecane	Decane	PCE		
1	5 wt% ADPODS, 3 wt% AMA	0-9	0	25			x	Neg	
2	5 wt%ADPODS, 3 wt% AMA	0	0-9	25			x	Neg	
3	5 wt% ADPODS, 3 wt% AMA	3	0-9	25			x	Winsor type I	
4	2.5 wt% Polysorbate 80, 2.5 wt% AMA	0	0-7	25			x	Winsor type I-III-II	Middle phase at 3.0-3.5 wt% $CaCl_2$
5	2.5 wt% IPA, 5 wt% AMA	0	0-1	25			x	Winsor type I-III	Middle phase at 0.7-0.9 wt% $CaCl_2$
6	3 wt% AOT	0-20	0	15-40	x	x		Neg	
7	4 wt% AOT	0-20	0	15-40	x	x		Neg	
8	5 wt% AOT	0-20	0	15-40	x	x		Neg	
9	3 wt% Polysorbate 80	0-20	0	15-40	x	x		Neg	
10	4 wt% Polysorbate 80	0-20	0	15-40	x	x		Neg	

Table A-1 (continue).

No	Surfactant system	Salinity scan		Temperature scan (°C)	Oil			Results	NOTE
		wt% NaCl	wt% $CaCl_2$		Hexadecane	Decane	PCE		
11	5 wt% Polysorbate 80	0-20	0	15-40	x	x		Neg	
12	2 wt% ADPODS, 4 wt% AOT	0-20	0	25	x	x		Winsor type I-III	Middle phase at 7.0-8.5 wt%NaCl for hexadecane and 6.0-8.5 wt% NaCl for decane
13	2 wt% ADPODS, 4 wt% AOT	5.0, 8.5	0	15-40	x	x		Winsor type I,III	Not changed from the reesults at 25°C
14	5 wt% Polysorbate 60	0-1.0	0	25-60	x	x		Neg	
15	5 wt% Polysorbate 60	0	0-1.0	25-60	x	x		Neg	
16	4 wt% Polysorbate 60, 0.5 wt% AOT	0-1.0	0	25-60	x	x		Neg	
17	4 wt% Polysorbate 60, 0.5 wt% AOT	0	0-1.0	25-60	x	x		Neg	
18	3 wt% Polysorbate 60, 0.5 wt% AOT	0-1.0	0	25-60	x	x		Neg	
19	5 wt% Polysorbate 60, 0.5 wt% AOT	0	0-1.0	25-60	x	x		Neg	

Table A-1 (continue).

No	Surfactant system	Salinity scan		Temperature scan (°C)	Oil			Results	NOTE
		wt% NaCl	wt% $CaCl_2$		Hexadecane	Decane	PCE		
20	5 wt% AOT, 5 wt% Span 80,1.5 wt% ADPODS	2.0	0	15-40	x	x		Winsor type II for hexadecane and decane	
21	2 wt% AOT, 3 wt% Span 80, 1.5 wt% ADPODS	2.0	0	30	x	x		Neg	
22	0.125 wt% $C_{12}EO_5$	0.585	0	25-60	x	x		Neg	Turbidity changed

Table A-2 Phase height and relative volume of water and oil phase in microemulsion formation with 5 wt% ADPODS, 3 wt% AMA and PCE at different NaCl and $CaCl_2$ concentration.

No.	wt% NaCl	wt% $CaCl_2$	Total Height (cm)	Upper Phase Height (cm)						Lower Phase Height (cm)					
				1	2	3	average	SD	Relative Volume	1	2	3	average	SD	Relative Volume
1	0.0	0.0	6.9	3.9	3.8	3.9	3.9	0.1	0.56	3.0	3.1	3.0	3.0	0.1	0.44
2	3.0	0.0	6.9	3.6	3.5	3.6	3.5	0.0	0.51	3.4	3.4	3.4	3.4	0.0	0.49
3	3.0	1.0	6.9	3.6	3.6	3.6	3.6	0.0	0.52	3.3	3.3	3.3	3.3	0.0	0.48
4	3.0	2.0	6.9	3.6	3.6	3.6	3.6	0.0	0.51	3.4	3.4	3.4	3.4	0.0	0.49
5	3.0	3.0	6.9	3.6	3.6	3.6	3.6	0.0	0.51	3.4	3.4	3.4	3.4	0.0	0.49
6	3.0	4.0	6.9	3.5	3.5	3.4	3.5	0.1	0.50	3.4	3.4	3.5	3.4	0.1	0.50
7	3.0	5.0	6.9	3.5	3.5	3.5	3.5	0.0	0.50	3.5	3.5	3.5	3.5	0.0	0.50
8	3.0	6.0	6.9	3.6	3.7	3.7	3.7	0.1	0.53	3.3	3.2	3.3	3.3	0.1	0.47
9	3.0	7.0	6.9	3.6	3.6	3.6	3.6	0.0	0.51	3.4	3.4	3.4	3.4	0.0	0.49
10	3.0	8.0	6.9	3.7	3.7	3.7	3.7	0.0	0.53	3.3	3.3	3.3	3.3	0.0	0.47
11	3.0	9.0	6.9	3.6	3.6	3.6	3.6	0.0	0.52	3.3	3.3	3.3	3.3	0.0	0.48

Table A-3 Height and relative volume of water and oil phase in microemulsion formation with 2.5 wt% Polysorbate 80, 2.5 wt% AMA and PCE at different $CaCl_2$ concentration.

