การเพิ่มการละลายโดยสารลดแรงตึงผิวเพื่อการบำบัดสารประกอบโลหะอินทรีย์

นายศีลาวุธ ดำรงศิริ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2553

SURFACTANT ENHANCED SOLUBILIZATION FOR ORGANOMETALLIC COMPOUND REMOVAL

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A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Environmental Management
(Interdisciplinary Program)
Graduate School
Chulalongkorn University
Academic Year 2010

Thesis Title	SURFACTANT ENHANCED SOLUBILIZATION FOR ORGANOMETALLIC COMPOUND REMOVAL
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ศีลาวุธ ดำรงศิริ : การเพิ่มการละลายโดยสารลดแรงตึงผิวเพื่อการบำบัดสารประกอบโลหะอินทรีย์. (SURFACTANT ENHANCED SOLUBILIZATION FOR ORGANOMETALLIC COMPOUND REMOVAL) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ. ดร. จันทรา ทองคำเภา, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม:ดร. ปัญจพร เวชยันต์วิวัฒน์, Prof. David A Sabatini, Ph.D., จำนวนหน้า 184 หน้า.

งานวิจัยนี้มีเป้าหมายเพื่อบำบัดพื้นที่ปนเปื้อนสารประกอบโลหะอินทรีย์ ด้วยเทคนิคการใช้สารลดแรงตึงผิวโดยใช้กลไกการละลาย เตตระเอทิลเลท (ทีอีแอล)เป็นสารปนเปื้อนที่ต้องการศึกษา แต่เนื่องจากความเป็นพิษและความยุ่งยากในการใช้งาน จึงจำเป็นต้องมีการศึกษาเพื่อหาสารที่จะใช้เป็นสารตัวแทนของทีอีแอลในการทดลอง ทีอีแอลได้ถูกวิเคราะห์ในเบื้องต้นเพื่อหาค่าคาร์บอนสายตรงเทียบเท่า (อีเอซีเอ็น) ของทีอีแอล โดยอีเอซีเอ็นเป็นเกณฑ์ตัวหนึ่งในการเลือกตัวแทน ซึ่งพบว่าทีอีแอลมีค่าอีเอซีเอ็นอยู่ในช่วง 6.04 ถึง 7.68 จากคุณลักษณะที่เป็นสารประกอบโลหะอินทรีย์ ไดบิวทิวตินไดคลอไรด์ (ดีบีที) ถูกคัดเลือกมาเป็นตัวแทน - และเพื่อให้ได้อีเอซีเอ็นใกล้เคียงกับทีอีแอล สารตัวแทนคือสารผสมของไดบิวทิวตินไดคลอไรด์ (ดีบีที) กับเดกเคนที่อัตราส่วนโมล เท่ากับ 0.038 ต่อ 0.962 และสารผสมของดีบีทีกับเปอร์คลอโรเอทิลีนที่อัตราส่วนโมลที่เท่ากัน

สารลดแรงตึงผิวหลายระบบได้ถูกทดลองเพื่อทดสอบการเกิดไมโครอิมัลชันกับสารตัวแทน ระบบของสารละลายที่ถูกคัดเลือกคือ โซเดียมไดเฮกซิลซัลโฟซักซิเนต 3.6 เปอร์เซ็นต์โดยน้ำหนัก กับ โมโนแอลคิลไดฟีนิลออกไซด์ไดซัลโฟเนต 0.4 เปอร์เซ็นต์โดยน้ำหนัก ผลการทดลองชี้ให้เห็นว่าพีซีอีและเดกเคนถูกละลายเข้าไปที่ส่วนในของไมเซล-ทั้งในระบบสารเดี่ยวและสารผสม ลักษณะของไอโซเทอมของการละลายของดีบีทีชี้ว่า ดีบีทีถูกละลายที่พื้นผิวของไมเซลในระบบสารเดี่ยว การละลายของดีบีทีสูงขึ้นเมื่อผสมกับพีซีอีหรือเดกเคนซึ่งน่าจะเกิดจากการที่สารทั้งสองช่วยละลายดีบีทีให้เข้าไปอยู่ในส่วนในของไมเซล จึงสามารถสรุปได้ว่าดีบีทีมีพฤติกรรมการละลายคล้ายกับสารประกอบอินทรีย์ที่มีขั้ว

การละลายของพีซีอีและเดกเคนในสารละลายช่วงไหลออกในการทดลองแบบคอลัมน์มีความสัมพันธ์กับของความสามารถในการละลายของทั้งสอง และสามารถอธิบายได้ด้วยกลไกที่เกิดขึ้นเช่นเดียวกับการศึกษาในระบบไม่ต่อเนื่อง แต่ในกรณีของดีบีทีผลที่เกิดขึ้นไม่สามารถอธิบายได้ด้วยกลไกที่พบจากการศึกษาในระบบไม่ต่อเนื่อง ทั้งนี้พบว่าการละลายของดีบีทีนั้นต่ำมาก และเทคนิคแบบเกรเดียนไม่สามารถเพิ่มการละลายของดีบีทีในการทดลองแบบคอลัมน์ได้

การดูดซับของดีบีทีบนพื้นผิวของทรายเป็นสาเหตุของการละลายที่น้อยมากของดีบีที การทดลองเพื่อลดดูดซับของดีบีทีจึงดำเนินการ โดยการปรับค่าพีเอชของสารละลายของสารละแรงตึงผิวให้เป็นกรดแรง (พีเอช 1) ซึ่งทำให้ดีบีทีอยู่ในรูปของประจุบวก และเปลี่ยนพื้นผิวของทรายมีประจุบวก นอกจากนี้มีการทดลองที่ค่าพีเอชไปที่ 4 และ 9 พบว่าไม่สามารถทำให้ประสิทธิภาพการบำบัดดีบีทีเพิ่มขึ้นได้ ดังนั้นกล่าวได้ว่า การบำบัดสารผสมของดีบีทีโดยกลไกการละลายอาจไม่เหมาะสมหากตัวกลางเป็นทรายซึ่งเป็นซิลิกอนออกไซด์นั้นมีพื้นผิวเป็นลบตามธรรมชาติ.

สาขาวิชา การจัดการสิ่งแวดล้อม
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4989695920 : MAJOR ENVIRONMENTAL MANAGEMENT
KEYWORDS : SURFACTANT / MICROEMULTION / SOLUBILIZATION / ORGANOMETALLIC COMPOUND / DIBUTYLTIN DICHLORIDE

SEELAWUT DAMRONGSIRI: SURFACTANT ENHANCED SOLUBILIZATION FOR ORGANOMETALLIC COMPOUND REMOVAL.
THESIS ADVISOR: ASST. PROF. CHANTRA TONGCUMPOU, Ph.D.,
THESIS CO-ADVISORS: PUNJAPORN WESCHAYANWIWAT, Ph.D., PROF. DAVID A SABATINI, Ph.D., 184 pp.

The study was aimed to find the approach to clean up the contaminated site by surfactant flushing technique based on the solubilization mechanism. Even tetraethyl lead (TEL) is a focused contamination in this study, TEL surrogate was needed to be identified and used instead of TEL due to its toxicity and troublesome handling. The equivalent alkane carbon number (EACN) of TEL was determined and found to be about 6.04 to 7.68. This EACN value had been used as one of criteria for proper surrogate selection. Dibutyltin dichloride (DBT) was selected based on designed criteria of being organometallic compound. The surrogate oils were then prepared as the mixture of DBT and decane at the molar ratio of 0.038:0.962 and mixture of DBT and perchloroethylene (PCE) at the same ratio.

Various surfactants systems were tested to form a microemulsion with these surrogate oils. The selected surfactant solution was 3.6 wt.% sodium dihexyl sulfosuccinate and 0.4 wt.% monoalkyl diphenyloxide disulfonates. The solubilization study revealed that PCE and decane were solubilized into the core of these surfactant micelles in both single and mixed oil systems. The solubilization isotherm of DBT suggested that DBT solubilizes near the surface of the micelles in a single oil system. The DBT solubilization was increased if mixed with PCE or decane indicating that those oils may help facilitating the DBT into the core of micelles. It may be concluded that the DBT behaves like a polar organic compound.

The solubilization of PCE and decane were quantified from the effluent stream in the column experiment and compared the result to their solubilization capacity. The mechanism of solubilization of PCE and decane can be explained following the behavior found in batch study. However not for the case of DBT that the solubilization was found extremely low. Moreover, the gradient technique could not enhance the solubilization of DBT.

The adsorption of DBT onto sand surface was a major cause to limit DBT solubilization. The adsorption of DBT could be minimized by altering pH of surfactant solution to the very acidic condition (pH 1), where the DBT is a cationic form and the surface of sand possesses positively charges but this strong acidic condition is not applicable in an actual site remediation. At pH 4 and pH 9, the DBT removal efficiency was not promising. Thus, the removal of DBT-PCE mixture by solubilization was improper to be applied if the media naturally possess negative surface charge such as sand and silicon oxide.

Field of Study : Environmental Management Student's Signature Seelawut D.
Academic Year : 2010 Advisor's Signature ....
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ACKNOWLEDGEMENTS

I would like to express my gratitude to, Assistant Professor Dr. Chantra Tongcunpou my advisor and Dr. Punjaporn Weschayanwiwat and Professor David A Sabatini my co-advisors for their valuable suggestion, encouragement, and supports throughout my study.

My gratitude is also extended to Assistant Professor Dr. Manaskorn Rachakornkij, Dr. Aranya Fuangswasdi, Assistant Professor Dr. Ekawan Leupromchai, and Professor Dr. Chongrak Polprasert, for serving as thesis committee, for their recommendations and also useful suggestions.

Thanks to National Center of Excellence for Environmental and Hazardous Waste Management, Chulalongkorn University for the full scholarship and partially funding for the thesis work and all useful supporting facilities. THE 90th ANNIVERSARY OF CHULALONGKORN UNIVERSITY FUND (Ratchadaphiseksomphot Endowment Fund). The study was also funded by DuPont Company which gave me a great experience as a part of a tetraethyl lead remediation project.

I would like to express my sincere gratitude to Miss Chantana Intim, Miss Benjawan Noinumnon, and staffs of the NCE-EHWM for the helpful, knowledge and some laboratory technique. Thanks to Mr. Chaiwat Rongsayamanont for some suggestions and Ms. Lada Mathurasa for the aquifer material and facilitating information. In addition, I would like to thank all my friends for their friendly help and suggestions.

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LIST OF ABBREVIATIONS

°C	Degree celsius
μL	Microliter
ACN	Alkane carbon number
C16DPDS	monoalkyl diphenyloxide disulfonates
$Ca(NO_3)_2$	Calcium nitrate
$CaCl_2$	Calcium chloride
cm	Centimeter
CMC	Critical micelle concentration
DBT	Dibutyltin dichloride
DI	Deionized water
DNAPL	Dense non-aqueous phase liquid
EACN	Equivalent alkane carbon number
g	Gram
g/mL	Gram per milliliter
g/mole	Gram per mole
HCl	Hydrochloric acid
HLB	Hydrophile-lipophile balance
HNO_3	Nitric acid
IFT	Interfacial tension
L	Liter
LNAPL	Light non-aqueous phase liquid
M	Molar
mg	Milligram
mg tin/L	Milligram as tin per liter
mg/kg	Milligram per kilogram
mg/L	Milligram per liter
min	Minute
mL	Milliliter
mM	Millimolar
MW	Molecular weight

NaCl	Sodium chloride
NaOH	Sodium hydroxide
NAPL	Non-aqueous phase liquid
PCE	Tetrachloroethylene or Perchloroethylene
PV	Pore volume
PZC	Point of zero charge
RSD	Relative standard deviation
SDHS	Sodium dihexyl sulfosuccinate or Aerosal-MA
SDOS	Sodium dioctyl sulfosuccinate or Aerosal-OT
SEAR	Surfactant enhanced aquifer remediation
SP	Solubilization parameter
TCE	Trichloroethylene
TEL	Tetraethyl lead
wt.%	Percent weight by weight

CHAPTER I
INTRODUCTION

1.1 Introduction

Organometallic compounds are the compounds containing chemical bonds between a carbon and metal. Organometallic compounds have practical uses in many industries. In the old days, tetraethyl lead (TEL) was mixed with gasoline to help reduce knocking in automobiles. Due to the toxicity of lead, it is no longer used and has been replaced by other organometallic compounds such as ferrocene or methylcyclopentadienyl manganese tricarbonyl (MMT) (USEPA, 1999). The spillage of highly toxic organometallic compounds that occurs during the production, transportation, use, and disposal stages causes severe soil and groundwater contamination.

Tetraethyl lead is an organometallic substance that had been used as an additive in gasoline to raise the octane number. Since it can cause severe health effects, especially to child development, the United States Environmental Protection Agency (US EPA) has been phasing out this poisonous substance since 1973. However, the soil and groundwater associated with several TEL production plants remain contaminated (US EPA, 1999). A site containing an old TEL production plant of the DuPont Company was used in a case study of this type of contamination. TEL and its solvent leaked and seeped to the complex aquifer in the underground. Nowadays, many pumping wells still remain in operation to prevent that harmful organometallic compound from leaking out of the controlled contaminated area. This type of contamination shows up in many types of sites such as abandon gas stations and storage sites, where an effective remediation technique needs to be applied. Even TEL could be degraded chemically and biologically, the degradation via microorganism seems to be limited on the triethyl lead (Gallert et al., 2002 and 2004). The chemical oxidation was also studied (Andreottola et al., 2008) however, it seems not be suitable for the in-situ remediation. Thus, the removal of organometallic compounds such as TEL from the subsurface is a challenge approach.

Surfactant enhanced aquifer remediation (SEAR) using a microemulsion technique has been applied to remediate organic contamination over the past decade (Shiau et al., 1996; Dwarakanath et al., 1999; Sabatini et al., 2000; Wu et al., 2000, 2001; Childs et al., 2004). To investigate the remediation of TEL from a contaminated site using microemulsion, a TEL surrogate is needed because TEL is troublesome to handle.

The first part of the study was to indentify a surrogate to be used in place of TEL. Three criteria were identified to represent the intrinsic properties of TEL: (1) being an organometallic compound, (2) having a similar equivalent alkane carbon number (EACN), and (3) having a similar density.

Organotin compounds have been used as catalysts, stabilizers in plastic industries, and wood preservatives, and in agricultural biocides and antifouling paints for ship hulls. Dibutyltin dichloride (DBT), an organotin compound, is a promising TEL surrogate due to its toxicity, which is less than TEL's, along with its lower cost availability in market, thus making DBT much safer to work with and easier to obtain than TEL. DBT is an organotin commonly used as a stabilizer in polyvinyl chloride (PVC) products such as packaging materials, bottles, pipes, and mouldings; in manufacturing processes; and as the catalyst in many chemical reactions. From widely use in industries resulted DBT be extensively distributed and contaminated in the environment (RPA, 2003).

The second part of this work demonstrates the surfactant's ability to form microemulsions with an oil surrogate and describes the solubilization behavior of DBT. Four surfactants were applied to form the microemulsion solution with the oil surrogate. The third part provides a simulation of the remediation of a contaminated aquifer using a column experiment. The initial amounts of the trapped surrogate oil, the mobilization of the surrogate oil, and the solubilization in the effluent solution were investigated to evaluate the removal efficiency of the treatment system. Finally, the pH was altered to minimize the adsorption of DBT to the sand surface.

To summarize an overall work, a surrogate for TEL was investigated based on the three intrinsic properties of TEL. Then, the surfactant solutions capable of forming microemulsions with the TEL surrogate were investigated and tested to determine their efficiency in column experiment simulations. The ultimate objectives of this work are to identify the best approach and for cleaning out contaminated soil by SEAR using solubilization mechanism.

CHAPTER II of this thesis is the theoretical backgrounds required to understand the content in following chapters. The CHAPTER III summarizes all chemical and materials applied in this study. The overall methods used in the experiment were included in this chapter. For CHAPTER IV, V, VI, and VII, they had been written as manuscript format for each experimental part which included introduction, materials, method, and result within each chapter. CHAPTER VIII is the overall conclusion of this study and recommendation for future work.

1.2 Objectives of the study

The primary objective of this research is to clean up the organometallic compound (in case of TEL) contaminated soil using a surfactant enhanced aquifer remediation technique using the solubilization mechanism. The trapped compound in the subsurface must be released and solubilized into the surfactant solution, which can be extracted to the treatment plant above ground. The sub-objectives are as follows:

1. To identify the proper TEL's surrogate for the preliminary study based on it being an organometallic compound with a similar EACN and similar density.
2. To identify suitable surfactant microemulsion systems in the presence of each TEL's surrogate.
3. To observe the effects of an organometallic compound on solubilization by a surfactant microemulsion solution in batch and column studies.
4. To remove the TEL's surrogate using microemulsion in the column study.
5. To investigate the effects of the gradient approach on TEL's surrogate removal.

1.3 Hypotheses

Suitable surfactant microemulsion solutions can release the trapped organometallic compound (TEL's surrogate) and its metabolites from soil pores and enabling them to be solubilized into the surfactant micelles.

1.4 Scope of study

The overall work can be divided into five parts.

1.4.1 TEL surrogate investigation

Due to TEL is a very toxic compound, complicated provision and difficult to handle, the surrogate of TEL was designed to be used instead of TEL. This first phase of the investigation aims to find the proper surrogate for TEL in order to investigate the solubilization potential and solubilization behavior of the organometallic compound. The metal atom contained in the molecule of the contaminant may have an effect on its solubilization into surfactant micelles, and since organometallic compounds generally posses their metabolites, the surrogate in the study should be an organometallic compound. The EACN is a parameter indicating the oil's hydrophobicity. It is very important that a compound posses the same EACN usually able to form the same microemulsion using the same surfactant system. Therefore, having an equivalent EACN and being organometallic were important parameters in order to find the proper surfactant system capable of forming microemulsions with TEL. Another important property in the remediation of a contaminated site is the density of the contaminant. The density of the surrogate should, therefore, be similar to that of TEL to imitate the vertical migration problem in the column experiment. Thus, the threefold criterion was used for selecting the surrogate: (1) being organometallic, (2) being DNAPL, and (3) having a similar EACN as TEL.

The EACN of TEL and the surrogate was determined by a method proposed by Salager et al. (1979). Four known ACN hydrocarbon compounds (pentane, hexane, octane, and decane) were used to establish the empirical relation between the EACN and S* of the surfactant system following Salager's equation. From this empirical relation along with the S* of the TEL mixture, the EACN of TEL can be calculated.

Based on the first criteria, DBT was selected for this study as a surrogate since it is an organometallic compound and DNAPL; it is also widely used and less toxic compared to TEL. However, because DBT is solid at room temperature and has a very low EACN, thus, it had to be mixed with another oil to increase the EACN to be close to that of TEL. Therefore, DBT was mixed with another oil to obtain the other appropriate properties according to our criteria for being used as a TEL surrogate. In case, PCE and decane were used to mix with DBT describing in CHAPTER III.

1.4.2 Phase behavior study

Many surfactant solubilization studies have focused on organic contaminants but it is rare to find one on organometallic compounds. The phase behavior study of the microemulsion was performed to understand the behavior of the surfactant with the surrogate oil. The desired behavior is a type I microemulsion (oil in water) to type III microemulsion (middle phase). From a practical standpoint, it is most important that the system must be type I so that the oil solubilizes into the water phase. Type III also could be applied but the notably low IFT must be considered.

1.4.3 Solubilization study

The solubilization of each compound by the surfactant system was measured. In the experiment with the mixed oil, the solubilization of each compound was quantified separately. The DBT was measured as total tin. Then the solubilization of each compound was discussed. Our preliminary study showed that the phase behavior remained the same between days 2 to 4, after that, such behavior changed and it was irreversible, which may had been caused by degradation. Thus, to prevent this type of uncertainly, the solubilization of the system was evaluated after 2 days.

1.4.4 Column experimental study

This phase of the study simulated a lab-scale treatment to observe the performance of the selected surfactant solution. The column experiments were simply performed by flooding the surfactant solution through the packed media, which was contaminated with the surrogate oil. Ottawa sand (20-30 mesh) was applied as the packed media. The TEL surrogate was used to contaminate the sand under a saturation condition. Every column was packed using the same packing procedure to obtain an analogue packed column. The aqueous surfactant solution was then flooded through the column and the effluent solution was collected and analyzed for solubilized contaminants. The gradient technique was also applied to measure the improvement.

1.4.5 Study on the effect of pH

The pH of the surfactant solution was altered to improve the efficiency of the system. HCl was used for pH decreasing as it did not precipitate with tin, and chloride ions also appeared in the system from the dissociation of salt. NaOH was applied to adjust pH to a basic condition. The effect of pH was used to investigate the phase behavior, solubilization of contaminant, and improvement of the treatment efficiency in the column experiment. A pH of 1 was designed to prove the assumption that at this pH the adsorption of DBT should be minimized. Effect of pH on-living organisms could be ignored for this case since living organisms are not expected to be present in the aquifer. The effect on the soil matrix was of greater concern. Acidic and basic conditions in the groundwater were possible, as pH ranged from 4 to 9. Thus, pH was adjusted to the most useful range for practical applications.

CHAPTER II

THEORETICAL BACKGROUNDS AND LITERATURE REVIEWS

2.1 Tetraethyl lead

Tetraethyl lead (TEL) is a neutral organometallic compound which was discovered by Charles Kettering in 1921, a general motor (GM) corporation researcher. It is an organometallic substance which was used as an additive in gasoline to raise the octane number. Emission of lead from road vehicles was accumulated in the environment, where human can directly expose causing severe health effect especially to child development. The United States Environmental Protection Agency (US EPA) has initiated to phase out this poisonous substance since 1973. Nowadays, it has been discontinued in many countries. However, some businesses are allowed to continue using TEL such as in aviation gasoline, racing gasoline, and recreational marine. Currently, the largest use of alkyl-lead occurs in aviation gasoline for general aviation (piston-engine) aircraft. In 1998, the aviation industry used approximately 295.3 million gallons of leaded gasoline, which is estimated to contain 1.39 million pounds of TEL (US EPA, 1999a). TEL emissions containing lead are still found on airport fuel terminals, bulk plants-aviation gasoline, bulk plants-leaded racing and other non-road vehicle gasoline, and spills from fuel loading, transfer, storage and fueling (US EPA, 1999). Several TEL production plants have also proved to be contaminated both in soil and groundwater (US EPA, 1999).The leakage from underground storage of gas station is a source of TEL contamination in every countries used leaded gasoline which became a point of concerned in Canada (Patriarche and Campbell, 1999). More evidences of contamination were found in refinery sites such as in Louisiana (US EPA, 2000), New York (US EPA, 2002), and Oklahoma (Department of Environmental Quality, 2005) and in air force base like in Alaska (US EPA, 1999b).

TEL possesses very high dangerous potential, resulting from lead element containing in the molecule. Generally, lead in metallic forms gets into human body via ingestion or inhalation of particles borne lead. Importantly, TEL and other alkyl-lead are easily absorbed through the skin (US EPA, 1999). Direct contact with TEL can be resulted in irritating to the eyes, the skin and the respiratory tract which may be fatal if contacting at high level. Once lead entering the body, it interferes the function of normal cell and a number of physiologic processes. It primarily affects the peripheral and central nervous systems, the blood cells, and metabolism of vitamin D and calcium. The toxicity on reproductive system also occurs. Initial symptoms of alkyl-lead poisoning include anorexia, insomnia, tremor, weakness, fatigue, nausea and vomiting, mood shifts such as aggression or depression, and impairment of memory. In case of acute poisoning, the possible health effects include mania, convulsions, delirium, fever, coma, and even death. Children are at a higher risk of lead poisoning than adults due to their lower body weights and developing neurological systems. Health effects for children include premature births, reduced birth weight, decreased intelligence, learning and hearing difficulties, and reduced growth. Childhood lead poisoning, mostly caused by the ingestion or inhalation of inorganic lead compounds in soil and dust which is a widely recognized public health problem (US EPA, 1999). The TEL is also very toxic to aquatic organisms. The substance may cause long-term effects in the aquatic environment (ICSC, 2003; Sigma-Aldrich, 2007)

The organometallic compounds can be degraded chemically and biologically in the environment (Gadd et al., 1993). TEL is a non-persistent compound. Nevertheless, it breaks down in the environment to other forms of organolead which are much more persistent, eventually forming stable inorganic lead. In an aquatic environment, TEL was firstly degraded to mono-ionic triethyl lead, which was in turn degraded to di-ionic diethyl lead, and finally to Pb^{2+} (Rhue et al., 1992). The degradation of TEL in soil was observed by Ou et al. (1994). The degraded products of TEL are still toxic to human and environment.

TEL is a hydrophobic compound with very low water solubility of 0.2 to 0.3 mg/L at 0 to 38 ºC (Feldhake and Stevens, 1963) making it trend to be adsorbed on soil material, but is highly soluble in hydrophobic solvents such as gasoline, benzene, and hexane. On the other hand, ionic ethyl-lead species, such as triethyl lead, diethyl lead, including many decomposed products, are not soluble in hydrophobic solvents but highly soluble in water (Feldhake and Stevens, 1963). The metabolite of TEL is also toxic and quite persistent making it possible to be carried long distances in ground water. Solid inorganic leads are stable and insoluble and thus, not easily to be leached to ground water. However, the leaching may occur under acidic conditions or when lead concentrations are extremely high let it may not be accepted if it settle near the aquifer.

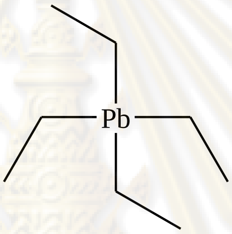
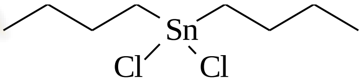
The treatment of TEL by biodegradation seem to be limited on the triethyl lead (Gallert et al., 2002 and 2004). The chemical oxidation was also studied (Andreottola et al., 2008) but seem not suit to the in-situ remediation. Thus, the removal of organometallic compounds such as TEL from the subsurface is a challenge approach. The surfactant enhanced aquifer remediation (SEAR) is a promising technique showing a great potential by enhancing the solubilization of organometallic compounds and its metabolites into the surfactant aggregates as demonstrated high efficiency on remediation of soil contaminated with leaded gasoline (Ouyang et al., 1996; Leser and Wingrave, 2000).

2.2 Dibutyltin dichloride

To investigate the remediation of TEL from contaminated site using microemulsion technique, the surrogate is needed to find and used instead of TEL due to its troublesome handle. Organometallic compounds of tin were interested as they are in the same group with lead. Some of them were take in to considerate its toxicity, density, and their structure. Tetrabutyltin has similar structure but has high toxicity similar to TEL and not has much high density. Monobutyltin is soluble in water. Tributyltin is a good choice but its toxicity is still very high. Thus, the dibutyltin was come in to consideration. The dibutyltin dichloride (DBT) shows high potential to be used as TEL surrogate. Regarding to being organometallic compound of tin which is in the same group with lead, and has high density, toxicity which DBT is less than TEL, the availability in market with lower cost, thus much safer to work with and easier to obtain than TEL (Thongkorn, 2007). The TEL and DBT properties are showed in Table 2.1.

About 350 ton of trialkyl-tin compounds are used annually as pesticides, biocides, and systhesis process, whilst about 18,000 ton of mono and dialkyl-tin compounds (including DBT) are used annually as stabilizers for polyvinyl chloride (PVC), catalysts for various products and in glass coating resulting in an extensive distribution in the environment (RPA, 2003).

Table 2.1 Properties of TEL and DBT

Properties	**Tetraethyl lead**	**Dibuthyltin dichloride**
IUPAC name	Tetraethylplumbane	dibutyl(dichloro)stannane
Physical form	Colorless oily liquid	Colorless solid
Formula	$Pb(C_2H_5)_4$	$Cl_2Sn(C_4H_9)_2$
Structure		
Molecular weight (g/mole)	323.44	303.83
Density (g/mL at 25°C)	1.653	1.360
Water solubility (mg/L)	0.29	36
Toxicity LD_{50} (oral rat, mg/kg^{-1})	12.3	50

Source: Physical properties obtained from Sigma-Aldrich material safety data sheet (Sigma-Aldrich, 2007)

DBT is harmful for eyes, ingestion and inhalation system, and able to be absorbed through the skin. The possible risk to the unborn child has also found. The target organs of DBT are similar to TEL that are the central nervous system, respiratory system, eyes, immune system, reproductive system, and skin. It can be accumulated in the food chain and pose potential effects on human health (Dopp et al., 2007). Organotin compounds are amongst the most toxic anthropogenic agents that have been released into the environment (Gibb et al., 1988). Even at 1–2 ng/L, tributyltin (TBT) causes both chronic and acute toxic effects in sensitive aquatic organisms, such as algae, zooplankton, molluscs and the larval stage of some fishes (Gibb and Bryan. 1996). Out of concern for the marine environment, the use of organotin compounds was prohibited in all marine antifouling paints in the EU beginning 1 July 2003.

Organotin compounds are also found in landfill leachates. Pinel-Raffaitin reported that up to nine organotin compounds (i.e. methyltin, ethyltin, butyltin and mixed methyl-ethyltins) were detected in landfill leachates at concentrations ranging from 0.01 to 6.5 mg(Sn)/L, which were 1–38% of the total tin concentration in landfill (Pinel-Raffaitin et al., 2008). Huang and Matzner (2004) detected organotin compounds and metabolites in forest soils of the Lehstenbach catchment (German Fichtelgebirge Mountains) showing that degradation to methyltin and butyltin was slow (half-lives from 0.5 to 15 years). They found that the soil degradation rates of mono-/di- substituted organotin were higher than tri-substituted organotin. Stepwise dealkylation was observed in all cases of di-substituted organotin, but only in some cases of tri-substituted organotin (Huang and Matzner, 2004).

The widely distribution of organotin compounds resulting in more challenge clean-up technique requirement. Study on using DBT as TEL surrogate, not only give us a benefit for achieve goal of remediation itself, but also provides a tendency success for TEL remediation too.

2.3 Non aqueous phase liquid

Non aqueous phase liquid (NAPL) refers to the contaminants that remain undiluted with water but as the original bulk liquid in the subsurface such as the spilled oil. It is generally trapped in the soil pore. The region of subsurface containing residual oil and pooled oil is referred as the source zone. Groundwater flowing through the source zone slowly dissolves the trapped oil phase to aqueous phase plumes of contamination hydraulically down-gradient from the source zone. Some NAPL compounds are resistant to biodegradation and less adsorbed therefore, becoming substantial aqueous phase plumes. Other NAPL compounds are relatively immobile in groundwater which is highly retarded relative to the rate of groundwater flow. However, some NAPLs are highly toxic at even very low concentration in groundwater possessing an unacceptable risk to human health and the environment. In unsaturated zone, the NAPLs with high volatility can cause vaporized NAPL contamination.

The density of oil is a major parameter which is easy to quantify but important for site remediation approach. The oils which have higher density than water are called the dense non aqueous phase liquids (DNAPLs). The fact that DNAPLs are denser than water allowing them to migrate downward to the significant depths below the water table through the unconsolidated deposits and the fractured bedrock until it finally accumulates as DNAPL pool at the surface of impermeable layer (Taylor et al., 2001) that complicated the treatment. Light non aqueous phase liquids (LNAPL) are in contrast that lighter than water and trend to accumulate at the surface of ground water. Furthermore, DNAPLs are mostly slightly soluble in water, but toxic, making DNAPL source zones can persist for many decades. The mobilization as DNAPL oil was a major concern for treatment design.

2.4 Equivalent alkane carbon number (EACN)

The alkane carbon number (ACN) is defined as oil hydrophobicity of linear *n*-alkane with correspondence to its carbon number (i.e., ACN of hexane = 6). For the non-alkane oils such as benzene, the new wording was designated so-called the equivalent alkane carbon number or “EACN” which is applicable in surfactant work. The oil EACN concept was initiated by Wade et al. (1977), where the EACN of the non-alkane oils was determined by comparing the optimum microemulsion formulation at the same physicochemical environment to those of *n*-alkanes. Baran et al. (1994) demonstrated the method to determine the EACN of chlorinated hydrocarbons such as tetrachloroethylene, 1,2-dichlorobenzene, and trichloroethylene. However, the EACN discovery for organometallic compound (i.e., TEL) is rare at the moment. Understanding the oil EACN is useful for designing surfactant systems that suit for solubilizing that oil (Wu et al., 2000; 2001). Consequently, this research is one of the very first works determining the EACN of organometallic compound.

When there are more than one oil in the mixture, the EACN of oil mixture can be determining based on pseudocomponent assumption (Baran et al., 1994). Based on this assumption, the composition of solubilized oil are equal to the composition of the excess oil. The $EACN_{mix}$ of the oil mixture is computed by linear mixing rule, Equation 2.1.

$$EACN_{mix} = \sum_{i} x_i \cdot EACN_i \tag{2.1}$$

where $EACN_{mix}$ is EACN of oil mixture; $EACN_i$ is EACN of component i in the oil mixture; χ_i is mole fraction of component i in the oil mixture. However, when the very difference polarity oil are mixed together, the actual EACN tends to deviate from the line produced by this linear equation (Shiau et al., 1996).

2.5 Surfactants

Surfactants are amphipathic molecules that consist of a polar or hydrophilic portion (known as surfactant’s head) and a non-polar or hydrophobic portion (known as surfactant’s tail) (Rosen, 2004). The polar head group interacts strongly with water molecules by dipole-dipole or ion-dipole interactions. These interactions result in the hydrophilic behavior of the surfactants. The non-polar tail group interacts weakly with the water molecules in an aqueous environment. Thus, the interaction between water molecules tends to extrude the surfactant’s tail out of the water region due to their hydrophobic behavior. As a consequence, the surfactants accumulate at various interfaces rather that dissolve freely in aqueous solution (Schramm et al., 2003; Tadros, 2005).

Surface tension is a force per unit length required to pull apart the surface molecule in order to permit expansion of the surface by movement into it of molecule from the phase underneath it. Molecules at the surface or interface of the liquid have potential energies greater than the molecule in the interior of the liquid due to the different attractive interaction energy between molecule at the interface with the interior of it bulk phase and molecule at the interface with another bulk phase. When a water soluble surfactant add into a system of water and oil, the surfactants molecules adsorb at the interface thus replace the water molecule at the interface, the interaction across the interface is now between hydrophilic group of that surfactant and water molecules on a side of the interface and between hydrophobic group of surfactant and oil molecules on another side of the interface. These interactions are now much stronger and less different. As the result, the interfacial tension of the system is decreased. The surface and interfacial tension decrease as the surface concentration of surfactant increase until the surface concentration reach the maximum value.

At high concentration of surfactant, the surfactant molecules are aggregated into the cluster called micelle. The concentration which the first micelle formed called critical micelle concentration (CMC). The formation of micelles is recognized as a result of both the tendency of hydrophobic parts to avoid energetically unfavorable contacts with aqueous media, and the desire for the hydrophilic parts to maintain contact with the aqueous environment. In aqueous micelles (see Figure 2.1), each monomer orients its hydrophilic part in contact with aqueous phase and its hydrophobic part into the interior of the aggregate. After the point of CMC, the surface tension and interfacial tension (IFT) was negligible decreased. But the solubilization of oil into micelles was became considered.

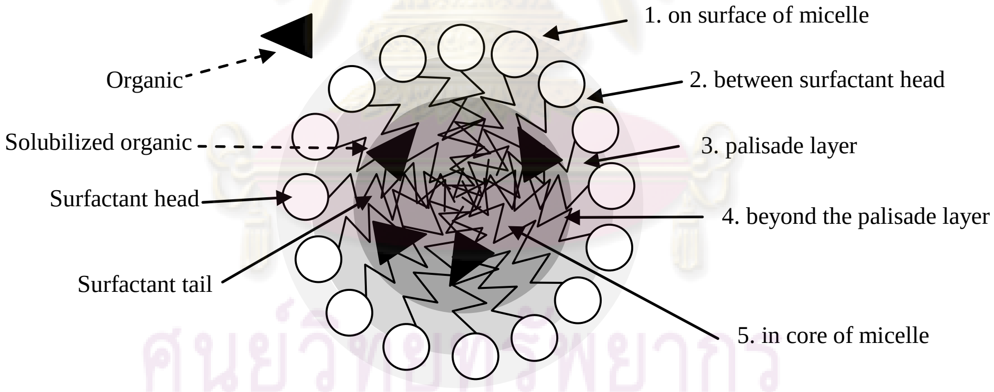


Figure 2.1 Schematic of aqueous surfactant micelle

At the surfactant concentration lower than CMC, the IFT decrease with increase of surfactant concentration until reach the CMC while the solubilization is negligible. And after the CMC the IFT is quite constant while the solubilization was increase as the surfactant increase as a result of formed micelles (see Figure 2.2).

Solubilization is an important property of surfactant which is the result from partitioning of the contaminant into the oil like core of the micelle formed in the water. The solubilization occur at a number of different location in micelle: 1) on the surface of micelle, 2) between the hydrophilic head group, 3) palisade layer between hydrophilic head group and first few carbon atom, 4) more deeply beyond the palisade layer and 5) in the core of micelle (see Figure 2.1). The solubilization region depends on the interaction between surfactant and solubilizate (Rosen, 2004). Thus, the surfactant can mix water-insoluble compounds with water forming an emulsion solution (Schramm et al., 2003; Tadros, 2005).

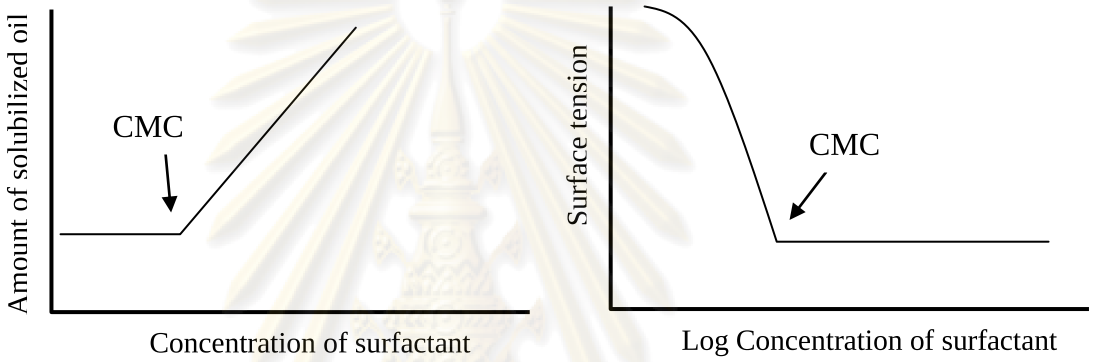


Figure 2.2 The relation of CMC to the IFT and solubilization of organic compound (adapted from Rosen, 2004)

The locus of solubilization seem complicated but in the manner of depth, from surface to core of micelle, solubilization region in micelles seem to related to the polarity of oil. it may divided into three main locations of oils solubilized inside the surfactant micelle: 1.) polar surface region (surfactant head groups) 2.) palisade layer (between surfactant tails) and 3.) hydrophobic core. Upon these regions, non-polar oils are solubilized in the micelle core region whereas semi-polar and polar oils preferably solubilized at the palisade and surface regions, respectively (Szekeres et al., 2005).

Under the suitable condition, i.e., surfactant and salt concentration, the size of formed micelles is about < 0.1 µm producing the stable micelles solution so called microemulsion. The microemulsion is thermodynamically stable and the formation of micelle is spontaneous (Sabatini et al., 2000). The difference between emulsion and microemulsion are their particle size and stability (Paul and Moulik, 2001).

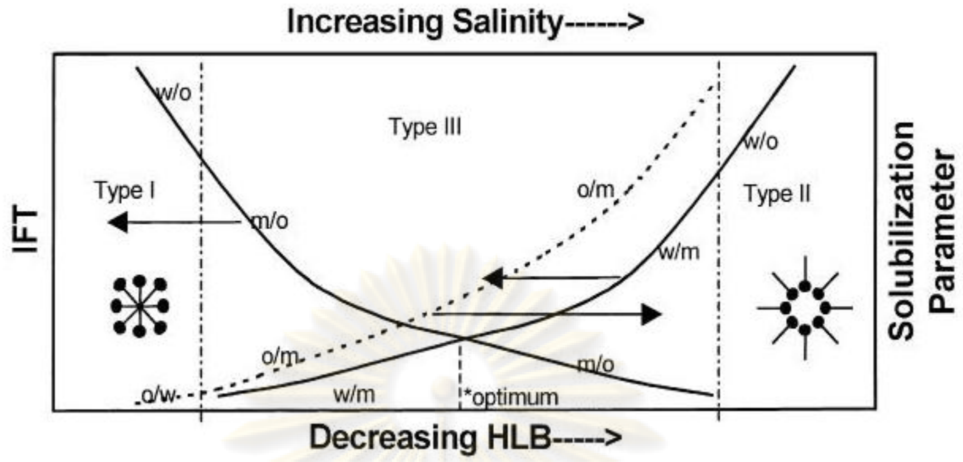


Figure 2.3 Winsor phase diagram adapted from Sabatini et al. (2000)

The microemulsion yields the ultra-low IFT, large interface area, capacity to solubilize both aqueous and oil soluble compounds (Paul and Moulik, 2001). Normally, there are three types of microemulsion showed in Figure 2.3. Type I (oil in water): the surfactant shows the hydrophilic behavior. Micelles form in water phase thus oil is emulsified into water. Type II (water in oil): the surfactant shows the lipophilic behavior. Micelles form in oil phase that water is emulsified into oil. Type III (optimum condition with three phases): micelles separate from both phases and form its own middle phase. Type I and III microemulsion are benefit on the surfactant base remediation of organic contamination which is performed by many studies (Dwarakanath et al., 1999; Sabatini et al., 2000; Wu et al., 2000). Hydrophilic surfactant trend to product type I while the hydrophobic one trend to product type II that also depend on the oil type. The types of microemulsion can be driven from I to III and II by the adjusting of hydrophile-lipophile balance (HLB) by the mixing between hydrophilic and hydrophobic surfactant and the increasing of salinity in the ionic surfactant system.

