REMOVAL OF THE MIXTURE OF TRIBUTYLTIN AND TETRACHLOROETHYLENE USING MICROEMULSION TECHNIQUE COUPLE WITH NEUTRAL BUOYANCY CONCEPT

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การกำจัดสารปนเปื้อนผสมระหว่างสารไตรบิวทิลทินกับเตตระคลอโรเอทิลีนโดยวิธีไมโครอิมัลชันร่วมกับการปรับแรงลอยตัวให้เป็นกลาง

นางสาวจารุวรรณ ตาฬวัฒน์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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Thesis Title	REMOVAL OF THE MIXTURE OF TRIBUTYLTIN AND TETRACHLOROETHYLENE USING MICROEMULSION TECHNIQUE COUPLE WITH NEUTRAL BUOYANCY CONCEPT
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จารุวรรณ ตาฬวัฒน์ : การกำจัดสารปนเปื้อนผสมระหว่างสารไตรบิวทิลทินกับเตตระคลอโรเอทิลีนโดยวิธีไมโครอิมัลชันร่วมกับการปรับแรงลอยตัวให้เป็นกลาง (REMOVAL OF THE MIXTURE OF TRIBUTYLTIN AND TETRACHLOROETHYLENE USING MICROEMULSION TECHNIQUE COUPLE WITH NEUTRAL BUOYANCY CONCEPT) อ.ที่ปรึกษาวิทยานิพนธ์หลัก ผศ.ดร.จันทรา ทองคำเภา, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม Prof. David A. Sabatini, 98 หน้า.

งานวิจัยนี้ได้ศึกษาถึงความเป็นไปได้ในการใช้วิธีไมโครอิมัลชันร่วมกับการปรับแรงลอยตัวให้เป็นกลาง เพื่อกำจัดสารปนเปื้อนผสมระหว่างสารไตรบิวทิลทินกับเตตระคลอโรเอทิลีนออกจากระบบน้ำใต้ดิน สารไตรบิวทิลทินเป็นสารโลหะอินทรีย์ที่มีอันตรายร้ายแรงใช้ผสมในสีทาเรือ เพื่อป้องกันการเกาะตัวของเพรียงส่งผลให้ลดการใช้พลังงานน้ำมันในการขับเคลื่อนเรือ สารไตรบิวทิลทินมักอยู่ในรูปของสารผสม ดังนั้นงานวิจัยนี้จึงศึกษาสารไตรบิวทิลทินในรูปของสารผสมกับเตตระคลอโรเอทิลีนซึ่งเป็นตัวทำละลายอินทรีย์ที่ใช้แพร่หลาย สารทั้งสองตัวนี้มีความหนาแน่นมากกว่าน้ำ ดังนั้นการกำจัดการปนเปื้อนสารทั้งสองตัวนี้ออกจากระบบใต้ดินต้องคำนึงถึงการป้องกันการไหลลงสู่ชั้นน้ำใต้ดินที่ลึกลงไป แอลกอฮอล์ถูกเลือกให้เป็นตัวช่วยในการปรับแรงลอยตัวของสารปนเปื้อนผสมนี้ให้ใกล้เคียงกับสภาวะล้อมรอบ ดังนั้นการศึกษาส่วนใหญ่จะทำในสภาวะที่มีแอลกอฮอล์ผสมอยู่ด้วย ผลการศึกษาเป็นดังต่อไปนี้คือ ค่าอีเอซีเอ็น (EACN: Equivalent Alkane Carbon Number) ของไตรบิวทิลทิน มีค่าเฉลี่ยอยู่ที่ 11.17 ในขณะที่ ค่าอีเอซีเอ็นของสารผสม 60 % โดยน้ำหนักของไตรบิวทิลทิน กับ 40% โดยน้ำหนักของเตตระคลอโรเอทะลีนซึ่งเป็นสารผสมที่ใช้เป็นหลักในการทดลองครั้งนี้ มีค่าเท่ากับ 6.5 โดยค่านี้ใกล้เคียงกับค่าอีเอซีเอ็นของ เตตระเอทิลเลดซึ่ง เป็นสารปนเปื้อนโลหะอินทรีย์ที่สำคัญอีกตัวหนึ่งเช่นกัน ระบบที่เลือกใช้ในการศึกษา อย่างละเอียดคือ ระบบของ 3.6 wt % SDHS + 0.4 wt% C16 DPDS ที่ความเข้มข้น 3 wt% NaCl โดยเปรียบเทียบกันระหว่างแอลกอฮอล์สองชนิดคือ เอ็นบิวทิลแอลกอฮอล์(n-BuOH) และ เทอเชียรีบิวทิลแอลกอฮอล์ (tert-BuOH หรือ TBA) การทดลองได้ศึกษาทั้งแบบกะและแบบต่อเนื่อง โดยการศึกษาได้เน้น ถึงความสามารถในกำจัดสารไตรบิวทิลทินและเตตระคลอโรเอทิลีน และความสามารถในการลดความหนาแน่นของเฟสน้ำมัน ระบบที่ศึกษามีการใช้สัดส่วนของแอลกอฮอล์และสารลดแรงตึงผิวที่แตกต่างกัน ในการศึกษาแบบต่อเนื่องมีทั้งระบบที่ใช้ขั้นตอนเดียวเพื่อเปรียบเทียบระหว่างการใช้สารลดแรงตึงผิวอย่างเดียวกับที่มีแอลกอฮอล์ผสม และระบบที่ใช้สองขั้นตอนโดยในขั้นตอนแรกจะเป็นการใช้แอลกอฮอล์อย่างเดียวเพื่อลดความหนาแน่นของสารปนเปื้อนให้ได้ระดับหนึ่งก่อน แล้ว จึงตามด้วยขั้นตอนที่สองที่มีสารลดแรงตึงผิวเป็นส่วนผสม ผลปรากฏว่าระบบที่สามารถกำจัดสารปนเปื้อนได้อย่างมีประสิทธิผลในการปรับแรงลอยตัวให้เป็นกลางหรือน้อยกว่าน้ำ คือระบบที่ต้องทำเป็นสองขั้นตอนโดยขั้นตอนแรกจะชะคอลัมน์ด้วยสารละลายเกลือที่อิ่มตัวด้วย n-BuOH จากนั้น ชะด้วยสารละลายสารลดแรงตึงผิว 3.6 wt % SDHS + 0.4 wt% C16 DPDS ที่ความเข้มข้น 3 wt% NaCl ที่ถูกทำให้อิ่มตัวด้วย n-BuOH เช่นกัน โดยที่รูปแบบหลักในการกำจัดอยู่ในรูปของ เหลวที่ไม่ใช่น้ำ(NAPL) โดยที่ 82.09% สำหรับสารไตรบิวทิลทิน และ 85.23% สำหรับสารเตตระคลอโรเอทิลีนของที่ถูกกำจัดออกมาได้มีความหนาแน่นน้อยกว่าน้ำล้อมรอบ ในขณะที่ 13.24% TBT และ 5.74% PCE ของที่ถูกกำจัดออกมาได้ อยู่ในรูปที่มีความหนาแน่นมากกว่าน้ำ แต่ก็ไม่มากนัก คือมีความหนาแน่นอยู่ ที่1.063 $mg.L^{-1}$ โดยที่ใช้สารชะล้างทั้งหมดประมาณ 40 เท่าของปริมาตรช่องว่างระหว่างเม็ดทรายที่บรรจุในคอลัมน์

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต ……………………………………………………..
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JARUWAN TALAWAT: REMOVAL OF THE MIXTURE OF TRIBUTYLTIN AND TETRACHLOROETHYLENE USING MICROEMULSION TECHNIQUE COUPLE WITH NEUTRAL BUOYANCY CONCEPT. ADVISOR: ASST. PROF. CHANTRA TONGCUMPOU, Ph.D., CO-ADVISOR: PROF. DAVID A. SABATINI, Ph.D., 98 pp.

This research studied the feasibility of using microemulsion technique couple with neutral buoyancy concept to remove the mixture of tributyltin (TBT) and tetrachloroethylene (PCE) from subsurface system. TBT is a hazardous organometal and was used as a biocidal paint to prevent barnacle adhesion to marine vessel. TBT was usually used as a mixture so this study used it as a mixture with PCE which was a common organic solvent so it was likely to be found coexisting with other organic contaminant. Both TBT and PCE are dense non aqueous phase liquid (DNAPL), therefore prevention of downward migration had to be considered when carrying out the removal process. Addition of alcohol was selected as a means to adjust the density of the contaminant to be closed to that of the surrounding water. Hence, most of the experiments in this study were carried out in the presence of alcohol. Major finding in this research were as follows. Hydrophobicity of organometallic under study, tributyltin (TBT), was characterized as an equivalent alkane carbon number (EACN) and was determined to be 11.17 by using Salager's equation and linear mixing rule. The TBT-PCE mixture under focused was the mixture of 60 wt% TBT with 40 wt% PCE and had its EACN calculated to be 6.5 which was closed to the EACN of tetraethylead, another important organometal. The surfactant system selected for detail investigation was the system of 3.6 wt% SDHS + 0.4 wt% C16 DPDS at 3wt% NaCl (4 wt% total surfactant) with two alcohol types, n-butanol (BuOH) and tert-butanol (TBA). The study was conducted in both batch and continuous flow study by focusing on the removal of TBT and PCE and the density modification of mobilized NAPL. Performance of different alcohol and surfactant concentration were studied. In the continuous flow study, the flushing schemes were explored for both single step flushing which compared between the surfactant system with and without alcohol addition and two-step flushing which used only alcohol addition in the first step to adjust the density and added surfactant in the second step to reduce interfacial tension. Results from six column studies showed that the most efficient system for removal of TBT and PCE while having the density of mobilized NAPL lower than surrounding aqueous phase was the system with two- step flushing with saturated BuOH. The system was preflushed with saturated BuOH solution with 3 wt% NaCl and followed by 3.6 wt% SDHS + 0.4 wt% C16 DPDS at 3wt% NaCl saturated with BuOH. The main removal mechanism was mobilization at which 82.09% of TBT and 85.23% of PCE from total removal was removed as light nonaqueous phase liquid (LNAPL). There was some small DNAPL mobilization occurred but the density was already modified to1.063 mg.L^{-1}, and it was accounted for 13.24% for TBT and 5.74% for PCE from their total removal. The total applied flushing solution was 40 times of the volume between pore space of the sand packed in the column.

Field of Study : Environmental Management Student's Signature ....
Academic Year : 2012 Advisor's Signature ....
Advisor's Signature ....

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CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

Figure **Page**

Figure **Page**

Page

Figure

ABBREVIATIONS

AMA	a tradename of sodium dihexyl sulfosuccinate
AOT	a tradename of sodium dioctyl sulfosuccinate
A/S	alcohol to surfactant mass ratio
BuOH	n-butyl alcohol
C16DPDS	C16 diphenyloxide disulfonate
DNAPL	dense nonaqueous phase liquid
Dowfax	a tradename of C16 diphenyloxide disulfonate
EACN	equivalent alkane carbon number
HLB	hydrophillic lipophillic balance
Kow	octanol-water partitioning coefficient
LNAPL	light nonaqueous phase liquid
P80	polysorbate 80; tween 80; polyoxyethylene(20) sorbitan monooleate
PCE	perchloroethylene; tetrachloroethylene
S*	optimum salinity
SDHS	sodium dihexylsulfosuccinate
SDOS	sodium dioctylsulfosuccinate
SEAR	surfactant enhanced aquifer remediation
SPo	solubilization parameter for oil
SPw	solubilization parameter for water
TBA	tert-butyl alcohol
TBT	tributyltinchloride; tributyltin
TEL	tetraethyllead
TRI-PLOT	a spreadsheet program for plotting ternary phase diagram
1φ	one miscible phase

CHAPTER I

INTRODUCTION

1.1 BACKGROUND FOR THE STUDY

Dense nonaqueous phase liquids (DNAPLs) are of major concern in groundwater contamination. Beside their toxicity and low biodegradability, they also have high density and low water solubility. Being denser than aqueous phase causes DNAPL to move downward into deeper layers of subsurface material. Their immiscibility with water causes them to be easily trapped within pore spaces by interfacial tension and capillary forces (Childs et al., 2004). Conventional site remediation technique is a pump and treat system with water but it is ineffective for treatment of contaminant at the residual level due to its inability to counteract the capillary force holding contaminants within the pore space. When contaminated water is pumped to the surface, this trapped residual liquid will subsequently contaminate the adjacent clean water that come to replace. Therefore the volume of contaminated water kept increasing as the treatment continued (Harwell et al., 1999).

Surfactant enhanced aquifer remediation (SEAR) had been studied as a mean to remediate residual DNAPL contaminants from the subsurface (Hofstee et al., 2003; Kostarelos et al., 1998; Lunn and Kueper, 1999; Ramburg et al., 2004), but very limited research has been conducted on organometallic compounds.

Most organometallic compounds are harmful to the environment. For example, tributyltin (TBT) poses a threat to marine life causing imposex in gastropod and interfering spawning in fish (Shimasaki et al., 2003) and tetraethyllead (TEL) can cause casualty in human (Stasik et al., 1969). Many organometallic compounds are DNAPLs. For example, the density of TEL and TBT are 1.65 and 1.20 $g.mL^{-1}$, respectively, with the logarithms of octanal/water coefficient (Kow) equal to 4.15 and 3.42, respectively (Arnold et al., 1997; Wang et al., 1996). TEL was intensively used as a major antiknock agent in gasoline in the past and caused widespread contamination especially in many manufacturing sites and gasoline stations (Gallert and Winter, 2002). In the present days, it is still allowed to be added to aviation and racing gasoline. TBT was used as a biocide in paint formulation and has been found in contaminated sites, landfill leachate, including coastal and fresh water sediment (Mersiowsky et al., 2001; Mora et al., 2003). Use of biocidal paint containing TBT had been prohibited for a boat smaller than 25 meters in several countries. However, there are still several countries that permitted its use, and the ships that were painted there can be transported oversea and spread the contamination. (Craig et al, 2003).

Concerns of vertical migration of DNAPLs have led to the study of density modifying additives as a means to convert it to achieve neutral buoyancy (Hofstee et al., 2003; Kostarelos et al., 1998; Lunn and Kueper, 1999; Ramburg et al., 2004). Partitioning alcohols are the main density modifiers proposed for density adjustment. They can act as swelling agents that increase the volume of the organic phase and thus reduce the density of the oil contaminants. These swelling behaviors can be DNAPL specific and the system conditions must be considered (Kostarelos et al., 1998; Lunn and Kueper, 1999; Taylor et al., 2004). While other density modifiers have been proposed, such as polyaphron and foaming agent (Vidrine et al., 2000; Zhong 2011), in this study, we focus on alcohols as density modifiers due to their widespread availability and convenient applicability.

Organometallic substances are usually applied industrially as a mixture. For instance, TBT is usually added to the biocidal paint at around 19.5 wt% - 22.5 wt% (Mogul et al., 1996). TEL was also mixed with dibromoethane and dichloroethane in the molar ratio of 1:0.5:1 (Falta et al., 2005). Therefore, in this study we evaluated the mixture of TBT and tetrachloroethylene (PCE). PCE is a common organic solvent so it is likely to be found coexisitng with other organic contaminants. It also has DNAPL characteristics and is problematic for downward vertical migration. TBT was chosen because it is an important environmental contaminant that has seen only limited research on its remediation.

1.2 OBJECTIVES

The main objective is to develop the optimal flushing system based on neutral buoyancy concept couple with microemulsion system in order to remove the mixture of TBT and PCE. This main objective can be divided into five sub-objectives as follow:

1. To characterize the hydrophobicity of TBT and the mixture of TBT with PCE.
2. To study phase behavior of the microemulsion formation from variation of oil samples, surfactant types, alcohol types, and salt concentration.
3. To develop flushing solutions that can form microemulsion and promote neutral buoyancy with the mixture.
4. To find solubilization capacity of the mixture by the selected flushing systems and their ability to modify oil density to prevent vertical migration.
5. To conduct column study to investigate the removal mechanism, removal efficiency of different flushing systems.

1.3 HYPOTHESES

The hypotheses for this study are as follows:

1. Surfactant system can form microemulsion with the mixture of tributyltin and tetrachloroethylene and enhance its removal.

2. Neutral buoyancy approach can be coupled with microemulsion technique to prevent downward migration.

1.4 SCOPE OF THE STUDY

This research aims to find the optimum flushing solution and flushing scheme to clean up the residual saturation of the mixture of tributyltin and tetrachloroethylene based on microemulsion technique coupled with neutral buoyancy concept. Firstly, hydrophobicity characteristics of the oil samples were investigated by finding equivalent alkane carbon number (EACN). Secondly, several surfactant systems were screened and selected for further study by using phase behavior study. Each surfactant systems included surfactant(s), alcohol, salt, and water in various proportion and type. The next step was the investigation of the candidate flushing solution in their abilities to modify density of the microemulsion and to solubilize oil samples. Final investigations were conducted in column with flow through conditions to simulate the environments where this flushing solution is intended to be applied. The materials packed in the column was synthetic material, Ottawa sand.

Several surfactants were investigated as candidates for the surfactant system to be used for further study. The main focus was on anionic surfactants such as sodium dihexyl sulfosuccinate (SDHS), sodium dioctyl sulfosuccinate (SDOS), and C16 diphenyloxide disulfonate (C16 DPDS). These surfactants were chosen because they were reported to form microemulsion with dibutyltin chloride (DBTDC) which is also an organometallic (Thongkorn, 2007; Damrongsiri et al., 2010). In addition, twin-head anionic surfactant, C16 DPDS, had been proposed as a suitable surfactant for site remediation due to its high solubilization potential, high precipitation resistance, and low adsorption to subsurface matrix (Deshpande et al., 2000). Polysorbate (P80) was also investigated due to their nonpolar nature which might enhance solubilization of nonpolar organometallic in the surfactant solution.

1.5 BENEFITS OF THE STUDY

These results can be used to gain some insight for finding an optimum flushing solution and flushing scheme for remediation of site contaminated with the DNAPLs mixture of organometallic compounds and chlorinated solvents at residual saturation for future environmental restoration.

1.6 ORGANIZATION OF THE CONTENT

The first half of this study focused on understanding phase behavior of DNAPL mixture of TBT and PCE in the presence of surfactants and alcohols, the effect of alcohol to surfactant ratio to its density modification and solubilization capacity. These batch study results are discussed in Chapter IV. The later half focused on continuous flow study which perform in both single step flushing and two step flushing. The effect of alcohol addition into surfactant solution on density modification, removal mechanism and efficiency were investigated. These flushing solutions and flushing schemes are discussed in Chapter V. Theoretical background and literature review is provided in Chapter II while methodology is presented in Chapter III. Conclusion and recommendations are in Chapter VI.

CHAPTER II

THEORETICAL BACKGROUNDS AND LITERATURE REVIEWS

2.1 ORGANOMETALLICs AND CHLORINATED HYDROCARBON

2.1.1 Organometallics

Many organometallics are dense nonaqueous phase liquid (DNAPL). For example, the density of tetraethyllead and tributyltin are 1.65 and 1.20 g.mL^{-1}, respectively. Organometallics are substances that are usually highly toxic to both vertebrate and invertebrate. Their usages posed danger to both workers and the environment. For example, ingestion or inhalation of tetraethyllead can cause human casualty (Stasik et al., 1969). The threat of organotin on marine life included imposex causing in gastropod and sprawning inhibition in fish (Jamari, 1999). TBT was first used to kill some snail species being hosts for Schistoma that transmits disease to human. It was also used to prevent fouling of marine vessel hulls by colonization of marine animal such as barnacle. This colonization is not only damage the marine surface but also caused the vessel to be heavy and have high fuel consumption (Champ, 2000).

Organometallics usually have high bioconcentration factor (BCF), with BCF of 300 and 3,000 for tetraethyllead and tributyltin, respectively. This is due to the fact that they have lipophillic portion attached to the heavy metal enabling them to pass through membrane easily and get accumulated up through the food chain. This lipophillic portion also enable them to penetrate blood brain barrier which is normally protect inorganic metal from affecting the central nervous system (Boonsaneau, 1997).

2.1.2 Chlorinated hydrocarbons

Tetrachloroethylene, with its common name as perchloroethylene (PCE), is a commonly used organic solvent due to its low flammability and good solvent characteristic. As a result, it was found as a common contaminant in the USA National Priorities List sites (Kibbey et al., 2002). Many studies had been carried out to decontaminate it but there still is no common practice on how to recover it aboveground due to its vertical migration problem (Ramsburg et al., 2004; Taylor et al., 2004). Besides, it is never been studied as a mixture with tributyltin which might cause it to behave differently. This study investigated its removal as an oil mixture in which the research findings might be able to be used as a case study for cleaning up a chemical mixture of organometallic and chlorinated solvent in the future.

2.2 MICROEMULSION AND GROUNDWATER REMEDIATION

Miscibility of groundwater and contaminant is an important aspect in cleaning up groundwater contamination. Its benefit is that it will be easy to be transported from the contaminated spot to above ground facility where the contaminant can be separated and further treated. Surfactant-based microemulsion formation can promote this miscibility since it can reduce interfacial tension between the two phases. The degree of miscibility depends on droplet size. If the droplet sizes are very small (10 - 100 nm), the two phases become transparent and it is called a microemulsion. If the two phases are miscible but show some turbidity due to the droplet sizes around 1-10 μm, it is called an emulsion. Droplet size in the microemulsion can be very small while maintaining thermodynamically stability because they have very low interfacial tension of 10^{-2} – 10^{-3} mN/m. In case of emulsion which is not thermodynamically stable but kinetically stable, the interfacial will be in the range of 1-10 mN/m.

2.2.1 Surfactant and micelle formation

Surfactant structure composes of the hydrophilic head and lipophillic tail. The hydrophilic head can be anionic, cationic, nonionic, switterionic, or amphoteric. The length of the lipophillic tails can be used as an indication of the hydrophobicity of the surfactant molecules. Accumulation of surfactant molecule in the solution up until a certain concentration can cause conformation of surfactant monomers to form aggregate called micelle (Figure 2.1). This concentration is called CMC (critical micelle concentration) (Rosen, 2004). This phenomenon was driven by the increasing of entropy. The water molecules surrounding the lipophillic part of the surfactant molecule was liberated due to formation of micelle yielding overall entropy of the system to be increased (Bourrel and Schechter, 1988).

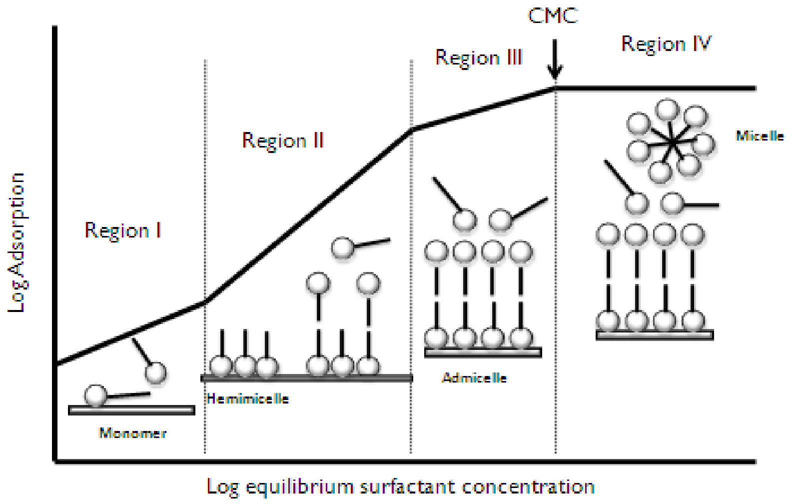


Figure 2.1 Diagram showing interaction among surfactant monomers over a range of surfactant concentration (Charoensaeng et al., 2008)

2.2.2 Microemulsion type and Windsor R-ratio

Microemulsion can be classified into three types depending on which phase are the continuous phase. Oil in water (o/w or type I) microemulsion has water as a continuous phase; while water in oil (w/o or type II) microemulsion has oil as a continuous phase (Rosen, 2004). Bicontinuous microemulsion (middle phase or type III) usually contains equal amount of oil and water so both of them are considered as continuous phases. These microemulsion types can undergo phase transition if the system condition changed. Winsor had studied this transition systematically and showed that phase transition can be changed from type I to type III to type II by increasing salinity or decreasing HLB (Figure 2.2).

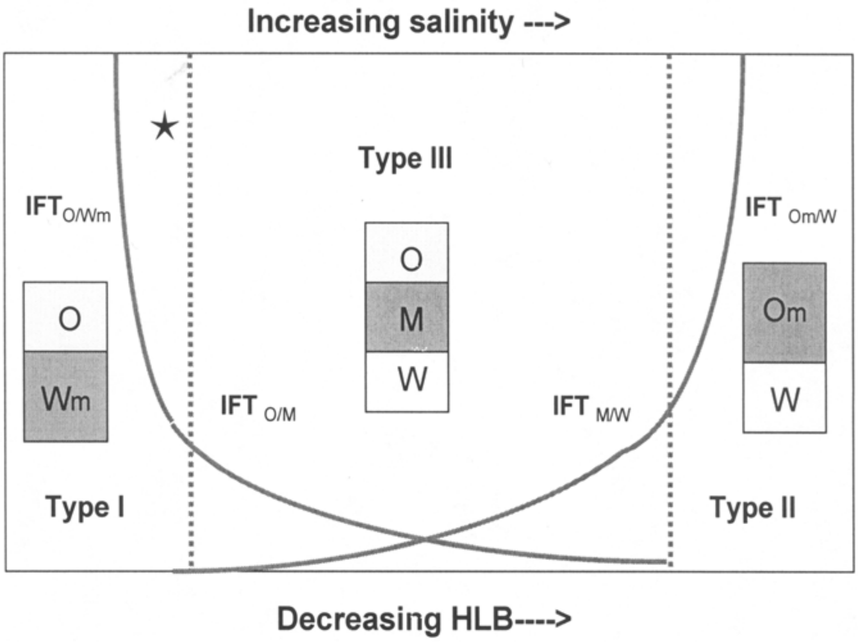


Figure 2.2 Windsor phase diagram showing phase transition by increasing salinity and decreasing HLB (Tongcumpou et al., 2003)

Windsor R ratio, which is a ratio of lipophillic interaction of surfactant with oil (Aco) over the hydrophilic interaction of surfactant with water (Acw), has been used extensively to represent microemulsion type formation. This ratio includes interaction among oil molecule (Aoo) and among lipophillic part of surfactant molecule (A_{LL}) in the numerator and interaction among water molecule (Aww) and among hydrophillic part of surfactant molecule (A_{HH}) in the denominator (Bourrel and Schechter, 1988). The R ratios of <1, >1, and 1 imply that the microemulsion type are type I, II, and III, respectively.

$$R = \frac{A_{CO} - A_{OO} - A_{LL}}{A_{CW} - A_{WW} - A_{HH}} \qquad (2.1)$$

2.2.3 Surfactant enhanced aquifer remediation

Application of a conventional pump and treat system to remediate several superfund sites in the US had been shown to be ineffective in cleaning up the sites. This is due to the fact that contaminant liquid is trapped within the pores of the subsurface medium by capillary force. After the contaminated water is pumped to the surface, this trapped residual liquid will subsequently contaminate the adjacent clean water that come to replace. Therefore, the volume of contaminated water will keep increasing as the treatment continue (Harwell et al., 1999).