No.	wt% $CaCl_2$	Total Height (cm)	Upper Phase Height (cm)						Middle Phase Height (cm)						Lower Phase Height (cm)					
			1	2	3	average	SD	Relative Volume	1	2	3	average	SD	Relative Volume	1	2	3	average	SD	Relative Volume
1	0.0	6.9	3.3	3.2	3.3	3.3	0.1	0.47	0.0	0.0	0.0	0.0	0.0	0.00	3.6	3.7	3.6	3.6	0.1	0.53
2	1.0	6.9	3.7	3.7	3.7	3.7	0.0	0.53	0.0	0.0	0.0	0.0	0.0	0.00	3.3	3.3	3.3	3.3	0.0	0.47
3	2.0	6.9	0.3	0.3	0.2	0.2	0.0	0.03	3.6	3.5	3.6	3.5	0.0	0.51	3.1	3.2	3.2	3.1	0.0	0.45
4	3.0	6.9	1.4	1.4	1.4	1.4	0.0	0.20	2.5	2.5	2.5	2.5	0.0	0.36	3.0	3.0	3.0	3.0	0.0	0.43
5	4.0	6.9	2.3	2.4	2.4	2.4	0.1	0.34	1.6	1.7	1.6	1.6	0.1	0.24	3.0	2.8	2.9	2.9	0.1	0.42
6	5.0	6.9	2.7	2.7	2.7	2.7	0.0	0.38	1.4	1.4	1.4	1.4	0.0	0.20	2.9	2.9	2.9	2.9	0.0	0.41
7	6.0	6.9	2.7	2.7	2.7	2.7	0.0	0.38	1.5	1.5	1.4	1.4	0.0	0.21	2.8	2.8	2.9	2.8	0.0	0.41
8	7.0	6.9	2.8	2.7	2.7	2.7	0.1	0.40	1.4	1.4	1.4	1.4	0.0	0.20	2.7	2.8	2.8	2.8	0.1	0.40
9	8.0	6.9	2.7	2.7	2.7	2.7	0.0	0.39	1.4	1.4	1.4	1.4	0.0	0.20	2.8	2.8	2.8	2.8	0.0	0.41
10	9.0	6.9	2.9	2.9	2.9	2.9	0.0	0.42	1.6	1.7	1.7	1.7	0.1	0.24	2.4	2.3	2.3	2.3	0.1	0.34
11	10.0	6.9	2.8	2.9	2.9	2.9	0.1	0.42	1.5	1.5	1.5	1.5	0.0	0.22	2.6	2.5	2.5	2.5	0.1	0.37
12	11.0	6.9	3.0	3.0	3.0	3.0	0.0	0.43	0.0	0.0	0.0	0.0	0.0	0.00	3.9	3.9	3.9	3.9	0.0	0.57
13	12.0	6.9	3.0	3.1	3.0	3.0	0.1	0.44	0.0	0.0	0.0	0.0	0.0	0.00	3.9	3.8	3.9	3.9	0.1	0.56
14	13.0	6.9	3.0	3.0	3.0	3.0	0.0	0.43	0.0	0.0	0.0	0.0	0.0	0.00	3.9	3.9	3.9	3.9	0.0	0.57
15	14.0	6.9	3.0	3.0	2.9	2.9	0.0	0.43	0.0	0.0	0.0	0.0	0.0	0.00	4.0	4.0	4.0	4.0	0.0	0.57

Table A-4 Density of water and oil phase in microemulsion formation with 5 wt% ADPODS, 3 wt% AMA and PCE at different NaCl and $CaCl_2$ concentration.

No.	wt% NaCl	wt% $CaCl_2$	Phase	Volume (µL)				Mass (g)				Density (g/cm^3)
				no. 1	no. 2	no. 3	average	no. 1	no. 2	no. 3	average	
1	0.0	0.0	Upper	20	20	20	20	0.0302	0.0301	0.0301	0.0301	1.5067
2			Lower	20	20	20	20	0.0203	0.0202	0.0203	0.0203	1.0133
3	3.0	0.0	Upper	20	20	20	20	0.0299	0.0298	0.0297	0.0298	1.4900
4			Lower	20	20	20	20	0.0206	0.0207	0.0206	0.0206	1.0317
5	3.0	1.0	Upper	20	20	20	20	0.0309	0.0308	0.0309	0.0309	1.5433
6			Lower	20	20	20	20	0.0206	0.0210	0.0212	0.0209	1.0467
7	3.0	2.0	Upper	20	20	20	20	0.0297	0.0297	0.0298	0.0297	1.4867
8			Lower	20	20	20	20	0.0209	0.0212	0.0210	0.0210	1.0517
9	3.0	3.0	Upper	20	20	20	20	0.0317	0.0316	0.0316	0.0316	1.5817
10			Lower	20	20	20	20	0.0206	0.0209	0.0208	0.0208	1.0383
11	3.0	4.0	Upper	20	20	20	20	0.0315	0.0314	0.0312	0.0314	1.5683
12			Lower	20	20	20	20	0.0211	0.0212	0.0210	0.0211	1.0550
13	3.0	5.00	Upper	20	20	20	20	0.0309	0.0380	0.0380	0.0356	1.7817
14			Lower	20	20	20	20	0.0210	0.0212	0.0210	0.0211	1.0533
15	3.0	6.0	Upper	20	20	20	20	0.0317	0.0318	0.0317	0.0317	1.5867
16			Lower	20	20	20	20	0.0212	0.0215	0.0214	0.0214	1.0683
17	3.0	7.0	Upper	20	20	20	20	0.0317	0.0317	0.0316	0.0317	1.5833
18			Lower	20	20	20	20	0.0216	0.0222	0.0220	0.0219	1.0967
19	3.0	8.0	Upper	20	20	20	20	0.0318	0.0316	0.0318	0.0317	1.5867

Table A-4 (continue).

No.	%NaCl	$\%CaCl_2$	Phase	Volume (μL)				Mass (g)				Density (g/cm^3)
				no. 1	no. 2	no. 3	average	no. 1	no. 2	no. 3	average	
20	3.0	9.0	Lower	20	20	20	20	0.0216	0.0219	0.0218	0.0218	1.0883
21			Upper	20	20	20	20	0.0307	0.0307	0.0305	0.0306	1.5317
22			Lower	20	20	20	20	0.0218	0.0219	0.0218	0.0218	1.0917

Table A-5 Density of water and oil phase in microemulsion formation with 2.5 wt% Polysorbate 80, 2.5 wt% AMA and PCE at different $CaCl_2$ concentration.

No.	$\%CaCl_2$	Phase	Volume (μL)				Mass (g)				Density (g/cm^3)
			no. 1	no. 2	no. 3	average	no. 1	no. 2	no. 3	average	
1	0.0	Upper	20	20	20	20	0.0311	0.0312	0.0311	0.0311	1.5567
2		Lower	20	20	20	20	0.0198	0.0198	0.0198	0.0198	0.9900
3	1.0	Upper	20	20	20	20	0.0302	0.0301	0.0302	0.0302	1.5083
4		Lower	20	20	20	20	0.0197	0.0203	0.0200	0.0200	1.0000
5	2.0	Upper	20	20	20	20	0.0311	0.0310	0.0311	0.0311	1.5533
6		Lower	20	20	20	20	0.0198	0.0202	0.0198	0.0199	0.9967
7	3.0	Upper	20	20	20	20	0.0271	0.0271	0.0271	0.0271	1.3550
8		Lower	20	20	20	20	0.0199	0.0206	0.0203	0.0203	1.0133
9	4.0	Upper	20	20	20	20	0.0308	0.0309	0.0308	0.0308	1.5417
10		Lower	20	20	20	20	0.0202	0.0202	0.0201	0.0202	1.0083

Table A-5 (continue).