The microemulsion phase transition from type I to II is governed by the hydrophilicity and lipophilicity of the system as described by R ratio and the molecular interaction (per unit interfacial area) (Bourrel and Schechter, 1998) which is the interaction between surfactant, oil and water molecules in the system as show in Equation 2.2.

$$R = \frac{A_{CO} - A_{OO} - A_{LL}}{A_{CW} - A_{WW} - A_{HH}} \tag{2.2}$$

where A_{CO} is the interaction between the surfactant and the oil, A_{CW} is the interaction between the surfactant and the aqueous phase, A_{LL} and A_{HH} are self-interaction between their lipophilic tail and between their hydrophilic head of the surfactant, respectively. The parameters A_{WW} and A_{OO} are self-interaction in the water phase and oil phase, respectively. The numerator of the equation represents the net interaction of the lipophilic portion of the surfactant at the interface, while the denominator represents the hydrophilic part of the interface. Bourrel and Schechter also indicated that the optimum formulation corresponds to R values equal to 1, or when the interactions of the lipophilic and hydrophilic regions are in balance. For R<<1, the interface becomes more hydrophilic, and a micellar solution or O/W microemulsions exists. At R>>1, inverse micelles form and the solution becomes a W/O microemulsion.

2.6 Surfactant enhanced aquifer remediation (SEAR)

The SEAR is generally applied to contaminated sites at the source zone. The source zone is separated from the outer area and groundwater flow by sheet pile. Then the SEAR is performed by flushing the surfactant solution through the injection well and pumping out at the extraction well. The surfactant in flushing solution flows through the contaminated aquifer, source zone, to remove the contaminant via the mechanisms informed previously. The surfactant solution containing NAPL extracted from aquifer is then subsequently treated by the treatment plant.

In the remediation by pump and treat, the contaminant aqueous capacity depends on the aqueous solubility of the contaminant. When surfactant is added to the aqueous phase, the micelles are formed; the solution capacity is enhanced by the solubilization mechanism which is partitioning of organic contaminant into micelles. Apparent aqueous solubility is enhanced, the actual aqueous solubility unchanged, the increased solubility is the portion that is in micelles (West and Harwell, 1992; Childs et al., 2006). Rosen provide a good defined of the solubilization: the spontaneous dissolving of a substance which is solid, liquid, or gas by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduce thermodynamic activity of the solubilized material (Rosen, 2004). Both soluble and insoluble substances are dissolved by the solubilization mechanism; the important of this phenomenon is that it makes the insoluble compound can be dissolved in the solvent. A major practical important is the formation of products containing water-insoluble ingredients which can replace the use of organic solvent.

The efficiency of the surfactant solution can be express in many ways. The enhance solubility of contaminant can be expressed as Sw*/Sw that is the ratio of the appearance aqueous solubility to the true aqueous solubility (Kile and Chiou, 1989); this parameter include the enhancement by both monomer and micelles form. Solubilization Parameter (SP) is the ratio of contaminant volume and surfactant weight in the middle phase (West and Harwell, 1992). The solubilization capacity of middle phase microemulsion is defined by the solubilization parameters as Equation 2.3 and 2.4 (Healy and Reed, 1977):

$$SP_o = V_o / M_s \tag{2.3}$$

and

$$SP_w = V_w / M_s \tag{2.4}$$

where SP_o and SP_w are solubilization parameters for oil and water, respectively; V_o and V_w are volumes of oil and water solubilized in the surfactant solution, respectively; and M_s is the total mass of surfactant(s) present, excluding the mass of alcohol (if used).

Mobilization is the movement that the non-aqueous phase liquid (NAPL) moves as its own phase. In the residual zone, the force that traps the NAPL is capillary force which is proportional to the IFT at the oil/water interface and the force that pushes it from the pore is the result of pressure drop per unit distance (ΔP/L). The energy require to form the increased interfacial area is the IFT multiply by the increasing area. Thus, if the IFT is very low, the mobilization can occur at low ΔP/L (West and Harwell, 1992). In the surfactant base remediation, the surfactant is added into mixture of oil and water and accumulates at the oil/water interface, it product the lower interfacial tension between oil/water interface and resulting in the mobilization (Sabatini et al., 2000). In case of Type III microemulsion, it products very low oil/water interfacial tension and ultra high contaminant solubilization; the very low IFT in this region tend to mobilize the trapped oil (West and Harwell, 1992; Sabatini et al., 2000).

For the contaminant recovery in the soil matrix, mobilization is highly more effective than solubilization (Dwarakanath et al., 1999; Shiau et al., 2000). But the mobilization of DNAPL is a cause of vertical migration of the DNAPL that promotes the movement of contaminant to the deeper zone which product the new and more complicate contamination. Thus, the careful on the occurrence of mobilization is very important to design a SEAR for a contaminated site. Vertical migration is a very concern for the subsurface remediation. Especially for DNAPL, the downward migration may create a new deeper contaminated area which make the remediation are not succeeded and also product a more complicate problem. The mobilized DNAPL may be moved until reach an impermeable layer and accumulate as the DNAPL pool. The cause of vertical migration can be divided into two mechanisms. First is the mobilization of DNAPL which product the major influence in vertical migration and be concerned by many researchers. Since the interfacial tension is responsible for trapping the oil in soil pore, the significant reduction in IFT promotes an easy released of the oil from the porous media. Thus, to design a SEAR technique for a contaminated site, the occurrence of mobilization should be mitigated.

Although the solubilization offers low removal efficiency in comparison to mobilization, it has low potential to create the vertical migration. So, the solubilization is the preferable mechanism for the SEAR process.

Huh (1979) establish the *Chun-Huh relationship* that is $S^2 \alpha 1/IFT$. Since the IFT decrease continuously from type I to type III region, from the Chun-Hun relationship solubilization potential increase continuously from type I to type III region until reach the optimum point. So, in the surfactant mixture, when the mixture is design for increase the solubilization capacity, the mobilization potential is also increase too.

Due to the most significant induce mechanism is the IFT; the mechanism of oil removal can be adjusted simply for ionic surfactant by shifting the salinity of the surfactant mixture. The salinity can be changing continuously and economically in the field which is an advantage of using ionic surfactant over nonionic surfactant (Dwarakanath et al., 1999).

To control the vertical migration, many ideas were proposed. The initial principle to prevent mobilization is the avoiding of type III on flushing condition (West and Harwell, 1992) that product very low IFT between surfactant solution and oil. It is also important that in type I microemulsion, the contaminant is solubilized into aqueous phase.

A numeric model preferred to use for predict the mobilization is the trapping number introduced in 1996 by Pennell et al (Pennell et al., 1996). The model describes the relation between the residual saturation of oil in the soil column and the IFT, density of trapped oil, viscosity, and velocity of flushing solution. Sabatini and coworker suggest that surfactant systems can be formulated to obtain the maximum solubilization of oil in the water phase without forming a middle phase microemulsion, known as a supersolubilization system (Sabatini et al., 2000). This region located near the boundary of type I and type III. To prevent the mobilization, Sabatini and coworker (Sabatini et al., 2000) introduced gradient concept that sequentially adjusts the surfactant solution which product the interfacial tension value from high to low. This approach can prevent the vertical migration and still maintain the remedial efficiency.

2.7 Surfactant selection

Surfactant is the basic chemical in the mixture used to increase contaminant aqueous solubility and modify oil/water interface to improve efficiency. So, the surfactant selection is very important. Surfactant mixture should have similar HLB values to that of the oils in order to achieve maximum stabilization (Wu et al., 2001; Acosta et al., 2003; Rosen, 2004). That is more hydrophobic oil can form better emulsion by lower HLB surfactant. This proper surfactant require less electrolyte, higher solubilization capacity, and faster coalescence, lower viscosity, thus it is more economical (Acosta et al., 2003). This study show that if selected surfactant too much different HLB from the oil, the mixture require more additive such as electrolyte and linker and also product lower quality emulsion too.

In addition, the use of high dosage of NaCl is not an amenable approach to subsurface remediation (Shiau et al., 1994). Traditional cosurfactant such as medium chain length alcohol utilized to prevent the formation of liquid crystal may not be useful due to their toxicity (Shiau et al., 1994).

2.8 Salager's equation

Microemulsion formulation is largely a trial-and-error process. Empirical models can help to expedite this trial-and-error process. For systems containing hydrocarbon, anionic surfactant, alcohol, and salinity; the following relationship named Salager equation (Equation 2.5) has proven to be valid (Salager et al., 1979):

$$\ln S^* \quad = K(EACN) + f(A) - \sigma + a_T(T - 25) \qquad (2.5)$$

where S^* is the optimum salinity of the microemulsion system; EACN is an equivalent alkane carbon number of oil; $f(A)$ is a function of alcohol type and concentration; σ is the parameter indicating the characteristic of surfactant; a_T is a coefficient accounted for temperature effect.

This equation can be modified into a reduced form as shown in Equation 2.6 if the system is applied at the same temperature using the same the surfactant type and concentration without alcohol addition.

$$\ln S^* \quad = K(EACN) + c \qquad (2.6)$$

where c = a constant value which can be obtained from the plot between ln S* vs EACN and then used in the study.

2.9 Literature Review

Feldhake and Stevens (1963) observed for the solubility of TEL in water. They extracted TEL from their degradation products using pentane. No degradation products of TEL were detected in pentane phase. The TEL solubility was 0.2-0.3 mg/L at 0-38 ºC.

Ou et al (1994) observed for the biological and chemical degradation of tetraethyllead in soil. They found that transformation of TEL to ionic forms in soil occurred both biologically and chemically. The degradation products were triethyl lead and diethyl lead. Mineralization of TEL in soil was a microbially mediated process (base on present of CO_2). After 28 d of incubation, no TEL could be detected in their soil samples and considerable amounts of ionic ethyllead species were present suggests that TEL is less persistent in soil than its degradation products, ionic ethyllead species. This study did not determine the distribution of individual ionic ethyllead species.

Ouyang et al. (1996) study on the removing of TEL from the contaminated soil by microemulsion. The column contained leaded gasoline initially 30% residual saturation. The flooding was done sequentially by saline solution (0.01 M NaCl) and surfactant solution (mixture of sodium lauryl sulfate and n-pentanol), respectively. The 1.6 pore volume of saline solution could displace 41% of total applied gasoline; leave 59% as residual gasoline. The first result agrees with the expected result from capillary number. Then the column was flushed by 6.4 pore volume of surfactant solution which has interfacial tension of 0.03 Nm^{-1}. As the result, 95% of residual gasoline and 90% of residual lead was removed. They also found that the TEL is not stable; it was degraded 74% in 48 hr that was the retention time in the column.

Pennell et al. (1994) studied on PCE recovery by using four column experiments to determine the recovery ability of surfactant solution. The first two column were flushed by 4% polyoxyethylene (POE) (20) sorbitan monooleate (Tween80), resulting in the removal of 90% and 97% of the residual PCE from 20-30 and 40-120 mesh Ottawa sand, respectively. Micellar solubilization was the main mechanism which observed to be rate limited base on: (a) the disparity between initial steady-state concentrations of PCE in the column effluent and equilibrium value measured in batch experiments; and (b) the increase in effluent concentrations of PCE following periods of flow interruption. In the following two experiments, surfactant mixtures of sodium sulfosuccinates show the removed > 99% of the residual PCE from soil columns packed with 40-270-mesh Ottawa sand. The mobilization was the dominated (80%) removal mechanism, the interfacial tension between surfactant solution and PCE were 0.09 dyn/cm in the system of 1:1 sodium diamyl/dioctyl sulfosiccinate and 0.57 dyn/cm for 4:1 sodium dihexyl/dioctyl sulfosiccinate. The results indicated that ultra-low interfacial tensions (< 0.00l dyn/cm) are not required to achieve significant PCE mobilization when buoyancy forces are important.

Pennell e al. (1996) studied the potential to mobilization of the DNAPL using PCE. The mobilization was induced under the IFT 47.8 to 0.09 dyn/cm. Trapping number was established as the relation of viscous, buoyancy, and capillary force acting to retain organic liquid in the porous medium. The critical trapping number value which begins the mobilization is about 2×10^{-5} to 5×10^{-5}, and the complete displacement of PCE can be observed at about 1×10^{-3}. The interplay of viscous and buoyancy force were showed in the horizontal column experiment. PCE saturation curves were expressed as a function of the total trapping number (N_T) for four ranges of Ottawa sand. This study showed the potential including buoyancy force to PCE mobilization and provides a new approach to predict the mobilization of DNAPL.

The study of Dwarakanath et al. (1999) was carried out using a variety column for selecting and evaluating the suitable surfactant for subsurface remediation. The contaminant in the study were tetrachloroethylene (PCE), trichloroethylene (TCE), jet fuel, and dense non-aqueous phase liquid from a site at Hill Air Force Base, UT. Both Ottawa sand and Hill field soil were using in the experiment. The surfactants selected for column study based on high contaminant solubilization, fast coalescence, and absence of liquid crystal phase or gel during the phase behavior experiment. The objectives of experiments were to recovers more than 99% of contaminant, low adsorption of surfactant, and little or no lost of hydraulic conductivity. The result from the mobilization experiment show 80% of contaminant was recovered as free phase. The peak of contaminant aqueous concentration were observed at about 1 pore volume, follow by rapid decline to low concentration within 3 pore volume. The mobilization was prevented in solubilization experiment by trapping number concept.

The effluent contaminant concentration reach a high value and keep quite constant observed as a plateau concentration until 5 to 10 pore volume, following by a decline to low value. The increasing of viscosity by adding little polymer in surfactant solution resulting in the longer plateau of high effluent concentration duration that lead the system require less pore volume of remedial solution in treatment. For the mobilization study, the hydraulic gradient was observed increase until the oil bank reaches the outflow end piece of column, following by the decline to lower value. The hydraulic gradient of solubilization study were observed as the same trend to the mobilization experiment, the hydraulic gradient increase until the surfactant breakthrough and follow by the declining. The increasing viscosity increased the hydraulic gradient. The very high, unacceptable, hydraulic gradient was observed in the mixture of 1.4% sodium dioctyl sulfosuccinate (SDOS), 0.6% sodium dihexyl sulfosuccinate (SDHS) with jet fuel (JP4). The following experiment found the reducing of breakthrough indicating the plugging of soil pore. Another column test using SDOS also found the reducing of permeability even the water flood was performed. The addition of alcohol (8% secondary butyl alcohol) to SDOS mixture can be used to reduce this plugging. The result of this study indicated that SDHS was a preferred surfactant which could be applied in the treatment with no significant loss of permeability even the addition of polymer, very low sorption loss and also show 99.9% removal of contaminant. The experiment also indicated that the recovery mechanism could be conducted by simply adjust the salinity which can be adjusted continuously in field work. This is an advantage of using anionic surfactant.

Sabatini et al. (2000) investigated the key issue for the subsurface remediation of DNAPL, which were economic consideration, minimizing surfactant loss, maximizing contaminant extraction, and surfactant regeneration. They showed the use of capillary curve to optimize the contaminant solubility while minimize the mobilization. Finally, they exhibited the gradient approach which increases solubilization potential without mobilization. Gradient technique is the idea to remove the oil fraction that most readily to be mobilized first and remove the other fraction subsequently. The contaminated packed column was flooded by the surfactant system which product not too low IFT to prevent mobilization of oil while solubilize a fraction of residual oil, then switch to more robust surfactant system producing lower IFT and higher solubilization in step by step.

Taylor et al. (2001) conducted the batch, column, and two-dimensional box experiment to investigate the effect of rate-limited solubilization and low permeability lenses in the surfactant flushing. The surfactant used in the study is Tween80. Batch experiment was carried out to determine the solubilization capacity, density, viscosity and the interfacial tension. The result of column experiment shows that the solubilization of PCE was limited at Darcy velocity of 0.8 to 8.2 cm/hr and high up during period of flow interruption. The effluent concentration data were used to determine the effective mass transfer coefficient which shows the dependent on Darcy velocity. The 2-D box was packed with contain the lenses of low permeability soil to investigate the effect of heterogeneous of subsurface, the. The result show rate limit solubilization and the PCE was became pool above the low permeability layer which reduce the PCE recovery compare to the result of column study. This study demonstrated the potential impact of both mass transfer limitation and subsurface layering on the PCE remediation.

Lee et al. (2001) performed the column tests to examine the effect of surfactant solution condition on the removal of toluene. The result show the optimum condition of 4% (v/v) sodium diphenyl oxide disulfonate, pH of 10, temperature of 20°C, and 4 mL/min of flow rate. The toluene removal was 95% which higher than the un-adjusted condition of 6-19%.

Gallert and Winter (2002) studied on the removal of TEL from highly TEL contaminated sandy soil from a producing company. Soil samples were supplied with oxygen or oxygen and minerals at different water saturation to observe the present of microbial degradation. The long-term elution of TEL from contaminated soil was carried out using glass columns using oxygen-saturated water. They found that TEL was completely eluted from the sandy soil within 260 days that converted to triethyllead by chemical or microbiological reaction. The triethlylead was 60–80% of the maximal amount that could be formed from TEL by a single dealkylation. This indicated that about 20–40% of the triethyllead were apparently further degraded. A little diethlylead were found in water. This triethyllead concentration was observed highly toxic for non-adapted microorganisms. Only little alkyllead degradation occurred even a readily degradable carbon source was added while the fast growth of bacteria observed.

Tongcumpou et al. (2003) investigated the relationship between microemulsion phase behavior and detergency for oily soils. Surfactant phase behavior was evaluated for hexadecane and motor oil which large hydrophobic character. Three surfactants with a wide range of hydrophilic/lipophilic character were used: alkyl diphenyl oxide disulfonate (highly hydrophilic), dioctyl sodium sulfosuccinate (intermediate character), and sorbitan monooleate (highly hydrophobic). This mixed surfactant bridge the hydrophilic/lipophilic gap between the water and the oil phases and lead to form microemulsions which product substantial solubilization and ultra-low interfacial tension. The microemulsion phases could be observed for both systems with hexadecane and motor oil using the salinity of 0 to 25%. The mixture of anionic and nonionic show the robust to temperature (20 to 60 °C in the study) compared to single one. The supersolubilization region promotes high solubilization parameter while the interfacial tension was not low as the middle phase region. The interfacial tension and solubilization follows the *Chun-Huh* equation.

The study of Childs et al. (2004) was the extension of the Sabatini et al (2000). The goal of the gradient system is the maximizing of the solubilization capacity of the contaminant by the type one microemulsion while minimizing the mobilization. They establish the gradient curve which is the modification of trapping and capillary curve. Gradient curve is the present of DNAPL residual saturation as the function of interfacial tension and microemulsion viscosity. The study also showed that the addition of gradient step, smooth of IFT changing, resulting in the dramatically reduce of mobilization.

Gallert and Winter (2004) study on the degradation of alkyllead compounds to inorganic lead in contaminated soil. They found that tetraalkyllead contaminated in soil could be eliminated by elution with oxygenated water as ionic tri- and dialkyllead species into the circulating water in the soil columns or the groundwater at the contaminated site. Trialkyllead degradation rates at high (7 mg/L) and low concentrations (1.5 mg/L) were in the same range. However, dialkyllead species were formed more than could be degraded at the higher trialkyllead concentrations. About 54% of the lead was converted to inorganic lead after 2 years of elution with oxygenated water. If a triethyllead-elimination rate of about 125 mg/L.d would also apply for in situ conditions, the contaminated soil could be remediated in about 19 years.

Childs et al. (2006) reported a PCE removal by surfactant solution from a control test cell at Dover National Test Site. The surfactant formulation was SDHS, isopropanol and calcium chloride. The flushing promotes a high concentration of PCE (supersolubilization) without vertical PCE migration. The flushing were operated in both vertical circulation and line drive configurations. The 68% of overall PCE removal achieved after 10 pore volume. The residual saturation was reduced from 0.7% to 0.2%, PCE concentration in the groundwater was reduce from 37-190 mg/l to 7.3 mg/l. The recycle of surfactant solution decrease the required mass of surfactant by 90%. In the upward vertical circulation flow, the 80% PCE removal was obtain in 5 pore volume. The multilevel sampler shows the most of trapped oil was localized in the secluded region of the aquifer which results in the lower PCE concentration in the groundwater.

Pabute et al. (2007) apply the gradient approach system for PCE surfactant flushing. The gradient using base on the variation of interfacial tension between surfactant solution and contaminant: electrolyte gradient for anionic surfactant system and temperature gradient for nonionic surfactant system. In the column experiment, mixture of monoalkylate diphenyl oxide disulfonate (C16DPDS) and SDHSwas using to form microemulsion; with gradient system, the PCE can be removed more than 99% without mobilization. This technique also studied to remove decane and hexadecane from fabric by temperature gradient 30 to 45 °C. The n-dodecyl pentaethylene glycol. The result shows that the gradient system can remove two oil better than washing at a constant temperature.

Zhao et al. (2005) presented the solubilization of phenanthrene and the extraction of it from spiked soil by sodium castor sulfate (SCOS) which is the surfactant from castor oil producing from reproducible resource. The experiment compare with the commercial surfactants: Triton X-100, Tween 80, Brij35, sodium dodecylbenzene sulfonate and sodium dodecyl sulfate. SCOS forms stable microemulsion and behave like a separate bulk phase in concentrating organic solute. The solubility enhancement of phenanthrene increase as the concentration of SCOS increase. In contrast with the effect of conventional surfactant, a sharp inflection of surface tension in the CMC study did not show but decrease continuously. SCOS show largest mass solubilization ratio among the surfactant in the study in both soil-free and soil-water experiment. The partitioning coefficients of phenanthrene between emulsified phase and aqueous phase is slightly larger than those between the micellar pseudo phase and the aqueous phase. The extraction experiment show high and fast desorption of phenanthrene perhaps due to its high solubilization capacity.

Zhou et al. (2004) studied on the solubilization of pyrene by four anionic-nonionic mixed surfactant-sodium dodecyl sulfate (SDS) with Triton X-405 (TX405), Brij35, Brij58, and Triton X-100 (TX100)-was studied. The molar solubilization ratio (MSR) of pyrene in mixed surfactant are found larger that those predicted by ideal mixing rule. The effect on MSR for pyrene follow the order of SDS-TX405> SDS-Brij35> SDS-Brij58> SDS-TX100 which increase with the increase in the HLB value of nonionic surfactant in the mixed system. The K_{mc} of the SDS-TX405 was greater than the ideal value but the SDS-Brij35, SDS-Brij58, SDS-TX100 were smaller. The CMCs of four systems show the lower than the ideal CMC of mixed system. The mixing effect of mixed surfactant on MSR for pyrene can be attributed to the reduction of CMC and the increasing or decreasing of K_{mc}.

Zhao et al. (2007) studied on the micellar solubilization of trichloroethene (TCE), perchloroethene (PCE) and their mixture (TCE–PCE) by mixed nonionic and anionic surfactant, Triton X-100 (TX100) and sodium dodecylbenzene sulfonate (SDBS) in DNAPL/water systems was presented. Generally, nonionic surfactants have interaction with oil better than anionic one but they loss from system by partition to organic phase. In this study, the TX100 losses into TCE and TCE–PCE phases were great when single TX100 was used, whereas those into PCE phase were much less, while no partitioning of SDBS into DNAPLs was observed. In mixed surfactant systems, SDBS decreased greatly the partition loss of TX100 into DNAPLs. The extent of TX100 partition decreased with the amount of SDBS increasing and the polarity of DNAPL decreasing. TX100 and SDBS formed mixed micelles in the solution phase. The inability of SDBS to partition into DNAPLs and the mutual affinity of SDBS and TX100 in the mixed micelle controlled the partitioning of TX100 into DNAPL phase. The solubilization of TX100-SDBS solution was greater than the individual SDBS system (equal total surfactant concentration). The work presented here demonstrates that mixed nonionic–anionic surfactants may be probably potentially better systems than the corresponding single ones.

Thongkorn et al. (2007) studied on the remediation of soil contaminated by organometallic compound. The TEL was concerned contaminant but the surrogate was used in their experiments due to toxicity of TEL. Their study established a linear equation between optimum salinity and EACN by using linear alkanes in the phase scan experiment for the optimum salinities determination in order to determine EACN of TEL which would be used as one criteria for selecting the TEL surrogate. Two linear equations derived from two surfactant systems: solution of 2 wt.% SDHS 2 wt.% Tween80 and solution of 2 wt.% SDHS 2 wt.% SDOS. Consequently, the EACN of TEL was quantified from these two surfactants solution at 6.04 and 7.68. The other two criteria of TEL surrogate were being an organometallic compound and being DNAPL. However, it is rarely to find any compound possessed all those three properties and having low toxicity. DBT was then introduced and mixed with oil to make it has properties similar to TEL. Some alkanes were mixed with DBT to obtain the designed EACN. As the result, DBT-decane mixture was found to have similar EACN (7.2) to TEL and thus used as TEL surrogate. Then the study on phase study, solubilization measurement and column experiment was carried out for some surfactant solution.

CHAPTER III

MATERIALS AND METHODOLOGY

3.1 Materials

3.1.1 Organic compounds

Analytical grade TEL and DBT were purchased from Sigma-Aldrich Co. Perchloroetylene (PCE) was purchased from Ajax-Finechem. The *n*-alkane series including pentane (Fluka), hexane (LabScan), octane (Carlo Erba), and decane (from Fluka) were used to establish the empirical relationship between *S** and oil's ACN. Decane also used as the solvent for DBT in the same manner of PCE.

DBT-PCE mixture and DBT-decane mixture were used as surrogate of TEL as described the criteria for selection in CHAPTER IV. They were prepared and stored no longer than one week.

Table 3.1 Organometallic compound properties

Properties	Tetraethyl lead	Dibutyltin dichloride
Physical form	Colorless oily liquid	Colorless solid
Formula	$Pb(C_2H_5)_4$	$Cl_2Sn(C_4H_9)_2$
Molecular weight (g/mole)	323.44	303.83
Density (g/mL at 25°C)	1.653	1.360
Water solubility (mg/L)	0.29	36
Toxicity LD_{50} (oral rat, mg/kg^{-1})	12.3	50

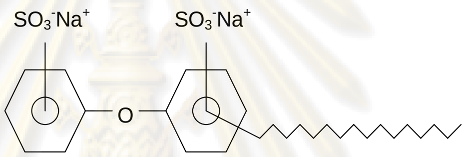
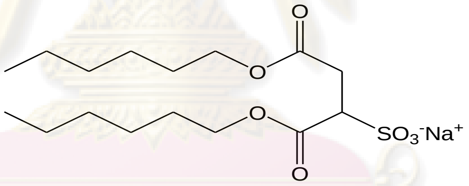
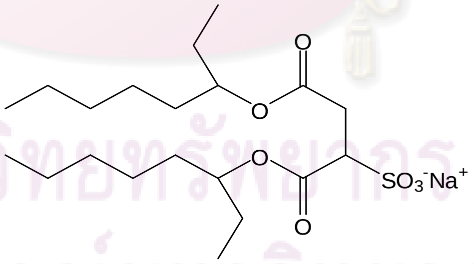
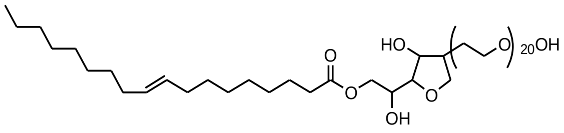
Source: Physical properties obtained from Sigma-Aldrich material safety data sheet

3.1.2 Surfactants

The anionic surfactants consisted of monoalkyldiphenyloxide disulfonates (C16DPDS, trade name of Dowfax8390 with 36% active) was supplied by Dow Chemical Co., sodium dihexyl sulfosuccinate (SDHS, trade name of AMA with 80%

active) and sodium dioctyl sulfosuccinate (SDOS, trade name of AOT with 100% active) are purchased from Fluka Co. The nonionic surfactant, sorbitan monooleate with 20 ethoxy groups (trade name of Tween80 with 100% active) was purchased from BDH Co. The IUPAC name, CAS number, and chemical formulas were supplied below and in Table 3.2. All surfactant solutions applied in the experiment were prepared freshly before used.

Table 3.2 Properties of surfactant used in this study.

Surfactants	**Type**	**Structure**	**MW (g/mol)**	**HLB**
Monoalkyl, diphenyloxide disulfonates (C16DPDS)	anionic		642	71.5*
Sodium dihexyl sulfosuccinate (SDHS)	anionic		388.45	16.6*
Sodium dioctyl sulfosuccinate (SDOS)	anionic		444.57	10.2*
Sorbitan monooleate (20 ethoxy groups) (Tween80)	nonionic		1308	15.0**

Note: *   HLB value for anionic surfactants were calculated based on Davies method.
** HLB value for nonionic was developed by Griffin (Tadros, 2005).

C16DPDS, Chemical Formula: $C_{28}H_{40}Na_2O_7S_2$

IUPAC name: disodium 2-hexadecyl-3-(2-sulfonatophenoxy)benzenesulfonate

CAS Number: 65996-95-4

SDHS, Chemical Formula: $C_{16}H_{29}NaO_7S$

IUPAC name: sodium 1,4-dihexoxy-1,4-dioxobutane-2-sulfonate

CAS Number: 3006-15-3

SDOS, Chemical Formula: $C_{20}H_{37}NaO_7S$

IUPAC name: sodium 1,4-bis(2-ethylhexoxy)-1,4-dioxobutane-2-sulfonate

CAS Number: 78207-03-1

Tween80, Chemical Formula: $C_{64}H_{124}O_{26}$

IUPAC name: 2-[2-[3,5-bis(2-hydroxyethoxy)oxolan-2-yl]-2-(2-hydroxyethoxy)ethoxy]ethyl (E)-octadec-9-enoate

CAS Number: 9005-65-6

3.1.3 Electrolyte

Analytical grade sodium chloride (NaCl, 100%) and calcium chloride ($CaCl_2$, 100%) were purchased from LabScan. Analytical grade calcium nitrate ($Ca(NO_3)_2$, 100%) used in column experiment was from Ajax Finechem.

3.1.4 Soil materials

The 20-30 mesh Ottawa sand (Fisher Scientific) was applied as the soil media in the column experiment. It was washed by DI water and dry before packed into column. The aquifer soil was derived from a site at Rayong supplied by Department of Groundwater Resources. It was washed by tap water until the washing water was clear after left to precipitate in 10 minute and wash again by DI water, it was dried at 100 ºC, then sieved to 20-30 mesh in order to comparison. The organic matter was 0.07%, measured by soil-fertilizer-environment scientific development project, Kasetsart University. Zeta potential of Ottawa sand was measured by electrophoretic apparatus (zeta-meter system 3.0^+, zeta-meter Inc.) to quantify the point of zero charge (PZC). However, we could know only that the PZC of Ottawa sand and sieved aquifer soil was lower than 3. However, the PZC of Ottawa sand from a literature was about 1.5 (Railsback, 2006).

3.2 Methodology

Overall experimental methods are explained in this section. Details in each experiment and more procedure information were informed in that such chapter. Here is the core of the experiment for the following chapters: CHAPTER IV, V, VI, and VII.

3.2.1 Create the oil surrogate.

The criteria which the oil surrogate should have were being the organometallic compound, similar EACN, and similar density. Thus, the EACN of TEL, focused organometallic compound in the study, must be indentified primary. Salager's relation was applied for quantification of EACN by the established linear empirical equation (Equation 2.6).

Equation 2.6 is the relation between EACN (or ACN for alkane oil) of oil and optimum salinity of the system. The pentane (ACN = 5), hexane (ACN = 6), octane (ACN = 8), and decane (ACN = 10) was applied in the experiment. Equal volume of oil and aqueous surfactant was added in 1 mL tube (0.5 mL each) with stopper. The surfactant solution of 2 wt.% SDOS and 2 wt.% Tween80 with various concentration of NaCl were added into the tubes, and then equal volume of a *n*-alkane was added into the tubes. The tubes were immediately sealed, gently shook for 1 min, and equilibrated for 1 day. Solubilization parameter (SP, Equation 2.3 and 2.4) was quantified by measuring the change of the volume of oil phase and aqueous phase as indicated by a changing of solution height using the digimatic height gages (Model series 192, Mitutoyo). The graphs between SP_o and wt.% NaCl, and between SP_w and wt.% NaCl were plotted on the same chart and the $S*$ was then determined as an intercept of these two plots. The same procedures were done with other *n*-alkanes in the series. The empirical relationship between *S** and alkane oils' ACN was established. The mixture of TEL and hexane in a mole fraction ratio of 0.2:0.8 was prepared and used for investigating the EACN of TEL. The experiments needed to be set up in a hood under a nitrogen atmosphere glove bag purchased from Sigma-Aldrich (Germany) in order to prevent TEL degradation and a direct contact to air. The same procedure was applied to other surfactant systems: 2 wt.% SDOS and 2 wt.% SDHS.

Then, after the EACN of TEL was derived. A number of solutions containing organotin (DBT) mixed with solvent(s) at various mole fraction ratios of DBT in solvent(s) (such as hexane) were prepared. These mixed oils were tested by the same procedure with surfactant systems. The mixed oils that yield the same *S** which responded to EACN similar to of TEL, was used as the TEL surrogate for further study.

3.2.2 Phase study

The part is to find the surfactant solution which could form microemulsion thus the criteria to select the surfactant solution was that the system giving the transition phase form Winsor type I to type III microemulsion.

Some surfactants (C16DPDS, SDHS, SDOS, and Tween80) were prepared at 4 wt.% total concentration with varied salt concentration and some mixed couple surfactant ratio. The microemulsion formation systems were conducted in 1 mL tubes with equal volume of surfactant aqueous solution and oil surrogate. These tubes were then immediately sealed with stopper and gently shook for 1 minute.

Initially, the phase formation was observed every day for several day and found that the phase keep steady during after 1 day to 4 day and disappear subsequently which could not reversible. Thus, the samples were selected to stand for 2 days at 25 ºC.

3.2.3 Solubilization study

This study was done to observe the solubilization capacity of contaminants into surfactant solution. In CHAPTER V, it was done by mixed 5 mL of surfactant solution at various salinity and oil together. , gently shook to mix, and let it stand for 2 day, then separated aqueous for measurement. However, in CHAPTER VII, the methodology was developed for easier separation, thus, derived more accurate result. The 25 mL of selected surfactant at various salinities were prepared in 50 mL separation funnel then 2 mL of oil surrogate was added, gently shook to mix it, and let it stand for 2 day. The aqueous surfactant solution was then separated from the oil phase. It is very important that we could loss some volume of surfactant solution, even though 25 mL was profuse for measurement, it did not allow any oil drop dispersed into the surfactant solution. In case of middle phase appeared, it was collected and mixed with aqueous phase and measured as mixed solution.

The solubilized PCE and decane was measured by gas chromatography (Clarus 500, PerkinElmer) with FID detector connected with headspace auto sampler (Turbomatrix 40, Perkin Elmer). Nirogen gas was used as carrier gas. The sample volume of 100 µL was equilibrated by headspace auto sampler using the temperature of 80 ºC for 30 min before injected to the GC system. The column flow was controlled by pressure at 6 psi. The oven temperature was 140 ºC isotopic system.

DBT was measured as total tin in the solution. The samples were digested by microwave digester (Ethos pro, Milestone) before measured for tin by ICP-OES system (Vista-MPX, Varian). The digestion procedure was adapted from digestion method described by Hargreaves (Hargreaves et al., 2004), 500 µL of sample was mixed with 9 mL hydrochloric acid (65%) and 3 mL of nitric acid (37%) and temperature program started with the increasing of temperature to 175 ºC within 13 min and the holding at 175 ºC for another 10 minutes. It should be noted that even nitric acid is a better one for digestion of organic compounds, tin could be precipitated with nitrate. Therefore Hargreaves et al. (2004) developed this method to prevent that problem. However, in this experiment, very tiny floating oil slough was observed in the digested solution but it did not affect the calibrated curve. Thus, some samples which were suspected had high organic content was reduced the sample to 250 µL to ensure the digestion procedure.

3.2.4 Column study

Column packing and residual oil preparation procedure was adapted from Childs et al. (2004) and Acosta et al. (2003). The column and pumping system is in Figure 3.1. Two pumping systems were prepared, the joints and valves of the system are made from stainless. The pumping system (*A*) was connected to the effluent end of column and then the water was pumped to displace air in the pumping pipe line. After that the water was drained out until the surface of water equals to the bottom filter.

The Ottawa sand was packed into column by wet packing technique to avoid the air bubbles retain in the sand column. About 50 mL of water and 200 g of Ottawa sand were prepared in each beaker and weighted with beaker. The water was gradually filled into column, where the height of sand filled each time was about 2 cm. The water at surface level was maintaining about 4 cm above the sand surface. The sand was stirred and packed every time after filled to dispel all air bubbles. When the sand was packed to reach the height of 16 cm, the water was drained out, which was collected, until the surface of water in column reach the top surface of sand. Then the remaining water was then weighted again (with its beaker) to calculate the pore volume of packed column. The same procedure was also used for the experiment with aquifer soil. The pore volume ($\forall_p$) was the different weight of water in beaker before (W_{w1}) and after packed the sand (W_{w2}) divided by the density of water (D_W) as show in Equation 3.1.

$$\forall_p = \frac{(W_{W1} - W_{W2})}{D_W} \tag{3.1}$$

The sand was also weighted to know the mass of sand in the column. Then, when the sand was saturated with water, the influent pumping system (*B*) with *flow adapter* was fitted to the top of column. The water was then flushed from the effluent in up flow direction to dispel the air at the top of column and influent pipe line. Then, when there was no air in every part of column system, the flow was stopped and the pumping system at the effluent was removed. Now the column was packed and ready to use. Then, 10 pore volumes of degassed water containing 0.01 M $Ca(NO_3)_2$, which functioned as the synthetic groundwater, was pumped to influent line at the pore velocity of 2 cm/min.

Residual saturation was established by replace the water in the column by DBT-PCE mixture using the head different technique in up-flow direction. The oil was filled to the column at the height of about 16 cm. Then, 10 pore volumes of synthetic ground water were injected at the pore velocity of 2 cm/min. (ten time of surfactant flushing) to flush the free phase oil out.

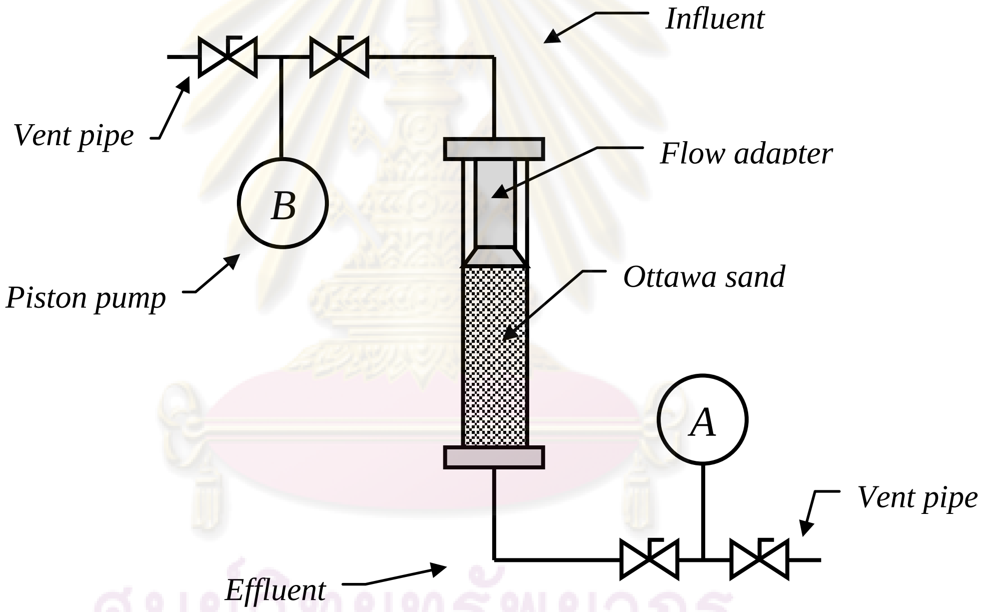


Figure 3.1 Experimental setup for column experiments.

The amount of entrapped oil was quantified, in the same manner of pore volume, from a mass balance of the oil before and after the contamination procedure. The volume of retained oil (V_{oil}) can be calculated from the weight of oil with the container before (W_{oil1}) and after (W_{oil2}) saturation procedure and the oil density (D_{oil}) (see Equation 3.2).

$$V_{oil} = \frac{(W_{oil1} - W_{oil2})}{D_{oil}} \tag{3.2}$$

The residual saturation was calculated as the volume of retained oil divide by pore volume of the saturated area. Then, this prepared column was flowed by 1 PV of DI water and follow by flooding with the surfactant solution at the pore velocity of 0.2 cm/min (adopted from Childs et al., 2004) to observe the solubilized contaminant in the effluent and the treatment efficiency. The pore velocity relates to the mobilization potential. Flow rate of 0.38 mL/min was used for the column calculating from this pore velocity, porosity, and the column diameter. The effluent were collected by fraction collector (RediFrac, Pharmacia Biotech), 20 min per sample. The surfactant flooding was stop when the PCE or decane was absent. Mobilized oil fraction was removed as fast as possible and measured by weight. Then sample was keep to measure for solubilization of PCE and DBT as tin.

