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REMOVAL AND CONCENTRATION OF PYRENE FROM CONTAMINATED SOIL USING A PHASE SEPARATION OF MIXED CATIONIC AND ANIONIC SURFACTANTS SOLUTION

Mr. Putchaya Thunhapran

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By	Mr. Putchaya Thunhapran
Field of Study	Environmental Management
Thesis Principal Advisor	Punjaporn Weschayanwiwat, Ph.D.
Thesis Co-advisor	Professor John F. Scamehorn, Ph.D.

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……………………………………Dean of the Graduate School
(Assistant Professor M.R. Kalaya Tingsabadh, Ph.D.)

THESIS COMMITTEE

……………………………………Chairperson
(Assistant Professor Manaskorn Rachakornkij, Ph.D.)

……………………………………Thesis Principal Advisor
(Punjaporn Weschayanwiwat, Ph.D.)

John Scamehorn……………………Thesis Co-advisor
(Professor John F. Scamehorn, Ph.D.)

……………………………………Member
(Chantra Tongcumpou, Ph.D.)

……………………………………External Member
(Chalothorn Sophonwutikul, Ph.D.)

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การศึกษานี้เป็นการประเมินแนวทางใหม่ในการใช้สารละลายผสมของสารลดแรงตึงผิวชนิดประจุบวก (ดีแทบ) และชนิดประจุลบ (ดาวแฟ๊ก) เพื่อกำจัดไพรีนออกจากดิน การศึกษาการดูดซับของสารลดแรงตึงผิวบนดินและความสามารถในการละลายไพรีนโดยสารละลายดีแทบ สารละลายดาวแฟ๊ก และสารละลายผสมระหว่างดีแทบและดาวแฟ๊กที่อัตราส่วนผสมโดยโมลที่ 1.5:1, 1:1, 1:1.5 และ 1:2 พบว่าดีแทบดูดซับบนดินได้มากขึ้นเมื่อความเข้มข้นสูงขึ้น ขณะที่ดาวแฟ๊กไม่ดูดซับบนดิน สำหรับผลการศึกษาความสามารถในการละลายไพรีนโดยสารละลายของสารลดแรงตึงผิวพบว่า สารละลายผสมระหว่างดีแทบและดาวแฟ๊กที่อัตราส่วนผสมทุกอัตราส่วนมีความสามารถในการละลายไพรีนได้มากกว่าสารละลายดีแทบและสารละลายดาวแฟ๊กที่ไม่ได้ผสม ผลการศึกษาการดูดซับของสารลดแรงตึงผิวบนดินและความสามารถในการละลายไพรีนโดยสารละลายของสารลดแรงตึงผิวพบว่าสารละลายผสมระหว่างดีแทบและดาวแฟ๊กที่อัตราส่วนผสมโดยโมลที่ 1:1 ถูกเลือกเพื่อนำไปใช้ในการศึกษาผลของความเข้มข้นทั้งหมดของสารลดแรงตึงผิวผสมและตัวเติม (แคลเซียมคลอไรด์และตัวเชื่อมที่ชอบน้ำมัน) ต่อการกำจัดไพรีนออกจากดิน ผลการศึกษาพบว่าส่วนผสมของสารลดแรงตึงผิวที่เหมาะสมที่สุดที่สามารถกำจัดไพรีนออกจากดิน คือ สารละลายผสมระหว่างดีแทบและดาวแฟ๊กที่อัตราส่วนผสมโดยโมลที่ 1:1 ความเข้มข้นทั้งหมดของสารลดแรงตึงผิวผสม 20 มิลลิโมลาร์ แคลเซียมคลอไรด์ 0.025 เปอร์เซ็นต์โดยน้ำหนัก และโดเดคานอล 1 มิลลิโมลาร์ ซึ่งสามารถกำจัดไพรีนได้สูงสุดถึง 87.5 เปอร์เซ็นต์ หลังจากนั้นระบบของสารลดแรงตึงผิวผสมที่ประกอบด้วยตัวเติมแต่ละชนิดและไม่มีตัวเติมถูกปรับอัตราส่วนผสมโดยโมลของสารละลายผสมระหว่างดีแทบและดาวแฟ๊กเพื่อก่อให้เกิดการแบ่งวัฏภาคของสารละลายของสารลดแรงตึงผิวผสมนี้ และเพื่อศึกษาความสามารถในการเพิ่มความเข้มข้นของสารจากการแบ่งวัฏภาคดังกล่าว ผลการศึกษาพบว่าการแบ่งวัฏภาคโดยสารละลายผสมระหว่างดีแทบและดาวแฟ๊กที่อัตราส่วนผสมโดยโมลที่ 2:1 ที่ประกอบด้วยแคลเซียมคลอไรด์ 0.025 เปอร์เซ็นต์โดยน้ำหนัก มีความสามารถในการทำให้สารเข้มข้นขึ้นได้ดีที่สุด ซึ่งไพรีนและสารลดแรงตึงผิวส่วนใหญ่จะสะสมอยู่ในวัฏภาคที่เข้มข้นไปด้วยสารลดแรงตึงผิว นอกจากนี้ยังพบว่าความสามารถในการเพิ่มความเข้มข้นของไพรีนและสารลดแรงตึงผิวสูงถึง 3,200 เท่าอีกด้วย

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ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์ร่วม John Scamehorn

4989452720 : MAJOR ENVIRONMENTAL MANAGEMENT

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PUTCHAYA THUNHAPRAN : REMOVAL AND CONCENTRATION OF PYRENE FROM CONTAMINATED SOIL USING A PHASE SEPARATION OF MIXED CATIONIC AND ANIONIC SURFACTANTS SOLUTION. THESIS PRINCIPAL ADVISOR: PUNJAPORN WESCHAYANWIWAT, THESIS COADVISOR: JOHN F. SCAMEHORN, 148 pp.

A new approach using mixed cationic surfactant (DTAB) and anionic surfactant (DOWFAX) for pyrene removal from contaminated soil was proposed. In this study, surfactant adsorption onto soil and pyrene solubilization by pure DTAB, pure DOWFAX and mixtures of DTAB:DOWFAX at molar ratios of 1.5:1, 1:1, 1:1.5, and 1:2 were investigated. The results showed that DTAB adsorption onto soil increases with concentration, while DOWFAX does not adsorb onto soil. The DTAB:DOWFAX at all studied molar ratios showed the greater pyrene solubilization over those of DTAB and DOWFAX alone. From the surfactant adsorption and pyrene solubilization results, the DTAB:DOWFAX at 1:1 molar ratio was selected for further use to investigate the effects of total surfactants concentration and additives ($CaCl_2$ and lipophilic linkers) addition on pyrene removal from contaminated soil. The results showed that the optimal surfactant formulation is DTAB:DOWFAX at 1:1 molar ratio with 20 mM total surfactants concentration, 0.025%wt $CaCl_2$, and 1 mM dodecanol, where the highest pyrene removal of 87.5% was achieved. These surfactant systems with and without each additive were later on adjusted the molar ratio of DTAB:DOWFAX to induce the aqueous surfactant two-phase (ASTP) system to investigate the preconcentration ability. The results showed that the ASTP system formed by DTAB:DOWFAX at 2:1 molar ratio and 0.025%wt $CaCl_2$ exhibited the best preconcentration ability, where most of pyrene and surfactants accumulate in a small volume of the surfactant-rich phase, and the pyrene and surfactant partition ratios were as high as 3,200.

Field of study..Environmental Management.. Student's signature P. Thunhapran

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LIST OF ABBREVIATIONS

°C	Degree Celsius
AMA	Sodium dihexyl sulfosuccinate
ASTP system	Aqueous surfactant two-phase system
Brij 35	Polyoxyethylene (23) dodecanol
BTEX	Benzene, Toluene, Etylbenzene, and Xylene
C12	Carbon 12
C16	Carbon 16
C8	Carbon 8
$CaCl_2$	Calcium chloride
CMC	Critical micelle concentration
CPE	Cloud point extraction
CTAB	Cetyl trimetyl ammonium bromide
DNAPL	Dense nonaqueous phase liquid
DPCl	Dodecyl-pyridinium chloride
DPDS or DOWFAX	Alkyldiphenyloxide disulfonates
DTAB	4 - (Dodecyldimetyl ammonium) butirate
DTAB	Dodecyltrimethylammonium bromide
g	Gram
HOC	Hydrophobic organic compound
KCl	Potassium Chloride
K_m	Micelle-water partitioning coefficient
K_{ow}	Octanol-water partitioning coefficient
L	Liter
LiCl	Lithium Chloride
mg/kg	Milligram per kilogram
mg/L	Milligram per liter
$MgCl_2$	Magnesium Chloride
mL	Milliliter
mM	Millimolar
mol/L	Mole per liter

MSR	Molar solubilization ratio
NaBr	Sodium Bromide
NaCl	Sodium Chloride
NAPL	Nonaqueous phase liquid
nm	Nanometer
OE	Oxyethylene
PAH	Polycyclic aromatic hydrocarbon
PCE	Tetrachloroethylene
PODD	Pentamethyl-octadecyl-1,3-propane diammonium dichloride
POE	Polyoxyethylene
ppb	Part per billion
ppm	Part per million
PZC	Point of zero charge
rpm	Round per minute
SC	Solubilization capacity
SDS	Sodium dodecyl sulfate
SEAR	Surfactant enhanced aquifer remediation
SL	Sodium laurate
SOS	Sodium octyl sulfate
TCE	Trichloroethylene
TOC	Total organic carbon
TPH	Total petroleum hydrocarbon
Triton X-100 or TX100	Octylphenoxypolyethoxy(9-10)ethanol
Triton X-114 or TX114	Octyl phenol polyethylene glycol ether
Triton X-305 or TX305	Octylphenoxypolyethoxy(30)ethanol
Tween 20	Polyoxyethylene sorbitan monolaurate
Tween 60	Polyoxyethylene sorbitan monostearate
Tween 80	Polyoxyethylene sorbitan monooleate
V	Volume
VOC	Volatile organic compound

CHAPTER I

INTRODUCTION

1.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic chemicals consisting of two or more fused benzene rings in a linear, angular, or cluster arrangement (Ladislao et al., 2004). This class of compounds is of increasing attention because of their toxic, mutagenic and carcinogenic properties (Potin et al., 2004). They are emitted into the environment as a result of natural processes including forest fires and volcanic eruptions; and of anthropogenic activities such as road traffic, fossil fuel utilization, chemical manufacture, and oil spills (Volkering et al., 1992).

Pyrene, one of high molecular weight PAHs consisting of four fused benzene rings, has been commercially used in the production of dyes, pesticides, pharmaceuticals, and plastics; and as a starting material for the synthesis of benzo(a)pyrene (www.epa.gov/epaoswer/hazwaste/minimize/factshts/pyrene.pdf). In addition, it is ubiquitous in the environment resulting from an incomplete combustion of fossil fuels (Faust, 1993). Pyrene is one of 16 PAHs that have been listed as the US EPA priority pollutants due to its toxicity, mutagenicity, low biodegradability, and environmental persistence (Volkering et al., 1992; Cheung and Kinkle, 2005). Misuse, accidental spillage, and improper disposal of PAHs including pyrene have resulted in an extensive subsurface contamination that is a major environmental concern (Mohamed and Mahfoodh, 2006). When this contaminant is in aquifers, its transport with water is limited and adsorbing strongly onto soil is preferred according to its low vapor pressure, low water solubility, and high interfacial tension with water (Grimberg et al., 1995).

Generally, there are several technologies for clean-up of organic pollutants contaminated subsurface soil and groundwater such as pump and treat, solvent flushing, phytoremediation, and bioremediation. However, in many cases, these methods have proven to be ineffective, expensive, unreliable, and often required an extended time periods for adequate clean up (Reddy et al., 1995). For example, by mean of bioremediation for contaminated soil, organic compounds need to be in a liquid phase to be used by microorganisms (Eftekhari, 2000). In addition, some organic compounds, especially PAHs are limited to be degraded by microorganism due to their toxicity, low bioavailability, and strong adsorptive capacity to soil (Liang et al., 2007). For pump and treat, nowadays, this technology is not considered as the most appropriate alternative for aquifer remediation due to the long time requirement to achieve the cleanup goals and the ineffectiveness of the system (Khan et al., 2004).

To solve these problems, the surfactant-based separations have been considered as the alternative technologies for enhancing contaminant removal from media because these technologies use environmentally friendly surfactants as the separating agent and have low energy requirement (Kimchuvanit et al., 2000). The phase separation of surfactant solution is known as an aqueous surfactant two-phase (ASTP) system. A well-known example of ASTP system that can be applied to extract the target solutes from water and other environmental metric such as soil is the cloud point extraction (CPE) that utilizes the cloud-point feature of nonionic surfactants. A temperature-induced phase separation has been successfully used in extraction, preconcentration, separation, and/or purification of various species such as heavy metals and organic compounds (Trakultamupatam et al., 2002; Kimchuvanit et al., 2000; Tong et al., 1998). From previous study, CPE technique was effectively applied in decontamination of oil polluted soil (Hiller and Wandruszka, 2004).

Recently, mixed surfactants are of great interest in scientific and industrial applications because they are less expensive than pure surfactants and also often provide better performance. The performance of mixed surfactant systems is often superior as compared to that of a single surfactant system, especially mixed cationic-anionic surfactants. Cationic-anionic surfactant mixtures often exhibit synergistic effects and provide more favorable properties in several aspects: high surface activity, enhanced adsorption, enhanced solubilization, lower interfacial tension, and much lower critical micelle concentration, as compared with those of the individual surfactant at the same total concentration (Silva and Viseu, 1998). In addition, aqueous mixtures of oppositely charged surfactants exhibit interesting phase behavior similar to that of nonionic surfactants, which is the ASTP (Tong et al, 1999). An ASTP system formed by cationic-anionic surfactant mixtures was reported by

Zhao and Xiao (1996). This system has been used for the extraction of biomaterials and organic compounds (Tong et al., 1999; Mao et al., 2002). When a cationic and an anionic surfactants are mixed at certain total surfactant concentrations and molar ratios, the solution separates spontaneously into two aqueous phases, even at ambient temperature for some systems. One phase is rich, and the other phase is lean in both of surfactants (Zhao and Xiao, 1996).

In comparison between a conventional extraction system formed by nonionic surfactants and a novel extraction system formed by mixtures of cationic and anionic surfactants, the former takes place only above a critical temperature known as the cloud point but the latter can be operated at low temperature if the surfactant concentration and composition are suitable (Khaolerk, 2006). Therefore, a new ASTP extraction system does not require an addition of energy for increasing temperature as CPE (Xiao et al., 2000). Moreover, ASTP system is safe, nontoxic, and nonflammable. So, it represents a relatively environmentally benign extraction technique (Hao et al., 2006). At present, the ASTP extraction system formed by mixtures of cationic and anionic surfactants was successfully applied for extraction and preconcentration organic contaminants from aqueous solution (Krutlert, 2004; Kunanupap, 2004; Khaolerk, 2006; Intasara, 2006). Currently, there is no study of ASTP formed by cationic-anionic surfactant mixtures for clean-up organic contaminants from soil. Therefore, from its characteristics and advantages, the ASTP extraction system formed by the mixtures of cationic and anionic surfactants is a promising technique to clean up soil contaminated with organic compounds. In this study, this technique was applied to clean-up pyrene contaminated soil.

1.2 Objectives

The main objective of this research was to clean-up pyrene contaminated soil using the mixtures of cationic and anionic surfactants as separating agents. The extracted solution containing pyrene was consequently reduced the volume by adjusting the system to form an aqueous surfactant two-phase (ASTP) system. The sub-objectives were as follows:

1. To study the surfactant adsorption onto soil and pyrene solubilization by surfactant solutions both individual surfactant and mixed surfactants at various molar ratio of cationic to anionic surfactants in order to determine a suitable surfactant system that optimizes the surfactant adsorption along with pyrene solubilization.
2. To determine the effects of surfactant concentration and additives addition (such as electrolyte and lipophilic likers) on pyrene removal from contaminated soil.
3. To induce the ASTP condition by adjusting the surfactant composition in order to preconcentrate pyrene in the surfactant-rich phase.

1.3 Hypotheses

An aqueous solution containing mixtures of cationic and anionic surfactants can be applied to remove pyrene from contaminated soil effectively and the aqueous surfactant two-phase (ASTP) system can be afterward induced to preconcentrate pyrene in the surfactant-rich phase.

1.4 Scope of the study

A homogeneous solution of cationic-anionic surfactant mixtures was utilized to clean-up pyrene from contaminated soil at constant pyrene concentration of 200 mg pyrene/kg soil. Dodecyltrimethylammonium bromide (DTAB) and alkyldiphenyloxide disulfonate (DPDS or trade name of DOWFAX 8390) were used as cationic and anionic surfactants. Silica sand with low iron content was used as a model porous medium in this study. Pyrene contaminated soil was obtained from the spiking of pyrene solution onto silica sand.

The surfactant adsorption onto soil and solubilization of pyrene by pure surfactants (DTAB and DOWFAX) and mixed surfactants (DTAB:DOWFAX) at molar ratios of 1:1, 1:1.5, 1:2, and 1.5:1 were investigated in order to select a suitable surfactant system that optimized the surfactant adsorption onto soil and pyrene solubilization. These molar ratios of DTAB:DOWFAX used in this study were proved to form homogeneous, single phase solutions without surfactant precipitation (Krutlert, 2004; Kunanupap, 2004).

Later on, surfactant concentration at a suitable surfactant composition obtained from previous studies was varied in order to investigate the effects of surfactant concentration on pyrene removal from contaminated soil at ambient temperature in batch experiment. After an appropriate surfactant system at certain concentration that provided the optimal efficiency of pyrene removal was obtained, this system in the presence of additives including electrolyte and lipophilic linkers were studied. Calcium chloride ($CaCl_2$) was utilized as the electrolyte in order to study the effects of its concentration on pyrene removal from contaminated soil. The *n*-alcohols varied alkyl chain length C8, C12, and C16 (octanol, dodecanol, and hexadecanol) were used as the lipophilic linkers. The effects of alcohol chain length and concentration on pyrene removal from contaminated soil were investigated. The comparison on pyrene removal efficiency received from each effect was revealed. Afterward, the surfactant systems that provided the suitable pyrene removal efficiency of each effect were induced to form the ASTP system by adjusting the surfactant composition in order to preconcentrate the surfactants and solubilized pyrene into a small volume of the surfactant-rich phase. Then, the preconcentration ability in term of the surfactant and pyrene partition ratios, the fractional surfactant-rich phase volume, the percentage of pyrene extracted in the surfactant-rich phase, and concentration of pyrene remaining in surfactant-dilute phase were determined.

CHAPTER II

THEORECTICAL BACKGROUND AND LITERATURE REVIEW

2.1 Pyrene

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds consisting of two or more fused benzene rings in a linear, angular, or cluster arrangement. PAHs include a class of organic priority pollutants causing serious environmental and public health concern due to the following characteristics: (1) chronic health effects, especially carcinogenicity; (2) microbial recalcitrance; (3) high bioaccumulation potential; and (4) low removal efficiencies by traditional treatment processes. They are classified as both carcinogenic and noncarcinogenic compounds. Carcinogenic PAHs refer to fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene. Non-carcinogenic PAHs refer to naphthalene, acenaphthylene, acenapthene, fluorene, anthracene and phenanthrene. Their occurrence in the environment is partly the result of natural processes including forest fires and volcanic eruptions, and partly due to anthropogenic activities including the incomplete combustion of fossil fuels, accidental discharge during transport, use and disposal of petroleum products, and incineration of wastes (Hurst et al., 1996; Ladislao et al., 2004; Rivas, 2006).

Pyrene, also known as benzo(def)phenanthrene and β-pyrene, is a one of high molecular weight PAHs consisting of four fused benzene rings (Faust, 1993). It has been commercially used in the production of dyes, pesticides, pharmaceuticals, and plastics and as a starting material for the synthesis of benzo(a)pyrene (www.epa.gov/epaoswer/hazwaste/minimize/factshts/pyrene.pdf). Besides, it is everywhere in the environment due to a product of incomplete combustion of fossil fuels (Faust, 1993). According to its toxicity, mutagenicity, carcinogenicity, low biodegradability, and persistence in environment, this compound is one of 16 PAHs that has been listed as one of US EPA priority pollutants (Keith and Telliard, 1979;

Volkering et al., 1992). Although a large body of literature exists on the toxicity and carcinogenicity of PAHs, toxicity data for pyrene are not available. No human data were available that addressed the toxicity of pyrene (Faust, 1993). Pyrene can be released to the environment through misuse, accidental spillage, and improper disposal (Ladislao et al., 2004). Therefore, it is commonly found in air, soil, sediments, surface water, and aquifer (Juhasz and Naidu, 2000).

In ambient air, the amount of pyrene is directly decreased by photolysis or it may adsorb onto particulate matter and may be moved to long distance transport depending on the particle size distribution and climatic conditions. In aquatic environment, this contaminant can strongly adsorb onto sediments and particulate matter, and slightly or moderately bioconcentrate in aquatic organisms, but it tends not to hydrolyze. Moreover, it may be decreased due to biodegradation and photolysis close to the surface of waters. Apart from water problems, pyrene is extensively contaminated onto soil. In surface soil, when it is released into soil, it tends to strongly adsorb onto soil, but it will not hydrolyze or evaporate from soils and surfaces. Additionally, its concentration may be decreased due to appreciable biodegradation (www.speclab.com/compound/c129000.htm). An important environmental concern is pyrene contaminated aquifers including subsurface soil and groundwater (Mohamed and Mahfoodh, 2006). When it is discharged to aquifers, its transportation in water is limited and prefers to strongly adsorb onto soil resulting in high persistence due to its low vapor pressure, low water solubility, and high interfacial tension with water (Grimberg et al., 1995). From these reasons, an extensively subsurface contamination with pyrene is considered as a serious environmental problem. Oregon Department of Environmental Quality reported the data of chemicals that were released to environment. The data in 1994 showed that at Former Unocal Terminal 0022 Site in Clatsop County Oregon, U.S.A., pyrene was found in groundwater and soil at concentration about 0.035 and 5,700 ppm, respectively (www.deq.state.or.us/lq/ECSI/ecsidetailfull.asp?seqnbr=1646#siteinfo).

In general, bioremediation has been used for clean-up of PAHs including pyrene contaminated soil. Valentin et al. (2007) studied the biodegradation of four different PAHs including pyrene by the white-rot fungus in a spiked marsh soil operated in a slurry reactor system. The initial pyrene concentration in soil slurry system was about 50 mg/kg soil. The results showed that the concentrations of pyrene up to 30 mg/kg soil were degraded by these microorganisms after 30 days of operation. However, the application of bioremediation has some limitations. Some chemicals are not amenable to biodegradation such as heavy metals, radionuclides and some chlorinated compounds (Boopathy, 2000). Especially, the bioremediation of soil contaminated with PAHs is often limited by the PAH bioavailability due to their toxicity, low water solubility, and high soil-water distribution ratios (Volkering et al., 1992). Therefore, sites that are contaminated with high concentration of PAHs including pyrene, bioremediation may not be considered as an effective remedial technology. To solve these problems, surfactant-based separation technologies considered as the alternative technologies may be used for enhancing removal efficiency of organic compounds including PAHs from contaminated soil because these technologies use environmentally friendly surfactants as the separating agent and have low energy requirement (Kimchuvanit et al., 2000).

2.2 Surfactant

2.2.1 Introduction

Surfactants, an abbreviation of surface active agents, are amphipathic molecules consisting of two dissimilar parts: a hydrophilic head and a hydrophobic tail as shown in Figure 2.1 (Eftekhari, 2000; Rouse, 2001). This combination makes the surfactant ambivalent; the hydrophilic head group is attracted to polar environments, such as water, while the hydrophobic tail comprised a long chain hydrocarbon is attracted to nonpolar environments, for example oil. Consequently, the surfactant can dissolve either in water or oil and have the capability to solubilize water or oil to create homogeneous system (Uppgård, 2002).

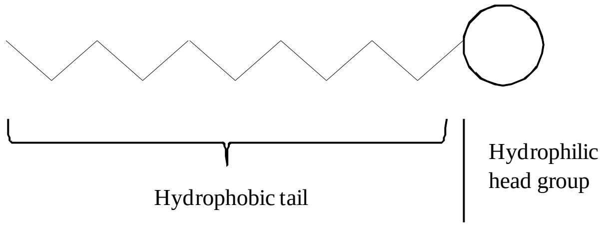


Figure 2.1 Schematic diagram of surfactant molecule (Eftekhari, 2000)

Surfactants are an important class of chemicals that are widely used in products ranging from detergents, pharmaceuticals, and food products to fuel additives. Moreover, they play a major role in the oil industry, for example in enhanced and tertiary oil recovery. They are also occasionally used for environmental protection, e.g. in oil slick dispersants. Recently, surfactants have applied in such high-technology areas such as electronic printing, magnetic recording, biotechnology, microelectronics and viral research (Rosen, 2004; Tadros, 2005; Suchomel, 2006).

2.2.2 Types of surfactant

Surfactants are normally classified into four types according to the charge on the polar head group consisting of anionic, cationic, nonionic and zwitterionic. The examples of various surfactant types are as illustrated in Table 2.1. Differences in the chemistry of surfactants due to the nature of the hydrophobic tails (degree of branching, carbon number, aromaticity) are usually less pronounced than those due to the nature of the hydrophilic head group (Li, 2000).

Anionic surfactants are molecules that bear a negative charge on the hydrophilic head. The most commonly used head groups are carboxylates, sulphates, sulphonates and phosphates. This type of surfactant can adsorb onto the positively charged surface (such as alumina) with theirs negatively charged hydrophilic head oriented to the surface and theirs hydrophobic tail oriented away from that surface (Rosen, 1989). They are widely used in many industrial applications due to their relatively low cost of manufacture and they are used in practically every type of detergent (Tadros, 2005). Moreover, they are applied in petroleum recovery due to their high aqueous solubility and repulsion from soils that possess a negative surface charge (Ouyang et al., 1995).

Cationic surfactants are molecules that bear a positive charge at the hydrophilic head. Their head groups are usually comprised of an amino or quaternary nitrogen group. They can adsorb onto the negatively charged surface (i.e. clay and silica at neutral pH) with theirs positively charged hydrophilic head oriented toward the surface and theirs hydrophobic tail oriented away from that surface (Rosen, 1989). The prime use of cationic surfactants is their tendency to adsorb at negatively charged surfaces, e.g. anticorrosive agents for steel, flotation collectors for mineral ores, dispersants for inorganic pigments, antistatic agents for plastics, anticaking agent for fertilizers, and as bactericides. Due to the positive charge on the head group giving the strong substantively on negatively charged fibers such as cotton and hair, they are used as fabric and hair conditioners (Tadros, 2005).

Nonionic surfactants are molecules without charges at the hydrophilic head group. They contain a polyoxyethylene group as the soluble head group (Ouyang et al., 1995). The water solubility of nonionic surfactants depends on the length of the ethoxylated chain such as the longer it is, the greater its solubility. They can adsorb onto the surface with either the hydrophilic or the hydrophobic group oriented toward the surface depending on the nature of surface. The major use of these surfactants is a composition in foods and drinks, pharmaceuticals and skin care products (Rosen, 1989).

Zwitterionic (Amphoteric) surfactants consist of both cationic and anionic groups at the hydrophilic head depending on pH of solution. In acid pH solutions, the molecules acquire a positive charge and behave like cationic surfactants whereas in alkaline pH solutions they become negatively charged and behave like anionic surfactants. They can adsorb onto both positively charged and negatively charged surfaces without changing the charge of the surface significantly. Zwitterionic surfactants have excellent dermatological properties. They also exhibit low eye irritation and are often used in shampoos and other personal care products, especially cosmetics (Rosen, 2004; Tadros, 2005).