No.	%CaCl$_2$	Phase	Volume (µL)				Mass (g)				Density (g/cm^3)
			no. 1	no. 2	no. 3	average	no. 1	no. 2	no. 3	average	
11	5.0	Upper	20	20	20	20	0.0313	0.0312	0.0313	0.0313	1.5633
12		Lower	20	20	20	20	0.0202	0.0204	0.0204	0.0203	1.0167
13	6.0	Upper	20	20	20	20	0.0309	0.0309	0.0310	0.0309	1.5467
14		Lower	20	20	20	20	0.0207	0.0202	0.0205	0.0205	1.0233
15	7.0	Upper	20	20	20	20	0.0317	0.0318	0.0319	0.0318	1.5900
16		Lower	20	20	20	20	0.0203	0.0208	0.0205	0.0205	1.0267
17	8.0	Upper	20	20	20	20	0.0290	0.0302	0.0301	0.0298	1.4883
18		Lower	20	20	20	20	0.0203	0.0206	0.0205	0.0205	1.0233
19	9.0	Upper	20	20	20	20	0.0309	0.0308	0.0310	0.0309	1.5450
20		Lower	20	20	20	20	0.0202	0.0203	0.0203	0.0203	1.0133
21	10.0	Upper	20	20	20	20	0.0300	0.0298	0.0301	0.0300	1.4983
22		Lower	20	20	20	20	0.0203	0.0204	0.0203	0.0203	1.0167
23	11.0	Upper	20	20	20	20	0.0296	0.0298	0.0298	0.0297	1.4867
24		Lower	20	20	20	20	0.0208	0.0207	0.0207	0.0207	1.0367
25	12.0	Upper	20	20	20	20	0.0309	0.0308	0.0309	0.0309	1.5433
26		Lower	20	20	20	20	0.0204	0.0203	0.0203	0.0203	1.0167
27	13.0	Upper	20	20	20	20	0.0289	0.0290	0.0287	0.0289	1.4433
28		Lower	20	20	20	20	0.0201	0.0204	0.0205	0.0203	1.0167
29	14.0	Upper	20	20	20	20	0.0293	0.0292	0.0295	0.0293	1.4667
30		Lower	20	20	20	20	0.0205	0.0204	0.0205	0.0205	1.0233

Table A-6 Density of water and oil phase in microemulsion formation with 0.125 wt% $C_{12}EO_5$, 0.585 wt% NaCl and decane at different temperature.

No.	Temperature (°C)	Phase	Volume (μL)				Mass (g)				Density (g/cm^3)
			no. 1	no. 2	no. 3	average	no. 1	no. 2	no. 3	average	
1	25	Upper	20	20	20	20	0.0208	0.0206	0.0208	0.0207	1.0367
2		Lower	20	20	20	20	0.0147	0.0145	0.0145	0.0146	0.7283
3	30	Upper	20	20	20	20	0.0207	0.0205	0.0202	0.0205	1.0233
4		Lower	20	20	20	20	0.0149	0.0148	0.0149	0.0149	0.7433
5	35	Upper	20	20	20	20	0.0208	0.0203	0.0206	0.0206	1.0283
6		Lower	20	20	20	20	0.0147	0.0147	0.0146	0.0147	0.7333
7	40	Upper	20	20	20	20	0.0203	0.0207	0.0210	0.0207	1.0333
8		Lower	20	20	20	20	0.0140	0.0146	0.0150	0.0145	0.7267
9	45	Upper	20	20	20	20	0.0211	0.0211	0.0212	0.0211	1.0567
10		Lower	20	20	20	20	0.0149	0.0146	0.0147	0.0147	0.7367
11	50	Upper	20	20	20	20	0.0211	0.0210	0.0211	0.0211	1.0533
12		Lower	20	20	20	20	0.0150	0.0148	0.0150	0.0149	0.7467
13	55	Upper	20	20	20	20	0.0207	0.0209	0.0199	0.0205	1.0250
14		Lower	20	20	20	20	0.0150	0.0149	0.0149	0.0149	0.7467
15	60	Upper	20	20	20	20	0.0214	0.0209	0.0210	0.0211	1.0550
16		Lower	20	20	20	20	0.0149	0.0147	0.0149	0.0148	0.7417

Table A-7 Density of water and oil phase in microemulsion formation with 0.125 wt% $C_{12}EO_5$, 0.585 wt% NaCl and hexadecane at different temperature.

No.	Temperature (°C)	Phase	Volume (μL)				Mass (g)				Density (g/cm^3)
			no. 1	no. 2	no. 3	average	no. 1	no. 2	no. 3	average	
1	25	Upper	20	20	20	20	0.0215	0.0210	0.0212	0.0212	1.0617
2		Lower	20	20	20	20	0.0153	0.0154	0.0154	0.0154	0.7683
3	30	Upper	20	20	20	20	0.0208	0.0205	0.0204	0.0206	1.0283
4		Lower	20	20	20	20	0.0155	0.0156	0.0156	0.0156	0.7783
5	35	Upper	20	20	20	20	0.0215	0.0211	0.0213	0.0213	1.0650
6		Lower	20	20	20	20	0.0151	0.0152	0.0153	0.0152	0.7600
7	40	Upper	20	20	20	20	0.0216	0.0213	0.0218	0.0216	1.0783
8		Lower	20	20	20	20	0.0153	0.0155	0.0154	0.0154	0.7700
9	45	Upper	20	20	20	20	0.0209	0.0209	0.0208	0.0209	1.0433
10		Lower	20	20	20	20	0.0150	0.0153	0.0152	0.0152	0.7583
11	50	Upper	20	20	20	20	0.0205	0.0209	0.0206	0.0207	1.0333
12		Lower	20	20	20	20	0.0154	0.0154	0.0153	0.0154	0.7683
13	55	Upper	20	20	20	20	0.0212	0.0212	0.0124	0.0183	0.9133
14		Lower	20	20	20	20	0.0154	0.0153	0.0157	0.0155	0.7733
15	60	Upper	20	20	20	20	0.0207	0.0211	0.0214	0.0211	1.0533
16		Lower	20	20	20	20	0.0151	0.0157	0.0155	0.0154	0.7717

Table A-8 Interfacial tension of microemulsion system with 5 wt% ADPODS, 3 wt% AMA and PCE at different NaCl and $CaCl_2$ concentration.