CHAPTER IV

THE EACN AND THE SURROGATE OIL

The study in this part was carried out together with Prangtong Thongkorn (Thongkorn, 2007), a master student, to establish the linear empirical relations using Salager's relation concept. From first part of the experiment (3.2.1), two linear empirical relations derived from two surfactant system. The EACN of TEL was determined which was about 6.04 to 7.68. The detailed results were supplied in APPENDIX A. Only the part of EACN quantification of TEL was contributed to the manuscript. After the EACN of TEL was quantified, the surrogate oil was then identified by Thongkorn (2007) using the same procedure Among some alkane: octane, decane, and dodecane; decane was selected according to the finding that it can rise the EACN to the desired value and could form middle phase with the surfactant solution in the procedure of EACN determination. The result showed that mixture of DBT and decane at mole ratio of 0.038:0.962 had EACN similar to TEL (EACN = 7.2), decane was a light oil having density of 0.748 g/mL. Thus, the mixture of DBT-PCE at the same mole ratio was applied to be used as another surrogate in further experiment. The new surrogate (DBT-PCE mixture) could rises the density up to 1.587 g/mL and become a DNAPL, however, PCE lowered the EACN of the mixture to be at 0.3.

4.1 Paper's title and authors

The title of this manuscript was proposed to be "EACN and Microemulsion Phase Behavior of Organometallic Mixtures". The contributed authors were Prangthong Thongkorn, Seelawut Damrongsiri, Punjaporn Weschayanwiwat, Chantra Tongcumpou, and David A. Sabatini.

4.2 Abstract and key words

Surfactant enhanced solubilization was evaluated for organometallic compound removal from contaminated sand using the conducted. Tetraethyl lead (TEL) has been implicated as a cause of contamination worldwide. Due to the toxicity and difficulty in the handling of TEL, this work aimed to explore a new substance for use as a TEL surrogate for research and to investigate the capability of surfactant microemulsion solution to remove TEL surrogate contamination in soil. The criteria for TEL surrogate selection were stipulated. Salager's concept was applied to determine the hydrophobicity (defined by equivalent alkane carbon number, EACN) of TEL and as a consequence, dibutyltin dichloride (DBT) mixed with decane at a molar ratio of 0.038:0.962 was found to be the most suitable TEL surrogate since the EACN of this oil mixture was close to that of TEL (EACN_{TEL}= 6.04-7.23). A surfactant system comprised of 3.6 wt.% sodium dihexyl sulfosuccinate and 0.4 wt.% monoalkyl diphenyloxide disulfonate was investigated for solubilization of the surrogate oil andapplied to flush the sand column contaminated by such oil. The results indicate that the surrogate oil could be solubilized into surfactant solution as expected. Nevertheless, the phenomenon in the column experiment behaved differently as the solubilization of DBT was impeded by the surfactant solution. Both organic and inorganic behavior was observed and affected on treatment.

Key words: dibutyltin dichloride (DBT); tetraethyl lead (TEL); equivalent alkane carbon number (EACN); microemulsion; surfactant;

4.3 Introduction

Tetraethyl lead (TEL) - an organometallic compound - was extensively used as an anti-knock additive in gasoline beginning in the 1920s (Rhue et al., 1992). It is considered a toxic substance due to its harmful effects on humans and the environment. The use of TEL in gasoline for automobiles was banned by the United States Environmental Protection Agency (USEPA) in 1973. As a consequence, leaded gasoline production and consumption declined. However, TEL production over a long period resulted in widespread contamination. At present, the addition of TEL in fuel is limited to airplanes and racing cars (Ouyang et al., 1996; Unob et al., 2003).

Some study to solve this problem was done using several methods. The degradation of TEL in soil was observed by Ou et al. (1994). In an aquatic environment, TEL was firstly degraded to mono-ionic triethyl lead, which was in turn degraded to di-ionic diethyl lead, and finally to Pb^{2+} (Rhue et al., 1992). The organometallic compounds can be degraded chemically and biologically in the environment (Gadd et al., 1993). The treatment of TEL contaminated packed soil column by biodegradation seem to be limited on the triethyl lead (Gallert et al., 2002 and 2004). The chemical oxidation was also studied (Andreottola et al., 2008) but seem not suit to the in-situ remediation. TEL is a non-persistent compound. Nevertheless, it can break down in the environment to other forms of organolead which are much more persistent, eventually forming stable inorganic lead. The degraded products of TEL are still toxic to human and environment.

TEL is a hydrophobic compound with very low water solubility of 0.2 to 0.3 mg/L at 0 to 38 ºC (Feldhake and Stevens, 1963) making it trend to be adsorbed on soil material, but is highly soluble in hydrophobic solvents such as gasoline, benzene, and hexane. On the other hand, ionic ethyl-lead species, such as triethyl lead, diethyl lead, including many decomposed products, are not soluble in hydrophobic solvents but highly soluble in water (Feldhake and Stevens, 1963). The metabolite of TEL is also toxic and quite persistent making it possible to be carried long distances in ground water. Solid inorganic leads are stable and insoluble and thus, not easily to be leached to ground water. However, the leaching may occur under acidic conditions or when lead concentrations are extremely high, let it not be accepted if it settle near the aquifer.

Thus, the removal of TEL from the subsurface is a challenge approach. A robust remedial technique known as the surfactant enhanced aquifer remediation (SEAR) has been found to be a promising method to mitigate contamination of organic compounds (Shiau et al., 1996; Dwarakanath et al., 1999; Harwell et al., 1999; Sabatini et al., 2000; Uchiyanma et al., 2000; Wu et al., 2000, 2001; Acosta et al., 2003; Child et al., 2004). The removal of leaded gasoline from a packed soil column using surfactant solution was investigated by Ouyang et al. (1996) and the washing of TEL from soil and equipment was also studied by Laser and Wingrave. (2000). Thus, surfactant-enhanced solubilization may be a potential technique to remove the organometallic compound from contaminated areas rather than using a degradation approach which leaves the derivatives of heavy metal in place.

In order to investigate the approach for TEL removal, surrogates which are less toxic were needed to be selected So, this research was primarily aimed to find a surrogate oil to be used for experiments instead of TEL, owing to the fact the TEL itself is very toxic and difficult to handle. Important criteria of compound to be used in the experiment with surfactant wok are the equivalent alkane carbon number or "EACN". The organic compound which has similar EACN tends to be able to form the same type of microemulsion with the surfactant mixture in the same range of HLB. For example, the surfactant solution which could form type III microemulsion with hexane also has high potential to form type III (not type I or type II) microemulsion with limonene too (EACN of limonene is about 6, Szekeres et al, 2007).

The alkane carbon number (ACN) is defined as the degree of hydrophobicity of linear linear alkane with correspondence to its carbon number (i.e., ACN of hexane = 6). For the nolinear alkane oils such as benzene, in order to compare with ACN, the term the equivalent alkane carbon number or "EACN" was defined. The oil EACN concept was initiated by Cayias and co-workers (Cayias et al., 1976), where the EACN of the nonlinear alkane oils can be determined by comparing the optimum microemulsion formulation in the same physicochemical environment as that of linear alkanes. Understanding the EACN of oil is useful for designing the surfactant systems that can enhance the solubilization of that oil (Wu et al., 2000; 2001).

When there are more than one types of oil in the mixture, the EACN of oil mixture can be determined based on pseudocomponent assumption (Baran et al., 1994). By this assumption, the compositions of solubilized oil are equal to the compositions of the excess oil. The $EACN_{mix}$ of the oil mixture is computed by linear mixing rule, Equation 4.1.

$$EACN_{mix} = \sum_i x_i \cdot EACN_i \qquad (4.1)$$

where $EACN_{mix}$ is EACN of oil mixture; $EACN_i$ is EACN of component i in the oil mixture; χ_i is mole fraction of component i in the oil mixture.

To determine the EACN of oils, the surfactant microemulsion formation coupled with Salager's Equation was used as shown in several studies (Wu et al., 2000; Baran et al., 1994). Salager found that the optimum salinity (S^*), which is the point at which equal volume of water and oil solubilized into middle phase microemulsion (Winsor type III), can be stated by the following empirical equation (Salager et al., 1979):

$$\ln S^* = K(EACN) + f(A) - \sigma \qquad (4.2)$$

where S^* is optimum salinity, K is a constant, $f(A)$ is a value specific to the alcohol utilized, and σ is a characteristic surfactant parameter. This equation can be modified into a reduced form as shown in Equation 4.3 if the system is applied at the same temperature using the same the surfactant and same concentration without alcohol addition.

$$\ln S^* = K(EACN) + c \qquad (4.3)$$

where c = a constant value, thus, easier to establish and used in the study. Thus, $(EACN)_M$ can be substituted into Equation 4.3, resulting in:

$$\ln S_{mix}^* = K(EACN_{mix}) + c \qquad (4.4)$$

As the S* was defined as the point that oil and water solubilized into middle equally, the solubilization capacity (SP) is the expedient parameter. The solubilization capacity of middle phase microemulsion is defined by the SP (Healy and Reed, 1977) as

$$SP_o = V_o/V_s \qquad (4.4)$$

and

$$SP_w = V_w/V_s \qquad (4.5)$$

where SP_o and SP_w are solubilization parameters for oil and water, respectively; V_o and V_w are volumes of oil and water solubilized in the surfactant solution, respectively; and V_s is the volume of surfactant(s) present, excluding the alcohol volume (if used).

4.4 Materials and methods

4.4.1 Materials

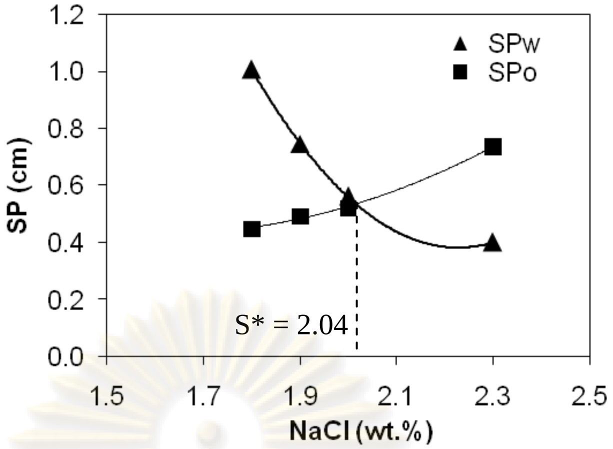
Analytical grade TEL and DBT purchased from Sigma-Aldrich Co. were used as contaminants. The linear alkane series including pentane (Fluka), hexane (LabScan), octane (Carlo Erba) and decane (Fluka) were used to establish the empirical relationship between *S** and (E)ACN of oil (Salager's Equation). The surfactants used in this research were sodium dihexyl sulfosuccinate (SDHS, trade name of Aerosal MA with 80% active) and sodium dioctyl sulfosuccinate (SDOS, trade name of Aerosal OT with 100% active) were purchased from Fluka Co; and a sorbitan monooleate with 20 ethoxy groups (trade name of Tween80 with 100% active) was purchased from BDH Co. Sodium chloride (analytical grade) was purchased from LabScan and used for salinity scan. All chemicals in this research were used as received without further purification.

4.4.2 Experimental Procedures

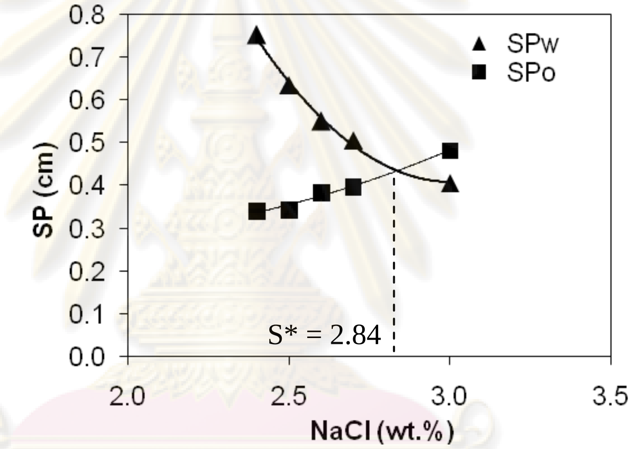
Parameters in Salager's Equation were first established using the following method. Equal volume of linear alkane oil and aqueous phase were added to a 1 mL tube (0.5 mL each) with stopper. The aqueous phase contained a mixture of 2 wt.% SDOS, 2 wt.% Tween80 and sodium chloride at various concentrations. The tubes were immediately sealed, gently shaken for 1 minute and equilibrated for 1 day. The *S** of each linear alkane oil could be obtained based on the solubilization parameter (*SP*) method. *SP* was quantified by measuring the change of the volume of the oil and aqueous phases as indicated by changing solution height as shown in Equations (4.4) and (4.5). The graph of values for *SP* for oil and aqueous phases (SP_o and SP_w, respectively) and concentration of NaCl of each linear alkane system was plotted. The S^* was indicated by the intersection of SP_o and SP_w. By the same manner, the mixture of TEL and hexane in a mole ratio of 0.2:0.8 was prepared and used for investigating the EACN of TEL. The same method was applied to another surfactant system: 2 wt.% SDOS and 2 wt.% SDHS. Next, a number of solutions containing DBT mixed with solvent(s) with various molar ratios of DBT in solvent(s) were prepared. Microemulsions were formed with these mixed oils using the procedure discussed above. The mixed oils yielding EACN values close to that of TEL were used as the TEL surrogate for further study.

4.5 Results and discussion

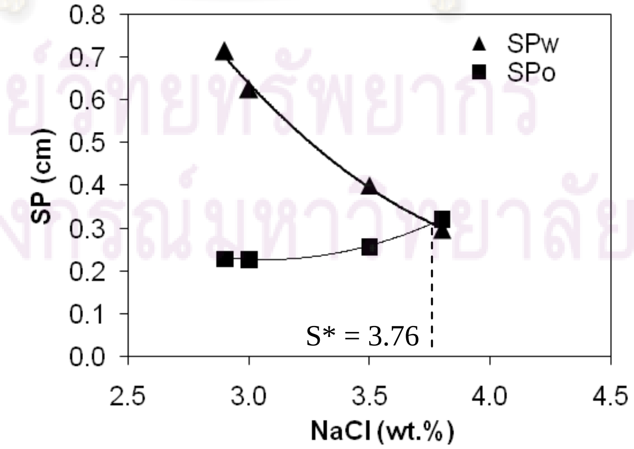
Both surfactant mixtures, SDOS/Tween80 and SDOS/SDHS, were able to form microemulsion with alkanes ranging from ACN = 5 (pentane) to ACN = 10 (decane). The system of SDOS/Tween80 was formulated with 3 linear alkanes including hexane (ACN = 6), octane (ACN = 8) and decane. The volume of phase change and phase transition could be observed in each system. The S^* of each oil could be obtained from the intersection point of plots between SP_w and SP_o versus wt.% NaCl. From this procedure, the S^* of the 3 linear alkanes could be obtained. The results were show in Figure 4.1 and 4.2. The S^* of hexane, octane and decane were determined as 2.04, 2.84 and 3.76, respectively. For a system of SDOS/SDHS, the S^* with 3 linear alkane oils: the S^* of pentane, hexane and octane were also achieved by the same procedures and were 1.49, 1.85, and 2.94, respectively.



(a)

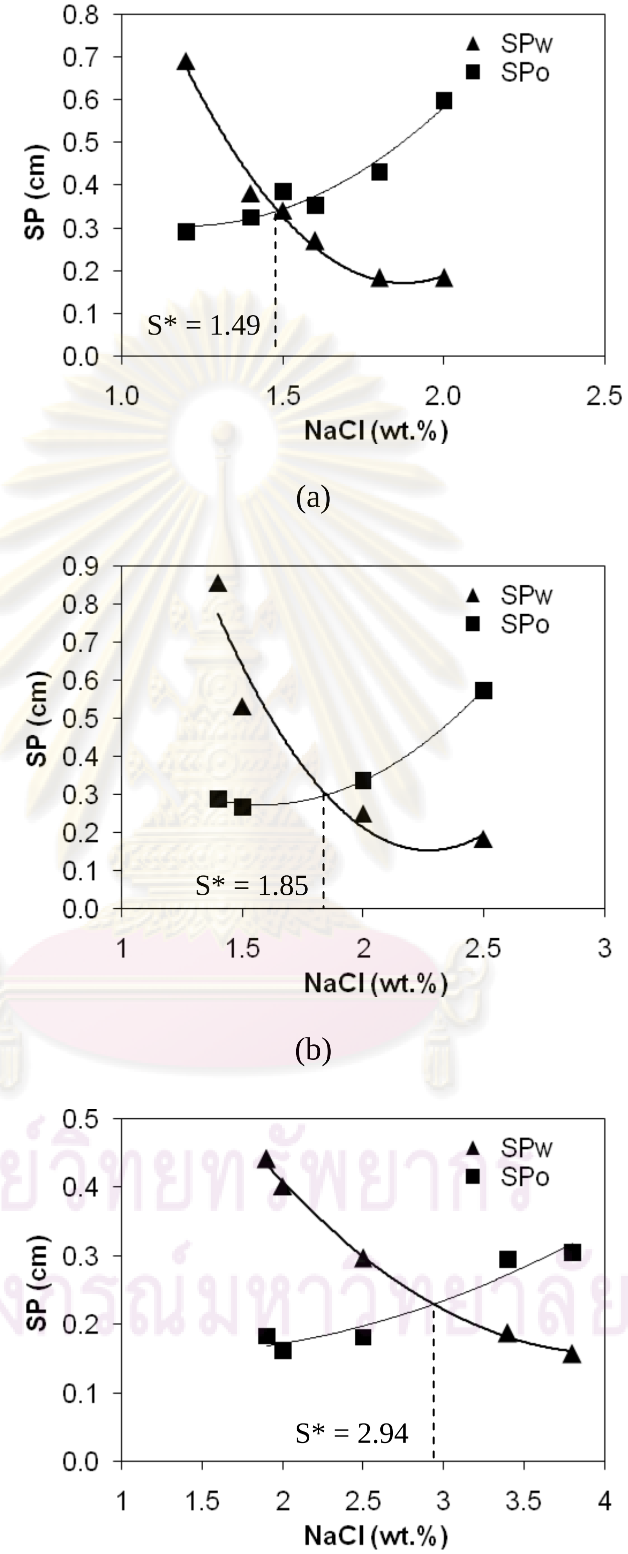


(b)



(c)

Figure 4.1 Plot of SP_w and SP_o with NaCl and the optimum salinity in solution of 2 wt.% SDOS and 2 wt.% Tween80 (a) hexane (b) octane (c) decane



(a)

(b)

(c)

Figure 4.2 Plot of SP_w and SP_o with NaCl and the optimum salinity in solution of 2 wt.% SDOS and 2 wt.% SDHS (a) pentane (b) hexane (c) octane

The natural logarithm of *S** was plotted against the oils' EACN as shown in Figure 4.3. Thus, the empirical equation between ln*S** and EACN for SDOS/Tween80 system was $\ln S^* = 0.1529\ \mathrm{EACN} - 0.1959$ and for SDOS/SDHS system was $\ln S^* = 0.2273\ \mathrm{EACN} - 0.7419$. The coefficient of determination from both systems were higher than 99% (R-square > 0.99).

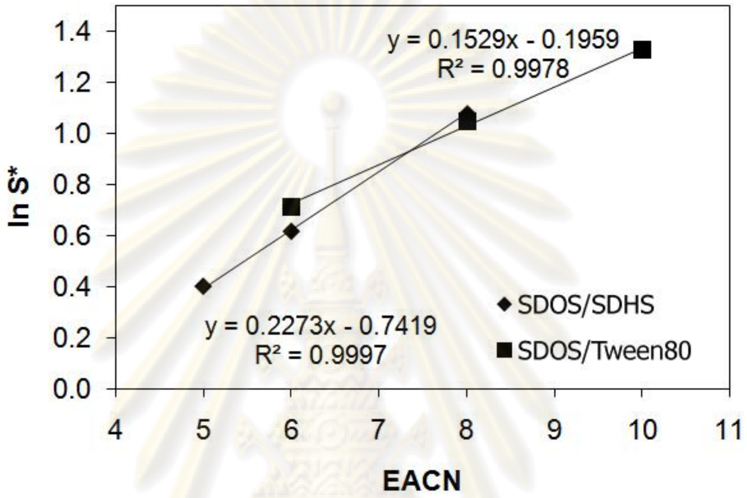


Figure 4.3 Linear relation between the natural logarithm of *S** and EACN by the surfactant solution of 2 wt.% SDOS 2 wt.% Tween80 and 2 wt.% SDOS 2 wt.% SDHS

To quantify the EACN of TEL, high purity TEL was mixed with hexane at a mole ratio of 0.2:0.8. The mixed TEL solution was used to form microemulsion with both surfactant systems. The obtained *S** from SDOS/Tween80 system and from SDOS/SDHS system were 2.06 and 2.01 which respond to the EACN of 6.008 and 6.34, respectively. Then, the EACN of pure TEL was calculated by Equation 4.1 and found to be 6.04 and 7.68, via system of SDOS/Tween80 and SDOS/SDHS, respectively.

4.6 Conclusions

The microemulsion formation between surfactant and mixed oils was applied to investigate the EACN of TEL and its surrogate using Salager's Equation and a linear mixing rule. The surfactant solution of SDOS/Tween80 found to be form middle phase with of hexane, octane and decane while the surfactant solution of SDOS/SDHS could be formed with pentane, hexane, and octane. The linear relation between ln S* and EACN was established with high coefficient of determination. The EACN of TEL was found to be 6.04 and 7.68 by SDOS/Tween80 and SDOS/SDHS, respectively.

CHAPTER V

SOLUBILIZATION CAPACITY AND SOLUBILIZATION BEHAVIOR OF OIL SURROGATE

From CHAPTER IV as we propose an oil surrogate that was mixture of DBT and decane at molar ratio of 0.038:0.962 which has the properties of being organometallic compound and has similar EACN but the density was different, it was light oil. It is must mention that we could not found the oil surrogate which has all three properties as designed criteria. Thus, in this CHAPTER, another oil surrogate was then proposed that was the mixture of DBT and PCE at the same molar ratio in order to represent the properties of being organometallic and has similar density (but different EACN) that for observed for mobilization in CHAPTER VI and VII. The same ratio was designed for compare the result. Both oil mixtures were applied in this study.

This is the result from solubilization study (3.2.3). Some surfactant mentioned in CHAPTER III was tried to form microemulsion with this surrogate oil. But only the solution of 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with $CaCl_2$ showed the phase transition from type I to type III, thus, applied in the solubilization study. The solubilization result was discussed and composed to be the following paper. The detailed results were provided in APPENDIX B.

5.1 Manuscript's title and authors

The title of this manuscript was "Solubilization of dibutyltin dichloride with surfactant solutions in single and mixed oil systems" The contributed authors were Seelawut Damrongsiri, Chantra Tongcumpou, Punjaporn Weschayanwiwat, and David A. Sabatini. This paper was already published in Journal of Hazardous Materials (2010), volume 181, page 1109–1114.

5.2 Abstract and key words

The harmful effects of organometallic compounds and their metabolites on the environment and human health require the development of more effective remediation methods. Surfactant enhanced remediation has been considered as a potential method for the removal of organometallic compounds; however, additional understanding is needed about the solubilization processes of these compounds. The surfactant enhanced solubilization of dibutyltin dichloride (DBT), an organometallic compound, was the focus of this research. In addition, the synergistic effects of DBT solubilization in perchloroethylene (PCE) and decane mixtures were evaluated. The results indicate that PCE and decane were solubilized into the core of these surfactant micelles in both single and mixed oil systems. DBT solubilization was limited when DBT alone was present (single oil system), and the nature of the solubilization isotherm suggests that DBT solubilization tended to occur near the micelle surface in a single oil system. DBT solubilization was found to increase when present in the PCE and decane oil mixture. PCE and decane may have facilitated the solubilization of DBT because they were solubilized in the micelle core. From this study, it may be concluded that the DBT behaves like polar oil such as dodecanol, having properties of a polar organic compound.

Key words: Organometal; Dibutyltin dichloride; Perchloroethylene; Solubilization

5.3 Introduction

Organometallic compounds (i.e., compounds containing bonds between carbon and a metal) have been employed in numerous applications. For example, they have been used as catalysts, stabilizers in plastic industries, wood preservatives, agricultural biocides, and antifouling paints made for ship hulls. Tetraethyl lead and tetramethyl lead, in particular, have been combined with gasoline as an antiknock agent. The spillage of these highly toxic organometallic compounds during their production, transport, and/or blending has caused severe soil and groundwater contamination problems (USEPA, 1999).

Organotin compounds have also been used in a range of applications. Tetra-substituted compounds have been used as intermediates in the synthesis of other organic chemicals (RPA, 3003). Tri-substituted organotins are used as biocides, pesticides, antifouling boat paints, and intermediates in the production of other chemicals (RPA, 2003). Mono- and di-substituted organotins are generally grouped together and used as polyvinyl chloride (PVC) stabilizers, as catalysts, and in glass coating. About 18,000 tons per year of mono- and dialkyl-tin compounds, were sold in EU in 2002, resulting in their extensive distribution in the environment (RPA, 2003). Their properties of organotin compounds depend on the numberof organic groups that are bonded with tin (RPA, 2003). Organotins have been shown to accumulate in the food chain and pose a potential risk to human health (Cao et al., 2009). Organotin compounds are also found in landfill leachates. Pinel-Raffaitin reports that up to nine organotin compounds (e.g., methyltin, ethyltin, butyltin, and mixed methy-ethyltins) have been detected in landfill leachates at concentrations ranging from 0.01 mg tin/L to 6.5 mg tin/L, which totaled 1–38 wt.% of the tin concentration in the landfill (Pinel-Raffaitin et al., 2008). Huang and Matzner (2004) detected organotin compounds and metabolites in a forest soils showing that the degradation rates of methyltin and butyltin are slow (with half-lives from 0.5 years to 15 years).

Unlike other organic contaminants, bioremediation cannot sufficiently eliminate the risks associated with organometallic compounds since the resulting heavy metal metabolites (such as tin or lead) remain at the contamination site. Thus, the removal of organometallic compounds from the subsurface is a preferable approach. Surfactant enhanced aquifer remediation (SEAR) is a promising method for increasing the solubilization of organometallic compounds and their metabolites in soil and aquifers contaminated with leaded gasoline and other organic solvents (Ouyang et al. 1996; Leser and Wingrave, 2000). However, when a metal is present in the organic structure of a surfactant solution, it may alter its solubilization behavior; thus, a better understanding of the solubilization behavior of organometallic compounds is required.

Surfactants are amphipathic molecules consisting of a hydrophilic region (the head) and hydrophobic region (the tail). The polar head group of a surfactant interacts strongly with water molecules, resulting in the surfactant's hydrophilic behavior. In contrast, the hydrophobic tail groups dislike water. Thus, when a surfactant's critical micelle concentration (CMC) is surpassed, the surfactant forms colloidal aggregates called micelles with tail groups clustered together in the interior and shielded from water by the hydrophilic heads (Rosen, 2004). In the presence of salt, the size of a thermodynamically stable micelle can increase from several nanometers to hundreds of nanometers.

When these nanosize stable micelles solubilize oil they are known as microemulsions, which are translucent and form spontaneously (Sabatini et al. 2000). The main difference between an ordinary emulsion (i.e., a macroemulsion) is that only microemulsion possess the thermodynamically stable property (Paul and Moulik, 2001). In addition, microemulsion systems produce very low interfacial tension (IFT) and are capable of solubilizing both aqueous and oil soluble compounds. There are generally three types of microemulsions. Type I (oil in water) microemulsions form in the water phase with oil solubilized in the aqueous micelles. Type II (water in oil) form in the oil phase, where water is solubilized into the reverse micelles. In Type III (intermediate between Type I and Type II) microemulsion, the surfactant aggregated micelles separate from both phases and form a new thermodynamically stable middle phase. The type of microemulsion formed depends primarily on the properties of both the oil and surfactant(s) in the system. Hydrophilic surfactants tend to produce Type I microemulsions, while hydrophobic surfactants produce Type II microemulsions. Microemulsions can transition from being Type I to Type III and then Type II when the hydrophile–lipophile balance (HLB) of the system is reduced the surfactant system becomes more oil soluble. This can happen, for example, by increasing the salinity or adjusting the mixture of the hydrophilic and hydrophobic surfactants. Type I and Type III microemulsions have been used in surfactant-based remediation of organic contamination (Sabatini et al. 2000; Paul and Moulik, 2001; Dwarakanath et al., 1999).

Theoretically, the structure of the oil or solubilizate determines its locus of solubilization in a micelle (Rosen, 2004). The location of oil solubilization in a micelle can be (1) on the surface of a micelle, (2) within the hydrophilic head group, (3) on the palisade layer between the hydrophilic head group and first few carbon atoms, (4) beyond the palisade layer, and (5) at the core of the micelle (Schramm et al., 2003; Tadros, 2005). This work aims to better understand the solubilization behavior of organometallic compounds by investigating the solubilization of dibutyltin dichloride in surfactant solutions. Dibutyltin dichloride (DBT) was selected for this study as a surrogate for tetraethyl lead (TEL) because DBT is less toxic and is thus much safer to work with and easier to obtain than TEL. DBT was selected due to the fact that it is also an organometallic compound. However, since DBT is solid at room temperature, PCE and decane were added to obtain a mixture of non-aqueous phase liquids (DNAPL), which can represent the organometallic contaminants found in groundwater. The enhanced understanding gained on the solubilization of organotin compounds will help to guide the design of a surfactant system to enhance organometallic remediation with a high level of efficiency.

5.4 Materials and methods

5.4.1 Materials

Analytical grade DBT was purchased from Sigma–Aldrich Co., perchloroethylene (PCE) was purchased from Ajax Finechem, and analytical grade decane was purchased from Fluka Co. Two anionic surfactants were studied: C16 diphenyloxide disulfonate (C16DPDS), with the trade name Dowfax8390, was supplied by Dow Chemical Co., and sodium dihexyl sulfosuccinate (SDHS), known as AMA, was purchased from Fluka Co. Analytical grade calcium chloride ($CaCl_2$) and sodium chloride (NaCl) were purchased from LabScan and used for the salinity scans. All chemicals in this study were used as received without further purification.

5.4.2 Methods

5.4.2.1 Preparation of the mixed oil

DBT–PCE and DBT–decane, the mixed oils used in this study, were combined at the molar ratio of 0.038:0.962. This ratio was adapted from a study by Thongkorn et al. (2008), that investigated the removal of tetraethyl lead (TEL) using an oil surrogate with similar properties to TEL (an organometallic compound) and a similar equivalent alkane carbon number (EACN). In their study, a DBT–decane mixture with amolar ratio of 0.038:0.962 was selected as the TEL surrogate. At this molar ratio, the mixed oil surrogate (DBT–decane) was a light non-aqueous phase liquid (LNAPL). Thus, since TEL is denser than water, the selected liquid for mixing with DBT as the surrogate is the dense non-aqueous phase liquid (DNAPL). This DNAPL TEL surrogate was prepared by combining DBT with both PCE and decane. The same molar ratio of DBT and decane of 0.038:0.962 used in the previous work by Thongkorn et al. was used in this work for the purpose of comparison. DBT was selected because it has properties similar to that of TEL, its lower toxicity than TEL, its availability in the market, and its lower cost; all in all, these factors made it an attractive TEL surrogate option (Thongkorn et al., 2008).

5.4.2.2 Phase behavior and solubilization studies

Single surfactant systems of C16DPDS and SDHS at various salinities were mixed with the surrogate oil (a mixture of DBT and PCE at the molar ratio of 0.038:0.962). The binary system of C16DPDS was coupled with SDHS at varying weight ratios from 0 to 1 at 0.1 intervals (with 4 wt.% total). This was also carried out with the surrogate to observe its phase behavior. The samples were mixed and equilibrated for one day in storage cupboard. Afterward, the samples were placed at room temperature, 25 ºC, for 4 h to observe their phase behavior. The system selected from the scan was the one providing a transition from a Type I microemulsion to the Type III boundary. Subsequently, the selected formula was prepared in the batch study to investigate the solubilization. The same procedure was also performed using the DBT–decane mixture. The solubilization of the oil surrogate in surfactant solutions was carried out by preparing equal volumes of the oil surrogate and the selected surfactant solution in 10 mL screw cap tubes (5 mL each) of oil and water. The samples were mixed and equilibrated at 25 ºC for two day. The aqueous phase samples were measured to determine their solubilized tin values and PCE or decane values. Meanwhile, solubilization experiments for individual PCE, decane, and solid

DBT in the same surfactant solutions were also conducted. Each sample received 0.05 g of DBT in solid form.

5.4.2.3 Measurement of PCE, decane, and tin

The solubilized PCE and decane values were measured by a gas chromatography (Clarus 500, Perkin–Elmer) with a flame ionization detector (FID) connected to a headspace auto sampler (Turbomatrix 40, Perkin–Elmer). Helium gas was used as a carrier gas. The sample volume of 100 μL was equilibrated by the headspace auto sampler at 80 ºC for 30 min before being injected to the gas chromatography (GC) system. The oven temperature was 140 ºC for the isotopic system in which a peak of PCE was observed at 2.81 minute and that of decane was observed at 3.18 minute. DBT was measured as the total tin in the solution. The samples were digested by a microwave digester (Ethos pro, Milestone) before being measured for their tin contents by an inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Vista-MPX, Varian). The digestion procedure was adapted from the method described by Hargreaves et al. (2004).

5.5 Results and discussion

In order to achieve a middle-phase (i.e., Type III) microemulsion, a proper microemulsion system makes use of a surfactant with an HLB closest to that of the oil to be formulated (Wu et al., 2000; Acosta et al., 2003). Frequently, microemulsion formation requires additives such as salt and alcohol to form a microemulsion (Acosta et al., 2003). In this study, a mixture of surfactants C16DPDS and SDHS was selected to form the microemulsions.

5.5.1 Phase study

5.5.1.1 Phase behavior of DBT–PCE

When the single surfactant systems were evaluated, 4 wt.% C16DPDS was found to form a Type I microemulsion. This result was expected for C16DPDS since it is rather hydrophilic and there has been no report that it can form a Type III microemulsion by itself without any additives such as co-surfactant or alcohol. In the system with 4 wt.% SDHS, a Type III microemulsion was observed without any salt because the HLB of the surfactant was much lower than that of C16DPDS. This enabled it to be well suited to form a microemulsion with the target oil. C16DPDS was then mixed with SDHS to decrease the HLB of the C16DPDS system, and the mixture is expected to have the potential to formulate a microemulsion phase transition with the mixture of DBT–PCE.

To mixtures of C16DPDS and SDHS at various weight ratios, we added varying concentration of a salt, NaCl or $CaCl_2$, to observe their microemulsion phase transitions. This is referred to as salinity scan. The results show that only the systems containing a C16DPDS fraction equal to or less than 0.1 exhibited the transition from Type I to Type III. Thus, the mixture selected for the further experiments contained SDHS and C16DPDS at a ratio of 0.9:0.1 (3.6 wt.% SDHS and 0.4 wt.% C16DPDS). The phase transition was observed at 3 wt.% NaCl for the system with NaCl scan and at 0.3 wt.% for the system with $CaCl_2$ scan.

The phase behavior of the systems clearly demonstrates that a lower amount of $CaCl_2$ was needed to achieve a Winsor Type I to Type III phase transition as compared to the amount of NaCl required. This finding agrees with the study of Cheng and Sabatini (2001). Furthermore, Cheng and Sabatini (2002) explained that polyvalent cations (Ca^{2+} and Al^{3+}) have much higher surface charge densities and associate more strongly with the micelles of anionic surfactants than monovalent cations and, thus, are much more effective in decreasing the system HLB to promote the formation of a middle-phase microemulsion. Based on these results, the surfactant mixture comprised of 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with $CaCl_2$ was selected for the solubilization study.

5.5.1.2 Phase behavior of DBT–decane

The EACN of the DBT–decane mixture is much higher than that of the DBT–PCE mixture due to the fact that the alkane carbon number (ACN) of decane (10) is much higher than the EACN of PCE (2.9) (Baran et al., 1994). Thus, it can be presumed that the very hydrophilic (high HLB) C16DPDS would be able to form an o/w emulsion with the DBT–decane mixture. The same mixed surfactant system containing 3.6 wt.% SDHS and 0.4 wt.% C16DPDS was put through salinity scans, with both NaCl and $CaCl_2$, to determine their effects on the mixed DBT–decane surrogate oil. Unlike the system with DBT–PCE, a phase transition was not clearly observed with NaCl. Instead, phase separation was found when the NaCl content was greater than 5 wt.%. Experiments with $CaCl_2$ did not found phase transition in the range of 0.1–1.0 wt.% (0–90 mM) and phase separation did not occur in the $CaCl_2$ system. Therefore, since the $CaCl_2$ system did not cause phase separation it was selected for use in the solubilization study.

5.5.2 Solubilization study

In order to evaluate the solubilization behavior of the three oils (DBT, PCE, and decane), each oil was solubilized individually (single oil) and in the two mixtures (DBT–decane and DBT–PCE) were solubilized in the surfactant mixture selected from the phase study (containing 3.6 wt.% SDHS and 0.4 wt.% C16DPDS). The solubilization results of DBT, PCE, and decane individual and in binary mixtures are illustrated in Figure 5.1 (DBT–PCE) and 5.2 (DBT–decane).

5.5.2.1 Solubilization of individual oil in the surfactant mixture

In the systems of single oil (DBT or PCE or decane), only PCE was found to dramatically increase in aqueous concentrations as the $CaCl_2$ concentration increased. The solubilization of decane increased by about 0.46 mM and that of PCE by 5.1 mM for ever 1.0 mM increase of the salt, respectively (see slopes of the equations in

Figure 5.1. and 5.2). In contrast, DBT solubilization remained virtually constant (see the equation in Figure 5.1 and 5.2 for DBT-single).

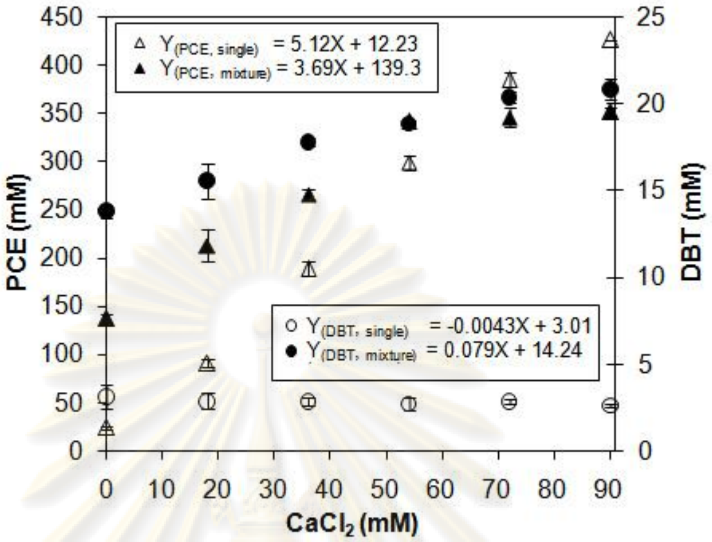


Figure 5.1 Solubilization of PCE and DBT in the system containing 3.6 wt.% SDHS and 0.4 wt.% C16DPDS at various $CaCl_2$ concentrations with individual oil and DBT–PCE mixture.

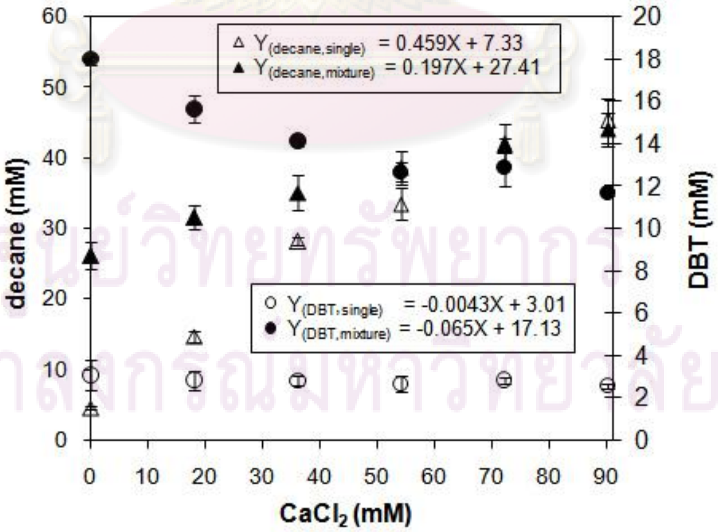


Figure 5.2 Solubilization of decane and DBT in the system containing 3.6 wt.% SDHS and 0.4 wt.% C16DPDS at various $CaCl_2$ concentrations with individual oil and DBT–decane mixture.

To help to understand the impact of salt addition on solubilization it is helpful to consider the effect of increasing salt on the surfactant itself. The addition of salt to the anionic surfactant solution decreased the repulsion occurring between head groups within the anionic surfactant head group, and resulted in the closer packing of the surfactant head group as the aggregation numbers increased and the curvature decreased.