To improve pump and treat technique, surfactant enhanced aquifer remediation has been of much interest. Surfactant is a chemical which has two natures in one molecule. It has hydrophilic head group and hydrophobic tail. It can reduce surface tension between pollutant and the soil matrix. As a result, pollutants can either solubilize into the aqueous phase or detach from the pore space and mobilize with the flowing water. Thus, it can be used to remove the pollutants from the aquifer to be transported above ground. For example, only 6.6 pore volume was needed to flush out 93% trimethylbenzene and 75.2% dichlorobenzene from a test cell in a contaminated site in the USA (Ouyang et al., 1996; Harwell et al., 1999).

Microemulsions have high capability to solubilize and mobilize contaminants from the subsurface to above ground facility, where the contaminant can be separated for further treatment. However, specific surfactant systems are required for certain pollutants due to differences in both pollutant and surfactant characteristics. For example, polar substances are well solubilized in the polar outer region of the micelle, while nonpolar chemical tends to be localized in the inner core region. Some chemicals stay in the palisade layer (between surfactant tails) with their location depending on their hydrophobicity (Rosen, 2004).

2.3 HYDROPHOBICITY CHARACTERISTICS OF OIL AND SURFACTANTS

Two common measurements of a contaminant's hydrophobicity are the octanol/water coefficient (Kow) and equivalent alkane carbon number (EACN) (Queste et al., 2007). This study uses the EACN as a means to characterize hydrophobicity because it is very useful for microemulsion formulation. EACN represents the equivalent n-alkane for a given compound, for example, hexane has an EACN of six. Oils having similar EACN values have similar optimum salinity, which is the salinity at which oil and water are equally soluble in the surfactant middle phase microemulsion solution (Thongkorn, 2007). Thus compounds with a higher EACN number are more hydrophobic.

The hydrophobicity - hydrophillicity characteristics of contaminants and surfactant are major factors contributing to their ability to form microemulsion with one another. Equivalent Alkane Carbon Number (EACN) and Hydrophilic Lipophillic Balance (HLB) are used as expressions of these characteristics for organic oils and surfactant, respectively.

One way for EACN determination is finding optimum salinity for a certain type of surfactant system that can cause lowest interfacial tension between surfactant solution and oil sample and then using Salager's equation to calculate the EACN. This equation is derived from empirical relationship between the optimum salinity and the number of carbon in a series of straight chain hydrocarbon forming microemulsion with the same surfactant system as being used with oil sample. Their relationships are as follow:

$$\ln S^* = K(EACN) + f(A) - \sigma + aT\,(T - 25) \qquad (2.2)$$

where S* is the optimum salinity

$f(A)$ is a function of alcohol type and concentration

σ is a parameter specific for a particular surfactant system

aT is a constant related to temperature effect

If the system has no alcohol addition, uses the same surfactant, and is carried out at the same temperature, the above equation will be as follow:

$$\ln S^* = K(EACN) + C \quad \text{where } C \text{ is a constant} \qquad (2.3)$$

Determination of HLB was originated from experimentation and used mainly for nonionic surfactant. Normally, it is a scale starting from 1 to 40 in which the higher number represent the higher hydrophilicity (Rosen, 2004; Thongkorn, 2007) Calculation based on structural formula had also been developed as well as calculation that can be used with ionic surfactant. Davies has derived HLB for a range of specific functional groups which could be found within a surfactant molecule. The number can be substituted into the following equation to find the resulting HLB of that surfactant.

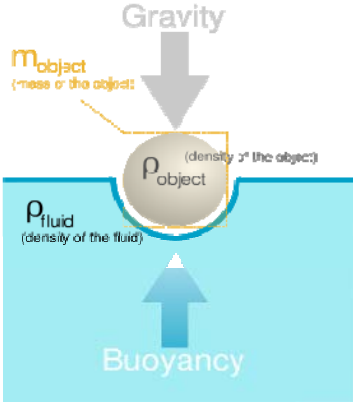
$$\text{HLB} = 7 + \sum \text{hydrophilic HLB} - \sum \text{hydrophobic HLB} \qquad (2.4)$$

2.4 NEUTRAL BUOYANCY AS MEANS TO PREVENT VERTICAL

Neutral buoyancy is a state where the force acting on an object in an upward direction equals to the one in a downward direction. According to Ramsburg and Pennell (2002), neutral buoyancy occurred at the point where the bond number is zero. The bond number (N_B) is the number that represents the ratio of buoyancy and capillary force as shown in equation 2.5 where $\Delta\rho$ is the density difference between the aqueous and oil phase (ρ_w- ρ_o), g is gravitational constant, k_i is intrinsic permeability of the medium, k_{rw} is the relative permeability of the aqueous phase, γ_{ow} is interfacial tension between the organic and aqueous phase, and θ is the contact angle (Pennell et al., 1996; Ramsburg and Pennell, 2002).

$$N_B = \Delta\rho g k_i k_{rw} / \gamma_{ow}\cos\theta \qquad (2.5)$$

Given that buoyancy force equals to the weight of the displaced fluid with an equal volume to that of the displacing object, then the force balance at neutral buoyancy state can be written as follow:



$$\boxed{\rho_1 V_1 g = \rho_2 V_2 g}$$

where ρ_1, ρ_2 are density of a liquid and an object respectively

V_1 V_2 are volume of a liquid and an object respectively

Figure 2.3 Schematic diagram showing neutral buoyancy condition (Wikipedia, 2012).

Application of the above relationship to the non aqueous phase liquid contaminant in the groundwater indicated that the contaminant will sink or float depending on whether it has higher or lower density than the groundwater respectively. Therefore, using surfactant to remediate dense non aqueous phase liquid (DNAPL) in contaminated aquifer has been a challenge due to the potential downward vertical migration of the detached oil. As a result, it can cause the DNAPL to move deeper into the finer layer and become more difficult to be cleaned up.

Partitioning alcohols have been studied as a mean to enable DNAPL to approach neutral buoyancy. They act as a swelling agent that increase the volume of organic phase and thus reduce the density of the oil contaminants (Ramsburg et al., 2004). Several kinds of alcohol had been applied to remediate the subsurface contamination. Ethanol was used as cosolvent to reduce interfacial tension (Ramsburg et al., 2004; Brooks et al., 2004), while propanol, butanol, and hexanol were used as a swelling alcohol to achieve oil density adjustment.

Some manipulation of oil density to achieve neutral buoyancy had been carried out by pre-flooding the media with alcohol to adjust the density and followed by surfactant solution flooding to reduce the interfacial tension (Kostarelos et al., 1998; Lunn and Kueper, 1999; Ramsburg et al., 2004; Taylor et al., 2004). As a result, the detached oils were expected to be pumped out together with the flushing solution.

Flushing sequences are as important as flushing solutions. Using butanol as a pre-flood solution and surfactant as a flooding solution had been shown to cause more mobilization than using the mixture of butanol and surfactant together in the pre-flood solution (Ramsburg et al., 2004). The alcohol partitioning behaviors are DNAPL specific and the system conditions are needed to be considered (Hofstee et al., 2003; Ramsburg et al., 2004). Therefore, gaining an understanding of the effect of the flushing solution and flushing sequence on the removal behavior is necessary for successful site-specific remediation.

2.5 LITERATURE REVIEWS

Caponetti et al. (1992) investigated the role of alcohol to surfactant ratio on microemulsion formation of pentanol, hexanol, heptanol, and octanol with hexadecane and potassium oleate by using small angle neutron scattering. They found out that for a given alcohol, increasing alcohol to surfactant ratio increased the amount of alcohol at the interface but the total amount of alcohol in the particle decreased due to decreased particle dimension. For a fixed alcohol to surfactant ratio, increasing hydrophobicity of the alcohol caused lower fraction of alcohol at the interface.

Pennell et al. (1996) performed column experiments to investigate the onset of tetrachloroethylene (PCE) mobilization during surfactant flushing. They reduced interfacial tension between oil and aqueous phase from 47.8 to 0.09 dyne/cm in four size fractions of Ottawa sand by using four different surfactant solutions. They introduced the total trapping number as an expression for forces involved in PCE mobilization process including viscous, buoyancy, and capillary force. They found that the critical value for all sand fractions fell within the range of 2×10^{-5} to 5×10^{-5}.

Kostarelos et al. (1998) introduced a concept of neutral buoyancy to counter the problem of vertical migration. The flushing solution of 4% dihexylsulfosuccinate at 0.6% salinity with and without the addition of 8% isopropanol were compared. The results showed that alcohol addition reduced the density of microemulsion from 1.028 g/cm^3 to 1.003 g/cm^3 but the solubility of trichloroethylene in the microemulsion was also reduced from 5.9% to 3.3% by weight. However, they focused the neutral buoyancy concept on the microemulsion form in the aqueous phase. Their companion paper also applied the mathematical model for neutral buoyancy on the basis that no free NAPL phase mobilization occurred.

Martel et al. (1998) showed the necessity of adding solvent to the flushing solution in addition to surfactant and alcohol in order to increase the removal efficiency of a mixture of heavy aliphatics, aromatics, and chlorinated hydrocarbons. They compared two kinds of solvent and found that toluene is better than limonene. However the amount that toluene which can be mixed with the flushing solution was small comparing to the amount of solvent needed to get the optimum performance. Therefore, the optimum flushing solution contained the mixture of toluene and limonene.

Dwarakanath and Pope (1998) had extended the application of a partitioning interwell tracer test on identifying location and extent of contamination in an aquifer. They proposed using EACN of both contaminant and partitioning alcohol as tools to estimate partitioning coefficients of alcohol tracers in both NAPLs and water phase. Their initial step was to correlate the EACN of linear alkane with the logarithm of partitioning coefficient of various alcohols to obtain a linear regression. After that, they use those relationships with some numerically modification to obtain a binary equation accounted for both NAPLs and alcohol EACNs. The NAPLs under focused in their study were PCE, TCE, and jet fuel.

Lunn and Kueper (1999) demonstrated that multiple-step alcohol floods can recover tetrachloroethylene better than single alcohol flood. Their flushing process included a 10% isobutanol preflood, a composite alcohol of 65% ethylene glycol & 35% propanol (v/v) mainflood, and a xanthan gum polymer solution postflood. Their system were arranged in an upflow gradient direction which means that they also had pressure from injected solution as a counteract force for gravitation. Their flushing system yielded good performance since they achieved 99.8% recovery while maintaining neutral buoyancy. However, the amount of total flushing solution needed was quite high, almost three times as required by single step ethanol flushing.

Harwell et al. (1999) compared the removal mechanisms between solubilization and mobilization by using different surfactant systems that yield different degree of interfacial reductions. The mixed surfactant of ethoxylated sorbitol ester with di(ethylhexyl)sulfosuccinate at a ratio of 45:55 (w/w) had caused PCE trapped in sand column to mobilize and yielded a removal rate over 40 times the single surfactant system of sodium dodecyl benzene sulfonate.

Sabatini et al. (2000) summarized key technical and economic issues for surfactant enhanced groundwater remediation. They illustrated the importance of solubility enhancement, interfacial tension, viscosity, and density in selecting an appropriate surfactant system. They suggested the use of site-specific capillary curve to optimize solubilization. They also introduced the concept of surfactant gradient system to progressively increase the solubilization while minimize mobilization and vertical migration. They demonstrated that a mixed surfactant system of a branched alkyl (C14-C15) propyloxylated sulfate and a mono-dihexadecyl diphenyloxide disulfonate with a salinity gradient of 0%, 0.6%, and 1.0% $CaCl_2$ can remove 94.3% PCE without mobilization occurring.

Wu et al. (2001) performed column study with glass bead packed in a vertically oriented 2.5 cm I.D. 15.0 cm length column. Residual hexadecane in the column was decontaminated using two stages flooding of 2%AOT/2%Tween 80 with 5% and 7% NaCl, respectively. Percent recovery of 100.3% was obtained with 50% from mobilization, 31.4% from Type I microemulsion, and 18.9 % from middle phase microemulsion.

Kibbey et al. (2002) investigated the partitioning efficiency of n butanol into chlorobenzene, trichloroethylene, and tetrachloroethylene with and without addition. They found out that addition of surfactant required higher alcohol in aqueous phase to achieve the same partitioning as without addition of surfactant. They suggested the application of macroemulsion flushing and stressed on prevention of dilution of alcohol concentration in the flushing solution.

Hoftee et al. (2003) conducted column experiments using a flushing solution consisted of a mixture of 23% water, 23% hexanol, and 54% isopropanol. They arranged their column in an up-flow direction and pumped their flushing solution at a fix discharge rate. They varied the initial density of DNAPLs and column permeability to investigate the required flow velocity and the removal patterns. An equation was presented to relate the critical specific discharge to the initial density difference between the groundwater and the DNAPL.

Ramberg et al. (2004) used two-dimensional sand columns to compare three different flushing systems in their ability to prevent vertical migration and to recover PCE from the contaminated sand spot. The three systems were as follow: 1) a single flood of 4% AMA + 0.05% $CaCl_2$ 2) a preflood of 6% butanol and a mainflood with 4% (4AMA:1AOT) + 20% butanol + 0.05% $CaCl_2$ 3) a preflood of 4.7% tween 80 + 1.3% span 80 + 15% butanol emulsion and a mainflood of 10% AMA + 5% butanol + 0.1 % $CaCl_2$ + 1.5% NaCl. They found that the first system caused vertical migration into the fine sand layer while the other two can prevent that. Even though the second and third system recovered about the same amount of PCE but their mechanisms were different. The high proportion of PCE removed by the second system was done by free phase mobilization while the majority of PCE removed by the third system was recovered in aqueous phase.

St-Pierre et al. (2004) conducted sand column experiments to evaluate efficiency of different flushing solutions in removing trichloroethylene at residual concentration. The tested solutions were 20%, 50%, 80% ethanol; 20%, 50% propanol; 85% butanol; and 20%, 50% of the mixture of ethanol and butanol with SAS surfactant. The highest recovery of 99.5% was obtained using the mixed solution of 33.3% ethanol and 16.7% SAS. They also investigated the application of tie-line slope in constructed phase diagram to predict the major removal mechanisms.

Robert et al. (2006) optimized TCE dissolution in surfactant solution by using xanthan gum polymer. Multiple steps flushing were preflushing the system with 0.5g/L xanthan gum solution and mainflushing with the solution mixture between 0.5 g/L xanthan gum and surfactant (W2722/SAS) in various concentration. Surfactant concentration in the main flush was increased from 0.5% to 2% and to 5% with the flushing pore volume (PV) of 1.52 PV, 1.2 PV, and 3.75 PV, respectively. It was found that the polymer increased the solution viscosity and TCE dissolution. However, there was plugging of the inflow screen due to bacterial growth or microgel formation associated with the polymer.

Ervin and Ramsburg (2009) studied the alcohol partitioning as a tracer to DNAPL spatial distribution. The NAPL and alcohol under studied were trichloroethylene and 2-octanol. They found that the partitioning coefficient of 2-octanol were non linear with six folded increased of the partitioning coefficient above the aqueous concentration of 300 mg.L^{-1}. Therefore, the simulation for alcohol partitioning in the column experiment had to account for this nonlinearlity otherwise the prediction could not represent the actual phenomena.

CHAPTER III

RESEARCH METHODOLOGY

The research methodology is divided into two parts. The first one is a batch study to find hydrophobicity characteristic of TBT, to study phase behavior of the oil mixture, and to develop flushing solution. The second part is a continuous flow study which performs in both single step flushing and two- step flushing to study removal mechanism and DNAPL density modification. The experimental framework is shown in Figure 3.1.

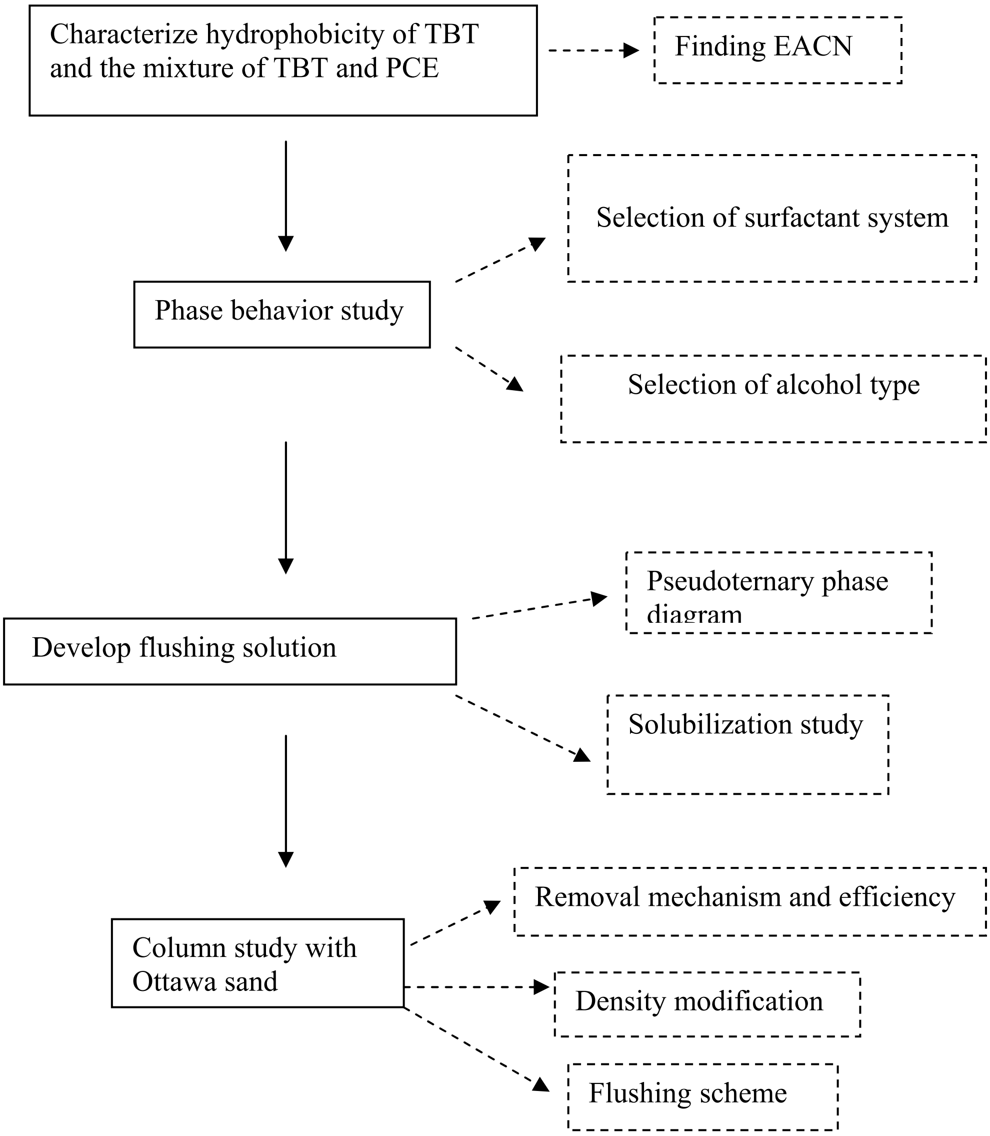


Figure 3.1 Experimental framework

3.1 MATERIALS

3.1.1 Organometallic and organic compounds

Tributyltinchloride (TBT) was purchased from Sigma-Aldrich Co. Tetrachloroethylene (PCE) was purchased from Ajax-Finechem. The *n*-alkane series, pentane, hexane, octane, and decane were purchased from Fluka, LabScan, Carlo Erba, and Fluka, respectively. Isopropyl alcohol, n-butyl alcohol, and tert-butyl alcohol were purchased from Labscan. N-pentanol and n-hexanol were purchased from Merck.

3.1.2 Surfactants

Sodium dihexylsulfosuccinate (SDHS), with the common name AMA, and sodium dioctylsulfosuccinate (SDOS), known as AOT, were purchased from Fluka Co. C16 diphenyloxide disulfonates (C16 DPDS) with the tradename Dowfax 8390, was supplied by Dow Chemical Co. Polyoxyethylene (20) sorbitan monooleate (Polysorbate 80; P80, known as Tween 80) was purchased from BDH Co.

3.1.3 Water and electrolyte

Water used in the experiment was deionized water with the resistivity of 18 $M\Omega\ cm^{-1}$. Sodium chloride (NaCl) was purchased from Labscan and Calcium nitrate ($Ca\ (NO_3)_2$) was purchased from Ajax Finechem.

3.1.4 Column packing material

This column study tried to imitate source zone contamination that saturated with contaminant DNAPL. The geological under interest is shallow and unconsolidated aquifer at which the general contaminations are likely to occur. Therefore, ottawa sand (20-30 mesh) purchased from Fisher Scienctific Co. was used for packing column. The sand had size range about 0.6-0.85 mm which was considered as coarse sand. This size range was selected because it render higher hydraulic conductivity than fine or medium sand; and groundwater was likely to prefer flowing through these layer. In addition, this size range was also applied in the study carried out by Thongkorn (2007) and Damrongsiri (2010) which also study organometallic contamination in groundwater. The results obtained in this research then can be further compared.

Table 3.1 Chemical and physical properties of TBT and PCE

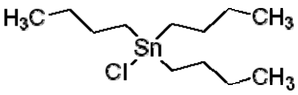
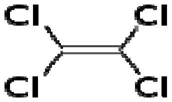
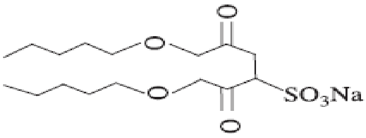
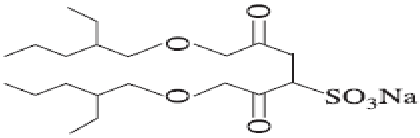
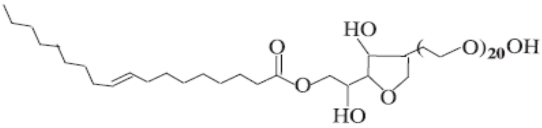
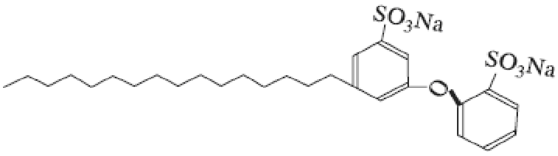
Properties	TBT	PCE
Physical form	Clear to brown liquid	Clear colorless liquid
Molecular formula	$Sn(C_4H_9)_3\,Cl$	C_2Cl_4
Molecular structure		
Molecular weight	325.49	165.8
Density	1.2	1.6
Water solubility	0.007 mg/L	100 mg/ L
Boiling point	171-173 @ 25 mmHg	121
Melting point	-9	- 22.8
Toxicity (LD 50)	126-224 mg/kg (oral/rat)	2629 mg/kg (oral/rat)
Log Kow	4.1	3.4
Vapor pressure	0.04 mmHg (25)	18.47 mmHg (25)
BCF	3000 – 4500	39 - 49

Table 3.2 Properties of surfactants used in this study

Surfactant	Structure	MW	HLB	Type
AMA (SDHS)		388.45	16.1	Two-tailed anionic
AOT (SDOS)		444.57	14.2	Branched two tail anionic
Tween 80 (P80)		1308	15.0	Ethoxylated nonionic
Dowfax 8390 (C16DPDS)		642	71.5	Twin headed anionic

3.2 METHODOLOGY: HYDROPHOBICITY CHARACTERIZATION OF OIL SAMPLES

3.2.1 Finding the surfactant system for middle phase formation with TBT and a series of straight chain alkane.

To find the EACN of oil, one first finds a surfactant system that is able to form middle phase microemulsion with the oil (Thongkorn, 2007). Thus, surfactant systems with varying hydrophilic-lipophillic balance (HLB) were examined for the TBT DNAPL. It was found that the SDHS, which has HLB of 16.15 as calculated by using Davies Method (Lange, 1999; Tadros, 2005), can form a middle phase microemulsion with TBT. However, when this system (4 wt% SDHS) was studied with a range of straight chain alkane (C5-C10) at salinity of 0 wt%-3 wt% NaCl, middle phase formations did not occur. In addition, the system of 2 wt% SDOS & 2 wt% SDHS as well as 2 wt% SDOS & 2 wt% P80 that had been found to form middle phase with a series of straight chain alkane (C5-C10) (Thongkorn, 2007) did not form middle phase microemulsion with TBT at 0 wt% - 5 wt% NaCl.

Therefore, octadecane and decane were mixed with TBT at varying ratio to adjust its hydrophobicity. The mixture of TBT:octadecane at the mass ratio of 0.4, 1.0, and 2.3 and TBT:decane at the mass ratio of 0.4 and 1.1 were investigated. Results showed that the mixture of TBT:decane at the mass ratio of 0.4 can form middle phase with the surfactant system of 2 wt% SDOS & 2 wt% SDHS. This TBT/decane mixture then was used to find EACN of TBT in the next step.