Table 2.1 Classification of surfactant molecules

Classification	Example	Chemical Formula
Anionic	Sodium dodecyl sulfate (SDS)	$CH_3(CH_2)_{11}SO_4^-Na^+$
Cationic	Cetyl trimetyl ammonium bromide (CTAB)	$CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$
Nonionic	Polyoxyethylene (23) dodecanol (Brij 35)	$CH_3(CH_2)_{11}(OCH_2CH_2)_{23}OH$
Zwitterionic	4 - (Dodecyldimetyl ammonium) butirate (DAB)	$CH_3(CH_2)_{11}N^+ (CH_3)_2(CH_3)COO^-$

Source: Bezerra et al, 2005

2.2.3 Surfactant adsorption

One of the characteristic features of surfactants is their tendency to adsorb at the surface/interface mostly in an oriented fashion. Surfactant adsorption is a process of transfer of surfactant molecules from bulk solution phase to the surface/interface. The adsorption of surfactants at the solid-liquid interface play an important role in many technological and industrial applications, such as detergency, mineral flotation, corrosion inhibition, dispersion of solids, oil recovery and so on (Paria, 2003; Paria and Khilar, 2004). However, the adsorption of surfactants has some disadvantages in their applications for enhanced oil recovery and surfactant-enhanced soil remediation because it results in surfactant loss and reduced surfactant mobility. Moreover, surfactant adsorption may create new adsorption sites for hydrophobic compounds and also leads to a significant reduction in their effectiveness to remove the contaminants from the soils (Noordman et al., 2000; Rodrı´guez-Cruz et al, 2005).

The adsorption of surfactants at the solid/liquid interface is strongly influenced by the number of factors: (1) the nature of structural groups on the solid surface, i.e. highly charged sites or non-polar sites, (2) the nature of surfactant molecule such as the nature of hydrophilic head groups (ionic or nonionic) or hydrophobic groups (long or short, straight-chain or branched, aliphatic or aromatic), (3) the environment of the aqueous phase such as pH, temperature, presence of electrolyte, and presence of other additives such as alcohol, urea, and etc (Rosen, 1989).

2.2.3.1 Mechanism of surfactant adsorption

There are several mechanisms by which surface-active molecules may adsorb onto the solid substrates from aqueous solution. Generally, adsorption of surfactants involves single ions rather than micelles (Rosen, 1989; Paria and Khilar, 2004).

a) Ion exchange: Replacement of counter ions adsorbed onto the substrate from the solution by similarly charged surfactant ions.

b) Ion pairing: Adsorption of surfactant ions from solution onto oppositely charged sites unoccupied by counter ions.

c) Acid - Base Interaction: Adsorption occurs by either hydrogen bond between substrate and adsorbate or Lewis acid - Lewis base reaction.

d) Hydrophobic bonding: Adsorption occurs by this mechanism when there is an attraction between the hydrophobic group of an adsorbed molecule and a molecule present in the solution.

e) Adsorption by polarization of ¶ electrons: Adsorption occurs by this mechanism when the surfactant contains electron-rich aromatic nuclei and the solid adsorbent has strongly positive sites, the attraction between electron rich aromatic nuclei of the adsorbate and positive sites on the adsorbent results adsorption.

f) Adsorption by dispersion forces: Adsorption by London-van der Waals force between adsorbate and adsorbent increases with increasing the molecular weight of the adsorbate.

2.2.3.2 Equilibrium adsorption of surfactant (adsorption isotherm)

The study of equilibrium of surfactant adsorption is important to determine the maximum amount adsorbed per unit area or mass of the adsorbent and to determine the adsorption isotherm. The amount of surfactant adsorbed onto the soil solid can be expressed by Equation 2.1 (adapted from Rosen and Li, 2001).

$$q = \frac{(C_{in} - C_{eq})\,V}{g} \tag{2.1}$$

where: q = Mass of surfactant adsorbed to soil normalized by the mass of soil (g surfactant/ g soil)

C_{in} = Initial surfactant concentration (mol/L)

C_{eq} = Equilibrium surfactant concentration (mol/L)

V = Volume of solution (L)

g = Weight of soil solid (grams)

Adsorption of surfactant at the solid-liquid interface is usually characterized by adsorption isotherm. Adsorption isotherm is obtained by determining “depletion of the surfactant due to adsorption onto solid surface at constant temperature”. The amount of surfactant adsorbed per unit mass or unit area of the solid by varying the surfactant concentration is plotted against equilibrium concentration (Paria, 2003). The example of the typical adsorption isotherm of ionic surfactants onto oppositely charged surface is shown in Figure 2.2. In general, a typical isotherm can be divided into four regions when plotted on a log-log scale.

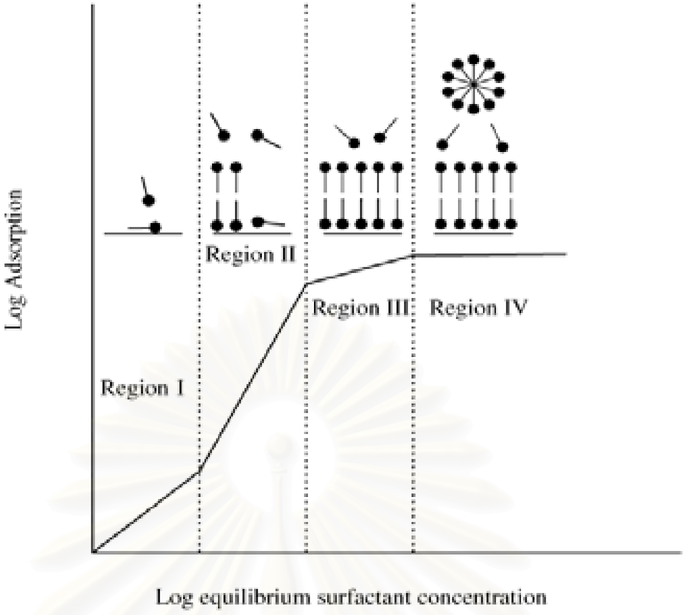


Figure 2.2 Schematic diagram of a typical surfactant adsorption isotherm (Adak et al, 2005)

Region 1 is a region of low adsorption densities and followed as Henry's law. This region occurs at very low surfactant concentration and surfactants are adsorbed as monomers and did not interact with one another. The adsorption in this region results primarily from electrostatic interaction between surfactant ions and the oppositely charged solid surface. Adsorption increases linearly with concentration and the slope of the curve is approximately one.

Region 2 is indicated by the sharp increase in the slope of the isotherm. At the onset of region 2, surfactant species begin to form surface aggregates, solloids (surface colloids), including hemi-micelles, admicelles, etc., due to lateral interaction between hydrocarbon chains. Hemi-micelles and admicelles occur at the surfactant concentrations below critical micelle concentration (CMC) depending on their structures are formed as being local monolayers or local bilayers, respectively. The hemi-micelle is considered as a monolayer that has head groups adsorb on the solid surface whereas tail groups are contacted with the aqueous solution. The admicelle is considered as a bilayer with a lower layer of head groups adsorbs on the solid surface and an upper layer of head groups is toward to the solution. Due to this additional driving force resulting from the lateral association with the electrostatic interaction still active, the adsorption density exhibits a sharp increase in this stage.

Region 3 shows a slower rate of adsorption than region 2. When the solid surface is electrically neutralized by the adsorbed surfactant ions, the electrostatic attraction is no longer operative and adsorption takes place due to lateral attraction alone with a reduced slope.

Region 4 is the plateau adsorption region. When the surfactant concentration reaches critical micelle concentration (CMC), the surfactant monomer activity becomes constant and any more increase in concentration contributes only to the micellization in solution and it does not change the adsorption density. The adsorption in this region is mainly through lateral hydrophobic interaction between the hydrocarbon chains. In regions 3 and 4, surfactant molecules adsorb with a reversed orientation (head groups facing the bulk solution) resulting in a decrease in the hydrophobicity of the particles in this region (Paria and Khilar, 2004; Adak et al., 2005; Zhang and Somasundaran, 2006).

2.2.4 Micellization

Micellization is an important phenomenon in detergency and solubilization. When surfactants are dissolved in solution, theirs hydrophobic groups distort the structure of water by breaking hydrogen bond between water molecules resulting in an increase of the free energy of the system. So, the system responds in some ways to minimize the free energy and then surfactant molecules are expelled to the surfaces or interfaces of the system, with their hydrophobic groups oriented to minimize contact with the water molecules. The surface of water becomes covered with a single layer of surfactant molecules (monomers) with their hydrophobic groups oriented predominantly toward the air and their hydrophilic groups attach onto the water. This decrease in the dissimilarity of two phases contacting each other at the surface results in a decrease in the surface tension (Rosen, 1989).

At low surfactant concentration in an aqueous solution, the monomers mainly adsorb at the air/water interface. When surfactant concentrations are increased, the surface is more adsorbed and concentrated by monomers. If their concentrations are increased above a certain threshold called the critical micelle concentration (CMC), another way to minimize the free energy is to reorient themselves into colloidal-sized clusters, known as micelles. This phenomenon is called micellization or micelle formation (Hill, 1999; Paleologos et al., 2005). Typically, normal micelles consist of 60 – 100 monomers and are at equilibrium with a surfactant concentration in solution close to CMC (Matinez et al., 2000). Surfactant micelles contain two portions. One is the hydrophobic tail portions of surfactant molecules within their interior while the other is the hydrophilic portions of surfactant molecules within micelle exterior (reported by Murphy, 1998). The polar exterior of micelle imparts high aqueous solubility while the nonpolar interior acts as a pseudo-oil phase which nonpolar organic compounds may partition (Shiau et al., 1994). However, depending on the specific surfactant and solution conditions, micelles can adopt a variety of shapes, ranging from roughly spherical to ellipsoidal as demonstrated in Figure 2.3 (Scamehorn et al., 2004; Paleologos et al., 2005).

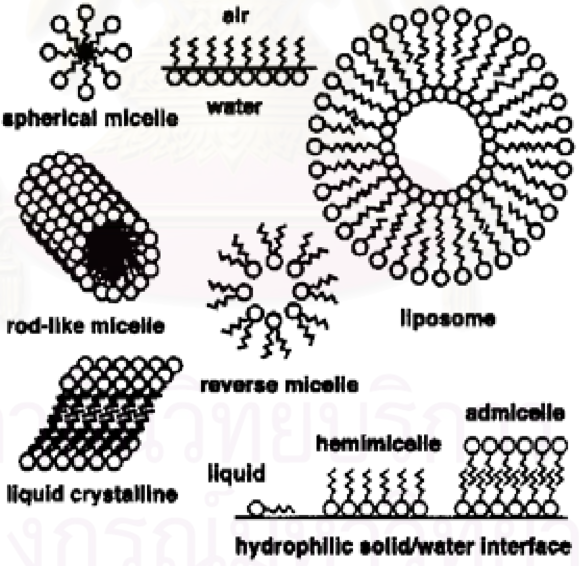


Figure 2.3 Typical surfactant aggregates (Scamehorn et al., 2004)

Surfactant molecule contributes differently to a given property when present as monomer versus in a micelle. The CMC can be determined by plotting a physicochemical property of the solution such as osmotic pressure, turbidity, solubilization, magnetic resonance, surface tension, equivalent conductivity and selfdiffusion versus the surfactant concentration as illustrated in Figure 2.4. Different measurements yield slightly different CMC values depending upon the technique used because the formation of micelles occurs over a small concentration range. Different techniques are sensitive to different concentrations in this range (Lokar, 2004; Tadros, 2005).

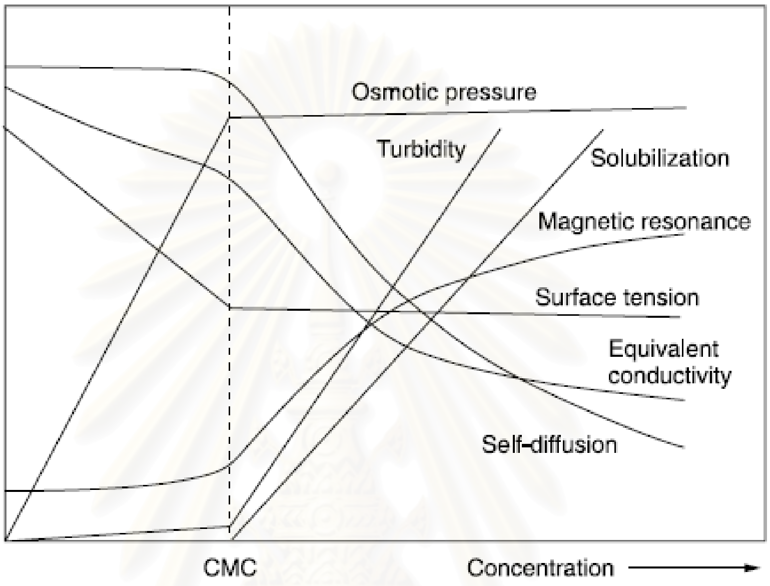


Figure 2.4 Changes in the surfactant concentration dependence of a wide range of physicochemical changes around the critical micelle concentration (CMC)

In general, the CMC can be measured by carrying out surface tension measurements on a series of different surfactant concentrations. Surfactants exhibit a specific surface tension curve as a function of the concentration. Initially the surfactant molecules increasingly enrich themselves at the water surface. During this phase the surface tension decreases linearly with the logarithm of the surfactant concentration. When the CMC is reached, i.e. when the surface is saturated with surfactant molecules, a further increase in surfactant concentration no longer has any appreciable influence on the surface tension (KRÜSS GmbH, 2007).

Factor affecting the CMC and micellization are structure of surfactant (hydrophobic volume, chain length, head group area), temperature, additive, pH, surfactant concentration and surfactant composition (for surfactant mixtures) (Rosen, 1989; Murphy and Taggart, 2002; Renoncourt, 2005). Within any class of surface active agent, the CMC decreases with increasing chain length of the hydrophobic portion (alkyl group). Generally, nonionic surfactants have lower CMC than their corresponding ionic surfactants of the same alkyl chain length. Incorporation of a phenyl group in the alkyl group increases its hydrophobicity to a much smaller extent than increasing its chain length with the same number of carbon atoms. The valency of the counter ion in ionic surfactants has a significant effect on the CMC, for example increasing the valency of the counter ion from 1 to 2 can reduce the CMC (Rosen, 1989; Tadros, 2005). Moreover, the addition of additives such as electrolyte and alcohol in aqueous surfactant solution can cause a change in the CMC. For example, the addition of electrolyte (NaCl) to a solution of SDS anionic surfactant dramatically lowers the CMC (Kim et al., 2000). The presence of alcohols such as butanol, pentanol, and hexanol in an anionic surfactant, namely potassium dodecanoate can also cause a decrease in CMC (Tadros, 2005).

2.2.5 Micellar structure and shape

2.2.5.1 Morphologies of aggregates

The structures of aggregates formed by surfactants in aqueous solution are spherical micelles, rod-like micelles (wormlike micelles), bilayers, inverted structures, and etc as shown in Figure 2.3. The aggregation structures of surfactants in aqueous solution depend on the chemical structure of surfactant and solution condition such as concentration, temperature, pH and ionic strength. These structures can transform from one to another when the solution are changed (Uppgård, 2002; Aswal, 2003; Buwalda, 2001).

(A) Spherical micelles

Spherical micelles are clusters consisting of hydrophobic tails in the inner core with the hydrophilic head groups facing to water. Normally, unbranched single-tailed surfactants possess a conical shape and aggregate to form spherical micelles in aqueous solution above their CMC. Spherical micelles usually consist of

40-100 monomers and are approximately 5 nm in diameter (Holmberg et al., 2003; Buwalda, 2001).

(B) Wormlike micelles

Wormlike micelles are formed by surfactants whose monomer shape resembles a truncated cone. Both theoretical and experimental studies show that wormlike micelles are long (several tens of micrometers) and flexible. The presence of wormlike micelles in aqueous solution is often reflected by an increase in relative viscosity. Viscoelastic solutions are formed upon increasing the surfactant concentration. The viscoelasticity indicates that an entangled network of wormlike micelles has been formed. Formation of these micelles can be induced by addition of strongly binding counter ions to ionic surfactants in aqueous solution (Buwalda, 2001).

(C) Vesicles

Generally, surfactant molecules possessing one head group and two alkyl tails form vesicles in aqueous solution. Vesicles form curved bilayers similar to those of lamellar phase. The hydrophobic tails are the inner core of bilayer while the hydrophilic head groups are located at bilayer/water interface. A vesicle is a shell which encapsulates an aqueous interior. Vesicles range in diameter from 20 nm to several micrometers and can be either unilamellar or multilamellar. Vesicles formed from pure surfactants are metastable and eventually revert to the flat bilayer state and ultimately precipitate as crystalline materials (Rosen, 1989; Bulwada, 2001).

(D) Reverse Micelles

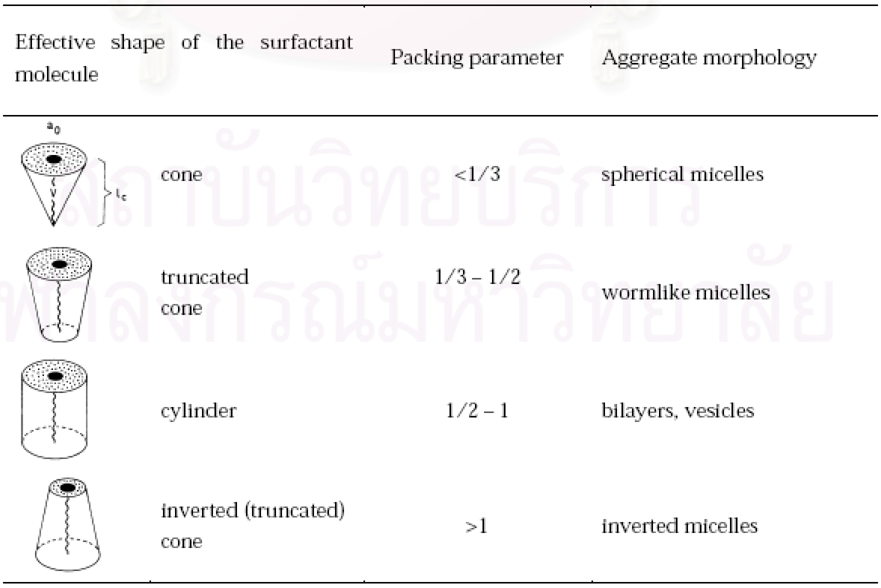
Reverse micelles have the opposite structure arrangement to the normal micelles where the water is in the core which surrounding by the surfactant polar head groups. The hydrocarbon chains face to the non-polar solvent, for example oil (Holmberg et al., 2003).

2.2.5.2 Packing parameter

Aggregate morphology is mainly determined by a delicate balance between attractive hydrophobic interactions of surfactant tails and electrostatic repulsions of surfactant head groups. The molecular architecture of a given surfactant determines the type of aggregate into which a surfactant associates in aqueous solution. The relationship between the shape of the surfactant monomer and the morphology of aggregate is represented by the packing parameter. The packing parameter (P) can be calculated from equation (2.2). In this equation, V is the volume of the hydrocarbon part of the surfactant, *l* is the chain length of the extended all-trans alkyl tail, and a_0 is the mean cross-sectional (effective) head group surface area.

$$P = V/a_0 l \qquad (2.2)$$

Surfactants where $0<P<1/3$ form micelles in aqueous solution. If $1/3<P<1/2$ wormlike micelles are formed whereas surfactants with $1/2<P<1$ form vesicles. Inverted (reversed) structures are formed when $P>1$. The relationship of the architecture of surfactant monomer and aggregate morphology is demonstrated in Figure 2.5 (Rosen, 1989; Buwalda 2001).



Effective shape of the surfactant molecule		Packing parameter	Aggregate morphology
	cone	<1/3	spherical micelles
	truncated cone	1/3 – 1/2	wormlike micelles
	cylinder	1/2 – 1	bilayers, vesicles
	inverted (truncated) cone	>1	inverted micelles

Figure 2.5 Relationship between the shape of surfactant monomers and aggregate morphology (Bulwada, 2001)

2.2.5.3 Micellar aggregation number

Micellar aggregation number is a number of surfactant monomers within a micelle. Generally, a conventional fluorescent probe method has been used to calculate aggregation numbers of several types of surfactants. The aggregation numbers in aqueous solution increase with an increase in the length of the hydrophobic group (greater *l*), a decrease in the number of OE units in POE nonionic surfactants (smaller a_0), and an increase in the binding of the counterions with the micelle in ionic surfactans (smaller a_0). In addition, these numbers decrease with an increase in the size of the hydrophilic head groups of surfactant (larger a_0) (Rosen, 1989; Renoncourt, 2005).

2.2.6 Solubilization

One of the important properties of surfactants that is directly related to micelle formation is solubilization. Solubilization is defined as the spontaneous dissolving of a substance (solid, liquid, or gas) by reversible interaction with surfactant micelles in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of solubilized material (Rosen, 1989).

The solubilization capacity (SC) is a measure of the amount of a compound (solubilizate) that can be solubilized in a surfactant solution, relative to the amount of surfactant in the micelles (Hill, 1999). The SC of surfactants with the same hydrophilic head group generally increases with increasing alkyl tail length (Rosen, 1989). Hill (1999) stated that the size and shape of micelles affects the solubilization capacity of surfactants. The SC of a given micellar solution is dependent on the micellar volume available for solubilization. Micelles contain different regions with varying polarity and the SC of a given compound within the micelle will be determined by the volume of the regions, in which the compound is solubilized, as well as the concentration of the compound in those regions (Hill, 1999). The exact location in the surfactant micelle at which solubilization occurs (locus of solubilization) varies with the nature of material solubilized and is of importance in that it reflects the type of interaction occurring between surfactant and solubilizate. In general, solubilization is believed to occur at a number of sites within micelle: (1) on the micelle surface; (2) between the hydrophilic head groups; (3) in the palisade layer; (4) more deeply in the palisade layer; and (5) within the hydrophobic core of the micelle. The palisade layer is the region which marks the transition between the hydrophilic outer layers and the hydrophobic core. It contains both hydrophobic and hydrophilic groups. Small polar molecules, such as short-chain phenols, in aqueous medium are generally solubilized in the shallow palisade layer of surfactant micelles or by adsorption at the micelle-water interface. In contrast, quite hydrophobic and nonpolar solubilizates tend to reside only in the hydrophobic cores of surfactant aggregates. Large polar molecules, such as long-chain alcohols, are solubilized between surfactant molecules in the palisade layer with the polar groups of solubilizates oriented toward the polar groups of surfactant molecules and nonpolar portions pointed toward the interior of the micelles. Alternatively, larger hydrophobic space in surfactant aggregates could result in greater solubilization of hydrophobic species such as PAHs in aqueous medium (Rosen, 1989; Acosta et al., 2003; Swe et al., 2006).

The solubilization capacity or solubilizing power can be characterized by the molar solubilization ratio, MSR, and the micelle-water partitioning coefficient, K_m. MSR is a measure of the solubilization capacity of a surfactant solution for a particular solute. MSR refers to the moles of the solute solubilized per mole of surfactant in the micelles and is determined by the slope of the graph of surfactant concentration versus solute concentration in mol/L. In addition to MSR, the effectiveness of solubilization can also be expressed in terms of the partition coefficient, K_m, of the organic compound between micelles and the aqueous phase. The partition coefficient can be expressed in Equation 2.3.

$$K_m = X_m / X_a \tag{2.3}$$

Where X_m and X_a are the mole fractions of solute in micelles and the aqueous phase, respectively. The value of X_m can be calculated as X_m = MSR/(1+ MSR), and X_a can be expressed as $X_a = C_{eq}/C_{eq}+55.55$, where C_{eq} is the equilibrium concentration of the organic solute in water alone, and 55.55 is the inverse molar volume of water. In solubilization studies, C_{eq} is the water solubility concentration of the organic solute (Reported by Fuangswasdi et al., 2006).

The solubilization ability is influenced by many factors such as the structure of surfactant and solubilizate, organic additives, and temperature. For hydrocarbon or long-chain polar compounds that are solubilized in the interior of micelle or deep in the palisade layer, the amount of solubilizate increases with an increase in the size of micelle. Thus, any factor that causes an increase in either the diameter of micelle or its aggregation number can be expected to increase the solubilization capacity. For nonpolar solubilizate, if surfactant has a longer hydrophobic tails meaning a greater the aggregation number of micelle, surfactant micelle provides a higher solubilization capacity for these compounds. For polar compounds, very few generalizations relating the degree of solubilization to the structure of surfactant can be made from available data, since solubilization can be in both the inner and outer regions of micelles. Moreover, the temperature has the effect on the solute solubilization by surfactant solution. For ionic surfactant, the increasing temperature can enhance the extent of solubilization both polar and nonpolar solubilizates due to an increase in thermal agitation causing more space available for solubilization in the micelle. For nonionic surfactant, it is quite complex since the temperature of system relates to its cloud point. For nonpolar solubilizates, the solubilization increases with an increase in the temperature and the increase becoming very rapid as the cloud point is approached (Rosen, 1989; Rosen, 2004).

Besides, the addition of additives such as electrolyte and lipophilic linkers in the surfactant solution affects to the solubilization ability. The addition of small amount of electrolyte to ionic surfactant solutions increases the extent of solubilization of hydrocarbons that are solubilized in the inner core of micelle and decreases that of polar compounds that are solubilized in the outer region of palisade layer. The presence of electrolyte in the ionic surfactant solution decreases the repulsion between the similarly charged ionic surfactant head groups, thereby decreasing CMC and increasing the aggregation number and volume of micelles. The increase in aggregation number of micelles can cause an increase in the solubilization for hydrocarbon in the inner core of micelle (Rosen, 1989). Recently, there are many researches that studied the effect of electrolyte in surfactant solution on the solubilization of solute. For example, Kim et al. (2000) studied the effect of electrolyte on pyrene solubilization of dodecyl sulfate (anionic) micelles and found that the addition of a suitable amount of electrolyte in the micellar dodecyl sulfate solutions increases the solubility of pyrene as compared to the results obtained from this surfactant solution alone.

On the other hand, the presence of lipophilic linkers in surfactant solution can enhance the solute solubilization capacity (Graciaa et al., 1993; Salager et al., 1998; Uchiyama et al., 2000). The concept of lipophilic linkers was first introduced by Graciaa et al. (1993). The lipophilic linker is a molecule that orientates along the surfactant tails and promotes orientation of oil molecules further into the oil phase. Thus, lipophilic linkers serve as a link between oil molecules and the surfactant tails (Sabatini et al., 2003). The long-chain alcohols with C8 or higher behave as lipophilic linkers. When lipophilic linker dissolves in the surfactant solution, they are adsorbed at palisade layer of surfactant micelle, where its hydrophilic head orients toward the micelle-water interface while its alkyl chain intercalates into the hydrophobic region of micelle and also interacts with the surfactant tails. From these reasons, it can cause the inner core of micelle has a higher degree of hydrophobicity. Thus, the addition of long-chain alcohol as lipophilic linker tends to have more favorable for non-polar or hydrophobic solute solubilization (Graciaa et al, 1993; Tan and O’Haver, 2004). Recently, there are many researches reporting that the addition of lipophilic linker into surfactant solution increases the solubilization capacity of solute. Salager et al. (1998) studied the effect of alcohol concentration, chain length of the alcohol, and hydrophobicity of the oil on the solubilization enhancement of the different linker formulations. The main finding of this research is that the solubilization enhancement was not proportional to the lipophilic linker concentration. Rather, after reaching a certain ratio of lipophilic linker to surfactant, the solubilization enhancement plateaus, and further increasing the concentration of the lipophilic linker no longer enhances the solubilization capacity. Later on, Uchiyama et al. (2000) investigated the effect of lipophilic linker on the solubilization capacity of anionic surfactant microemulsion systems. N-Alkyl alcohols are utilized as lipophilic linkers in middle-phase microemulsions of trichloroethylene, tetrachloroethylene, and hexane. The lipophilic linker effect increases the solubilization capacity of the anionic surfactant system. The solubilization parameter for both hydrocarbons and chlorinated hydrocarbon oil increases as a function of alcohol concentration. As the alkyl chain length of the alcohol linker molecule increases, the solubilization capacity increases. Moreover, Tan and O'Haver (2004) studied the impact of lipophilic linkers (long chain alcohols: octanol, decanol, and dodecanol) on the adsolubilization of styrene by Triton X nonionic surfactant at the water-silica interface. They found that the adsolubilization of styrene are promoted by the linkers. The increasing the hydrophobic chain length and the concentration of linker in the system can enhance the styrene adsolubilization capacity, though the impact of increasing hydrophobic tail length stops at dodecanol.