No.	wt% NaCl	wt% $CaCl_2$	Winsor type	IFT (mN/m)				
				1	2	3	average	SD
1	0.0	0.0	I	5.897	5.897	5.895	5.897	0.001
2	3.0	0.0	I	0.845	0.847	0.846	0.846	0.001
3	3.0	1.0	I	0.521	0.520	0.521	0.520	0.000
4	3.0	2.0	I	0.612	0.613	0.611	0.612	0.001
5	3.0	3.0	I	0.460	0.460	0.460	0.460	0.000
6	3.0	4.0	I	0.401	0.399	0.400	0.400	0.001
7	3.0	5.0	I	0.393	0.393	0.393	0.393	0.000
8	3.0	6.0	I	0.331	0.332	0.332	0.332	0.001
9	3.0	7.0	I	0.310	0.309	0.311	0.310	0.001
10	3.0	8.0	I	0.367	0.368	0.368	0.368	0.000
11	3.0	9.0	I	0.235	0.234	0.235	0.235	0.001

Table A-9 Interfacial tension of microemulsion system with 2.5wt% Polysorbate 80, 2.5 wt% AMA and PCE at different $CaCl_2$ concentration.

No.	wt% $CaCl_2$	Winsor type	IFT (mN/m)				
			1	2	3	average	SD
1	0.0	I	N.D.	N.D.	N.D.	N.D.	x
2	0.5	I	0.103	0.104	0.101	0.103	0.002
3	1.0	III	0.054	0.058	0.056	0.056	0.002
4	1.5	III	0.065	0.065	0.065	0.065	0.000
5	2.0	III	0.036	0.035	0.035	0.035	0.001
6	2.5	III	N/A	N/A	N/A	N/A	x
7	3.0	III	N/A	N/A	N/A	N/A	x
8	3.5	III	N.D.	N.D.	N.D.	N.D.	x
9	4.0	III	N.D.	N.D.	N.D.	N.D.	x
10	4.5	III	N.D.	N.D.	N.D.	N.D.	x
11	5.0	III	N.D.	N.D.	N.D.	N.D.	x
12	5.5	II	N.D.	N.D.	N.D.	N.D.	x
13	6.0	II	N.D.	N.D.	N.D.	N.D.	x
14	6.5	II	N.D.	N.D.	N.D.	N.D.	x
15	7.0	II	N.D.	N.D.	N.D.	N.D.	x

N.D.* indicates value not determined

N/A** indicates value cannot measured

Table A-10 Interfacial tension of microemulsion system with 0.125 wt% $C_{12}EO_5$, 0.585 wt% NaCl and decane at different temperature.

No.	Temperature (^oC)	IFT (mN/m)				
		1	2	3	average	SD
1	25	0.574	0.576	0.578	0.576	0.002
2	30	0.240	0.240	0.240	0.240	0.000
3	35	0.254	0.258	0.254	0.255	0.002
4	40	0.282	0.282	0.282	0.282	0.000
5	45	0.284	0.287	0.285	0.285	0.002
6	50	0.367	0.368	0.367	0.367	0.001
7	55	0.349	0.350	0.351	0.350	0.001
8	60	0.767	0.766	0.767	0.767	0.001

Table A-11 Interfacial tension of microemulsion system with 0.125 wt% $C_{12}EO_5$, 0.585 wt% NaCl and hexadecane at different temperature.

No.	Temperature (^oC)	IFT (mN/m)				
		1	2	3	average	SD
1	25	1.484	1.485	1.486	1.485	0.001
2	30	0.565	0.566	0.566	0.566	0.001
3	35	0.376	0.376	0.374	0.375	0.001
4	40	0.440	0.442	0.442	0.441	0.001
5	45	0.269	0.273	0.271	0.271	0.002
6	50	0.396	0.395	0.396	0.396	0.000
7	55	0.606	0.605	0.605	0.605	0.001
8	60	0.634	0.635	0.636	0.635	0.001

Appendix B Experimental Data of Column Study.

Table B-1 Relationship between ADPODS concentration and absorbance measured by UV-VIS spectrophotometer.

wt% ADPODS	ADPODS Concentration (mg/L)	Area				
		1	2	Average	SD	%RSD
0	0	0.000	0.000	0.000	0.000	0.000
1	10000	0.108	0.108	0.108	0.000	0.000
3	30000	0.312	0.311	0.312	0.001	0.227
4	40000	0.388	0.389	0.389	0.001	0.182
5	50000	0.483	0.483	0.483	0.000	0.000

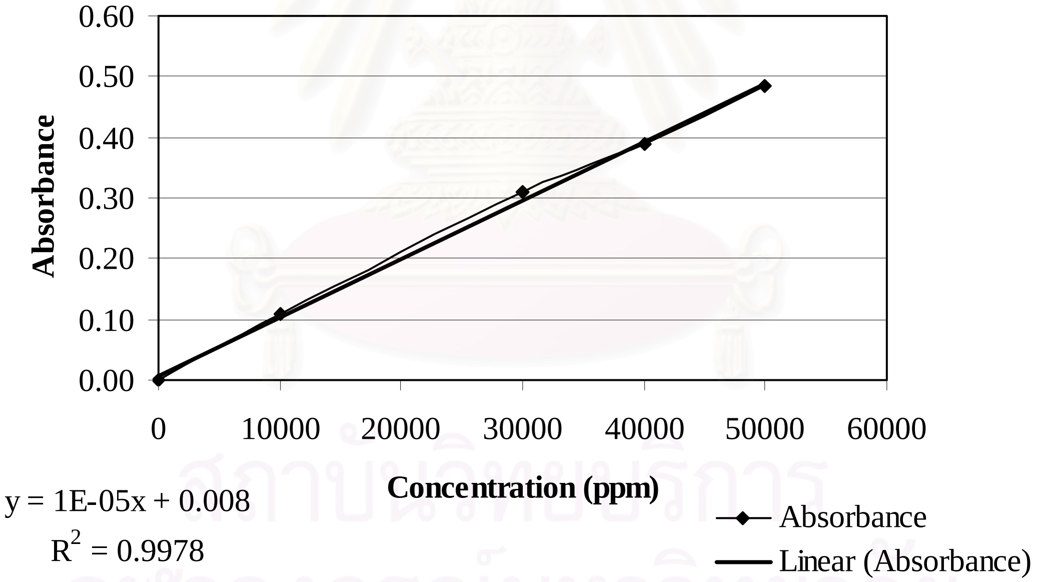

Figure B-1 Relationship between ADPODS concentration and absorbance measured by UV-VIS spectrophotometer.

Table B-2 Adsorption data of ADPODS on Ottawa sand.