Consequently, the space in the palisade layer was limited due to the occupancy of salt, while the space between the palisade layer and the inner core, which encompasses the first few carbons of the surfactant's tails, expanded. Based on the rule of thumb that the solubilization behavior of all solubilizates corresponded to their locus of solubilization within the micelle (Rosen, 2004), solubilization PCE that is hydrophobic and slightly polar was then facilitated by the expansion of both inner core and palisade layer. In contrast, solubilization of non-polar and hydrophobic decane occurs only in the inner core region of the microemulsion. Thus, the solubilization results indicate that PCE and decane were solubilized into the core of the micelles as the salinity increased, whereas DBT, the highest polar among these three oils, which by, its highly polar nature is expected to solubilized the near head group region, was consequently found remain constant or even slightly decreased in solubilization by an increase of salt (slope near zero and slightly negative for the DBT equation in Figure 5.1).

5.5.2.2 Solubilization of DBT and PCE as an oil mixture

The solubilization of DBT and PCE as a mixed oil was evaluated with the same surfactant solution, 3.6 wt.% SDHS and 0.4 wt.% C16DPDS, with varying $CaCl_2$ concentrations. The results shown in Figure 5.1 compare the solubilization of each single oil and each oil when present in the binary mixture. When $CaCl_2$ was increased from 0 mM to 90 mM, the solubilization of DBT behaved synergistically. The solubilization of DBT increased by around 0.08 mM for every 1.0 mM addition of $CaCl_2$, yet no increase was observed in the absence of PCE. Furthermore, even at zero $CaCl_2$, solubilization increased from 3 mM with DBT alone to 14 mM with DBT in PCE.

These results suggest the occurrence of the co-solvent effect from DBT and PCE, which may have heightened DBT solubilization as the amount of mixed oil was increased. DBT was likely solubilized at the palisade layer and may have partitioned in the outer layer of the core by solubilizing with PCE. Subsequently, at high salt contents where space for DBT is even more limited, DBT prefers to partition into PCE and hence reduces the concentration of solubilized PCE in the micelle. Therefore, the ratio of the solubilization enhancement of PCE in the individual oil system was higher than that of the mixed oil system: 51 mM and 37 mM for the individual oil system and mixed oil system, respectively. In addition, our preliminary experiments confirmed the occurrence of the co-solvent effect between PCE and DBT; the water solubility of DBT increased from 0.44 mM to 1.81 mM in the system containing PCE.

5.5.2.3 Solubilization of DBT and decane as an oil mixture

The solubilization of decane in the DBT–decane mixture using the same surfactant solution (3.6 wt.% SDHS and 0.4 wt.% C16DPDS) showed a similar trend to solubilization of PCE in the DBT–PCE mixture. However, and in contrast to the results for DBT–PCE mixture, DBT solubilization in this case decreased as $CaCl_2$ increased when DBT was mixed with decane (see Figure 5.2). It may be assumed that the close packing effect from the salt addition had a stronger influence than the co-solvent effect.

5.5.2.4 Solubilization behavior

The increased solubilization of both PCE and decane in the surfactant solution results is consistent with the behavior reported in a study on the effects of a lipophilic linker (Uchiyama et al, 2000). The lipophilic linker in a system has been shown to enhance the solubilization capacity of the anionic surfactant (Acosta et al., 2003; Uchiyama et al, 2000). In this present study, DBT is believed to play a role as a lipophilic linker and hence is what enhanced solubilization in the system. Acosta et al. (Acosta et al., 2003) reported that lipophilic linker molecules modify the equilibrium interfacial properties that serve as a link between oil molecules and the surfactant tails. This explanation also applies to lipophilic linker behavior when the linker partitions into the organic phase, and the partitioning into the oil phase is higher when that oil is a polar oil (Sabatini et al, 2003). As described above, DBT performed in a manner similar to that of a lipophilic linker (like dodecanol), which may be due to the DBT’s asymmetric molecular structure, caused by the hydrophobic part of its alkyl chain group combining with the hydrophilic part.

It should be noted that the molar ratio of the initial mixed oil of both systems (mixed DBT–PCE and mixed DBT–decane), at 0.038:0.962, was found to increase in aqueous-based surfactant solutions and decrease as the salt concentrations increased (see Figure 5.3).

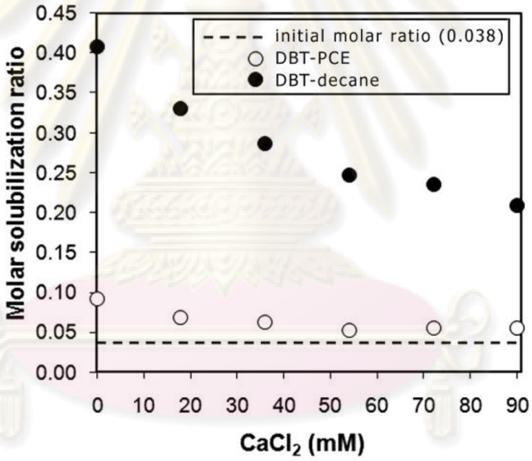


Figure 5.3 Molar ratio solubilization of DBT–PCE and DBT–decane in the systems containing the 3.6 wt.% SDHS and 0.4 wt.% C16DPDS mixture at various CaCl$_2$ concentrations

This solubilization phenomenon agrees with the preferential solubilization behavior of polar oil in mixed organics (Graciaa et al., 1993), in which the solubilized polar to non-polar oil molar ratio is higher than that of the excess phase and decreases as the salinity increases. In the case of the DBT–PCE oil mixture, even though it may be considered as polar oil, DBT can be assumed to have higher polarity due to its lower EACN. Based on this assumption, the oil molar ratio’s effect on solubilization in this present study is consistent with the behavior reported by Szekeres et al. (2005).

5.5.2.5 Loci of DBT, PCE, and decane in the micelle

From the pseudo-component assumption, it is well known that oils are solubilized in different locations in micelles depending on their molecular structure and polarity (Szekeres et al., 2005). The three solubilization locations in a micelle (Rosen, 2004) may be summarized as follows: the polar surface region, the palisade layer (between the surfactant tails), and the hydrophobic core (see Figure 5.4). When binary mixtures of polar and non-polar oils are solubilized, the non-polar oil is solubilized into the inner core, while the polar oil is solubilized in both the core and the palisade layer (Graciaa et al., 1993; Szekeres et al., 2005). Therefore, the ratio of polar oil in the micelles tends to be higher than that of a non-polar organic as it is able to be solubilized in all micellar regions. The composition of solubilized oil in the core is considered to be the same as it is in the excess phase, whereas the polar surface region and the palisade layer are dominated by polar oil (see Figure 5.4). Increasing salinity makes the micelles swollen and enlarges the hydrophobic core, causing solubilization in micelles to be preferentially enhanced in the core. As a result, increasing salinity can cause the solubilization ratio to approach the excess phase value (Uchiyama et al., 2000).

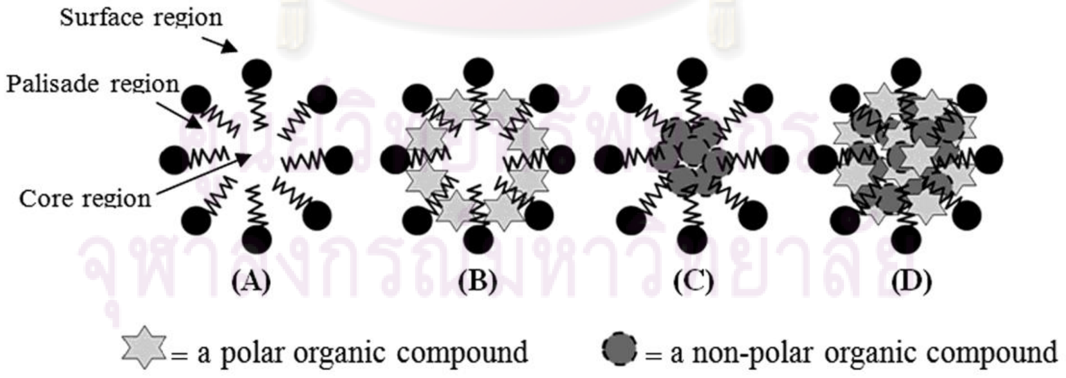


Figure 5.4 Loci of polar and non-polar solubilizates in a micelle (adapted from Tadros, 2005). (A) surfactant micelle, (B) solubilization region of polar organic compound, (C) solubilization region of non-polar organic compound, (D) solubilization region of mixture of non-polar and polar organic compound.

A different situation was observed when two oils with similar polarity values were solubilized. Zhao et al. (2007) studied the solubilization of trichloroethylene (TCE, EACN = −3.8), PCE, and a TCE–PCE mixture (1:1, by volume). The solubilization values of individual TCE and PCE by 1 wt.% sodium dodecyl benzene sulfonate were about 43 mM and 14 mM, respectively, while TCE and PCE with the TCE–PCE mixture were 19 mM and 13 mM (totaling 32 mM).

As can be seen from these results, total solubilization values are greatly impacted by polarity of the molecule being solubilized. The amount of solubilization increased in conjunction with polarity for PCE, the TCE–PCE mixture, and individual TCE. This finding helps us to understand the different solubilization mechanisms observed in our study. It indicates that PCE and TCE may solubilize in the same micelle region, resulting in the reduction of their solubilization when they are mixed together. Up to this point, it can be summarized that DBT behaves like a polar oil, not like a hydrophobic oil. This makes DBT more similar to the polar oil dodecanol, which has been used in studies on lipophilic linkers (Acosta et al., 2003;, Uchiyama et al. 2000; Sabatini et al, 2003) and the solubilization of mixed polar and nonpolar oils (Graciaa et al., 1993; Szekeres et al., 2005).

5.6 Conclusion

Organometallic compounds can be solubilized into surfactant micelles. Their solubilization potential depends on the chemical’s polarity and molecular structure, and the size or the metal element in its molecule. The solubilization behavior of DBT was similar to that of polar oil; DBT also exhibited an effect close to that of a lipophilic linker. The selected surfactant systems used for this study exhibited Type I to Type III microemulsion phase transitions, which are expected to provide the highest solubilization due to the swelling of micelles close to the phase transition. The solubilization behavior of the organometallic compounds maybe similar to that of general organic compounds in that the location of the solubilization region depends on the polarity of the chemical. The discussion here is based on the assumption that DBT is a polar organic compound, and this general rule of thumb was used to describe the solubilization trend. The increase in the aggregation number obtained from increasing salinity enhanced the solubilization of non-polar compounds in the core and decreased the solubilization of polar organic compounds in the palisade layer region.

Understanding of the solubilization behavior of organometallic compounds is crucial to the design of efficient surfactant enhanced remediation systems. The similarity of the organometallic solubilization behavior observed in this research to that of non-metallic organic oils, for which there is previous research on, indicates that the well established solubilization concepts of non-metallic oils may be applicable to organometallic compounds. However, in soil treatment practices, the sorption of organometallic compounds on soil and their degradation should be studied, as they may have significant effects on phase formation, solubilization, and treatment efficiency.

CHAPTER VI
COLUMN EXPERIMENT

This chapter was focusing on the results obtained from the column experiment (3.2.4). Both oil surrogates (mixtures of DBT-decane and DBT-PCE) were used in the study. The Ottawa sand was used as the soil media. The surfactant solution applied in the study was the same formulation used in the solubilization study (CHAPTER V) which were the solution of 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with $CaCl_2$. Single surfactant flooding and gradient surfactant flooding were carried out. The detailed results were available in APPENDIX C.

6.1 Paper's title and authors

The title of this manuscript was “Removal of dibutyltin dichloride mixture by anionic surfactant solution: Column study” The contributed authors were Seelawut Damrongsiri, Chantra Tongcumpou, and David A. Sabatini.

6.2 Abstract and key words

Surfactant enhanced remediation has been considered as a potential method for the removal of organometallic compounds. The previous study show that solubilization of dibutyltin dichloride (DBT) was similar to the polar organic compound. The column experiment was carried out to observe the occurring during surfactant flooding through the DBT contaminated aquifer. The plug flow was obtained in the experiment indicated by tracer study. Mixture of DBT-perchloroetylene (DBT-PCE) and DBT-decane were applied as the contaminant. Solubilization tendency of PCE and decane in every experiment were similar to the general organic compound found in some literatures that governed by rate limited mechanism. Solubilization of DBT was obstructed. The concentration of DBT was just a slice of its solubilization capacity even most of DBT was still trapped in the packed sand column. The gradient surfactant flooding could not drive the solubilization of DBT. The adsorption of DBT was suspected to be the cause of problem. The result indicated that DBT may show the properties of both organic and inorganic compound, it could be solubilized by solvent and surfactant and may also able to be absorbed on sand.

Key words: organometallic compound; dibutyltin dichloride (DBT); surfactant; column experiment; solubilization

6.3 Introduction

Organometallic compounds (i.e., compounds containing bonds between carbon and a metal) have been employed in numerous applications. For example, they have been used as catalysts, stabilizers in plastic industries, wood preservatives, agricultural biocides, and antifouling paints made for ship hulls. Tetraethyl lead and tetramethyl lead, in particular, have been combined with gasoline as an antiknock agent. The spillage of these highly toxic organometallic compounds during their production, transport, and/or blending has caused severe soil and groundwater contamination problems (USEPA, 1999). However, the study on TEL remediation in laboratory was concerned on the risk of such very dangerous organolead including it degradation products. The base knowledge about of organometal remediation by surfactant should be awareness. The experiments turn to start on lower risk compound such as organotin.

Organotin compounds have also been used in a range of applications such as an intermediates in the synthesis of other organic chemicals, biocides, pesticides, antifouling boat paints, di-substituted organotins are generally grouped together and used as polyvinyl chloride (PVC) stabilizers, as catalysts, and in glass coating. About 18,000 tons per year of mono- and dialkyl-tin compounds, were sold in EU in 2002, resulting in their extensive distribution in the environment (RPA, 2003). Organotins have been shown to accumulate in the food chain and pose a potential risk to human health (Cao et al., 2009). Organotin compounds are also found in landfill leachates. Pinel-Raffaitin reports that up to nine organotin compounds (e.g., methyltin, ethyltin, butyltin, and mixed methy-ethyltins) have been detected in landfill leachates at concentrations ranging from 0.01 mg tin/L to 6.5 mg tin/L, which totaled 1–38 wt.% of the tin concentration in the landfill (Pinel-Raffaitin et al., 2008). Huang and Matzner (2004) detected organotin compounds and metabolites in a forest soils showing that the degradation rates of methyltin and butyltin are slow (with half-lives from 0.5 years to 15 years).

Unlike other organic contaminants, bioremediation cannot sufficiently eliminate the risks associated with organometallic compounds since the resulting heavy metal metabolites (such as tin or lead) remain at the contamination site. Thus, the removal of organometallic compounds from the subsurface is a preferable approach. Surfactant enhanced aquifer remediation (SEAR) is a promising method for increasing the solubilization of organometallic compounds and their metabolites in soil and aquifers contaminated with leaded gasoline and other organic solvents (Ouyang et al., 1996; Leser and Wingrave, 2000).

Pump and treat method is an old style aquifer treatment aided from flow of water. The surfactant solution is used to modify pump and treat method via release and solubilize the contaminant into solution which increases the treatment efficiency called surfactant enhanced aquifer remediation (SEAR).

The mechanisms occurred in the subsurface are solubilization by the micelles and the mobilization by the very low oil/water interfacial tension. When surfactant is added into mixture of oil and water, surfactant monomer accumulates at the oil/water interface that lower the interfacial tension between oil/water interface, by greatly reduction of IFT, the trapped oil is mobilized (Pennell et al., 1996; Sabatini et al., 2000).

Mobilization is vastly effective than solubilization in manner of oil removal (Pennell et al., 1994; Dwarakanath et al., 1999; Shiau et al., 2000) but however it is a cause of vertical migration, movement of contaminant to the deeper zone, of the DNAPL that product the new and more complicate contamination problem.

Solubilization is an important property of surfactant which is the result from partitioning of the contaminant into the oil like core of the micelle formed in the water. A major practical important is the formation of products containing water-insoluble ingredients which can replace the use of organic solvent. The capacity of treating solution is enhanced by the solubilization mechanism which is partitioning of organic contaminant into micelles. Apparent aqueous solubility is enhanced, the actual aqueous solubility unchanged, the increased solubility is the portion that is in micelles (West and Harwell., 1992; Childs et al., 2006). Even the solubilization is quite low recovery efficiency in comparison to mobilization, but it has low potential to create the vertical migration. So, the solubilization is the preferable mechanism for the SEAR.

Hun, 1979 establish the Chun-Hun relationship that is the relation between S^2 and 1/IFT. The IFT decrease while solubilization potential increase continuously from type I to type III region until reach the optimum point. Thus, when a surfactant system is designed for increase the solubilization capacity, the mobilization potential is also increase too. Due to the most significant induce mechanism is the IFT; the mechanism of oil removal can be adjusted simply for ionic surfactant by shifting the salinity of the surfactant mixture. The salinity can be changing continuously and economically in the field which is an advantage of using ionic surfactant over nonionic surfactant (Dwarakanath et al., 1999).

To prevent the mobilization, Sabatini et al. (2000) introduced gradient concept that sequentially adjusts the surfactant solution which can prevent the vertical migration and still maintain the remedial efficiency. As the idea, DNAPL will be removed by solubilize the most mobilizable DNAPL fraction first. The system performs by flushing the column using surfactant solution from high IFT to minimize the mobilization of trapped oil then when the residual saturation decrease, the system was shift to lower IFT to release oil that trapped stronger but not too low IFT to increase solubilization capacity while maintain prevent mobilization. Thus, lower IFT and higher solubilization than the single surfactant flushing could be achieved with minimizing mobilization.

The dibutyltin dichloride (DBT), an organotin compound, was an attractive TEL surrogate option (Thongkorn et al., 2008) because it is a organometallic compound which has less toxic and is thus much safer to work with and easier to obtain than TEL. It was mixed with decane at the mole ratio of 0.038:0.962 to make the resulted mixed oil has similar Equivalent Alkane Carbon Number (EACN) to TEL (Thongkorn et al., 2008). The EACN of DBT-decane mixture is 7.2 while the EACN of TEL is between 6.04 to 7.68 (Thongkorn et al., 2007 and 2008). However, mixture of DBT-decane is a light oil with the density of 0.748 g/mL). Thus, the DBT was coupled with PCE at the same ratio, 0.038:0.962, in order to comparison, was used as an mixture of organometallic compound which has high density similar to TEL (Damrongsiri et al., 2010). The DBT-PCE mixture has the density of 1.587 g/mL with EACN of 0.3. The solubilization of DBT and mixture of DBT as TEL surrogate were carried out in previous study (Damrongsiri et al., 2010). It was indicated that DBT was able to be solubilized in the same manner with polar organic compound which solubilized in the outer part of micelles of the experimented surfactant solution. In this study those oil was applied in the column experiment to simulate for treatment of a contaminated aquifer.

6.4 Materials and methods

6.4.1 Materials

Analytical grade DBT were purchased from Sigma-Aldrich Co. Perchloroetylene (PCE) was purchased from Ajax Finechem. Analytical grade decane was purchased from Fluka Co. The anionic surfactants consisted of C16 diphenyloxide disulfonates (C16DPDS), trade name Dowfax8390, and were supplied by Dow Chemical Co. Sodium dihexyl sulfosuccinate (SDHS) known as AMA was purchased from Fluka Co. Analytical grade calcium chloride was purchased from LabScan. Analytical grade sodium chloride (NaCl, 100%) and calcium chloride ($CaCl_2$, 100%) were purchased from LabScan. Analytical grade calcium nitrate ($Ca(NO_3)_2$, 100%) used in column preparation was from Ajax Finechem.

All chemicals in this research were used as received without further purification. The surfactant solution using in the experiment was the mixture of 3.6 wt.% SDHS and 0.4 wt.% C16DPDS. This surfactant system was applied in previous work (Damrongsiri et al., 2010). The 20-30 mesh Ottawa sand (Fisher Scientific) was applied as the soil media in the experiment. It was washed by DI water and dry before packed into column.

6.4.2 Methods

6.4.2.1 Column packing procedure

Column packing and residual oil preparation procedure was adapted from Childs et al. and Acosta et al. (Childs et al., 2004; Acosta et al., 2003). The column and pumping system is in Figure 6.1. Two pumping systems were prepared, the joints and valves of the system are made from stainless. The pumping system (*A*) was connected to the effluent end of column and then the water was pumped to displace air in the pumping pipe line. After that the water was drained out until the surface of water equals to the bottom filter.

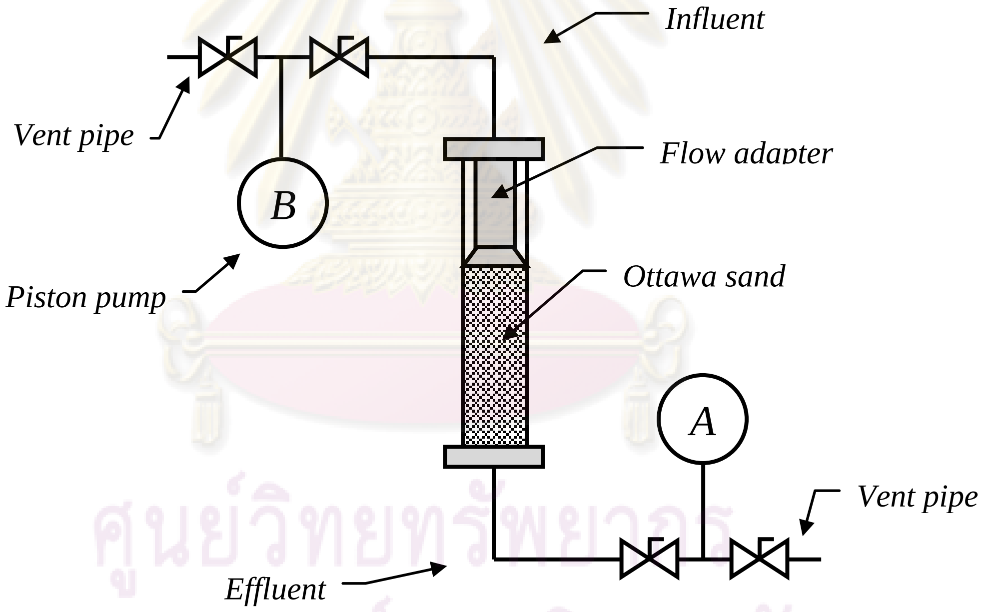


Figure 6.1 Experimental setup for column experiments.

The 20-30 mesh Ottawa sand was washed by de-ionized water, dried, and packed into column by wet packing technique to avoid the air bubbles retain in the sand column. About 50 mL of water and 200 g of Ottawa sand were prepared in each beaker and weighted with beaker. The water was gradually filled into column, where the height of sand filled each time was about 2 cm. The water at surface level was maintaining about 4 cm above the sand surface. The sand was stirred and packed every time after filled to dispel all air bubbles. When the sand was packed to reach the height of 16 cm, the water was drained out, which was collected, until the surface of water in column reach the top surface of sand. Then the remaining water was then weighted again (with its beaker) to calculate the pore volume of packed column.

The pore volume ($\forall_p$) was the different weight of water in beaker before (W_{w1}) and after packed the sand (W_{w2}) divided by the density of water (D_W) as show in Equation 6.1.

$$\forall_p = \frac{(W_{W1} - W_{W2})}{D_W} \tag{6.1}$$

The sand was also weighted to know the mass of sand in the column. Then, when the sand was saturated with water, the influent pumping system (*B*) with *flow adapter* was fitted to the top of column. The water was then flushed from the effluent in up flow direction to dispel the air at the top of column and influent pipe line. Then, when there was no air in every part of column system, the flow was stopped and the pumping system at the effluent was removed. Now the column was packed and ready to use. Then, 10 pore volumes of degassed water containing 0.01 M $Ca(NO_3)_2$, which functioned as the synthetic groundwater, was pumped to influent line at the pore velocity of 2 cm/min.

Residual saturation was established by replace the water in the column using the head different technique that details depend on the density of oil. The up-flow replacement was used for DNAPL (DBT-PCE mixture) while down-flow replacement was applied for LNAPL (DBT-decane mixture) that for LNAPL we need to invert the column to became effluent end on top and influent end at bottom. The oil was filled to the column at the height of about 16 cm. Then, 10 pore volumes of synthetic ground water were injected at the pore velocity of 2 cm/min. (ten time of surfactant flushing) to flush the free phase oil out.

The amount of entrapped oil was quantified, in the same manner of pore volume, from a mass balance of the oil before and after the contamination procedure. The volume of retained oil (V_{oil}) can be calculated from the weight of oil with the container before (W_{oil1}) and after (W_{oil2}) saturation procedure and the oil density (D_{oil}). (see Equation 6.2).

$$V_{oil} = \frac{(W_{oil1} - W_{oil2})}{D_{oil}} \qquad (6.2)$$

The residual saturation was calculated as the volume of retained oil divide by pore volume of the saturated area. Then, this prepared column was flooding with the surfactant solution at the pore velocity of 0.2 cm/min (adopted from Childs et al., 2004) to observe the solubilized contaminant in the effluent and the treatment efficiency. The pore velocity relates to the mobilization potential. Flow rate for the column was calculated from this pore velocity, porosity, and the column diameter. The effluent were collected by fraction collector (RediFrac, Pharmacia Biotech), 20 min per sample. The surfactant flooding was stop when the PCE or decane was absent.

6.4.2.2 Tracer study

The tracer test and calculation was adapted from Tchobanoglous et al., 2003. Tracer study was done to know the actual flow characteristics of packed column. The column was packed in the same way of treatment study. The tracer was bromide. Theoretically, tracer is introduced into the influent end of the reactor with a pulse injection but that idea could not be applied to our experiment, our flow was very low and the effluent was need to collected by a period time. In addition, we want to know the appearance flow character through the influent pipe, pump, joint, packed column until to the effluent end. Thus, in our tracer study, after the column was packed already, 10 mg/L of bromide solution was replaced the water reservoir and flow continuously. The effluent was collect by fraction collector by every 10 min. Bromide concentration was plotted versus pore volume to make a response curve. The curve is in a form of cumulative curve so, it was calculated by reveres the method showing in Tchobanoglous et al., (2003) to turn to normal distribution curve to compute the column characteristic.

6.4.2.3 PCE and decane measurement

The solubilized PCE and decane was measured by gas chromatography (Clarus 500, PerkinElmer) with FID detector connected with headspace auto sampler (Turbomatrix 40, Perkin Elmer). Nirogen gas was used as carrier gas. The sample volume of 100 µL was equilibrated by headspace auto sampler using the temperature of 80 ºC for 30 min before injected to the GC system. The column flow was controlled by pressure at 6 psi. The oven temperature was 140 ºC isotopic system.

6.4.2.4 DBT measurement

DBT was measured as total tin in the solution. The samples were digested by microwave digester (Ethos pro, Milestone) before measured for tin by ICP-OES system (Vista-MPX, Varian). The digestion procedure was adapted from digestion method described by Hargreaves (Hargreaves et al., 2004), 500 µL of sample was mixed with 9 mL 65 wt.% hydrochloric acid and 3 mL of 35 wt.% nitric acid and temperature program started with the increasing of temperature to 175 ºC within 13 min and the holding at 175 ºC for another 10 minutes. It should be note that general digestion using only nitric acid is may resulting in the precipitation of tin.

6.4.2.5 Extraction

There were three steps. 1) After the surfactant flooding was stopped, sand was then transfer to 250 mL glass bottle with cap. The extraction was done by fill 100 mL of surfactant solution at 0.5 wt.% $CaCl_2$ and shake for one day to extract surfactant solution soluble of remaining mixed oil, then separate the surfactant solution out and wash with DI water, collect those surfactant solution and washing water, and adjusted the volume to 250 mL by volume metric flask to measure the PCE or decane and DBT. 2) Then fill 100 mL of 12.5 wt.% HCl solution in to bottle and shake for another one day to extract the fraction that may solubilize in acid condition, then separate the acid solution and wash with DI water, collect those solutions and adjust the volume to 250 mL to measure for DBT (HCl concentration became 5 wt.%). 3)

Finally dry the sand and weight 5 g of sand (triplicates) to perform the same DBT digestion procedure with sample to extract the possibly adsorbed DBT in any forms from sand.

6.4.2.6 Result analysis

The result was divided to five fractions: 1) mobilized fraction, 2) solubilized fraction, 3) extracted by surfactant solution, 4) extracted by acid, and 5) extract from sand. All amount was derive from the measurement. The mass from fraction 1 and 2 was considered as treated fraction and fraction 3, 4, and 5 were the amount of PCE, decane and DBT which still remain after treatment. The total mass was the accumulation of those five fractions. The percentage of treatment efficiency was calculated as the treated fraction divided by total mass.

6.5 Results and discussion

6.5.1 Packed column properties

The properties of all packed columns in the experiment were demonstrated in Table 6.1. The same procedure was performed on the packing of column in order to make every column were most analogous. The flow was calculated base on the desired pore velocity of 0.2 cm/min and porosity of that packed column which the calculated flow were between 0.35-0.39 mL/min. Nonetheless, the actual flow used in the experiment was 0.38 mL/min which resulting in a small fluctuate of pore velocity (pore velocity was 0.20±0.01 cm/min) that respond to retention time of 79±2 min. Residual saturation (Rs) is the amount of oil that remains in the sand pore in percent unit (100% mean oil replace entire sand pore in column). The amount of surfactant solution to be used in the flushing were normalized by calculated to pore volume unit (PV) to exclude the effect of different pore volume size of each column.

Table 6.1 The properties of packed columns in the experiment

Surfactant system / mixed oil	Pore Volume (mL)	Porosity	Retention time (min)	Rs (%)
0.0 wt.% $CaCl_2$ / DBT-PCE	30.46	0.376	80	12.9
0.2 wt.% $CaCl_2$ / DBT-PCE	31.11	0.384	82	14.6
0.4 wt.% $CaCl_2$ / DBT-PCE	29.60	0.365	78	17.7
0.4 wt.% $CaCl_2$ / DBT-decane	30.54	0.377	80	18.1
0.8 wt.% $CaCl_2$ / DBT-decane	30.01	0.370	79	22.2
Gradient $CaCl_2$ / DBT-PCE	28.67	0.349	75	17.4

6.5.2 Tracer study

The resident time of the tracer respond curve calculated from the difference of the time water flowed from the reservoir to the top of column (68.1 min) and from the reservoir out as effluent (148.0 min) was 79.9 min while the retention time obtained by the calculation from average pore volume of column and actual flow was 79 min. These two values were agreed very well indicating that the quantification of pore volume and flow measurement were reliable. According to Tchobanoglous et al (2003) reported that a reactor having Morrill dispersion index (MDI) of equal or less than 2 can be considered as plug flow reactor, therefore, our packed column which had MDI of 1.25 (see APPENDIX C), could be considered as plug flow.

6.5.3 Single surfactant system

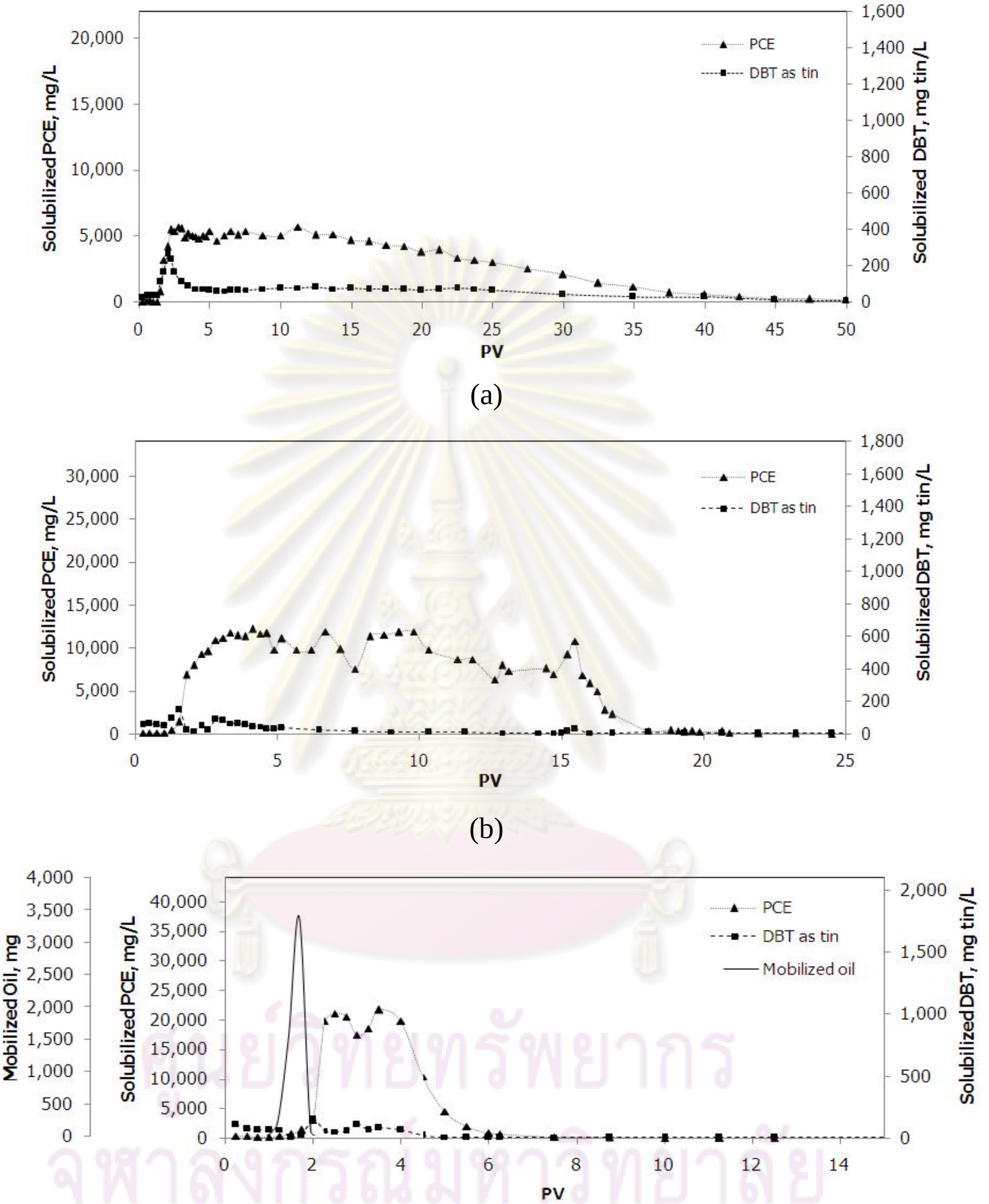
Figures 6.2 and 6.3 show the plots of the column experiments as solubilization and mobilization of the DBT-PCE and DBT-decane mixture, respectively. The surfactant applied in the study with DBT-PCE mixture were 3.6 wt.% SDHS 0.4 wt.% C16DPDS without $CaCl_2$ (Solution A), with 0.2% $CaCl_2$ (Solution B), and with 0.4 wt.% $CaCl_2$ (Solution C). For the column of DBT-decane mixture, the surfactant solutions were 3.6 wt.% SDHS 0.4 wt.% C16DPDS with 0.4 wt.% $CaCl_2$ (Solution C), and 0.8 wt.% $CaCl_2$ (Solution D),. The maximum value of Y axis is set to the equilibrium solubilization for the expedient consideration.

6.5.3.1 Mobilization

The DBT-PCE mixture was removed from the column via mobilization only by the Solution C at around 75% while the DBT-decane mixture was mobilized by Solution C and Solution D at around 40% and 50% respectively. Mobilized oil fraction was observed before solubilization occurred. These results follow the general trend as reported by other studies (Dwarakanath et al., 1999; Sabatini et al., 2000; Childs et al., 2004) indicating that once the IFT between two different phases is decreased by surfactant monomers were firstly at interface and reduced IFT resulting to mobilization of a certain amount of trapped oil, and once micelles were formed solubilization was then occurred (Rosen, 2004). Front of surfactant stream come with low surfactant concentration follow by main stream with design surfactant concentration. So that once the surfactant concentration was higher than its CMC, oil starts to be solubilized into micelles while the IFT does not decrease any more.

6.5.3.2 Solubilization

The maximum solubilization of PCE in the column experiments were 5,100, 11,000, and 20,000 mg/L for the surfactant systems of Solution A, Solution B and Solution C, respectively. As compared to the maximum solubilization capacity of PCE obtained from the solubilization study with the same surfactant solution as shown in Table 6.2 (Damrongsiri et al., 2010), the solubilization of PCE in the column experiments were 20%, 30%, and 45% of their solubilization capacity. The similar manner was observed in the experiment with DBT-decane mixture. The maximum solubilized decane from the column experiment were 2,400 and 4,300 mg/L for the surfactant systems of Solution C and Solution D, respectively, which were only 50% and 70% of their solubilization capacity in batch experiment. However, one can observe from Table 6.2 that DBT has much lower solubilization than PCE and decane in the column experiment. This indicated that ratio of DBT and PCE (or decane) in the trapped sand of the column have been changed once they were solubilized in the surfactant solution (effluent from the columns).

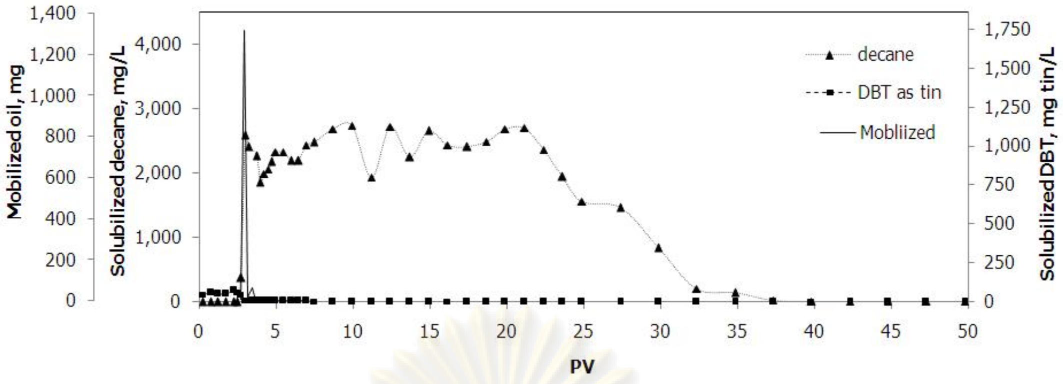


(a)

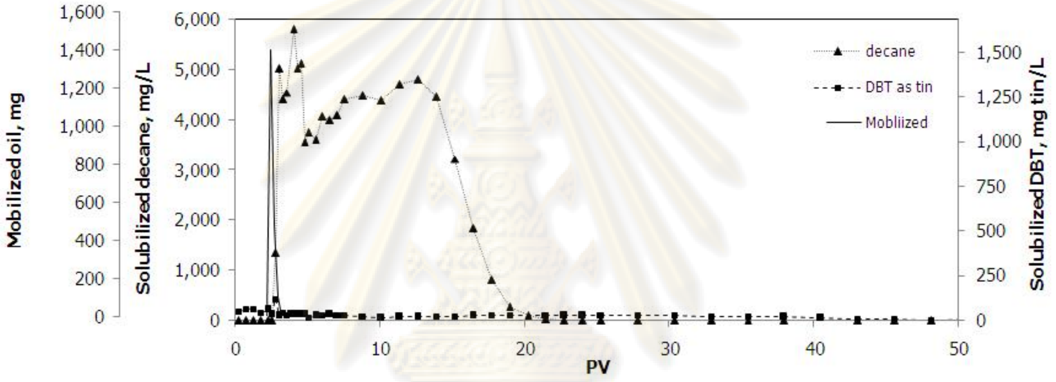
(b)

(c)

Figure 6.2 Effluent result of column experiment with DBT-PCE mixture by single surfactant flooding, (a) 3.6 wt.% SDHS 0.4 wt.% C16DPDS without $CaCl_2$ (Solution A), (b) 3.6 wt.% SDHS 0.4 wt.% C16DPDS with 0.2% $CaCl_2$ (Solution B), and (c) 3.6 wt.% SDHS 0.4 wt.% C16DPDS with 0.4 wt.% $CaCl_2$ (Solution C)



(a)



(b)

Figure 6.3 Effluent result of column experiment with DBT-decane mixture by single surfactant flooding, (a) 3.6 wt.% SDHS 0.4 wt.% C16DPDS with 0.4 wt.% $CaCl_2$ (Solution C), and (b) 3.6 wt.% SDHS 0.4 wt.% C16DPDS with 0.8% $CaCl_2$ (Solution D)

Those solubilization values from the column study were only occurred as a fraction of the solubilization capacity. Since the solubilization is the rate limited mechanism, the shorter contact time in the column experiment may be the possibly cause that lower solubilization (Pennell et al., 1994; Taylor et al., 2001). The retention times in every column were similar, however, higher percentage of solubilization capacity was observed in the system with higher salinity. Thus the different percentage of solubilization capacity was respond to the shorter equilibrium time of system located close to middle phase (higher salinity) (Dwarakanath et al., 1999).

Table 6.2 Solubilization of contaminant in solubilization study (Damrongsiri et al., 2010)

Surfactant system / mixture oil	**Solubilization capacity**	
	mg/L	
	PCE	**DBT**
0 wt.% Ca / DBT-PCE	22,000	1,600
0.2 wt.% Ca / DBT-PCE	34,000	1,800
0.4 wt.% Ca / DBT-PCE	44,000	2,100
	decane	**DBT**
0.4 wt.% Ca / DBT-decane	4,500	1,860
0.8 wt.% Ca / DBT-decane	6,000	1,680

The PCE (and decane) concentration in the effluent was dramatically increased within the first 5 PV of the surfactant solution flushing until reach plateau and then declined gradually to trace concentration (see Figures 6.2 and 6.3). The volume of surfactant solution requires to remove the entire PCE in the column was different depending on solubilization of PCE in such surfactant system and initial residual PCE. In contrast to solubilization capacity, DBT was removed only in the first 5 PV with very low concentration as compared to PCE and decane and after the sixth PV of surfactant flushing, DBT was found almost none in the effluent. However, it did not mean complete removal occur. So, it can be expected that DBT still remained in the packed column. The limitation of DBT solubilization in the packed column needed to be understood. So, the further experiment had been conducted by gradient surfactant system as will be described in the next session.