2.3 Cationic-anionic surfactant mixtures

Mixed surfactant systems are much favored from the view point of economy and performance. They are less expensive than pure surfactants and also often provide better performance. The performance of mixed surfactant systems is often superior as compared to that of a single surfactant system. Thus, surfactant mixtures are commonly used in practical applications. For example, in skin care applications, the synergism in surfactant mixtures decreases the total surfactant concentration and consequently reduces skin irritation. Cleaning formulations often include anionic mixtures to maximize solubilization and nonionic surfactants to maximize the water hardness tolerance. In the case of mixtures containing zwitterionic surfactants, betaines are widely used as foam booster in commercial shampoos or in hair conditioners (Kang et al., 2001; Diaz et al, 2005). In addition, mixed surfactant systems are also of great theoretical interest. A mixed micellar solution is a representation of a mixed micelle, mixed monolayer at the air/solution interface, and mixed bilayer aggregate at the solid interface. Mixed surfactants can be applied over a wider range of temperature, salinity, and hardness conditions than the individual ones (Kang et al., 2001; Zhou and Zhu, 2004).

Generally, mixtures of cationic and anionic surfactants use to be described as incompatible in the formulation because they may form a precipitate when they are brought together in an aqueous solution and cannot be used as surface active agents (Li and Liu, 1995). This is a major disadvantage as far as their application viewpoints are considered. However, soluble cationic-anionic surfactant mixtures can be formed successfully if either a cationic surfactant or an anionic surfactant or both have a large hydrophilic group. Therefore, these mixtures can be utilized as surface active agents (Mehreteab and Loprest, 1988; Kang et al., 2001). Cationic-anionic surfactant mixtures show remarkably different physicochemical properties due to the strong electrostatic interaction between the surface active cation and anion (Li and Liu, 1995; Kang et al., 2001). Moreover, mixed cationic-anionic surfactants often exhibit synergistic effects and provide more favorable properties in several aspects: high surface activity, enhanced adsorption, enhanced solute solubilzation capacity, lower interfacial tension, and much lower critical micelle concentrations, as compared with those of the individual surfactant with the same total concentration (Silva and Viseu, 1998). Many researches are proven that the mixtures of cationic and anionic surfactants exhibit the synergistic effects in several aspects.

Kunanupap (2004) studied the CMC determination of DTAB cationic surfactant, DOWFAX anionic surfactant, and DTAB:DOWFAX mixtures. They found that the mixture of DTAB and DOWFAX surfactants offers the synergistic effect by a decrease in the CMC value to be much lower than DTAB and DOWFAX alone. Additionally, Yatcilla et al. (1996) reported that the mixtures of CTAB and SOS surfactants (cationic-anionic surfactant mixtures) yield lower CMC value than CTAB and SOS alone.

Fuangswasdi et al. (2006) studied the solubilization of styrene and ethylcyclohexane by cationic-anionic surfactant mixtures. PODD and SDS were utilized as cationic and anionic surfactants, respectively. The results showed the mixtures of SDS and PODD provide a higher solubilization of styrene and ethylcyclohexane as compared to SDS and PODD alone.

Aqueous mixtures of cationic and anionic surfactants display many unique features. Combinations of cationic and anionic surfactants in aqueous solution assemble into a wide range of aggregate morphologies in aqueous solution that are completely different from those formed from the individual surfactants. Cationic-anionic surfactant mixtures may aggregate into spherical micelles, wormlike micelles, vesicles, lamellar phases, and a precipitate. The type of aggregate formed can be modified by the molecular architecture of the mixed cationic-anionic surfactants, e.g. by variation of the asymmetry of the alkyl surfactant tails, by branching of one of the tails, and by changing the stochiometry of the mixture (Bulwada, 2001). When cationic and anionic surfactants are simply mixed, the surfactant aggregates are formed and provide more tightly packed according to the strong reduction in the repulsion forces between their oppositely charged head groups causing the smaller effective head group area. In addition, the volume of the alkyl surfactant tails are increased resulting from the interaction between two types of surfactant tails. Correspondingly, an increase in the volume of aggregation offers a greater solubilization capacity for solute therein. If one of the surfactants is present in a small excess, the cationic-anionic surfactant mixtures spontaneously form closed vesicles that provide more available sites for solubilization and also offers a higher solute solubilization capacity than normal micelles (Renoncourt, 2005).

In addition, aqueous mixtures of oppositely charged surfactants exhibit interesting phase behavior similar to that of nonionic surfactant called aqueous surfactant two phase (ASTP) systems (Tong et al., 1999; Mao et al., 2002).

2.4 Surfactant utilization for the environmental application

2.4.1 Surfactant enhanced aquifer remediation (SEAR)

Currently, subsurface contamination with hydrophobic organic compounds (HOCs) is a serious environmental concern. HOCs are immiscible in water and tend to adsorb onto soil, and also may be present as discrete phases in the subsurface. These organic compounds often enter the subsurface as a separate organic phase or nonaqueous phase liquid (NAPL). Under normal flow regimes, this NAPL is immobile and frequently represents a long-term source of aquifer contamination. Removal of NAPLs from contaminated soils is difficult due to their low water solubility and high interfacial tension. In the past, the traditional method for clean-up soils and aquifers contaminated with NAPL organic contaminants is a pump-and-treat with water (Lee et al., 2001). However, this method is not considered as the most appropriate alternative for aquifer remediation due to the long time requirement to achieve the cleanup goals and the ineffectiveness of the system (Khan et al., 2004).

The surfactant flushing technology, also refers to surfactant enhanced aquifer remediation (SEAR), is a promising technology for removing organic liquids from subsurface and has proven to be applicable to the removal of NAPLs. This technique is based primarily on two important processes: (1) micellar solubilization of NAPLs and (2) mobilization of entrapped NAPLs due to interfacial tension reductions (Pennell et al., 1993; Pennell et al., 1994). A combined effect of mobilization and solubilization can take place when mobilized DNAPL ganglia are dissolved into the aqueous phase. The SEAR technique consists of the injection of a surfactant solution into the contaminated zone and the extraction of water, surfactants and contaminants with subsequent treatment of the extracted water at the surface. However, the technique requires additional costs compared to conventional pump-and-treat method on a short term. These costs originate from additional measurements to be made (e.g. tests for the toxicity, mobilizing capacities, biodegradability, etc.), the cost of surfactants and the more expensive decontamination of the extracted water. On the other hand, the use of surfactants will reduce the remediation duration, and hence costs related to remediation time (Pennell et al., 1993; Childs et al., 2006).

In the past, there are many researches that successfully applied SEAR technology for clean-up organic compounds from contaminated soil. Lee et al. (2005) studied the application of nonionic surfactant for in-situ flushing to diesel contaminated site in Korea. Sorbitan monooleate (2%wt) was mixed with uncontaminated groundwater and then the solutions were flushed through the site. The results showed 88% of the initial total petroleum hydrocarbon (TPH) concentration was removed from the pilot site with 5 pore volumes. The amount removed was more than 75 times than flushing by water alone. Later on, Childs et al. (2006) studied microemulsion solution to remove tetrachloroethylene (PCE) from a control test cell at the Dover National Test Site. The surfactant formulation (sodium dihexyl sulfosuccinate (AMA), isopropanol and calcium chloride) was able to achieve a high concentration of PCE in swollen micelles (supersolubilization) without vertical PCE migration. The results showed that after flushing for 10 pore volumes, the overall PCE removal was 68%. In addition, the residual PCE saturation was reduced from 0.7% to 0.2%, and the concentration of PCE in the groundwater was reduced from 37–190 mg/L prior flushing to 7.3 mg/L after flushing. Recycling the surfactant solution reduced the required surfactant mass by 90%.

2.4.2 Surfactant-based separation technology

Surfactants can play an important role in separation science. The unique tendency of surfactants to adsorb at interfaces and to form micelles in solution lead to separation ability called surfactant based separation technologies. These technologies represent ones of the most promising new separation techniques to emerge over the past few decades with potential for advance improvements in industrial and analytical separations. The examples of surfactant-based separation techniques include cloud point extraction, surfactant-enhanced ultrafiltration, froth flotation, and foam fractionation. Moreover, these techniques are utilized for many environmental applications such as in-situ or ex-situ remediation of contaminated soil, wastewater and groundwater clean-up, removal of ink to permit recycling of paper and plastic (Scamehorn and Harwell, 2000).

2.4.2.1 Cloud Point Extraction (CPE)

The phase separation of surfactant solution is known as an aqueous surfactant two-phase (ASTP) system. The cloud point extraction (CPE), one of ASTP, is based on the phase separation properties of aqueous nonionic surfactant solutions (Katsaounos et al., 2002). When micellar solutions of a nonionic surfactant are heated above a narrow temperature range called as cloud-point temperature (Martinez et al., 2000), the solutions become turbid and then separate into two isotropic phases. One phase is separated from the bulk aqueous solution and concentrated in surfactant micelles called the surfactant-rich phase or coacervate phase. The other phase is dilute in surfactant micelles called the surfactant-dilute phase, in which the surfactant concentration will be approximately equal to the critical micelle concentration (CMC). Upon cooling, this phenomenon is reversible and then a single phase is again obtained (Kimchuwanit et al., 2000; Ferrera et al., 2004). For environmental applications, if an aqueous solution contains organic pollutants is mixed with a nonionic surfactant, organic solutes in water tend to solubilize in micelles and concentrate in coacervate phase (Kimchuwanit et al., 2000; Trakultamupatam et al., 2002). Therefore, from the characteristic of CPE, it has been successfully used in the extractive preconcentration, separation and/or purification of various species, ranging from metal ions to organic compounds of environmental concern (Tong et al., 1998; Nascentes and Arruda, 2003).

From previous studies, CPE has been successfully used for removal organic compounds from contaminated soil and water. Hiller and Wandruszka (1994) investigated cloud point extraction for clean-up oil contaminated soil. A nonionic surfactant employed was Triton X-114. In the practical clean-up, the results showed that 85-98% of the oil present in the soil was found to be trapped in the micellar phase of the separated washing liquid. A 15-min washing time with 3-5% detergent was found to be sufficient for this degree of contaminant removal from soil containing 0.009-0.017% oil, using a liquid: solid ratio of 5:2. Kimchuwanit et al. (2000) studied the extraction of trichloroethylene (TCE) from water using cloud point extraction. Octylphenoxypoly(ethyleneoxy)ethanol was used as a nonionic surfactant. The results showed that 91% of TCE was extracted into the surfactant-rich phase in one stage. TCE concentration in surfactant-rich can be over two orders of magnitude greater than in the surfactant-dilute phase. Increasing temperature, surfactant concentration, and adding of NaCl can improve the fraction of TCE extracted. Trakultamupatam et al. (2002) applied CPE for removal of benzene, toluene, and ethylbenzene from wastewater. A nonionic surfactant, t-octylphenolpolyethoxylate, was used as the separating agent. The results were reported that the aromatic contaminants tend to solubilize into the surfactant aggregates and concentrate in the surfactant-rich phase. The concentration of the solutes in the surfactant-rich phase increases as temperature, added electrolyte concentration, and degree of alkylation of the aromatic solutes increase.

The cloud point of micellar solutions can be changed by the addition of additives, for example salt, alcohol, other surfactants, polymers, and some organic or inorganic compounds, which can cause an increase or decrease on the phase micellar solubility. Gu and Galera-Go´mez (1999) investigated the effect of polar organic liquids (alcohols, acids, ethers, ketones, esters, etc.) on the cloud point of Triton X-100 in aqueous solutions. The results showed that the addition of polar organic liquids that are infinitely miscible in water increases its cloud point while the presence of polar organic liquids that are partially soluble in water decreases the cloud point of the surfactant. In another application, the same researchers studied the changes caused by addition of surfactants as Triton X-100 (nonionic), SDS (anionic), and CTAB (cationic) on the cloud point of Triton X-114, and the influence of several electrolytes on the cloud point of these mixed micellar media. Generally, the cloud point of an aqueous mixture of two nonionic surfactants is an intermediate value of those when they are used alone. Related to the mixed micellar media formed by nonionic and ionic surfactants, the researchers proved that the addition of SDS or CTAB increases the cloud point of a 1%wt Triton X-114 solution from 25 to 74°C. The increase hydrophilic characteristic of the micellar phase can be explained by the following: the ionic surfactant molecules added are incorporated into nonionic micelles, changing the surface charge and increasing the repulsion among micelles, which makes them more hydrophilic. On the other hand, the addition of electrolytes increases or decreases the surfactant cloud point. These effects are respectively known as “salting-in” and “salting-out.” They have a minor magnitude in the micellar medium formed by pure nonionic surfactants. However, when they are added in a mixed micellar media such as those formed by Triton X-100 and SDS or CTAB, the cloud point is drastically reduced (Gu and Galera-Go´mez, 1999).

2.4.2.2 Aqueous Surfactant Two-Phase (ASTP) extraction system formed by cationic-anionic surfactant mixtures

Of late, ASTP systems formed by cationic-anionic surfactant mixtures have been extensively used for the extractive separation of biomaterials and organic compounds (Tong et al., 1999; Mao et al., 2002). When two oppositely charged ionic surfactants are mixed at certain concentration and molar ratio, the solution becomes turbid and the phase separation can occur similar to that exhibits for nonionic surfactant system. One phase is concentrated in surfactant aggregates known as the surfactant-rich phase while the other phase is dilute in surfactant aggregates called the surfactant-dilute phase (Xiao et al., 2000; Mao et al., 2002). The phase behavior of these systems depend on the molar ratio of cationic to anionic surfactant in the mixture, the overall surfactant concentration and the nature of the surfactant, i.e., chain length, type of polar head and of counterion. An outstanding property of this system is the ability of cationic-anionic surfactant mixture to spontaneously form catanionic vesicles which can remain stable for years (Yatcilla et al., 1996; Renoncourt, 2005). Compared to temperature-induced aqueous two-phase systems formed by nonionic surfactants or cloud point extraction, a new ASTP system can be operated at desired temperature even at ambient in some systems. Unlike the phase separation of nonionic surfactant, the phase separation takes place only above a critical temperature. In addition, ASTP extraction system formed by cationic and anionic surfactants represents entirely aqueous systems not involving to the organic solvents. Thus, they are safe, nontoxic, and nonflammable which represent relatively environmentally benign extraction media (Hao et al., 2006).

There are many factors affecting the ASTP system formed by mixed cationic and anionic surfactants such as surfactant composition and concentration, temperature, electrolytes, and pH. In general, the ASTP system occurs at certain composition and concentration. The regions that the phase separation takes place are different for each mixture. Phase separation can be found in the region that cationic or anionic is in excess or even at equimolar. It is demonstrated that the effect of molar ratio is quite strong (Zhao and Xiao, 1996; Xiao et al., 2000; Yin et al., 2002; Shang et al., 2007). Moreover, the temperature has an effect on the ASTP system by changing in the structure of surfactant aggregates, for example the transition from normal micelles to vesicles which affect to the solubility of surfactant (Mao et al., 2002; Renoncourt, 2005). The presence of electrolytes affects to the ASTP system. The addition of salts generally tends to screen the electrostatic repulsion between surfactant aggregates and promotes larger aggregate formation such as the transformation of small micelles into larger structures (lamellar structures or vesicles) causing a higher solute solubilization (Yin et al., 2002). Additionally, the addition of acids (hydrochloric, acetic, nitric, and sulfuric acid) or base (sodium hydroxide) can alter the phase behavior by changing the phase volume ratio and inducing precipitation (Tong et al., 1998; Tong et al., 1999).

In the past, an ASTP system formed by cationic and anionic surfactant mixtures was successfully utilized for removal of organic pollutants from water. Kunanupap (2004) studied on the effect of operating conditions on benzene removal using an ASTP system formed by mixed DTAB and DOWFAX as a cationic and an anionic surfactant. The high benzene and surfactant partition ratio and extremely low fractional surfactant-rich phase volume proved the ASTP technique could be applied to extract and preconcentrate the pollutant from wastewater. 72% of benzene was extracted and preconcentrated in surfactant-rich phase at ambient temperature of 30 °C with the total surfactants concentration of 50 mM at 2:1 molar ratio of DTAB:DOWFAX within a single stage.

Krutlert (2004) investigated the effect of electrolytes on BTEX removal using an ASTP system technique formed by DTAB:DOWFAX mixtures (cationic-anionic surfactant mixtures). The results showed that most of contaminants concentrate in the surfactant-rich phase. Moreover, the extraction of BTEX from wastewater at 50 mM of total surfactants concentration with 2:1 molar ratio of DTAB:DOWFAX in the presence of electrolytes (LiCl, NaCl, KCl and $MgCl_2$) can be enhanced as compared with in the absence of electrolytes. At 1 M NaCl, 95% of xylene, 92% of ethylbenzene, 90% of toluene, and 79% of benzene are extracted into the surfactant-rich phase, respectively. In addition, different cation type of electrolytes can equally enhance VOC extraction efficiency.

Khaolerk (2006) applied a phase separation of cationic and anionic surfactant mixtures for PCE removal from wastewater. The total surfactants concentration of mixed DTAB:DOWFAX solution at 2:1 molar ratio was investigated ranging from 30 to 100 mM. The results showed that total surfactants concentration of 70 mM is the most suitable condition that 91.4% of PCE is extracted into the surfactant-rich phase or 8.6% of PCE remains in the surfactant-dilute phase.

From the literature reviews, the applications of an ASTP system formed by cationic-anionic surfactant mixtures for organic compounds removal from soil have never been studied before. From the advantages and characteristics of this ASTP system as mention above, an ASTP system formed by the mixtures of cationic and anionic surfactants is a promising technique to clean-up organic contaminants including pyrene from contaminated soil effectively.

CHAPTER III

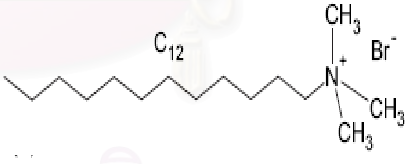
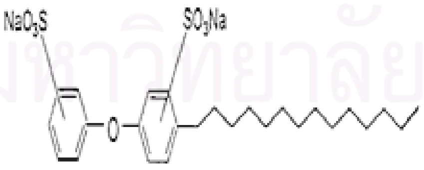
METHODOLOGY

3.1 Material

3.1.1 Surfactants

A cationic surfactant, dodecyltrimethylammonium bromide (DTAB) with a purity of 99% was purchased from Robiot Co., Ltd (Nanjing, China). A twin-head anionic surfactant, alkyldiphenyloxide disulfonates (DPDS or trade name of DOWFAX 8390) with 35% active was contributed from Dow Chemical Co., Ltd. (West Virginia, USA). Their properties were listed in Table 3.1.

Table 3.1 Physical and chemical properties of the studied surfactants

Surfactant	MW (g/mol)	Chemical Structure	CMC (mM)
Dodecyltrimethylamonium bromide, $C_{15}H_{34}BrN$	308.3		13.55 (1)
Alkyldiphenyloxide disulfonate, $C_{16}H_{33}C_{12}H_7O(SO_3Na)_2$	642		0.5 (2)

(1) Bagha et al. (2007), (2) Lee et al. (2002)

3.1.2 Contaminant

The contaminant used in this research was pyrene. It was purchased from Aldrich Chemical Company with a purity of 98%. Pyrene was a yellow crystalline solid. The physical and chemical properties of pyrene were shown in Table 3.2.

Table 3.2 Physical and chemical properties of pyrene

Formula	$C_{16}H_{10}$⁽¹⁾
Molecular weight (g/mol)	202.26⁽¹⁾
Boiling point (ºC)	404⁽²⁾
Melting point (ºC)	156⁽²⁾
Vapor pressure (mmHg) at 25 ºC	$2.50 \times 10^{-6(1)}$
Water solubility (mg/L) at 25 ºC	$1.30 \times 10^{-1(1)}$
Log K_{ow}	4.88⁽¹⁾
Specific gravity	1.271⁽²⁾

(1) LaGrega et al. (2001), (2) Reported by Faust (1993)

3.1.3 Silica sand

Silica sand with low iron content was purchased from Fisher Scientific Co., Ltd. with a particle size about 40 – 100 mesh (0.149 – 0.4 mm). It was chosen as a model porous medium because it had high hydraulic conductivity, low cation exchange capacity and low organic carbon content (Lee et al., 2002) and so called in this study as a soil.

3.1.4 Lipophilic linkers

Octanol, dodecanol, and hexadecanol used as the lipophilic linkers in this study were purchased from Merck Ltd. (Germany) with a purity of 99%, Fluka Chemica (Switzerland) with a purity of 99.5%, and Fluka Chemica (Germany) with a purity of 99%, respectively. Their properties were shown in Table 3.3.

Table 3.3 Physical and chemical properties of lipophilic linkers

Descriptions	**Octanol**	**Dodecanol**	**Haxadecanol**
Formula	$C_8H_{18}O$	$C_{12}H_{26}O$	$C_{16}H_{34}O$
Color/Form	Colorless liquid	Colorless liquid	Solid white crystals
Molecular weight (g/mol)	130.22	186.33	242.45
Boiling point (ºC)	194 – 195	259	334
Melting point (ºC)	-16 > -17	24	49.3
Vapor pressure (mmHg) at 25 ºC	7.94×10^{-2}	8.48×10^{-4}	3.06×10^{-6}
Water solubility (mg/L) at 25 ºC	540	4	1.34×10^{-5}
Log K_{ow}	3.00	5.13	6.65
Specific gravity	0.8270	0.8309	0.8187

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

3.2 Experimental Procedures

3.2.1 Adsorption of surfactants onto soil

Adsorption of DTAB, DOWFAX, and DTAB:DOWFAX mixtures at molar ratios 1.5:1, 1:1, 1:1.5, and 1:2 onto soil were carried out in batch experiments at equilibrium condition. Two grams of silica sand was placed in test tubes and then

10 mL of DTAB aqueous solution at concentrations of 2, 4, 6, 8, and 10 mM was added (solid to liquid ratio = 1:5). The same manner was applied in the case of pure DOWFAX aqueous solution except the studied concentrations are 0.2, 0.4, 0.6, 0.8, 1, 2, 4, 6, 8, and 10 mM and the solid to liquid ratio was studied at 1:2 and 1:5. For the mixtures of DTAB:DOWFAX aqueous solution at molar ratios of 1.5:1, 1:1, 1:1.5, and 1:2, the solid to liquid ratio of 1:5 was applied at total surfactant concentrations of 2, 4, 6, 8, and 10 mM.

Consequently, the test tubes were horizontally shaken at 100 rpm for 24 hrs at 25ºC, where the shaking time for 24 hrs was assured to be more than enough for equilibrium adsorption. After shaking, the samples were then centrifuged at 3000 rpm for 20 min. The supernatants were collected and analyzed for surfactant concentrations. The DOWFAX concentration was determined by UV-visible spectrophotometer. The DTAB concentration was measured using TOC analyzer. For DTAB:DOWFAX mixtures at all studied molar ratios, the total surfactants concentration was measured by TOC analyzer. Three replicates were done for each experimental condition. The mass of surfactants adsorbed onto the soil was determined from material balance. Given the mass of surfactants sorbed and the mass of soil, a value of q (mass of chemical adsorbed on soil normalized by the mass of soil) could be calculated as Equation 2.1 (modified from Noordman et al., 2000).

3.2.2 Solubilization study

The solubilization of pyrene by surfactants was studied in batch experiments. This study was divided into four sub-experiments (modified from Zhu and Feng, 2003; Fuangswasdi et al., 2006).

3.2.2.1 Equilibrium time determination for pyrene solubilization by surfactant

The equilibrium time to be sufficient for reaching maximum solubilization of pyrene by surfactant was determined. Only one surfactant system of DTAB:DOWFAX solution at 1:1.5 molar ratio was applied and three replicates were performed in this experiment. Pyrene of 0.05 grams as solid crystal was placed in a series of test tubes and then 10 mL of surfactant solution at concentration of 1 mM was added. The amount of pyrene added (0.05 grams) was many times in excess of its apparent solubility, thus crystalline phase of pyrene needed to be observed at the end of experiment. The test tubes were subsequently capped and shaken at 100 rpm at 25ºC for 5 days. The samples were collected from each tube everyday for 5 days and then centrifuged at 3000 rpm for 20 min to separate the undissolved solute from the aqueous phase. An appropriate aliquot of the supernatant solution was carefully withdrawn using an autopipette and diluted to 10 mL with 5 mL methanol. The concentration of pyrene in solution was measured using UV-visible spectrophotometer.

3.2.2.2 Pyrene solubilization by single and mixed surfactants

The solubility of pyrene in pure DTAB, pure DOWFAX, and mixtures of DTAB:DOWFAX at molar ratios of 1.5:1, 1:1, 1:1.5, and 1:2 at various surfactant concentrations were investigated. Triplicate tests were performed in each condition. The same procedure was applied as previously described in section 3.2.2.1 except the samples were equilibrated for certain duration obtained from equilibrium time determination study and the concentration of surfactants at each prepared molar ratio were varied. The concentration of pyrene was analyzed using UV-visible spectrophotometer. At the end of this experiment, the solubilization capacity was determined in term of molar solubilization ratio (MSR) and micelle-water partitioning coefficient (K_m).

3.2.2.3 Effects of electrolyte in surfactant solution on pyrene solubilization

To investigate the effects of electrolyte in surfactant solution on pyrene solubilization, the surfactant composition that optimized pyrene solubilization capacity via MSR and log K_m resulting from section 3.2.2.2 was used in this experiment. $CaCl_2$ was utilized as the electrolyte. The concentration of $CaCl_2$ used in this study was fixed at 0.025%wt.

The solubility of pyrene in the solution of a suitable surfactant composition at various concentrations with constant 0.025%wt of $CaCl_2$ was carried out. Three replicates were performed in this experiment. The same procedure was applied as previously described in section 3.2.2.1 except the samples were equilibrated for certain duration obtained from equilibrium time determination study. The concentration of pyrene was analyzed by using UV-visible spctrophotometer. At the end of this study, the solubilization capacity of surfactants in the presence of $CaCl_2$ in terms of MSR and log K_m were determined.

3.2.2.4 Effects of lipophilic linkers in surfactant solution on pyrene solubilization

This experiment aimed to evaluate the effects of lipophilic linkers in surfactant solution on pyrene solubilization. The surfactant composition that optimized pyrene solubilization capacity via MSR and log K_m resulting from section 3.2.2.2 was utilized. Three types of *n*-alcohols including octanol, dodecanol, and hexadecanol were used as lipophilic linkers in this study. A total mole of surfactant to total mole of alcohol at 10:1 was applied for octanol and dodecanol, where the hexadecanol could be prepared only at its water solubility (1.34×10^{-5} mg/L) due to the fact that it is almost insoluble in either water or surfactant solution.

The solubility of pyrene in the solution of an appropriate surfactant composition with lipophilic linkers at various surfactant and linkers concentrations was investigated. Triplicate tests were performed in this experiment. The same procedure was applied as previously described in section 3.2.2.1 except the samples were equilibrated for certain period obtained from equilibrium time determination study. The concentration of pyrene was measured by using UV-visible spctrophotometer. At the end of this study, the solubilization capacity of surfactants in the presence of lipophilic linker in terms of MSR and log K_m were determined.