Initial Concentration (ppm)	Ceq (ppm)			Blank (ppm)	Adsorption Concentration (ppm)			q (mg/g ottawa sand)				
	1	**2**	**3**		**1**	**2**	**3**	**1**	**2**	**3**	**Average**	**SD**
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10000	10000.00	9907.41	10000.00	10030.86	30.86	123.46	30.86	308.64	1234.57	308.64	617.28	534.58
20000	19935.79	20128.41	20032.10	20064.21	128.41	-64.21	32.10	1284.11	-642.05	321.03	321.03	963.08
30000	29951.85	29951.85	30048.15	30016.05	64.21	64.21	-32.10	642.05	642.05	-321.03	321.03	556.04
40000	40051.48	40051.48	40051.48	40085.80	34.32	34.32	34.32	343.20	343.20	343.20	343.20	0.00
50000	50103.52	50000.00	50103.52	50082.82	-20.70	82.82	-20.70	-207.04	828.16	-207.04	138.03	597.67

Table B-3 Relationship between PCE concentration and area measured by gas chromatography with headspace autosampler.

PCE Concentration (ppb)	Area				
	1	2	Average	SD	%RSD
0	0.00	0.00	0.00	0.00	0.00
100	228557.91	216765.18	222661.55	8338.72	3.75
250	578649.19	600959.48	589804.34	15775.76	2.68
500	1092376.32	1124127.61	1108251.97	22451.55	2.03
1000	2389186.17	2386492.19	2387839.18	1904.93	0.08

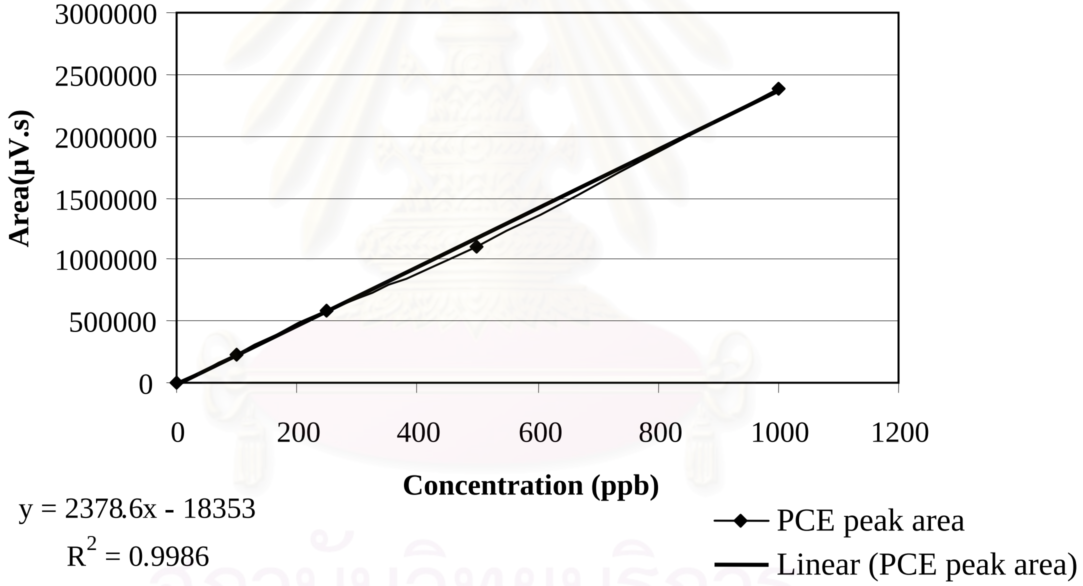

Figure B-2 Relationship between PCE concentration and area measured by gas chromatography with headspace autosampler.

Table B-4 PCE concentration and accumulation at different pore volume of column study flushing with surfactant gradient system.

No.	PV	PCE Concentration (ppm)						PCE Accumulation (ppm)
		1	2	3	Average	SD	%RSD	
1	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.6	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.8	1191.00	1234.00	1215.00	1213.33	21.55	1.78	1213.33
6	1.0	4043.00	3988.00	4400.00	4143.67	223.69	5.40	5357.00
7	1.2	5750.00	5857.00	5544.00	5717.00	159.09	2.78	11074.00
8	1.4	5421.00	5645.00	5371.00	5479.00	145.92	2.66	16553.00
9	1.6	6055.00	5913.00	5908.00	5958.67	83.46	1.40	22511.67
10	1.8	6943.00	7310.00	7211.00	7154.67	189.87	2.65	29666.33
11	2.0	10600.00	10781.00	10858.00	10746.33	132.45	1.23	40412.67
12	2.2	5739.00	5389.00	5547.00	5558.33	175.28	3.15	45971.00
13	2.4	5586.00	5551.00	5855.00	5664.00	166.33	2.94	51635.00
14	2.6	7343.00	7421.00	7250.00	7338.00	85.61	1.17	58973.00
15	2.8	13902.00	14028.00	13965.00	13965.00	63.00	0.45	72938.00
16	3.0	13176.00	13289.00	13163.00	13209.33	69.30	0.52	86147.33
17	3.2	17911.00	17514.00	18368.00	17931.00	427.35	2.38	104078.33
18	3.4	25923.00	26053.00	25013.00	25663.00	566.66	2.21	129741.33
19	3.6	24539.00	23842.00	24236.00	24205.67	349.49	1.44	153947.00
20	3.8	33154.00	32566.00	32633.00	32784.33	321.89	0.98	186731.33

Table B-4 (continue).

No.	PV	PCE Concentration (ppm)						PCE Accumulation (ppm)
		1	2	3	Average	SD	%RSD	
21	4.0	40057.00	43647.00	42390.00	42031.33	1821.68	4.33	228762.67
22	4.2	74708.00	72190.00	73682.00	73526.67	1266.17	1.72	302289.33
23	4.4	41054.00	41771.00	41969.00	41598.00	481.41	1.16	343887.33
24	4.6	49020.00	49950.00	51748.00	50239.33	1386.82	2.76	394126.67
25	4.8	61117.00	59596.00	58500.00	59737.67	1314.24	2.20	453864.33
26	5.0	37966.00	36922.00	38270.00	37719.33	707.04	1.87	491583.67
27	5.2	10084.00	10469.00	10225.00	10259.33	194.78	1.90	501843.00
28	5.4	5127.50	5388.00	5267.00	5260.83	130.36	2.48	507103.83
29	5.6	907.00	938.00	927.00	924.00	15.72	1.70	508027.83
30	5.8	901.00	907.00	892.00	900.00	7.55	0.84	508927.83
31	6.0	1212.00	1193.00	1209.00	1204.67	10.21	0.85	510132.50
32	6.2	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
33	6.4	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
34	6.6	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
35	6.8	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
36	7.0	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
37	7.2	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
38	7.4	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
39	7.6	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
40	7.8	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
41	8.0	0.00	0.00	0.00	0.00	0.00	0.00	510132.50

Table B-4 (continue).