6.5.4 Gradient surfactant system

From the problem of DBT limited solubilization, this gradient was proposed to improve the DBT solubilization. The salinity and pore volume of each shifting step was estimated from previous single flushing experimental result. The gradient system was ideal to first remove the residual oil which most readily fraction to be mobilized using not too low IFT resulting by a surfactant system and following by the more robust system sequentially (Sabatini et al., 2000; Childs et al., 2004). One pore volume of water was flow through the column before follow by surfactant solution. The surfactant solution used in this gradient study was the 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with different $CaCl_2$ concentration. Initial residual oil was 20%. The effluent results were plotted as in Figure 6.4.

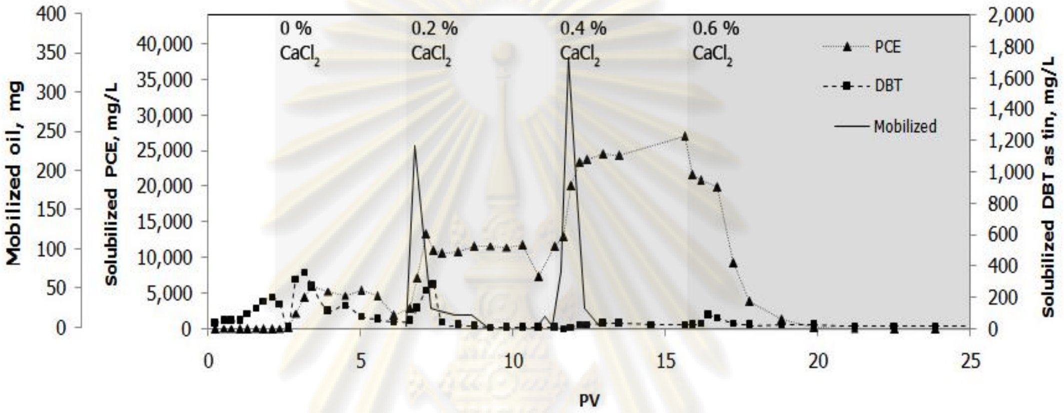


Figure 6.4 Effluent result of gradient surfactant system

The flushing was started by 4 PV of surfactant system without $CaCl_2$ follow by 4.5 PV of surfactant system with 0.2 wt.% $CaCl_2$, 4 PV of surfactant system with 0.4 wt.% $CaCl_2$), and surfactant system with 0.6 wt.% $CaCl_2$ until finished the flooding. The mobilization was not observed for the first gradient of 4 PV of surfactant solution without $CaCl_2$, however about 450 and 600 mg of oil was mobilized (15% of total trapped oil) once the next portions of surfactant solution with increasing salinities to 0.2 wt.% and 0.4 wt.%, respectively. In comparison, this mobilization result seemed different from the experiment of single surfactant flushing by solution of 3.6 wt.% SDHS, 0.4 wt.% C16DPDS and 0.2 wt.% $CaCl_2$ that mobilized fraction just in the negligible amount. The explanation is that the surfactant with 0.2 wt.% $CaCl_2$ was flow into the column when the remaining Rs was about 15.7%, while in single flushing experiment with the same salt has the Rs only 12%.

The mobilization occurred during the salinity of surfactant was changed indicating that too much residual oil still remain when the shifted the salinity that thus induce the mobilization by the lower IFT. This could be prevented by increase the pore volume of each salinity used to additional reducing of Rs.

Solubilization of PCE increased with increasing salinity sequentially before fall down when have no more residual oil remain. At 25 PV, completely removal was observed for PCE (15% by mobilization and 85% by solubilization). About 40% of DBT was removed (60% remain) that 15% by mobilization and 25% by solubilization. By this experimental result, the gradient technique could not help improve the solubilization of DBT.

6.5.5 Discussion on the removal of DBT from packed sand column

By the column experiment both single and gradient flooding, percentage of solubilization of DBT were found extremely low. The solubilization of The highest value observed in surfactant system without $CaCl_2$ in the experiment with DBT-PCE mixture which just about 70 mg/L or around 4% of it solubilization capacity. Due to the totally difference for the result found with PCE and decane, it indicated that the limitation of contact time and contact area may not be a parameter to govern this phenomena. The adsorption of DBT on sand surface was suspected to be the cause of this problem.

At the end of each experiment, almost PCE and decane was removed out, while a fraction of DBT was still remaining in the column. For system without $CaCl_2$, almost PCE was removed at about 50 PV while 20% of DBT was still remained, even the percent removal of DBT of this column was seem high but this due to the large volume of treatment solution flushing through the column. In experiment with surfactant system with 0.2 wt.% $CaCl_2$, PCE was completely removed at 20 PV while 80% of DBT was still remained. For system with 0.4 wt.% $CaCl_2$ which the mobilization occurred, 70% of residual oil was unstrapped out off the column by mobilization. PCE removal was done at only 8 PV and 80% of DBT was removed, but in those DBT removal, 70% of them was removed via mobilization thus only 10% of DBT was solubilized. This result showing that we could not remove DBT by solubilization efficiently. In the decane experiments, 55% and 75% of DBT was removed at the end of the study by surfactant system with 0.4 and 0.8 wt.% $CaCl_2$, respectively, however, 40% and 50% of that resulted from mobilization.

6.5.6 Extraction result

In order to prove if DBT (or its metabolite) was adsorbed on sand in the packed column the extraction was carried out to determine the amount of remaining DBT in the column. A significant fraction of DBT was extracted during the extraction process. Some amount of DBT was extracted in first step using the surfactant solution. The solubilized DBT in first step was still far less than the solubilization capacity (37 mg tin/L out of 250 mg tin/L) indicating that DBT could not be desorbed from sand by surfactant solution. A larger fraction of DBT was seemed to be extracted in the second step which performed by strong hydrochloric acid. The forms of these tin compounds in our acid solution were unknown. However, the remaining tin on sand may be in the initial form as DBT or may be degraded to some metabolite or even in inorganic forms which preferable adsorbed on sand. Most of DBT was extracted from sand in this second step. The tin extracted from third step was absent or in a negligible amount.

6.6 Conclusion

The solubilization of PCE and decane in column effluent was related to the value derived from solubilization experiment that could be explained by rate limited mechanism. Nonetheless, the solubilization of DBT in column experiment was very low and not relate to the trend of solubilization study indicating that the contact time and contact area was not only limited mechanism for solubilization of DBT. Completely removal of PCE and decane could be achieved reasonable but did not for DBT which the maximum solubilization in column experiments were not more than 4% of their solubilization capacity. The gradient approach which shift the surfactant system to high salinity was found unable to induce the higher the solubilization of DBT in column effluent. The result indicated that the surfactant flushing either single solution or gradient approach are not appropriate procedures for DBT removal in contaminated soil. However, the finding from this study indicates clearly that mobilization was a key mechanism to remove DBT; however, the vertical migration has to be concern.

As we have known that the components in the solubilization study and the column study were different due to there was no solid phase (sand) in the solubilization study. So the sorption of DBT on the sand packed in the column can be expected to be occurred since it contains inorganic moiety part. As a consequence, the sorption behavior of DBT should be concerned to eliminate this problem.

CHAPTER VII

EFFECT OF pH ON DBT REMOVAL

From CHAPTER VI, we found that the DBT could be removed from packed sand column. An altering form of DBT and surface charge of packed media has a potential to minimize the adsorption of DBT. Thus, the experiments were carried out again including the phase study (3.2.2), solubilization study (3.2.3), and column study (3.2.4) to investigate the effect of pH of the surfactant solution on the DBT removal. Both Ottawa sand and aquifer soil were applied in the study. A manuscript has been written based on this study. The experimental results were presented in the APPENDIX D.

7.1 Paper's title and authors

The title of this manuscript is "Effect of pH on removal of dibutyltin dichloride by anionic surfactant solution" The contributed authors were Seelawut Damrongsiri, Chantra Tongcumpou, and David A. Sabatini.

7.2 Abstract and key words

The previous study showed that solubilization of dibutyltin dichloride (DBT) in the anionic surfactant solution was similar to that of polar organic compound. However, the solubilization of DBT from packed sand column was impeded due to the adsorption of positively charged DBT (cationic form) onto the negative surface charge of sand. The adjustment of pH to alter the form of DBT and surface charge of sand to minimize the problem was then studied. The result showed that the adsorption of DBT could be prevented when the pH of system was adjusted to 1, where DBT remained the cationic form and the surface charge of sand became positive. The pH 4 where DBT was in cationic form and pH 9 where DBT possessed a neutral form were studied. It was found that the adsorption of DBT was still significant at both pHs. However, too low pH will affect the properties of an aquifer and the living organism

in that soil. Thus, the pH adjustment was not suit to be used to lessen the adsorption of DBT onto the negatively surface charge, such as sand and silicon oxide, in order to promote the removal of DBT from contaminated aquifer by solubilization. On the other hand, another mechanism − mobilization may need to be considered.

Key words: organometallic compound; dibutyltin dichloride; surfactant; pH; adsorption; solubilization

7.3 Introduction

Organometallic compounds (i.e., compounds containing bonds between carbon and metal) have been employed in numerous applications, for example, being used as catalysts, stabilizers in plastic industries, wood preservatives, agricultural biocides, and antifouling paints for ship hulls. Tetraethyl lead (TEL) and tetramethyl lead, in particular, have been combined with gasoline as an anti-knock agent. A spillage of these highly toxic organometallic compounds during their production, transport, and/or blending has caused severe soil and groundwater contamination problems (USEPA, 1999). The study on TEL remediation in laboratory was concerned regarding risk of itself and its degraded products. However, the fundamental knowledge on organometal remediation by surfactant solution should be carried out. The experimental procedure then started with organometal compound such as organotin.

Organotin compounds have also been used in a range of applications such as intermediates in the synthesis of other organic chemicals, biocides, pesticides, antifouling boat paints. Di-substituted organotins are generally grouped together and used as polyvinyl chloride (PVC) stabilizers, as catalysts, and used in glass coating. About 18,000 tons per year of mono- and dialkyl-tin compounds, were sold in EU in 2002, resulting in their extensive distribution in the environment (RPA, 2003). Organotins have been shown to accumulate in the food chain and pose a potential risk to human health (Cao et al., 2009). Organotin compounds are also found in landfill leachates. Pinel-Raffaitin and his group reports that up to nine organotin compounds (e.g., methyltin, ethyltin, butyltin, and mixed methy-ethyltins) have been detected in landfill leachates at concentrations ranging from 0.01 mg tin/L to 6.5 mg tin/L, which was accounted as 1–38 wt.% of the tin concentration in the landfill (Pinel-Raffaitin et al., 2008). Huang and Matzner (2004) detected the organotin compounds and their metabolites in a forest soils showing that the degradation rates of methyltin and butyltin are slow with half-lives from 0.5 to 15 years.

Unlike other organic contaminants, bioremediation cannot sufficiently eliminate the risks associated with organometallic compounds since the resulting heavy metal metabolites (such as tin or lead) remain at the contamination site. Thus, the removal of organometallic compounds from the subsurface is a preferable approach. Surfactant enhanced aquifer remediation (SEAR) is a promising method for increasing the solubilization of organometallic compounds and their metabolites in soil and aquifers contaminated with lead gasoline and other organic solvents (Ouyang et al., 1996; Leser and Wingrave, 2000).

Pump and treat method is a conventional aquifer treatment aided from the flow of water. The modified pump and treat method by surfactant solution called surfactant enhanced aquifer remediation (SEAR) is proven to be more effective, where the contaminant is solubilized and released into the surfactant solution.

The mechanisms occurred in the subsurface are solubilization of contaminant by the surfactant micelles and the mobilization of contaminant by the very low oil/water interfacial tension. When the surfactant is added into a mixture of oil and water, surfactant monomer accumulates at the oil/water interface that lower the interfacial tension between oil/water interface, by greatly reduction of IFT, the trapped oil is mobilized (Sabatini et al., 2000). Mobilization is vastly effective than solubilization for oil removal purpose (Dwarakanath et al., 1999; Shiau et al., 2000). However, a vertical migration tends to occur causing a movement of DNAPL contaminant to the deeper zone that generates a new and more complicate contamination problem. Solubilization is an important property of surfactant which is a result of contaminant’s partitioning into the oil-like core of the surfactant micelles formed in the water. Therefore, the water-insoluble ingredients can be soluble in aqueous phase without the use of the organic solvent. Although the solubilization possesses quite low recovery efficiency in comparison to mobilization, it has low potential to create the vertical migration thus make it become the preferable mechanism for DNAPL treatment by SEAR.

The dibutyltin dichloride (DBT), an organotin compound, was selected to be studied here because it has properties similar to that of TEL. It has a lower toxicity than TEL and is available in the market with lower cost resulted in an attraction to be used as the TEL surrogate (Thongkorn et al., 2008). It was mixed with decane at the molar ratio of 0.038:0.962 to make the resulted mixed oil having similar properties to TEL (being organometallic compound with similar Equivalent Alkane Carbon Number; EACN to TEL). The DBT was also coupled with perchloroethylene (PCE) at the same ratio, 0.038:0.962, in order to make a comparison (being organometallic compound with similar density to TEL) (Damrongsiri et al., 2010). The solubilization of DBT in surfactant solution was carried out in the previous study (Damrongsiri et al., 2010). The result indicated that DBT was able to be solubilized at the outer part of micelles in the same manner as polar organic compound. The remediation of the mixtures of organometallic compound and solvents; DBT mixed with PCE and DBT mixed decane; was conducted in the column study. The result revealed that PCE and decane were removed in the typical manner like several organic oils while the removal of DBT was unusual. The solubilization of DBT was extremely limited, which the solubilized concentration of DBT was found only 1-4% of the solubilization capacity at plateau and declined to trace concentration level. Most of DBT still remained in the column while the solubilized decane and PCE were about 30-50% of their solubilization capacities. A limit of solubilization rate (Pennell et al., 1994; Dwarakanath et al., 1999; Taylor, 2001) could be used to explain the solubilization of PCE and decane but not for DBT. Thus, the sorption of DBT onto media was suspected to be the major cause of this limited solubilization.

The sorption of DBT in clay-rich sediments was studied by Hoch et al. (2003) as a function of pH (4-8) in a wide salinity range. The total organic carbon (TOC) of these sediments was low. The maximum sorption was found at zero salinity and pH 6. The sorption trend could be expected as showed in Figure 7.1 that the sorption was reduced when pH deviates from pH 6. The mechanism of sorption was discussed by extrapolated from some sorption studies of tributyltin (TBT) and monobutyltin (MBT). DBT was anticipated to have the pH dependent dissociation reaction in the same manner as TBT and MBT. When pH is higher than its pk_a, DBT was expected to be in a neutral form as $DBT\text{-}OH_2$ and at pH lower than its pk_a being in a cationic form as $DBT\text{-}OH^+$ or DBT^{2+}. The driving force of DBT sorption occurring between pH 4-7 was an electrostatic interaction between anionic clay surface and cationic form of DBT.

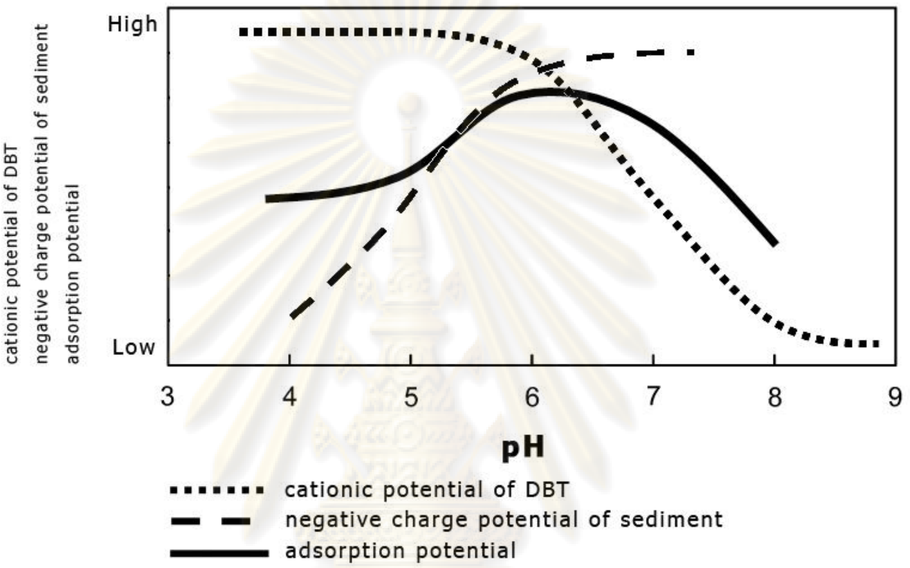


Figure 7.1 Sorption percentage of DBT onto sediment as a function of pH (rebuild from Hoch et al., 2003)

The pH affected to both surface properties of media and aquatic chemistry of DBT. The PZC of sediment in the experiment was about 4. The pk_a of DBT was expected to be about 7 (Hoch et al., 2003). Thus, the negative surface charge of sediment and cationic potential of DBT could be estimated as shown in Figure 7.1, which resulted in such adsorption. When pH decreases, the DBT presents in a cationic form, while the negative surface charge of clay deceases. In the contrary, when the pH increases, the negative surface charge of clay increases while DBT become neutral form. Thus, either way the adsorption reduced.

The hypothesis was raised that the pH adjustment may improve the efficiency of DBT solubilization by surfactant in the column experiment. If we adjust the system to lower the pH, DBT will be in a cationic form and the negative surface charge of sand will also decrease. The electrostatic force will reduce thus the sorption will be declined and the solubilization of tin in inorganic form will be. In the contrary at higher pH, DBT will be in a neutral form that may hinder the sorption and enhance solubilization of neutral form DBT into surfactant micelles.

7.4 Materials and methods

7.4.1 Material

7.4.1.1 Chemicals

Analytical grade DBT was purchased from Sigma-Aldrich. Perchloroetylene (PCE) was purchased from Ajax Finechem. The anionic surfactant consisted of C16 diphenyloxide disulfonates (C16DPDS), which has a trade name of Dowfax8390 was supplied by Dow Chemical. Sodium dihexyl sulfosuccinate (SDHS) known as AMA was purchased from Fluka. Analytical grade of calcium chloride and sodium chloride were purchased from LabScan. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Carlo ERBA and used to adjust the pH. Nitric acid (HNO_3) purchased from Carlo ERBA and HCl were applied in digestion procedure. All chemicals in this research were used as received without further purification.

The surfactant solution using in the experiment was the mixture of 3.6 wt.% SDHS and 0.4 wt.% C16DPDS, which was the same system used in the previous work (Damrongsiri et al., 2010).

The DBT-PCE mixture at molar ratio of 0.038:0.962 was used to investigate the solubilization capacity and solubilization behavior by Damrongsiri et al. (2010). DBT-decane mixture was used as an oil surrogate, which has similar properties to TEL including being an organometallic compound and having a similar EACN. The DBT-PCE mixture at the same molar ratio was also applied to represent the organometallic mixture which has similar density to TEL.

7.4.1.2 Ottawa sand and aquifer soil

The Ottawa sand supplied from Fisher Scientific at 20-30 mesh was applied as the soil media in the experiment. It was washed by DI water and dried prior to packing in the column. The aquifer soil was obtained from a site of department of groundwater resources at Rayong Province, Thailand. It was washed by a tap water until the washing water was clear after leaving for precipitation for 5 minutes and washed again by DI water. Then, it was dried at 100 ºC in the oven and sieved to 20-30 mesh similar to Ottawa sand to avoid the particle size effect in comparative study. The organic matter was 0.07% measured by soil-fertilizer-environment scientific development project, Kasetsart University. Zeta potential of Ottawa sand was measured by electrophoretic apparatus, zeta-meter system 3.0^{+} (zeta-meter Inc.) to investigate the PZC. However, we could only know that the PZCs of Ottawa sand and sieved aquifer soil were lower than 3. However, the PZC of Ottawa sand from literature was reported about 1.5 (Railsback, 2006).

7.4.2 Methods

7.4.2.1 pH adjustment

To adjust the surfactant solution to acidic condition, the HCl was selected to be used in this study because tin could precipitate with nitrate. After the acidic pH was adjusted to pH 4 or pH 1, that solution was kept for at least 3 days and tested if the pH still remained as prepared. The NaOH was used to adjust the solution for basic condition. In case of basic pH, the carbon dioxide can dissolve into the solution, which will decrease the pH after the solution was left for a while (surfactant itself also affects the pH). Thus, certain amount of NaOH was added to adjust the pH of surfactant solution to have an equilibrium pH at pH 9 in the present of carbon dioxide. As the result, 20 mM of NaOH was added and the pH 9 was obtained after three day and maintained at pH 9±0.2 at least another 3 days.

7.4.2.2 PCE and decane measurement

The solubilized PCE and decane were measured by gas chromatography (Clarus 500, PerkinElmer) with FID detector connected with headspace auto sampler (Turbomatrix 40, Perkin Elmer). Nitrogen gas was used as a carrier gas. The sample volume of 100 µL was equilibrated in the chamber of headspace auto sampler using at 80 ºC for 30 min before injected to the GC system. The column flow was controlled at constant pressure at 6 psi. The oven temperature was kept constant at 140 ºC.

7.4.2.3 DBT measurement

DBT was measured as total tin in the solution. The samples were digested by microwave digester (Ethos pro, Milestone) before total tin was measured by ICP-OES system (Vista-MPX, Varian). The digestion procedure was adapted from method described by Hargreaves (Hargreaves et al., 2004), where 500 µL of sample was mixed with 9 mL HCl (65%) and 3 mL of HNO_3 (37%). The temperature was programmed to reach 175 ºC within 13 minutes and hold there for 10 minutes.

7.4.2.4 Phase study and solubilization study

The phase study was observed by mixing 0.5 mL of surfactant solution and 0.5 mL of DBT-PCE mixture together in 1 mL tube with stopper and equilibrated for 2 days at controlled temperature of 25 ºC following the condition applied in the preliminary study. The system of DBT-decane was also carried out in the same manner. The Winsor type I/III boundary of each system were observed.

The solubilization study was carried out in 50 mL separatory funnel. The 25 mL of surfactant solution of which pH was already adjusted, at each salinity was inserted into the funnel followed by 2 mL of mixed oil. The solution was shaken gently until it well mixed prior to settling by nature. The equilibrium was reached within 2 days. Then, the separated phase of surfactant solution was taken out to measure for the concentration of PCE, decane and DBT (as total tin).

7.4.2.5 Column packing procedure and experiment

Column packing and residual oil preparation procedures were adapted from Childs et al. (2004) and Acosta et al. (2003). The column and pumping system were shown in Figure 7.2. Two pumping systems were prepared. The joints and valves of the flowing system were made from stainless steel. The pumping system (*A*) was connected to the effluent end of column and then the water was pumped to displace the air in the pumping pipe line. After that the water was drained out until the surface of water was equaled to the bottom filter.

The Ottawa sand was packed into the column by the wet packing technique to avoid the air bubbles retaining in the sand column. About 50 mL of water and 200 g of Ottawa sand were prepared in separated beakers and weighted the whole beaker. The water and sand were gradually filled into the column in an alternate fashion, where the height of sand filled each time was about 2 cm. The water at surface level was maintained about 4 cm above the sand surface. The sand was packed and stirred every time after filled to dispel the air bubbles.

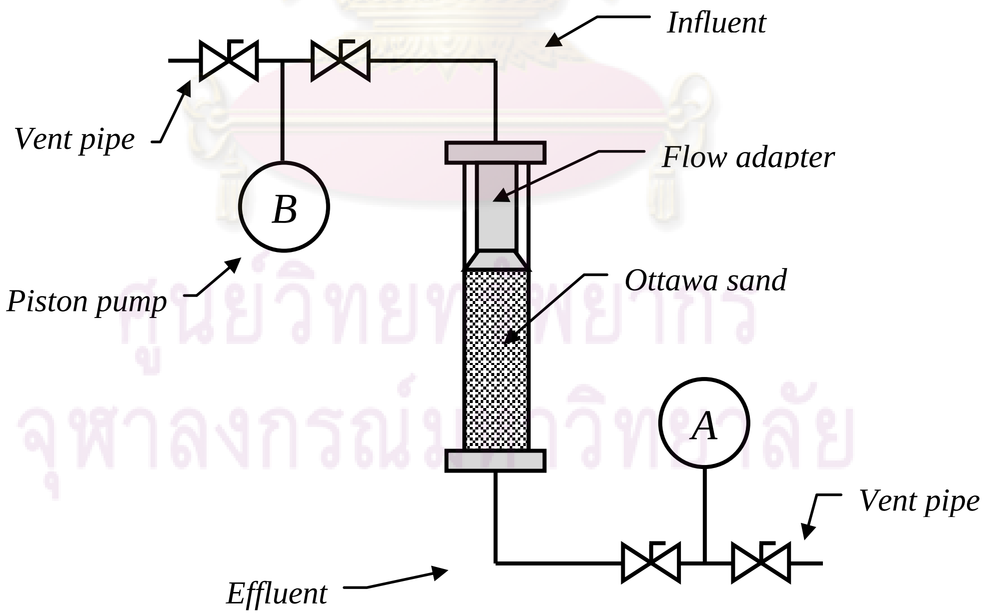


Figure 7.2 Experimental setup for column experiments.

When the sand was packed to reach the height of 16 cm, the water was drained out and collected, until the surface of water in the column reach the top surface of sand. Then the collected water was then weighted again together with its beaker to quantify the pore volume of packed column. The same procedure was also applied to the column packed with aquifer soil. The pore volume ($\forall_p$) was the different weight of water in beaker before (W_{w1}) and after packed the sand (W_{w2}) divided by the density of water (D_W) as shown in Equation 7.1.

$$\forall_p = \frac{(W_{W1} - W_{W2})}{D_W} \tag{7.1}$$

The sand was also weighted to evaluate the mass of sand packed in the column. When the sand was saturated with water, the influent pumping system (*B*) with *flow adapter* was fitted to the top of the column. The water was then flushed from the effluent in upflow direction to dispel the air at the top of column and influent pipe line. When there was no air left in the system, the flow was stopped and the pumping system at the effluence was removed. At this point, the column was packed and ready to be used. Then, 10 pore volumes of degassed water containing 0.01 M $Ca(NO_3)_2$, which was functioned as the synthetic groundwater, was pumped through the influent line at the pore velocity of 2 cm/min.

The condition at residual saturation was established by replacing the water in the column by DBT-PCE mixture using the head different technique in upflow direction. The oil mixture was filled to the column at the height of about 16 cm. Then, 10 pore volumes of synthetic groundwater was injected at the pore velocity of 2 cm/min, which was ten times of surfactant flushing velocity, to flush the free phase oil out.

The amount of entrapped oil was quantified, in the same manner of pore volume, from a mass balance of the oil before and after the contamination procedure. The volume of retained oil (V_{oil}) can be calculated from the weight of oil within the container before (W_{oil1}) and after (W_{oil2}) saturation procedure and the oil density (D_{oil}) (see Equation 7.2).

$$V_{oil} = \frac{(W_{oil1} - W_{oil2})}{D_{oil}} \tag{7.2}$$

The residual saturation was calculated as the volume of retained oil divide by pore volume of the saturated area. Then, this prepared column was flowed by 1 PV of DI water followed by surfactant solution flushing at the pore velocity of 0.2 cm/min (adopted from Childs et al., 2004) to observe the solubilized contaminant in the effluent. The removal efficiency of contaminant by the surfactant solution can be evaluated. The pore velocity relates to the mobilization potential. Flow rate of solution fed into the column was related to pore velocity, porosity, and the diameter of column. The effluents were collected by a fraction collector (RediFrac, Pharmacia Biotech) at 20 min per sample. The surfactant flushing was stopped when the PCE or decane was absent in the flushed solution. Mobilized oil fraction was removed and measured by its weight. Then, the samples were kept to measure for the solubilization of PCE and DBT later on.

7.4.2.6 Detailed Method part 1: experiment at pH 1, 7, 9 using $CaCl_2$ as electrolyte

The experiment in part 1 was desired to investigate if pH affects the DBT sorption. The desired pH for acidic condition was pH 1 in order to change the surface charge of the Ottawa sand to a little positive as the PZC of the silica oxide is around 2 (Railsback, 2006) while the desired basic condition was at pH 9. The surfactant solution was composing of 3.6 wt.% SDHS, 0.4 wt.% C16DPDS and used $CaCl_2$ as the electrolyte. The pH of surfactant solution was adjusted before use. Both DBT-PCE and DBT-decane mixture were applied in phase study and solubilization study. Then, the surfactant solution without $CaCl_2$ and with 0.2 wt.% $CaCl_2$ were selected to apply in the column study, which use DBT-PCE mixture as the contaminant. The Ottawa sand was applied in this experiment.

7.4.2.7 Detailed Method part 2: experiment at pH 4, 7, 9 using NaCl as electrolyte

The experiment in part 2 was aimed to adjust the surfactant to more applicable. The same surfactant was used while NaCl was applied rather than $CaCl_2$ to avoid the precipitation at basic pH. The pHs in the experiments were 4, 7, and 9. Only DBT-PCE mixture was applied in this part. The phase study and solubilization study were carried out in the same manner as the first part. Both Ottawa sand and sieved aquifer soil were used in the column experiment.

7.4.2.8 Extraction

When the experiment was completed, the extraction was carried out to quantify the remaining contaminants in the column. There were three steps; 1) After the surfactant flushing was stopped, sand was then transferred into 250 mL glass bottle with cap. The extraction was done by filling 100 mL of surfactant solution into the bottle and shaking for one day to extract the remaining mixed oil, which is soluble in the surfactant solution. The surfactant solution was withdrawn and the sand was washed by DI water. The surfactant solution and washing water were collected and adjusted the volume to 250 mL in a volume metric flask to measure the concentration of PCE and DBT. 2) A 100 mL of 12.5 wt.% HCl solution was filled in a bottle and shaken for one day to extract the contaminant fraction that is soluble in acid condition. The acid solution was withdrawn and the sand in bottle was washed by DI water. Those solutions were collected and adjusted the volume to 250 mL prior to measuring for the DBT concentration (HCl concentration became 5 wt.%). 3) Finally the sand was dried and 5 g of sand with three replicates were subjected to the digestion procedure on the same procedure as done for DBT in order to extract all possible DBT in any forms adsorbed onto sand out.

7.4.2.9 Result analysis

The samples were divided to five fractions: 1) mobilized fraction, 2) solubilized fraction, 3) extracted by surfactant solution, 4) extracted by acid, and 5) extract from sand. The mass of contaminant derived from fraction 1 and 2 were considered as treated fraction, while ones from fraction 3, 4, and 5 were the amount of remaining contaminant after treatment. The total mass was the accumulation of those five fractions. The percentage of treatment efficiency was calculated as the treated fraction divided by total mass.

7.5 Results and discussion

7.5.1 Packed column properties

The properties of packed columns in the experiment were demonstrated in Table 7.1. The same preparation procedure was performed to ensure the consistency of columns' property. The flow rate was calculated based on the constant pore velocity of 0.2 cm/min (Childs et al., 2004) and actual porosity of the packed column resulting in s slightly different flow rate required for each packed column. Therefore, the actual flow rate used in the experiment was set at 0.38 mL/min. The retention time, thus, was different in each packed column (see Table 7.1). All experiments with Ottawa sand have similar retention time while the experiments with sieved aquifer soil has 20 min longer retention time. Residual saturation (Rs) is the amount of oil that remains in the sand pore in percent unit (100% means oil replaced entire sand pore in column). The amount of surfactant solution to be used for flushing was normalized in term of pore volume unit (PV) to exclude the effect of different pore volume size of each column.

7.5.2 Result part 1: experiment at pH 1, 7, 9 using $CaCl_2$ as electrolyte

The surfactant solution was 3.6 wt.% SDHS, 0.4 wt.% C16DPDS, and $CaCl_2$ as the electrolyte. The studied pH was 1, 7 and 9. The experimental results at pH 9 were excluded because the precipitation of $CaCl_2$ was occurred. The pH of surfactant solution without adjustment was about 7±0.04. It was found that the boundary of Winsor type I/III at pH1 was shifted to 0.2 wt.% $CaCl_2$ as compared to 0.4 wt.% $CaCl_2$ at pH 7. This might be the effect of high ionic strength in the aqueous solution similar to the effect of electrolyte addition.

Table 7.1 Properties of packed columns.

Column	Pore Volume (mL)	Porosity	Retention time (min)	Rs (%)
Part 1				
20-30 mesh Ottawa sand with surfactant solution of 3.6 wt.% SDHS 0.4 wt.% C16DPDS without electrolyte				
pH 7	30.5	0.38	80	13.8
pH 1	30.7	0.38	81	15.5
20-30 mesh Ottawa sand with surfactant solution of 3.6 wt.% SDHS 0.4 wt.% C16DPDS with 0.2 wt.% $CaCl_2$				
pH 7	29.5	0.36	78	17.2
pH 1	30.6	0.38	80	18.4
Part 2				
20-30 mesh Ottawa sand with surfactant solution of 3.6 wt.% SDHS 0.4 wt.% C16DPDS and 1 wt.% NaCl				
pH 4	29.6	0.37	78	15.5
pH 7	29.1	0.36	77	18.7
pH 9	30.7	0.38	81	11.3
20-30 mesh aquifer soil with surfactant solution of 3.6 wt.% SDHS 0.4 wt.% C16DPDS and 1 wt.% NaCl				
pH 4	37.7	0.47	99	9.8
pH 7	39.5	0.49	104	9.9
pH 9	38.8	0.48	102	9.8

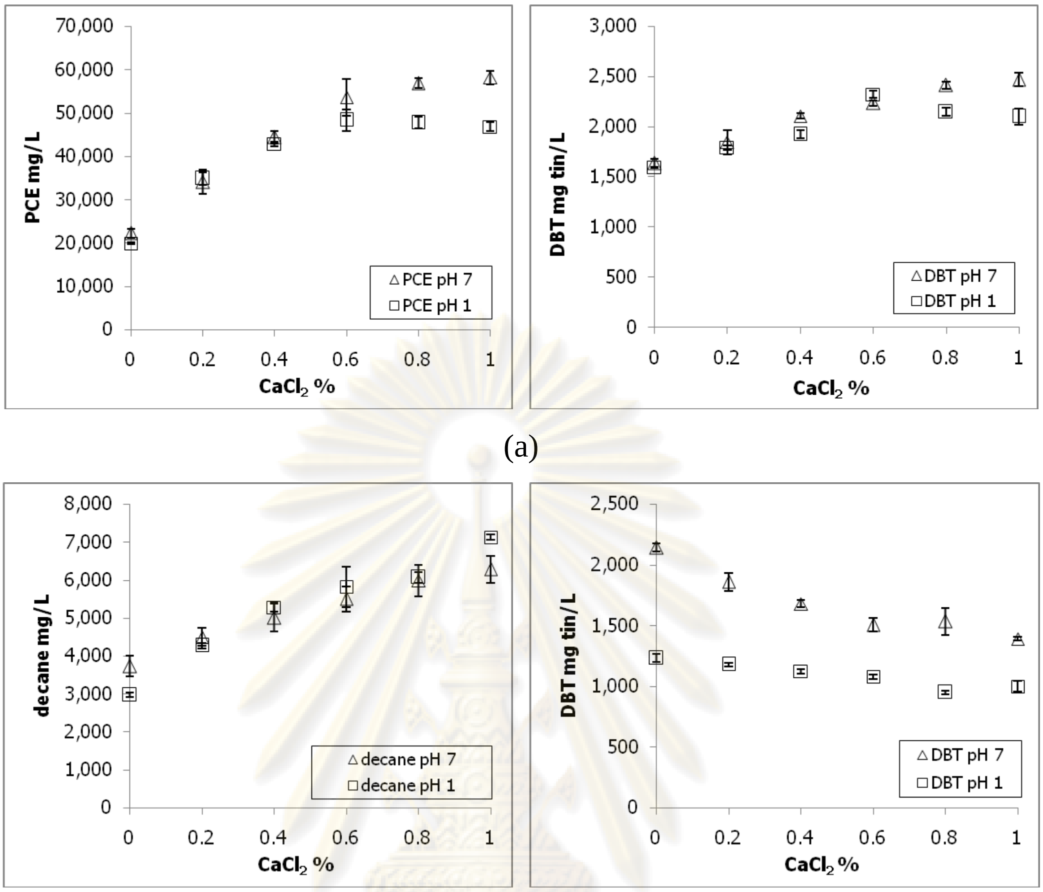
R ratio and the molecular interaction (Bourrel and Schechter, 1998) is a good approach to describe hydrophilicity and lipophilicity of the surfactant system. It is the interaction between surfactant, oil and water molecules in the system as show in Equation 7.3.

$$R = \frac{A_{CO} - A_{OO} - A_{LL}}{A_{CW} - A_{WW} - A_{HH}} \qquad (7.3)$$

where A_{CO} is the interaction between the surfactant and the oil, A_{CW} is the interaction between the surfactant and the aqueous phase, A_{LL} and A_{HH} are self-interaction between their lipophilic tail and between their hydrophilic head of the surfactant, respectively. The parameters A_{WW} and A_{OO} are self-interaction in the water phase and oil phase, respectively. The numerator of the equation represents the net interaction of the lipophilic portion of the surfactant at the interface, while the denominator represents the hydrophilic part of the interface. Bourrel and Schechter also indicated that the optimum formulation corresponds to R values equal to 1, or when the interactions of the lipophilic and hydrophilic regions are in balance. For R<<1, the interface becomes more hydrophilic, and a micellar solution or O/W microemulsions exists. High ionic strength reduces the repulsion between ionic head group of surfactant that promote the interaction among those surfactant head group (A_{hh}) and possibly the activity between surfactant and water (A_{cw}) resulting in the increase of R value (Rosen, 2004). However, it was just a slight shift.

The solubilized decane, PCE, and DBT was quantified using two oil mixtures: DBT-decane and DBT-PCE (see Figure 7.3). The amount of solubilized decane and PCE in systems at pH 1 and 7 were similar while that of DBT was observed to be pH dependent for the system of DBT-decane, where the solubilized DBT at pH 1 was lower. The acidic environment did not have much affect onto these surfactants as their head group was sulfate. Nevertheless, there were some studies on a surfactant which was splittable at low pH (Chen et al., 2000a and 2000b).

The column experiment was carried out using the surfactant solution of 3.6 wt.% SDHS 0.4 wt.% C16DPDS without $CaCl_2$ and with 0.2 wt.% $CaCl_2$ in order to compare the result with previous study. Mixture of DBT-PCE mixture was selected to be used as the contaminant. The properties of packed sand columns were comparable. The concentrations of PCE and DBT (as total tin) in the effluent were plotted as shown in Figure 7.4 and 7.5. About 55% and 75% of treated oil were mobilized at pH 1 by the systems without $CaCl_2$ and with 0.2 wt.% $CaCl_2$, respectively. Large amount of mobilized oil indicated the lower IFT of the system at pH 1 than at pH 7. The lower IFT may be a result of the high ionic strength that reduced the repulsion between ionic surfactant head groups thus, promoted the sorption of surfactant onto the interface (Rosen, 2004).



(a)

(b)

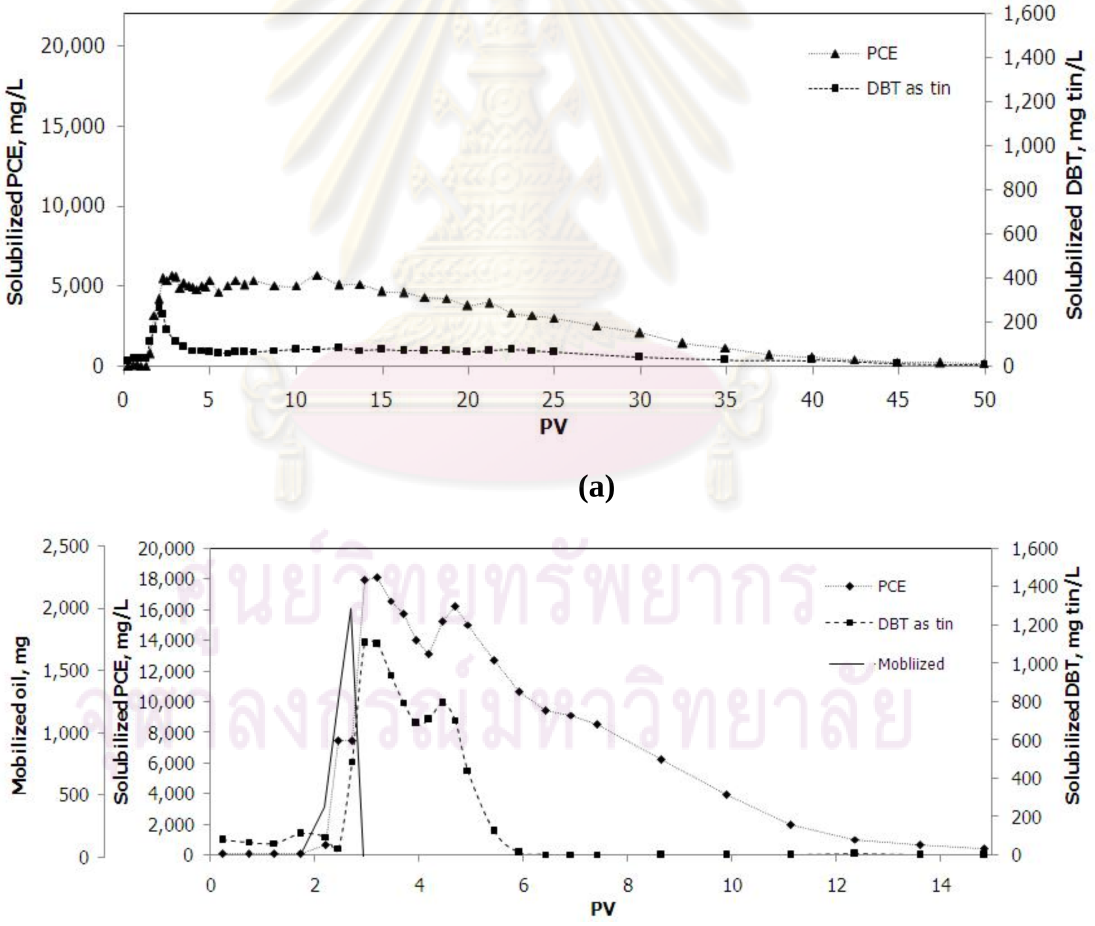
Figure 7.3 Batch solubilization result of 3.6 wt.% SDHS 0.4 wt.% C16DPDS using $CaCl_2$ as electrolyte at pH 7 and 1 for (a) DBT-PCE mixtute and (b) DBT-decane mixture.