3.2.2. Finding EACN of TBT

A salinity scan was carried out by gently mixing an equal volume of a series of straight chain alkanes (pentane, hexane, octane, and decane) with the surfactant mixture of 2 wt% SDOS & 2 wt% SDHS at varying wt% of NaCl (1 wt% - 4 wt% with 0.2 wt% interval) and left at room temperature for 24 hours to reach equilibrium. Only the systems that show middle phase formation were used for finding solubilization parameters of oil (SPo) and water (SPw). SPo and SPw are parameters that represent the ratio of oil and water solubilized in the middle phase to the surfactant within the same region, respectively. The relationship between the two parameters with percent salinity vary in the inverse direction and the two trend lines intersect at the salt concentration which we call optimum salinity (S*). The optimum salinities of the four oils were then plotted against their alkane carbon number to obtain a Salager's equation (Thongkorn, 2007), $\ln S^* = K(EACN) + C$. Then a salinity scan of TBT/decane mixture at the mass ratio of 0.4 with the surfactant system of 2 wt% SDOS & 2 wt% SDHS at varying wt% of NaCl was carried out. After optimum salinity of the TBT/decane mixture was identified, EACN was then calculated from the obtained Salager's equation. Even though a single oil and single surfactant was recommended to use for finding optimum salinity in the middle phase (Queste et al., 2007), the mixture of TBT with decane at the mass ratio of 0.4 was used in this study for reasons described above. EACN of TBT was then calculated by using linear mixing rule ($EACN = \sum x_i(EACN)_i$, where x_i and $EACN_i$ are a mole fraction and an EACN of a chemical i in the mixture, respectively.

3.3 METHODOLOGY: PHASE BEHAVIOR STUDY

The effect of surfactant type, alcohol to surfactant ratio, salinity, and oil mixture proportion on phase behavior of the oil samples were investigated in the phase behavior study. This is due to the fact that most contaminants are usually occurred as a mixture in various proportion in which their phase behaviors with a particular surfactant system can be dramatically different.

3.3.1 Selection of surfactant system

The mixture of TBT/PCE at the mass ratio of 0.25 and 1.50 (equal to 20 wt% and 60 wt% TBT, respectively) were used to form phase behavior study with five surfactant systems. TBT concentration in the mixture was varied based on an assumption that the oil ratio in the mixture might vary from place to place and the applied system should perform well in a wide range of TBT proportion. The tested surfactants were twin headed anionic surfactant (C16DPDS), two tailed anionic surfactant (SDHS, SDOS), and ethoxylated nonionic surfactant (P80) (Table 3.2). The surfactants were mixed at varying ratio to cover a range of hydrophilic-lipophillic balance (HLB) as follows: 2 wt% SDHS & 2 wt% SDOS (HLB= 15.20); 2 wt% SDHS & 2 wt% P80 (HLB=15.58); 4 wt% SDHS (HLB=16.15); 3.6 wt% SDHS &

0.4 wt% C16DPDS (HLB= 22.09); and 2 wt% SDHS & 2 wt% C16DPDS (HLB= 43.83).

Since an addition of alcohol was explored in this study as a density modifier, the optimum surfactant system should also have good performance under the presence of alcohol. Therefore, n-butyl alcohol was also added into surfactant systems at varying alcohol concentration of 0 wt%, 1.6 wt%, 3.2 wt%, and 4.8 wt% while all experiments were carried out at total surfactant concentration of 4 wt%. Laser pointer-aided observation (λ = 650 nm ± 10 nm) was used to identify o/w or w/o microemulsion by detecting the light scattering of swollen micelles whether they are in the aqueous phase (Type I), in the oil phase (Type II), or in the middle phase (Type III). This technique of using a laser pointer to locate microemulsion type was also used by other researchers (Queste et al., 2007). In addition, using a laser pointer with a wavelength of 630 nm - 660 nm had been used to indicate the occurrence of colloidal suspension of micelles of the size 79 nm (Qiao et al., 2010) which was within the size range of the microemulsion (10 nm -100 nm) (Rosen, 2004). In case no light scattering was observed, it was assumed that the micelle or swollen micelle concentration might be very small and have little or no oil solubiliized within the micelle.

For further detailed investigation, the TBT/PCE mixture with the mass ratio of 1.50 was used. The selection was based on a calculated EACN of the mixture obtained from this research (6.5) which was close to the EACN of tetraethyllead (6.0 - 7.0), another organometal (Thongkorn, 2007), so it can be used for further comparison as warranted.

3.3.2 Selection of alcohol type

Phase behavior of the oil mixture of TBT/PCE at a mass ratio of 1.5 with the selected surfactant system under the presence of other alcohol types (isopropyl alcohol, tert-butyl alcohol, and n-pentanol) was studied.

Experiments were conducted in a similar fashion as in the study to find optimum surfactant system but only the oil mixture at mass ratio of 1.5 was applied. Phase behavior of the oil mixture of TBT/PCE at a mass ratio of 1.5 with the selected surfactant system under the presence of other alcohol types (isopropyl alcohol, tert-butyl alcohol, and n-pentanol) was studied. The study was carried out using the surfactant systems of 3.6 wt% SDHS & 0.4 wt% C16 DPDS with total alcohol concentration of 0 wt%, 1.6 wt%, 3.2 wt%, and 4.8 wt% and NaCl concentration of 2.4 wt%, 3.0 wt%, and 3.6 wt%.

3.4 METHODOLOGY: DEVELOP FLUSHING SOLUTION

Pseudoternary phase diagram and solubilization study were used as tools to develop flushing solution with the details are as following:

3.4.1 Pseudoternary phase diagram

Three experiments were set up using similar technique but with different starting combination among three vertices of the diagram (a surfactant brine solution, an oil mixture, and an alcohol). The surfactant used in this experiment was the mixed surfactant of SDHS: C16DPDS at a mass ratio of 9:1 with 3 wt% NaCl. The oil mixture was 60 wt% TBT and 40 wt% PCE. Two types of alcohol, n-butyl alcohol (BuOH) and tert-butyl alcohol (TBA), which were selected from phase behavior study were used. The variation details are as follows:

3.4.1.1 Variation ratios of surfactant and mixed oil as initial combination

Different concentrations of surfactant solution (4 wt%, 6 wt%, 8 wt%) were mixed with oil mixture at varying volume ratio of 0.2:0.8, 0.4:0.6, 0.6:0.4, 0.8:0.2, and 0.9:0.1. Two types of alcohols, n-butanol and tert- butanol, were separately added to the solutions with different compositions until they either became one miscible phase or have phase conversion. Compositons of three constituents were used to plot pseudo ternary diagram by TRI-PLOT (Graham & Midgley, 2000).

3.4.1.2 Variation ratios of alcohol and mixed oil as initial combination

Only 4 wt% surfactant concentration was investigated. This step began with mixture of alcohols and oil mixture at volume varying ratio of 0.9:0.1, 0.7:0.3, 0.5:0.5, and 0.3:0.7. The 4wt% surfactant solutions were then added until phase separation occurred. Pseudo ternary phase diagram were subsequently plotted by TRI-PLOT (Graham & Midgley, 2000) using relative volume of each constituent.

3.4.1.3 Variation ratios of surfactant and mixed oil as initial combination

In order to cover more area in the phase diagram, starting material had been alternated. Mixtures of alcohols (n-butanol and tert- butanol) with the surfactant solution at varying volume ratios of 0.9:0.1, 0.7:0.3, 0.5:0.5, and 0.3:0.7 were prepared. The oil mixtures were then slowly added until phase conversion occurred and data were plotted into TRI-PLOT.

3.4.2 Solubilization study

The mixture of TBT-PCE in an amount of 4 mL was mixed with 4 mL of surfactant solutions. The investigated surfactant systems were the mixture of SDHS and C16DPDS at a weight ratio of 9:1 with total surfactant concentration of 2 wt% and 4 wt%. N-butyl alcohol and tert-butyl alcohol were used in this study with the alcohol to surfactant mass ratios of 0, 0.4, 0.8, 1.0, 1.2 and 1.6. The test tubes were then sealed, gently shaken, and left at room temperature for 3 days to reach equilibrium condition after which PCE, TBT, surfactant concentration, and oil phase density were determined.

3.5 METHODOLOGY: CONTINUOUS FLOW STUDY

Since most groundwater remediation was applied on-site in continuous flow mode, column studies were set up to imitate the contamination at residual saturation. This methodology section of continuous flow study consists of column setting, alcohol partitioning study, single step flushing, and two step flushing.

3.5.1 Column setting

Sand columns were set up to simulate residual saturation in the contaminated saturated zone. The packing procedure was adapted from Thongkorn (2007) and Damrongsiri (2010). The purposes of the study are to investigate the removal mechanism, removal efficiency, and density modification by carrying out chemical analysis to analyze the performance of the flushing system quantitatively.

The flow through experiments were conducted using glass column (2.5 cm inner diameter and 30 cm length) equipped with an adjustable flow adapter from KONTES (Chromatography columns, KONTES CHROMAFLEX ^{TM}). The columns were wet and stir packed to avoid air bubble accumulation. A small amount of water and sand was gradually added into the column until the height of 17 cm of wet sand is reached while keeping the water on top of the sand at all times. The amount of water and sand were measured before and after packing for the calculation of pore volume. The water that had been used up to fill pore space in the column is called one pore volume. Keeping air bubble-free conditions is important in all step of packing to prevent the dead spot in the flow channel. Vent pipes in both upward and downward system are used for this purpose (Figure 3.2).

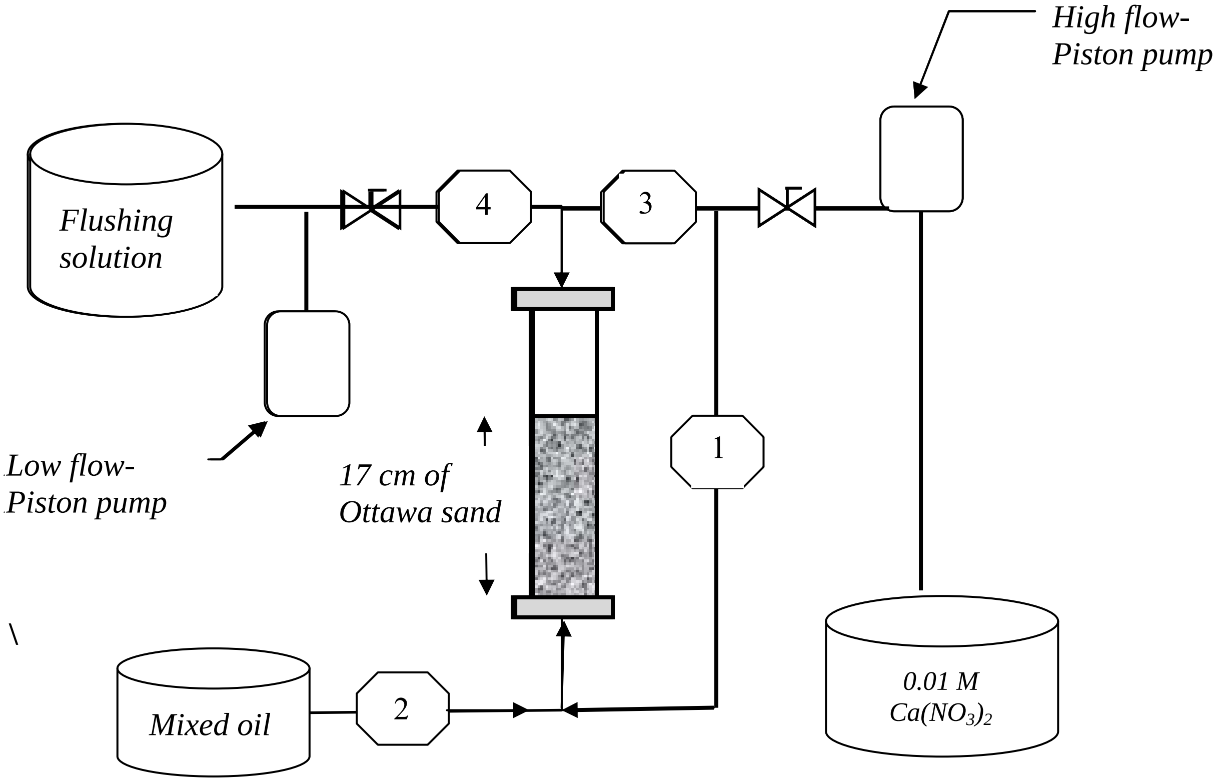


Figure 3.2 Column setting including 3 way valve for gas venting to create air-free packing condition. Two pumping systems with low and high flow rate for upward and downward flow configurations. Column setting and running sequence were shown in number 1, 2, 3, and 4.

After no air bubble was observed in the column, the deionized water was switch to the 0.01 M Ca(NO$_3$)$_2$ solution to imitate groundwater condition. Further column runnings were sequentially carried out in four steps as shown in Figure 3.2. Firstly, the simulated groundwater was flow through the column in an upward direction with high flow rate pistol pump (Model QG50, Fluid metering Inc.) at a flow rate of 4.0 mL.min^{-1}(10 times the designed operation flow rate) for 10 pore volume.

Secondly, residual oil saturation was established by loading oil sample into the column in an upward manner until the oil reached the top of the column. The loading technique was adapted from Damrongsiri (2010) by using head difference upward loading between the oil sample and the top of sand column. The column was left for 3 hours to increase the contact time between the residual oil and packed sand. Thirdly, oil sample in the column beyond saturation were removed by flushing downward with about 10 pore volumes of simulated groundwater at a flow rate 10 times the designed operation flow rate until no free oil phase observed in the outlet. This un-trapped oil was captured as both free oil phase and solubilized phase which were then deducted from the amount of oil loaded into the column. The result was the actual residual oil that was saturated in the column. The column with this residual oil was then ready for treatment comparison. Fourthly, the selected flushing solutions were then introduced into the column by down ward flow using another piston pump (Model QG6, Fluid metering Inc.) which set the flow velocity at fixed operation flow rate of 0.4 ±0.03 $mL.min^{-1}$.

A fraction collector (Model Frac 920, Amersham Bioscience) was used to collect the effluent from the column every 20 minute. The aqueous samples from the vials were analyzed directly for PCE and alcohol concentration by GC-HS. TBT was analyzed as total tin concentration by ICP-OES (Vista-MPX, Varian) with prior digestion with microwave system (Ethos pro, Milestone). The mobilized oil sample were removed from the aqueous phase right after the sampling and the composition of oil sample were instrumentally analyzed with prior dilution with 4 wt % surfactant + 3 wt% NaCl. The sand samples after each column treatment were firstly extracted by 4 wt% surfactant solution for 1 day and subsequently by 5wt% HCl for another 1 day. Chemical analysis was also carried out on extraction solution of the sand sample. The resultant mass in the extracted solution were sequentially subtracted from the total mass before calculation for total removal.

3.5.2 Alcohol partitioning study

TBA and BuOH were used to conduct partitioning study between the TBT-PCE mixed oil phase and aqueous phase with and without the presence of surfactant. The experiments were carried out in a similar fashion as in the phase behavior study but focused more on density modification which play major roles in promoting neutral buoyancy and critical point for phase conversion.

3.5.2.1 Alcohol partitioning with no addition of surfactant

TBA and BuOH were tested to find the minimum amount needed to cause phase conversion of the mixed oil under studied. Different alcohol to mixed oil mass ratio (3.5:0.5, 3.0:1.0, 2.5:1.5, 2.0:2.0, 1.5:2.5, 1.0:3.0, and 0.5:3.5) were used as initial composition in the batch study. Equal amounts of 3 wt% NaCl solution were mixed with those varying ratio of oil and alcohol and leave for 24 hr to reach equilibrium. Density modification and chemical composition of both oil and aqueous phase were determined. It showed that minimum alcohol concentration in the aqueous phase causing phase conversion from DNAPL to LNAPL were 14.5 wt% and 4.8 wt% for TBA and BuOH, respectively. Therefore, brine solution with 14.5 wt% TBA and 4.8 wt% BuOH were selected for further study in continuous flow mode of two step flushing scheme.

3.5.2.2 Alcohol partitioning with an addition of surfactant

From column study results, BuOH was selected for further improvement. Before the last column was set up, a study on alcohol partitioning between mixed oil phase and surfactant solution aqueous phase was carried out to study the effect of initial surfactant concentration on alcohol concentration in the oil phase at equilibrium. Mixed oil with an amount of 2ml were added to 5 ml of flushing solution with five initial surfactant concentration (0 wt%, 2 wt%, 4 wt%, 6 wt%, 8 wt%) at 3% NaCl. Then BuOH was slowly added to each tube until the mixed oil approached density modified phase conversion. Final phase conversions were achieved through centrifuge at 2500 rpm for 3 minutes. Density modification and chemical composition of both oil and aqueous phase were determined.

3.5.3 Flushing scheme

All six column studies had been carried out using 3.6% AMA & 0.4% Dowfax at 3% NaCl. The column studies were performed in both single step flushing and two step flushing with the detail of flushing solution in each flushing scheme as following

3.5.3.1 Single step flushing

Three flushing solutions were used as followings: 1) with only 3.6% AMA & 0.4% Dowfax at 3% NaCl; 2) with 6% AMA & 0.4% Dowfax at 3% NaCl + 4.8% tert-butanol and 3) with 6% AMA & 0.4% Dowfax at 3% NaCl + 4.8% n-butanol. The flushing time was about 16 pore volume for all three columns.

3.5.3.2 Two step flushing

Two column studies had been set up to study the effect of two step flushing in improving density modification capability to approach neutral buoyancy. The first one was preflushing the column with 14.5% TBA + 3 wt% NaCl for about 15 pore volume and followed by 4 wt% total surfactant (3.6 wt% SDHS + 0.4 wt% C16DPDS + 3 wt% NaCl) with 12.5% TBA until only small amount of oil was detected in the effluent. The second one was preflushing the column with 4.8% BuOH + 3 wt% NaCl for about 15 pore volume and followed by 4 wt% total surfactant (3.6 wt% SDHS + 0.4 wt% C16DPDS + 3 wt% NaCl) with 3 wt% BuOH until the effluent had only small amount of solubilized oil.

Finally, the column study was carried out using the two step flushing scheme with BuOH as a density modifying agent. The first step used 3% NaCl brine solution saturated with BuOH and followed by the 4% surfactant solution saturated with BuOH. The saturated solutions were prepared by thoroughly mixing an excess amount of BuOH with the solutions and left at room temperature for 3 days with an excess BuOH cover the top of the solution. The solutions were slowly stirred intermittently and the top excess was removed before being applied in the column study. The duration for alcohol pre flushing for this column was increased to 20 pore volume to give more partitioning time to the residual oil.

3.6 ANALYTICAL METHOD

3.6.1 Quantification of TBT as tin

Aqueous sample with an amount of 0.3 ml was mixed with 3 ml of 65 wt% nitric acid and 9 ml of 37 wt% hydrochloric acid in the vessel. The digestion condition adapted from Thongkorn (2007) and Damronsiri (2010) with the temperature ramping from room temperature to 175 ºC within 13 min and holding there at 175 ºC for 15 minutes. The samples were vented in the digester for 30 minutes before left at room temperature until the vessel cooled down. Since the digester operated at the condition based on the reference vessel, the samples of a close range of PCE concentration were grouped together to be digested in the same batch and the sample of highest PCE concentration was selected as reference vessel. (microwave digestion were carried out after PCE quantification). The volume of final solutions were made to 25 ml with milliQ water and analyzed by ICP –OES (Vista-MPX, Varian) at 283.998 nm.

3.6.2 Quantification of PCE, TBA and BuOH

PCE and alcohol in the aqueous effluent was analyzed using Gas Chromatography (Clarus 500, PerkinElmer) with FID detector equipped with head space auto sampler (Turbomatrix 40, PerkinElmer). Aqueous sample with an amount of 100 µL was incubated in the thermostat of head space auto sampler at 50 ºC for 30 minutes with the temperature for needle and transfer line of 55 ºC and 60 ºC, respectively. The oven temperature program was set up at 50 ºC for 3 minutes and ramped up to 80 ºC in 3 minutes. Retention times for PCE, BuOH, and TBA are 5.68, 3.59, and 2.84 minutes, respectively.

3.6.3 Quantification of anionic surfactant

Surfactant concentration was analyzed using two phase titration method adapted from Liu et al (2004) with dodecyltrimethylammonium bromide (DTAB) as a cationic titrant and dichloromethane (DCM) as an organic phase. The titration procedure was carried out by mixing 1 ml of an aqueous sample as titrand with 25 ml of deionized water, 15 ml of DCM, and 10 ml of indicator solution (prepared according to manufacturer instruction, BDH). Then titrate with 5 mM of DTAB cationic titrant until the end point was reached (the organic phase changed from pink color to colorless).

3.6.4 Determination of oil and aqueous phase density

Since NAPL phase samples having organomettallic TBT as a major component are highly toxic, the experiments were planned in manners that minimize the waste produced. Therefore, the sample with an amount of only 100.00 µl was used in gravimetrically measurement by a 4 digit balance (Sartorious) with five replicates and the average value was used for further analysis. The accuracy of measurements was found to be within ±0.0001 g.mL^{-1} by calibration with a density meter (Model DMA35, Anton Parr) using n-butyl alcohol at 25°C. This density meter requires about 3 ml of sample per each measurement resulting in 15 ml of sample per five replicates comparing with 500 μl by gravimetrically measurement. Given this high accuracy, high precision balance was used for density measurement throughout the study. The average density of five replicates was then used for further analysis in the results and discussion section. The measurement of phase density using high precision scale were also employed by other researchers (Jeong et al., 2009; Martel et al., 1993).

CHAPTER IV

MICROEMULSION FORMATION AND PHASE BEHAVIOR

Microemulsion formation was used as a tool to determine phase behavior of TBT /PCE mixed oil in the presence of surfactants and alcohols as a density modifying agent. Understanding the behavior of the TBT/PCE oil mixture under different conditions helps in designing effective removal system for DNAPL organometallic TBT mixture while prevent vertical migration. This chapter consists of four parts. Firstly, the hydrophobicity of TBT was characterized as an equivalent alkane carbon number (EACN). Secondly, phase behaviors of TBT/PCE oil mixture under different surfactant systems with variation of alcohol to surfactant and salinity scanning were performed for selection of surfactant system and alcohol type. Thirdly, pseudoternary phase diagrams were constructed as a preliminary visual observation for alcohol selection. Finally, solubilization study was also carried out to study the effect of alcohol to surfactant ratio to its density modification and solubilization capacity.

4.1 HYDROPHOBICITY CHARACTERIZATION OF TBT

The hydrophobicity of oil of interest can be characterized as an average equivalent alkane carbon number (EACN) by applying Salager's equation and linear mixing rule (Baran,et al., 1994; Thongkorn, 2007). In order to find EACN of TBT, a range of surfactant solutions were investigated to find the surfactant system that can form middle phase microemulsion with both TBT and a series of alkanes with known EACNs. Then the carbon number of each alkane was plotted versus the natural log(ln) values of each optimum salinity (S*). The Salager's equation was then obtained from the linear correlation. The details are as following:

4.1.1 Phase transition study of TBT with variation of surfactant system

SDHS and C16 DPDS were investigated for their ability to form phase transition with organometallic TBT. They were mixed in various ratios to cover a range of HLB (16.15-43.80) as calculated by Davies method. Salinity scanning was performed in the range of 0-5% NaCl. The surfactant and sodium salt were initially mixed by vortex mixing and only the one that no phase separation occurred were used to studied with TBT oil. Even though HLB cannot exactly represent the hydrophobicity of the applied surfactant system since it did not account for the salinity, it still can be used to compare different surfactant systems under studied. Results had shown that TBT could form middle phase microemulsion with 8% SDHS and showed clear phase transition at 2- 4%NaCl. For lower surfactant concentration, at 4% SDHS, middle phase microemulsion was formed at 3% NaCl with no appeared transition, and there was no middle phase formation at 2%SDHS. These results indicated that TBT might need high surfactant concentration or high aggregation number in order to be solubilized within the micelle. For the system of mixed surfactant, there was no middle phase formation for the mixture of SDHS and SDOS at any mixing ratio (Table 4.1).

Consequently, an alkane series with known EACNs (5, 6, 8, and 10 carbons) were investigated for their ability to form middle phase microemulsion with 4% SDHS at 0-3% NaCl which is the system that can form middle phase with TBT, the oil of interest but there was no middle phase microemulsion formation occurred.

Table 4.1 Phase transition study of TBT with various surfactant systems under salinity scanning and their results of salinity that middle phase transition occurred.

Surfactant system	**HLB**	**wt% NaCl**	**Observation for phase behavior****
1. 2% SDHS / 2% C16 DPDS	43.80	0-5%	NP
2. 3.2% SDHS / 0.8% C16 DPDS	27.22	0-5%	NP
3. 3.6% SDHS / 0.4% C16 DPDS	21.69	0-4%	NP
4. 3.8% SDHS / 0.2% C16 DPDS	18.90	0-3%	NP
5. 3.9% SDHS / 0.1% C16 DPDS	17.90	0-3%	NP
6. 8 % SDHS	16.15	0-3%	2-4 %NaCl
7. 4% SDHS	16.15	0-3%	3% NaCl
8. 2% SDHS	16.15	0-3%	NP

Note ** "NP" refers to no phase transition or microemulsion was observed and percentage of NaCl refers to the range of NaCl concentrations that phase transition occurred in those systems

4.1.2 Phase transition study of TBT with the surfactant system of 2wt%SDOS + 2wt%SDHS and 2wt%SDOS + 2wt%P80

According to Thongkorn (2007), two surfactant systems had been developed that could form middle phase microemulsion with the oils of known EACNs. They were 2%SDOS + 2%P80 and 2%SDOS + 2%SDHS but only the surfactant system of 2%SDOS + 2%SDHS could form phase transition with the mixture of DBT/decane (with DBT at a mole fraction of 0.01-0.05). Nevertheless, since TBT is more hydrophobic than DBT, both surfactant system were chosen as a base system to which TBT would adjust for its EACN finding.