3.2.3 Soil contamination

Silica sand was used as a model porous soil in these experiments. Methanol was utilized as a solvent for dissolving pyrene. A solution of pyrene in methanol was spiked into soil. Pyrene contaminated soil was prepared in each test tube. To obtain 200 mg pyrene/ kg soil (ppm), 0.25 mL of a stock pyrene solution of 2,000 mg/L was added into 2.5 g of soil contained in the test tubes. Then, pyrene contaminated soil prepared in each test tube was left over night in the fume hood to evaporate the methanol (adapted from Eftekhari, 2000 (fine sand); Zhou and Zhu, 2007 (soil with 0.52 % organic carbon content)). The presence of pyrene in soil could be in various features such as small precipitates mixed with soil texture, coated layer on soil grain, etc. However, we assured the concentration of pyrene spiked on soil using the back extraction after soil spiking.

3.2.4 Effects of surfactant concentration on pyrene removal

To evaluate the effects of total surfactant concentration on pyrene removal, the surfactant composition that optimized from the surfactant adsorption study along with the pyrene solubilization study was used in this experiment. The surfactant concentrations at suitable surfactant composition were varied in six concentrations (5, 10, 20, 30, 40, 50, and 60 mM). This experiment was performed in batch experiments. Pyrene contaminated soil of 2.5 grams was placed in test tubes and then 2.5 mL of surfactant solution at various concentrations was added (solid to liquid ratio = 1:1). The test tubes were subsequently capped. These tubes were shaken at 100 rpm for certain duration obtained from 3.2.2.1 and then centrifuged at 3000 rpm for 20 min to separate the undissolved solid from the aqueous phase. An appropriate aliquot of the supernatant solution was carefully withdrawn using the autopipette and diluted to 10 mL with 5 mL methanol. The concentration of pyrene in solution was measured using UV-visible spectrophotometer. Three replicates were performed in this experiment. At the end of this study, the efficiency in term of pyrene removal from contaminated soil was investigated (adapted from Zhou and Zhu, 2007).

3.2.5 Effects of additives addition on pyrene removal

To evaluate the effects of additives addition on pyrene removal from contaminated soil, two groups of additives utilized in this study were electrolyte and lipophilic linkers. An appropriate surfactant system at certain concentration obtained from section 3.2.4 that yielded the optimized efficiency of pyrene removal was utilized in this experiment. The effects of additives addition on pyrene removal were carried out in batch experiments. This experiment was divided into three cases.

3.2.5.1 Effects of electrolyte addition on pyrene removal

To investigate the effects of electrolyte addition on pyrene removal from contaminated soil, $CaCl_2$ was used as the electrolyte for this study. $CaCl_2$ concentrations that imitated to groundwater condition were varied in five concentrations: 0.005, 0.01, 0.025, 0.04, and 0.05%wt. Pyrene contaminated soil of 2.5 grams was placed in test tubes and then 2.5 mL of the appropriate surfactant concentration resulted from 3.2.4 with different $CaCl_2$ concentrations was added. Then the same procedure was applied as previously described in section 3.2.4. Triplicate tests were carried out for this experiment. At the end of this study, the effect of $CaCl_2$ concentration on pyrene removal was determined.

3.2.5.2 Effects of lipophilic linkers on pyrene removal

To evaluate the effects of lipophilic linkers on pyrene removal from contaminated soil, three types of *n*-alcohols including octanol, dodecanol, and hexadecanol were proposed to be used as lipophilic linkers in this study. However, it was found that hexadecanol, which is a solid crystal, cannot be utilized since it has very low water solubility (1.34×10^{-5} mg/L) with high degree of hydrophobicity ($\log K_{ow} = 6.65$). Thus, it cannot be prepared at the same concentration as the other two alcohols. From these reasons, only two types of alcohols consisting of octanol and dodecanol were actually used in this experiment. Each type of lipophilic linkers was varied in three concentrations: 1, 2, and 4 mM as corresponded to total mole of surfactants to total mole of alcohols: 20:1, 10:1, and 5:1, respectively. Pyrene contaminated soil of 2.5 grams was placed in test tubes and then 2.5 mL of the appropriate surfactant concentration resulted from 3.2.4, with various types and molar ratios of lipophilic linkers, was added. Afterward, the same procedure was applied as previously described in section 3.2.4. Three replicates were performed in this study. At the end of this experiment, the efficiency in term of pyrene removal was investigated.

3.2.5.3 Effect of the optimal surfactant formulation on pyrene removal

In this experiment, the effect of the optimal surfactant formulation on pyrene removal from contaminated soil was investigated. The optimal surfactant formulation was selected from the results of each effect such as the surfactant formulation with optimized salt concentration, the surfactant formulation with optimized linker concentration, the surfactant formulation with the combination of salt and linker. Pyrene contaminated of soil 2.5 grams was placed in test tubes and then 2.5 mL of the optimal surfactant formulation was added. The same procedure was applied as previously described in section 3.2.4. Three replicates were performed in this experiment. Then, the efficiency in term of pyrene removal was determined. At the end of this study, the comparison on pyrene removal efficiency received from each surfactant formulation was revealed.

3.2.6 The preconcentration ability of ASTP system

This experiment was carried out in the batch experiment. After the surfactant system that offered the optimized pyrene removal efficiency of each effect was obtained, the solution of these surfactant systems was used to extracted pyrene from contaminated soil over again. The extraction of pyrene from contaminated soil was scaled-up five times. Pyrene contaminated soil of 12.5 grams was placed in the vials and then 12.5 mL of the suitable surfactant system obtained from each effect was added. These vials were capped and then shaken at 100 rpm for certain duration obtained from 3.2.2.1. Afterward, the supernatant was gradually poured into a separated vial. Later on, this solution was adjusted by an appropriate surfactant composition in order to induce a phase separation at ambient temperature. The molar ratio of mixed surfactants (DTAB:DOWFAX) that could induce a phase separation with highest surfactant and contaminant partition ratios was at 2:1 (Kunanupap, 2004; Khaolerk, 2006). After the phase separation occurred, the solution was separated into two phases. One phase was the surfactant-rich phase while the other phase was the surfactant-dilute phase. The concentrations of DOWFAX, and pyrene in both phases were analyzed. It should be noted that the total surfactants concentration was calculated base on DOWFAX concentration in this experiment. At the end of this study, the fractional rich-phase volume, the surfactant and pyrene partition ratios, the percentage of pyrene accumulated in the surfactant-rich phase, and the remained pyrene concentration in the surfactant-dilute phase were determined.

3.2.7 Analysis of surfactants and pyrene concentrations

The concentration of DOWFAX was measured by UV-visible spectrophotometer (Thermo Spectronic, Model Helios Alpha) at 240 nm with no interference of pyrene. The concentration of DTAB was determined by TOC Analyzer (TOC-VCPH). For the concentration of DTAB:DOWFAX mixtures in the surfactant adsorption study, the total surfactants concentration was measured by TOC Analyzer (TOC-VCPH). The pyrene concentration was determined by using UV-visible spectrophotometer (Thermo Spectronic Model Helios Alpha) at 333.6 nm (Zhu and Feng, 2003; Zhou and Zhu, 2004). The absorptive value is controlled in range of 0 to 1 absorbance unit.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Adsorption of surfactants onto silica sand

This study aimed to observe the adsorption of pure DTAB, pure DOWFAX, and mixtures of DTAB:DOWFAX at molar ratios of 1.5:1, 1:1, 1:1.5, and 1:2 onto silica sand. These molar ratios of DTAB:DOWFAX solution have been proven to be homogeneous, single phase solution without surfactant precipitation.

The adsorption isotherm for DTAB onto silica sand was demonstrated in Figure 4.1. Mass of surfactant adsorbed to soil normalized by the mass of soil (q) was plotted as a function of equilibrium surfactant concentration (C_{eq}). The result showed that the adsorption of DTAB onto silica sand linearly increases with increasing DTAB concentration. For the adsorption of DOWFAX, it was observed that DOWFAX does not adsorb onto silica sand at all. Due to the fact that the surface of silica sand is negatively charged surface at neutral pH (PZC of silica sand is 2 as reported by Kim and Lawler (2005)), the cationic surfactant that bears a positive charge at the hydrophilic head can adsorb onto this surface according to the electrostatic interaction whereas the anionic surfactant that has a negatively charged repels from that surface (Rosen, 1989; Atay et al, 2002). This finding is consistent with previous research done by Fuangswasdi et al. (2006). They studied the adsorption of PODD cationic surfactant and SDS anionic surfactant onto silica and found that PODD increasingly adsorbs onto silica with increasing its concentrations while SDS adsorption is negligible onto silica. Moreover, Rouse and Sabatini (1993) also reported that anionic surfactants have potential for being more resistant to adsorb in sandy soils due to charge repulsion from the negatively charged soil surfaces. The sorption isotherm of DTAB in this study is classified as a linear sorption isotherm where the amount of sorbed surfactant linearly increases with increasing the equilibrium concentration, which is common found in real environment when the sorbate concentrations are typically low. Sorption parameter in term of distribution coefficient (K_d) for DTAB was shown in Table 4.1.

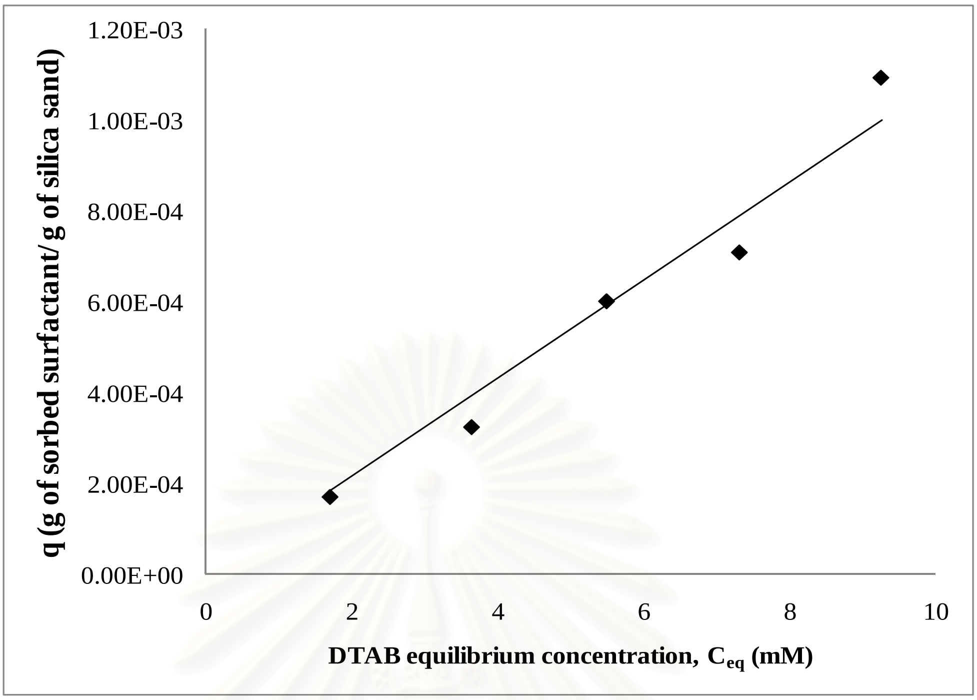


Figure 4.1 Adsorption isotherm for DTAB onto silica sand

For DTAB:DOWFAX at all studied molar ratios, the adsorption onto silica sand was expected to increase with respect to the presence of DTAB only in the solution resulting from nil DOWFAX adsorption as described above. Figure 4.2 illustrated the adsorption isotherms for DTAB considering only DTAB existed in DTAB:DOWFAX solution at all studied molar ratios onto silica sand. The K_d values accounted only for DTAB sorption at these molar ratios were summarized in Table 4.1.

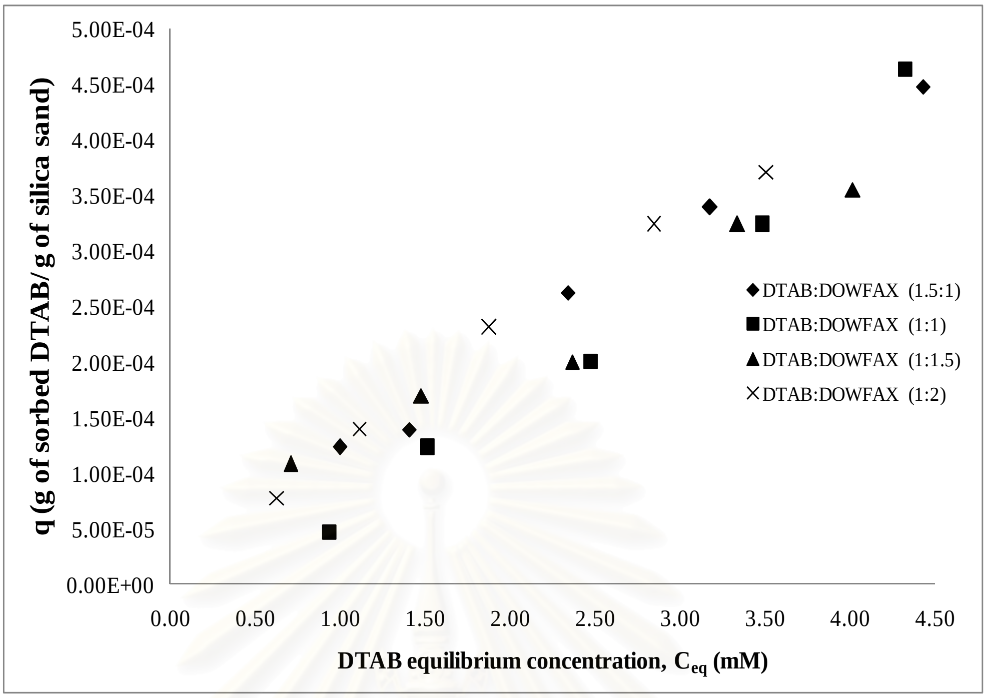


Figure 4.2 Adsorption isotherms for DTAB presented in DTAB:DOWFAX at molar ratio of 1.5:1, 1:1, 1:1.5, and 1:2 onto silica sand

Table 4.1 Distribution coefficient (K_d) for pure DTAB and DTAB in DTAB:DOWFAX at various molar ratios

Surfactant system	**K_d value (L/g)**
DTAB alone	3.50E-04
DTAB in DTAB:DOWFAX (1.5:1)	3.37E-04
DTAB in DTAB:DOWFAX (1:1)	3.11E-04
DTAB in DTAB:DOWFAX (1:1.5)	3.01E-04
DTAB in DTAB:DOWFAX (1:2)	3.63E-04

From Figure 4.2, it is obvious that the amount of DTAB presented in DTAB:DOWFAX solution at all studied molar ratios increasingly adsorbs onto silica sand over the range of its concentrations. Moreover, the adsorption trends of DTAB existed in DTAB:DOWFAX at these molar ratios are similar. From Table 4.1, it was found that K_d values for DTAB alone and DTAB presented in DTAB:DOWFAX at all studied molar ratios are not much different with the deviation of 8%. Thus, it was confirmed that the presence of DOWFAX in DTAB:DOWFAX solution at these molar ratios does not affect the adsorption of DTAB onto silica sand. This finding corresponds to earlier study done by Fuangswasdi et al. (2006). They compared the adsorption of PODD and SDS:PODD at molar ratio of 1:10 onto silica and found that the adsorption of PODD and SDS:PODD onto silica are virtually the same at PODD concentration greater than 0.1 mM. Therefore, the addition of SDS concentration does not significantly affect the adsorption of PODD.

From the consideration of the surfactant loss, we found that DTAB loses due to the adsorption onto silica sand about 6.23±0.65%. For DTAB:DOWFAX at all studied molar ratios, if we considered the total surfactant loss, it was found the percentage of surfactant loss for DTAB:DOWFAX at these molar ratios by the adsorption is as low as 1.58±0.34%. However, it was known that DOWFAX does not adsorb onto silica sand. If we considered the surfactant loss of only DTAB exited in DTAB:DOWFAX at all studied molar ratios, we found that DTAB presented in DTAB:DOWFAX at these molar ratios loses from the adsorption about 6.35±1.25%. From this finding, it was concluded that the small amount of DTAB loses due to the adsorption onto silica sand.

4.2 Equilibrium time determination for pyrene solubilization by surfactant

In this study, the equilibrium time for pyrene to reach the maximum solubilization in surfactant solution was investigated. Only single surfactant system, DTAB:DOWFAX at a molar ratio of 1:1.5 with total surfactants concentration of 1 mM, was utilized in this experiment and the samples were collected everyday for 5 days to measure the concentration of pyrene in the surfactant solution. The concentration of pyrene in surfactant solution at various times was demonstrated in Figure 4.3.

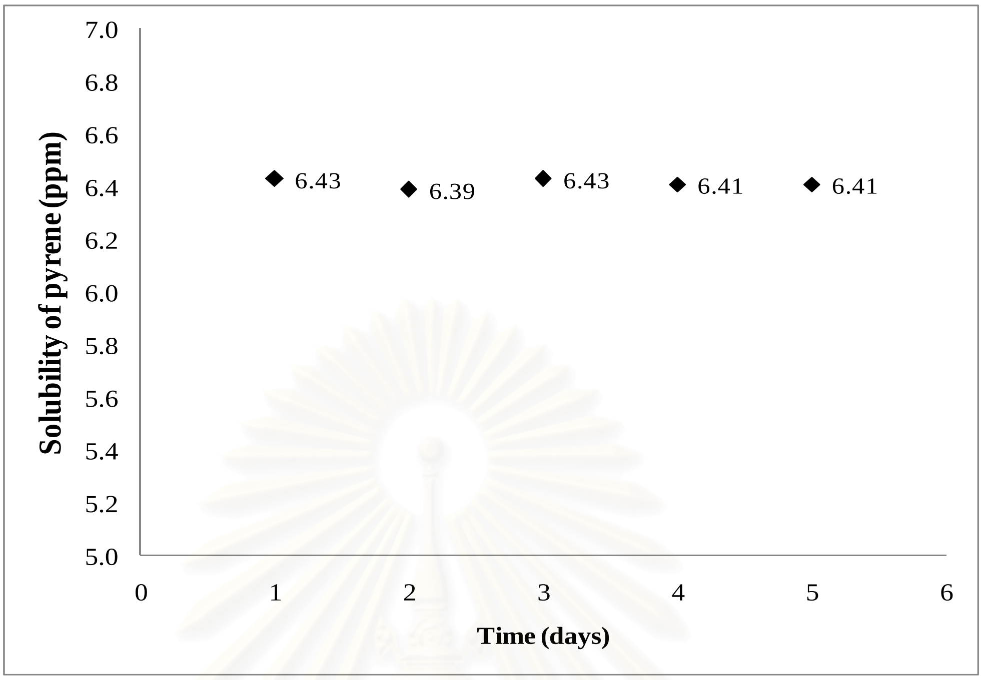


Figure 4.3 The concentration of pyrene in surfactant solution at various time (System: DTAB:DOWFAX at 1:1.5 molar ratio with total surfactants concentration of 1 mM at 25 ºC)

From Figure 4.3, the results showed that there is no change in the solubility of pyrene by DTAB:DOWFAX surfactant solution at 1:1.5 molar ratio with 1 mM of total surfactants concentration after 1 day. Therefore, a 24-hour can be considered as the equilibrium time for maximum pyrene solubilization by this surfactant system and was applied throughout the experiments. This finding is consistent with the previous study done by Paria and Yuet (2006) on the determination of equilibrium time for adequate naphthalene solubilization by surfactants. They found that the equilibrium condition was approached within 24 hours for naphthalene solubilization.

4.3 Pyrene solubilization by single and mixed surfactants

In this study, the solubilization of pyrene by pure DTAB, pure DOWFAX, and mixed DTAB:DOWFAX at molar ratios of 1.5:1, 1:1, 1:1.5, and 1:2 was evaluated as shown in Figure 4.4, where the apparent solubility of pyrene was plotted as a function of surfactant concentration. It was found that the solubility of pyrene increases linearly with surfactant concentration beyond their critical micelle concentration (CMC) both in single and mixed surfactants. In addition, the solubilities of pyrene in mixed DTAB:DOWFAX at all studied molar ratios are higher than those in DTAB and DOWFAX solution alone. The slope of the plot in Figure 4.4 represents the MSR and thus, the K_m can be calculated. The MSR and log K_m values were summarized in Table 4.2.

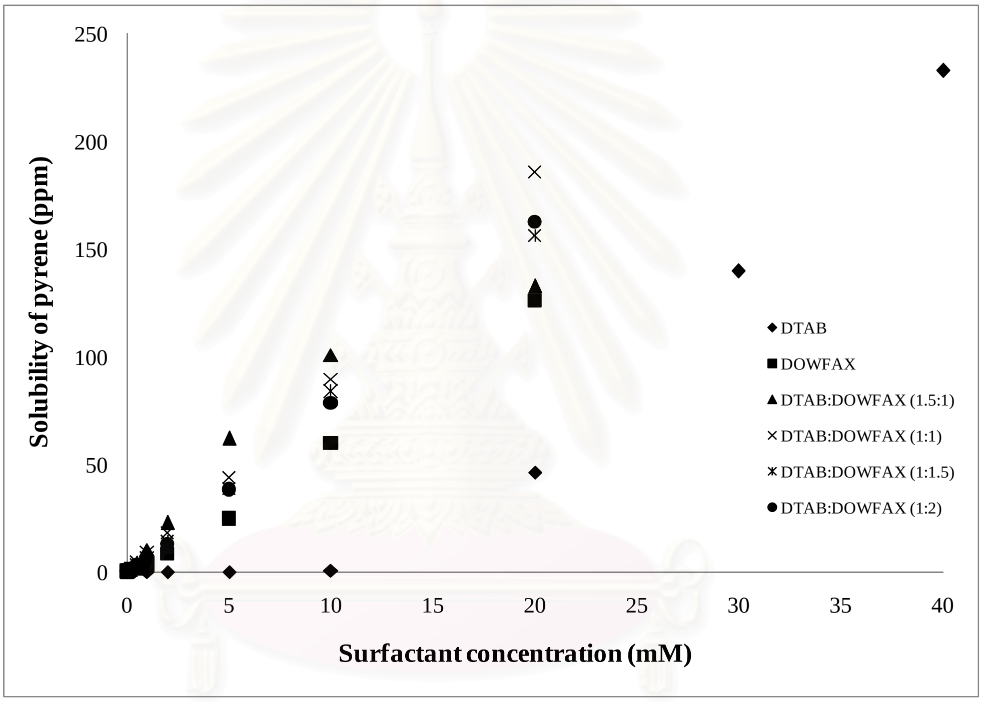


Figure 4.4 Pyrene solubilization in the solution of DTAB, DOWFAX, and DTAB:DOWFAX mixtures at molar ratios of 1.5:1, 1:1, 1:1.5, and 1:2 at 25 ^{o}C

Table 4.2 Molar solubilization ratio (MSR) and log micelle-water partitioning coefficient (log K_m) of pyrene at different DTAB:DOWFAX molar ratios

DTAB:DOWFAX	**1:0**	**1.5:1**	**1:1**	**1:1.5**	**1:2**	**0:1**
MSR	0.032	0.060	0.045	0.039	0.040	0.031
Log K_m	6.43	6.69	6.57	6.51	6.52	6.41

From Table 4.2, it was observed that the MSR and log K_m values of DTAB:DOWFAX mixtures at all studied molar ratios are higher than those of DTAB and DOWFAX alone. Thus, the mixed cationic-anionic surfactants show the synergistic effect resulting in a higher pyrene solubilization capacity than the individual ones. Since pyrene has low water solubility with high degree of hydrophobicity (log K_{ow} = 4.88), it tends to solubilize in the hydrophobic core of surfactant aggregates (Mohamed and Mahfoodh, 2006). For the mixed cationic and anionic surfactant systems, the tightly packed bilayer vesicles may spontaneously form as a result of a reduction of the repulsion forces between their oppositely charged head groups. In addition, these cationic-anionic surfactant aggregates have a larger aggregation number resulting in greater interactions between their hydrophobic chains and having a larger hydrophobic core region than the normal micelles formed by individual ionic surfactants. (Buwalda, 2001; Renoncourt, 2005). From these reasons, cationic-anionic surfactant aggregates yield a higher pyrene solubilization capacity than individual ionic surfactant micelles. Similar results were observed in previous study done by Mohamed and Mahfoodh (2006) on pyrene solubilization by anionic surfactant (SDS), nonionic surfactant (Tween 80), and mixed SDS/Tween 80. They found that the mixtures of SDS/Tween 80 exhibit the synergistic effect as shown by a higher pyrene solubilization than SDS and Tween 80 alone. The observed synergism by mixed SDS-Tween 80 for pyrene solubilization was explained in term of the interaction between their hydrophobic chains, which are co-aggregated in the mixed micellar core, where pyrene tends to solubilize. In addition, this finding is in close agreement with the previous work done by Fuangswasdi et al. (2006). They studied the solubilization of nonpolar ethylcyclohexane by anionic surfactant (SDS), cationic surfactant (PODD), and mixed SDS:PODD. They found that the mixtures of SDS/PODD show a higher solubilization of ethylcyclohexane as compared to those of SDS and PODD alone.

Earlier study on pyrene solubilization by single nonionic and mixed anionic-nonionic surfactants (TX100, Brij35, TX305, SDS/TX100, SDS/Brij35, and SDS/TX305) reported the log K_m values of 5.90, 5.86, 5.65, 5.99, 6.45, and 6.50, respectively (Zhu and Feng, 2003). It was found that our log K_m values of DTAB:DOWFAX mixtures at all studied molar ratios were higher than those observed in single nonionic and mixed anionic-nonionic surfactant systems.

From surfactant adsorption and pyrene solubilization studies, the suitable surfactant system was selected for further use to study the effects of surfactant concentration on pyrene removal from contaminated soil. For adsorption study, we found that only DTAB sorbs onto silica sand. For pyrene solubilization study, we found that the DTAB:DOWFAX at molar ratio of 1.5:1 has the highest pyrene solubilization as shown by the highest MSR and log K_m values. However, at total surfactant concentration greater than 10 mM of this surfactant molar ratio, the solubility of pyrene decreases due to a high viscosity of the solution. Therefore, in practical application, this mixture is not appropriate to be used for clean up the contaminated soil. From these reasons, the DTAB:DOWFAX at 1:1 molar ratio that provides a similar pyrene solubilization capacity to that of at 1.5:1 and uses less DTAB composition was considered as the suitable surfactant system to be used in the next experimental sections.

4.4 Effects of total surfactant concentration on pyrene removal

This experiment aimed to investigate the effects of total surfactant concentration on pyrene removal from contaminated soil. The initial concentration of pyrene used in this experiment was 200 mg/kg soil (ppm). A solution of pyrene in methanol was spiked into soil. Before this experiment was done, the back extraction of pyrene from contaminated soil was investigated in order to ensure that the spiked soil has the pyrene concentration of 200 mg/kg soil. Methanol was used as the extractant. From the back extraction, 99% of pyrene recovery from contaminated soil was achieved. Therefore, the spiking technique was proven to be valid and the prepared spiked soil was presumed to have the pyrene concentration of 200 mg/kg soil.

The effects of total surfactant concentration on pyrene removal were demonstrated in Figure 4.5, where the percentage of pyrene removal was plotted against the total surfactant concentration. It was observed that the percentage of pyrene removal increases with increasing total surfactant concentration. Obviously, pyrene removal efficiency of DTAB:DOWFAX at 1:1 molar ratio almost linearly increases with increasing concentration ranging from 5-30 mM. At the total surfactant concentration higher than 30 mM, pyrene removal efficiency slightly increases.