The solubilization of PCE from the systems at pH 7 and pH 1 were similar and agreed well with results observed by other studies (Pennell et al., 1994; Dwarakanath et al., 1999; Sabatini et al., 2000). The solubilization began when the surfactant solution was entered the column, solubilization increased sharply then remained there at plateau region until most of the trapped organic was depleted from column. The solubilization then decreased gradually until zero. The solubilization observed in this study could be described by the rate limited solubilization (Pennell et al., 1994; Dwarakanath et al., 1999; Taylor, 2001). The DBT solubilization of DBT at pH 7 was found to be quite low although most of DBT still presented in the column, which complied will with result found from previous study. Surprisingly, the trend of DBT solubilization at pH 1 was similar to general oil. This was better than expected.

Table 7.2 Solubilization study and plateau value from column experiment.

Surfactant with	Solubilization capacity		Column (at plateau)			
	mg/L		mg/L		% of capacity	
wt.% $CaCl_2$	**PCE**	**DBT (as tin)**	**PCE**	**DBT (as tin)**	**PCE**	**DBT (as tin)**
			pH 7			
Without $CaCl_2$	22,000	1,600	5,100	*np**	23	-
0.2 wt.% $CaCl_2$	34,000	1,800	11,000	*np*	32	-
			pH 1			
Without $CaCl_2$	20,000	1,600	16,000	850	80	53
0.2 wt.% $CaCl_2$	34,000	1,800	20,000	760	59	42

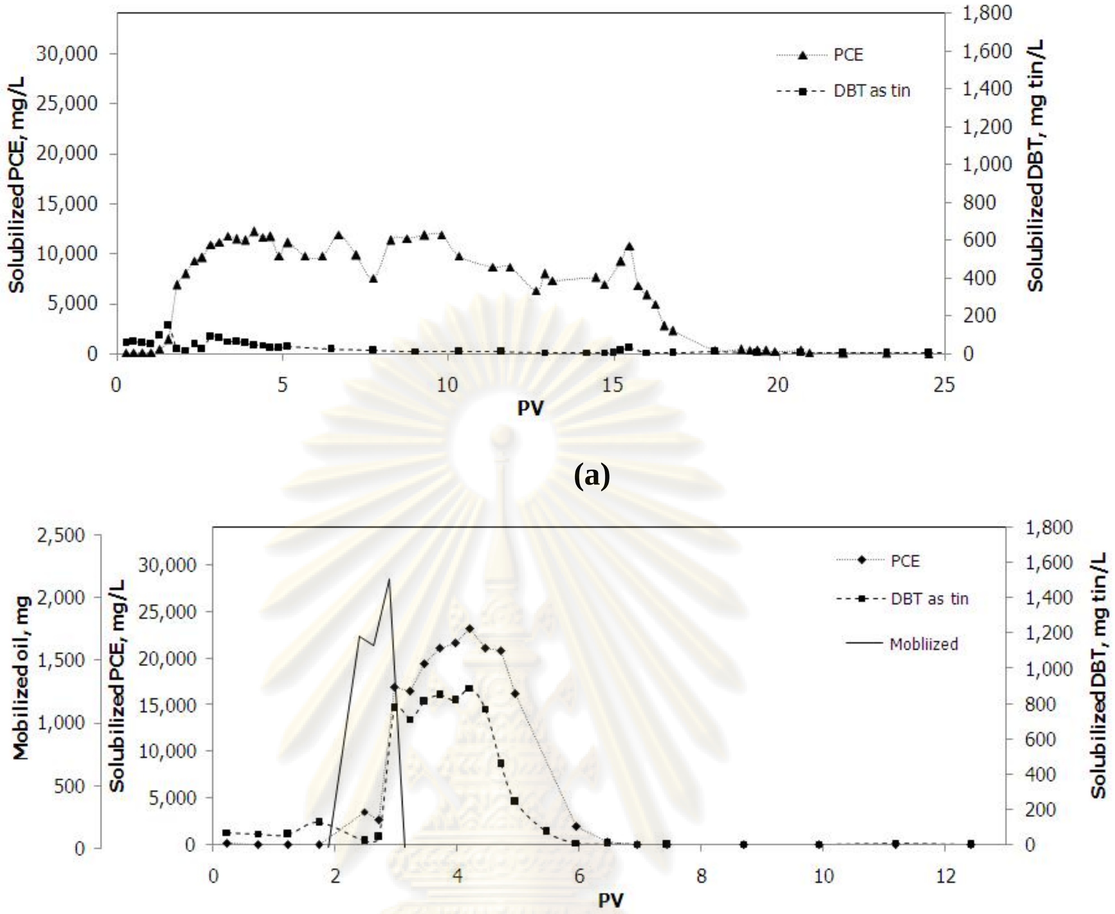
* *np* mean plateau region can not be observed



(a)

(b)

Figure 7.4 Effluent result for system of 3.6 wt.% SDHS 0.4 wt.% C16DPDS without $CaCl_2$ at (a) pH7 and (b) pH 1.



(a)

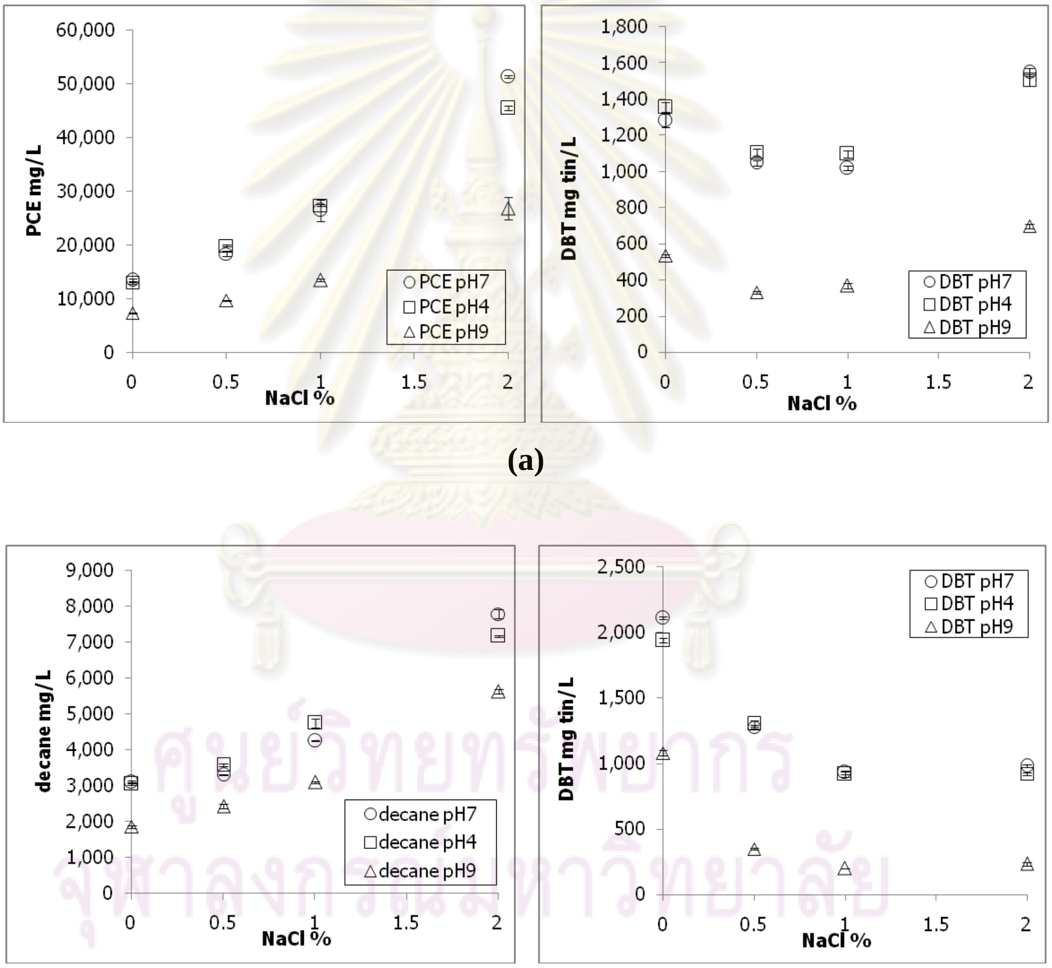
(b)

Figure 7.5 Effluent result for system of 3.6 wt.% SDHS 0.4 wt.% C16DPDS with 0.2 wt.% $CaCl_2$ at (a) pH7 and (b) pH 1.

The comparison on solubilization study was shown in Table 7.2. The solubilization result of the system at pH 1 observed to have a higher percentage of solubilization capacity than at neutral pH system for both PCE and DBT. It is important to note that the maximum solubilization of DBT at pH 1 was high up to 50% of their solubilization capacity. This proved that the sorption of DBT was the cause of limited solubilization and the altering of DBT’s form and sand surface charge by adjusting pH could help preventing the problem. Under this situation, DBT could be removed in the same manner with general organic oil. The extraction result show that there was not DBT left in the packed column after surfactant flushing.

7.5.3 Result part 2: experiment at pH 4, 7, 9 using NaCl as electrolyte

To prevent the precipitation of $CaCl_2$, the NaCl was applied with the same surfactant solution of 3.6 wt.% and SDHS 0.4 wt.% C16DPDS with three pHs at 4, 7 and 9. The pH of surfactant solution without adjustment was about 6.9±0.03 while the adjusted pHs were 4±0.07 and 9±0.07. The observation after 2 days revealed that the boundaries of Winsor type I/III at 1 wt.% NaCl at these 3 pHs were the same.



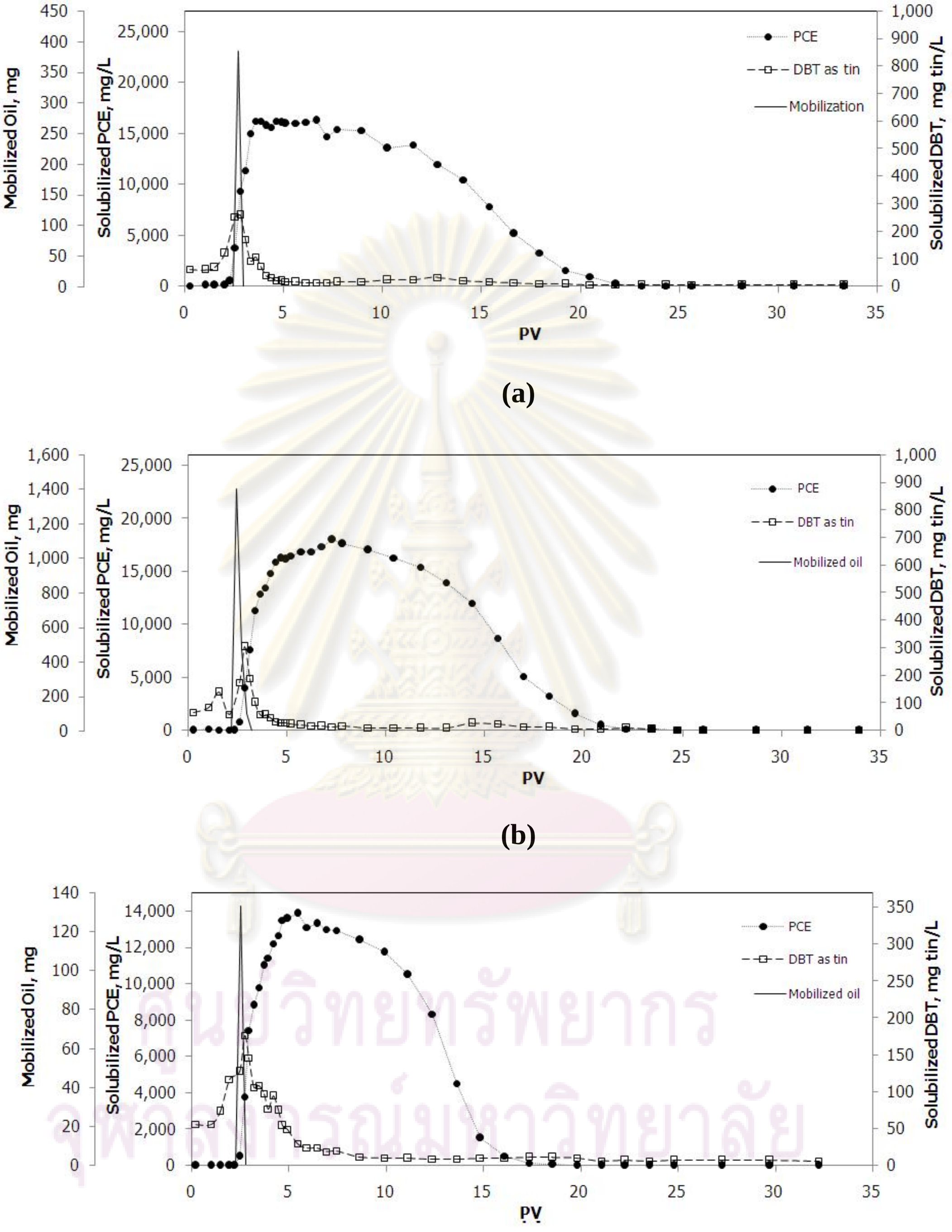
(a)

(b)

Figure 7.6 Batch solubilization result of 3.6 wt.% SDHS 0.4 wt.% C16DPDS using NaCl as electrolyte at pH 4, 7, and 9 for (a) DBT-PCE mixture and (b) DBT-decane mixture.

The solubilized decane, PCE, and DBT were investigated and shown in Figure 7.6a and 7.6b. The different solubilization capacity at various salinities was already discussed in Damrongsiri et al. (2010). Solubilization trend of systems at pH 4 and 7 were similar that at pH 1. It was quite clear that adjusting pH to acidic condition did not affect the solubilization of this surfactant system. However, solubilization at pH 9 was observed to be reduced. In fact, both phase study and solubilization study were expected that the boundary of Winsor type I/III may shift to lower salinity at pH 9 and the solubilization should be higher than that at neutral pH due to the effect of sodium ion from NaOH.

The column studies were carried out using the Ottawa sand and sieved aquifer soil. The column packed with sieved aquifer soil has a higher pore volume and porosity (see Table 7.1) resulting in a longer retention time for 20 minutes. The effluent streams were collected and analyzed for the mobilization and solubilization as shown in Figure 7.7 for column packed with the Ottawa sand and in Figure 7.8 for column packed with sieved aquifer soil. The solubilization of PCE in the effluent form all experiments were similar, where the solubilization steeply increased prior to reaching a plateau, declining gradually afterwards until only a trace amount of oil being observed with respect to time indicating that most of the trapped oil had already been removed. Solubilization of PCE at pH 4 and 7 were similar as discussed previously for the system at pH 1. The solubilization at plateau was between 50 to 60% of their solubilization capacity (see Table 7.3) for the experiment at pH 4 and 7. The system at pH 9 illustrated a great plateau solubilization value which high up to 90 % of its solubilization capacity, by the way, its capacity was lower than acidic and neutral pH. The reason of what happen at pH 9 was still unknown.

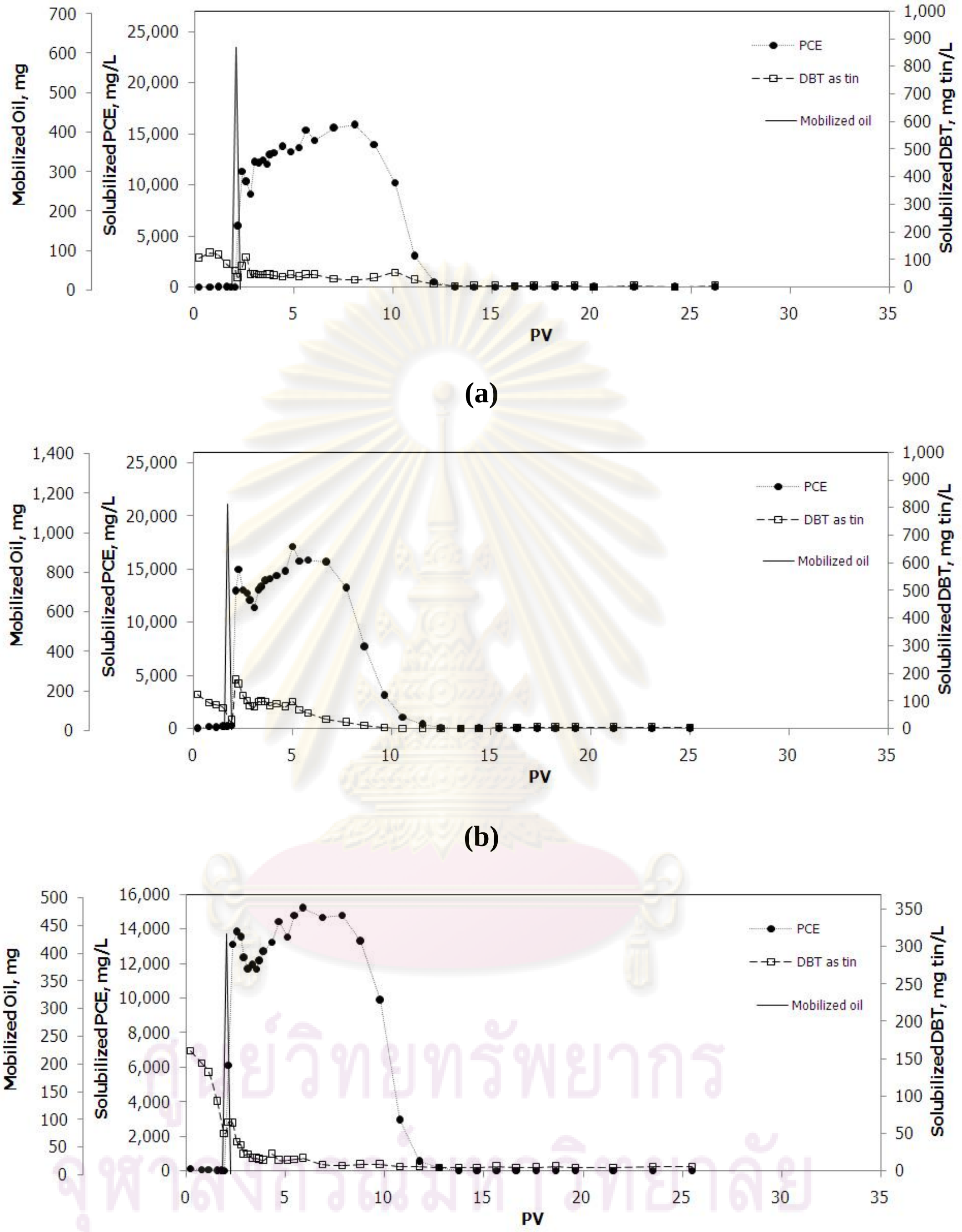


(a)

(b)

(c)

Figure 7.7 Effluent result from packed column of Ottawa sand which residual DBT-PCE mixture flooded with 3.6%SDHS 0.4C16DPDS 1% NaCl at (a) pH4, (b) pH 7 and (c) pH 9.



(a)

(b)

(c)

Figure 7.8 Effluent result from packed column of 20-30 mesh aquifer soil which residual DBT-PCE mixture flooded with 3.6%SDHS 0.4C16DPDS 1% NaCl at (a) pH 4, (b) pH 7 and (c) pH 9.

Solubilization trend (see Table 7.3) of DBT at pH 4 and 9 were indifferent from that at pH 7 that were very limited. To be focused on solubilization of DBT, the fraction of DBT removed by solubilization was considered only. As the result, 24, 21, and 22 mg of DBT (as total tin) were removed by 33 PV (990 mL) of surfactant solution at pH 4, 7, and 9, respectively, from the column packed by Ottawa sand, while 24, 27, and 17 mg of DBT (as total tin) were removed by 26 PV (990 mL) of surfactant solution at pH 4, 7, and 9, respectively, from the column packed by sieved aquifer soil. Those results could be considered indifferent. The altering of pH to be pH 4 or pH 9 could not help minimizing the adsorption of DBT from the media used in this study. The extraction results also confirm that most of DBT still remain in the packed column.

Table 7.3 Solubilization of PCE and DBT from solubilization study and plateau value from column experiment.

pH	**Solubilization capacity**		**Column (at plateau)**			
	mg/L		**mg/L**		**% of solubilization capacity**	
	PCE	**DBT (as tin)**	**PCE**	**DBT (as tin)**	**PCE**	**DBT (as tin)**
Experiment with Ottawa sand						
4	24300	900	15,400	*np**	56	-
7	25300	1,300	15,800	*np*	60	-
9	14700	600	12,700	*np*	86	-
Experiment with sieved aquifer soil						
4	24300	900	14,200	*np*	52	-
7	25300	1,300	14,600	*np*	55	-
9	14700	600	13,800	*np*	94	-

* *np* mean plateau region can not be observed

7.6 Conclusion

The limited solubilization of DBT was caused by the adsorption of DBT onto the sand packed in the column. It was the resulting of electrostatic interaction between DBT and negative surface charge of sand. The effect of pH on the solubilization of surfactant solution was observed. Solubilization of PCE, decane and DBT was not affected by acidic pH irrespective to the type of electrolyte presented as show in

Figure 7.3 and 7.5. However, at pH 9, the basic condition reduce the solubilization of all experimented organic.

The altering of pH of surfactant solution could lessen the adsorption of DBT onto the surface as observed in the column study at pH 1. However, it was found that pH 4 was not sufficient to prevent the adsorption because the surface charge of sand was still negative while DBT was in a positive form. The column study at pH 1 indicated the lower IFT between surfactant solution and oil, which may be due to the high ionic strength from added HCl that help reducing the repulsion among ionic surfactant head groups and promoting the sorption of surfactant to the interface. In addition, the changed form of DBT to a neutral one by adjusting the system to pH 9 could not help improving the treatment efficiency. To prevent the adsorption of DBT onto sand, a modification of DBT to cationic form and the surface of sand to a positive charge was required by lowering the pH such as to pH 1. Too strong acidic condition could affect to the aquifer properties as well as the living organism in that soil. However, a slight pH shifting was not adequate to prevent the adsorption of DBT. Therefore, it was concluded that pH adjustment was not appropriate to be done to prevent the adsorption of DBT. As a consequence, the removal of DBT-PCE mixture by solubilization was improper to be applied if the media naturally possess negative surface charge such as sand and silicon oxide because the adsorption of the cationic form of organometallic compounds onto negatively charge surface could not be avoided. It would lessen the removal efficiency, cause a very long treatment time and require large volume of treatment solution unacceptably. On the other hand, the experimental result at pH 1 indicated that most of DBT can be removed easily by mobilized together their solvent, which was agreed well with previous study (Damrongsiri et al., 2010). The modified mobilization technique, or even ex-situ remediation may be a better choice to solve the organometallic contamination problem.

CHAPTER VIII
CONCLUSIONS

8.1 The EACN and the surrogate

Although the study aimed to clean out tetraethyl lead (TEL) from the source zone, the surrogate oil was applied in place of TEL in the initial study to minimize the experimenter's health risks. The three important properties considered for finding an appropriate oil surrogate were that it needed to (1) be an organometallic compound because a study on the solubilization of an organometallic compound was rare; (2) have a similar EACN to that of TEL because an oil that has a similar EACN normally produces similar phase behavior when used in the same surfactant system; and (3) have a similar density to that of TEL in order to study its vertical migration and mobilization. The EACN of TEL was quantified using Salager's relation technique (Salager et al., 1979) which was about 6.04 to 7.23. However, we could not find a surrogate that had all three of the desired properties.

Dibutyltin dichloride (DBT) was selected as the most match, as it is an organometallic compound of the same group with lead that is less toxic and more economically feasible and conveniently obtainable. Furthermore, the contamination of organotin including DBT has been concerned (RPA, 2003; Dopp et al., 2007; Cao et al., 2009). Since DBT is a solid polar compound, it needed to be mixed with an organic liquid to make it into a liquid and raise its EACN to 6-7 and to give it a similar density to that of TEL. The resulting DBT mixture, however, possessed only two of the three required properties. Finally, the oil surrogate used was a mixture of DBT and decane at molar ratio of 0.038:0.962. It was an organometallic compound, and had a similar EACN to that of TEL. A mixture of DBT and PCE at the same molar ratio was also used in order to study the vertical migration and compare the results. The mixture of DBT and PCE was an organometallic compound with a similar density (but different EACN). Thus, there were two oil surrogates used in this study.

8.2 Solubilization behavior

The experiment began with the phase study to observe the phase behavior in order to select the system for the solubilization study. The selected surfactant system was the combination of 3.6 wt.% SDHS 0.4 wt% C16DPDS with $CaCl_2$. Thongkorn (2007) also used this surfactant mixture in her study.

The solubilization of individual PCE, decane, and DBT, and the DBT-PCE and DBT-decane mixtures at various salinity levels was investigated. The results indicate that the solubilization of DBT and perhaps other organometallic compounds was similar to that of normal organic oil, making the solubilization regions dependent upon their polarity.

8.3 Column experiment

The solubilization and mobilization trends of both PCE and decane oil mixtures were harmonious with the general column experimental results of the previous studies (Sabatini et al., 2000; Childs et al., 2004). They related to the value derived from the solubilization experiment and could be explained by the rate limited solubilization mechanism (Pennell et al., 1994; Dwarakanath et al., 1999; Taylor et al., 2001). Conversely, the DBT concentration found in trace concentrations even though a large amount of DBT still remained in the packed column. The improper removal of DBT via solubilization could be blamed on the extremely limited solubilization. The results derived from the gradient technique also showed that the solubilization of DBT was very low. However, the study results also pointed out that mobilization was a mechanism capable of removing DBT by moving it together with its solvent; however, vertical migration remains a concern.

8.4 Effect of pH on DBT removal

DBT likely has a dissociation reaction, so the forms of DBT are depended upon pH. DBT is in cationic form at pH lower than 7 that tend to be adsorbed by the negative charge of sand surface (Hoch et al., 2003). The adsorption of DBT could be prevented if this electrostatic interaction can be minimized. The experimental results show that very low pH (i.e., pH 1) the adsorption of DBT to the sand surface was then minimized.

Thus the removal of DBT-PCE and DBT-decane mixtures by solubilization was poor as sand (silicon oxide) naturally has a negative surface charge. The adsorption of the cationic form of organometallic compounds could not be avoided.

8.5 Outlook on cost analysis

This part aims to discuss on application perspective of this technique focusing on cost of the treatment compare to pump and treat method used for a similar contaminant. However, to analyze in more details on cost and expense as an in situ treatment may not be possible due to the limitation of information. As a consequence, the following discussion is focusing on general perspective of in-situ site treatment by some methods published by the investigation of Federal Remediation Technologies Roundtable (FRTR). For the cost estimation proposed here is only to compare the pump and treat method with surfactant solution flushing which is the proposed technique. The expense is calculated based on the information from the column study.

As mentioned in the CHAPTER I, the purpose of this study was to investigate the approach for TEL removal from contaminated site at DuPont Company in Delaware, USA. The case study was the old DuPont's TEL production plan which now a day closed down and no longer produces TEL at the site. The contaminated area has been prohibited for any purpose but leave it for remediation. The TEL and its solvent were contaminated to the complexes aquifer as DNAPLs. The excavation on this site was impractical due to several limitations, thus, the in-situ treatment was only approach for remedy this contamination site.

The goal of treatment was to remove the source of contaminant. According to the case studies published by FRTR in the website (*www.frtr.gov*) reveal that the goal for contaminant source removal could not be achieved by using pump and treat methods. The source of NAPLs which still remains in the aquifer caused the reborn of contaminant concentration in groundwater after the remediation.

Even the biological degradation which is considered to be a good approach for remediate the plume of contaminant, it seems to be improper for this case as almost microorganism in soil could not survive in the condition of high concentration of toxic compound contaminated in aquifer. Some cases using chemical oxidation such as permanganate showed insignificantly different from pump and treat method since the reaction occur only with dissolved contaminant in soil water and once r the chemical injection stopped, the contaminant concentration was reborn if the source of DNAPLs still remain.

To simplify cost analysis comparative study, the following discussion will compare the cost estimation between pump and treat method and our surfactant solution flushing which can be considered as modified pump and treat known as SEAR approach. These two methods were similar construction, remedial system, and offsite treatment. The remedial system consisted of sheet pile, injection well and extraction well, pumping system, and storage for extracted solution. One addition for SEAR is the surfactant solution, storage, and injection system which also the addition capital cost. However, the higher solubilization in SEAR resulting in shorter operation time which reduces the operation and maintenance cost.

The actual cost for each section may not be estimated as mentioned earlier. Thus the comparison demonstrates the two methods based on column experiment by considering the packed column in this study as a contaminated aquifer. The packed column has pore volume of 30 mL and the retention of 80 minute. The trapped PCE is about 7,000 mg and DBT about 200 mg. For pump and treat method, assuming that the solubility obtained by flushing with water for both PCE and DBT are 50 mg/L (steady entire operation), thus, the volume required to remove all trapped PCE and DBT are 140 L and 4 L, respectively. So, 140 L is needed to remove all contaminant in this packed column responding to total time of 6,140 hrs (> 8 months with the flow rate of 0.38 mL/min).

If the SEAR is applied, the addition capital cost relies on storage, and injection system that may double cost of old style pump and treat. The amount of surfactant depends on volume of solution used entire flushing (if the solution is not regenerated). Another addition cost is also from surfactant used in the flushing solution which may be considered double cost on treatment. However, the shorter time and less flushing solution of the treatment may compensate the higher cost from surfactant addition.

If consider the formulation obtained from this study: 3.6 wt.% SDHS 0.4 wt.% C16DPDS without $CaCl_2$, the estimated surfactant solution require to remove all PCE was 55 PV but for DBT was 110 PV as adsorption occurred. The 110 PV is 3.3 L responding to time of 144 hrs at the same flow rate. Compare to pump and treat method, the surfactant solution flushing decreased the operation time from 8 months to 6 day. For the same surfactant mixture but if the solution at pH 1 was applied (mobilization occurred and not practical by too low pH), only 16 PV of surfactant solution is required for complete contaminant removal and reduce the operation time to be 21 hrs or less than a day.

In conclusion, the SEAR increases the capital cost about twice as compare to pump and treat method but able to reduce the operation period for more than forty times. The shorter operation period would directly reflect the operation cost i.e., equipment replacement, field inspection and so on. This may need for some sites that require short operation time. However, the treatment of contaminant and surfactant, or regeneration of surfactant is another expense to be concerned.

8.6 Overall Conclusions

From this study using DBT as a representative of organometallic compound, it can conclude that organometallic compound behaves similar to normal organic compound that solubilization behavior depending on their polarity. Meanwhile the column experimental result also shows that DBT is able to behave like an inorganic compound that could be adsorbed by electrostatic interaction depending on their dissociated forms. From these two properties in one molecule of organometallic compound led to a more complication technique needed for the remediation.

The study demonstrates that if the electrostatic interaction was stronger than the micelle partition, the solubilization by surfactant will be obstructed, thus the target compound will adsorb on media while this mechanism is not a concern for general organic compound remediation. This problem is able to take place as long as the organometallic compounds are in cationic form and the aquifer media has negative surface charge, which it is usually found in natural condition. The PZC of soil media was needed to concern to apply the surfactant solubilization on the removal of organometallic compound which able to form to ionic forms. The cationic forms of organometallic compounds may cause a serious removal efficiency problem, requiring an unacceptably long treatment time and large volume of the treatment solution.

Nevertheless, our result also indicated that mobilization of DBT together with their solvent flushing was a potential method to remove this organometallic compound that can overwhelm the adsorption problem. The modified mobilization technique may be a better choice to solve the organometallic contamination problem as well as vertical migration of the contaminant.

8.7 Application for TEL and other organometallic compounds

The overall process of SEAR to remediate organic compound is to remove the trapped contaminant from subsurface aquifer and collect it for further treatment. The key to remove the contaminant are to untrapped the contaminant from soil pore and solubilized it into surfactant micelle. Another addition factor for organometallic compound is to prevent the adsorption of possibly ionic forms of it. The adsorption via electrostatic interaction between ionic forms of organometallic compound and surface charge of sand could make the treatment ineffective. Silicon oxide and kaolinite have negative surface charge at neutral pH while aluminum oxide and magnesium oxide show the positive surface properties. The forms of organometallic compound such as organotin and organolead are in neutral forms or cationic forms that may interact strongly with negative surface charge of soil media.

Thus, not only the suitable surfactant matching to the organic compounds by EACN or HLB concept, the adsorption due to electrostatic interaction must be concern. The forms of organometallic compounds caused by dissociation reaction, or the degradation must be identified. While the PZC of soil material is also must be known to avoid the ineffective treatment during the operation.

The extracted contaminant is then go to the separation process to recovery the surfactant and the contaminant was then treated by oxidation process or by biodegradation if low concentration of contaminant or even incineration process. The remaining inorganic residual in case of lead also require further treatment.

The SEAR is normally designed only for source zone. The contaminated area beyond the source zone usually appears in the large scale with low concentration of contaminant. This may deal with biodegradation or the active barrier.

8.8 Recommendations for Future Study

As mentioned in the previous conclusion, the better procedure to remove an organometallic compound should be based on mobilization. However, since most of organometallic compounds having much higher density than flushing solution, the vertical migration will be another concern. In order to avoid this problem, further work should be conducted on buoyancy concept by adding additive compound to lower density of the bulk solution after flushing the contaminated soil.

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APPENDICES

APPENDIX A

Experimental result for CHAPTER IV

Table A.1 Solubilization parameter (SP) of system of hexane in 2 wt.% SDOS 2 wt.% Tween80 solution

NaCl	**Solubilization Parameter for oil (SP_o)**					
wt.%	**rep 1**	**rep 2**	**rep 3**	**Avg**	**SD**	**%RSD**
1.8	0.443	0.463	0.441	0.449	0.012	2.71
1.9	0.494	0.492	0.495	0.494	0.002	0.31
2.0	0.502	0.515	0.546	0.521	0.023	4.34
2.3	0.712	0.738	0.763	0.738	0.026	3.46
NaCl	**Solubilization Parameter for water (SP_w)**					
wt.%	**rep 1**	**rep 2**	**rep 3**	**Avg**	**SD**	**%RSD**
1.8	0.998	1.033	0.995	1.009	0.021	2.09
1.9	0.716	0.748	0.778	0.747	0.031	4.15
2.0	0.537	0.575	0.58	0.564	0.024	4.17
2.3	0.387	0.418	0.399	0.401	0.016	3.89

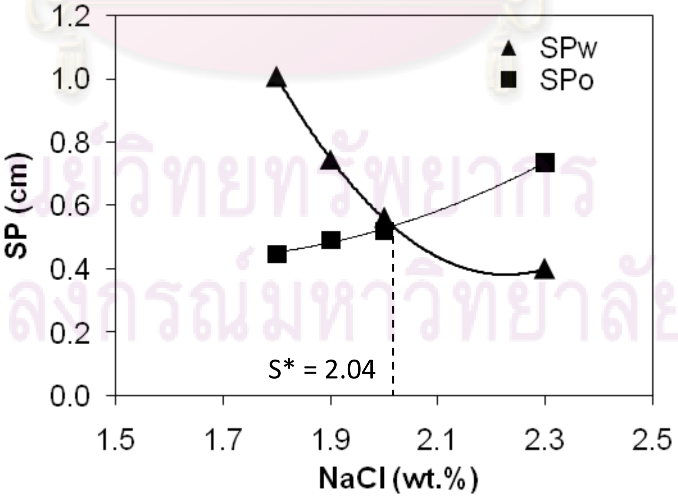

Figure A.1 Plot of SP_w and SP_o with NaCl and the optimum salinity of hexane in 2 wt.% SDOS 2 wt.% Tween80 solution

Table A.2 Solubilization parameter (SP) of system of octane in 2 wt.% SDOS 2 wt.% Tween80 solution

NaCl	**Solubilization Parameter for oil (SPo)**					
wt.%	**rep 1**	**rep 2**	**rep 3**	**Avg**	**SD**	**%RSD**
2.4	0.325	0.35	0.347	0.341	0.014	4.01
2.5	0.367	0.33	0.336	0.344	0.020	5.77
2.6	0.374	0.384	0.396	0.385	0.011	2.86
2.7	0.411	0.393	0.386	0.397	0.013	3.25
3.0	0.484	0.484	0.478	0.482	0.003	0.72
NaCl	**Solubilization Parameter for water (SPw)**					
wt.%	**rep 1**	**rep 2**	**rep 3**	**Avg**	**SD**	**%RSD**
2.4	0.756	0.751	0.749	0.752	0.004	0.48
2.5	0.627	0.623	0.656	0.635	0.018	2.83
2.6	0.556	0.544	0.551	0.550	0.006	1.10
2.7	0.488	0.52	0.512	0.507	0.017	3.29
3.0	0.399	0.405	0.417	0.407	0.009	2.25

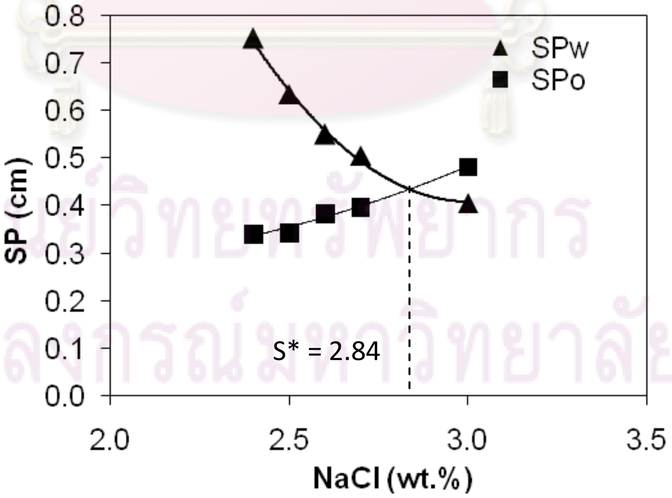

Figure A.2 Plot of SP_w and SP_o with NaCl and the optimum salinity of octane in 2 wt.% SDOS 2 wt.% Tween80 solution

Table A.3 Solubilization parameter (SP) of system of decane in 2 wt.% SDOS 2 wt.% Tween80 solution

NaCl	**Solubilization Parameter for oil (SPo)**					
wt.%	**rep 1**	**rep 2**	**rep 3**	**Avg**	**SD**	**%RSD**
2.9	0.239	0.228	0.222	0.230	0.009	3.75
3.0	0.209	0.218	0.259	0.229	0.027	11.66
3.5	0.248	0.29	0.237	0.258	0.028	10.83
3.8	0.32	0.292	0.352	0.321	0.030	9.34
NaCl	**Solubilization Parameter for water (SPw)**					
wt.%	**rep 1**	**rep 2**	**rep 3**	**Avg**	**SD**	**%RSD**
2.9	0.721	0.71	0.712	0.714	0.006	0.82
3.0	0.637	0.631	0.608	0.625	0.015	2.45
3.5	0.404	0.391	0.41	0.402	0.010	2.42
3.8	0.318	0.286	0.291	0.298	0.017	5.77

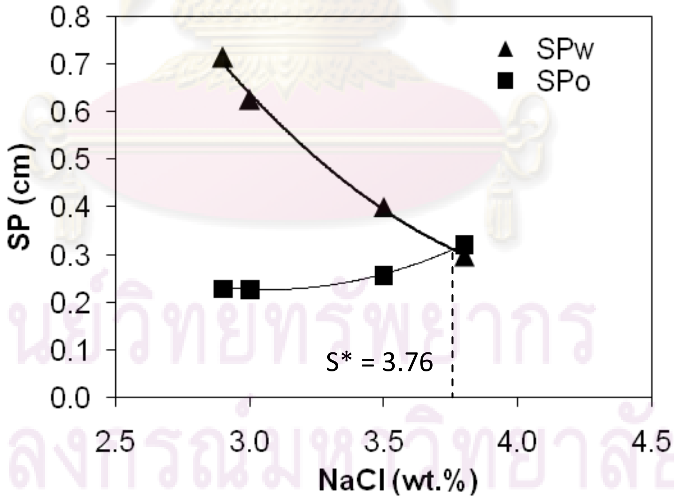

Figure A.3 Plot of SP_w and SP_o with NaCl and the optimum salinity of decane in 2 wt.% SDOS 2 wt.% Tween80 solution