From previous experiment in section 4.1.1, it appeared from visual observation that IFT decreased as % Dowfax and HLB decreased (the interfacial layer between the oil phase and aqueous phase were less convex or more flat). Together with the results of alkane series that can form middle phase with 2%SDHS +2%SDOS (HLB=15.20) but did not form middle phase with 4%SDHS (HLB=16.15), it implied that TBT and SDHS exhibited somewhat less hydrophobicity than C5-C10 alkane.

Therefore, it might be possible to mix TBT with an alkane of high EACN such as decane or octadecane to render more hydrophobicity to the TBT mixture. TBT was then mixed with decane at the mixing mass ratio of 0.4 and 1.1 and with octadecane at the mixing mass ratio of 0.4, 1.0, and 2.3. Subsequently, the mixtures were tested with the above mentioned two surfactant systems**.**

Table 4.2 TBT mixtures of varying mass ratio with decane and octadecane under studied with two surfactant systems of 2 wt% SDOS + 2wt% P80 and 2 wt% SDOS + 2wt% SDHS by salinity scanning.

Surfactant system	**Oil mixture**	**Mixing mass ratio**	**wt% NaCl**	**Observation for phase behavior****
2 wt% SDOS + 2 wt% P80	TBT:Decane	0.4	0-4%	NP
		1.1	0-4%	NP
	TBT:Octadecane	0.4	0-4%	NP
		1.0	0-4%	NP
		2.3	0-4%	NP
2 wt% SDOS + 2wt% SDHS	TBT:Decane	0.4	0-4%	1-3%
		1.1	0-4%	NP
	TBT:Octadecane	0.4	0-4%	NP
		1.0	0-4%	NP
		2.3	0-4%	NP

Note ** “NP” refers to no phase transition or microemulsion was observed and percentage of NaCl refers to the range of NaCl concentrations that phase transition occurred in those systems

Table 4.2 showed that only the mixture of TBT/decane at the mass ratio of 0.4 can form middle phase with the surfactant system of 2 wt% SDOS + 2 wt% SDHS. This TBT/decane mixture then would be used to find EACN of TBT.

Prior to finding EACN of TBT, the Salager’s equation had to be obtained. A salt scan was conducted for the surfactant solution of 2 wt% SDHS + 2 wt% SDOS and a series of straight chain alkane (pentane, hexane, octane, and decane) to form microemulsion to determine the optimum salinity (S*) of each alkane. Then the carbon number of each alkane was plotted versus the natural log(ln) values of each S* as shown in Fig.4.1(a-d). The Salager’s equation obtained from the linear correlation of the plot is $\ln S^* = 0.1818(EACN) - 0.6659$.

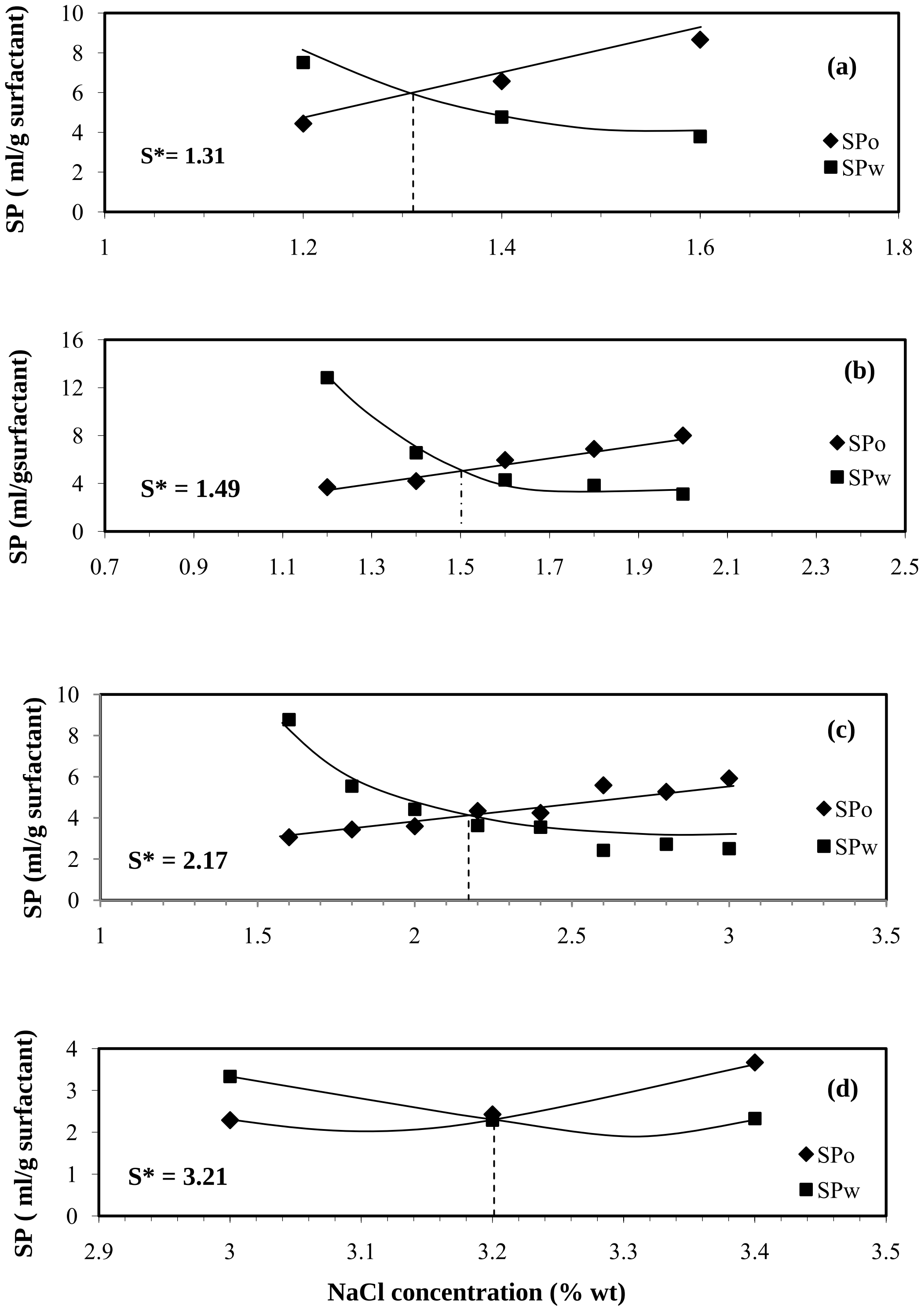


Figure 4.1 Solubilization parameter (SP) of oil (SPo) and water (SPw) in the middle phase microemulsion systems of a series of straight chain alkane: pentane **(a)**; hexane **(b)**; octane **(c)**; and decane**(d)** with the surfactant solution of 2wt% SDHS and 2wt% SDOS over a period of salinity scan.

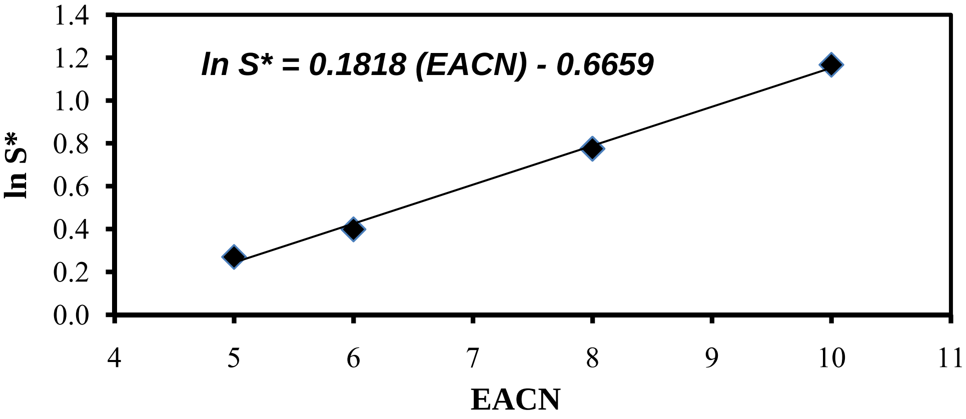


Figure 4.2 Salager's plot of the natural log optimum salinity (ln S*) versus alkane carbon number (pentane, hexane, octane, and decane) of the microemulsion systems formation of the alkane with the surfactant solution: 2wt% SDHS and 2wt% SDOS with salinity scan.

Next the optimum salinity for the oil mixture of TBT and decane at a mass ratio of 0.4 was determined using the same surfactant solution with the results shown in Figure 4.3(a-c). The S* of the mixed oil (TBT and decane) were used to determine EACN of the mixed oil from the Salager's equation. The linear mixing rule was later used for calculation of the EACN of TBT from the obtained EACN of the TBT-decane oil mixture. The averaged EACN value for TBT was 11.17 from the range of experimental values from 8.90 - 13.33 with the standard deviation of 2.22. This value can be used as an estimate since this method is based on the assumption that all surfactant resides within the middle phase layer, and that the oil mixture of TBT/decane interacted with the surfactant system as single oil so the linear mixing rule can be applied. Nevertheless, this value can be used as a guide for selection of an optimum surfactant for microemulsion formation and for selection of the proper composition of TBT and PCE to obtain the oil mixture having EACN close to the EACN of tetraethylead, another organometallic compound.

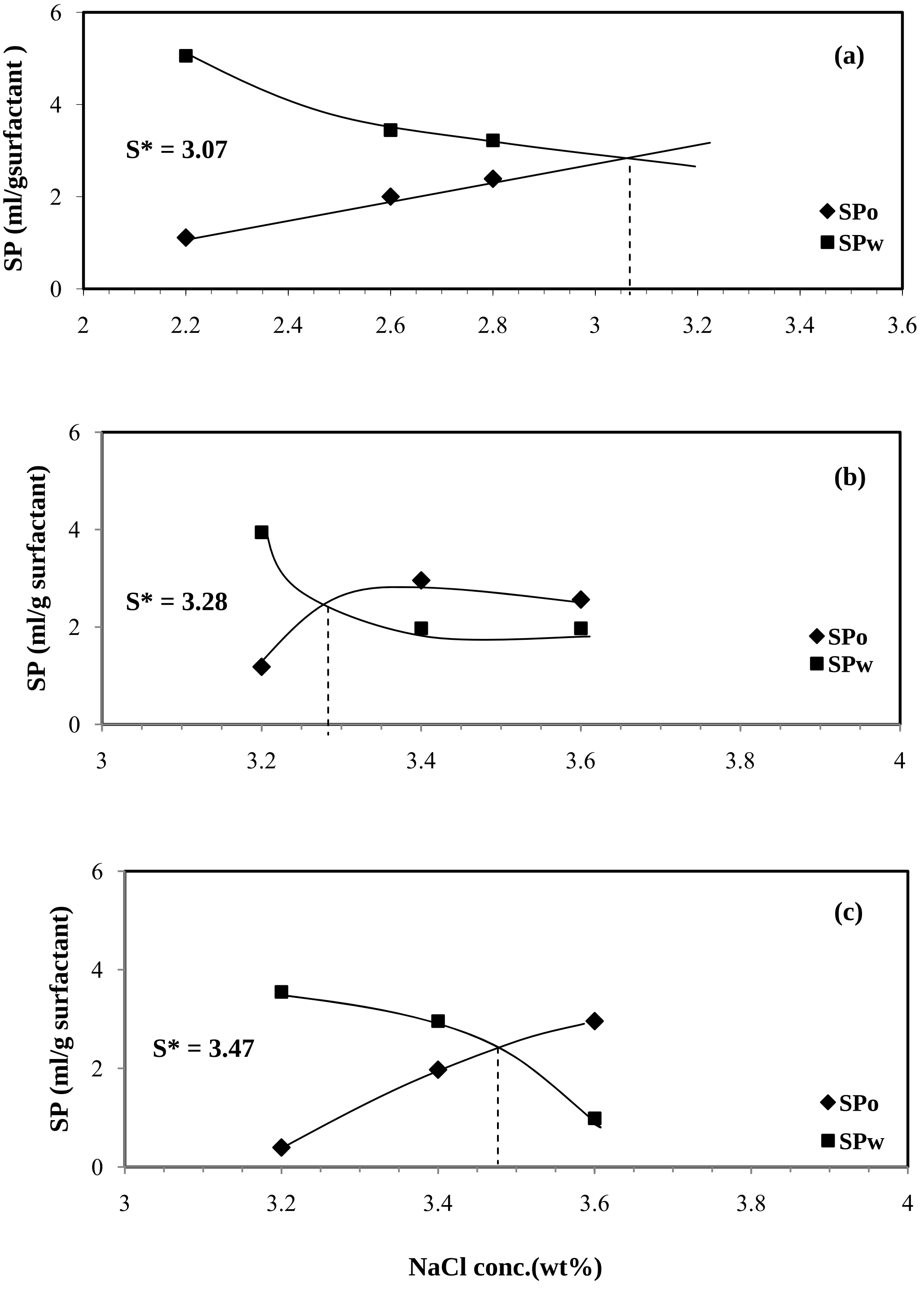


Figure 4.3 Solubilization parameter (SP) of oil (SPo) and water (SPw) in the middle phase microemulsion systems of the mixture of TBT:decane at a mass ratio of 0.4 for experimental set ups at three different times (a,b,c) with the surfactant solution of 2wt% SDHS and 2wt% SDOS over a period of salinity scan.

4.2 PHASE BEHAVIOR STUDY

4.2.1 Phase behavior study for surfactant selection

Phase behaviors of the five surfactant systems with two oil mixture ratios and varying alcohol and salinity were studied and the results were shown in Table 4.3. In general, addition of alcohol is expected to enhance the phase transition of the microemulsion as we can see in the phase behavior of pure PCE oil in the surfactant system of 4 wt% SDHS. However, addition of TBT turned out to prevent the microemulsion formation of the oil mixture with most of the system studied. These might imply distinct characteristic of organometallic TBT that behave not quite as a general polar oil since it has both nonionic and ionic nature in the same molecule.

The surfactant system that enabled microemulsion phase transition for various TBT proportion was the systems of 3.6 wt% SDHS & 0.4 wt% C16 DPDS at 3 wt% salinity. An addition of 0.4 wt% hydrophilic surfactant, C16 DPDS, with its reported HLB of 71.5, to the 3.6 wt% SDHS solution with its HLB of 16.15, as calculated by using Davies Method (Lange, 1999; Tadros, 2005), improved the system of only 4 wt% SDHS. The twin-headed C16 DPDS could help to expand a micelle space by increasing repulsion between head groups following by increasing space for polar or polarizable compounds (Rosen, 2004). However, increasing proportion of C16 DPDS from 0.4 wt% to 2.0 wt% caused the surfactant system to be too hydrophilic for TBT and no microemulsion was formed with the oil mixture of 60 wt% TBT.

Table 4.3 Phase behaviors study and salinity scanning of the oil samples with various surfactant systems under different concentration of n-butyl alcohol

Surfactant system	HLB [a]	wt % NaCl	PCE (EACN =2.9[b])				PCE + 20 wt% TBT (EACN= 3.8[c])				PCE + 60 wt% TBT (EACN=6.5[c])			
			wt% BuOH				wt% BuOH				wt% BuOH			
			0	1.6	3.2	4.8	0	1.6	3.2	4.8	0	1.6	3.2	4.8
4% SDHS	16.15	0.0	-[d]	-	-	-	-	-	-	-	-	-	-	-
		0.6	-	-	-	III	-	-	-	-	-	-	-	-
		1.2	-	-	I	III	-	-	-	-	-	-	-	-
		1.8	-	I	III	II	I	III	-	-	I	-	-	-
		2.4	I[e]	III	II	II	I	III	-	-	I	-	-	-
		3.0	III[g]	III	II	II	III	II	-	-	II	-	-	-
		3.6	III	II[f]	II	II	III	II	-	-	II	-	-	-
2% SDHS + 2% SDOS	15.20	0.0	-[d]	-	-	-	I	-	-	-	-	-	-	-
		0.6	I[e]	-	-	-	II	-	-	-	-	-	-	-
		1.2	II[f]	II	II	II	II	-	-	-	II	II	-	-
		1.8	II	II	II	-	II	-	-	-	-	-	-	-
		2.4	II	II	-	-	II	-	-	-	-	-	-	-
		3.0	II	-	-	-	II	-	-	-	-	-	-	-
		3.6	II	-	-	-	II	-	-	-	-	-	-	-
2% SDHS + 2% P 80	15.58	0.0	-[d]	-	-	-	-	-	-	-	-	-	-	-
		0.6	-	I	I	I	-	-	-	-	-	-	-	-
		1.2	I[e]	I	I	III	-	-	-	-	-	-	-	-
		1.8	I	I	III	II[f]	I	I	I	I	-	-	-	-
		2.4	I	III[g]	II	II	I	II	II	II	I	I	-	-
		3.0	I	III	II	II	I	II	II	II	I	I	-	-
		3.6	I	II	II	II	III	II	II	II	I	III	-	-
2% SDHS +2% C16 DPDS	43.83	0.0	-[d]	-	-	-	-	-	-	-	-	-	-	-
		0.6	-	-	-	-	-	-	-	-	-	-	-	-
		1.2	-	-	-	-	-	-	-	-	-	-	-	-
		1.8	-	-	-	-	-	-	-	-	-	-	-	-
		2.4	-	-	-	I	-	-	-	-	-	-	-	-
		3.0	-	-	I	I	-	-	I	I	-	-	-	-
		3.6	-	I[e]	I	III[g]	II[f]	I	I	I	-	-	-	-
3.6 wt% SDHS + 0.4 wt% C16 DPDS	22.09	0.0	-	-	-	-	-	-	-	-	-	-	-	-
		0.6	-	-	-	-	-	-	-	-	-	-	-	-
		1.2	-	-	-	I	-	-	-	-	-	-	-	-
		1.8	-	-	I	III	-	I	I	I	I	-	-	-
		2.4	-[d]	I	III	II	I	I	II	II	I	I	-	-
		3.0	I[e]	III[g]	III	II	I	III	II	II	I	III	-	-
		3.6	I	III	II[f]	II	I	III	II	-	I	II	II	II

[a] Calculated by using Davies Method (Lange, 1999; Tadros, 2005) [b]Wu et al., 2001 [c] Calculated by using linear mixing rule (Baran et al., 1994) [d] Assumed little or no oil solubilized within the micelle [e] Assumed microemulsion Type I [f]Assumed microemulsion Type II [g] Assumed microemulsion Type III

The surfactant system of 2 wt% SDHS + 2 wt% P80 performed better than the system of 2 wt% SDHS + 2 wt% C16 DPDS with the presence of both TBT and BuOH as shown in Table 4.3. This might due to steric repulsion caused by available monovalency of TBT with mixed anionic micelle while an addition of P80, a nonionic surfactant, reduced this steric effect and some microemulsions occurred.

4.2.2 Phase behavior study for alcohol selection

Phase behavior of the oil mixture of TBT/PCE at a mass ratio of 1.5 with the selected surfactant system under the presence of other alcohol types (isopropyl alcohol, tert-butyl alcohol, and n-pentanol) was studied. The study was carried out using the surfactant systems of 3.6 wt% SDHS & 0.4 wt% C16 DPDS with total alcohol concentration of 0 wt%, 1.6 wt%, 3.2 wt%, and 4.8 wt% and NaCl concentration of 2.4 wt%, 3.0 wt%, and 3.6 wt%. Tert-butyl alcohol (TBA) was chosen for further comparison with n-butyl alcohol (BuOH) due to its ability to form both Type II and III microemulsions as shown in Table 4.4. This selection was made based on criteria that the selected alcohol should have properties that can partition well into the oil phase. This requirement is likely to be met if the microemulsion type is w/o (Type II) or middle phase (Type III) microemulsion. In addition, TBA and BuOH can form both Type II and III microemulsion at high alcohol concentration which can promote neutral buoyancy. They can also form microemulsion at the salt concentration required for the selected surfactant system. Isopropyl alcohol is highly water soluble so it tends to stay in the water and form Type I microemulsion or at most Type III in which neutral buoyancy of oil phase is harder to be developed. For n-pentanol, even though it can form Type II but at high alcohol and salt concentration, it was not able to form microemulsion with the oil mixture.

Table 4.4 Phase behavior of the oil mixture with the surfactant systems of 3.6 wt% SDHS + 0.4 wt% C16 DPDS under different alcohol type and salt concentration**.**

Alcohol type	LogKow	wt % NaCl	60 wt% TBT+ 40 wt% PCE			
			wt % alcohol			
			0	1.6	3.2	4.8
Isopropyl alcohol	0.05[a]	2.4	I[e]	I	I	-[f]
		3.0	I	I	I	I
		3.6	I	I	III[g]	III
Tert- butyl alcohol	0.35[b]	2.4	I	I	I	I
		3.0	I	I	I	III
		3.6	I	I	III	II[h]
n-butyl alcohol	0.88[c]	2.4	I	I	-	-
		3.0	I	III	-	-
		3.6	I	II	II	II
n-Pentanol	1.51[d]	2.4	I	I	I	I
		3.0	I	III	-	-
		3.6	I	II	II	-

[a-d] National Center for Biotechnology Information, 2012 [e] Assumed microemulsion Type I [f]Assumed little or no oil solubilized within the micelle [g] Assumed microemulsion Type III [h] Assumed microemulsion Type II

4.3 PSEUDOTERNARY PHASE DIAGRAMS

A ternary phase diagram is generally used to represent phase behavior of the three component system since it can display the complex relationship among the compositions when changing one component affect the overall behavior and relative composition (Bourrel and Schechter, 1988). The system under investigation of this study consisted of six components; 1) TBT, 2) PCE, 3) alcohol, 4) surfactant, 5) water, 6) NaCl. Therefore, it might be difficult to portray the real behavior as originally intended by the true ternary diagram. Therefore, the main emphasis in constructing the diagram was on phase conversion over a wide range of relative composition of the system since we need to minimize the risk associated with vertical migration which occurred when the oil in the system was DNAPL.

The pseudo ternary phase diagrams in this study were used to approximately represent the phase behavior of the mixed oil (60 wt% TBT and 40 wt% PCE) under different alcohol and surfactant concentration. The mixed oil was represented as one pseudo phase on one vertex; and the 4 wt% total surfactant (3.6 wt% SDHS + 0.4 wt% C16DPDS + 3 wt% NaCl) was represented as another pseudo phase on another vertex.

The pseudoternary phase diagrams in this study were plotted using a spreadsheet program called TRIPLOT (Graham and Midgley, 2000). The three vertices of the diagrams were an oil mixture of TBT-PCE (at a mass ratio of 1.5), an alcohol (either TBA or BuOH), and a surfactant brine solution with 4 wt% total surfactant concentration (3.6 wt%SDHS and 0.4 wt% C16DPDS at 3 wt% NaCl).

Each diagram represented phase behavior of the oil mixture under a wide range of relative composition of mixed oil, surfactant solution, and alcohol. Figure 4.4a and 4.4b were obtained from systems having TBA and BuOH as density modifying agents, respectively. The area labeled DNAPL and LNAPL represent the system with two phases in which the oil phase was DNAPL and LNAPL, respectively. The white area labelled 1φ indicated that there was only one miscible phase at that overall composition. The results showed that the surfactant system with BuOH produced larger LNAPL region than the one with TBA. This suggested the lower risk of vertical migration by the system using BuOH than the system using TBA as we can see from the trend of the dash line in the diagram. The dash line (- - -) represent the overall composition as 4% surfactant solution was gradually added to the starting combination of alcohol to mixed oil at volume ratio of 0.6:0.4. BuOH also had been reported to produce a bigger microemulsion formation area than other alcohols (ethanol, isopropyl alcohol, 1-propanol) with soybean oil and surfactants (Brij58, Span 80) by Kantarci et al. (2002).

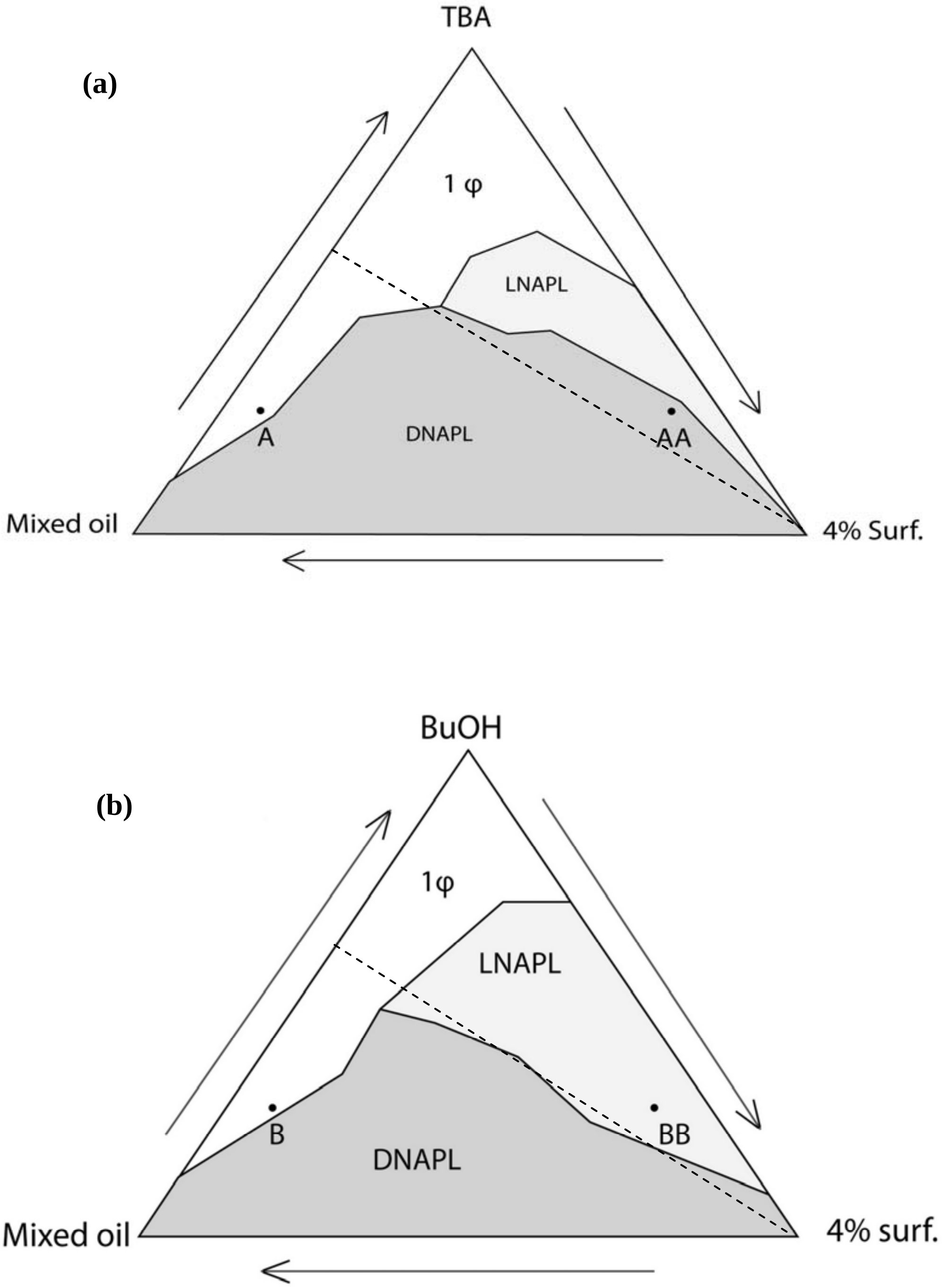


Figure 4.4 Pseudo ternary phase diagrams expressing phase behavior of the mixed oil (60 wt% TBT and 40 wt% PCE); the 4wt% surfactant brine solution (3.6 wt% SDHS + 0.4 wt% C16DPDS at 3 wt% NaCl) and; two types of alcohols TBA (a) and BuOH (b) where A, AA and B, BB are the points at the same composition, respectively. The dash line (----) represents the overall composition as 4% surfactant solution was gradually added to the starting combination of alcohol to mixed oil at volume ratio of 0.6:0.4.