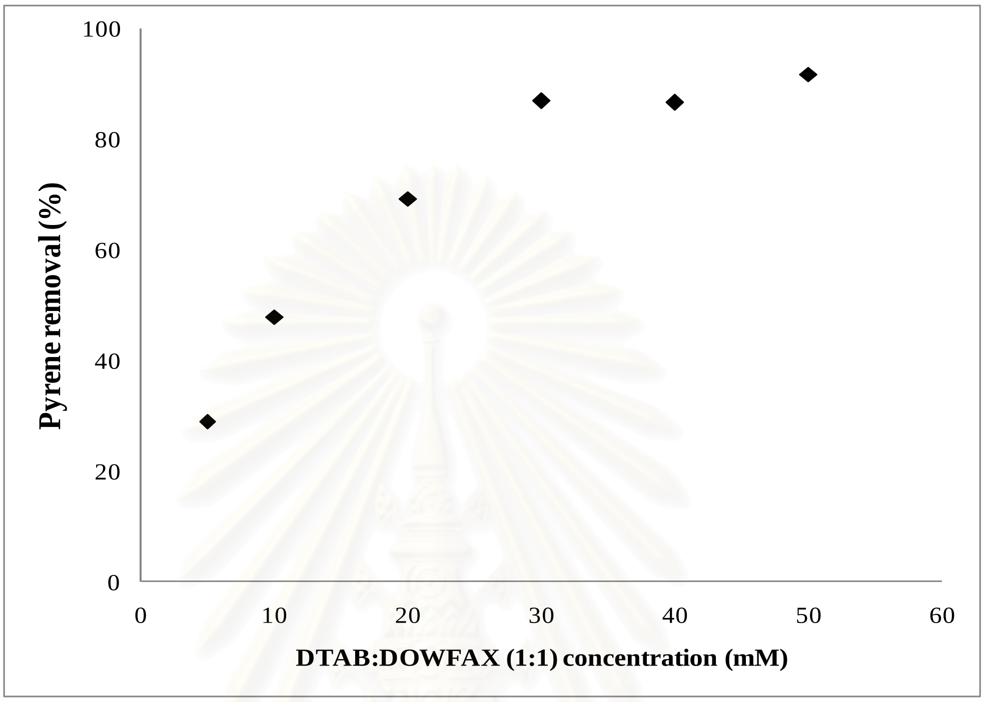


Figure 4.5 Effects of total surfactant concentration on pyrene removal (%) (System: DTAB:DOWFAX at 1:1 molar ratio without additives)

From this finding, it was worthwhile to note that this system was very effective using a very low solid to liquid ratio of 1:1, meaning that only 2.5 mL of surfactant solution is used to clean-up 2.5 g of pyrene contaminated soil, but can achieve the pyrene removal up to 90% as compared to previous work on the desorption of phenanthrene from contaminated soil at phenanthrene concentration of 308 ppm using anionic-nonionic mixed surfactants where the solid to liquid ratio was as high as 1: 10 to reach the same range of phenanthrene removal (Zhou and Zhu, 2007). Although phenanthrene (3 fused benzene rings) has a little bit less degree of hydrophobicity as compared to pyrene (4 fused benzene rings), it requires the volume of surfactant solution 10 times greater. The total concentration of mixed anionic-nonionic surfactant solution used was 12 mM which was lower than one used in this study.

From this experiment, DTAB:DOWFAX at 1:1 molar ratio with total concentration of 20 mM considered as the most suitable surfactant system was used in next experiments in order to study the effects of additives on pyrene removal from contaminated soil because this condition provided the moderate efficiency of pyrene removal; thus, was expected to demonstrate how the addition of suitable amount of additives can enhance the pyrene removal efficiency.

4.5 Effects of additives on pyrene removal

4.5.1 Effects of electrolyte addition on pyrene removal

This experiment aimed to investigate the effects of electrolyte on pyrene removal from contaminated soil. $CaCl_2$ was used as the electrolyte in this study since $CaCl_2$ imitated the groundwater condition. The effects of $CaCl_2$ addition on pyrene removal from contaminated soil were evaluated as shown in Figure 4.6, where the percentage of pyrene removal was plotted as a function of $CaCl_2$ concentration. Obviously, the percentage of pyrene removal increases with an increase in $CaCl_2$ concentration up to 0.025%wt and then decreases above 0.025%wt. Thus, surfactant system of DTAB:DOWFAX at 1:1 molar ratio, total surfactants concentration of 20 mM with 0.025% wt of $CaCl_2$ addition offers the pyrene solubilization as high as 83.5% as compared to 69.1% without additive.

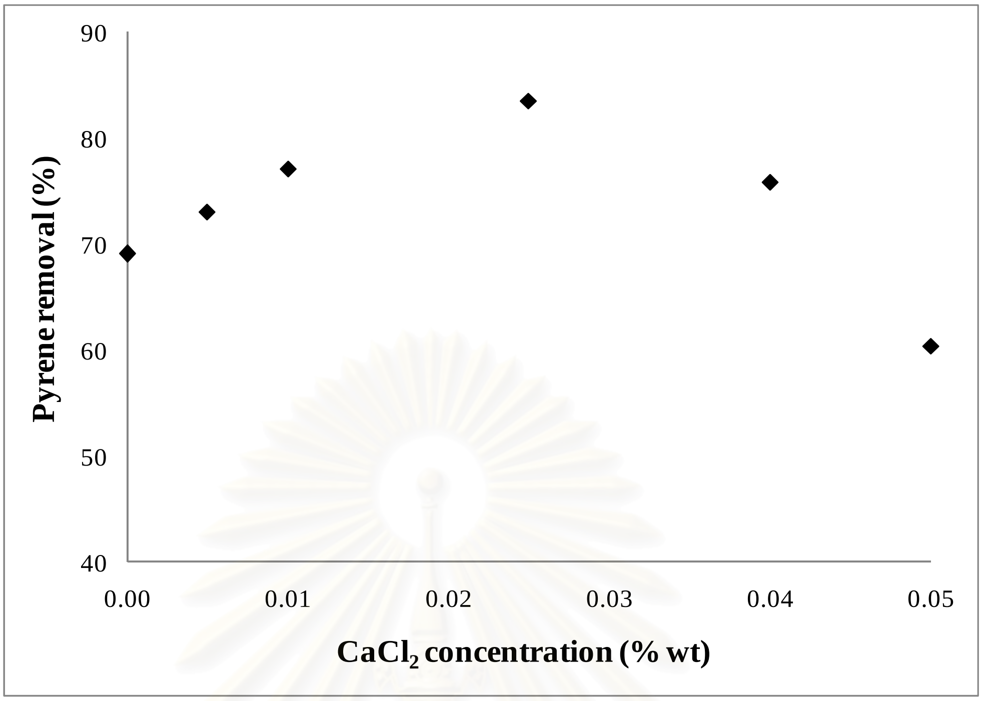


Figure 4.6 Effects of $CaCl_2$ concentration on pyrene removal (%) (System: DTAB:DOWFAX at 1:1 molar ratio with 20 mM of total surfactants concentration)

From this finding, it was observed that a certain salt concentration can enhance the efficiency of pyrene removal from contaminated soil resulted from an increase of pyrene solubilization capacity. This was confirmed in the next experiment that illustrated the effects of electrolyte in surfactant solution on pyrene solubilization via MSR and log K_m. However, if the concentration of $CaCl_2$ was too high (more than 0.025%wt), the surfactant solutions become cloudy with high viscosity. It is possible that there is a phase transition of the surfactant aggregates in such a way that lose its capability for solubilizing organic solutes, which was consistent with previous research done by Brasher et al. (1995). They studied the effect of NaBr addition on the phase behavior of CTAB/SOS surfactant mixtures (mixed cationic-anionic surfactants) and found that the addition of salt alters the electrostatic interaction and contributes to the changes in free energy of aggregation. Thus, the equilibrium phase behavior and surfactant aggregate properties change. The phase behavior of mixed CTAB:SOS system apparently changes when electrolyte is added, especially a vesicle to micelle transition occurring in this surfactant system with increasing salt concentration at certain surfactant compositions.

4.5.2 Effects of lipophilic linkers on pyrene removal

This experiment aimed to investigate the effect of lipophilic linkers addition into mixed cationic-anionic surfactants solution on pyrene removal from contaminated soil. Three straight chain alcohols consisting of octanol (C8), dodecanol (C12), and hexadecanol (C16) were proposed to utilize as the lipophilic linkers in this study. However, it was found out that hexadecanol, which is a solid crystal, cannot be used since it has very low water solubility (1.34 x 10^{-5} mg/L or 0.0134 ppb) with high degree of hydrophobicity (log K_{ow} = 6.65). It cannot be prepared at the same concentration as the other two alcohols used in this study. Thus, only two types of alcohols, which are octanol and dodecanol, were used. These alcohols were varied in three concentrations: 1 mM, 2 mM, and 4 mM as corresponded to total moles of surfactants to total moles of alcohols: 20:1, 10:1, and 5:1, respectively.

The effects of lipophilic linkers on pyrene removal from soil were illustrated in Figure 4.7, where the percentage of pyrene removal was plotted as a function of alcohol concentration. It was found that the percentage of pyrene removal increases sharply with increasing octanol concentration at 1 mM and then slightly increases above 1 mM. Similar trend was observed on dodecanol addition. From these results, it was observed that the surfactant system of DTAB:DOWFAX at 1:1 molar ratio, total surfactants concentration of 20 mM with dodecanol concentration of 4 mM provides the pyrene solubilization as high as 86.7% comparing with 69.1% without additives.

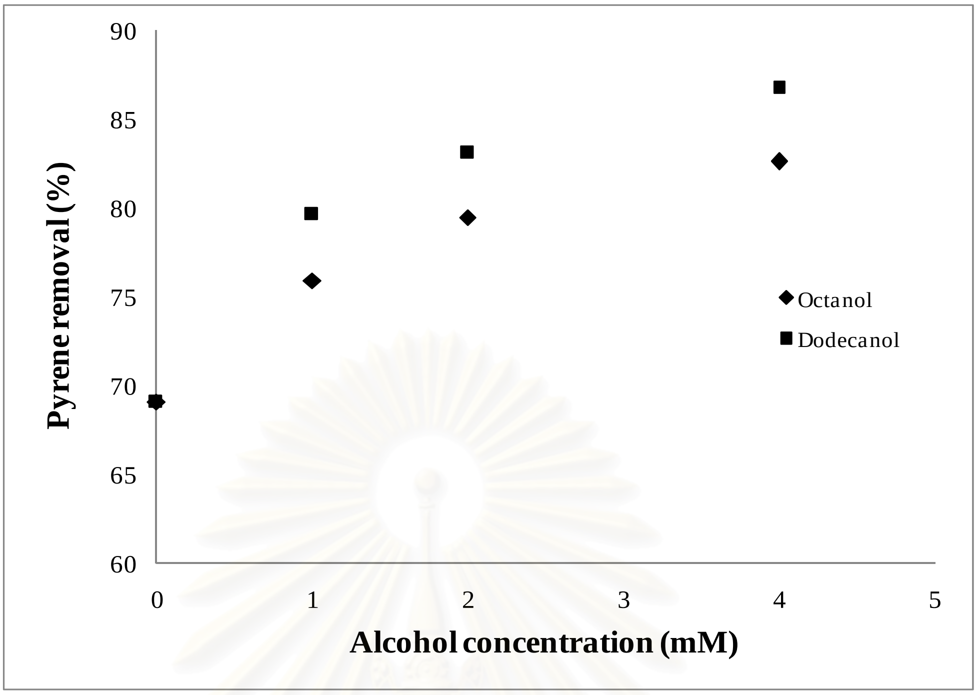


Figure 4.7 Effects of lipophilic linkers on pyrene removal (%) (System: DTAB:DOWFAX at 1:1 molar ratio with 20 mM total surfactants concentration)

From this finding, it was noted that the addition of long-chain alcohols both octanol and dodecanol in the mixed cationic-anionic surfactants solution can enhance the solubilization of pyrene and also increases the percentage of pyrene removal from contaminated soil compared to the results obtained from the same surfactant solution without alcohol. In addition, it was observed that at the same alcohol concentration, the pyrene removal efficiency upon the addition of dodecanol is higher than that of octanol. Thus, the efficiency of pyrene removal increases with increasing the alcohol-chain length in the surfactant solution. Since surfactant aggregates containing dodecanol provide more degree of hydrophobicity in the inner core of micelles, where pyrene tends to solubilize, than the surfactant aggregates with octanol, the surfactant solution with dodecanol provides a higher pyrene solubilization capacity as compared to surfactant solution with octanol. Similar results were observed in previous work done by Tan and O’Haver (2004). They investigated the effects of lipophilic linkers (long-chain alocohols: octanol, decanol, and dodecanol) on the adsolubilization of styrene in Triton X nonionic surfactant at water/silica interface. The results showed that the presence of linkers can promote the styrene adsolubilization. Increasing the hydrophobic chain length and increasing the concentration of linker in the system increase the adsolubilization of styrene. This discussion was confirmed through the next experiment that demonstrated the effects of lipophilic linkers in surfactant solution on pyrene solubilization via MSR and log K_m. Moreover, this finding is consistent with work done by Kim and Lee (2002). They studied the effects of medium-chain alcohols (butanol, pentanol, and hexanol) in the nonionic surfactant solutions (Tween 20, Tween 60, and Tween 80) on the diesel removal from contaminated sandy soil. In their work, the medium-chain alcohol behaves as co-surfactant and aligns along with surfactant molecule where the interior core region is not expanded as compared to the long-chain alcohols, where the locus of solubilization is deeper into the core of surfactant micelles, thus lengthen the diameter of hydrophobic core. As a consequence, the addition of long-chain alcohol tends to have more beneficial for non-polar solute solubilization than the addition of medium-chain alcohol. In this study, they found that the addition of medium-chain alcohol in Tween solutions increases the diesel removal efficiency as compared to the results obtained from Tween solutions without alcohol. In addition, the diesel removal efficiency increases with an increase in alkyl-chain length of alcohol in the cases of Tween 60 and Tween 80.

4.5.3 Effect of the optimal surfactant formulation on pyrene removal

After the effects of total surfactant concentration and additives addition on pyrene removal were investigated, the effect of the optimal surfactant formulation on pyrene removal was evaluated. The optimal surfactant formulation was selected from the results of each effect. From the consideration on the effects of lipophilic linkers on pyrene removal, it was found that the dodecanol concentration of 4 mM offers the highest pyrene removal efficiency as shown in Figure 4.7. However, the addition of 1 mM dodecanol in this surfactant solution shows a sharp increase in the pyrene removal efficiency as high as 10.5% from without additives and the rate of enhancement gradually declines with increasing dodecanol concentration. From this reason, dodecanol at 1 mM was selected as the suitable concentration instead of one at

4 mM. In conclusion, the DTAB:DOWFAX at 1:1 molar ratio with 20 mM total surfactants concentration, 0.025 % wt $CaCl_2$, and 1 mM dodecanol were selected as the optimal surfactant formulation. This surfactant system was prepared and tested for its proficiency and found that it gives the pyrene removal of as high as 87.5 %.

The comparison on pyrene removal efficiency among the best surfactant system obtained from each effect and the optimal surfactant formulation was shown in Figure 4.8.

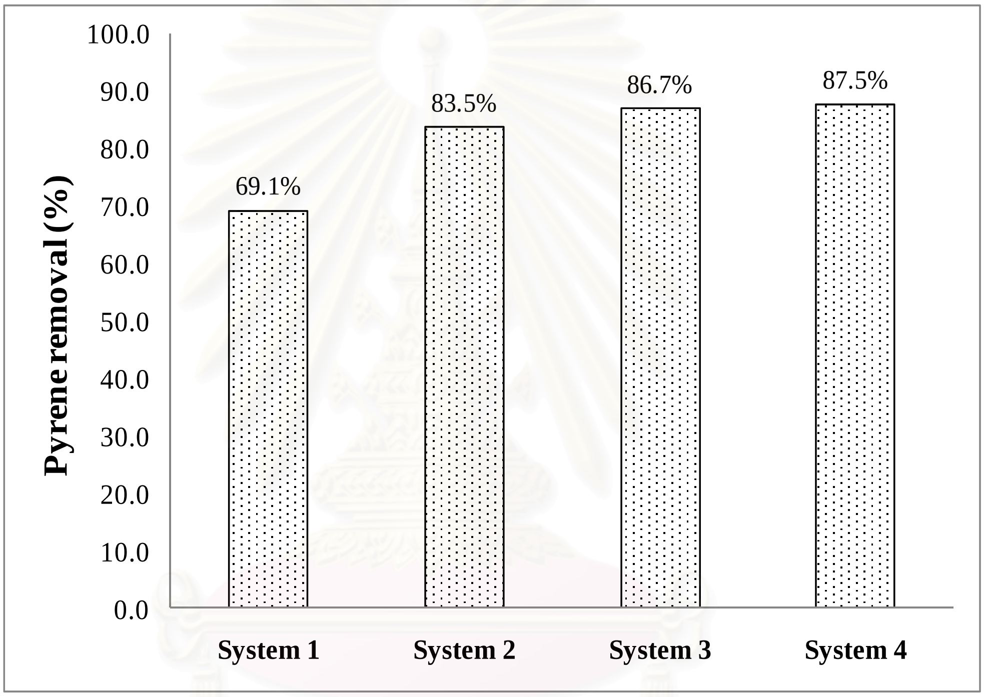


Figure 4.8 Comparison of the pyrene removal efficiency of each surfactant system (System 1: DTAB:DOWFAX at 1:1 molar ratio with 20 mM total surfactants concentration; System 2: DTAB:DOWFAX at 1:1 molar ratio with 20 mM total surfactants concentration and 0.025%wt $CaCl_2$; System 3: DTAB:DOWFAX at 1:1 molar ratio with 20 mM total surfactants concentration and 4 mM of dodecanol concentration; System 4: DTAB:DOWFAX at 1:1 molar ratio with 20 mM total surfactants concentration, 0.025%wt $CaCl_2$, and 1 mM dodecanol concentration)

From Figure 4.8, it was observed that the surfactant systems containing additives (system 2, 3, and 4) provide the higher pyrene removal efficiency as compared to the surfactant system without additives (system 1). In addition, we found that the pyrene removal efficiency of system 3 and system 4 are not much different. It should be noted that system 4 contains only 25% of dodecanol used in system 3 but supplemented by a low $CaCl_2$ concentration of 0.025%wt. An integration of salt and linker creates a synergism and yields the highest percentage of pyrene removal. Therefore, the addition of suitable amount of additives in the surfactant solution can enhance the efficiency of pyrene removal from contaminated soil effectively.

4.6 Effects of additives in surfactant solution on pyrene solubilization

4.6.1 Effects of $CaCl_2$ in surfactant solution on pyrene solubilization

In this experiment, the effects of $CaCl_2$ in surfactant solution on pyrene solubilization were investigated to explain if the solubilization capability for pyrene increases upon the addition of salt. The surfactant system used in this study was DTAB:DOWFAX at 1:1 molar ratio. A solution of mixed surfactants contained 0.025%wt of $CaCl_2$ in every surfactant concentration. Figure 4.9 demonstrated the effects of $CaCl_2$ in surfactant solution on pyrene solubilization. The apparent solubility of pyrene was plotted as a function of surfactants concentration. Obviously, the addition of $CaCl_2$ at concentration of 0.025%wt in DTAB:DOWFAX solution at 1:1 molar ratio increases the solubility of pyrene as compared with the results obtained from this surfactant solution alone. The slope of the plot in Figure 4.9 represents the MSR and thus, the K_m can be calculated. The MSR and log K_m values were summarized in Table 4.3.

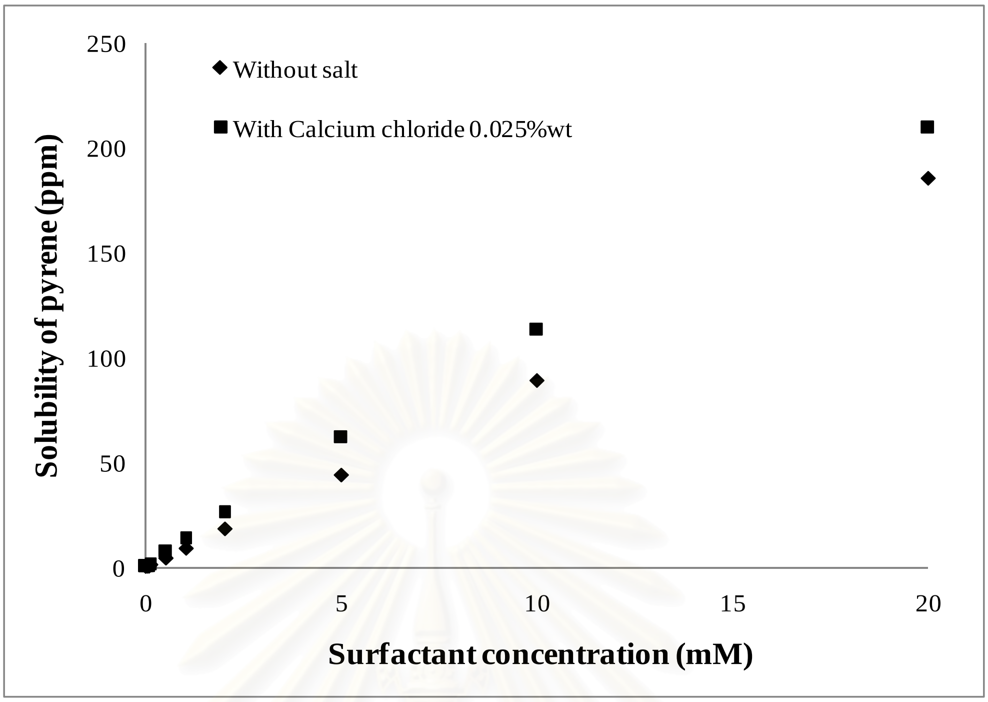


Figure 4.9 Effects of $CaCl_2$ (0.025 %wt) in DTAB:DOWFAX solution at 1:1 molar ratio on pyrene solubilization

Table 4.3 Molar solubilization ratio (MSR) and log micelle-water partitioning coefficient (log K_m) of pyrene for DTAB:DOWFAX at 1:1 molar ratio with and without $CaCl_2$

Surfactant system	MSR	Log K_m
DTAB:DOWFAX at 1:1 molar ratio	0.045	6.57
DTAB:DOWFAX at 1:1 molar ratio with 0.025%wt $CaCl_2$	0.053	6.64

From Table 4.3, it was found that the MSR and log K_m values of DTAB:DOWFAX solution at 1:1 molar ratio with 0.025%wt $CaCl_2$ are higher than those of DTAB:DOWFAX solution at 1:1 molar ratio alone. Thus, the presence of a suitable salt concentration in the mixed cationic-anionic surfactants solution can enhance the pyrene solubilization capacity. This finding is agreed with the fact that the addition of electrolyte in the ionic surfactant solution decreases the repulsion between the similarly charged ionic surfactant head groups causing a decrease in CMC as well as an increase in aggregation number and volume of micelles. The increase in aggregation number of micelles can create a more favorable hydrophobic region for pyrene to solubilize resulting in an increasing in pyrene solubilization (Rosen, 1989; Kim et al, 2000). Furthermore, this finding corresponds to research done by Zhu and Feng (2003). They studied the effects of inorganic salts on pyrene solubilization by SDS-Brij 35 (anionic-nonionic mixed surfactants) and reported that the addition of inorganic salt at concentration of 0.01 mmol/L in mixed SDS-Brij 35 solution can increase the solubility of pyrene as compared to one without salt addition.

4.6.2 Effects of lipophilic linkers in surfactant solution on pyrene solubilization

This study aimed to evaluate the effects of lipophilic linkers in surfactant solution on pyrene solubilization and the results could be used to support the finding on the effects of lipophilic linkers on pyrene removal from contaminated soil. The surfactant system of DTAB:DOWFAX at 1:1 molar ratio was used. Lipophilic linkers used in this study were octanol, dodecanol, and hexadecanol. A total mole of surfactants to total mole of alcohol at 10:1 was applied for octanol and dodecanol only. For hexadecanol, the molar ratio of 10:1 cannot be applied since the saturation of hexadecanol was found as shown by a solid crystal settled on the bottom of the tube. Therefore, the concentration of hexadecanol at its water solubility was prepared and mixed with surfactant solution instead, resulting in the corresponding total mole of surfactants to total mole of hexadecanol was 10:5.53 x 10^{-8}.

The effects of lipophilic linkers in surfactant solution on pyrene solubilization were illustrated in Figure 4.10, where the apparent solubility of pyrene was plotted as a function of total surfactants concentration. For octanol and dodecanol, it was found that the solubility of pyrene increases linearly with increasing octanol and dodecanol concentrations in DTAB:DOWFAX solution at 1:1 molar ratio. As compared the effects between octanol and dodecanol in the surfactant solution on pyrene solubilization, it was obvious that at the same surfactant concentration, the solubility of pyrene in surfactant solution with dodecanol is greater than that with octanol. For hexadecanol, it was observed that the solubility of pyrene in DTAB:DOWFAX solution at 1:1 molar ratio remains almost the same either with or without hexadecanol. The slope of the plot in Figure 4.10 represents the MSR and thus, the K_m can be calculated. The MSR and log K_m values were summarized in Table 4.4.

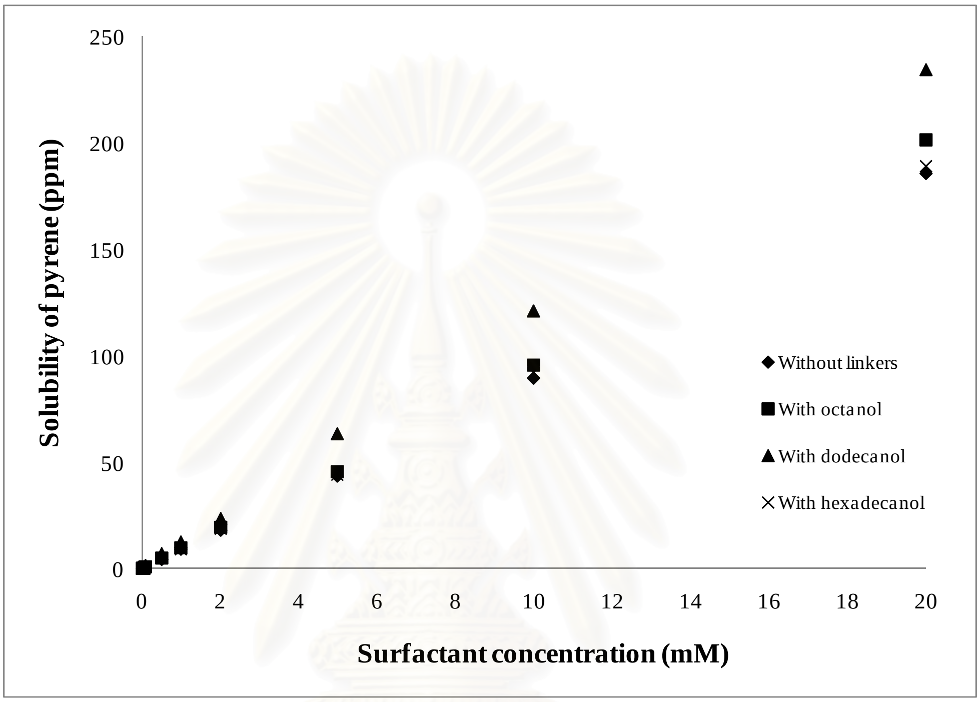


Figure 4.10 Effects of lipophilic linkers type on pyrene solubilization (System: DTAB:DOWFAX solution at 1:1 molar ratio and the total mole of surfactants to total mole of alcohol at 10:1 for octanol and dodecanol, and at 10:5.53 x 10^{-8} for hexadecanol)

Table 4.4 Molar solubilization ratio (MSR) and log micelle-water partitioning coefficient (log K_m) of pyrene for DTAB:DOWFAX at 1:1 molar ratio with and without lipophilic linkers at total mole of surfactants to total mole of alcohol at 10:1 for octanol and dodecanol, and at 10:5.53 x 10^{-8} for hexadecanol

Surfactant system	**MSR**	**Log K_m**
DTAB:DOWFAX at 1:1 molar ratio without linkers	0.045	6.57
DTAB:DOWFAX at 1:1 molar ratio with octanol	0.049	6.61
DTAB:DOWFAX at 1:1 molar ratio with dodecanol	0.059	6.68
DTAB:DOWFAX at 1:1 molar ratio with hexadecanol	0.046	6.58

From Table 4.4, it was found that the MSR and log K_m values of DTAB:DOWFAX solution at 1:1 molar ratio without linkers and with hexadecanol are similar. Thus, the presence of hexadecanol in surfactant solution does not change the solubilization of pyrene as compared with the results obtained from surfactant solution alone probably due to the fact that the amount of added hexadecanol is extremely low and the polarity of hexadecanol may be too low (being a very non-polar compound) resulting in a competition solubilization between hexadecanol and pyrene. On the other hand, the MSR and log K_m values of surfactant solution with octanol and dodecanol are higher than that of surfactant solution without linkers. Consequently, the addition of octanol and dodecanol in surfactant solution provide a higher pyrene solubilization. Furthermore, it was observed that DTAB:DOWFAX solution at 1:1 molar ratio with dodecanol offers the highest MSR and log K_m values.