Table A.4 Solubilization parameter (SP) of system of pentane in 2 wt.% SDOS 2 wt.% SDHS solution

NaCl	**Solubilization Parameter for oil (SPo)**					
wt.%	**rep 1**	**rep 2**	**rep 3**	**Avg**	**SD**	**%RSD**
1.2	0.287	0.298	na	0.293	0.008	2.66
1.4	0.334	0.317	0.329	0.327	0.009	2.67
1.5	0.386	0.387	na	0.387	0.001	0.18
1.6	0.342	0.349	0.371	0.354	0.015	4.27
1.8	0.42	0.444	na	0.432	0.017	3.93
2.0	0.592	0.606	na	0.599	0.010	1.65
NaCl	**Solubilization Parameter for water (SPw)**					
wt.%	**rep 1**	**rep 2**	**rep 3**	**Avg**	**SD**	**%RSD**
1.2	0.703	0.681	na	0.692	0.016	2.25
1.4	0.387	0.386	0.374	0.382	0.007	1.89
1.5	0.34	0.345	na	0.343	0.004	1.03
1.6	0.27	0.27	0.271	0.270	0.001	0.21
1.8	0.191	0.18	na	0.186	0.008	4.19
2.0	0.185	0.184	na	0.185	0.001	0.38

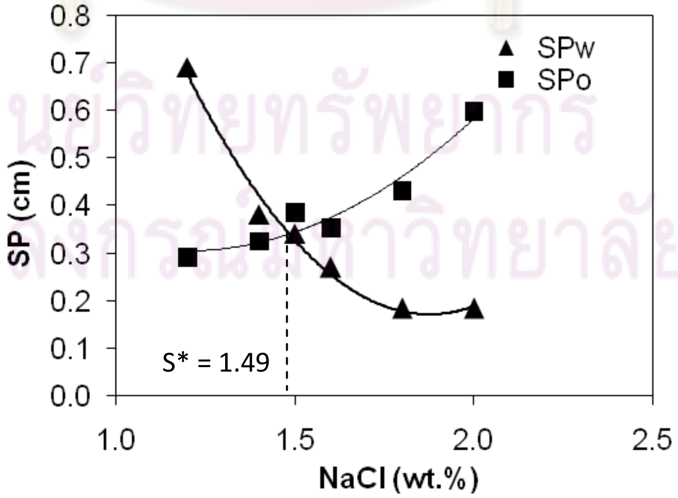

Figure A.4 Plot of SP_w and SP_o with NaCl and the optimum salinity of pentane in 2 wt.% SDOS 2 wt.% SDHS solution

Table A.5 Solubilization parameter (SP) of system of hexane in 2 wt.% SDOS 2 wt.% SDHS solution

NaCl	**Solubilization Parameter for oil (SPo)**					
wt.%	**rep 1**	**rep 2**	**rep 3**	**Avg**	**SD**	**%RSD**
1.4	0.288	0.289	0.291	0.289	0.002	0.53
1.5	0.265	0.277	0.262	0.268	0.008	2.96
2	0.337	0.336	0.34	0.338	0.002	0.62
2.5	0.577	0.572	0.575	0.575	0.003	0.44
NaCl	**Solubilization Parameter for water (SPw)**					
wt.%	**rep 1**	**rep 2**	**rep 3**	**Avg**	**SD**	**%RSD**
1.4	0.859	0.857	0.854	0.857	0.003	0.29
1.5	0.535	0.535	0.53	0.533	0.003	0.54
2	0.251	0.253	0.251	0.252	0.001	0.46
2.5	0.185	0.188	0.185	0.186	0.002	0.93

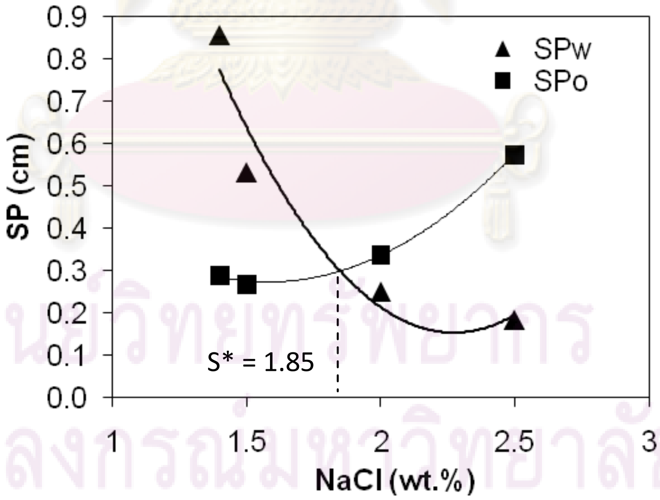

Figure A.5 Plot of SP_w and SP_o with NaCl and the optimum salinity of hexane in 2 wt.% SDOS 2 wt.% SDHS solution

Table A.6 Solubilization parameter (SP) of system of octane in 2 wt.% SDOS 2 wt.% SDHS solution

NaCl	**Solubilization Parameter for oil (SPo)**					
wt.%	**rep 1**	**rep 2**	**rep 3**	**Avg**	**SD**	**%RSD**
1.9	0.182	0.183	0.186	0.184	0.002	1.13
2	0.162	0.166	0.161	0.163	0.003	1.62
2.5	0.181	0.18	0.186	0.182	0.003	1.76
3.4	0.293	0.296	0.298	0.296	0.003	0.85
3.8	0.308	0.297	0.311	0.305	0.007	2.41
NaCl	**Solubilization Parameter for water (SPw)**					
wt.%	**rep 1**	**rep 2**	**rep 3**	**Avg**	**SD**	**%RSD**
1.9	0.441	0.44	0.444	0.442	0.002	0.47
2	0.401	0.403	0.402	0.402	0.001	0.25
2.5	0.29	0.299	0.301	0.297	0.006	1.98
3.4	0.188	0.184	0.192	0.188	0.004	2.13
3.8	0.158	0.161	0.153	0.157	0.004	2.57

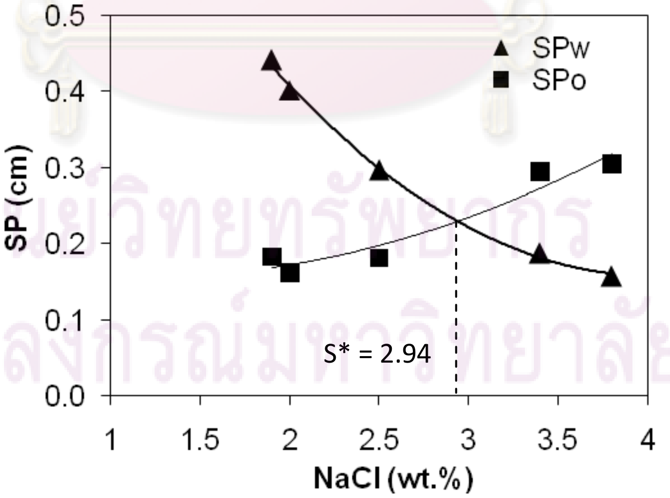

Figure A.6 Plot of SP_w and SP_o with NaCl and the optimum salinity of octane in 2 wt.% SDOS 2 wt.% SDHS solution

Table A.7 Relationship between ln S* and EACN of two surfactant systems

Alkane oil	EACN	Surfactant system			
		2 wt.% SDOS 2 wt.% Tween80		2 wt.% SDOS 2 wt.% SDHS	
		S*	ln S*	S*	ln S*
pentane	5			1.49	0.40
hexane	6	2.04	0.71	1.85	0.62
octane	8	2.84	1.04	2.94	1.08
decane	10	3.76	1.32		

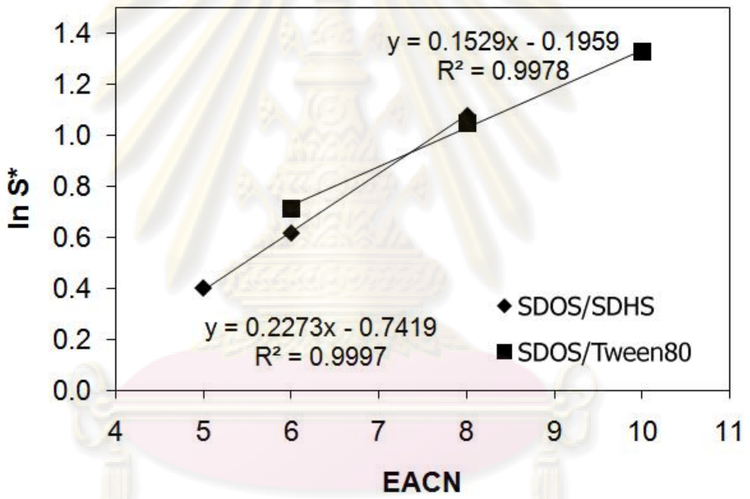

Figure A.7 Linear relation between the natural logarithm of *S** and EACN by the surfactant solution of 2 wt.% SDOS 2 wt.% Tween80 and 2 wt.% SDOS 2 wt.% SDHS

Table A.8 Solubilization parameter (SP) of system of TEL-hexane mixture at molar ratio of 0.2:0.8 in 2 wt.% SDOS 2 wt.% Tween80 solution

NaCl	**SP_o**	**SP_w**
wt.%	**cm**	**cm**
1.8	0.484	0.956
1.9	0.416	0.791
2.0	0.560	0.619
2.1	0.669	0.516
2.2	0.697	0.536
2.3	0.905	0.428

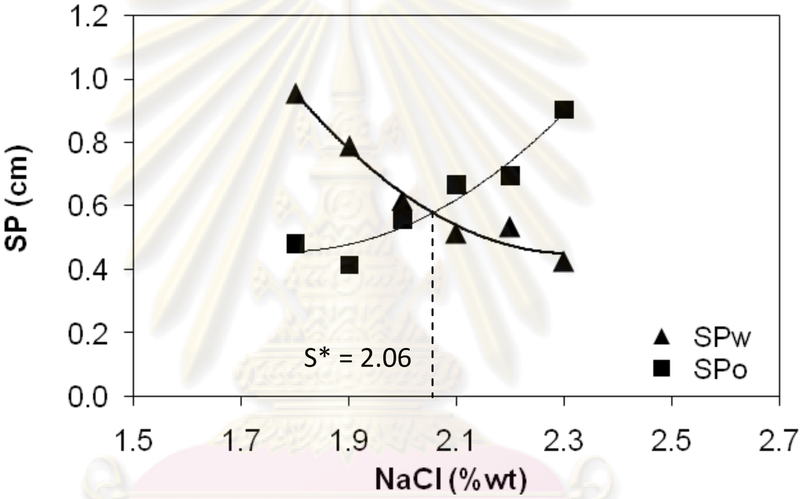

Figure A.8 Plot of SP_w and SP_o with NaCl and the optimum salinity of TEL-hexane mixture in 2 wt.% SDOS 2 wt.% Tween80 solution

Then the EACN of TEL could be calculated by Equation 2.6

$\ln S^* = K(EACN) + C$

$EACN = (\ln S^* - C) / K$

$EACN = (\ln 2.06 + 0.1959) / 0.1529$

$EACN = 6.008$

And from Equation 2.1, EACN of TEL-hexane mixture was 6.008, thus EACN of TEL was 6.04.

Table A.9 Solubilization parameter (SP) of system of TEL-hexane mixture at molar ratio of 0.2:0.8 in 2 wt.% SDOS 2 wt.% SDHS solution

NaCl	**SPo**	**SPw**
wt.%	**cm**	**cm**
1.5	0.105	0.548
1.7	0.229	0.405
2.0	0.270	0.271
2.2	0.292	0.216
2.5	0.489	0.162

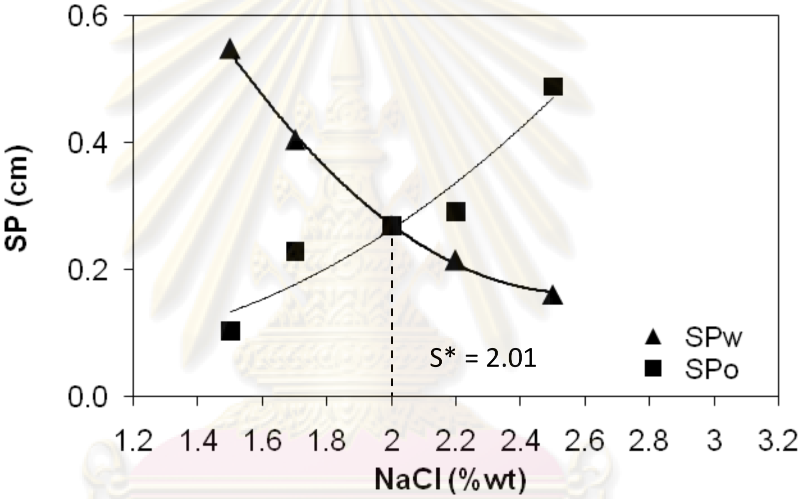

Figure A.9 Plot of SP_w and SP_o with NaCl and the optimum salinity of TEL-hexane mixture in 2 wt.% SDOS 2 wt.% SDHS solution

Then the EACN of TEL could be calculated by Equation 2.6

$$\ln S^* = K(EACN) + C$$

$$EACN = (\ln S^* - C) / K$$

$$EACN = (\ln 2.01 + 0.7419) / 0.2273$$

$$EACN = 6.34$$

And from Equation 2.1, EACN of TEL-hexane mixture was 6.34, thus EACN of TEL was 7.68.

APPENDIX B

Experimental result for CHAPTER V

Table B.1 Solubilization result of PCE in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using $CaCl_2$ as electrolyte.

wt.%	**in mg/L**					**%RSD**		**in mM**		
$CaCl_2$	**PCE**							**$CaCl_2$**	**PCE**	
	rep 1	**rep 2**	**rep 3**	**avg**	**SD**				**avg**	**SD**
0	4,201	3,796	3,927	3,975	206	5.2		0	23.97	1.24
0.2	15,088	14,285	15,822	15,065	769	5.1		18	90.85	4.63
0.4	30,122	32,491	31,348	31,320	1,185	3.8		36	188.87	7.14
0.6	48,366	50,786	49,529	49,561	1,210	2.4		54	298.86	7.30
0.8	62,406	64,922	63,972	63,767	1,271	2.0		72	384.53	7.66
1	70,618	70,596	70,471	70,562	79	0.1		90	425.51	0.48

Table B.2 Solubilization result of individual decane in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using $CaCl_2$ as electrolyte.

wt.%	**in mg/L**					**%RSD**		**in mM**		
$CaCl_2$	**Decane**							**$CaCl_2$**	**Decane**	
	rep 1	**rep 2**	**rep 3**	**avg**	**SD**				**avg**	**SD**
0	634	653	695	661	31	4.7		0	4.64	0.22
0.2	2,160	1,967	2,169	2,099	114	5.4		18	14.75	0.80
0.4	4,004	4,098	3,944	4,015	78	1.9		36	28.22	0.55
0.6	4,918	4,980	4,392	4,763	323	6.8		54	33.48	2.27
0.8	5,830	6,108	5,897	5,945	145	2.4		72	41.78	1.02
1	6,795	6,620	5,944	6,453	449	7.0		90	45.35	3.16

Table B.3 Solubilization result of individual DBT in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using $CaCl_2$ as electrolyte.

wt.%	**in mg/L**					**%RSD**		**in mM**		
$CaCl_2$	**Decane**							**$CaCl_2$**	**Decane**	
	rep 1	**rep 2**	**rep 3**	**avg**	**SD**				**avg**	**SD**
0	307	459	337	368	81	21.9		0	3.10	0.68
0.2	330	397	289	339	55	16.1		18	2.85	0.46
0.4	343	304	361	336	29	8.7		36	2.83	0.25
0.6	343	271	343	319	41	13.0		54	2.68	0.35
0.8	322	354	340	339	16	4.8		72	2.85	0.14
1	318	294	311	308	12	3.9		90	2.59	0.10

Table B.4 Solubilization result of decane using DBT-decane mixture in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using $CaCl_2$ as electrolyte.

wt.%	**in mg/L**					**%RSD**		**in mM**		
$CaCl_2$	**Decane**							**$CaCl_2$**	**Decane**	
	rep 1	**rep 2**	**rep 3**	**avg**	**SD**				**avg**	**SD**
0	3,447	3,753	3,984	3,728	269	7.2		0	26.20	1.89
0.2	4,672	4,599	4,225	4,499	240	5.3		18	31.62	1.69
0.4	4,581	5,151	5,265	4,999	366	7.3		36	35.13	2.57
0.6	5,500	5,833	5,176	5,503	329	6.0		54	38.67	2.31
0.8	6,077	5,536	6,339	5,984	409	6.8		72	42.05	2.88
1	6,667	6,151	6,008	6,275	347	5.5		90	44.10	2.44

Table B.5 Solubilization result of DBT using DBT-decane mixture in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using $CaCl_2$ as electrolyte.

wt.%	**in mg/L**					**%RSD**		**in mM**		
$CaCl_2$	**DBT**							**$CaCl_2$**	**DBT**	
	rep 1	**rep 2**	**rep 3**	**avg**	**SD**				**avg**	**SD**
0	2,118	2,177	2,127	2,141	32	1.5		0	18.03	0.27
0.2	1,786	1,935	1,854	1,858	75	4.0		18	15.65	0.63
0.4	1,668	1,655	1,714	1,679	31	1.9		36	14.14	0.26
0.6	1,449	1,507	1,557	1,504	54	3.6		54	12.67	0.46
0.8	1,421	1,636	1,539	1,532	108	7.0		72	12.91	0.91
1	1,371	1,400	1,399	1,390	16	1.2		90	11.71	0.14

Table B.6 Solubilization result of PCE using DBT-PCE mixture in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using $CaCl_2$ as electrolyte.

wt.%	**in mg/L**					**%RSD**		**in mM**		
$CaCl_2$	**PCE**							**$CaCl_2$**	**PCE**	
	rep 1	**rep 2**	**rep 3**	**avg**	**SD**				**avg**	**SD**
0	22,171	23,701	22,283	22,718	853	3.8		0	137.00	5.14
0.2	32,400	37,690	35,759	35,283	2,677	7.6		18	212.77	16.14
0.4	43,072	44,930	44,299	44,100	945	2.1		36	265.94	5.70
0.6	56,924	56,243	56,534	56,567	342	0.6		54	341.11	2.06
0.8	58,727	55,529	57,550	57,269	1,617	2.8		72	345.35	9.75
1	59,144	58,050	57,736	58,310	739	1.3		90	351.62	4.46

Table B.7 Solubilization result of DBT using DBT-PCE mixture in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using CaCl2 as electrolyte.

wt.%	**in mg/L**					**%RSD**		**in mM**		
$CaCl_2$	**DBT**							**$CaCl_2$**	**DBT**	
	rep 1	**rep 2**	**rep 3**	**avg**	**SD**				**avg**	**SD**
0	1,686	1,599	1,631	1,639	44	2.7		0	13.80	0.37
0.2	1,916	1,919	1,709	1,848	120	6.5		18	15.56	1.01
0.4	2,129	2,113	2,076	2,106	27	1.3		36	17.74	0.23
0.6	2,211	2,259	2,230	2,233	25	1.1		54	18.81	0.21
0.8	2,405	2,455	2,386	2,415	35	1.5		72	20.35	0.30
1	2,476	2,536	2,396	2,469	70	2.8		90	20.80	0.59

Table B.8 Molar solubilization ratio of DBT-PCE mixture and DBT-decane mixture in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using $CaCl_2$ as electrolyte.

$CaCl_2$	**DBT-PCE mixture**		**DBT-decane mixture**	
mM	**DBT**	**PCE**	**DBT**	**Decane**
0	0.092	0.908	0.408	0.592
18	0.068	0.932	0.331	0.669
36	0.063	0.937	0.287	0.713
54	0.052	0.948	0.247	0.753
72	0.056	0.944	0.235	0.765
90	0.056	0.944	0.210	0.790

APPENDIX C

Experimental result for CHAPTER VI

C.1 Tracer study

The same pumping system was applied for tracer study. The bromide solution was flowed from a reservoir through piston pimp, valve, and then, the top of column (Table C.1) then pass the packed column to the effluent end (Table C.2)

Table C.1 Bromide concentration at the top of column

Sample number	T_i	**PV**	A_i	$B=A_i-A_{i-1}$	$C_i=B_i/(T_i-T_{i-1})$	$D_i=C_ixT_i$	$E_i=T_i^2xC_i$
	Time		**Br**				
	min		**mg/L**				
1	30	0.37	0		0.0000	0.00	0.00
2	40	0.50	0.0415	0.04	0.0042	0.17	6.64
3	50	0.62	0.8544	0.81	0.0813	4.06	203.23
4	60	0.75	4.3365	3.48	0.3482	20.89	1253.56
5	70	0.87	7.9039	3.57	0.3567	24.97	1748.03
6	80	1.00	9.4427	1.54	0.1539	12.31	984.83
7	90	1.12	9.8818	0.44	0.0439	3.95	355.67
8	100	1.25	10.0731	0.19	0.0191	1.91	191.30
9	110	1.37	10.1584	0.09	0.0085	0.94	103.21
10	120	1.50	10.1525		0.0000	0.00	0.00
sum					*1.02*	*69.21*	*4846.46*

Mean resident time (R_t) = D_{sum}/C_{sum} = 68.13 min.

Table C.2 Bromide concentration at the effluent end of column.

Sample number	T_i	**PV**	A_i	$B=A_i-A_{i-1}$	$C_i=B_i/(T_i-T_{i-1})$	$D_i=C_ixT_i$	$E_i=T_i^2xC_i$
	Time		**Br**				
	min		**mg/L**				
1	110	1.37	0		0.0000	0.00	0.00
2	120	1.50	0.0746	0.07	0.0075	0.90	107.42
3	130	1.62	1.3628	1.29	0.1288	16.75	2177.06
4	140	1.75	4.5178	3.16	0.3155	44.17	6183.80
5	150	1.87	7.7966	3.28	0.3279	49.18	7377.30
6	160	2.00	9.5174	1.72	0.1721	27.53	4405.25
7	170	2.12	10.0168	0.50	0.0499	8.49	1443.27
8	180	2.25	10.1457	0.13	0.0129	2.32	417.64
9	190	2.37	10.2881	0.14	0.0142	2.71	514.06
10	200	2.50	10.3413	0.05	0.0053	1.06	212.80
11	210	2.62	10.2016		0.0000	0.00	0.00
sum					*1.03*	*153.11*	*22838.60*

Mean resident time (R_t) = D_{sum}/C_{sum} = 148.05 min

Table C.3 Calculated number for the Morrill dispersion index

Time	**Conc**	**Cumulative**	**Cumulative**
min	**mg/L**	**mg/L**	**percentage**
	A_i	$B_i = A_i+B_{i-1}$	$C_i = B_i/B_{sum}$
110	0.0000		
120	0.0075	0.0075	0.72
130	0.1288	0.13628	13.18
140	0.3155	0.4518	43.69
150	0.3279	0.77966	75.39
160	0.1721	0.9517	92.03
170	0.0499	1.00168	96.86
180	0.0129	1.01457	98.11
190	0.0142	1.02881	99.49
200	0.0053	1.03413	100.00
sum		*1.03413*	

Morrill dispersion index (MDI) = time at cumulative percentage at 90 / time at cumulative percentage at 10. The cumulative percentage at 10 was between 120 to 130 minute. In this range, the percentage increased by 12.46 in 10 minute. The cumulative percentage at 10 should at 120 + 10/12.46*(10-0.72) = 1*27.4* minute. The cumulative percentage at 90 was between 150 to 160 minute. In this range, the percentage increased by 16.64 in 10 minute. The cumulative percentage at 10 should at 150 + 10/16.64*(90-75.39) = *158.8* minute.

Thus, MDI = 158.8/127.4 = 1.25. Ideal plug flow has MDI of 1. Plug flow reactor has MDI less than 2.0 or equal (U.S. EPA, 1986 cited in Tchobanoglous et al. 2003) so this column could be considered as a plug flow column.

C.2 Result for column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS without $CaCl_2$

The packed column properties:

Pore volume = 31.16 mL
Porosity = 0.376
Trapped oil = 6.68 g (13.81 %Rs)

Table C.4 Results for the experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS without $CaCl_2$

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
0.25	55		24.05		-
0.50	121	1	35.39	0.23	-
0.75	58	1	36.07	0.50	-
1.00	48	2	37.64	0.78	-
1.25	52	2	37.62	1.06	-
1.50	800	5	111.49	1.63	-
1.75	3,182	21	166.81	2.69	-
2.00	4,197	49	263.31	4.32	-
2.25	5,489	85	236.76	6.22	-
2.49	5,367	127	166.87	7.76	-
2.74	5,708	169	na.	na.	-
2.99	5,570	212	112.42	9.88	-
3.24	4,878	251	na.	na.	-
3.49	5,148	289	87.85	11.40	-
3.74	5,047	328	na.	na.	-
3.99	4,948	366	74.27	12.63	-
4.24	4,816	403	na.	na.	-
4.49	5,027	441	74.01	13.76	-
4.74	4,963	479	na.	na.	-
4.99	5,368	518	63.78	14.81	-
5.49	4,632	594	60.41	15.75	-
5.99	5,031	667	62.39	16.68	-
6.49	5,365	746	64.78	17.65	-
6.99	5,093	826	65.20	18.64	-
7.48	5,357	905	68.24	19.65	-
8.73	5,061	1,103	74.56	22.37	-
9.98	5,025	1,295	78.29	25.27	-

Table C.4 (continue)

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
11.23	5,666	1,498	79.90	28.28	-
12.47	5,093	1,702	80.83	31.33	-
13.72	5,117	1,896	74.63	34.28	-
14.97	4,664	2,082	76.22	37.15	-
16.22	4,596	2,258	71.81	39.96	-
17.46	4,333	2,428	73.23	42.72	-
18.71	4,234	2,590	70.10	45.44	-
19.96	3,797	2,743	64.36	47.99	-
21.21	3,940	2,890	72.52	50.60	-
22.45	3,337	3,028	77.90	53.45	-
23.70	3,198	3,152	74.14	56.34	-
24.95	3,010	3,270	65.88	59.00	-
27.44	2,532	3,481	na.	na.	-
29.94	2,083	3,656	43.15	67.29	-
32.43	1,437	3,790	na.	na.	-
34.93	1,170	3,889	30.10	72.85	-
37.42	719	3,961	na.	na.	-
39.92	558	4,010	28.23	77.29	-
42.41	432	4,047	na.	na.	-
44.90	288	4,074	10.80	80.25	-
47.40	232	4,094	na.	na.	-
49.89	186	4,110	7.91	81.68	-

Result and calculation for PCE

Initial trapped PCE	=	6,228	mg	a
PCE dissolved during replacement	=	406	mg	b
Trapped result	=	5,822	mg	c = a-b
Mobilized PCE	=	0	mg	d
Solubilized PCE	=	4,110	mg	e
Extract by surfactant solution	=	28	mg	f
Extract by HCl solution	=	0	mg	g
Extract from sand	=	0	mg	h
Total mass measured	=	4,138	mg	i = d+e+f+g+h
Total treated	=	4,110	mg	j = d+e
Total remained	=	28	mg	k = f+g+h
% PCE removal	=	99	%	i / j * 100
Mass balance	=	71	%	i / c * 100

Result and calculation for DBT

Initial trapped DBT as tin	=	176	mg as tin
DBT dissolved during replacement	=	21	mg as tin
Trapped result	=	155	mg as tin
			mg as tin
Mobilized DBT	=	0	mg as tin
Solubilized DBT	=	82	mg as tin
Extract by surfactant solution	=	2	mg as tin
Extract by HCl solution	=	14	mg as tin
Extract from sand	=	0	mg as tin
			mg as tin
Total mass measured	=	98	mg as tin
Total treated	=	82	mg as tin
Total remained	=	16	mg as tin
% DBT removal	=	84	%
Mass balance	=	63	%

C.3 Result for column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 0.2 wt.% $CaCl_2$

The packed column properties:

Pore volume = 30.94mL
Porosity = 0.363
Trapped oil = 7.04 g (15.06 %Rs)

Table C.5 Results for the experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 0.2 wt.% $CaCl_2$

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
0.26	90		55.35		0
0.52	120	1	63.31	0.45	0
0.77	134	2	58.51	0.91	0
1.03	94	3	52.03	1.33	0
1.29	461	5	95.96	1.90	348
1.55	1,389	12	149.54	2.83	348
1.81	6,842	43	21.96	3.48	348
2.06	7,965	99	20.24	3.64	348
2.32	9,268	165	52.03	3.92	348
2.58	9,598	236	21.12	4.19	348
2.84	10,868	314	89.88	4.62	348
3.10	11,133	398	82.22	5.27	348
3.35	11,748	485	66.71	5.84	348
3.61	11,449	573	62.42	6.33	348
3.87	11,336	660	57.50	6.78	348
4.13	12,189	749	43.85	7.17	348
4.39	11,638	839	46.31	7.51	348
4.64	11,706	928	32.54	7.81	348
4.90	9,797	1,010	27.89	8.04	348
5.16	11,083	1,089	35.91	8.28	348
5.68	9,747	1,248	na.	8.28	348
6.19	9,789	1,396	na.	8.28	348
6.45	na.	1,396	24.35	9.43	348
6.71	11,874	1,561	na.	9.43	348
7.22	9,832	1,726	na.	9.43	348
7.74	7,522	1,858	16.13	10.19	348
8.26	11,335	2,001	na.	10.19	348

Table C.5 (continue)

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
8.77	11,540	2,175	na.	10.19	348
9.03	na.	2,175	13.38	10.76	348
9.29	11,846	2,352	na.	10.76	348
9.80	11,921	2,533	na.	10.76	348
10.32	9,814	2,698	10.99	11.22	348
11.35	8,686	2,979	na.	11.22	348
11.61	na.	2,979	9.54	11.61	348
11.87	8,674	3,111	na.	11.61	348
12.64	6,308	3,282	na.	11.61	348
12.90	7,985	3,336	7.71	11.94	348
13.16	7,297	3,395	na.	11.94	348
14.19	na.	3,395	7.53	12.23	348
14.45	7,625	3,678	na.	12.23	348
14.70	6,956	3,733	7.25	12.34	348
14.96	na.	3,733	4.27	12.38	348
15.22	9,228	3,856	18.54	12.47	348
15.48	10,792	3,933	31.81	12.66	348
15.74	6,814	3,999	na.	12.66	348
15.99	5,873	4,048	6.98	12.95	348
16.25	4,949	4,089	na.	12.95	348
16.51	2,751	4,118	na.	12.95	348
16.77	2,275	4,137	3.98	13.08	348
18.06	348	4,187	9.06	13.33	348
18.83	437	4,196	na.	13.33	348
19.09	390	4,199	na.	13.33	348
19.35	320	4,202	3.95	13.57	348
19.61	316	4,204	na.	13.57	348
19.86	271	4,206	na.	13.57	348
20.64	308	4,213	4.69	13.74	348
20.90	122	4,215	na.	13.74	348
21.93	69	4,218	3.40	13.89	348
23.22	69	4,220	2.66	14.01	348
24.51	10	4,222	2.88	14.11	348
25.80	0	4,222	1.64	14.20	348

Result and calculation for PCE

Initial trapped PCE = 6,567 mg
PCE dissolved during replacement = 151 mg
Trapped result = 6,416 mg

Mobilized PCE = 325 mg
Solubilized PCE = 4,222 mg
Extract by surfactant solution = 0 mg
Extract by HCl solution = 0 mg
Extract from sand = 0 mg

Total mass measured = 4,547 mg
Total treated = 4,547 mg
Total remained = 0 mg

PCE removal = 100 %
Mass balance = 71 %

Result and calculation for DBT

Initial trapped DBT as tin = 186 mg as tin
DBT dissolved during replacement = 34 mg as tin
Trapped result = 152 mg as tin

Mobilized DBT = 9 mg as tin
Solubilized DBT = 14 mg as tin
Extract by surfactant solution = 13 mg as tin
Extract by HCl solution = 69 mg as tin
Extract from sand = 5 mg as tin

Total mass measured = 110 mg as tin
Total treated = 23 mg as tin
Total remained = 87 mg as tin

DBT removal = 21 %
Mass balance = 72 %

C.4 Result for column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 0.4 wt.% $CaCl_2$

The packed column properties:

Pore volume = 33.27 mL

Porosity = 0.365

Trapped oil = 8.33 g (17.74 %Rs)

Table C.6 Results for the experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 0.4 wt.% $CaCl_2$

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
0.25	306		106.99		0
0.50	332	2	77.10	0.68	0
0.75	129	4	67.90	1.22	0
1.00	119	5	68.69	1.72	0
1.25	334	7	69.03	2.23	194
1.50	619	10	5.71	2.51	1,765
1.75	1,312	17	23.09	2.62	5,156
2.00	3,029	33	154.02	3.27	5,232
2.25	19,786	118	60.39	4.06	5,232
2.50	21,000	269	52.91	4.48	5,232
2.75	20,512	422	53.44	4.88	5,232
3.00	17,446	563	111.71	5.49	5,232
3.25	18,548	696	64.83	6.14	5,232
3.50	21,694	845	83.01	6.69	5,232
4.00	19,740	1,151	67.28	7.80	5,232
4.50	10,415	1,375	20.74	8.45	5,232
5.00	4,534	1,485	10.06	8.68	5,232
5.51	2,006	1,534	7.25	8.81	5,232
6.01	933	1,555	8.60	8.92	5,232
6.26	734	1,562	8.52	8.99	5,232
7.51	191	1,579	9.03	9.31	5,232
8.76	59	1,583	7.20	9.61	5,232
10.01	27	1,585	8.55	9.90	5,232
11.26	0	1,585	7.39	10.20	5,232
12.51	0	1,585	7.12	10.47	5,232
15.01	0	1,585	6.09	10.96	5,232
17.52	0	1,585	11.45	11.61	5,232
20.02	0	1,585	6.11	12.25	5,232

Result and calculation for PCE

Initial trapped PCE = 7,763 mg
PCE dissolved during replacement = na. mg
Trapped result = 7,763 mg

Mobilized PCE = 4,879 mg
Solubilized PCE = 1,585 mg
Extract by surfactant solution = 0 mg
Extract by HCl solution = 0 mg
Extract from sand = 0 mg

Total mass measured = 6,464 mg
Total treated = 6,464 mg
Total remained = 0 mg

PCE removal = 100 %
Mass balance = 83 %

Result and calculation for DBT

Initial trapped DBT as tin = 220 mg as tin
DBT dissolved during replacement = na. mg as tin
Trapped result = 220 mg as tin

Mobilized DBT = 138 mg as tin
Solubilized DBT = 12 mg as tin
Extract by surfactant solution = 18 mg as tin
Extract by HCl solution = 12 mg as tin
Extract from sand = 0 mg as tin

Total mass measured = 180 mg as tin
Total treated = 150 mg as tin
Total remained = 30 mg as tin

DBT removal = 83 %
Mass balance = 82 %

C.5 Result for column experiment with DBT-decane mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 0.4 wt.% $CaCl_2$

The packed column properties:

Pore volume = 30.54 mL
Porosity = 0.377
Trapped oil = 4.25 g (18.62 %Rs)

Table C.7 Results for the experiment with DBT-decane mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 0.4 wt.% $CaCl_2$

PV	decane		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
0.25	0		48.09		0
0.75	0	0	58.90	0.81	0
1.24	0	0	52.70	1.66	0
1.74	0	0	50.27	2.44	0
2.24	0	0	76.50	3.41	0
2.49	0	0	64.16	3.94	0
2.74	371	1	48.76	4.37	1,315
2.99	2,584	13	11.30	4.60	1,335
3.24	2,405	32	11.48	4.69	1,397
3.48	na.	32	7.79	4.76	1,397
3.73	2,259	40	7.66	4.82	1,397
3.98	1,851	56	8.72	4.88	1,397
4.23	1,988	70	7.66	4.94	1,397
4.48	2,056	86	7.49	5.00	1,397
4.73	2,174	102	7.24	5.06	1,397
4.98	2,320	119	7.34	5.11	1,397
5.47	2,319	154	6.71	5.22	1,397
5.97	2,187	188	6.61	5.32	1,397
6.47	2,191	222	6.17	5.42	1,397
6.97	2,434	257	5.60	5.51	1,397
7.47	2,475	294	4.58	5.58	1,397
8.71	2,676	392	2.95	5.73	1,397
9.95	2,731	495	3.33	5.85	1,397
11.20	1,934	583	2.83	5.96	1,397
12.44	2,720	672	2.28	6.06	1,397
13.69	2,244	766	1.89	6.14	1,397
14.93	2,651	859	3.22	6.24	1,397

Table C.7 (continue)

PV	decane		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
16.18	2,426	956	3.85	6.37	1,397
17.42	2,402	1,047	3.24	6.51	1,397
18.66	2,487	1,140	3.49	6.63	1,397
19.91	2,675	1,238	3.08	6.76	1,397
21.15	2,701	1,340	2.61	6.87	1,397
22.40	2,364	1,437	2.72	6.97	1,397
23.64	1,944	1,519	2.58	7.07	1,397
24.89	1,559	1,585	2.57	7.17	1,397
27.37	1,458	1,700	2.81	7.37	1,397
29.86	834	1,787	2.86	7.59	1,397
32.35	200	1,826	2.35	7.78	1,397
34.84	141	1,839	2.18	7.96	1,397
37.33	25	1,845	2.22	8.12	1,397
39.82	11	1,847	3.95	8.36	1,397
42.30	7	1,848	1.95	8.58	1,397
44.79	4	1,848	2.05	8.73	1,397
47.28	3	1,848	1.68	8.88	1,397
49.77	4	1,848	1.20	8.98	1,397

Result and calculation for decane

Initial trapped decane = 3,921 mg
Decane dissolved during replacement = 66 mg
Trapped result = 3,855 mg

Mobilized decane = 1,288 mg
Solubilized decane = 1,848 mg
Extract by surfactant solution = 2 mg
Extract by HCl solution = 0 mg
Extract from sand = 0 mg

Total mass measured = 3,138 mg
  Total treated = 3,136 mg
  Total remained = 2 mg

Decane removal = 100 %
Mass balance = 81 %

Result and calculation for DBT

Initial trapped DBT as tin = 129 mg as tin
DBT dissolved during replacement = 21 mg as tin
Trapped result = 108 mg as tin

Mobilized DBT = 42 mg as tin
Solubilized DBT = 9 mg as tin
Extract by surfactant solution = 15 mg as tin
Extract by HCl solution = 2 mg as tin
Extract from sand = 32 mg as tin

Total mass measured = 100 mg as tin
  Total treated = 51 mg as tin
  Total remained = 49 mg as tin

DBT removal = 51 %
Mass balance = 93 %

C.6 Result for column experiment with DBT-decane mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 0.8 wt.% $CaCl_2$

The packed column properties:

Pore volume = 30.01 mL
Porosity = 0.370
Trapped oil = 4.98 g (22.19 %Rs)

Table C.8 Results for the experiment with DBT-decane mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 0.8 wt.% $CaCl_2$

PV	decane		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
0.25	0		48.51	0.00	0
0.76	0	0	61.81	0.84	0
1.27	0	0	63.74	1.79	0
1.77	0	0	42.11	3.37	0
2.28	0	0	59.12	4.14	0
2.53	0	0	31.92	4.49	1,399
2.79	1,341	5	116.36	5.05	1,878
3.04	5,023	29	25.59	5.59	1,978
3.29	4,422	65	41.13	5.84	1,978
3.55	4,547	99	27.52	6.10	1,978
3.80	na.	99	31.50	6.33	1,978
4.05	5,811	178	31.79	6.57	1,978
4.31	5,020	219	31.12	6.81	1,978
4.56	5,120	258	32.33	7.05	1,978
4.81	3,547	291	32.20	7.29	1,978
5.07	3,741	318	16.36	7.48	1,978
5.57	3,597	374	25.11	7.79	1,978
6.08	4,072	432	27.07	8.19	1,978
6.59	4,005	494	30.31	8.63	1,978
7.09	4,098	555	28.21	9.07	1,978
7.60	4,406	620	27.72	9.50	1,978
8.86	4,489	789	20.53	10.41	1,978
10.13	4,390	958	11.08	11.01	1,978
11.40	4,715	1,131	17.95	11.57	1,978
12.66	4,799	1,311	18.53	12.26	1,978
13.93	4,472	1,488	20.99	13.01	1,978
15.20	3,223	1,634	19.78	13.78	1,978

Table C.8 (continue)

PV	decane		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
16.46	1,830	1,730	24.38	14.62	1,978
17.73	800	1,780	26.19	15.58	1,978
19.00	257	1,800	26.53	16.59	1,978
20.26	92	1,806	na.	16.59	1,978
21.53	12	1,808	26.40	18.60	1,978
22.79	4	1,809	24.32	19.56	1,978
24.06	3	1,809	25.23	20.50	1,978
25.33	3	1,809	27.22	21.50	1,978
27.86	3	1,809	27.70	23.59	1,978
30.39	3	1,809	26.64	25.65	1,978
32.93	2	1,809	22.77	27.53	1,978
35.46	2	1,810	20.47	29.17	1,978
37.99	2	1,810	18.19	30.64	1,978
40.52	na.	1,810	11.36	31.76	1,978
43.06	1	1,810	9.49	32.56	1,978
45.59	1	1,810	8.28	33.23	1,978
48.12	1	1,810	2.14	33.63	1,978
50.65	1	1,810	6.55	33.96	1,978

Result and calculation for decane

Initial trapped decane = 4,590 mg
Decane dissolved during replacement = 103 mg
Trapped result = 4,487 mg

Mobilized decane = 1,824 mg
Solubilized decane = 1,810 mg
Extract by surfactant solution = 0 mg
Extract by HCl solution = 0 mg
Extract from sand = 0 mg

Total mass measured = 3,634 mg
Total treated = 3,634 mg
Total remained = 0 mg

Decane removal = 100 %
Mass balance = 81 %

Result and calculation for DBT

Initial trapped DBT as tin = 151 mg as tin
DBT dissolved during replacement = 31 mg as tin
Trapped result = 120 mg as tin

Mobilized DBT = 60 mg as tin
Solubilized DBT = 34 mg as tin
Extract by surfactant solution = 10 mg as tin
Extract by HCl solution = 0 mg as tin
Extract from sand = 22 mg as tin

Total mass measured = 126 mg as tin
Total treated = 94 mg as tin
Total remained = 32 mg as tin

DBT removal = 75 %
Mass balance = 105 %

C.7 Result for column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS with gradient $CaCl_2$

The packed column properties:

Pore volume = 28.67 mL

Porosity = 0.349

Trapped oil = 8.33 g (18.3 %Rs)

Table C.9 Results for the experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS with gradient $CaCl_2$

PV	$CaCl_2$	PCE		DBT as tin		Mobilized oil
		concentration	cumulative	concentration	cumulative	cumulative
	wt.%	mg/L	mg	mg/L	mg	mg
0.27	*w	40		32.93		0
0.53	w	54	0	49.85	0.31	0
0.80	w	62	1	49.10	0.69	0
1.06	w	0	1	49.67	1.07	0
1.33	w	0	1	96.88	1.62	0
1.59	w	54	1	130.76	2.49	0
1.86	w	38	2	174.40	3.65	0
2.12	w	37	2	205.05	5.09	0
2.39	w	52	2	156.23	6.46	0
2.65	0	127	3	19.23	7.13	0
2.92	0	2,185	12	319.17	8.41	0
3.18	0	4,398	37	359.02	10.99	0
3.45	0	5,935	76	267.27	13.37	0
3.98	0	5,265	161	111.06	16.25	0
4.51	0	4,684	237	151.03	18.24	0
5.04	0	5,318	313	77.58	19.98	0
5.57	0	4,652	388	57.89	21.01	0
6.10	0	1,953	439	46.64	21.80	0
6.63	0	2,904	476	49.53	22.53	0
6.89	0.2	7,162	514	128.43	23.21	232
7.16	0.2	13,310	592	246.76	24.63	366
7.42	0.2	11,058	684	276.22	26.62	389
7.69	0.2	10,623	767	44.31	27.84	410
8.22	0.2	10,802	929	20.94	28.33	426
8.75	0.2	11,608	1,100	14.92	28.61	442
9.28	0.2	11,651	1,277	11.76	28.81	442
9.81	0.2	11,451	1,452	6.41	28.95	442

Table C.9 (continue)

PV	$CaCl_2$	PCE		DBT as tin		Mobilized oil
		concentration	cumulative	concentration	cumulative	cumulative
	wt.%	mg/L	mg	mg/L	mg	mg
10.34	0.2	11,778	1,629	4.07	29.03	442
10.87	0.2	7,301	1,774	4.92	29.10	442
11.40	0.2	11,551	1,917	4.43	29.17	457
11.66	0.4	12,970	2,010	1.95	29.19	528
11.93	0.4	20,028	2,135	10.13	29.24	872
12.20	0.4	23,285	2,300	24.59	29.37	1,037
12.46	0.4	23,747	2,479	29.17	29.57	1,061
12.99	0.4	24,526	2,846	29.68	30.02	1,061
13.52	0.4	24,348	3,217	29.70	30.47	1,061
14.58	0.4	na.	3,217	29.10	31.37	1,061
15.64	0.4	27,008	4,778	26.82	32.22	1,061
15.91	0.6	21,635	4,963	23.39	32.41	1,061
16.17	0.6	20,857	5,125	35.53	32.63	1,061
16.44	0.6	na.	5,125	84.74	33.09	1,061
16.70	0.6	19,926	5,435	71.15	33.68	1,061
17.23	0.6	9,212	5,656	33.96	34.48	1,061
17.76	0.6	3,751	5,755	21.26	34.90	1,061
18.82	0.6	1,318	5,832	25.65	35.61	1,061
19.88	0.6	160	5,854	21.89	36.33	1,061
21.21	0.6	66	5,858	18.45	37.10	1,061
22.53	0.6	40	5,860	19.59	37.82	1,061
23.86	0.6	36	5,862	15.45	38.49	1,061
25.19	0.6	35	5,863	15.96	39.09	1,061

* *w* = water

Result and calculation for PCE

Initial trapped PCE = 7,765 mg
PCE dissolved during replacement = 363 mg
Trapped result = 7,402 mg

Mobilized PCE = 990 mg
Solubilized PCE = 5,863 mg
Extract by surfactant solution = 0 mg
Extract by HCl solution = 0 mg
Extract from sand = 0 mg

Total mass measured = 6,853 mg
Total treated = 6,853 mg
Total remained = 0 mg

PCE removal = 100 %
Mass balance = 93 %

Result and calculation for DBT

Initial trapped DBT as tin = 220 mg as tin
DBT dissolved during replacement = 15 mg as tin
Trapped result = 205 mg as tin

Mobilized DBT = 28 mg as tin
Solubilized DBT = 39 mg as tin
Extract by surfactant solution = 10 mg as tin
Extract by HCl solution = 95 mg as tin
Extract from sand = 0 mg as tin

Total mass measured = 172 mg as tin
Total treated = 67 mg as tin
Total remained = 105 mg as tin

DBT removal = 39 %
Mass balance = 84 %

APPENDIX D

Experimental result for CHAPTER VII

D.1 Result for solubilization experiment of surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS using $CaCl_2$ as electrolyte at pH1 (Table D.1 to D.4)

Table D.1 Solubilization result of PCE from DBT-PCE in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using $CaCl_2$ as electrolyte at pH 1.