No.	PV	PCE Concentration (ppm)						PCE Accumulation (ppm)
		1	2	3	Average	SD	%RSD	
42	8.2	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
43	8.4	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
44	8.6	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
45	8.8	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
46	9.0	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
47	9.2	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
48	9.4	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
49	9.6	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
50	9.8	0.00	0.00	0.00	0.00	0.00	0.00	510132.50
51	10.0	0.00	0.00	0.00	0.00	0.00	0.00	510132.50

Table B-5 PCE concentration and accumulation at different pore volume of column study flushing without surfactant gradient system.

No.	PV	PCE Concentration (ppm)						PCE Accumulation (ppm)	PCE Mobilization (mL)	Accumulate PCE mobilization (g)
		1	2	3	Average	SD	%RSD			
1	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	1.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	1.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	1.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	1.6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	1.8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11	2.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12	2.2	997	1034	1010	1013.67	18.77	1.85	1.85	0.05	81.15
13	2.4	1243	1388	1300	1310.33	73.05	5.57	7.43	0.07	194.76
14	2.6	2750	2837	2555	2714.00	144.41	5.32	12.75	0.08	324.6
15	2.8	3012	3057	3183	3084.00	88.64	2.87	15.62	0.09	470.67
16	3.0	3144	3211	3105	3153.33	53.61	1.70	17.32	0.12	665.43
17	3.2	4179	4310	4291	4260.00	70.79	1.66	18.98	0.27	1103.64
18	3.4	4676	4731	4583	4663.33	74.81	1.60	20.59	0.43	1801.53
19	3.6	4598	4451	4587	4545.33	81.88	1.80	22.39	0.5	2613.03

Table B-5 (continue).

No.	PV	PCE Concentration (ppm)						PCE Accumulation (ppm)	PCE Mobilization (mL)	Accumulate PCE mobilization (g)
		1	2	3	Average	SD	%RSD			
20	3.8	5098	5115	5077	5096.67	19.04	0.37	22.76	0.62	3619.29
21	4.0	4697	4479	4545	4573.67	111.79	2.44	25.21	0.67	4706.7
22	4.2	3952	3897	3927	3925.33	27.54	0.70	25.91	0.65	5761.65
23	4.4	3577	3310	3583	3490.00	155.91	4.47	30.38	0.2	6086.25
24	4.6	3035	2942	3197	3058.00	129.05	4.22	34.60	0.1	6248.55
25	4.8	2141	2217	2196	2184.67	39.25	1.80	36.39	0.04	6313.47
26	5.0	1884	1798	1867	1849.67	45.54	2.46	38.85	0.03	6362.16
27	5.2	1109	1035	1083	1075.67	37.54	3.49	42.34	0.04	6427.08
28	5.4	998	973	924	965.00	37.64	3.90	46.25	0	6427.08
29	5.6	826	839	831	832.00	6.56	0.79	47.03	0	6427.08
30	5.8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
31	6.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	6.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
33	6.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
34	6.6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
35	6.8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
36	7.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
37	7.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
38	7.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
39	7.6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40	7.8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table B-5 (continue).

No.	PV	PCE Concentration (ppm)						PCE Accumulation (ppm)	PCE Mobilization (mL)	Accumulate PCE mobilization (g)
		1	2	3	Average	SD	%RSD			
41	8.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42	8.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
43	8.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
44	8.6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
45	8.8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
46	9.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
47	9.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
48	9.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
49	9.6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	9.8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
51	10.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix C Experimental Data of Washing Study

Table C-1 Relationship between decane concentration and absorbance measured by UV-VIS spectrophotometer.

PCE Concentration (ppm)	Area				
	1	2	Average	SD	%RSD
0	0.000	0.000	0.000	0.000	0.000
1000	0.081	0.082	0.082	0.001	0.868
2000	0.153	0.153	0.153	0.000	0.000
3000	0.235	0.234	0.235	0.001	0.302
4000	0.321	0.320	0.321	0.001	0.221
5000	0.398	0.398	0.398	0.000	0.000
6000	0.477	0.477	0.477	0.000	0.000
7000	0.557	0.557	0.557	0.000	0.000
8000	0.643	0.643	0.643	0.000	0.000
9000	0.714	0.714	0.714	0.000	0.000
10000	0.781	0.780	0.781	0.001	0.091

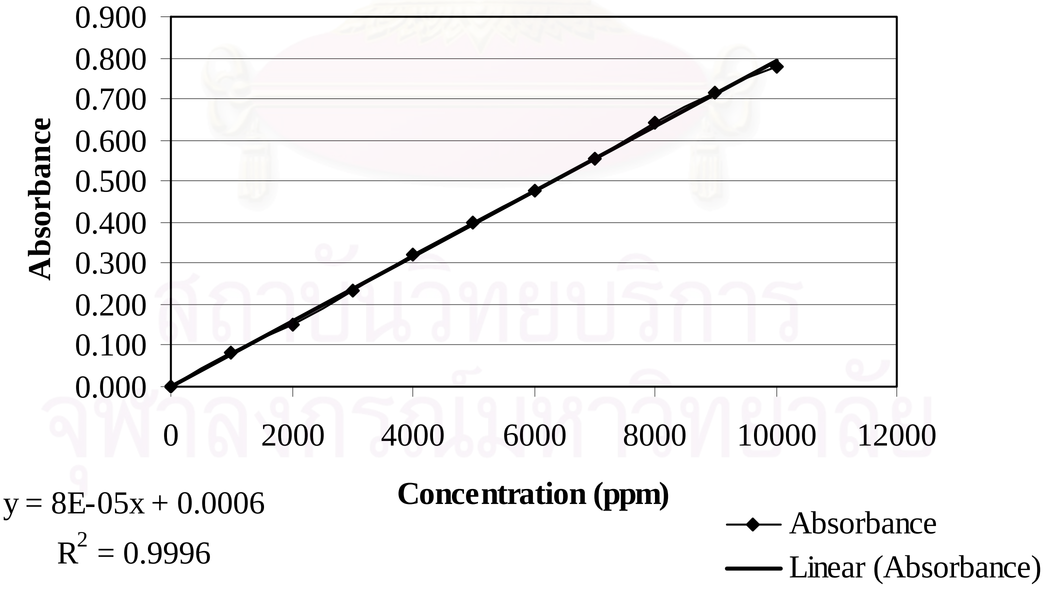

Figure C-1 Relationship between decane concentration and absorbance measured by UV-VIS spectrophotometer.