After the effects of lipophilic linkers in surfactant solution on pyrene solubilization via MSR and log K_m were investigated, the effects of alcohol concentration in surfactant solution at a certain concentration on pyrene solubilization were evaluated. In this study, octanol and dodecanol were only utilized because they can enhance the pyrene solubilization in surfactant solution as described above. The effects of alcohol concentration in DTAB:DOWFAX solution at 1:1 molar ratio with constant total surfactants concentration of 20 mM on pyrene solubilization were illustrated as shown in Figure 4.11, where the apparent solubility of pyrene was plotted against the alcohol concentration. Obviously, the solubility of pyrene increases linearly with increasing alcohol concentration both octanol and dodecanol. However, if the concentration of octanol and dodecanol greater than 4 mM, the surfactant solutions become cloudy and the surfactant precipitation was suspected to be occurred. Therefore, these solutions may lose the ability for solubilizing organic pollutants and are not appropriate for clean-up pyrene contaminated soil. It was found that the solubility of pyrene in surfactant solution with dodecanol is higher than that of with octanol at the same alcohol concentration.

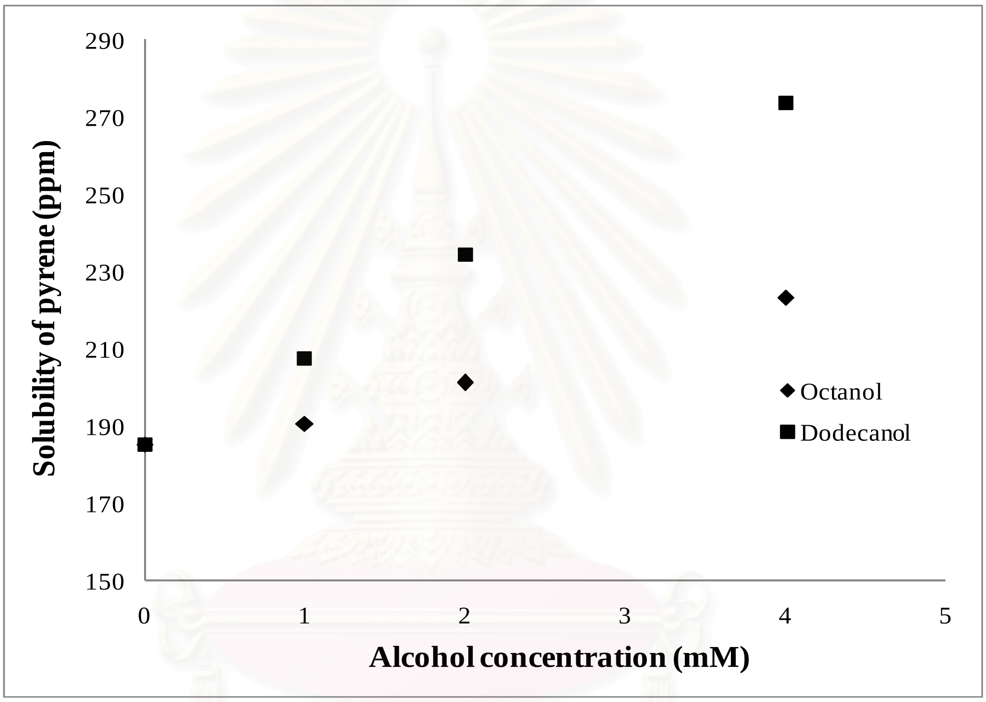


Figure 4.11 Effects of alcohol concentration in DTAB:DOWFAX solution at 1:1 molar ratio with constant total surfactants concentration of 20 mM on pyrene solubilization

From this finding, it was concluded that surfactant solution with lipophilic linkers (octanol and dodecanol) offers a higher pyrene solubilization capacity as compared to surfactant solution without additives. In addition, the presence of dodecanol in surfactant solution can enhance the pyrene solubilization greater than the addition of octanol in surfactant solution. Thus, an increase of alkyl-chain length of alcohol or alcohol concentration in surfactant solution increases the surfactant solubilization capacity for pyrene. This was described by the fact that when lipophilic linker dissolves in the surfactant solution, it tends to solubilize in the surfactant aggregates, where its hydroxyl group orients toward the hydrophilic region of surfactant aggregates, while its long alkyl chain penetrates into the hydrophobic core region of surfactant aggregates and also interacts with the hydrophobic surfactant tails. From these reasons, it can cause the inner core of surfactant aggregates, where pyrene tends to solubilize, possessed higher degree of hydrophobicity and hence has a greater potential for enhancing the solubilization capacity for pyrene (Graciaa et al, 1993; Tan and O'Haver, 2004). In addition, since dodecanol with C12 has a longer alkyl chain and a higher degree of hydrophobicity than octanol with C8, the alkyl chain of dodecanol can intercalate deeper into the inner core of surfactant aggregates and interact stronger with surfactant tails than the hydrocarbon chain of octanol. Therefore, surfactant aggregates containing dodecanol provide larger hydrophobic region than surfactant aggregates with octhanol (Kim and Lee, 2002). Thus, surfactant solution with dodecanol as a lipophilic linker offers a higher solubilization capacity for pyrene as compared to the one with octanol.

4.7 The preconcentration ability of ASTP system

Once the optimal surfactant system that yielded high pyrene removal efficiency from each effect was obtained, these surfactant systems were used to extract pyrene from contaminated soil over again. Afterward, the extracted surfactant solution containing pyrene was adjusted to a suitable surfactant composition (DTAB:DOWFAX at molar ratio of 2:1) in order to induce the ASTP system. By the new composition, the total surfactant concentration became 30 mM (previously at 1:1 molar ratio and total concentration of 20 mM). For the effects of lipophilic linkers on pyrene removal, it was found that the surfactant system with 4 mM dodecanol offers the highest percentage of pyrene removal as shown in section 4.5.2. However, this surfactant system with 4 mM dodecanol could not form the ASTP system after adjusting to a suitable surfactant composition. The solution is still homogeneous single cloudy phase. However, the surfactant system with 1 mM dodecanol proven to be able to form ASTP system after adjusting the surfactant composition was used in this study in stead of the former system at 4 mM dodecanol. This is quite consistent with previous research done by Mao et al (2002). They studied the phase transition induced by octane (additive) in ASTP system formed by DPCl/SL and DTAB/SL (cationic-anionic surfactant mixtures) and found that a certain amount of octane added in ASTP system formed by DPCl/SL and DTAB/SL can cause a phase transition from two-phase system to a single phase solution resulting from a transition of vesicles to normal micelles. Since dodecanol (log K_{ow} = 5.13) has a high degree of hydrophobicity as similar as octane (log K_{ow} = 4.00 - 5.18), thus the addition of octane or dodecanol in ASTP system formed by cationic-anionic surfactant mixtures may provide the similar trend of results on the phase transition. From this finding, it was possible that the presence of dodecanol (more than 1 mM) in ASTP system formed by DTAB:DOWFAX mixtures may cause the phase transition from ASTP system to single phase solution.

The results of an ASTP system formed by DTAB:DOWFAX mixtures with and without additives were summarized in Table 4.5. The comparison of surfactant and pyrene partition ratios and the percentage of pyrene accumulated in the surfactant-rich phase between an ASTP system formed by DTAB:DOWFAX mixtures with and without additives was shown in Figure 4.12.

Table 4.5 The ASTP system formed by DTAB:DOWFAX mixtures with and without additives at ambient temperature of 30 ºC

System	Fractional rich phase volume	DOWFAX concentration (mM)		Pyrene concentration (ppm)		Partition ratio		Pyrene accumulated in rich phase (%)
		Rich phase	Dilute phase	Rich phase	Dilute phase	Surfactant	Pyrene	
1	0.031	332.57	0.11	4,182.69	1.47	3,023.36	2,845.37	98.9
2	0.031	335.45	0.10	5,432.69	1.67	3,354.50	3,253.11	99.0
3	0.022	315.54	3.21	4,567.31	67.0	98.30	68.18	57.9
4	0.021	341.98	3.10	5,412.09	70.1	110.32	77.21	59.9

Note System 1: ASTP system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration without additive

System 2: ASTP system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration and 0.025%wt $CaCl_2$

System 3: ASTP system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration and 1 mM dodecanol

System 4: ASTP system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration, 0.025%wt $CaCl_2$, and 1 mM dodecanol

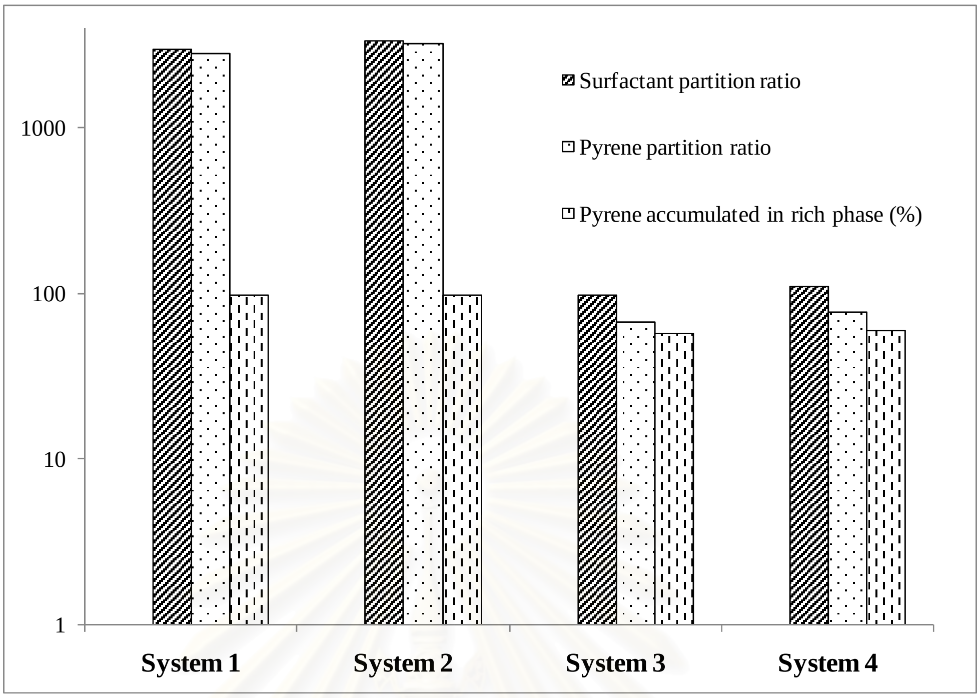


Figure 4.12 The comparison of surfactant and pyrene partition ratios and the percentage of pyrene accumulated in rich phase between an ASTP system formed by DTAB:DOWFAX mixtures with and without additives (System 1: ASTP system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration; System 2: ASTP system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration and 0.025%wt $CaCl_2$; System 3: ASTP system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration and 1 mM dodecanol; System 4: ASTP system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration, 0.025%wt $CaCl_2$, and 1 mM dodecanol)

From Table 4.5 and Figure 4.12, the results showed that system 1 and 2 offers a higher preconcentration ability as compared to system 3 and 4 considering from the surfactant and pyrene partition ratios and the percentage of pyrene accumulated in the surfactant-rich phase. For system 1 (without additives) and system 2 (with 0.025%wt $CaCl_2$), it was found that most of pyrene tends to solubilize in surfactant aggregates and thus concentrates in the surfactant-rich phase observing from the high percentage of pyrene accumulated in surfactant-rich phase. The partition ratio, which is the concentration of chemical in the surfactant-rich phase to that in the surfactant-dilute phase, of surfactant and pyrene are very high indicating a great preconcentration ability of both ASTP systems. In addition, it was observed that the fractional rich-phase volume is very low about 0.03 thus, both ASTP extraction systems have a potential for reducing the large volume of waste prior treatment or disposal, for example, 30 liters of the surfactant-rich phase was generated out of 1,000 liters of flushed surfactant solution meaning that 970 liters is the surfactant-dilute phase containing low concentrations of surfactants and pyrene, thus it may be discharged to the environment as the effluent if passed the regulation. This finding is agreed with many researches reporting that ASTP system formed by mixtures of cationic and anionic surfactants was successfully applied for extraction and preconcentration organic contaminants from aqueous solution (Krutlert, 2004; Kunanupap, 2004; Khaolerk, 2006; Intasara, 2006).

As compared the preconcentration ability of system 1 without additives and system 2 containing 0.025%wt $CaCl_2$, we found that the fractional rich-phase volume and the percentage of pyrene accumulated in surfactant-rich phase of system 1 and 2 are similar. Although the surfactant concentrations in both phases of system 1 and 2 are not much different, the pyrene concentration in the surfactant-rich phase of system 2 is higher than that of system 1 while the pyrene concentration in the surfactant-dilute phase of system 1 and 2 are not much different. From these reasons, the pyrene partition ratio of system 2 with 0.025%wt $CaCl_2$ is higher than that of system 1 without additives. It was possible that the higher pyrene partition ratio of system 2 with 0.025%wt $CaCl_2$ results from an increase of solubilization capacity of surfactant aggregates in the surfactant rich-phase upon the addition of electrolyte. This is consistent with previous research done by Yin et al (2002). They studied the effect of salt addition on phase separation of cationic-anionic surfactant mixtures and reported that the addition of salt can increase the aggregation number of micelles and also cause the transformation of small micelles to vesicles or lamellar structures resulting in an increase in solute solubilization capacity. Moreover, this finding corresponds to work done by Krutlert (2004). They studied the effect of electrolyte on BTEX removal from wastewater using ASTP system form by DTAB:DOWFAX mixtures. They found that the addition of NaCl can greatly enhance the extraction and preconcentration of benzene as shown by a doubling of benzene partition ratio upon the addition of 1.0 M NaCl. From this finding, it was concluded that the addition of $CaCl_2$ at concentration of 0.025%wt in the ASTP system formed by DTAB:DOWFAX mixtures can increase the preconcentration ability of pyrene.

For system 3 (with dodecanol) and system 4 (with $CaCl_2$ and dodecanol), it was found that the fractional-rich phase volume of system 3 and 4 are very low and lower than that of system 1 and 2 indicating that system 3 and 4 have a potential for reducing the large volume of waste greater than system 1 and 2. However, we found that the percentage of pyrene accumulated in the surfactant-rich phase of system 1 and 2 are higher than those of system 3 and 4 indicating that system 1 and 2 offers a greater preconcentration ability as compared to system 3 and 4. Furthermore, it was observed that the surfactant and pyrene concentrations in the surfactant-rich phase of system 3 and 4 are very high while those in the surfactant-dilute phase of system 3 and 4 are high too. From these reasons, the surfactant and pyrene partition ratios of system 3 and 4 are very low and much lower than those of system 1 and 2. Thus, the system 3 with dodecanol and system 4 with $CaCl_2$ and dodecanol provide a lower preconcentration ability as compared to system 1 without additives and system 2 with $CaCl_2$.

This finding is consistent with work done by Mao et al (2002) as previously described that the addition of a certain amount of octane into ASTP system formed by DPCl/SL and DTAB/SL can cause the phase transition from two-phase systems to single-phase solutions. Due to the fact that dodecanol and octane have the similar degree of hydrophobicity, the addition of octane or dodecanol in ASTP system formed by cationic-anionic surfactant mixtures may yield the similar results of phase transition. Although the surfactant system with 1 mM dodecanol and the surfactant system with 0.025%wt $CaCl_2$ and 1 mM dodecanol could form the ASTP system by the adjusting the suitable surfactant composition, the surfactant-dilute phase solution of both systems were cloudy with high surfactant and pyrene concentrations after the phase separation occurred. Therefore, it was possible that the presence of 1 mM dodecanol in ASTP system form in the DTAB:DOWFAX mixtures leads to some changes in microstructure of surfactant aggregates, which cannot be identified in this study. However, it was concluded that the presence of dodecanol in the ASTP system (system 3 and 4) decrease the preconcentration ability of pyrene. On the other hands, if a phase separation of surfactant solution or ASTP system was not considered, the dodecanol addition is of beneficial since it serves as a lipophilic linker and can enhance the pyrene solubilization resulting in an increase in pyrene partition ratio.

From this experiment, it was known that the phase separation or ASTP system formed by cationic-anionic surfactant mixtures can be induced by adjusting the surfactant composition (in this case, around the stoichiometric surfactant composition of DTAB:DOWFAX at 2:1 molar ratio and its vicinity). However, we found that an addition of a certain amount of $CaCl_2$ in mixed cationic-anionic surfactants solution can induce the phase separation of mixture of cationic-anionic surfactant system even at surfactant composition that naturally does not form ASTP (such as surfactant mixtures at surfactant composition not closed to the stoichiometric ratio). From this new finding, the surfactant system of DTAB:DOWFAX at 1:1 molar ratio with 20 mM total surfactants concentration was selected to study the preconcentration ability of ASTP system induced by the addition of $CaCl_2$. This surfactant system was used to extract pyrene from contaminated soil over again. Later on, 0.2%wt $CaCl_2$ was added into the extracted surfactant solution containing pyrene in order to induce the ASTP system. The comparison on the preconcentration ability of ASTP system induced by the adjusting the surfactant composition and by the addition of $CaCl_2$ was evaluated as shown in Table 4.6.

Table 4.6 The comparison on the preconcentration ability of ASTP system induced by adjusting the surfactant composition and by the addition of $CaCl_2$

System	Fractional rich phase volume	DOWFAX concentration (mM)		Pyrene concentration (ppm)		Partition ratio		Pyrene accumulated in rich phase (%)
		Rich phase	Dilute phase	Rich phase	Dilute phase	Surfactant	Pyrene	
A	0.031	332.57	0.11	4,182.69	1.47	3,023.36	2,845.37	98.9
B	0.040	232.67	1.07	3,166.21	18.0	217.45	175.90	87.0

Note System A: ASTP system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration (Induced by adjusting the surfactant composition)

System B: ASTP system formed by DTAB:DOWFAX at 1:1 molar ratio with 20 mM total surfactants concentration and 0.2%wt $CaCl_2$ (Induced by the addition of 0.2%wt $CaCl_2$)

From Table 4.6, as compared the preconcentration ability of system A and system B, it was obvious that the surfactant and pyrene partition ratios and the percentage of pyrene accumulated in the surfactant-rich phase of system A are higher than those of system B indicating that system A offers a greater preconcentration ability as compared to system B. In addition, we found that the fractional rich-phase volume of system A is lower than that of system B meaning that system A has a potential for reducing a volume of waste greater than system B. From this finding, it was concluded that the ASTP formed by cationic-anionic surfactant mixtures induced by adjusting the surfactant composition yields a greater preconcentration ability than one induced by the addition of salt. So, in summary, the presence of salt in the system of cationic-anionic surfactant mixture does not inhibit the ASTP extraction process. A certain amount of salt presented does not only enhance the solubilization of pyrene into the surfactant aggregates but also induce the phase separation even though the preconcentration ability is not very good as compared to an inducing by surfactant composition adjustment.

From the view point of pyrene removal based on pyrene solubilization into surfactant solution, we found that the optimal surfactant formulation containing linker and salt offers the highest pyrene removal efficiency and is suitable to be used for clean-up pyrene from contaminated soil. However, if we incorporated the reduction of waste generated aspect and the preconcentration ability possessing in the ASTP system, it was obvious that the ASTP system containing lipophilic linker provides a low preconcentration ability, while the ASTP system with salt and ASTP system without additives yield a high preconcentration ability of both pyrene and surfactant. The ASTP system containing salt provides the highest preconcentration ability. Thus, if we consider both pyrene removal and preconcentration ability of ASTP system, we found that the DTAB:DOWFAX at 1:1 molar ratio, 20 mM total surfactants concentration with the addition of 0.025%wt $CaCl_2$ is the best surfactant system because this surfactant system offers the high percentage of pyrene removal of 83.5%. In addition, this surfactant system can be induced the ASTP system by adjusting surfactant composition to the suitable one that provides the highest preconcentration ability where the partition ratios of both surfactant and pyrene are up to 3,200 indicating that the concentration of compounds in the surfactant-rich phase is more than 3,200 times higher than that of in the surfactant-dilute phase.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research aimed to study the effectiveness of mixed cationic and anionic surfactants solution to clean-up pyrene from contaminated soil and to induce the ASTP system by adjusting the surfactant composition in order to preconcentrate pyrene in the surfactant-rich phase. For adsorption study, the results showed that DTAB increasingly adsorbs onto silica sand with concentration while DOWFAX does not adsorb onto silica sand at all. For DTAB:DOWFAX at all studied molar ratios, the adsorption onto silica sand increases solely by the presence of DTAB in the solution. For pyrene solubilization study, the results demonstrated that the solubilization of pyrene by pure and mixed surfactants increases linearly with increasing surfactant concentration beyond the CMC. In addition, DTAB:DOWFAX at all studied molar ratios exhibited the synergistic effect as shown by the greater pyrene solubilization over DTAB and DOWFAX alone.

From the consideration of surfactant adsorption and pyrene solubilization results, we found that DTAB:DOWFAX at 1:1 molar ratio was the suitable surfactant system, which was further used to investigate the effects of total surfactants concentration on pyrene removal from contaminated soil. The results showed that DTAB:DOWFAX at 1:1 molar ratio at 20 mM total surfactants concentration, which yielded the moderate percentage of pyrene removal of 69.1% was considered as the most appropriate surfactant system to be further used. Later on, the effects of electrolyte and lipophilic linkers addition on pyrene removal from contaminated soil were evaluated. For $CaCl_2$ effects, we found that the surfactant system of DTAB:DOWFAX at 1:1 molar ratio at 20 mM total surfactants concentration with the addition of 0.025% wt $CaCl_2$ offers the pyrene removal as high as 83.5% or about 14% increase as compared to one without an addition of electrolyte. For the effects of lipophilic linkers, it was shown that DTAB:DOWFAX at 1:1 molar ratio at 20 mM total surfactants concentration with the addition of 4 mM dodecanol yields the pyrene removal of 86.7%, which was again higher than one without additive. In addition, it was observed that the pyrene removal efficiency increases with increasing the alcohol-chain length in the surfactant solution. In summary, the optimal surfactant formulation was found to be one which combines all additives, which is the DTAB:DOWFAX at 1:1 molar ratio with 20 mM total surfactants concentration, 0.025%wt $CaCl_2$, and 1 mM dodecanol, where the highest percentage of pyrene removal from contaminated soil of 87.5% was achieved. Thus, it was obvious that an integration of salt and linker creates the synergistic effect and yields the highest percentage of pyrene removal from soil.

From this finding, it was concluded that the presence of suitable amount of additives both electrolyte and lipophilic linkers can enhance the efficiency of pyrene removal from contaminated soil resulting from an increase of pyrene solubilization capacity. This was confirmed through the experiments that demonstrated the effects of electrolyte and lipophilic linkers in surfactant solution on pyrene solubilization. The DTAB:DOWFAX at 1:1 molar ratio was utilized in these experiments. The results demonstrated that the addition of $CaCl_2$ at concentration of 0.025% wt in DTAB:DOWFAX solution at 1:1 molar ratio increases the pyrene solubilization (shown by higher log K_m) as compared to the results obtained from this surfactant solution without salt. On the other hand, we found that DTAB:DOWFAX solution at 1:1 molar ratio with lipophilic linkers (octanol and dodecanol) offers a higher pyrene solubilization capacity as compared to one without linkers. The presence of dodecanol in surfactant solution increases the pyrene solubilization greater than the addition of octanol in surfactant solution. However, it was found that the presence of haxadecanol in the surfactant solution does not alter the pyrene solubilization as compared with the results of surfactant solution alone.

The surfactant systems that yielded the optimal pyrene removal from each effect were used to extract pyrene from contaminated soil over again. The extracted surfactant solution containing solubilized pyrene was afterward adjusted the surfactant composition to DTAB:DOWFAX at 2:1 molar ratio in order to form ASTP system. After the phase separation, the results showed that ASTP systems without additives and with $CaCl_2$ offer the greater preconcentration ability over those with dodecanol considering from the surfactant and pyrene partition ratios, and the percentage of pyrene accumulated in the surfactant-rich phase. Additionally, it was shown that the presence of 0.025% wt $CaCl_2$ in ASTP system yielded the highest preconcentration ability. The pyrene concentration in the surfactant-dilute phase was found as low as 1.67 ppm while the 99% of pyrene was extracted in the surfactant-rich phase. The surfactant and pyrene can be preconcentrated in the surfactant-rich phase in a small volume, where the surfactant and pyrene partition ratios are as high as 3,355 and 3,253, respectively.

From this study, we found that the addition of $CaCl_2$ at concentration of 0.2%wt in mixed DTAB:DOWFAX solution can also induce the ASTP system without adjusting the surfactant composition, where the molar ratio of DTAB:DOWFAX was still 1:1. As compared the preconcentration ability of ASTP system without additives induced by the surfactant composition and by the addition of $CaCl_2$, the results showed that ASTP system induced by the surfactant composition yields the greater preconcentration ability over that induced by the addition of salt.

In summary, it was shown that the mixed DTAB:DOWFAX surfactants solution was an excellent extracting agent for pyrene decontamination from soil. This solution can also form the ASTP system, where most of surfactants and pyrene can be concentrated in the surfactant-rich phase solution. This technique may be applied to extract the contaminants of environmental concern from environmental media (e.g. wastewater, groundwater, and subsurface soil) and to preconcentrate these wastes in a small volume of the surfactant-rich phase in order to reduce the large volume of wastes prior treatment or disposal.

5.2 Recommendations

In this study, the mixed DTAB and DOWFAX surfactants solution for clean-up pyrene from contaminated soil were carried out in batch experiments. For further study, the column experiments simulated the subsurface condition should be applied to investigate the effectiveness of mixed DTAB:DOWFAX solutions for decontamination of pyrene from soil in order to compare the results obtained from the batch experiments and the column experiments. In addition, this technique might be utilized for clean up pyrene from other soil types such as alumina or natural soil with organic content in order to investigate the effect of soil type on pyrene removal from contaminated soil using mixed DTAB:DOWFAX solutions. Moreover, this technique might be applicable for removal of mixed pollutants from contaminated soil, for example this mixed surfactants solution may be applied for flushing the soil contaminated with heavy metals along with hydrophobic compounds. It is possible that the mixed surfactant aggregates have a potential for solubilizing hydrophobic contaminants simultaneously binging heavy metals at the surfactants head. Heavy metals can be bounded around the micelle/water interface of surfactant aggregates while hydrophobic pollutants tend to solubilize in the hydrophobic core of surfactant aggregates. Besides, this system might be utilized for removal of other organic contaminants such as other recalcitrant PAHs and volatile organic compounds (VOCs) from contaminated soil. Furthermore, the other mixed cationic and anionic surfactants systems may be extended chosen to improve the efficiency of organic contaminants removal from contaminated soil.