$CaCl_2$	**PCE**					
	rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**RSD**
wt.%	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	19,802	19,714	20,032	19,849	164	0.83
0.2	35,847	35,424	33,195	34,822	1,425	4.09
0.4	42,960	42,289	43,171	42,807	461	1.08
0.6	49,981	45,544	49,388	48,304	2,409	4.99
0.8	46,634	47,278	49,264	47,725	1,371	2.87
1	45,857	46,620	47,958	46,811	1,064	2.27

Table D.2 Solubilization result of DBT from DBT-PCE in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using $CaCl_2$ as electrolyte at pH 1.

$CaCl_2$	**DBT as tin**					
	rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**RSD**
wt.%	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	19,802	19,714	20,032	19,849	164	0.83
0.2	35,847	35,424	33,195	34,822	1,425	4.09
0.4	42,960	42,289	43,171	42,807	461	1.08
0.6	49,981	45,544	49,388	48,304	2,409	4.99
0.8	46,634	47,278	49,264	47,725	1,371	2.87
1	45,857	46,620	47,958	46,811	1,064	2.27

Table D.3 Solubilization result of decane from DBT-decane in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using $CaCl_2$ as electrolyte at pH 1.

$CaCl_2$	**Decane**					
	rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**RSD**
wt.%	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	3,007	3,003	2,912	2,974	53	1.80
0.2	4,255	4,343	4,207	4,269	69	1.62
0.4	5,145	5,306	5,375	5,275	118	2.24
0.6	6,120	5,203	6,141	5,821	535	9.20
0.8	6,215	6,050	5,941	6,069	138	2.27
1	7,147	7,177	7,048	7,124	67	0.95

Table D.4 Solubilization result of DBT from DBT-decane in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using $CaCl_2$ as electrolyte at pH 1.

CaCl2	**DBT as tin**					
	rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**RSD**
wt.%	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	1,214	1,209	1,275	1,233	36	2.96
0.2	1,193	1,165	1,178	1,179	14	1.18
0.4	1,123	1,105	1,142	1,123	19	1.66
0.6	1,094	1,083	1,055	1,078	20	1.86
0.8	955	930	960	948	16	1.65
1	1,034	1,015	949	999	45	4.47

D.2 Result for solubilization experiment of surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS using NaCl as electrolyte at pH 4, 7 and 9 (Table D.5 to D.16).

Table D.5 Solubilization result of PCE from DBT-PCE in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using NaCl as electrolyte at pH 4.

NaCl	**pH**	**PCE**					
		rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**RSD**
wt.%		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	3.91	13,217	13,047	12,705	12,990	260	2.01
0.5	4.08	20,135	19,856	19,692	19,895	224	1.13
1	4.03	27,252	27,268	27,556	27,359	171	0.63
2	4.05	45,258	45,954	45,242	45,485	407	0.89

Table D.6 Solubilization result of DBT from DBT-PCE in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using NaCl as electrolyte at pH 4.

NaCl	**pH**	**DBT as tin**					
		rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**%RSD**
wt.%		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	3.91	1,382	1,332	1,355	1,356	25	1.87
0.5	4.08	1,081	1,107	1,121	1,103	21	1.86
1	4.03	1,112	1,076	1,100	1,096	18	1.69
2	4.05	1,529	1,467	1,514	1,503	33	2.17

Table D.7 Solubilization result of PCE from DBT-PCE in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using NaCl as electrolyte at pH 7.

NaCl	**pH**	**PCE**					
		rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**RSD**
wt.%		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	6.92	13,681	13,469	13,115	13,422	286	2.13
0.5	6.85	17,758	18,699	18,636	18,365	526	2.87
1	6.91	25,185	25,437	28,714	26,445	1969	7.44
2	6.89	51,664	51,109	51,239	51,337	290	0.57

Table D.8 Solubilization result of DBT from DBT-PCE in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using NaCl as electrolyte at pH 7.

NaCl	**pH**	**DBT as tin**					
		rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**%RSD**
wt.%		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	6.92	1,318	1,242	1,282	1,281	38	2.95
0.5	6.85	1,035	1,060	1,044	1,046	13	1.24
1	6.91	1,030	1,008	1,018	1,019	11	1.08
2	6.89	1,524	1,571	1,554	1,550	24	1.53

Table D.9 Solubilization result of PCE from DBT-PCE in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using NaCl as electrolyte at pH 9.

NaCl	**pH**	**PCE**					
		rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**RSD**
wt.%		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	9.05	8,015	8,233	7,996	8,081	132	1.63
0.5	8.89	10,772	10,628	10,618	10,673	87	0.81
1	8.94	14,607	14,975	14,427	14,791	260	1.76
2	8.99	31,680	29,599	27,155	29,478	2265	7.68

Table D.10 Solubilization result of DBT from DBT-PCE in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using NaCl as electrolyte at pH 9.

NaCl	**pH**	**DBT as tin**					
		rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**%RSD**
wt.%		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	9.05	540	525	538	535	8	1.49
0.5	8.89	323	336	333	331	7	2.08
1	8.94	363	355	384	367	15	4.07
2	8.99	688	712	696	699	12	1.75

Table D.11 Solubilization result of decane from DBT-decane in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using NaCl as electrolyte at pH 4.

NaCl	**pH**	**decane**					
		rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**%RSD**
wt.%		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	3.91	3,010	3,086	3,029	3,042	40	1.30
0.5	4.08	3,522	3,582	3,592	3,565	38	1.06
1	4.03	4,615	4,845	4,754	4,738	116	2.44
2	4.05	7,174	7,141	7,183	7,166	22	0.31

Table D.12 Solubilization result of DBT from DBT-decane in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using NaCl as electrolyte at pH 4.

NaCl	**pH**	**DBT as tin**					
		rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**%RSD**
wt.%		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	3.91	1,921	1,946	1,955	1,941	18	0.91
0.5	4.08	1,277	1,307	1,324	1,303	24	1.83
1	4.03	935	924	895	918	21	2.25
2	4.05	914	922	933	923	9	1.00

Table D.13 Solubilization result of decane from DBT-decane in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using NaCl as electrolyte at pH 7.

NaCl	**pH**	**decane**					
		rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**%RSD**
wt.%		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	6.92	3,109	3,127	3,062	3,099	34	1.08
0.5	6.85	3,289	3,324	3,284	3,299	22	0.66
1	6.91	4,225	4,257	4,238	4,240	16	0.39
2	6.89	7,916	7,662	7,772	7,783	127	1.63

Table D.14 Solubilization result of DBT from DBT-decane in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using NaCl as electrolyte at pH 7.

NaCl	**pH**	**DBT as tin**					
		rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**%RSD**
wt.%		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	6.92	2,127	2,103	2,109	2,113	12	0.59
0.5	6.85	1,278	1,265	1,293	1,278	14	1.11
1	6.91	948	917	933	933	15	1.64
2	6.89	969	986	991	982	11	1.17

Table D.15 Solubilization result of decane from DBT-decane in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using NaCl as electrolyte at pH 9.

NaCl	**pH**	**decane**					
		rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**%RSD**
wt.%		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	9.05	1,853	1,808	1,890	1,850	41	2.21
0.5	8.89	2,481	2,390	2,376	2,415	57	2.37
1	8.94	3,095	3,100	3,069	3,088	16	0.53
2	8.99	5,568	5,682	5,614	5,621	57	1.02

Table D.16 Solubilization result of DBT from DBT-decane in 3.6 wt.% SDHS 0.4 wt.% C16DPDS using NaCl as electrolyte at pH 9.

NaCl	**pH**	**DBT as tin**					
		rep 1	**rep 2**	**rep 3**	**avg**	**SD**	**%RSD**
wt.%		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
0	9.05	1,058	1,087	1,095	1,080	20	1.82
0.5	8.89	355	346	345	349	6	1.58
1	8.94	199	199	201	200	1	0.63
2	8.99	230	248	224	234	13	5.48

D.3 Result for column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS without $CaCl_2$ at pH 1 and use Ottawa sand as the media.

The packed column properties:

Pore volume = 30.71 mL

Porosity = 0.379

Trapped oil = 7.56 g (15.52 %Rs)

Table D.17 PCE and DBT in effluent for the column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS without $CaCl_2$ at pH 1

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
0.25	145		79.29		0
0.74	109	2	68.91	1.13	0
1.24	113	4	63.80	2.13	0
1.73	120	5	112.48	3.47	0
2.23	698	12	97.72	5.07	399
2.47	7,455	43	35.44	5.58	1,660
2.72	7,455	99	487.75	7.57	3,658
2.97	17,927	196	1108.20	13.63	3,658
3.22	18,115	333	1100.05	22.02	3,658
3.46	16,600	465	939.40	29.77	3,658
3.71	15,745	587	795.40	36.36	3,658
3.96	14,026	701	687.10	42.00	3,658
4.21	13,115	804	708.35	47.30	3,658
4.45	15,222	911	791.80	53.00	3,658
4.70	16,224	1,031	706.50	58.69	3,658
4.95	15,049	1,150	444.24	63.07	3,658
5.44	12,699	1,361	126.10	67.40	3,658
5.94	10,698	1,538	15.11	68.48	3,658
6.43	9,411	1,691	5.94	68.64	3,658
6.93	9,155	1,832	4.84	68.72	3,658
7.42	8,546	1,967	2.97	68.78	3,658
8.66	6,280	2,249	1.90	68.87	3,658
9.90	3,986	2,444	0.00	68.91	3,658

Table D.17 (continue)

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
11.14	2,026	2,558	0.73	68.92	3,658
12.37	1,061	2,617	7.56	69.08	3,658
13.61	655	2,649	0.00	69.22	3,658
14.85	471	2,671	0.00	69.22	3,658
16.09	0	2,679	0.00	69.22	3,658

Result and calculation for PCE

Initial trapped PCE = 7,054 mg a
PCE dissolved during replacement = 54 mg b
Trapped result = 7,000 mg c = a-b

Mobilized PCE = 3,411 mg d
Solubilized PCE = 2,679 mg e
Extract by surfactant solution = 0 mg f
Extract by HCl solution = 0 mg g
Extract from sand = 0 mg h

Total mass measured = 6,090 mg i = d+e+f+g+h
Total treated = 6,090 mg j = d+e
Total remained = 0 mg k = f+g+h

PCE removal = 100 % i / j * 100
Mass balance = 87 % i / c * 100

Result and calculation for DBT

Initial trapped DBT as tin = 200 mg as tin
DBT dissolved during replacement = 23 mg as tin
Trapped result = 177 mg as tin

Mobilized DBT = 96 mg as tin
Solubilized DBT = 69 mg as tin
Extract by surfactant solution = 1 mg as tin
Extract by HCl solution = 0 mg as tin
Extract from sand = 0 mg as tin
Total mass measured = 166 mg as tin
Total treated = 165 mg as tin
Total remained = 1 mg as tin

DBT removal = 99 %
Mass balance = 94 %

D.4 Result for column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 0.2 wt.% $CaCl_2$ at pH 1 and use Ottawa sand as the media.

The packed column properties:

Pore volume = 30.57 mL
Porosity = 0.377
Trapped oil = 8.94 g (18.43 %Rs)

Table D.18 PCE and DBT in effluent for the column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 0.2 wt.% $CaCl_2$ at pH 1

PV	**PCE**		**DBT as tin**		**Mobilized oil**
	concentration	**cumulative**	**concentration**	**cumulative**	**cumulative**
	mg/L	**mg**	**mg/L**	**mg**	**mg**
0.25	156		72.38		0
0.75	29	1	62.73	1.03	0
1.24	29	2	58.96	1.95	0
1.74	23	2	127.19	3.37	0
2.24	na.	2	na.	3.37	1,687
2.49	3,611	44	22.75	5.08	3,307
2.73	2,655	67	45.07	5.33	5,451
2.98	16,921	142	773.05	8.44	5,451
3.23	16,449	269	710.55	14.08	5,451
3.48	19,368	405	811.40	19.86	5,451
3.73	21,021	558	846.75	26.16	5,451
3.98	21,618	720	817.19	32.49	5,451
4.23	23,140	890	889.88	38.97	5,451
4.48	21,032	1,058	772.06	45.29	5,451
4.72	20,818	1,217	457.41	49.96	5,451
4.97	16,229	1,358	243.05	52.62	5,451
5.47	na.	1,358	73.73	55.03	5,451
5.97	1,957	1,634	13.96	55.70	5,451
6.46	310	1,652	8.93	55.87	5,451
6.96	0	1,654	5.60	55.98	5,451
7.46	0	1,654	2.32	56.04	5,451
8.70	0	1,654	5.02	56.18	5,451
9.94	0	1,654	3.64	56.35	5,451

Table D.18 (continue)

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
11.19	0	1,654	11.68	56.64	5,451
12.43	0	1,654	1.56	56.89	5,451

Result and calculation for PCE

Initial trapped PCE = 8,337 mg
PCE dissolved during replacement = 58 mg
Trapped result = 8,279 mg

Mobilized PCE = 5,083 mg
Solubilized PCE = 1,654 mg
Extract by surfactant solution = 0 mg
Extract by HCl solution = 0 mg
Extract from sand = 0 mg

Total mass measured = 6,737 mg
Total treated = 6,737 mg
Total remained = 0 mg

PCE removal = 100 %
Mass balance = 81 %

Result and calculation for DBT

Initial trapped DBT as tin = 236 mg as tin
DBT dissolved during replacement = 40 mg as tin
Trapped result = 196 mg as tin

Mobilized DBT = 144 mg as tin
Solubilized DBT = 57 mg as tin
Extract by surfactant solution = 1 mg as tin
Extract by HCl solution = 0 mg as tin
Extract from sand = 0 mg as tin

Total mass measured = 202 mg as tin
Total treated = 201 mg as tin
Total remained = 1 mg as tin

DBT removal = 100 %
Mass balance = 103 %

D.5 Result for column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 1 wt.% NaCl at pH 4 and use Ottawa sand as the media.

The packed column properties:

Pore volume = 29.62 mL
Porosity = 0.365
Trapped oil = 7.3 g (15.54 %Rs)

Table D.19 PCE and DBT in effluent for the column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 1 wt.% NaCl at pH 4.

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
0.26	85		62.61		0
1.03	107	2	60.13	1.40	0
1.54	113	4	68.07	2.37	0
2.05	122	6	119.54	3.80	0
2.31	512	8	na.	na.	0
2.57	3,819	25	253.52	6.63	0
2.82	9,360	75	258.24	8.58	384
3.08	11,375	153	170.81	10.21	384
3.34	14,984	254	92.24	11.21	384
3.59	16,222	372	105.99	11.96	384
3.85	16,222	495	73.50	12.64	384
4.11	15,746	617	39.97	13.08	384
4.36	15,575	736	32.59	13.35	384
4.62	16,185	857	21.69	13.56	384
4.88	16,063	979	18.58	13.71	384
5.13	15,938	1,101	17.65	13.85	384
5.65	15,969	1,343	15.05	14.10	384
6.16	16,076	1,587	13.78	14.32	384
6.67	16,240	1,832	13.72	14.53	384
7.18	14,702	2,068	13.47	14.73	384
7.70	15,383	2,296	15.29	14.95	384
8.98	15,289	2,879	16.71	15.56	384
10.26	13,539	3,427	23.49	16.32	384

Table D.19 (continue)

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
11.55	13,852	3,947	25.74	17.26	384
12.83	11,949	4,437	33.08	18.38	384
14.11	10,450	4,863	22.03	19.42	384
15.40	7,833	5,210	17.54	20.17	384
16.68	5,163	5,457	14.20	20.78	384
17.96	3,279	5,618	9.78	21.23	384
19.25	1,560	5,710	8.42	21.58	384
20.53	948	5,757	5.63	21.85	384
21.81	211	5,779	5.74	22.06	384
23.09	92	5,785	4.53	22.26	384
24.38	60	5,788	4.92	22.44	384
25.66	34	5,790	5.50	22.63	384
28.23	21	5,792	3.95	22.99	384
30.79	18	5,793	3.82	23.29	384
33.36	0	5,794	4.58	23.61	384

Result and calculation for PCE

Initial trapped PCE = 6,810 mg
PCE dissolved during replacement = 121 mg
Trapped result = 6,689 mg

Mobilized PCE = 358 mg
Solubilized PCE = 5,794 mg
Extract by surfactant solution = 0 mg
Extract by HCl solution = 0 mg
Extract from sand = 0 mg

Total mass measured = 6,152 mg
Total treated = 6,152 mg
Total remained = 0 mg

PCE removal = 100 %
Mass balance = 92 %

Result and calculation for DBT

Initial trapped DBT as tin = 193 mg as tin
DBT dissolved during replacement = 29 mg as tin
Trapped result = 164 mg as tin

Mobilized DBT = 10 mg as tin
Solubilized DBT = 24 mg as tin
Extract by surfactant solution = 74 mg as tin
Extract by HCl solution = 41 mg as tin
Extract from sand = 0 mg as tin

Total mass measured = 149 mg as tin
Total treated = 34 mg as tin
Total remained = 115 mg as tin

DBT removal = 23 %
Mass balance = 91 %

D.6 Result for column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 1 wt.% NaCl at pH 7 and use Ottawa sand as the media.

The packed column properties:

Pore volume = 29.13 mL
Porosity = 0.364
Trapped oil = 8.64 g (18.69 %Rs)

Table D.20 PCE and DBT in effluent for the column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 1 wt.% NaCl at pH 7.

PV	**PCE**		**DBT as tin**		**Mobilized oil**
	concentration	**cumulative**	**concentration**	**cumulative**	**cumulative**
	mg/L	**mg**	**mg/L**	**mg**	**mg**
0.26	15		65.93		0
1.04	138	2	84.12	1.71	0
1.57	61	3	138.16	3.40	0
2.09	32	4	58.22	4.89	0
2.35	25	4	na.	na.	0
2.61	860	8	175.16	6.67	1,399
2.87	4,033	26	303.30	8.48	1,878
3.13	7,628	70	188.31	10.35	1,978
3.39	11,334	143	102.01	11.46	1,978
3.65	12,888	235	59.34	12.07	1,978
3.91	13,441	335	56.19	12.51	1,978
4.17	14,830	442	46.76	12.90	1,978
4.44	15,872	559	33.12	13.20	1,978
4.70	16,242	681	29.41	13.44	1,978
4.96	16,140	804	27.50	13.66	1,978
5.22	16,476	928	22.67	13.85	1,978
5.74	16,856	1,181	19.51	14.17	1,978
6.26	16,888	1,437	16.39	14.44	1,978
6.78	17,366	1,698	15.15	14.68	1,978
7.31	17,965	1,966	12.62	14.89	1,978
7.83	17,585	2,237	17.25	15.12	1,978
9.13	16,990	2,893	10.44	15.64	1,978
10.44	16,278	3,526	9.29	16.02	1,978

Table D.20 (continue)

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
11.74	15,426	4,128	7.31	16.33	1,978
13.05	13,972	4,686	7.30	16.61	1,978
14.35	12,023	5,180	26.29	17.25	1,978
15.65	8,680	5,574	24.19	18.21	1,978
16.96	5,083	5,835	14.59	18.95	1,978
18.26	3,264	5,994	11.20	19.44	1,978
19.57	1,569	6,086	5.52	19.75	1,978
20.87	492	6,125	3.97	19.93	1,978
22.18	172	6,137	8.02	20.16	1,978
23.48	95	6,142	3.55	20.38	1,978
24.79	43	6,145	2.83	20.50	1,978
26.09	26	6,146	2.78	20.61	1,978
28.70	22	6,148	3.13	20.83	1,978
31.31	16	6,150	2.49	21.05	1,978
33.92	16	6,151	2.69	21.24	1,978

Result and calculation for PCE

Initial trapped PCE = 8,057 mg
PCE dissolved during replacement = 229 mg
Trapped result = 7,828 mg

Mobilized PCE = 1,844 mg
Solubilized PCE = 6,151 mg
Extract by surfactant solution = 0 mg
Extract by HCl solution = 0 mg
Extract from sand = 0 mg

Total mass measured = 7,995 mg
Total treated = 7,995 mg
Total remained = 0 mg

PCE removal = 100 %
Mass balance = 102 %

Result and calculation for DBT

Initial trapped DBT as tin = 228 mg as tin
DBT dissolved during replacement = 32 mg as tin
Trapped result = 196 mg as tin

Mobilized DBT = 52 mg as tin
Solubilized DBT = 21 mg as tin
Extract by surfactant solution = 39 mg as tin
Extract by HCl solution = 74 mg as tin
Extract from sand = 1 mg as tin

Total mass measured = 187 mg as tin
Total treated = 73 mg as tin
Total remained = 114 mg as tin

DBT removal = 39 %
Mass balance = 95 %

D.7 Result for column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 1 wt.% NaCl at pH 9 and use Ottawa sand as the media.

The packed column properties:

Pore volume = 30.66 mL
Porosity = 0.378
Trapped oil = 5.49 g (11.28 %Rs)

Table D.21 PCE and DBT in effluent for the column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 1 wt.% NaCl at pH 9.

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
0.25	11		56.13	0.00	0
0.99	12	0	56.36	1.28	0
1.49	16	0	73.52	2.27	0
1.98	9	1	116.91	3.72	0
2.23	15	1	na.	na.	0
2.48	504	3	127.13	5.57	133
2.73	3,778	19	176.39	6.72	133
2.97	7,445	62	145.94	7.95	133
3.22	8,803	123	106.25	8.91	133
3.47	9,787	194	108.95	9.73	133
3.72	10,976	273	97.80	10.51	133
3.97	11,416	358	76.55	11.17	133
4.21	12,182	448	94.15	11.82	133
4.46	12,644	542	75.00	12.46	133
4.71	13,464	641	54.14	12.96	133
4.96	13,569	744	49.12	13.35	133
5.45	13,845	952	30.17	13.95	133
5.95	13,086	1,157	24.12	14.36	133
6.44	13,291	1,357	24.12	14.73	133
6.94	12,972	1,557	19.23	15.06	133
7.44	12,922	1,754	19.87	15.36	133
8.68	12,391	2,235	11.78	15.96	133
9.91	11,704	2,693	10.64	16.38	133

Table D.21 (continue)

PV	PCE		DBT as tin		Mobilized oil
	concentration	**cumulative**	**concentration**	**cumulative**	**cumulative**
	mg/L	**mg**	**mg/L**	**mg**	**mg**
11.15	10,489	3,114	9.87	16.77	133
12.39	8,332	3,472	9.32	17.14	133
13.63	4,516	3,716	9.45	17.49	133
14.87	1,526	3,831	10.28	17.87	133
16.11	538	3,870	10.67	18.27	133
17.35	154	3,883	11.06	18.68	133
18.59	70	3,887	11.07	19.10	133
19.83	16	3,889	10.66	19.51	133
21.07	13	3,890	6.73	19.84	133
22.31	10	3,890	7.07	20.11	133
23.55	9	3,890	6.70	20.37	133
24.79	0	3,891	6.95	20.63	133
27.27	0	3,891	6.95	21.16	133
29.74	0	3,891	7.05	21.69	133
32.22	0	3,891	6.79	22.21	133

Result and calculation for PCE

Initial trapped PCE = 5,121 mg
PCE dissolved during replacement = 186 mg
Trapped result = 4,935 mg

Mobilized PCE = 124 mg
Solubilized PCE = 3,891 mg
Extract by surfactant solution = 0 mg
Extract by HCl solution = 0 mg
Extract from sand = 0 mg

Total mass measured = 4,015 mg
    Total treated = 4,015 mg
    Total remained = 0 mg

PCE removal = 100 %
Mass balance = 81 %

Result and calculation for DBT

Initial trapped DBT as tin = 145 mg as tin
DBT dissolved during replacement = 21 mg as tin
Trapped result = 124 mg as tin

Mobilized DBT = 4 mg as tin
Solubilized DBT = 22 mg as tin
Extract by surfactant solution = 11 mg as tin
Extract by HCl solution = 64 mg as tin
Extract from sand = 0 mg as tin

Total mass measured = 101 mg as tin
    Total treated = 26 mg as tin
    Total remained = 75 mg as tin

DBT removal = 26 %
Mass balance = 81 %

D.8 Result for column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 1 wt.% NaCl at pH 4 and use sieved aquifer soil as the media.

The packed column properties:

Pore volume = 37.7 mL
Porosity = 0.465
Trapped oil = 5.87 g (9.81 %Rs)

Table D.22 PCE and DBT in effluent for the column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 1 wt.% NaCl at pH 4.

PV	**PCE**		**DBT as tin**		**Mobilized oil**
	concentration	**cumulative**	**concentration**	**cumulative**	**cumulative**
	mg/L	**mg**	**mg/L**	**mg**	**mg**
0.20	34		104.34		0
0.81	78	1	123.79	2.60	0
1.21	0	2	116.72	4.43	0
1.61	0	2	82.31	5.94	0
1.81	64	2	na.	na.	0
2.02	66	3	62.45	7.04	7
2.22	5,943	25	34.11	7.41	14
2.42	11,361	91	75.32	7.82	22
2.62	10,318	174	111.14	8.53	31
2.82	9,143	248	45.10	9.13	40
3.02	12,196	329	49.98	9.49	49
3.23	12,118	421	47.51	9.86	59
3.43	12,452	514	46.02	10.21	69
3.63	12,071	608	44.80	10.56	80
3.83	12,916	703	45.41	10.90	91
4.03	13,171	802	41.27	11.23	102
4.44	13,738	1,006	38.86	11.84	114
4.84	13,292	1,212	45.04	12.48	126
5.24	13,691	1,417	37.50	13.10	140
5.65	15,416	1,638	45.64	13.74	153
6.05	14,388	1,864	45.77	14.43	168
7.06	15,536	2,433	32.45	15.92	184
8.06	15,859	3,029	27.63	17.06	201

Table D.22 (continue)

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
9.07	14,003	3,597	33.56	18.22	219
10.08	10,272	4,058	53.72	19.88	239
11.09	3,057	4,311	27.07	21.41	260
12.10	585	4,380	14.27	22.20	282
13.11	75	4,393	5.54	22.58	305
14.11	42	4,395	4.78	22.77	328
15.12	37	4,397	4.41	22.95	351
16.13	24	4,398	5.12	23.13	374
17.14	27	4,399	3.63	23.29	397
18.15	24	4,400	3.81	23.44	421
19.15	26	4,401	3.53	23.58	444
20.16	25	4,402	2.89	23.70	468
22.18	7	4,403	3.59	23.94	492
24.19	0	4,403	3.19	24.20	516
26.21	0	4,403	3.69	24.46	540

Result and calculation for PCE

Initial trapped PCE = 5,472 mg
PCE dissolved during replacement = 95 mg
Trapped result = 5,377 mg

Mobilized PCE = 573 mg
Solubilized PCE = 4,403 mg
Extract by surfactant solution = 0 mg
Extract by HCl solution = 0 mg
Extract from sand = 0 mg

Total mass measured = 4,977 mg
Total treated = 4,977 mg
Total remained = 0 mg

PCE removal = 100 %
Mass balance = 93 %

Result and calculation for DBT

Initial trapped DBT as tin = 155 mg as tin
DBT dissolved during replacement = 17 mg as tin
Trapped result = 138 mg as tin

Mobilized DBT = 16 mg as tin
Solubilized DBT = 24 mg as tin
Extract by surfactant solution = 30 mg as tin
Extract by HCl solution = 45 mg as tin
Extract from sand = 0 mg as tin

Total mass measured = 115 mg as tin
Total treated = 40 mg as tin
Total remained = 75 mg as tin

DBT removal = 35 %
Mass balance = 83 %

D.9 Result for column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 1 wt.% NaCl at pH 7 and use sieved aquifer soil as the media.

The packed column properties:

Pore volume = 39.49 mL

Porosity = 0.487

Trapped oil = 6.21 g (9.91 %Rs)

Table D.23 PCE and DBT in effluent for the column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 1 wt.% NaCl at pH 7.

PV	**PCE**		**DBT as tin**		**Mobilized oil**
	concentration	**cumulative**	**concentration**	**cumulative**	**cumulative**
	mg/L	**mg**	**mg/L**	**mg**	**mg**
0.19	0		125.04		0
0.77	228	3	96.49	2.53	0
1.15	98	5	87.49	3.92	0
1.54	212	7	76.64	5.17	0
1.73	221	9	na.	na.	0
1.92	379	11	30.48	5.99	1,145
2.12	12,923	62	175.26	6.77	1,145
2.31	14,998	168	160.61	8.04	1,145
2.50	13,062	275	121.07	9.11	1,145
2.69	12,772	373	102.43	9.96	1,145
2.89	12,058	467	84.98	10.67	1,145
3.08	11,422	556	78.70	11.30	1,145
3.27	13,018	649	98.38	11.97	1,145
3.46	13,321	749	96.83	12.71	1,145
3.66	13,916	853	98.86	13.46	1,145
3.85	14,130	959	84.19	14.15	1,145
4.23	14,446	1,177	92.95	15.50	1,145
4.62	14,776	1,399	78.60	16.80	1,145
5.00	17,131	1,641	100.47	18.16	1,145
5.39	15,808	1,891	70.00	19.46	1,145
5.77	15,860	2,132	57.61	20.43	1,145
6.74	15,650	2,731	35.92	22.20	1,145
7.70	13,213	3,279	22.80	23.32	1,145

Table D.23 (continue)

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
8.66	7,680	3,676	12.95	24.00	1,145
9.62	3,104	3,881	5.25	24.34	1,145
10.59	1,109	3,961	2.97	24.50	1,145
11.55	404	3,990	2.99	24.61	1,145
12.51	156	4,001	2.50	24.72	1,145
13.47	84	4,005	3.25	24.83	1,145
14.44	26	4,007	3.00	24.95	1,145
15.40	27	4,008	3.73	25.07	1,145
16.36	21	4,009	5.62	25.25	1,145
17.32	20	4,010	3.89	25.43	1,145
18.28	20	4,011	3.90	25.58	1,145
19.25	20	4,011	4.08	25.73	1,145
21.17	25	4,013	3.91	26.04	1,145
23.10	24	4,015	4.53	26.36	1,145
25.02	18	4,017	5.16	26.72	1,145

Result and calculation for PCE

Initial trapped PCE = 5,792 mg
PCE dissolved during replacement = 125 mg
Trapped result = 5,667 mg

Mobilized PCE = 1,068 mg
Solubilized PCE = 4,017 mg
Extract by surfactant solution = 0 mg
Extract by HCl solution = 0 mg
Extract from sand = 0 mg

Total mass measured = 5,084 mg
Total treated = 5,084 mg
Total remained = 0 mg

PCE removal = 100 %
Mass balance = 90 %

Result and calculation for DBT

Initial trapped DBT as tin = 164 mg as tin
DBT dissolved during replacement = 11 mg as tin
Trapped result = 153 mg as tin

Mobilized DBT = 30 mg as tin
Solubilized DBT = 27 mg as tin
Extract by surfactant solution = 26 mg as tin
Extract by HCl solution = 36 mg as tin
Extract from sand = 1 mg as tin

Total mass measured = 120 mg as tin
Total treated = 57 mg as tin
Total remained = 63 mg as tin

DBT removal = 48 %
Mass balance = 78 %

D.10 Result for column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 1 wt.% NaCl at pH 9 and use sieved aquifer soil as the media.

The packed column properties:

Pore volume = 38.77 mL
Porosity = 0.478
Trapped oil = 6.01 g (9.77 %Rs)

Table D.24 PCE and DBT in effluent for the column experiment with DBT-PCE mixture flushing with surfactant mixture of 3.6 wt.% SDHS 0.4 wt.% C16DPDS 1 wt.% NaCl at pH 9.

PV	**PCE**		**DBT as tin**		**Mobilized oil**
	concentration	**cumulative**	**concentration**	**cumulative**	**cumulative**
	mg/L	**mg**	**mg/L**	**mg**	**mg**
0.20	141		161.44	0.00	0
0.78	80	3	144.18	3.48	0
1.18	97	4	131.43	5.58	0
1.57	14	5	92.76	7.28	0
1.76	12	5	na.	na.	0
1.96	23	5	50.42	8.37	0
2.16	6,129	28	65.45	8.81	435
2.35	13,124	101	63.87	9.30	435
2.55	13,809	204	39.36	9.69	435
2.74	13,509	308	35.08	9.98	435
2.94	12,320	406	22.37	10.20	435
3.14	11,654	497	23.16	10.37	435
3.33	11,905	586	16.97	10.52	435
3.53	11,679	676	16.72	10.65	435
3.72	12,127	766	15.17	10.77	435
3.92	12,665	861	13.74	10.88	435
4.31	13,233	1,058	22.24	11.15	435
4.71	14,437	1,268	14.17	11.43	435
5.10	13,537	1,480	14.14	11.65	435
5.49	14,811	1,696	16.31	11.88	435
5.88	15,189	1,924	16.51	12.13	435
6.86	14,685	2,491	9.36	12.62	435
7.84	14,793	3,052	7.68	12.94	435

Table D.24 (continue)

PV	PCE		DBT as tin		Mobilized oil
	concentration	cumulative	concentration	cumulative	cumulative
	mg/L	mg	mg/L	mg	mg
8.82	13,279	3,585	8.46	13.25	435
9.80	9,863	4,025	8.20	13.57	435
10.78	2,931	4,268	6.18	13.84	435
11.76	557	4,334	5.79	14.07	435
12.74	216	4,349	5.18	14.27	435
13.72	47	4,354	5.34	14.47	435
14.70	44	4,355	5.09	14.67	435
15.68	28	4,357	5.59	14.88	435
16.66	31	4,358	4.95	15.08	435
17.64	29	4,359	4.47	15.25	435
18.62	29	4,360	5.45	15.44	435
19.60	34	4,361	4.83	15.64	435
21.56	40	4,364	5.16	16.02	435
23.53	32	4,367	6.11	16.45	435
25.49	32	4,369	6.09	16.91	435

Result and calculation for PCE

Initial trapped PCE = 5,607 mg
PCE dissolved during replacement = 232 mg
Trapped result = 5,375 mg

Mobilized PCE = 406 mg
Solubilized PCE = 4,369 mg
Extract by surfactant solution = 0 mg
Extract by HCl solution = 0 mg
Extract from sand = 0 mg

Total mass measured = 4,775 mg
Total treated = 4,775 mg
Total remained = 0 mg

PCE removal = 100 %
Mass balance = 89 %

Result and calculation for DBT

Initial trapped DBT as tin = 159 mg as tin
DBT dissolved during replacement = 22 mg as tin
Trapped result = 137 mg as tin

Mobilized DBT = 11 mg as tin
Solubilized DBT = 17 mg as tin
Extract by surfactant solution = 21 mg as tin
Extract by HCl solution = 48 mg as tin
Extract from sand = 1 mg as tin

Total mass measured = 98 mg as tin
Total treated = 28 mg as tin
Total remained = 70 mg as tin

DBT removal = 29 %
Mass balance = 72 %

BIOGRAPHY

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Publications:

1. Seelawut Damrongsiri, Chantra Tongcumpou, Punjaporn Weschayanwiwat, and David A. Sabatini. 2010. Solubilization of dibutyltin dichloride with surfactant solutions in single and mixed oil systems. Journal of Hazardous Materials 181: 1109-1114.
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He has carried out this research as a part of studied for a doctoral degree of Doctor of Philosophy Program in Environmental Management at graduate school, Chulalongkorn University. Under the management of National Center of Excellence for Environmental and Hazardous Waste Management.