Table C-2 Relationship between hexadecane concentration and absorbance measured by UV-VIS spectrophotometer.

PCE Concentration (ppm)	Area				
	1	2	Average	SD	%RSD
0	0.000	0.000	0.000	0.000	0.000
1000	0.083	0.084	0.084	0.001	0.847
2000	0.158	0.157	0.158	0.001	0.449
3000	0.239	0.239	0.239	0.000	0.000
4000	0.315	0.315	0.315	0.000	0.000
5000	0.396	0.397	0.397	0.001	0.178
6000	0.476	0.476	0.476	0.000	0.000
7000	0.546	0.545	0.546	0.001	0.130
8000	0.627	0.627	0.627	0.000	0.000
9000	0.713	0.713	0.713	0.000	0.000
10000	0.795	0.795	0.795	0.000	0.000

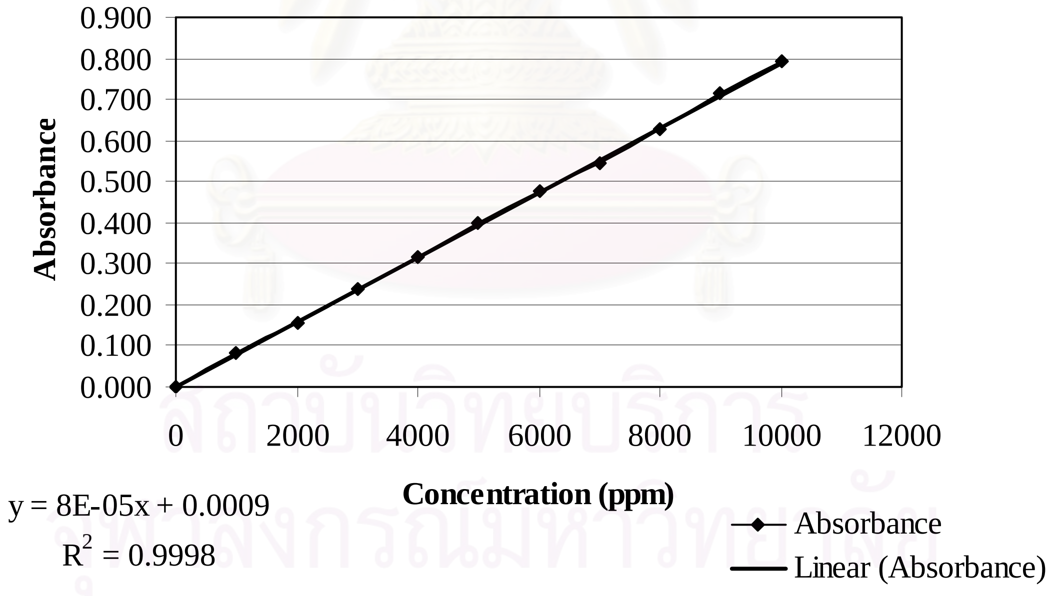

Figure C-2 Relationship between hexadecane concentration and absorbance measured by UV-VIS spectrophotometer.

Table C-3 Concentration of decane removal from polyester/cotton blend fabric at different temperature and other washing condition.

No.	Temperature (°C)	Condition	Absorbance				Concentration (ppm)						
			1	2	3	4	1	2	3	4	Average	SD	%RSD
1	30 to 45	Surfactant wash	0.039	0.044	0.046	0.042	491.524	559.158	582.751	526.875	540.077	39.652	7.342
2		Mix oils wash	0.047	0.042	x	x	587.965	532.815	x	x	560.390	38.997	6.959
3		Water wash	0.336	0.324	0.342	0.348	4242.247	4091.698	4321.964	4387.545	4260.864	127.469	2.992
4		Water wash with mix oils	0.371	0.405	x	x	4682.929	5105.810	x	x	4894.370	299.022	6.110
5		Unwash fabrics	0.565	0.530	0.527	x	7126.595	6683.055	6647.309	x	6818.986	266.996	3.915
6	45	Surfactant wash	0.056	0.049	0.058	0.056	712.969	612.951	734.164	705.328	691.353	53.672	7.763
7		Mix oils wash	0.067	0.058	x	x	844.349	832.090	x	x	838.220	8.668	1.034
8		Water wash	0.434	0.462	0.396	0.414	5479.609	5827.529	4993.330	5225.920	5381.597	357.514	6.643
9		Water wash with mix oils	0.382	0.383	x	x	4825.849	4836.621	x	x	4831.235	7.617	0.158
10		Unwash fabrics	0.529	0.491	0.512	x	6680.013	6191.846	6463.790	x	6445.216	244.613	3.795
11	40	Surfactant wash	0.053	0.050	0.049	0.052	670.509	627.821	613.036	656.430	641.949	26.210	4.083
12		Mix oils wash	0.071	0.066	x	x	890.150	827.185	x	x	858.668	44.523	5.185
13		Water wash	0.437	0.407	0.452	0.459	5518.114	5131.917	5699.788	5789.837	5534.914	291.466	5.266
14		Water wash with mix oils	0.442	0.482	x	x	5575.382	6085.330	x	x	5830.356	360.588	6.185
15		Unwash fabrics	0.615	0.638	0.587	x	7766.147	8055.850	7410.087	x	7744.028	323.449	4.177
16	35	Surfactant wash	0.054	0.055	0.054	0.065	687.332	688.848	687.307	722.611	696.525	17.406	2.499
17		Mix oils wash	0.069	0.072	x	x	873.915	906.420	x	x	890.168	22.985	2.582
18		Water wash	0.417	0.437	0.410	0.408	5266.029	5517.304	5171.524	5153.643	5277.125	167.539	3.175
19		Water wash with mix oils	0.409	0.443	x	x	5160.805	5586.929	x	x	5373.867	301.315	5.607
20		Unwash fabrics	0.517	0.497	0.487	x	6529.007	6274.323	6141.227	x	6314.852	197.041	3.120

Table C-3 (continue).

No.	Temperature (^oC)	Condition	Absorbance				Concentration (ppm)						
			1	2	3	4	1	2	3	4	Average	SD	%RSD
21	30	Surfactant wash	0.076	0.087	0.086	0.080	956.972	1091.954	1089.052	1011.012	1037.248	65.343	6.300
22		Mix oils wash	0.089	0.082	x	x	1127.547	1035.373	x	x	1081.460	65.177	6.027
23		Water wash	0.452	0.484	0.491	0.484	5699.618	6104.812	6197.684	6106.515	6027.157	222.628	3.694
24		Water wash with mix oils	0.448	0.474	x	x	5656.174	5984.028	x	x	5820.101	231.828	3.983
25		Unwash fabrics	0.613	0.629	0.549	x	7734.454	7939.170	6924.706	x	7532.777	536.460	7.122

Table C-4 %Decane removal from polyester/cotton blend fabric at different temperature and other washing condition.