For the ASTP system formed by the mixtures of cationic-anionic surfactants, it was shown that the ASTP system in this study has a potential for reducing the large volume of wastes. Moreover, this ASTP system can be operated at low temperature and does not require the addition of energy for raising temperature since the phase separation can be occurred by the suitable surfactant concentration and composition not by the critical temperature as in a case of nonionic surfactants. Thus, it was obvious that this technique is very beneficial in an economic viewpoint. For the future study, the ASTP system may be applied to extract and preconcentrate the other types of hazardous materials of environmental concerns. If this ASTP system formed by mixed cationic-anionic surfactants is applied for removal VOCs in the closed system, the concentrated surfactants presented in the surfactant-rich phase solution can be recovered for reuse using the air or vacuum stripper in order to strip these compounds out of the surfactant aggregates. Then, these concentrated surfactant solutions can be diluted with water to be used for other environmental applications.

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APPENDICES

APPENDIX A

Terms Notification

To investigate the preconcentration ability of aqueous surfactant two-phase (ASTP) system formed by cationic-anionic surfactant mixtures, these following terms are determined.

(i) Fractional rich-phase volume

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

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

$[\mathrm{V}]_{total}$ is the total volume of the solution

(ii) Surfactant partition ratio

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

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

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

(iii)Pyrene partition ratio

$$\text{Pyrene partition ratio } = \frac{[\mathrm{P}]_{rich}}{[\mathrm{P}]_{dilute}}$$

where $[\mathrm{P}]_{rich}$ is the concentration of pyrene in the surfactant-rich phase

$[\mathrm{P}]_{dilute}$ is the concentration of pyrene in the surfactant-dilute phase

(iv) The percentage of pyrene accumulated in the surfactant-rich phase

$$\%\text{Pyrene accumulated in the surfactant - rich phase} = \left[\frac{[\mathrm{P}]_{initial} - [\mathrm{P}]_{dilute}}{[\mathrm{P}]_{initial}}\right] \times 100$$

where $[\mathrm{P}]_{initial}$ is the initial concentration of pyrene in the extracted surfactant solution before phase separation

$[\mathrm{P}]_{dilute}$ is the concentration of pyrene in the surfactant-dilute phase

(v) Mass balance for pyrene

$$[(\mathrm{Fr}_\mathrm{R}) * (\mathrm{P})_\mathrm{R}] + [(1- \mathrm{Fr}_\mathrm{R}) * (\mathrm{P})_\mathrm{D}] = (\mathrm{P})_\mathrm{initial}$$

where (Fr_R) is the fractional rich-phase volume

$(\mathrm{P})_\mathrm{R}$ is the concentration of pyrene in the surfactant-rich phase

$(\mathrm{P})_\mathrm{D}$ is the concentration of pyrene in the surfactant-dilute phase

$(\mathrm{P})_\mathrm{initial}$ is the initial concentration of pyrene in the extracted surfactant solution before phase separation

(vi) Mass balance for total surfactant concentration

$$[(\mathrm{Fr}_\mathrm{R}) * (\mathrm{Surf})_\mathrm{R}] + [(1- \mathrm{Fr}_\mathrm{R}) * (\mathrm{Surf})_\mathrm{D}] = (\mathrm{Surf})_\mathrm{initial}$$

where (Fr_R) is the fractional rich-phase volume

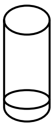
$(\mathrm{Surf})_\mathrm{R}$ is the concentration of surfactant in the surfactant-rich phase

$(\mathrm{Surf})_\mathrm{D}$ is the concentration of surfactant in the surfactant-dilute phase

$(\mathrm{Surf})_\mathrm{initial}$ is the initial concentration of surfactant in the extracted surfactant solution before phase separation

APPENDIX B

Table B-1 Results of preliminary study in the phase behavior of mixed cationic-anionic surfactants system

Surfactant system	Total surfactant conc. (mM)	Molar ratio	Temp (°C)	Phase appearance		Interfacial boundary
DTAB:DOWFAX	20	2:1	4		Upper: clear solution Lower: clear solution, oil-like, not much sticky	Unstable and clear interface
			30		Upper: clear solution Lower: clear solution, oil-like, not much sticky	Unstable and clear interface
DTAB:DOWFAX	30	2:1	4		Upper: clear solution Lower: clear solution, oil-like, not much sticky	Stable and clear interface
			30		Upper: clear solution Lower: clear solution, oil-like, not much sticky	Stable and clear interface
DTAB:DOWFAX	50	2:1	4		Upper: clear solution Lower: clear and viscous solution	Stable and clear interface
			30		Upper: clear solution Lower: clear and viscous solution	Stable and clear interface
DTAB:DOWFAX	100	2:1	4		Upper: clouded solution Lower: clear and highly viscous solution	Stable and clear interface
			30		Upper: clouded solution Lower: clear and highly viscous solution	Stable and clear interface

APPENDIX C

Table C-1 Determination of calibration curve of DOWFAX concentration measured by UV-visible spectrophotometer at wavelength of 240 nm (for adsorption of DOWFAX onto silica sand)

DOWFAX concentration (mM)	Absorbance at 240 nm
0.01	0.190
0.02	0.388
0.03	0.569
0.04	0.748
0.05	0.935

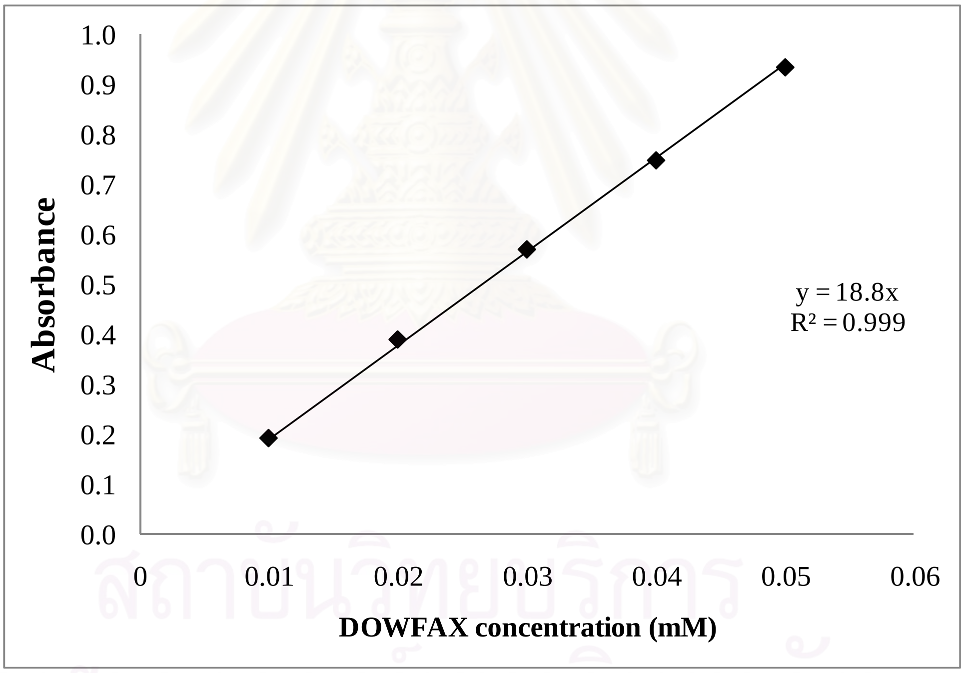


Figure C-1 Relationship between DOWFAX concentration (mM) and absorbance at 240 nm measured by UV-visible spectrophotometer (for adsorption of DOWFAX onto silica sand)

Table C-2 Determination of calibration curve of DTAB concentration measured by TOC analyzer (for adsorption of DTAB onto silica sand)

DTAB concentration (mM)	**TOC (mg/L)**
0.02	3.390
0.05	6.920
0.10	17.21
0.20	35.87
0.50	78.96
1.00	177.8

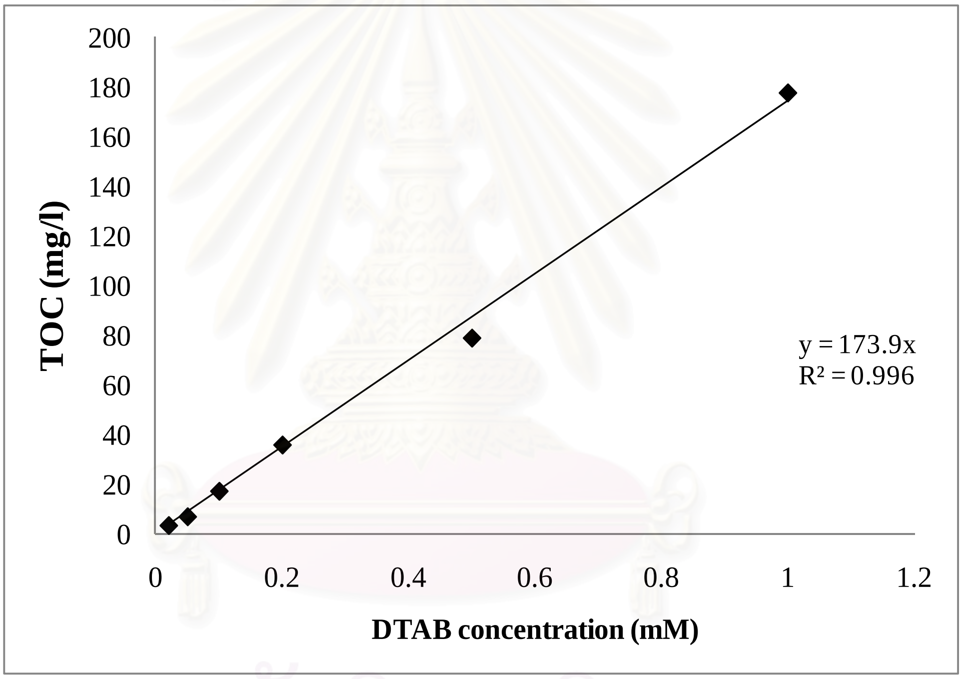


Figure C-2 Relationship between DTAB concentration (mM) and total organic carbon, TOC (mg/L) measured by TOC analyzer (for adsorption of DTAB onto silica sand)

Table C-3 Determination of calibration curve of DTAB:DOWFAX (1.5:1) concentration measured by TOC analyzer (for adsorption of DTAB:DOWAX at 1.5:1 molar ratio onto silica sand)

DTAB:DOWFAX (1.5:1) concentration (mM)	TOC (mg/L)
0.02	5.518
0.05	12.07
0.10	24.82
0.20	47.84
0.50	126.9

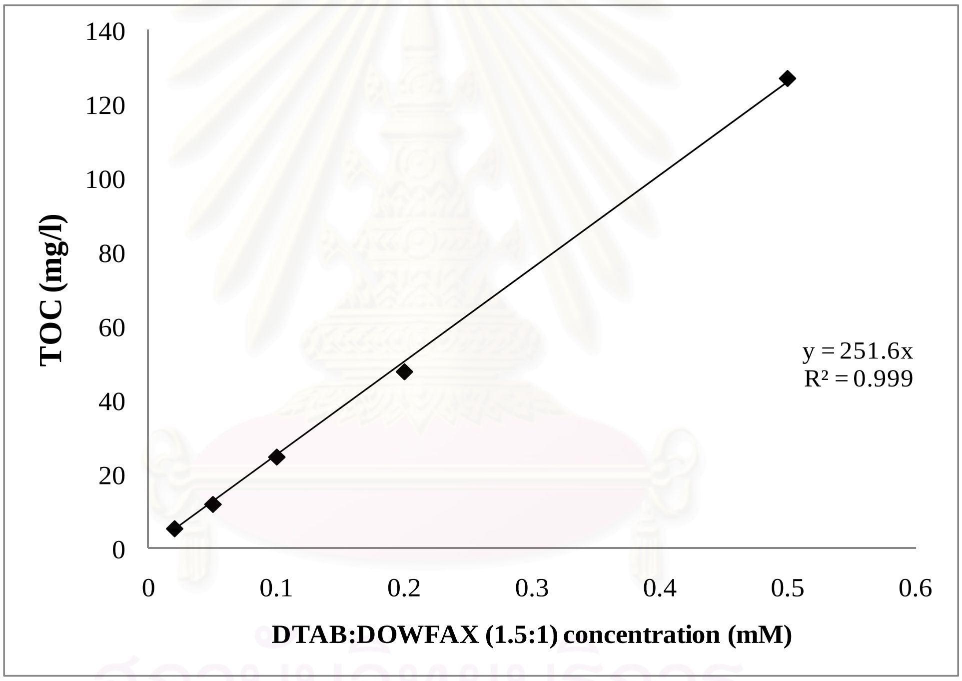


Figure C-3 Relationship between DTAB:DOWFAX (1.5:1) concentration (mM) and total organic carbon, TOC (mg/L) measured by TOC analyzer (for adsorption of DTAB:DOWFAX at 1.5:1 molar ratio onto silica sand)

Table C-4 Determination of calibration curve of DTAB:DOWFAX (1:1) concentration measured by TOC analyzer (for adsorption of DTAB:DOWAX at 1:1 molar ratio onto silica sand)

DTAB:DOWFAX (1:1) concentration (mM)	**TOC (mg/L)**
0.02	5.790
0.05	12.42
0.10	28.45
0.20	53.79
0.50	136.1

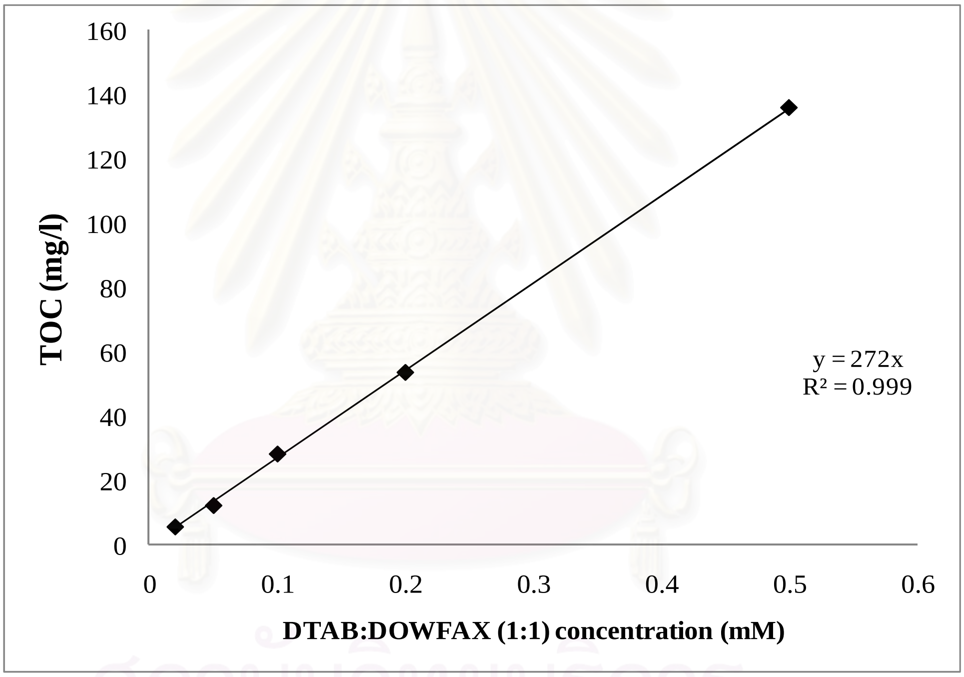


Figure C-4 Relationship between DTAB:DOWFAX (1:1) concentration (mM) and total organic carbon, TOC (mg/L) measured by TOC analyzer (for adsorption of DTAB:DOWFAX at 1:1 molar ratio onto silica sand)

Table C-5 Determination of calibration curve of DTAB:DOWFAX (1:1.5) concentration measured by TOC analyzer (for adsorption of DTAB:DOWAX at 1:1.5 molar ratio onto silica sand)

DTAB:DOWFAX (1:1.5) concentration (mM)	**TOC (mg/L)**
0.02	6.578
0.05	16.22
0.10	31.95
0.20	64.35
0.50	162.8

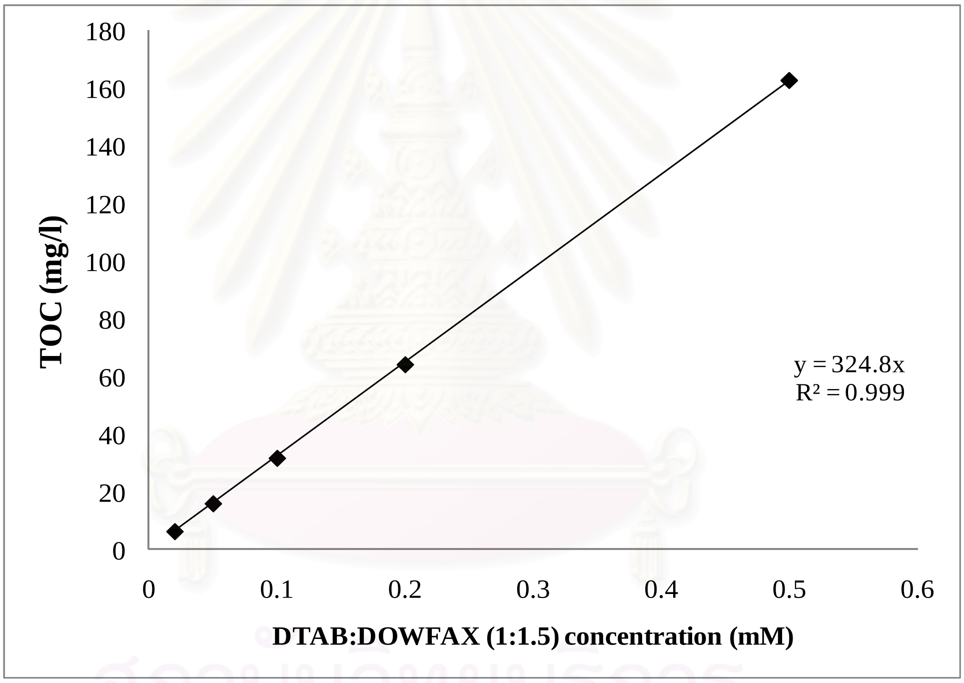


Figure C-5 Relationship between DTAB:DOWFAX (1:1.5) concentration (mM) and total organic carbon, TOC (mg/L) measured by TOC analyzer (for adsorption of DTAB:DOWFAX at 1:1.5 molar ratio onto silica sand)

Table C-6 Determination of calibration curve of DTAB:DOWFAX (1:2) concentration measured by TOC analyzer (for adsorption of DTAB:DOWAX at 1:2 molar ratio onto silica sand)

DTAB:DOWFAX (1:2) concentration (mM)	TOC (mg/L)
0.02	6.227
0.05	16.02
0.10	33.85
0.20	66.75
0.50	168.1

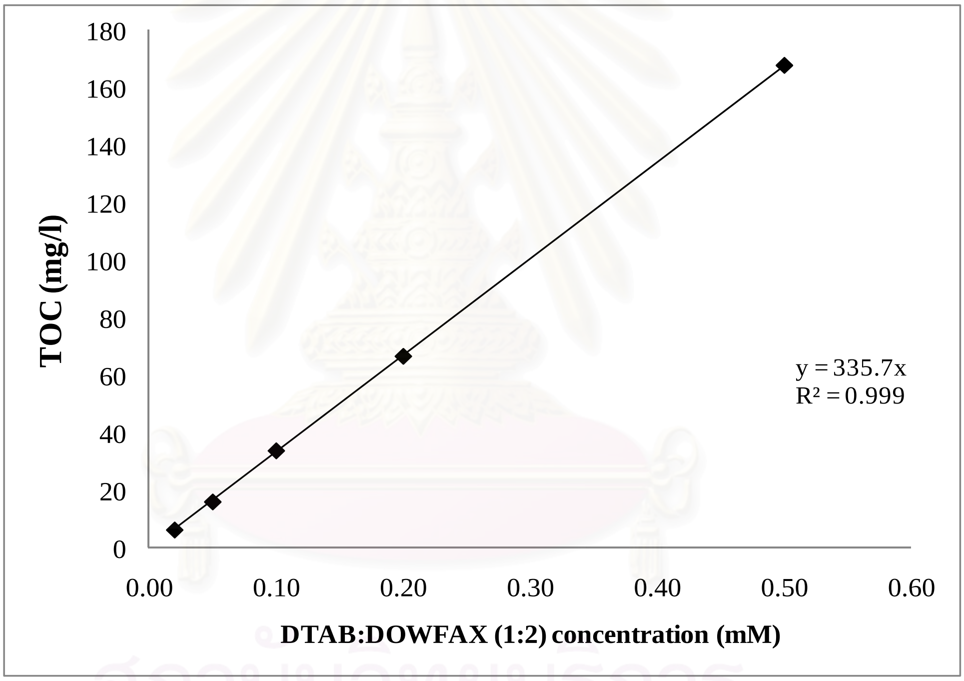


Figure C-6 Relationship between DTAB:DOWFAX (1:2) concentration (mM) and total organic carbon, TOC (mg/L) measured by TOC analyzer (for adsorption of DTAB:DOWFAX at 1:2 molar ratio onto silica sand)

Table C-7 Determination of calibration curve of DOWFAX concentration measured by TOC analyzer (for calculation of the adsorbed amount of DTAB presented in DTAB:DOWFAX at all studied molar ratios onto silica sand)

DOWFAX concentration (mM)	TOC (mg/L)	TOC area
0.02	8.398	14.710
0.05	19.87	34.810
0.10	38.42	67.340
0.20	77.00	134.96
0.50	184.6	323.63

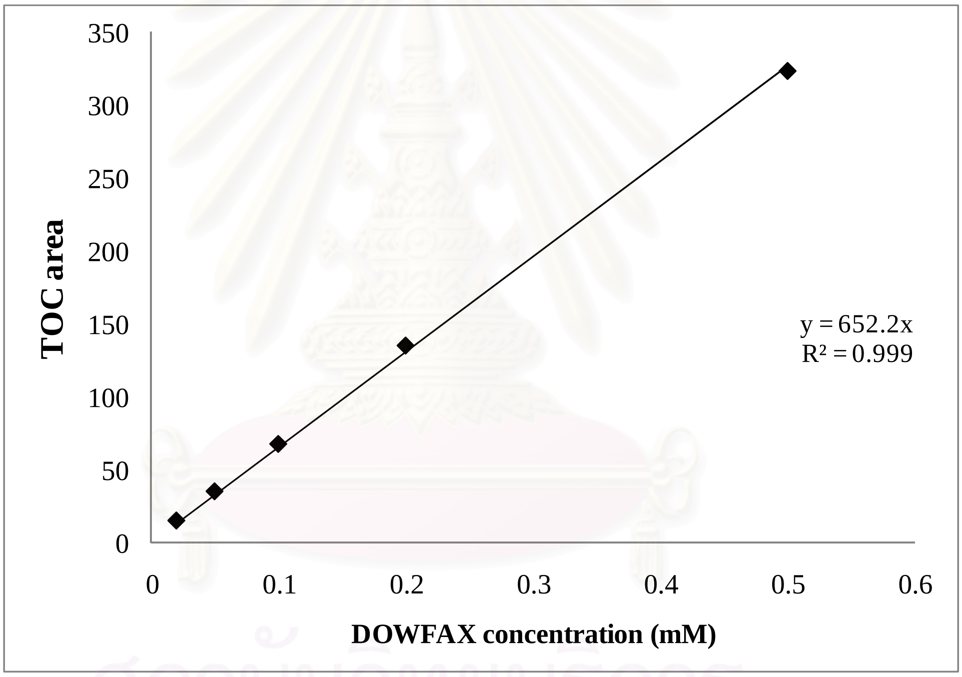


Figure C-7 Relationship between DOWFAX concentration (mM) and TOC area measured by TOC analyzer (for calculation of the adsorbed amount of DTAB presented in DTAB:DOWFAX at all studied molar ratios onto silica sand)

Table C-8 Determination of calibration curve of DTAB concentration measured by TOC analyzer (for calculation of the adsorbed amount of DTAB presented in DTAB:DOWFAX at all studied molar ratios onto silica sand)

DTAB concentration (mM)	TOC (mg/L)	TOC area
0.02	3.355	5.8750
0.05	7.884	13.810
0.10	15.71	27.540
0.20	32.47	56.910
0.50	83.86	147.00
1.00	177.8	311.64

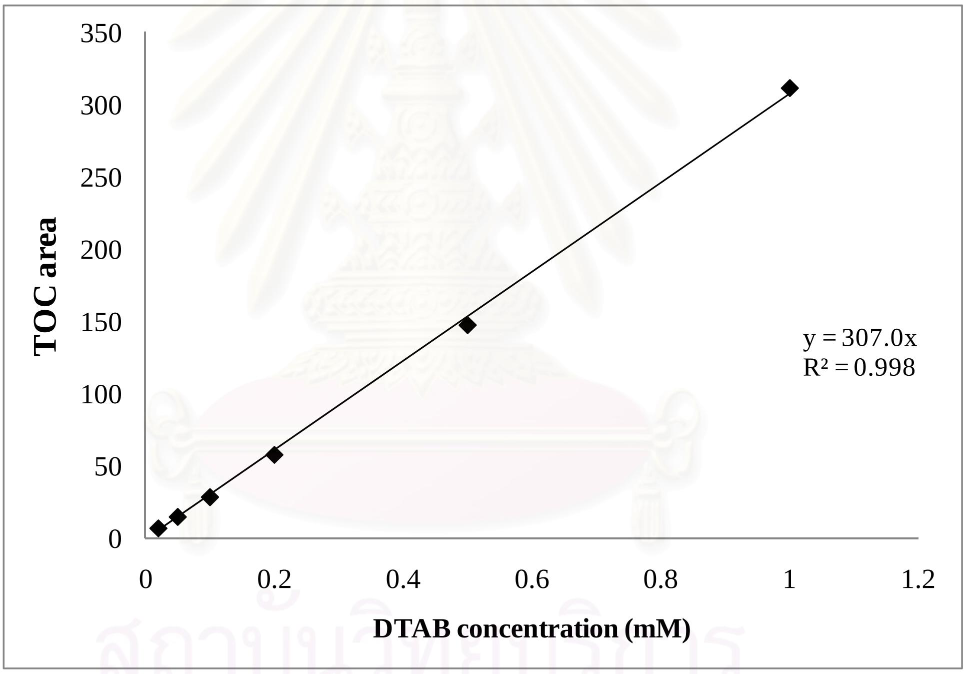


Figure C-8 Relationship between DTAB concentration (mM) and TOC area measured by TOC analyzer (for calculation of the adsorbed amount of DTAB presented in DTAB:DOWFAX at all studied molar ratios onto silica sand)

Table C-9 Determination of calibration curve of DOWFAX concentration measured by UV-visible spectrophotometer at wavelength of 240 nm (for the preconcentration ability of ASTP system)

DOWFAX concentration (mM)	Absorbance at 240 nm
0.01	0.193
0.02	0.394
0.03	0.585
0.04	0.790
0.05	0.985