The two diagrams also showed that as an alcohol concentration of the two systems having different alcohol (TBA vs BuOH) are equally fixed, the newly formed phases after the ratio of mixed oil to 4% surfactant were changed could be different. This can be seen from point A and B to point AA and BB in Fig. 4.4a & b (same composition but scanning from one point to other shows different transitions and phases). Factors that might contribute to these differences in phase behaviors are discussed in the following section.

4.4 EFFECT OF ALCOHOL TO SURFACTANT RATIO

This study compared the effects of alcohol type and alcohol to surfactant mass ratio (0, 0.4, 0.8, 1.0, 1.2, and 1.6) at total surfactant concentration of 2 wt% and 4 wt% on oil phase density modification and solubilization of TBT and PCE in the aqueous phase. In this experiment, the investigated surfactant systems were the mixture of SDHS and C16DPDS at the constant mass ratio of 9:1 (i.e. 3.6 wt% SDHS : 0.4 wt% C16 DPDS) and 3 wt% NaCl.

4.4.1 Effect on solubilization

4.4.1.1 PCE preferential solubilization

Solubilization behavior of TBT and PCE in the same surfactant system having TBA and BuOH had some similarity and differences. Figure 4.5 shows that the surfactant system with an addition of both TBA and BuOH influenced PCE preferential solubilization (all points above the dashed line indicate that PCE tends to partition into the surfactant solution and hence the TBT/PCE mass ratio in excess oil phase has increased from the initial ratio). This preference occurred even without alcohol added but it was more pronounced with the addition of TBA at higher total surfactant concentration than that when BuOH was used. Factors that govern the solubilization of the oil into surfactants solution can be from the oil properties as well as properties of the aqueous solution. However, compared to similar study on solubilization behavior of the mixture of PCE and dibutyltinchloride (DBT) in the similar surfactant system by Damrongsiri et.al (2010), the result at some extent is comparable. Their results reveal that the organometallic DBT preferred to solubilize in the surfactant solution more than those of the chlorinated solvent PCE. It indicated that the main factor contributing to this difference in organometallic and chlorinated solvent preferential solubilization were their hydrophobicity and polarity. In their oil mixture, DBT had higher polarity than PCE but the oil mixture in this study TBT has higher hydrophobicity than PCE. Therefore polarity of organometallic compounds plays an important part in their solubilization behaviors similar to that of other organic compounds.

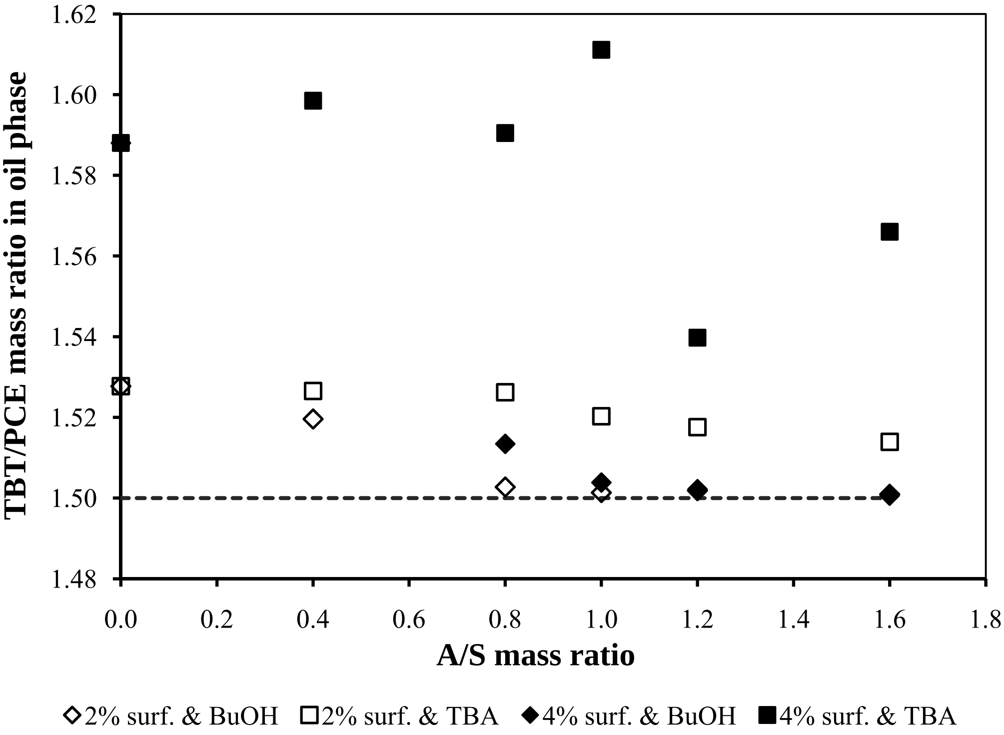


Figure 4.5 Mass ratio of TBT/PCE in the oil phase over a varying alcohol to surfactant (A/S) mass ratio using 2 wt% total surfactant concentration (1.8 wt% SDHS + 0.2 wt% C16DPDS at 3 wt% NaCl) and 4 wt% total surfactant concentration (3.6 wt% SDHS + 0.4 wt% C16DPDS at 3 wt% NaCl); and the dashed line represents the initial mass ratio of TBT/PCE in the mixed oil (0.6:0.4)

4.4.1.2 Solubilization capacity

The effect of A/S ratio can be seen in more details from the plot shown in Figure 4.6 a) and b). Solubility of both TBT and PCE gradually decreased as A/S ratio increased when BuOH was used as a density modifier but limited effect was observed for the system with TBA. This might be due to the fact that BuOH has higher log Kow than TBA, 0.88 vs 0.35, respectively (NCBI, 2012) and it had higher tendency to form w/o microemulsion. As the A/S increased the more surfactant in the system with BuOH would be incorporated into reverse micelle to form Type II microemulsion in the oil phase resulting in lower solubilization of the mixed oil. In addition, as A/S ratio increased, the volume of oil phase increased when BuOH was used as a density modifier more than when TBA was used. This indicates that BuOH is a better enhancer than TBA for w/o microemulsion formation of the mixed oil of TBT and PCE. This effect was also similar to a study done by Azira et.al which studied the effect of A/S ratio, using BuOH as an alcohol, on phase behavior of decane. It showed that at solution with higher A/S, type II microemulsion was a dominant phase (Azira et al., 2008).

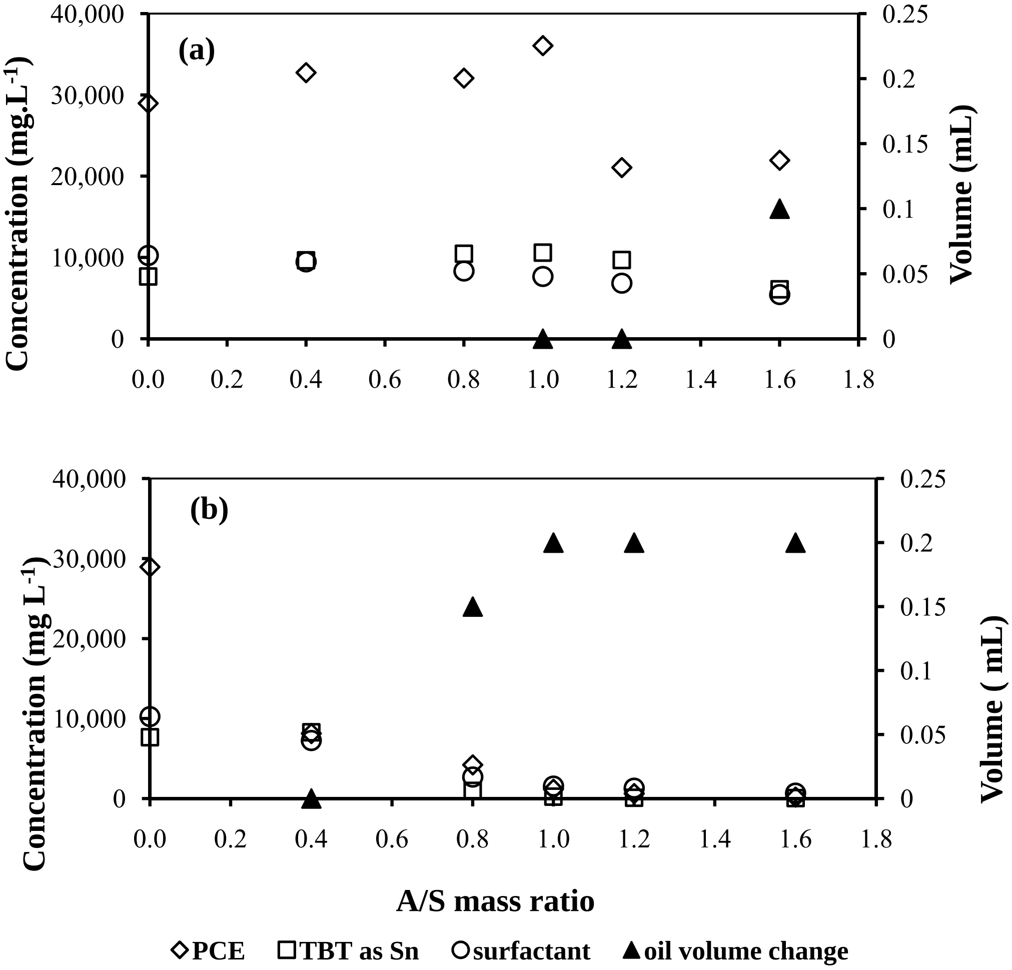


Figure 4.6 Effect of alcohol to surfactant (A/S) mass ratio on aqueous solubilization of PCE (◊), TBT (□), surfactant (○), and oil volume change (▲) in the system of 4% total surfactant brine solution (3.6 wt% SDHS + 0.4 wt% C16DPDS at 3 wt% NaCl) with an addition of two alcohols; TBA (a) and BuOH (b), respectively.

4.4.2 Effect on density modification

The results from solubilization study were coherent with the phase diagram on the fact that at high alcohol in the system, BuOH exhibited better performance for reducing TBT/PCE mixed oil density. In Figure 4.7 it was observed that both TBA and BuOH caused lower oil density when higher surfactant concentration was used (4 wt% vs 2 wt%) and both alcohols did not show much difference in oil density modification at low A/S ratio. However, BuOH caused lower oil density at high A/S ratio (1.6). This result showed that even though BuOH has higher density than TBA (0.81 g.mL^{-1} vs 0.78 g.mL^{-1} , respectively), but water volume that BuOH brought into the oil phase by w/o microemulsion formation was one more factor contributing to oil phase density reduction.

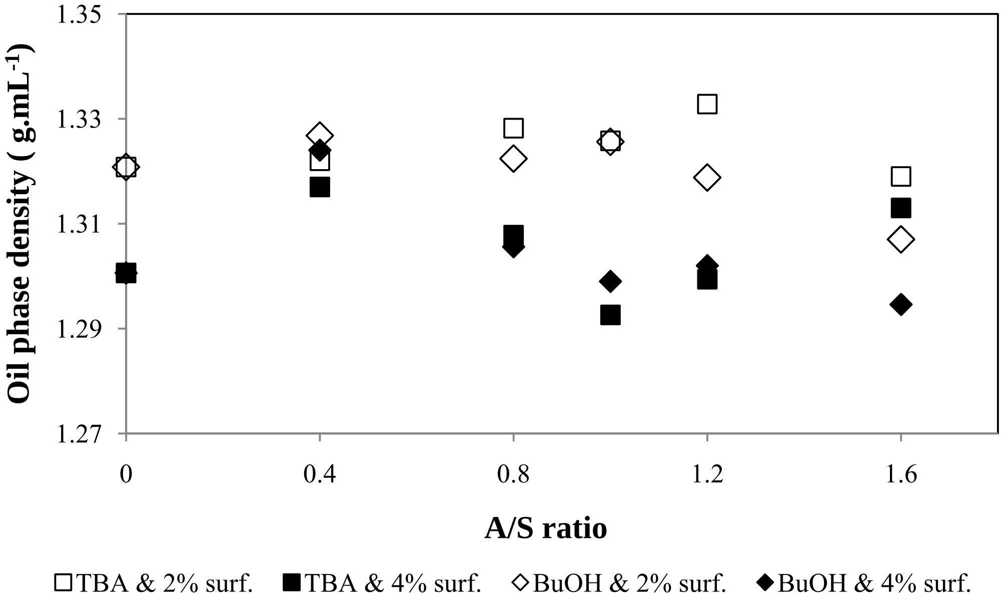


Figure 4.7 Oil phase density modification by TBA and BuOH at different mass ratio of alcohol to surfactant (A/S) using 2 wt% total surfactant concentration (1.8 wt% SDHS + 0.2 wt% C16DPDS at 3 wt% NaCl) and 4 wt% total surfactant concentration (3.6 wt% SDHS + 0.4 wt% C16DPDS at 3 wt% NaCl)

4.5 CONCLUSIONS

Flushing solution containing BuOH could be an advantage if mobilization would be used as a main removal mechanism since it produced larger LNAPL region in the pseudo ternary diagram rendering less risk associated with vertical migration of DNAPL. It also produce higher density reduction potential at high alcohol to surfactant ratio with lower solubilization in the aqueous phase requiring less downstream water treatment. Nevertheless the lower water solubility of BuOH has to be taken into account for designing delivery process into the subsurface. However, using TBA might be an advantage if an interest was put on higher solubilization capacity of flushing solution containing TBA and higher miscibility region it produced in pseudo ternary diagram.

Since it was shown that TBA and BuOH had both advantages and disadvantages, it is suggested that both of them should be further investigated by column study. The system with A/S ratio of 1.2 for both alcohol were selected for further study in column study to see the effect of continuous flow on the ability to modify oil phase density. The rationale for this selection based on their similar density modifying capability at this ratio but different solubilization capacity at different surfactant concentration. Therefore the performance in the continuous flow system with the chance of surfactant fluctuation can be studied in comparison to their phase behaviors.

CHAPTER V

CONTINUOUS FLOW STUDY

Advantages of both TBA and BuOH were demonstrated from the outcome of previous study. If mobilization would be the main removal mechanism, BuOH had an advantage over TBA for density modification but lower water solubility of BuOH had to be accounted for in designing delivery process into the ground. If solubilization would be under focused as a mechanism for site remediation, TBA had more advantage over BuOH. Nevertheless, it was shown that TBA and BuOH had both advantages and disadvantages, and it was suggestible that both of them should be further investigated by column study. The continuous flow study were performed in both single step flushing and two-step flushing. The first three columns applied single step flushing and the other three columns applied two-step flushing. The surfactant system under investigation for all six columns was 3.6% SDHS + 0.4 wt% C16DPDS at 3 wt% NaCl. Alcohol types and concentrations were varied to explore the possibility of density modification of mobilized NAPL to mitigate downward vertical migration.

5.1 SINGLE STEP FLUSHING: COMPARISON BETWEEN SURFACTANT SOLUTION WITH AND WITHOUT ALCOHOL ADDITION

Three column studies had been carried out to study removal mechanisms, removal efficiency, and oil density modification of single step flushing of which only surfactant was applied in column I while TBA and BuOH were added in column II and III, respectively. The details for each column were as follows: column I) 4 wt% total surfactant (3.6 wt% SDHS + 0.4 wt% C16DPDS); column II) 4 wt% total surfactant (3.6 wt% SDHS + 0.4 wt% C16DPDS) + 4.8 wt% tert-butanol (TBA) ; and column III) 4 wt% total surfactant (3.6 wt% SDHS + 0.4 wt% C16DPDS) + 4.8 wt% n-butanol (BuOH). All columns were performed at 3 wt% NaCl. The alcohol concentration of 4.8 wt% (A/S ratio = 1.2) was applied based on results from batch study that BuOH and TBA had similar performance at this ratio while showing high oil density reduction so the effect of continuous flow condition can be elucidated.

5.1.1 Removal of TBT and PCE from TBT-PCE oil mixture

Removal mechanisms and behavior of TBT and PCE were reported separately to study their preferential characteristic as found in the PCE preferential solubilization in the batch study. Figure 5.2 shows removal of TBT (a-c) and PCE (d-f) as solubilization relative to the highest solubilization and mobilization relative to the highest mobilization obtained from the study. The highest solubilization for TBT and PCE came from the batch study on solubilization at an alcohol to surfactant mass ratio of 1.2 (4.8 wt% alcohol). The highest mobilization per unit time came from column II with TBA addition.

The solubilization capacities of the three columns were such that TBT had highest solubilization in the system with TBA while PCE had highest solubilization in the system with only surfactant (as can be seen comparatively from number in each box of Figure 5.1a - f). This relative performances were similar to the results from batch study but the extent of solubilization in column I and II were lower than batch study while solubilization in column III was higher in column study than batch study. This might be the result from some preconditioning of the residual oil with BuOH during mobilization period since the solubilization of column III occurred after significant amount of mixed oil was removed by mobilization. Even though the flushing solution with BuOH addition yielded higher solubilization in column study than batch study, the extent of solubilization was still small. It benefit could better lie on polishing of residual NAPL after mobilization than using solubilization as main removal mechanism.

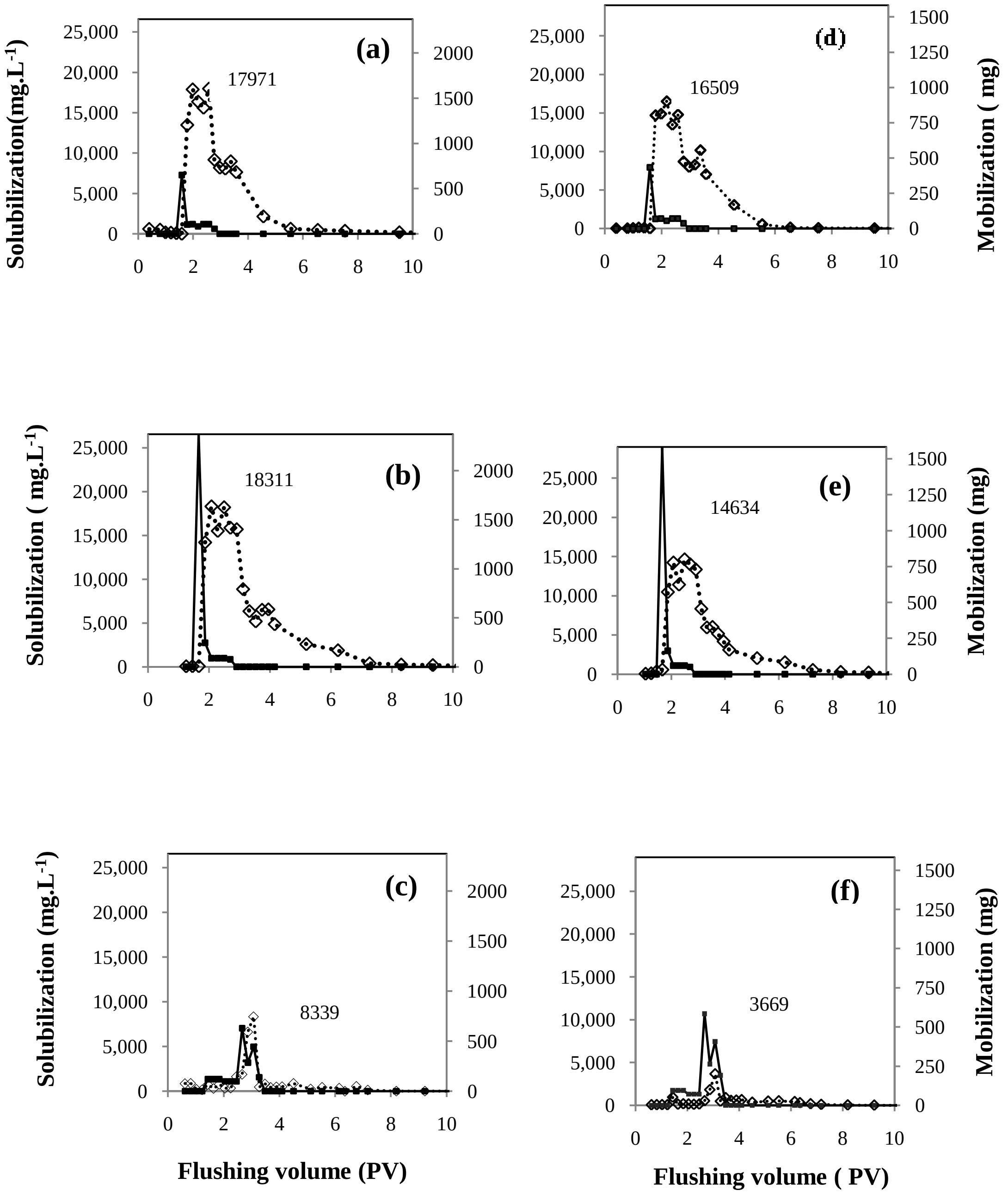


Figure 5.1 Solubilization (◊) and mobilization (■)of TBT **(a-c)** and PCE**(d-f)** during the flushing period from column I using 4 wt% total surfactant (3.6% SDHS + 0.4 wt% C16DPDS at 3 wt% NaCl) **(a,d)**; from column II using 4 wt% total surfactant + 4.8 wt% TBA **(b,e)**; and from column III using 4 wt% total surfactant +4.8 wt% BuOH **(c,f).**

Considering another removal mechanism, mobilization of the system with TBA and BuOH showed some differences. The amount of mobilized NAPL was highest at initial contact of surfactant front for the two systems of only surfactant and with TBA addition. For the system with BuOH addition, the mobilized NAPL was slowly released during initial contact with the surfactant front and the majority of mobilized oil came out in the later stage between 2.6th to 3.2th pore volume (PV). This might indicate that surfactant and BuOH were initially partitioned into the oil phase and form type II microemulsion. The good performance of BuOH in microemulsion formation was also found by a study carried out on dodecane by Choi et al. (1999). They found out that BuOH could penetrate into the lecithin interfacial layer between oil and water better than 1-propanol causing the reduction in film rigidity and the ease in microemulsion formation. This mobilization pattern of the system of BuOH might be an advantage in case of accident, the extent of damage would be minimized.

Comparing with phase behavior results of batch study, the results from column study suggested that alcohol partitioning into the NAPL phase were less than those at the equilibrium in the batch study. This can be seen by observation of middle phase microemulsion formation. From phase behavior study of the surfactant system of 3.6 wt%SDHS and 0.4 wt% C16DPDS at 3 wt% NaCl, TBA caused the middle phase microemulsion at 4.8 wt% alcohol, while BuOH produced middle phase microemulsion at 1.6 wt% alcohol. In the column studies running with 4.8 wt% alcohol for both TBA and BuOH, middle phase microemulsion was observed only in the column with BuOH. Since 1.6 wt% BuOH was needed to form middle phase microemulsion in the batch study, it was suggested that about three times of alcohol concentration at equilibrium was needed to be presented in the column to produce similar phenomena. Thus it was further suggested that increasing the TBA addition to about 14.4 wt% should produce similar outcome as with 4.8 wt% BuOH.

5.1.2 Density profiles of mobilized NAPL phase

Density modification by the three columns had different characteristics as shown in Figure 5.2. Mobilized NAPL from column I, using only surfactant, was eluded out in a closer range of density than mobilized NAPL from column II and III, having TBA and BuOH addition, respectively. The density of mobilized NAPL from column I was in a range of 1.274 - 1.312 g.mL^{-1}, while mobilized NAPL from column II and III were in a range of 1.194 - 1.311 g.mL^{-1} and 1.029- 1.275 g.mL^{-1}, respectively. The amount of mobilized NAPL from column I was quite stable over mobilization period while the majority of mobilized NAPL from column II, 3.956 g out of total 4.936 g, came out at one time with the highest density of 1.3112 g.mL^{-1}. Mobilized NAPL from column III came out in three ranges of density with the majority of NAPL, 3.102 g out of total 4.695 g, was removed within the density range of 1.1728-1.1696 g.mL^{-1} which was lower than mobilized NAPL from column II. This indicated that addition of BuOH in the flushing solution performed better than TBA as a density modifying agent. However, NAPL produced from the system with BuOH in the later stage of mobilization period were viscous and might obstruct the flow of flushing solution in the real application.