Temperature (^oC)	% oil removal			
	surfactant washing	water washing	surfactant washing with mix oils	water washing with mix oils
30	86.23	27.63	85.64	22.74
35	88.97	16.43	85.90	14.90
40	91.71	28.53	88.91	24.71
45	89.27	16.50	86.99	25.04
30 to 45	92.08	37.51	91.78	28.22

Table C-5 Hexadecane removal from polyester/cotton blend fabric at different temperature and other washing condition.

No.	Temperature (^{o}C)	Condition	Absorbance				Concentration (ppm)						
			1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**Average**	**SD**	**%RSD**
1	30 to 45	Surfactant wash	0.060	0.068	0.071	0.065	762.300	860.270	901.550	822.280	836.600	59.173	7.073
2		Mix oils wash	0.069	0.064	x	x	870.740	804.410	x	x	837.575	46.902	5.600
3		Water wash	0.262	0.240	0.274	0.270	3310.730	3042.000	3466.480	3415.600	3308.703	189.257	5.720
4		Water wash with mix oils	0.258	0.253	x	x	3260.760	3207.250	x	x	3234.005	37.837	1.170
5		Unwash fabrics	0.460	0.485	0.440	x	5822.070	6104.720	5566.990	x	5831.260	268.983	4.613
6	45	Surfactant wash	0.053	0.051	0.054	0.051	673.800	643.530	687.860	645.870	662.765	21.656	3.268
7		Mix oils wash	0.059	0.049	x	x	751.220	624.290	x	x	687.755	89.753	13.050
8		Water wash	0.264	0.284	0.285	0.295	3338.980	3593.980	3610.250	3738.390	3570.400	167.252	4.684
9		Water wash with mix oils	0.313	0.325	x	x	3965.020	4107.070	x	x	4036.045	100.445	2.489
10		Unwash fabrics	0.490	0.517	0.458	x	6197.900	6535.350	5796.690	x	6176.647	369.788	5.987
11	40	Surfactant wash	0.069	0.076	0.083	0.067	869.750	957.040	1056.070	849.190	933.013	94.426	10.121
12		Mix oils wash	0.077	0.081	x	x	972.320	1029.260	x	x	1000.790	40.263	4.023
13		Water wash	0.301	0.318	0.333	0.294	3805.100	4018.060	4207.630	3723.870	3938.665	218.038	5.536
14		Water wash with mix oils	0.323	0.314	x	x	4082.260	3970.840	x	x	4026.550	78.786	1.957
15		Unwash fabrics	0.445	0.465	0.387	x	5628.120	5879.810	4898.840	x	5468.923	509.493	9.316
16	35	Surfactant wash	0.095	0.087	0.079	0.069	1199.610	1098.240	1001.070	876.920	1043.960	137.738	13.194
17		Mix oils wash	0.068	0.077	x	x	863.100	977.930	x	x	920.515	81.197	8.821
18		Water wash	0.293	0.308	0.309	0.304	3711.820	3898.260	3906.560	3848.190	3841.208	90.029	2.344
19		Water wash with mix oils	0.304	0.296	x	x	3852.160	3747.550	x	x	3799.855	73.970	1.947
20		Unwash fabrics	0.505	0.501	0.419	x	6394.730	6337.320	5301.550	x	6011.200	615.245	10.235

Table C-5 (continue).

No.	Temperature (^{o}C)	Condition	Absorbance				Concentration (ppm)						
			1	2	3	4	1	2	3	4	Average	SD	%RSD
21	30	Surfactant wash	0.108	0.099	0.101	0.108	1360.760	1247.070	1274.120	1363.460	1311.353	59.651	4.549
22		Mix oils wash	0.104	0.091	x	x	1315.330	1147.370	x	x	1231.350	118.766	9.645
23		Water wash	0.353	0.384	0.365	0.360	4460.000	4852.820	4620.820	4558.800	4623.110	166.846	3.609
24		Water wash with mix oils	0.364	0.392	x	x	4601.850	4694.010	x	x	4647.930	65.167	1.402
25		Unwash fabrics	0.475	0.568	0.546	x	6009.970	7190.960	6913.150	x	6704.693	617.475	9.210

Table C-6 %Hexadecane removal from polyester/cotton blend fabric at different temperature and other washing condition.

Temperature (^{o}C)	% oil removal			
	surfactant washing	water washing	surfactant washing with mix oils	water washing with mix oils
30	80.44	31.05	81.63	30.68
35	82.63	36.10	84.69	36.79
40	82.94	27.98	81.70	26.37
45	89.27	42.20	88.87	34.66
30 to 45	85.65	43.26	85.64	44.54

Appendix D Experimental Data of Dynamic Interfacial Tension Study.

Table D-1 Dynamic interfacial tension of a 0.125 wt% $C_{12}EO_5$ and 0.585 wt% NaCl with decane.

Temperature (^oC)	Interfacial Tension (mN/m)					
	Time (min)					
	1	2	3	4	5	6
25	1.260	1.244	1.215	1.206	1.194	1.178
30	0.798	0.802	0.798	0.797	0.783	0.770
35	0.422	0.411	0.398	0.398	0.389	0.390
40	0.353	0.336	0.335	0.339	0.326	0.326
45	0.321	0.318	0.314	0.304	0.289	0.278
50	0.407	0.422	0.411	0.401	0.374	0.345
55	0.620	0.632	0.610	0.576	0.543	0.512
60	0.594	0.600	0.586	0.566	0.545	0.536

Table D-2 Dynamic interfacial tension of a 0.125 wt% $C_{12}EO_5$ and 0.585 wt% NaCl with hexadecane.

Temperature (^oC)	Interfacial Tension (mN/m)					
	Time (min)					
	1	2	3	4	5	6
25	2.124	2.020	1.937	1.860	1.821	1.802
30	1.448	1.412	1.357	1.311	1.256	1.212
35	0.959	0.925	0.884	0.850	0.809	0.764
40	0.670	0.633	0.601	0.565	0.539	0.523
45	0.302	0.301	0.299	0.297	0.295	0.294
50	0.274	0.267	0.267	0.267	0.263	0.259
55	0.195	0.196	0.196	0.194	0.193	0.200
60	0.210	0.211	0.205	0.208	0.212	0.200

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