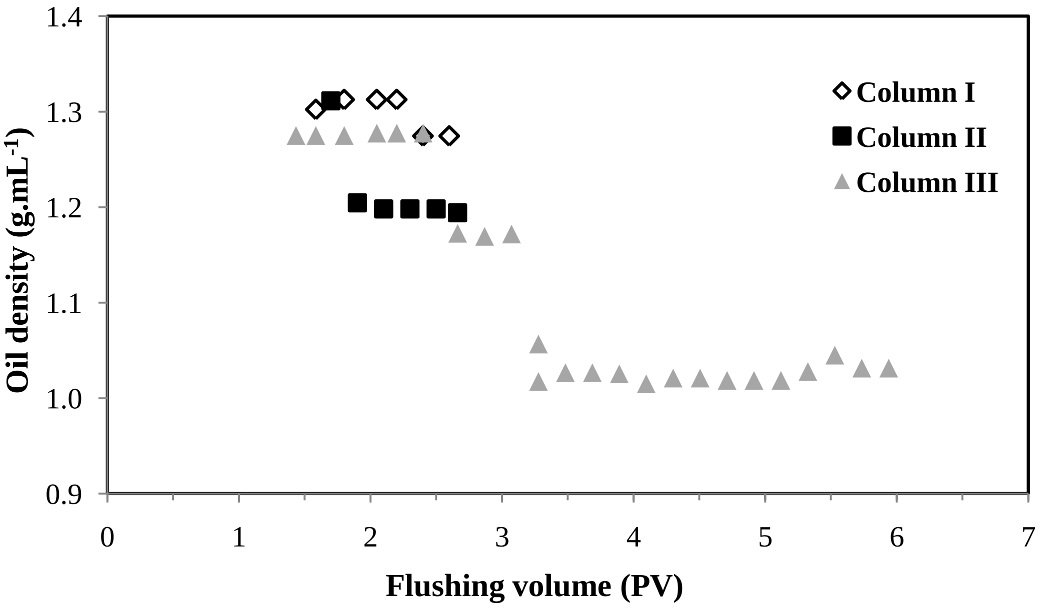


Figure 5.2 Density of free oil phase mobilized from column I using 4 wt% total surfactant (3.6% SDHS + 0.4 wt% C16DPDS at 3 wt% NaCl) **(♦)**; column II using 4 wt% total surfactant +4.8 wt% TBA **(■)**; and column III using 4 wt% total surfactant +4.8 wt% BuOH **(Δ)**. All mobilized oil samples are denser than aqueous phase (DNAPL).

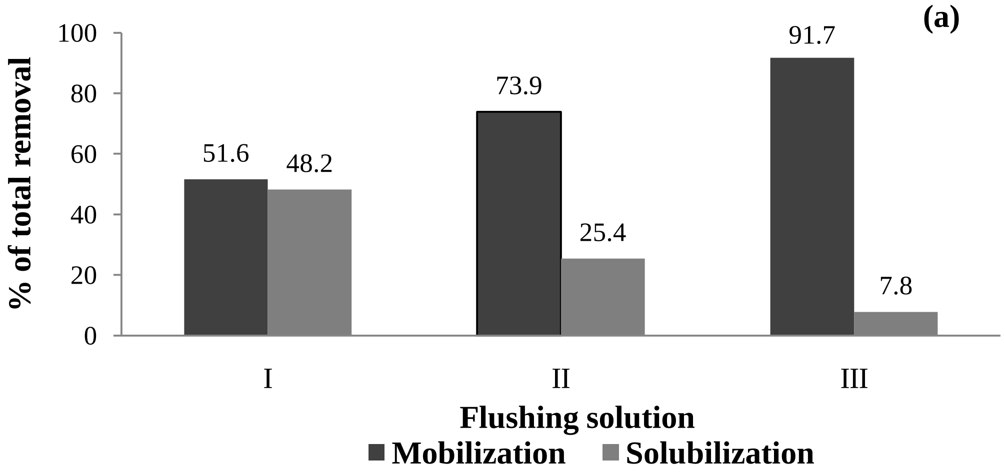
Considering relative density, mobilized NAPL from all three columns were denser than aqueous phase (DNAPL) with the conclusion that addition of 4.8 wt% BuOH could modified the density of mobilized NAPL better than an addition of 4.8 wt% TBA and with only surfactant. This might came from the fact that the majority of mobilized NAPL from column III came out at a later time than the other two columns so BuOH could be partitioned into NAPL phase over the longer period of time resulting in lower density of mobilized NAPL.

5.1.3 Removal mechanism of TBT and PCE

It was shown from results of the three column studies that removal mechanisms of PCE and TBT were different among the three flushing solutions. Similar trends were observed for PCE and TBT in increasing mobilization from no alcohol addition to with TBA and BuOH addition (Figure 5.3). It can be seen from increasing removal percentage of mobilization from 51.6% to 73.9% to 91.7% for TBT, and from 44.3% to 68.7% to 94.8% for PCE, respectively. These percentages were calculated based on a mass basis of total removal (mobilization and solubilization were added up to 100%, and mass balance for all columns can be seen in Appendix B). When alcohols were added, interfacial tension between the aqueous and NAPL phase were further decreased overcoming capillary force that held saturated NAPL within the pore space, resulting in more mobilized NAPL detached from the column. BuOH is more hydrophobic than TBA and likely to partition into the NAPL phase than TBA. As a result, the overall NAPL mass impacted by this interfacial tension reduction was higher with BuOH addition than with TBA addition resulting in relatively higher mobilization than solubilization as a removal mechanism.

Impact of solubilization reduction by addition of alcohol was also observed by Kostarelos et al. (1998). In their study, addition of isopropanol into the surfactant system of 4 % SDHS also reduced solubility of trichloroethylene from 5.9% to 3.3%. There was no mobilization visually observed since they also added xanthan gum to increase viscosity and their NAPL was applied in a spilled manner with about 2% residual saturation comparing with this study with average residual saturation about 16%. In addition, isopropanol is hydrophilic so it tended to stay in aqueous phase than partition into the NAPL phase as TBA and BuOH.

In the system with TBA addition from batch study, TBT had less solubilization than PCE at high surfactant concentration; while in the system with BuOH addition, TBT and PCE had about equal affinity for solubilization at high alcohol to surfactant ratio. For column study, the same trend applied that the system with BuOH helped solubilized both TBT and PCE out in the same proportion as in the mixed oil. This indicated that BuOH enhanced TBT solubilization relative to PCE more than TBA. It might be possible that BuOH help shielding the polar portion of TBT so that TBT can stay deeper into the core region and increase the amount of TBT within the micelle.



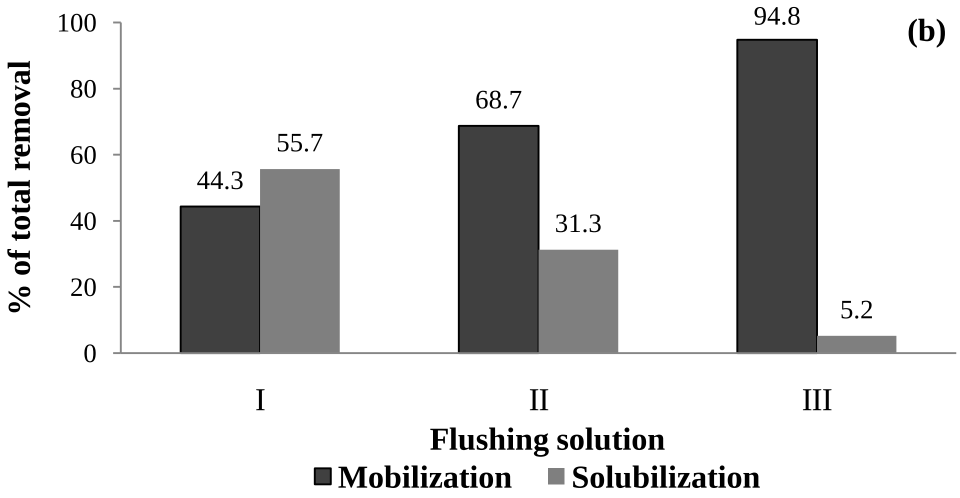


Figure 5.3 Removal mechanisms of TBT **(a)** and PCE **(b)** from column study using three different flushing solutions. Column I used 4 wt% total surfactant (3.6% SDHS + 0.4 wt% C16DPDS at 3 wt% NaCl) ; column II used 4 wt% total surfactant +4.8 wt% TBA ; and column III used 4 wt% total surfactant +4.8 wt% BuOH

From the study results, it was shown that addition of TBA and BuOH in the flushing solution and carried out flushing in a single step could not reduced the density of mobilized NAPL to be lower than the density of aqueous phase. As a result, the risk of downward vertical migration was still applied and further risk minimization was needed. Even though the system with BuOH had better performance in term of density modification, the higher volume of mobilized NAPL and some viscous phase produced at the later stage of mobilization was still a concern. Therefore, the two-step flushing was further investigated for both TBA and BuOH.

5.2 TWO-STEP FLUSHING

Further investigation of TBA and BuOH as a density modifying agent were performed in two-step flushing. The first step was applied to adjust the density of oil phase in situ while the second step was aimed to remove the density modified oil from the sand pore space. Before the column studies were carried out, alcohol partitioning were studied for both TBA and BuOH to identify the appropriate alcohol concentration in the flushing solution of the first step. The NaCl solution of 3 wt% was used as a base solution since this salt concentration was optimal for microemulsion formation with the mixed oil under studied (60 wt% TBT and 40 wt% PCE) and would also be applied in the second step flushing with surfactant addition.

5.2.1 Selection of alcohol concentration to modify NAPL phase density by in situ alcohol partitioning

Variation of alcohol to mixed oil ratios were used as initial compositions in the batch study. Each composition were mixed thoroughly with equal volume of 3 wt% NaCl solution and left for 24 hours to reach equilibrium. Density modification and chemical composition of both oil and aqueous phase were determined.

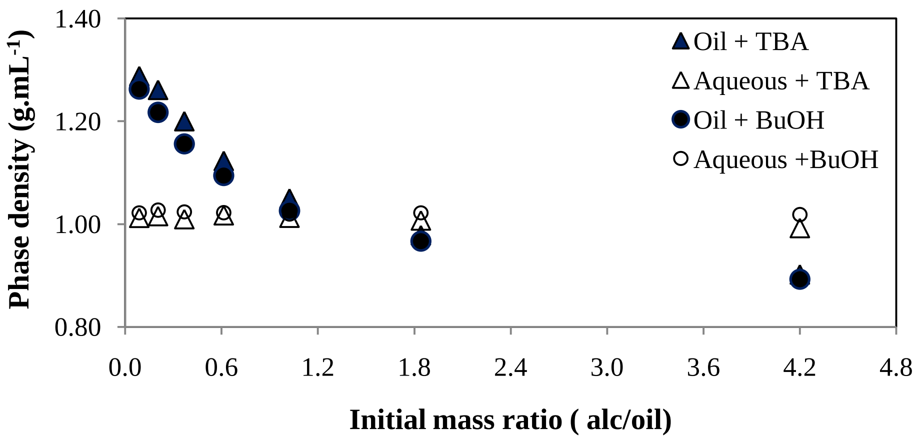


Figure 5.4 Density profiles of oil phase with TBA (▲); oil phase with BuOH (●); aqueous phase with TBA (Δ); and aqueous phase with BuOH (○) showing initial proportions of alcohol and oil that cause phase conversion from DNAPL to LNAPL.

From Figure 5.4, the NAPL phase density for both TBA and BuOH were sharply decreased between the initial alcohol to oil ratios of 0 to 1.0 and gradually decreased when it approached neutral buoyancy at the ratio of 1.8. Further increase of initial alcohol to oil ratio from 1.8 to 4.2 also decreased the NAPL phase density gradually. The NAPL phase density with TBA and BuOH as a density modifying agent at the initial mass ratio of 1.8 were 0.9784 and 0.9666 g.mL^{-1}, respectively.

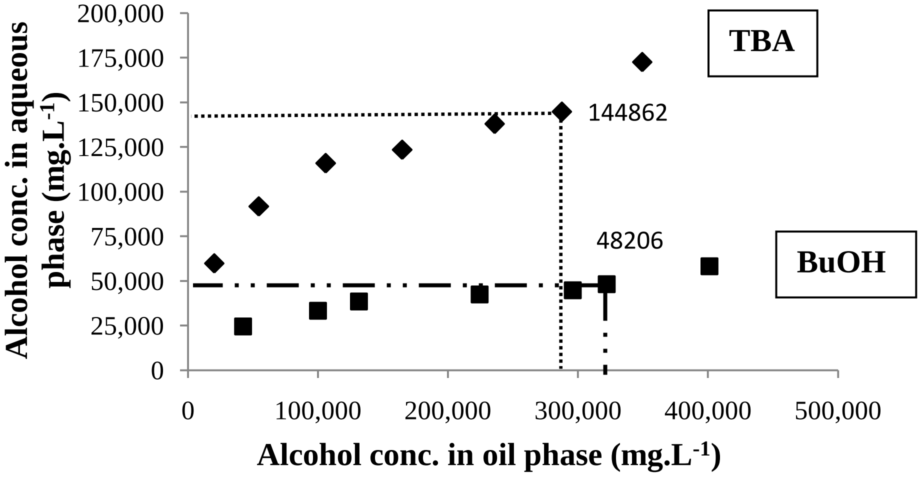
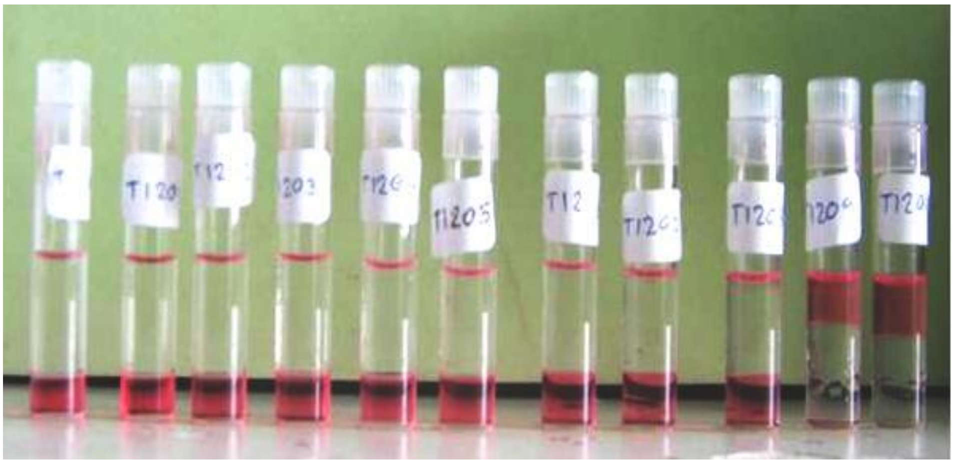


Figure 5.5 Alcohol partitioning curve of TBA and BuOH showing alcohol concentration in aqueous phase and oil phase. The dashed lines indicate alcohol concentration at the equilibrium where phase conversion from DNAPL to LNAPL with relative density approach neutral buoyancy for both alcohol types.

Figure 5.5 showed that the required TBA concentration in the aqueous phase to maintain phase conversion from DNAPL to LNAPL were higher than BuOH with the concentration about 14.5 wt% versus 4.8 wt% for BuOH. Their partitioning coefficients resulting from calculating their equilibrium concentration in the oil phase over aqueous phase at this initial ratio were 1.98 for TBA and 6.68 for BuOH. This suggested that BuOH was more efficient as a partitioning alcohol and a density modifying agent than TBA. However, performance in the continuous flow study might be different from batch study. Therefore, the brine solution with 14.5 wt% TBA and 4.8 wt% BuOH were selected as a basis for comparison in continuous flow mode of two step flushing scheme.

The alcohol concentrations in the second step were estimated based on an experiment carrying out to see the effect of alcohol back partitioning. The density modified mixed oil (LNAPL) with an alcohol to oil volume ratio of 1.6:1.0 were equilibrated with 4 wt% surfactant solution (3.6 wt% AMA+ 0.4 wt% Dowfax) containing different alcohol concentrations. The initial NAPL phase density resulting from mixing with equal alcohol to oil volume ratio of 1.6 were 0.9167 g.mL^{-1} for TBA and 0.9668 g.mL^{-1} for BuOH. From Figure 5.6, the minimum TBA concentration in the surfactant solution that could prevent phase conversion from LNAPL to DNAPL were 18 vol% (14 wt%), while it seemed that no phase conversion was observed in the oil of which density modified by BuOH even at 0% alcohol in the surfactant solution. The concentration of 16 vol% (12.5 wt%) was selected for TBA to compensate for the different initial oil density from the alcohol partitioning experiment which was 0.9784 g.mL^{-1}, while the concentration of 4 vol% (3 wt%) was selected for BuOH since there was some translucent observed in the oil phase indicating partitioning of surfactant and water into the oil phase which might help stabilize the phase density.

a)



b)

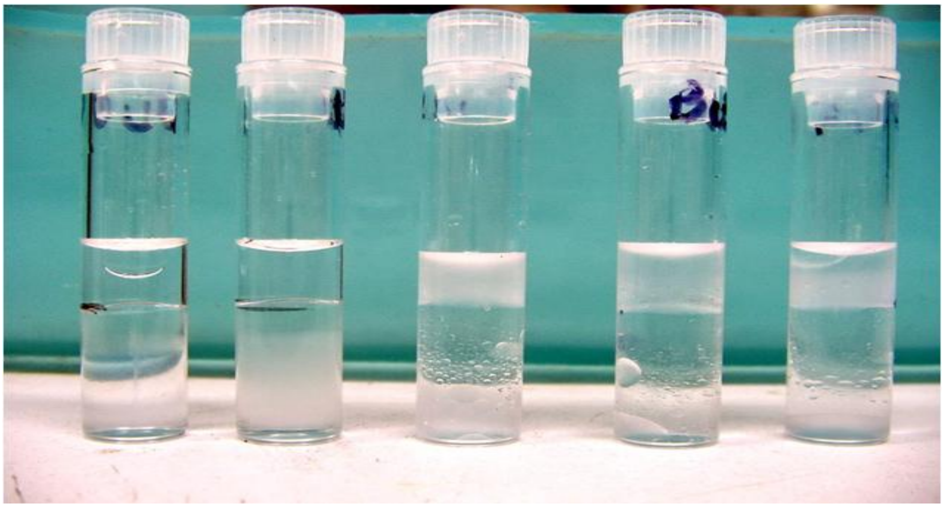


Figure 5.6 Effect of alcohol addition (volume %) in the 4 wt% surfactant solution (3.6 wt% AMA+ 0.4 wt% Dowfax) on prevention of alcohol back partitioning of TBA **a)** and BuOH **b)** from the density modified oil.

5.2.2 Two step flushing with TBA and BuOH as a density modifying agent

The brine solution of 3 wt% NaCl with 14.5 wt% TBA and 4.8 wt% BuOH were applied in the first step of continuous flow study to modify the density of mixed oil (60 wt% TBT and 40 wt% PCE) in the sand column with the residual saturation of 16.7% and 15.8%, respectively. Phase densities during mobilization period were measured for both NAPL and aqueous phase to compare their relative density over the mobilization time course. This observation would help to elucidate the difference in partitioning behavior between the two alcohols. Chemical compositions in the effluent and in the mobilized NAPL were also analyzed to investigate the removal pattern of TBT and PCE by both solubilization and mobilization mechanisms as a function of flushing volume.

5.2.2.1 Two-step flushing with TBA as a density modifying agent

The TBA two-step flushing, column IV, applied two step flushing scheme by pre-flushing with 14.5 wt% TBA + 3 wt% NaCl and following by the second step flushing solution of 3.6 wt% SDHS + 0.4 wt% C16DPDS + 3 wt% NaCl + 12.5 wt% TBA. During the first step, TBA and PCE concentration was monitored and the first step of pre-flushing with alcohol was terminated when there was some increase in PCE concentration in the aqueous effluent. From this study, the time it took for the first step of alcohol partitioning was about 15 pore volumes. After that, the flushing solution was changed to the surfactant solution and sample collections from column effluent were continued. The system performance was observed in both steps with the focus on the ability of TBA on modification of mobilized NAPL and the system characteristics during the mobilization period. During the mobilization period, NAPL phase was mobilized from the column together with aqueous phase in the effluent. The mobilized NAPL and the aqueous phase were separated immediately after sample collection. Chemical compositions in the aqueous effluent and in the mobilized NAPL phase were analyzed for TBT, PCE, and TBA. Phase densities were measured for both mobilized NAPL and aqueous phase. Concentration profiles of TBT and PCE were compared in respect to TBA concentration pattern and flushing time course. Relative phase densities of aqueous effluent and mobilized NAPL were explored over time course of mobilization.

5.2.2.1.1 System characteristics for the whole continuous flow study period

System characteristics of the TBA two-step flushing for the whole continuous flow period was shown in Figure 5.7. The concentration pattern of TBA, TBT, and PCE in the aqueous effluent in respect to flushing volume were observed. During the first step flushing, TBA concentration in the effluent was sharply increased between the 1st and 2nd PV and was quite stable afterwards. . After about 15 pore volume (14.9 PV) of flushing with 14.5 wt% TBA solution, the flushing solution was changed to the surfactant solution with 12.5 wt% TBA. Mobilized NAPL was detected in the effluent at the 15.9th PV which was about the time that the surfactant front would come out. This indicated that the mobilization process occurred at the initial contact between the residual oil and surfactant flushing solution. The mobilization period lasted for about 1.3 PV from the 15.9th to the 17.2th PV. Since this experiment focused on density modification of mobilized NAPL, the flushing was stop at the 18th PV where only small PCE was detected in the effluent. Analysis of TBT concentration required prior digestion so it was carried out later in the experiment.

From Figure 5.7, TBA concentration was decreased from the 14.4th to 15.9th PV indicating of alcohol partitioning into the oil phase. However, TBA concentration in the effluent was increased during the mobilization period. This additional TBA could be a result partially from the 12.5 wt% TBA concentration in the second step flushing solution and partially from back partitioning from the density modified NAPL. During mobilization period, PCE was the main solubilized specie in the effluent indicating of its preferential solubilization in the surfactant solution as observed in the batch study. At the later stage of mobilization period, PCE concentration in the effluent was small and the main solubilized specie in the effluent became TBT. The drawback of the TBA two- step flushing was that there was some mobilized NAPL detected during the 1th and 4th PV as the initial contact of TBA pre-flushing solution with the residual oil occurred. The density of this mobilized DNAPL was 1.264 g.mL^{-1} and % removal was accounted for 21.68 wt% and 3.64 wt% from total removal of PCE and TBT, respectively.

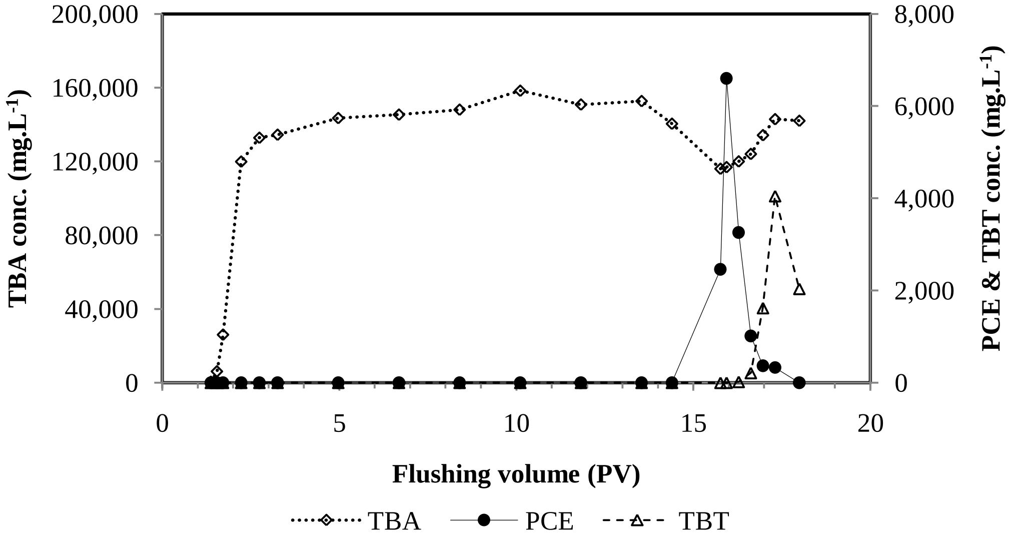


Figure 5.7 Composition profiles from the column with TBA two step flushing (pre-flushing with 14.5 wt% TBA and following by 3.6 wt% SDHS + 0.4 wt% C16DPDS + 3wt% NaCl + 12.5 wt% TBA) showing TBA (◊), PCE (●) , and TBT (▲) concentration in the aqueous effluent.

5.2.2.1.2 System characteristics during mobilization period

System characteristics during mobilization period were shown in Figure 5.8(a-b) as relative density of mobilized NAPL to aqueous phase and as concentration of TBA, TBT, and PCE in the mobilized NAPL. Surfactant and aqueous phase was calculated by subtraction of TBA, TBT, and PCE mass from total mobilized NAPL mass of each sample. The mobilization period lasted for about 1.3 PV (15.9 th-17.2th PV) by which the mobilized NAPL density slowly reduced from 1.089 to 1.0035 g.mL^{-1} but they were still denser than aqueous phase. The gradual decreasing of mobilized NAPL phase over the mobilization period suggested the TBA partitioning from the aqueous phase to the mobilized NAPL. However, the pattern of changing composition in the mobilized NAPL phase should also be considered. The decreasing of mobilized NAPL density from the 15.9th PV to 16.3th PV correspond to the decreasing of TBT and PCE concentration in the NAPL phase while the TBA concentration was quite stable. From the 16.3th PV to 16.8th PV, the TBT, PCE, and TBA concentration were quite stable but the density of mobilized NAPL was increased due to some increase of surfactant and aqueous phase in the NAPL phase.

Therefore, the changing composition of mobilized NAPL other than the alcohol concentration had to be taken into account for density modification capacity of the flushing system.

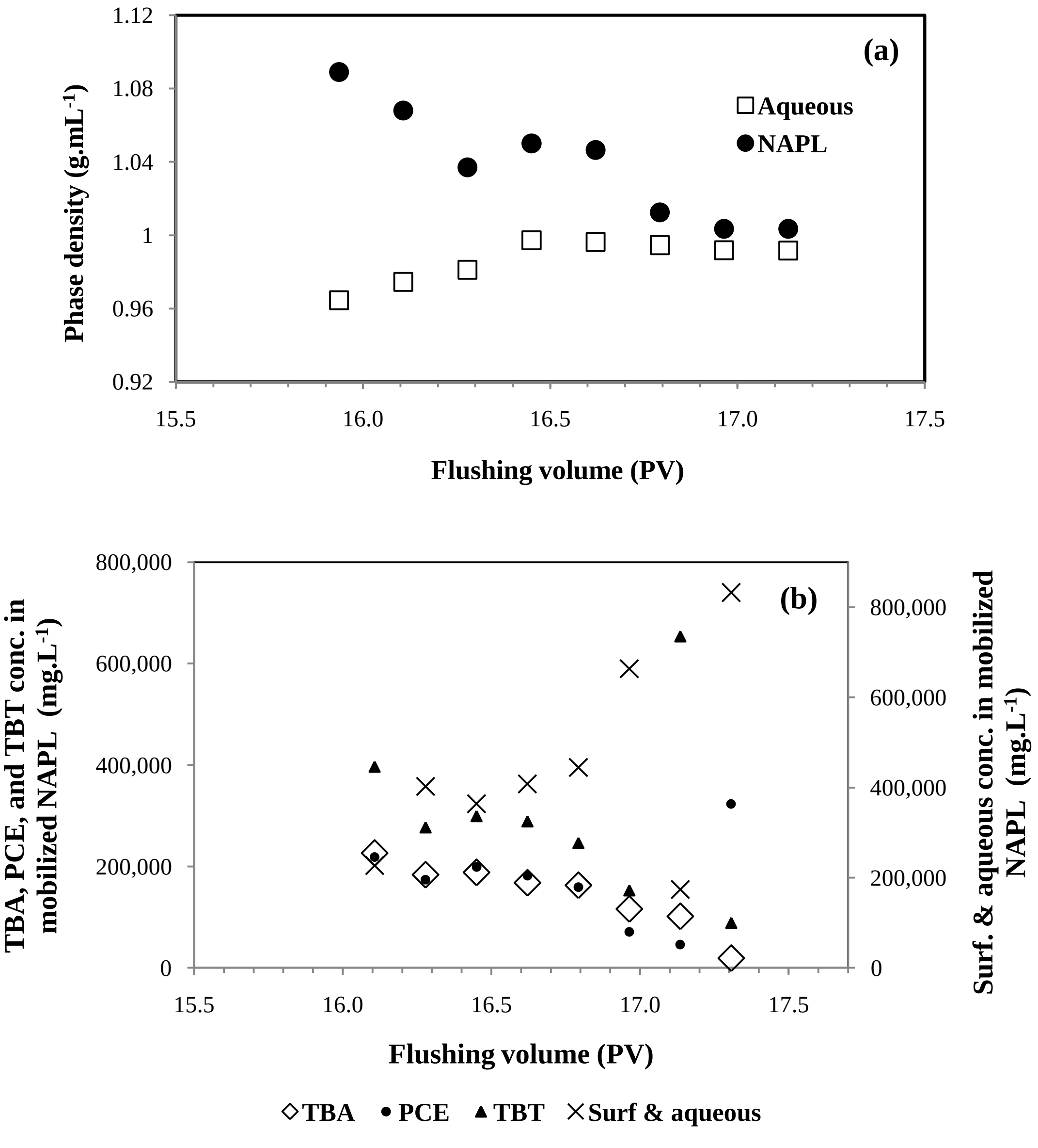


Figure 5.8 Mobilized NAPL characteristics during mobilization period of the system with TBA two step flushing shown as relative density **(a)** of mobilized NAPL(●) and aqueous phase(□); and as compositional profiles **(b)** of TBA (◊), PCE (●), TBT (▲), and surf.& aqueous (×) concentration in the mobilized NAPL.

5.2.2.2 Two-step flushing with BuOH as a density modifying agent

The BuOH two-step flushing, column V, applied two step flushing scheme by pre-flushing with 4.8 wt% BuOH + 3 wt% NaCl and following by the second step flushing solution of 3.6 wt% SDHS + 0.4 wt% C16DPDS + 3 wt% NaCl + 3 wt% BuOH. The duration for the first step BuOH solution flushing was about 15 pore volumes as to compare with the first step of TBA flushing. After that, the flushing solution was changed to the surfactant solution and sample collections from column effluent were continued. The system performance was observed in both steps with the focus on the ability of BuOH on modification of mobilized NAPL and the system characteristics during the mobilization period. During the mobilization period, NAPL phase was mobilized from the column together with aqueous phase in the effluent. The mobilized NAPL and the aqueous phase were separated immediately after sample collection. Chemical compositions in the aqueous effluent and in the mobilized NAPL phase were analyzed for TBT, PCE, and BuOH. Phase densities were measured for both mobilized NAPL and aqueous phase. Concentration profiles of TBT and PCE were compared in respect to BuOH concentration pattern and flushing time course. Relative phase densities of aqueous effluent and mobilized NAPL were explored over time course of mobilization.

5.2.2.2.1 System characteristics for the whole continuous flow study period

System characteristics of the BuOH two-step flushing for the whole continuous flow period was shown in Figure 5.9. The concentration pattern of BuOH, TBT, and PCE in the aqueous effluent in respect to flushing volume were observed. During the first step flushing, BuOH concentration in the effluent was quite fluctuated in a pattern that the BuOH concentration was increased to a certain concentration and then decreased for sometimes, and then the pattern was repeated but with the higher concentration reached. This pattern suggested that BuOH was required to be in the aqueous phase for a certain level before substantial partitioning into the NAPL phase occurred and once the alcohol in the oil phase increase the concentration of BuOH in the aqueous phase have to be in the higher level. This behavior indicated that the partitioning was not constant but need a certain concentration gradient. This was corresponding to the results from batch partitioning study showing that the partitioning coefficient was increased as the initial alcohol concentration in the aqueous phase increased. After about 15 pore volume (14.4 PV) of flushing with 4.8 wt% BuOH solution, the flushing solution was changed to the surfactant solution with 3 wt% BuOH.

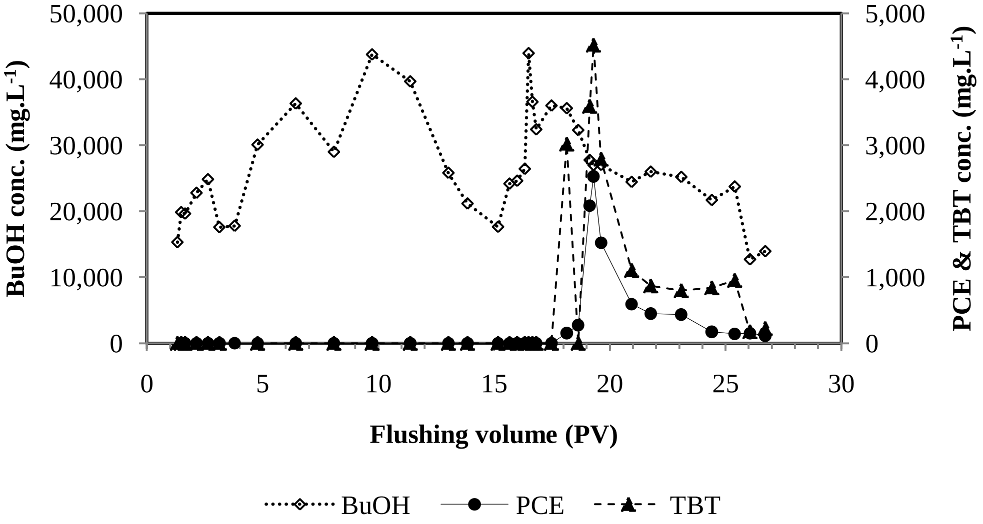


Figure 5.9 Composition profiles from the column using BuOH two step flushing (pre-flushing with 4.8 wt% BuOH and following by 3.6 wt% SDHS + 0.4 wt% C16DPDS + 3wt% NaCl + 3 wt% BuOH) showing BuOH (◊), PCE (●) , and TBT (▲) concentration in the aqueous effluent.

From Figure 5.9, after the second step flushing was started, BuOH concentration in the effluent began to rise up. This might partially due to the repetition of the up and down pattern of BuOH concentration as observed in the first step flushing and partially to the additional BuOH from the surfactant solution. The BuOH was decreased again at 16.5th PV and continue to decrease during the mobilization period. This indicated the tendency of BuOH to be in the NAPL phases in the presence of surfactant of the second step flushing. Mobilized NAPL was detected in the effluent at the 17.3th PV which was about 2 pore volume more than the time that the surfactant front would come out. There was no mobilization occurred at initial contact with the pre-flushing solution. This indicated that the mobilization process occurred after some BuOH and surfactant from aqueous phase partition into the residual oil. This is the advantage of BuOH over TBA as a density modifying agent in the first step flushing. The mobilization took place for about 2.6 PV from the 17.3th PV to the 19.9th PV, lasting longer than when using TBA in the first step flushing. At the early stage of mobilization, TBT was the main solubilized specie in the effluent. However, about equal affinity of TBT and PCE solubilization was observed in the later mobilization stage. This equal affinity of TBT and PCE for solubilization in the system with BuOH and surfactant solution was similar to the results from batch study and column study with single step flushing.

5.2.2.2.2 System characteristic during mobilization period

System characteristics during mobilization period were shown in Figure 5.10(a-b) as relative density of mobilized NAPL to aqueous phase and as concentration of BuOH, TBT, and PCE in the mobilized NAPL. Surfactant and aqueous phase was calculated by subtraction of BuOH, TBT, and PCE mass from total mobilized NAPL mass of each sample. The mobilization period lasted for about 2.6 PV (17.3 th-19.9th PV) by which the density of mobilized NAPL phase were quite stable over the whole mobilization period. The density range of this mobilized NAPL sample from the system with BuOH were 1.0604 to 1.0248 g.mL^{-1}, some of which were denser than the system with TBA two step flushing (1.089 to 1.0035 g.mL^{-1}). However, the density range of aqueous phase in the system of TBA (0.9646 – 0.9972 g.mL^{-1}) was lower than that of the system with BuOH (1.0092-1.0322 g.mL^{-1}) which then required lower density of mobilized NAPL in order to approach neutral buoyancy. Nevertheless, the mobilized NAPL from both column IV and V were still denser than aqueous phase.

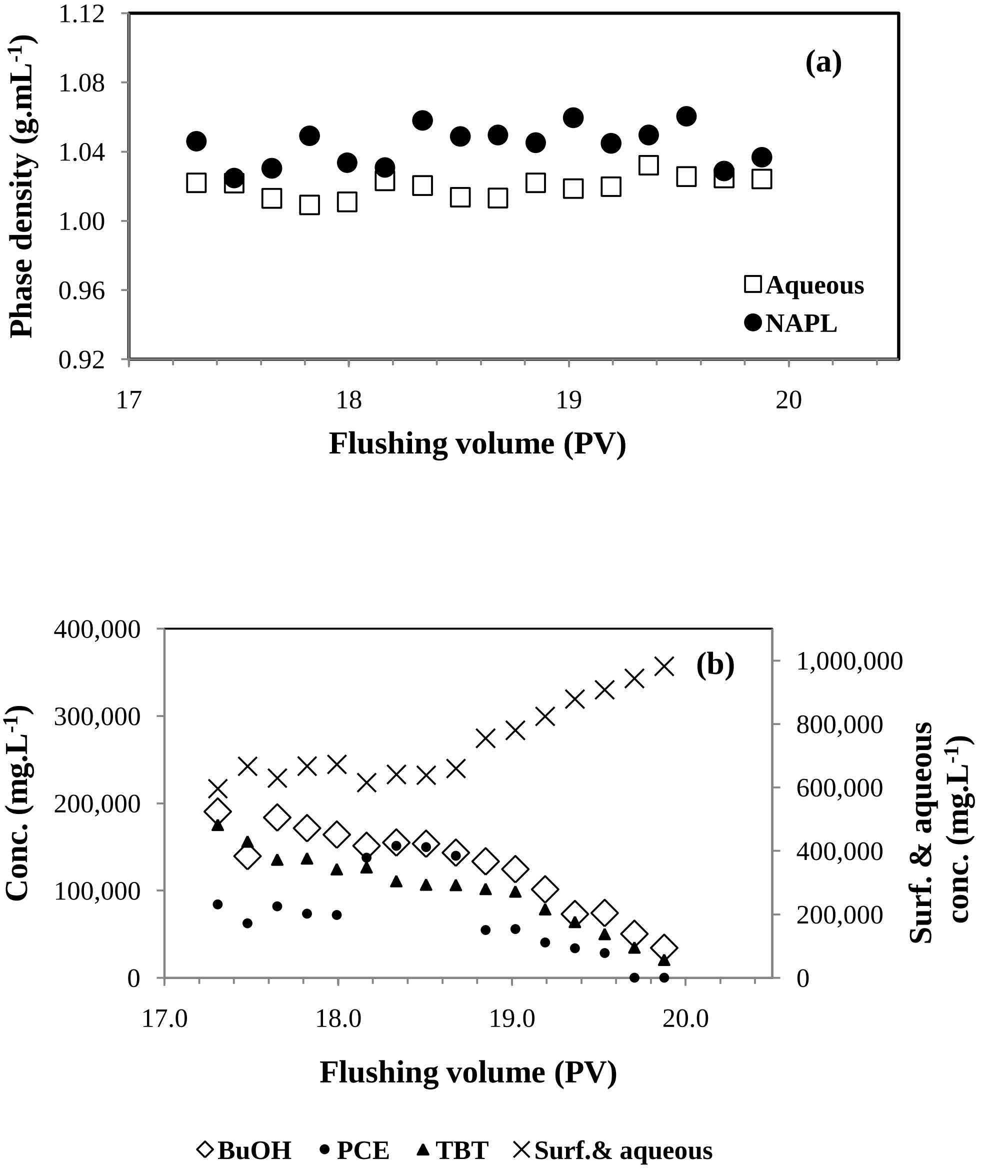


Figure 5.10 Mobilized NAPL characteristics during mobilization period of the system with BuOH two step flushing shown as relative density **(a)** of mobilized NAPL(●) and aqueous phase(□); and as compositional profiles **(b)** of BuOH (◊), PCE (●), TBT (▲), and surf.& aqueous (×) concentration in the mobilized NAPL.

Although the densities of mobilized NAPL were quite stable over the whole mobilization, the compositions within the NAPL phase were varied as can be seen in Figure 5.10b. The concentration of TBT and BuOH in the NAPL phase was gradually decreased from the early to the late stage of mobilization. The concentration of PCE was lower than TBT at the early and last stage of mobilization, while its concentration was higher than TBT in the middle stage of mobilization. This indicated that initial BuOH partitioning did not alter the mixed oil composition but once mobilization occurred, the partitioning pattern may be changed. From Figure 5.10a, the preferential solubilization of TBT was observed in the early stage of mobilization following by equal affinity for solubilization with PCE. This transition took place between the 18.1th PV to 18.4th PV and was corresponded to the period that PCE was found in a higher proportion than TBT in the mixed oil. This suggested that there might be a significant phase transition from TBT supersolubilization region to type II microemulsion as higher proportion of aqueous phase in the NAPL phase was also be found afterwards. However the extent of this TBT supersolubilization was still small compared with the single step flushing of columnIII with BuOH addition, 3018 vs 8339 mg.L^{-1}, respectively. This should be because the significant amount of TBT was already removed by mobilization. This should be a benefit since it would required less post treatment to remove TBT from aqueous phase.

Results from the two-step flushing showed that it had better performance than the single step flushing in density modification of mobilized NAPL to approach neutral buoyancy. In term of alcohol type comparison, the two step flushing with BuOH as a density modifying agent was selected for further improvement due to its lack of potential risk related to initial mobilization at the alcohol solution comparing to the system with TBA. It also required less quantity to achieve similar density conversion than the system with TBA. In addition, the cost of BuOH per unit volume was about twice lower than TBA. Then the system with BuOH was selected for the last column test in this study.

5.2.3 Selection of alcohol concentration for the system with BuOH as a density modifying agent under the presence of surfactant

Before the last column was set up, a batch study on alcohol partitioning between mixed oil phase and surfactant solution aqueous phase was carried out to study the effect of initial surfactant concentration on alcohol concentration in the oil phase at equilibrium. Mixed oil with an amount of 2ml were added to 5 ml of flushing solution with five initial surfactant concentration (0 wt%, 2 wt%, 4 wt%, 6 wt%, 8 wt%) at 3 wt% NaCl. Then BuOH was slowly added to each tube until the mixed oil approached density modified phase conversion. Final phase conversions were achieved through centrifuge at 2500 rpm for 3 minutes.

It was shown in Figure 5.11 that the density of both oil and aqueous phase at the point where phase conversion from DNAPL to LNAPL occurred were increased as surfactant concentration was increased. Their relative density was lower at high surfactant concentration (6 wt % and 8 wt %) than at low surfactant concentration (0 wt %, 2 wt %, and 4 wt %) with the increasing of both oil and aqueous phase. This might due to the fact that alcohol partitioning ratio was getting less at higher surfactant concentration at which additional surfactant outcompete the BuOH for space in the oil phase and, as a result, contributed to increased oil density.

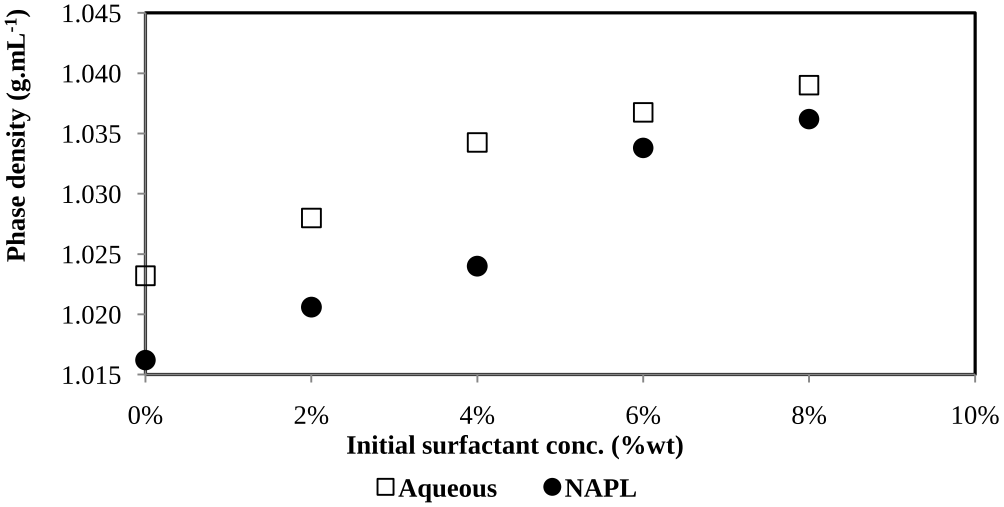


Figure 5.11 Effect of initial surfactant concentration on oil phase (●) and aqueous phase density (□) after phase conversion was achieved by BuOH addition at that particular initial surfactant concentration.

It was shown in Figure 5.12 (a,b) that BuOH had less oil partitioning at surfactant concentration of 6 wt% and 8 wt% than that of 4 wt% and 2 wt%. However, comparing with the partitioning study without surfactant, the partitioned BuOH in oil over BuOH in aqueous phase at this concentration was still higher than partitioning with alcohol alone (9.3 versus 6.68). This could come from the fact that surfactant incorporated BuOH into the oil phase by forming type II w/O microemulsion. Therefore BuOH performed as both a density modifying agent and a cosurfactant.

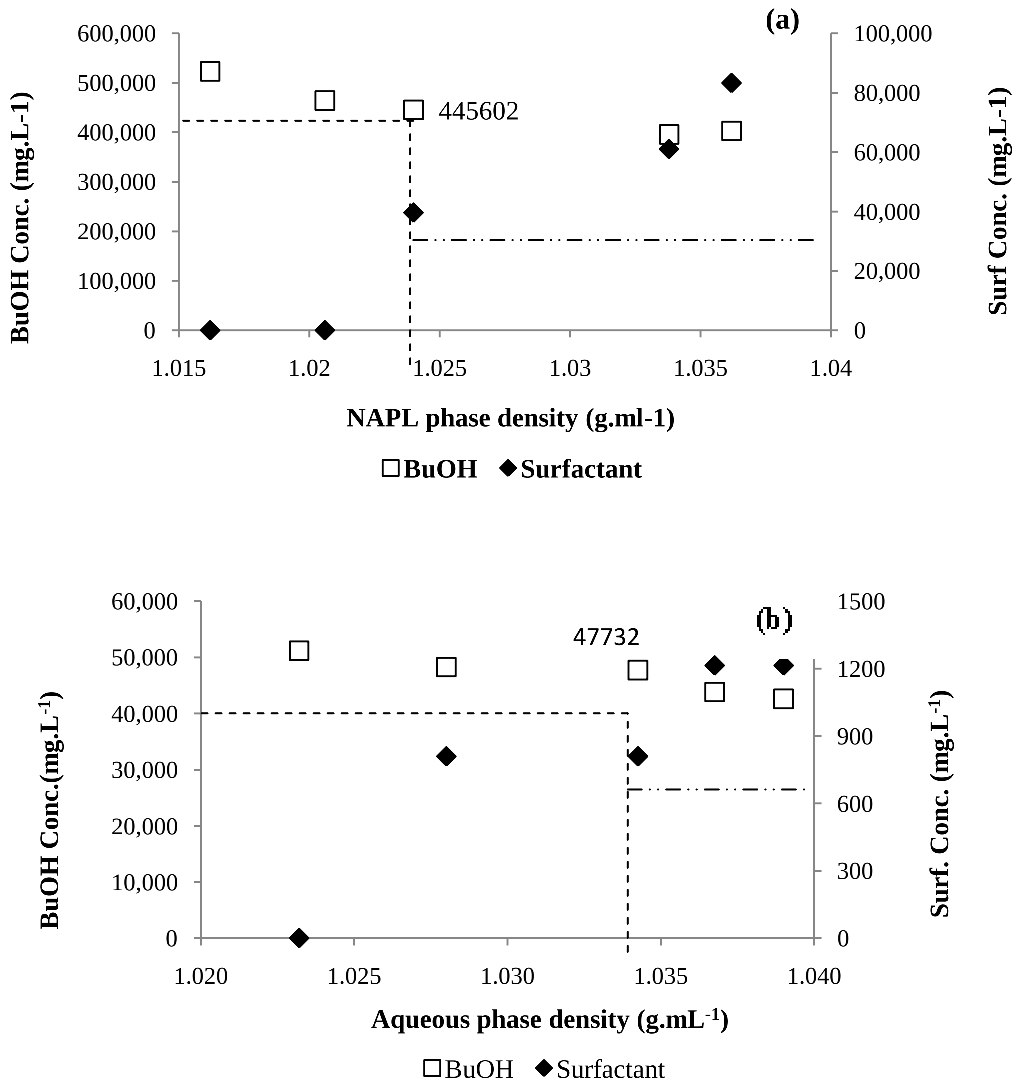


Figure 5.12 Concentration profiles of surfactant and BuOH in oil phase **(a)** and in aqueous phase **(b)** relative to the phase density

Figure 5.12 **(b)** indicated that it needed around 4.8 wt% BuOH in the aqueous phase in order to maintain LNAPL at equilibrium. BuOH at a concentration of 4.8 wt% is closed to saturation concentration of BuOH in the surfactant solution under studied (5.3 wt %), so the surfactant flushing solution will be saturated prior to applying in the next column study.

. 5.2.4 Performance of the selected system with saturated BuOH as a density modifying agent

The last column study was carried out using the two step flushing scheme with BuOH as a density modifying agent. The first step used 3% NaCl brine solution saturated with BuOH and followed by 3.6 wt% SDHS+ 0.4 wt% C16DPDS + 3 wt% NaCl saturated with BuOH. The saturated solutions were prepared by thoroughly mixing an excess amount of BuOH with the solutions and left at room temperature for 3 days with an excess BuOH cover the top of the solution. The solutions were slowly stirred intermittently and the top excess was removed before being applied in the column study. The duration for alcohol pre flushing for this column was increased to 23 pore volumes to give more partitioning time to the residual oil. The result showed that removal of the oil mixture in the form of LNAPL mobilized oil was achieved in the two-step flushing with saturated BuOH by which mobilization was the main removal mechanism of 82.09% for TBT and 85.23% for PCE.

5.2.4.1 System characteristics for the whole continuous flow study period

Figure 5.13 showed that the pre-flushing with saturated alcohol caused PCE preferential solubilization of mixed oil.in the continuous flow mode. As a result, during the first step, PCE was the main solubilized specie in the effluent which was not found in the first step flushing of under saturated BuOH solution. PCE removal during this first step flushing by aqueous solubilization was contributed to 3.82% from its total removal. In addition, the BuOH concentration in the effluent over the whole study did not varied as much as observed in the system with under saturated BuOH solution for both with and without surfactant addition which might be beneficial to operating condition. However, the drawback of using saturated BuOH was that there was some mobilized NAPL observed even in the first step of pre-flushing with only alcohol. This indicated that BuOH was partitioned into the oil phases sufficient enough to lower interfacial tension and overcome the capillary force between sand pore spaces. This DNAPL mobilization was accounted for 5.74% for PCE and 13.24% for TBT from their total removal. TBT and PCE had different removal mechanism during this first step flushing. PCE was removed by both solubilized and mobilized form, while TBT removal was in mobilized NAPL phase than solubilized phase. This might indicate that TBT interaction with BuOH without addition of surfactant did not enhance its interaction with aqueous phase as in the case of PCE with its smaller molecule, more hydrophillic and having double bond.

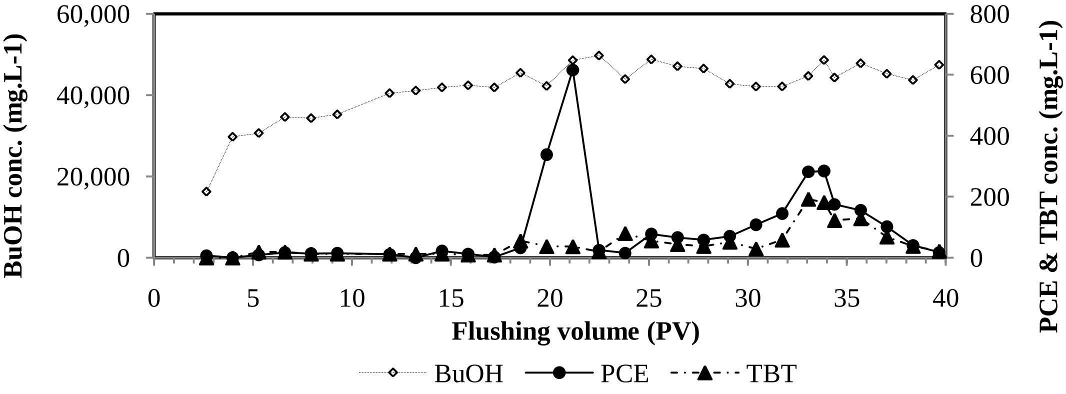


Figure 5.13 Composition profiles from the column with BuOH two step flushing (pre-flushing with 3 wt% NaCl saturated with BuOH and following by 3.6 wt% SDHS + 0.4 wt% C16DPDS + 3wt% NaCl saturated with BuOH) showing BuOH (◊), PCE (●) , and TBT (▲) concentration in the aqueous effluent..

The flushing solution was switched to the second step flushing solution of 3.6 wt% SDHS+ 0.4 wt% C16DPDS + 3 wt% NaCl saturated with BuOH at the 23.3th PV. The mobilization period during the second step flushing under this saturated alcohol condition occurred right after the surfactant front since the interfacial tension was supposed to be already low enough for mobilization even without surfactant enhancement. The mobilization continued until the 33.6th PV, lasting for 9 PV which was about 4 times longer than flushing with the surfactant solution having 3 wt% BuOH. In the later stage of mobilization period, there were some increases in TBT and PCE solubilization in the aqueous phase with PCE having preferential solubilization. Their solubilization were gradually decreased for both TBT and PCE until very small amounts were detected, and the flow was discontinued at the 40th PV.

5.2.4.2 System characteristic during mobilization period

System characteristics during mobilization period were shown in Figure 5.14(a-b) as relative density of mobilized NAPL to aqueous phase and as concentration of BuOH, TBT, and PCE in the mobilized NAPL. Surfactant and aqueous phase was calculated by subtraction of BuOH, TBT, and PCE mass from total mobilized NAPL mass of each sample. The major mobilization period lasted for 9 PV (24.6th - 33.6th PV) by which the density of mobilized NAPL phase were changing over time. The decreasing of mobilized NAPL density from the 24.6th to 26th PV was corresponded to the increasing of BuOH concentration in the NAPL phase. The additional BuOH in the mobilized NAPL could be a result from the higher partitioning coefficient of BuOH under the presence of surfactant than with only alcohol as found in the batch study (9.3 versus 6.68). However, as the majority of TBT and PCE were removed and more aqueous phase and surfactant was solubilized in the NAPL phase, the density of mobilized NAPL was increased from the 26th PV onward until the 28.8th PV and stabilized. The range of mobilized NAPL and aqueous phase densities during this mobilization period were 0.9394 - 1.0328g.mL^{-1} and 1.0064 – 1.0324g.mL^{-1}, respectively.

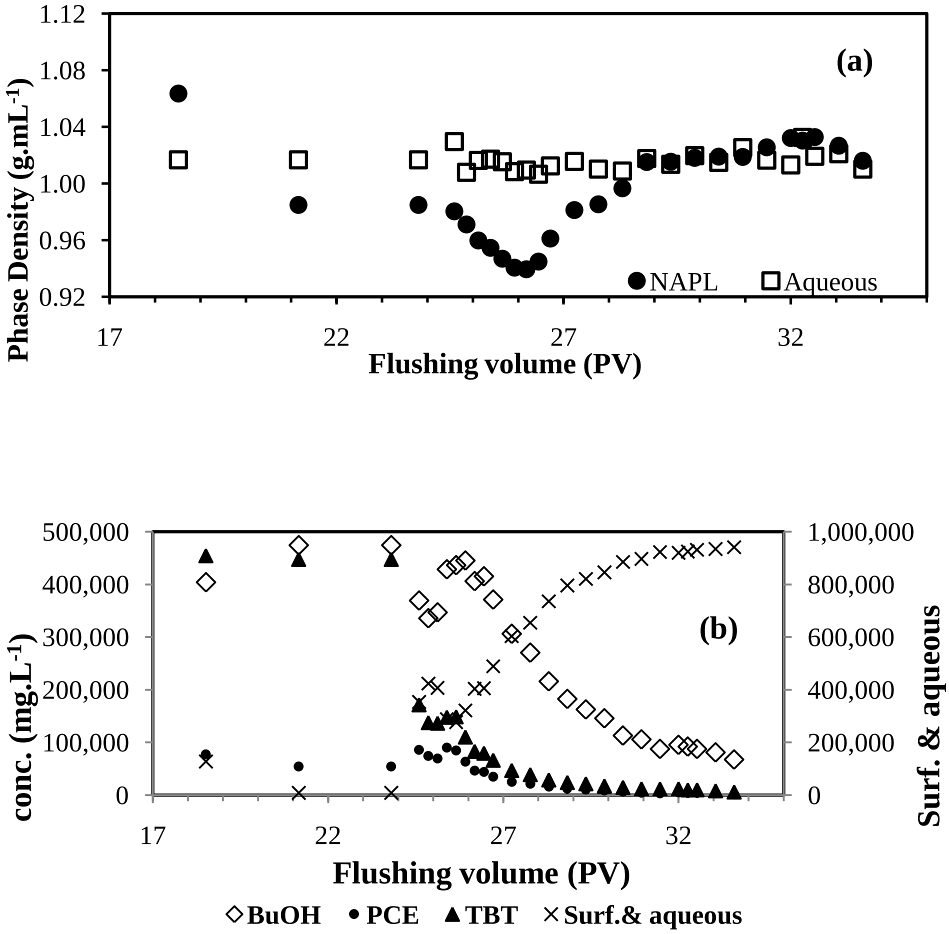


Figure 5.14 Mobilized NAPL characteristics during mobilization period of the system with saturated BuOH two step flushing shown as compositional profiles **(a)** of BuOH (◊), PCE (•), TBT (▲), and surf.& aqueous (×) concentration in the mobilized NAPL; and as relative density **(b)** of mobilized NAPL(•) and aqueous phase(□).

The density of the mobilized NAPL removed by the two-step flushing with the surfactant solution and saturated BuOH were lower than aqueous phase for most of the mixed oil removal. The removal of TBT and PCE as an LNAPL was accounted for 82.09 % and 85.23 % from total removal, respectively. There was some small DNAPL mobilization occurred in the first step flushing with saturated BuOH brine solution with the density already modified to 1.063g.mL^{-1}. This removal was accounted for 13.24% for TBT and 5.74% for PCE from their total removal.

5.3 CONCLUSIONS

From six column studies, removal of the oil mixture in the form of LNAPL mobilized oil was achieved in the two-step flushing with saturated BuOH by which mobilization was the main removal mechanism of 82.09% for TBT and 85.23% for PCE from total removal. Column conditions and system performances were summarized in Table 5.1. This study achieved the goal of removal the mixture of tributyltin chloride and tetrachloroethylene from the simulated contaminated material of high percentage of residual saturation while mitigating downward migration of the mobilized NAPL. Even though the number of total required flushing solution was quite high (40 pore volume), the obtained knowledge on its performance and removal mechanism can be useful for further detailed design of real site application.

Table 5.1 Column conditions and system performances

Column #	Flushing scheme	Flushing solution	Pre flushing with alcohol (PV)	Main flushing with surfactant solution (PV)	% Removal				Mobilized NAPL characteristics
					TBT		PCE		
					Mobilized	Solubilized	Mobilized	Solubilized	
1	Single step	4% Surf. + 3% NaCl	-	15.45	51.59	48.21	44.29	55.71	DNAPL
2	Single step	4% surf. + 4.8% TBA + 3% NaCl	-	16.60	73.89	25.36	68.74	31.26	DNAPL
3	Single step	4% surf. + 4.8% BuOH + 3% NaCl	-	16.38	91.70	7.85	94.80	5.20	DNAPL
4	Two step	1) 14.5% TBA + 3% NaCl	14.91		3.64		21.68		DNAPL
		2) 4%surf.+ 12.5% TBA + 3%NaCl		3.08	85.11	11.14	67.69	10.44	DNAPL
5	Two step	1) 4.8% BuOH + 3% NaCl	14.35		0.00		0.00		
		2) 4%surf.+ 3 % BuOH + 3% NaCl		13.41	84.84	14.98	88.50	9.19	DNAPL
6	Two step	1) Sat.BuOH +3% NaCl	23.27		13.24		5.74	3.82	DNAPL
		2) 4%surf.+ Sat.BuOH + 3% NaCl		16.4	**15.50**		**4.78**		**LNAPL**
					66.59	4.23	**80.45**	5.04	**LNAPL**

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The residual oil mixture of 60 wt% TBT and 40 wt% PCE can be removed by using microemulsion technique couple with neutral buoyancy concept. The mixed oil behavior s were investigated in both batch and column studies. Two main removal mechanisms, solubilization and mobilization were explored for their removal potential and density modification.

From batch study, hydrophobicity of organometallic under study, tributyltin (TBT), was characterized as an equivalent alkane carbon number (EACN) and was determined to be 11.17 by using Salager's equation and linear mixing rule. The EACN of the mixed oil (60 wt% TBT + 40 wt% PCE) was 6.5 which is close to the EACN of tetraethyllead, another concern organometallic compound. Phase behavior of several surfactant systems and salinity scanning had been studied by which the surfactant system of 3.6 wt% SDHS + 0.4 wt% C16 DPDS at 3wt% NaCl (4 wt% total surfactant) was selected. Alcohol used in this present study are n-butanol (BuOH) and tert-butanol (TBA). Pseudoternary phase diagrams of both TBA and BuOH were constructed. BuOH produced larger LNAPL region than TBA which should be beneficial to mobilization as a removal mechanism.

The column studies were carried out in a single step and two-step flushing. The results showed that two-step flushing performed better in term of mobilized NAPL density modification. To evaluate the behavior in different conditions, TBT and PCE were analyzed separately. From the batch study, the highest solubilization of TBT and of PCE were found in the systems with TBA and in the system with only surfactant, respectively. However, either the system with TBA or the system with only surfactant of the column study performed lower solubilization than those of the batch study both for TBT and PCE. Surprisingly, system with BuOH yielded better solubilization of both TBT and PCE in the column study than the batch study.

From single step flushing, the amount of mobilized NAPL was highest at the initial contact of surfactant for the two systems of using only surfactant and with TBA addition. For the system with BuOH addition, the mobilized NAPL was slowly released during the initial contact of surfactant and the majority of mobilized NAPL came out in the later stage.

Removal of the oil mixture in form of mobilized LNAPL was achieved in the two-step flushing with saturated BuOH by which mobilization was the main removal mechanism of 82.09% for TBT and 85.23% for PCE from total removal. There was some small DNAPL mobilization occurred, the density of the DNAPL was however, already modified to1.063 mg.L^{-1}. It was accounted for 13.24% for TBT and 5.74% for PCE from their total removal.

6.2 RECOMMENDATIONS

6.2.1 For further investigation

The obtained knowledge on system performance and removal mechanism especially from the last column study shows that it is possible to further minimize the DNAPL vertical migration. It can be either one of these two approaches. First, 4.8 wt% BuOH can be used in the first step with more flushing time (20 pore volume) and followed by the surfactant solution saturated with BuOH. Second, less time can be used in the first step of saturated alcohol pre-flushing, such as 10 pore volume, due to the fact that the oil characteristic during mobilization period indicated an additional alcohol partitioning from surfactant solution at a higher degree than with solution containing only alcohol.

Further study can be carried out on post flushing with 3 wt% NaCl and 0.01M $Ca(NO_3)_2$ to complete the decontamination process. In addition, surfactant concentration could be monitored along with other chemical composition to evaluate the possibility of surfactant recovery. This is due to the fact that the high aqueous content and low contaminant concentration were found in mobilized NAPL phase at the later stage of mobilization.

The mobilized NAPL containing TBT could be eliminated by incineration at a temperature above 1000 °C (Gkenakou , 2008). TBT in an aqueous phase can be photodegraded by UV or visible light with a photocatalyst (Bangkedphol et al., 2010), or it can be biodegraded at a low concentration (Mathurasa, 2011).

6.2.2 For further application

This flushing solution and scheme was suggested to be applied in situ on the site that are highly contaminated and have high percentage of source zone saturation. This high level of contamination was likely to be found on the manufacturing site or the site with major oil spill. The EACN of the contaminant mixture can be used to narrow down the choice of surfactant system and partitioning alcohol but cannot be used as a sole basis for flushing solution selection. This can be seen from the much different behavior of TBT (EACN=11.17) with dodecane (EACN =12) in microemulsion formation (experiment carried out in this study but data not shown). In addition, a study carried out by Queste et al.(2007) indicated that the difference behaviors of the organic compounds with the same EACN came from the differences in the monomeric solubility of surfactant in the oil phase.

Hydrophobicity play a major role as well as the molecular structure which dictated the ability of the contaminant molecules for various intermolecular interaction with the surrounding such as dispersion force, dipole-dipole, dipole-induced dipole, and hydrogen bonding (Schwarzenbach et al., 2003). Therefore, feasibility should be performed with the major contaminant in the area before the real application can be employed.

Water solubility of the orgametallic compound should also be considered since it also has major effect on operating conditions. Damrongsiri (2010) suggested pH adjustment for the decontamination of dibutyltin chloride with its water solubility of 36 mg.L^{-1} which might not be necessary for tributyltin chloride with its water solubility of 0.007 mg.L^{-1} (Environmental Protection Agency, 2012) which would be in an ionized form less than dibutyltin chloride in an aqueous phase.

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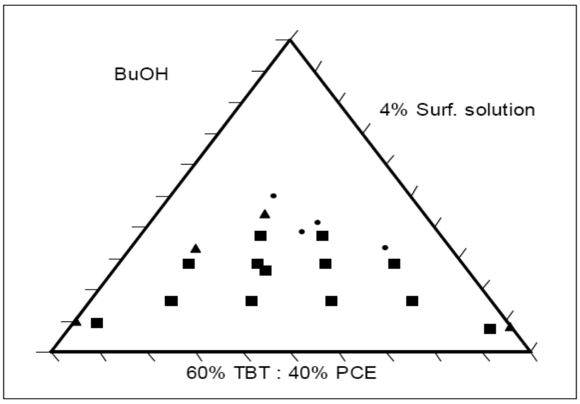
APPENDIX A



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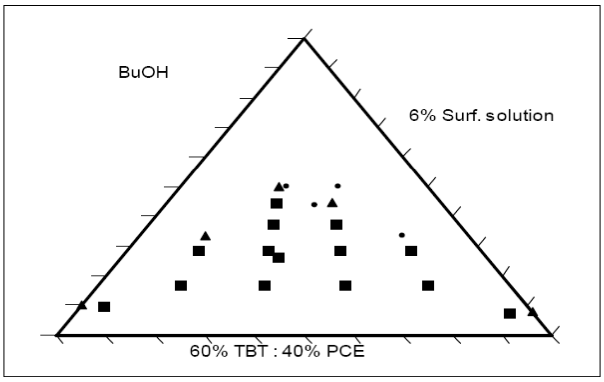

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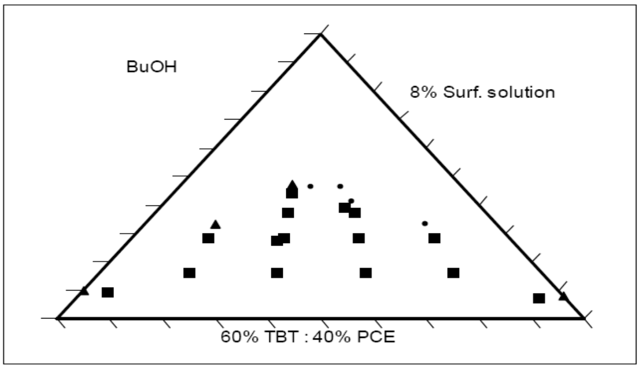
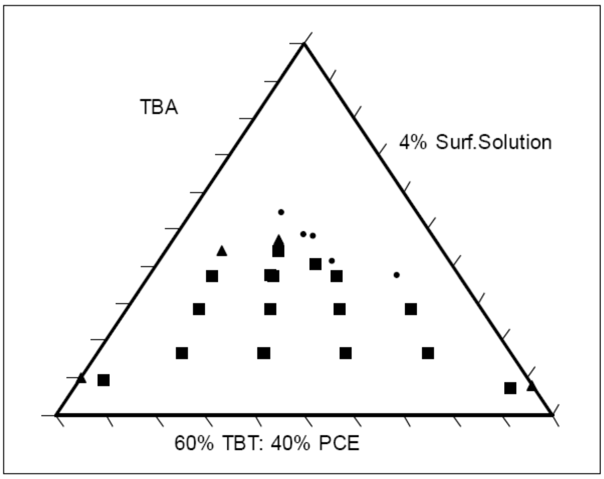
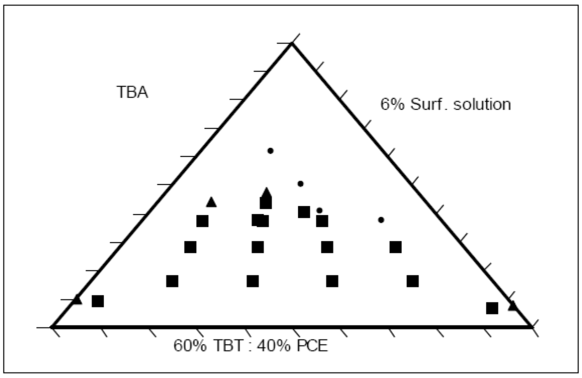


(c)

Figure A-1 Pseudo ternary phase diagram of n-BuOH with the mixed oil of 60 wt% TBT+40 wt% PCE and 4 wt% (a), 6 wt % (b), and 8 wt% (c) total surfactant concentration of SDHS and C16 DPDS at a mass ratio of 9:1 and 3 wt % NaCl. Each point in the diagram represents the two phase system with mixed as a DNAPL (■), an NAPL (●), and a miscible phase (▲).



(a)



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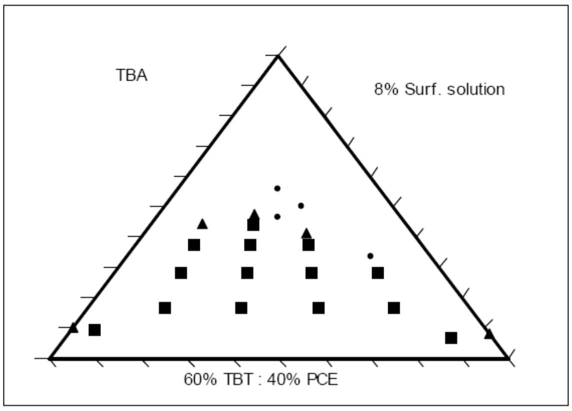

(c)

Figure A-2 Pseudo ternary phase diagram of TBA with the mixed oil of 60 wt% TBT/40 wt% PCE and 4 wt% (a), 6 wt % (b), and 8 wt% (c) total surfactant concentration of SDHS and C16 DPDS at a mass ratio of 9:1 and 3 wt % NaCl. Each point in the diagram represents the two phase system with mixed as a DNAPL (■), an NAPL (●), and a miscible phase (▲).

APPENDIX B

Table B-1 Relative density of oil and aqueous phase modified by TBA and BuOH at different initial alcohol to oil ratio with corresponding alcohol concentration in both oil and aqueous phase from the alcohol partitioning study without the presence of surfactant. The bold letter in the bottom two rows show condition of LNAPL phase.

Initial alcohol to oil volume ratio	**Initial alcohol to oil mass ratio**	**Density (g.mL^{-1})**				**Alcohol Concentration (mg.L^{-1})**				**Alcohol in oil to aqueous phase ratio**	
		TBA		**BuOH**		**TBA**		**BuOH**			
		Oil	Aqueous	Oil	Aqueous	Oil	Aqueous	Oil	Aqueous	TBA	BuOH
0.1	0.1	1.2882	1.0122	1.2625	1.0218	20183	59,874	42420	24,520	0.337091	1.730045
0.3	0.2	1.2614	1.0156	1.2174	1.0272	54486	91,758	100100	33,272	0.593801	3.0085
0.6	0.4	1.2004	1.0096	1.1560	1.0236	105981	115,880	131460	38,407	0.914577	3.422822
1.0	0.6	1.1232	1.0172	1.0942	1.0222	164833	123,471	224280	42,356	1.334996	5.295124
1.7	1.0	1.0498	1.0124	1.0260	1.0194	235810	137,942	296100	44,739	1.709492	6.61832
3.0	**1.8**	**0.9784**	**1.0070**	**0.9666**	**1.0218**	**287548**	**144,862**	**322000**	**48,206**	**1.985**	**6.6796**
7.0	**4.2**	**0.9020**	**0.9922**	**0.8926**	**1.0182**	**349390**	**172,643**	**401100**	**58,260**	**2.0238**	**6.8846**

Table B-2 Concentration of surfactant and alcohol in aqueous and oil phase from the alcohol partitioning study in the presence of surfactant

% Initial surf.	**surfactant concentration (mg/L)**		**BuOH concentration (mg/L)**		**BuOH in oil to aqueous phase ratio**
	In aqueous phase	**In oil phase**	**In aqueous phase**	**In oil phase**	
0%	0	0	51188	523362	10.22
2%	809	21839	48252	464191	9.62
4%	809	39633	47732	445602	9.34
6%	1213	61068	43843	395666	9.02
8%	1213	83311	42602	402870	9.46

Table B-3 Column conditions for both single step and two step flushing

Column #	Flushing solution	Residual oil (g)	Pore volume (ml)	Run time (PV)	Porosity	% Residual oil saturation	Time before enter column (PV)	Time switched to surfactant (PV)
1	4% Surf. + 3% NaCl	6.047	32.26	15.45	0.39	14.17	0.12	
2	4% surf. + 4.8% TBA + 3% NaCl	7.852	30.8	16.6	0.37	19.27	0.17	
3	4% surf. + 4.8% BuOH + 3% NaCl	5.953	31.2	16.38	0.37	14.42	0.16	
4	1) 14.5% TBA + 3% NaCl							
	2) 4%surf.+ 12.5% TBA + 3%NaCl	6.752	30.93	17.99	0.37	16.68	0.17	14.91
5	1) 4.8% BuOH + 3% NaCl							
	2) 4%surf.+ 3 % BuOH + 3%NaCl	6.656	32.14	27.76	0.38	15.8	0.12	14.35
6	1) Sat.BuOH +3% NaCl							
	2) 4%surf.+ Sat. BuOH + 3% NaCl	6.753	30.25	39.67	0.36	16.73	0.19	23.27

Table B-4 Removal of TBT and PCE from the residual oil saturation in six column studies performed for this research. Percent removal by two distinct removal mechanisms of mobilization and solubilization were reported as % removal from total % removal. Mass balance for each column were also included in the table.

Column#	**Flushing solutions**	**% Removal (Mobilization)**		**% Removal (Solubilization)**		**% Mass balance**	
		TBT	PCE	TBT	PCE	TBT	PCE
1	4% Surf. + 3% NaCl	51.59	44.29	48.21	55.71	64.55	75.18
2	4% surf. + 4.8% TBA + 3% NaCl	73.89	68.74	25.36	31.26	85.06	91.43
3	4% surf. + 4.8% BuOH + 3% NaCl	91.70	94.80	7.85	5.20	73.79	89.14
4	a) 14.5% TBA + 3% NaCl	3.64	21.68	11.14	10.44	64.19	58.69
	b) 4%surf.+ 12.5% TBA + 3%NaCl	85.11	67.69				
5	a) 4.8% BuOH + 3% NaCl	0.00	0.00	14.98	9.19	61.56	66.63
	b) 4%surf.+ 3 % BuOH + 3% NaCl	84.84	88.50				
6	a) Sat.BuOH +3% NaCl	13.24	5.74	4.23	8.86	74.88	44.15
	a) Sat.BuOH +3% NaCl	15.50	4.78				
	b) 4%surf.+ 5 % BuOH + 3% NaCl	66.59	80.45				

Table B-5 Solubilization of TBT and PCE in the six column studies camparing with the results from batch study

Flushing scheme	Flushing solutions	Solubilization ($mg.L^{-1}$)			
		TBT		PCE	
		Batch	Column	Batch	Column
Single step	1) 4 % surf + 3% NaCl	20999	17971	**28957**	**16509**
	2) 4% surf. +4.8% TBA + 3% NaCl	**26566**	**18311**	21046	14634
	3) 4% surf. +4.8% BuOH + 3% NaCl	271	8339	623	3669
Two step	4) 14.5% TBA + 3% NaCl	828		1830	
	4% surf. + 12.5% TBA + 3% NaCl		11099		6600
	5) 4.8% BuOH + 3% NaCl	23		0	
	4% surf. + 3% BuOH + 3% NaCl		4518		2527
	6) 3% NaCl + Sat. BuOH				
	4% surf. +Sat. BuOH + 3% NaCl	48	192	80	616

BIOGRAPHY

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1992- 1993 Environmental Quality Standard Division
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