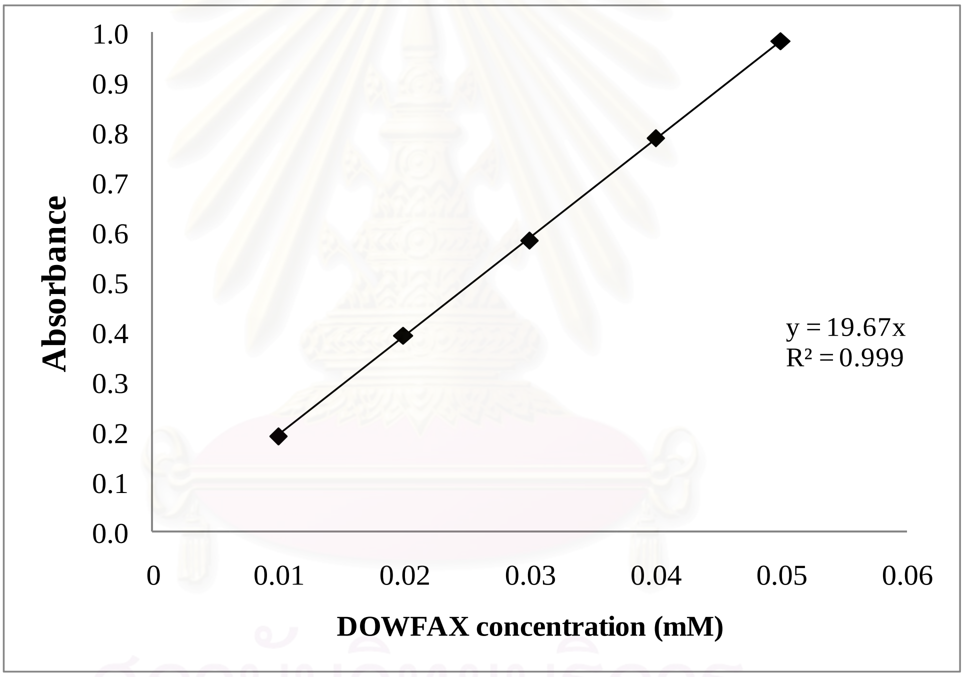


Figure C-9 Relationship between DOWFAX concentration (mM) and absorbance at 240 nm measured by UV-visible spectrophotometer (for the preconcentration ability of ASTP system)

Table C-10 Determination of calibration curve of pyrene concentration measured by UV-visible spectrophotometer at wavelength of 333.6 nm (The solution of pyrene was prepared in 50% of methanol)

Pyrene concentration (ppm)	**Absorbance at 333.6 nm**
0.5	0.098
1.0	0.189
2.0	0.371
3.0	0.547
4.0	0.723
5.0	0.915

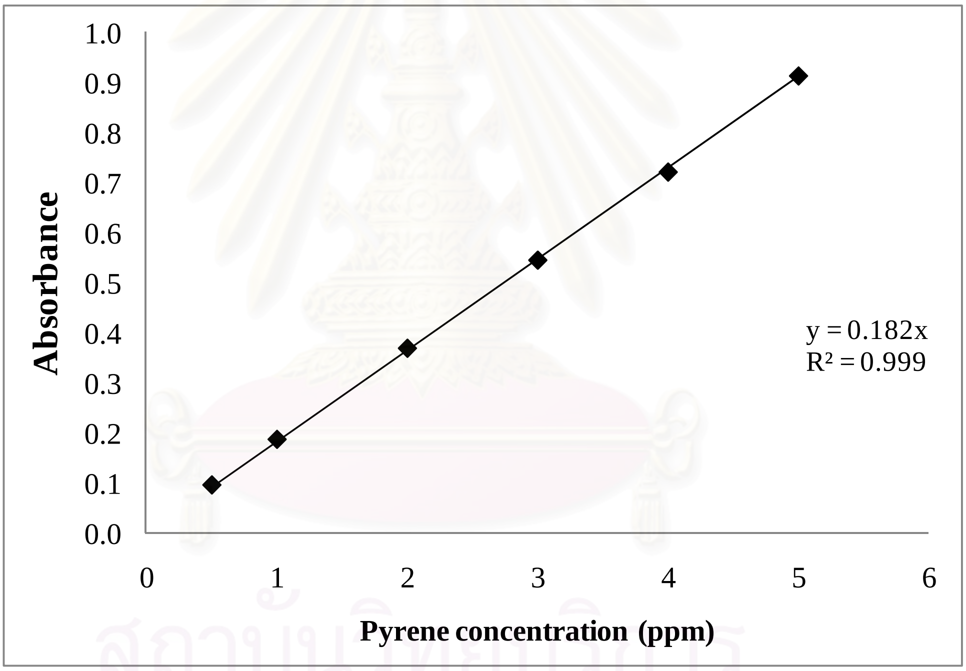


Figure C-10 Relationship between pyrene concentration (ppm) and absorbance at 333.6 nm measured by UV-visible spectrophotometer

APPENDIX D

Results of adsorption of surfactants onto silica sand

Table D-1 Results of adsorption of DOWFAX onto silica sand (solid to liquid ratio = 1:2)

Prepared DOWFAX concentration (mM)	**Blank**				**Sample**			
	Abs at 240 nm	Times dilutions	C_{in} (mM)	Average	Abs at 240 nm	Times dilutions	C_{eq} (mM)	Average
0.2	0.377	10	0.20	0.20	0.369	10	0.20	0.20
	0.385		0.20		0.368		0.20	
	0.383		0.20		0.375		0.20	
0.4	0.370	20	0.40	0.40	0.376	20	0.40	0.40
	0.369		0.40		0.370		0.40	
	0.381		0.40		0.369		0.40	
0.6	0.548		0.58	0.58	0.552		0.58	0.58
	0.552		0.58		0.550		0.58	
	0.550		0.58		0.552		0.58	
0.8	0.729		0.78	0.78	0.734		0.78	0.78
	0.727		0.78		0.731		0.78	
	0.730		0.78		0.737		0.78	
1.0	0.752	25	1.00	1.00	0.749	25	1.00	1.00
	0.747		1.00		0.747		1.00	
	0.753		1.00		0.750		1.00	
2	0.358	100	1.90	1.93	0.354	100	1.90	1.93
	0.363		1.90		0.368		2.00	
	0.367		2.00		0.365		1.90	
4	0.718		3.80	3.83	0.721		3.80	3.83
	0.722		3.80		0.720		3.80	
	0.732		3.90		0.726		3.90	
6	0.554	200	5.80	5.93	0.540	200	5.80	5.93
	0.562		6.00		0.568		6.00	
	0.558		6.00		0.561		6.00	
8	0.736		7.80	7.87	0.735		7.80	7.87
	0.741		7.80		0.746		8.00	
	0.748		8.00		0.738		7.80	
10	0.918		9.80	9.93	0.918		9.80	9.93
	0.933		10.00		0.936		10.00	
	0.949		10.00		0.943		10.00	

Note: C_{in} is the initial DOWFAX concentration (mM)

C_{eq} is the equilibrium DOWFAX concentration (mM)

Table D-2 Results of adsorption of DOWFAX onto silica sand (solid to liquid ratio = 1:5)

Prepared DOWFAX concentration (mM)	**Blank**				**Sample**			
	Abs at 240 nm	Times dilutions	C_{in} (mM)	Average	Abs at 240 nm	Times dilutions	C_{eq} (mM)	Average
0.2	0.371	10	0.20	0.20	0.368	10	0.20	0.20
	0.385		0.20		0.363		0.19	
	0.396		0.21		0.371		0.20	
0.4	0.373	20	0.40	0.40	0.378	20	0.40	0.40
	0.380		0.40		0.391		0.42	
	0.378		0.40		0.364		0.38	
0.6	0.559		0.60	0.59	0.553		0.58	0.59
	0.557		0.60		0.551		0.58	
	0.548		0.58		0.558		0.60	
0.8	0.738		0.78	0.79	0.732		0.78	0.79
	0.738		0.78		0.758		0.80	
	0.761		0.80		0.737		0.78	
1.0	0.755	25	1.00	1.00	0.750	25	1.00	1.00
	0.759		1.00		0.755		1.00	
	0.749		1.00		0.745		1.00	
2	0.372	100	2.00	2.00	0.375	100	2.00	2.00
	0.377		2.00		0.373		2.00	
	0.379		2.00		0.367		2.00	
4	0.735		3.90	3.90	0.730		3.90	3.90
	0.728		3.90		0.737		3.90	
	0.735		3.90		0.732		3.90	
6	0.559	200	6.00	6.00	0.560	200	6.00	6.00
	0.569		6.00		0.561		6.00	
	0.560		6.00		0.564		6.00	
8	0.748		8.00	8.00	0.743		8.00	8.00
	0.744		8.00		0.750		8.00	
	0.746		8.00		0.743		8.00	
10	0.936		10.00	10.00	0.940		10.00	10.00
	0.940		10.00		0.946		10.00	
	0.938		10.00		0.943		10.00	

Note: C_{in} is the initial DOWFAX concentration (mM)

C_{eq} is the equilibrium DOWFAX concentration (mM)

Table D-3 Results of adsorption of DTAB onto silica sand (solid to liquid ratio = 1:5)

Prepared DTAB concentration (mM)	**Blank**				
	TOC (mg/L)	**C_{in} (mM) (100 times dilution)**	**Average**	**STD**	**%RSD**
2	3.177	1.83	1.82	0.01	0.55
	3.188	1.83			
	3.155	1.81			
4	6.708	3.86	3.86	0.02	0.52
	6.728	3.87			
	6.674	3.84			
6	10.31	5.93	5.89	0.03	0.51
	10.20	5.87			
	10.20	5.87			
8	13.43	7.72	7.78	0.05	0.64
	13.59	7.81			
	13.57	7.80			
10	17.41	10.01	9.97	0.04	0.40
	17.29	9.94			
	17.32	9.96			
Prepared DTAB concentration (mM)	**Sample**				
	TOC (mg/L)	**C_{eq} (mM) (100 times dilution)**	**Average**	**STD**	**%RSD**
2	2.977	1.71	1.71	0.01	0.58
	2.978	1.71			
	2.960	1.70			
4	6.346	3.65	3.65	0.01	0.27
	6.371	3.66			
	6.328	3.64			
6	9.575	5.51	5.50	0.01	0.18
	9.544	5.49			
	9.551	5.49			
8	12.82	7.37	7.32	0.05	0.68
	12.75	7.33			
	12.64	7.27			
10	16.23	9.33	9.26	0.05	0.54
	16.08	9.25			
	16.03	9.22			

Note: C_{in} is the initial DTAB concentration (mM)

C_{eq} is the equilibrium DTAB concentration (mM)

Table D-4 Results of adsorption of DTAB:DOWFAX at 1.5:1 onto silica sand (solid to liquid ratio = 1:5)

Prepared DTAB:DOWFAX (1.5:1) concentration (mM)	**Blank**				
	TOC (mg/L)	**C_{in} (mM) (100 times dilution)**	**Average**	**STD**	**%RSD**
2	4.990	1.98	1.93	0.08	4.15
	4.994	1.98			
	4.634	1.84			
4	8.141	3.24	3.41	0.15	4.40
	8.807	3.50			
	8.785	3.49			
6	13.41	5.33	5.29	0.11	2.08
	13.02	5.17			
	13.53	5.38			
8	17.87	7.10	7.10	0.19	2.68
	17.38	6.91			
	18.32	7.28			
10	23.18	9.21	9.19	0.10	1.09
	22.84	9.08			
	23.32	9.27			
Prepared DTAB:DOWFAX (1.5:1) concentration (mM)	**Sample**				
	TOC (mg/L)	**C_{eq} (mM) (100 times dilution)**	**Average**	**STD**	**%RSD**
2	4.800	1.91	1.89	0.04	2.12
	4.803	1.91			
	4.617	1.84			
4	7.992	3.18	3.35	0.15	4.48
	8.705	3.46			
	8.574	3.41			
6	12.97	5.16	5.18	0.04	0.77
	13.14	5.22			
	12.96	5.15			
8	17.48	6.95	6.95	0.04	0.58
	17.38	6.91			
	17.55	6.98			
10	22.45	8.92	9.00	0.17	1.89
	23.13	9.19			
	22.34	8.88			

Note: C_{in} is the initial DTAB:DOWFAX (1.5:1) concentration (mM)

C_{eq} is the equilibrium DTAB DOWFAX (1.5:1) concentration (mM)

Table D-5 Results of adsorption of DTAB presented in DTAB:DOWFAX at 1.5:1 onto silica sand (solid to liquid ratio = 1:5)

DTAB:DOWFAX (1.5:1) concentration (mM)	Calculated DTAB concentration (mM) presented in DTAB:DOWFAX at 1.5:1 molar ratio	Blank			
		C_{in} (mM) (100 times dilution)	Average	STD	%RSD
2	1.2	1.15	1.08	0.12	11.1
		1.15			
		0.94			
4	2.4	1.25	1.50	0.22	14.7
		1.63			
		1.62			
6	3.6	2.56	2.51	0.15	5.98
		2.34			
		2.63			
8	4.8	3.40	3.40	0.27	7.94
		3.13			
		3.66			
10	6.0	4.73	4.72	0.10	2.12
		4.61			
		4.81			

DTAB:DOWFAX (1.5:1) concentration (mM)	Calculated DTAB concentration (mM) presented in DTAB:DOWFAX at 1.5:1 molar ratio	Sample			
		C_{eq} (mM) (100 times dilution)	Average	STD	%RSD
2	1.2	1.04	1.00	0.06	6.00
		1.04			
		0.93			
4	2.4	1.16	1.41	0.22	15.6
		1.57			
		1.50			
6	3.6	2.31	2.34	0.06	2.56
		2.40			
		2.30			
8	4.8	3.18	3.18	0.05	1.57
		3.13			
		3.22			
10	6.0	4.32	4.43	0.24	5.42
		4.71			
		4.26			

Note: C_{in} is the initial DTAB concentration (mM) presented in DTAB:DOWFAX at 1.5:1 molar ratio

C_{eq} is the equilibrium DTAB concentration (mM) presented in DTAB:DOWFAX at 1.5:1 molar ratio

Table D-6 Results of adsorption of DTAB:DOWFAX at 1:1 onto silica sand (solid to liquid ratio = 1:5)

Prepared DTAB:DOWFAX (1:1) concentration (mM)	**Blank**				
	TOC (mg/L)	**C_{in} (mM) (100 times dilution)**	**Average**	**STD**	**%RSD**
2	5.483	2.02	2.00	0.02	1.00
	5.403	1.99			
	5.393	1.98			
4	10.17	3.74	3.76	0.08	2.13
	10.47	3.85			
	10.07	3.70			
6	15.52	5.71	5.79	0.08	1.38
	15.75	5.79			
	15.93	5.86			
8	21.09	7.75	7.86	0.11	1.40
	21.34	7.85			
	21.67	7.97			
10	26.37	9.69	9.81	0.13	1.33
	26.64	9.79			
	27.05	9.94			
Prepared DTAB:DOWFAX (1:1) concentration (mM)	**Sample**				
	TOC (mg/L)	**C_{eq} (mM) (100 times dilution)**	**Average**	**STD**	**%RSD**
2	5.364	1.97	1.97	0.06	3.05
	5.527	2.03			
	5.205	1.91			
4	10.32	3.79	3.71	0.07	1.89
	9.989	3.67			
	9.969	3.67			
6	15.60	5.74	5.70	0.04	0.70
	15.51	5.70			
	15.43	5.67			
8	20.81	7.65	7.72	0.09	1.17
	20.93	7.69			
	21.26	7.82			
10	26.19	9.63	9.64	0.02	0.21
	26.15	9.61			
	26.26	9.65			

Note: C_{in} is the initial DTAB:DOWFAX (1:1) concentration (mM)

C_{eq} is the equilibrium DTAB DOWFAX (1:1) concentration (mM)

Table D-7 Results of adsorption of DTAB presented in DTAB:DOWFAX at 1:1 onto silica sand (solid to liquid ratio = 1:5)

DTAB:DOWFAX (1:1) concentration (mM)	**Calculated DTAB concentration (mM) presented in DTAB:DOWFAX at 1:1 molar ratio**	**Blank**			
		C_{in} (mM) (100 times dilution)	**Average**	**STD**	**%RSD**
2	1.0	1.01	0.97	0.03	3.09
		0.96			
		0.95			
4	2.0	1.56	1.60	0.12	7.50
		1.73			
		1.50			
6	3.0	2.48	2.61	0.12	4.60
		2.62			
		2.72			
8	4.0	3.54	3.70	0.17	4.59
		3.69			
		3.88			
10	5.0	4.43	4.63	0.20	4.32
		4.63			
		4.82			
DTAB:DOWFAX (1:1) concentration (mM)	**Calculated DTAB concentration (mM) presented in DTAB:DOWFAX at 1:1 molar ratio**	**Sample**			
		C_{eq} (mM) (100 times dilution)	**Average**	**STD**	**%RSD**
2	1.0	0.94	0.94	0.09	9.57
		1.03			
		0.85			
4	2.0	1.65	1.52	0.12	7.89
		1.46			
		1.44			
6	3.0	2.53	2.48	0.05	2.02
		2.48			
		2.43			
8	4.0	3.38	3.49	0.13	3.72
		3.45			
		3.64			
10	5.0	4.33	4.33	0.03	0.69
		4.31			
		4.36			

Note: C_{in} is the initial DTAB concentration (mM) presented in DTAB:DOWFAX at 1:1 molar ratio

C_{eq} is the equilibrium DTAB concentration (mM) presented in DTAB:DOWFAX at 1:1 molar ratio

Table D-8 Results of adsorption of DTAB:DOWFAX at 1:1.5 onto silica sand (solid to liquid ratio = 1:5)

Prepared DTAB:DOWFAX (1:1.5) concentration (mM)	**Blank**				
	TOC (mg/L)	**C_{in} (mM) (100 times dilution)**	**Average**	**STD**	**%RSD**
2	5.950	1.83	1.79	0.04	2.23
	5.704	1.76			
	5.825	1.79			
4	11.90	3.66	3.60	0.06	1.67
	11.73	3.61			
	11.51	3.54			
6	17.71	5.45	5.47	0.03	0.55
	17.87	5.50			
	17.73	5.46			
8	24.04	7.40	7.44	0.04	0.54
	24.15	7.44			
	24.25	7.47			
10	29.40	9.05	9.17	0.11	1.20
	30.10	9.27			
	29.82	9.18			
Prepared DTAB:DOWFAX (1:1.5) concentration (mM)	**Sample**				
	TOC (mg/L)	**C_{eq} (mM) (100 times dilution)**	**Average**	**STD**	**%RSD**
2	5.767	1.78	1.76	0.02	1.14
	5.640	1.74			
	5.728	1.76			
4	11.56	3.56	3.55	0.02	0.56
	11.45	3.53			
	11.55	3.56			
6	17.46	5.38	5.40	0.09	1.67
	17.31	5.33			
	17.85	5.50			
8	23.52	7.24	7.32	0.09	1.23
	23.69	7.29			
	24.10	7.42			
10	29.34	9.03	9.04	0.02	0.22
	29.44	9.06			
	29.32	9.03			

Note: C_{in} is the initial DTAB:DOWFAX (1:1.5) concentration (mM)

C_{eq} is the equilibrium DTAB DOWFAX (1:1.5) concentration (mM)

Table D-9 Results of adsorption of DTAB presented in DTAB:DOWFAX at 1:1.5 onto silica sand (solid to liquid ratio = 1:5)

DTAB:DOWFAX (1:1.5) concentration (mM)	**Calculated DTAB concentration (mM) presented in DTAB:DOWFAX at 1:1.5 molar ratio**	**Blank**			
		C_{in} (mM) (100 times dilution)	**Average**	**STD**	**%RSD**
2	0.8	0.85	0.78	0.07	8.97
		0.71			
		0.78			
4	1.6	1.70	1.59	0.12	7.55
		1.60			
		1.47			
6	2.4	2.47	2.50	0.08	3.29
		2.55			
		2.48			
8	3.2	3.53	3.59	0.06	1.67
		3.59			
		3.65			
10	4.0	4.04	4.25	0.20	4.71
		4.44			
		4.28			
DTAB:DOWFAX (1:1.5) concentration (mM)	**Calculated DTAB concentration (mM) presented in DTAB:DOWFAX at 1:1.5 molar ratio**	**Sample**			
		C_{eq} (mM) (100 times dilution)	**Average**	**STD**	**%RSD**
2	0.8	0.74	0.71	0.04	5.63
		0.67			
		0.72			
4	1.6	1.50	1.48	0.03	2.03
		1.44			
		1.50			
6	2.4	2.32	2.37	0.16	6.75
		2.24			
		2.54			
8	3.2	3.12	3.34	0.22	6.59
		3.33			
		3.56			
10	4.0	4.01	4.02	0.04	1.00
		4.06			
		3.99			

Note: C_{in} is the initial DTAB concentration (mM) presented in DTAB:DOWFAX at 1:1.5 molar ratio

C_{eq} is the equilibrium DTAB concentration (mM) presented in DTAB:DOWFAX at 1:1.5 molar ratio

Table D-10 Results of adsorption of DTAB:DOWFAX at 1:2 onto silica sand (solid to liquid ratio = 1:5)

Prepared DTAB:DOWFAX (1:2) concentration (mM)	**Blank**				
	TOC (mg/L)	**C_{in} (mM) (100 times dilution)**	**Average**	**STD**	**%RSD**
2	6.180	1.84	1.83	0.01	0.55
	6.114	1.82			
	6.180	1.84			
4	12.02	3.58	3.58	0.04	1.11
	12.03	3.58			
	12.05	3.59			
6	18.61	5.54	5.49	0.05	0.91
	18.42	5.49			
	18.31	5.45			
8	25.41	7.57	7.51	0.10	1.33
	25.38	7.56			
	24.83	7.40			
10	31.27	9.31	9.34	0.06	0.64
	31.58	9.41			
	31.26	9.31			
Prepared DTAB:DOWFAX (1:2) concentration (mM)	**Sample**				
	TOC (mg/L)	**C_{eq} (mM) (100 times dilution)**	**Average**	**STD**	**%RSD**
2	6.132	1.83	1.81	0.03	1.66
	5.973	1.78			
	6.124	1.82			
4	11.87	3.54	3.54	0.03	0.85
	11.82	3.52			
	11.97	3.57			
6	18.20	5.42	5.42	0.02	0.37
	18.24	5.43			
	18.12	5.40			
8	24.91	7.42	7.40	0.03	0.41
	24.87	7.41			
	24.75	7.37			
10	30.69	9.14	9.22	0.10	1.08
	31.32	9.33			
	30.83	9.18			

Note: C_{in} is the initial DTAB:DOWFAX (1:2) concentration (mM)

C_{eq} is the equilibrium DTAB DOWFAX (1:2) concentration (mM)

Table D-11 Results of adsorption of DTAB presented in DTAB:DOWFAX at 1:2 onto silica sand (solid to liquid ratio = 1:5)

DTAB:DOWFAX (1:2) concentration (mM)	Calculated DTAB concentration (mM) presented in DTAB:DOWFAX at 1:2 molar ratio	Blank			
		C_{in} (mM) (100 times dilution)	Average	STD	%RSD
2	0.7	0.69	0.68	0.02	2.94
		0.65			
		0.69			
4	1.3	1.20	1.21	0.01	0.83
		1.21			
		1.22			
6	2.0	2.13	2.03	0.09	4.43
		2.02			
		1.95			
8	2.7	3.18	3.06	0.19	6.21
		3.16			
		2.85			
10	3.3	3.69	3.75	0.11	2.93
		3.87			
		3.68			

DTAB:DOWFAX (1:2) concentration (mM)	Calculated DTAB concentration (mM) presented in DTAB:DOWFAX at 1:2 molar ratio	Sample			
		C_{eq} (mM) (100 times dilution)	Average	STD	%RSD
2	0.7	0.66	0.63	0.05	7.94
		0.58			
		0.66			
4	1.3	1.11	1.12	0.05	4.46
		1.08			
		1.17			
6	2.0	1.89	1.88	0.04	2.13
		1.91			
		1.84			
8	2.7	2.89	2.85	0.05	1.75
		2.87			
		2.80			
10	3.3	3.36	3.51	0.19	5.41
		3.72			
		3.44			

Note: C_{in} is the initial DTAB concentration (mM) presented in DTAB:DOWFAX at 1:2 molar ratio

C_{eq} is the equilibrium DTAB concentration (mM) presented in DTAB:DOWFAX at 1:2 molar ratio

Table D-12 Relationship between the equilibrium DTAB concentration, C_{eq} (mM) and mass of surfactant adsorbed to soil normalized by the mass of soil, q (g of adsorbed surfactant/ g of silica sand)

C_{eq} (mM)	q (g of adsorbed surfactant/ g of silica sand)	Slope of the plot between C_{eq} and q [g of surfactant/ (g of silica sand*mM)]	K_d (L/g)
1.71	1.70E-04	1.08E-04	3.50E-04
3.65	3.24E-04		
5.50	6.01E-04		
7.32	7.09E-04		
9.26	1.09E-03		

Table D-13 Relationship between the equilibrium DTAB concentration presented in DTAB:DOWFAX at 1.5:1 molar ratio, C_{eq} (mM) and mass of surfactant adsorbed to soil normalized by the mass of soil, q (g of adsorbed surfactant/ g of silica sand)

C_{eq} (mM)	q (g of adsorbed surfactant/ g of silica sand)	Slope of the plot between C_{eq} and q [g of surfactant/ (g of silica sand*mM)]	K_d (L/g)
1.00	1.23E-04	1.04E-04	3.37E-04
1.41	1.39E-04		
2.34	2.62E-04		
3.18	3.39E-04		
4.43	4.47E-04		

Table D-14 Relationship between the equilibrium DTAB concentration presented in DTAB:DOWFAX at 1:1 molar ratio, C_{eq} (mM) and mass of surfactant adsorbed to soil normalized by the mass of soil, q (g of adsorbed surfactant/ g of silica sand)

C_{eq} (mM)	q (g of adsorbed surfactant/ g of silica sand)	Slope of the plot between C_{eq} and q [g of surfactant/ (g of silica sand*mM)]	K_d (L/g)
0.94	4.62E-05	9.58E-05	3.11E-04
1.52	1.23E-04		
2.48	2.00E-04		
3.49	3.24E-04		
4.33	4.62E-04		

Table D-15 Relationship between the equilibrium DTAB concentration presented in DTAB:DOWFAX at 1:1.5 molar ratio, C_{eq} (mM) and mass of surfactant adsorbed to soil normalized by the mass of soil, q (g of adsorbed surfactant/ g of silica sand)

C_{eq} (mM)	q (g of adsorbed surfactant/ g of silica sand)	Slope of the plot between C_{eq} and q [g of surfactant/ (g of silica sand*mM)]	K_d (L/g)
0.71	1.08E-04	9.29E-05	3.01E-04
1.48	1.70E-04		
2.37	2.00E-04		
3.34	3.24E-04		
4.02	3.55E-04		

Table D-16 Relationship between the equilibrium DTAB concentration presented in DTAB:DOWFAX at 1:2 molar ratio, C_{eq} (mM) and mass of surfactant adsorbed to soil normalized by the mass of soil, q (g of adsorbed surfactant/ g of silica sand)

C_{eq} (mM)	q (g of adsorbed surfactant/ g of silica sand)	Slope of the plot between C_{eq} and q [g of surfactant/ (g of silica sand*mM)]	K_d (L/g)
0.63	7.71E-05	1.12E-04	3.63E-04
1.12	1.39E-04		
1.88	2.31E-04		
2.85	3.24E-04		
3.51	3.70E-04		

Table D-17 The percentage of surfactant loss for adsorption of DTAB onto silica sand

C_{in} (mM)	C_{eq} (mM)	Surfactant loss (%) $[(C_{in} - C_{eq})/ C_{in}]*100$	Average	STD
1.82	1.71	6.04	6.23	0.65
3.86	3.65	5.44		
5.89	5.50	6.62		
7.78	7.32	5.91		
9.97	9.26	7.12		

Table D-18 The percentage of surfactant loss for adsorption of DTAB:DOWFAX at all studied molar ratios onto silica sand

Surfactant system	C_{in} (mM)	C_{eq} (mM)	Surfactant loss (%) $[(C_{in} - C_{eq})/ C_{in}]*100$
DTAB:DOWFAX at 1.5:1 molar ratio	1.93	1.89	2.24
	3.41	3.35	1.76
	5.29	5.18	2.14
	7.10	6.95	2.07
	9.19	9.00	2.03
DTAB:DOWFAX at 1:1 molar ratio	2.00	1.97	1.34
	3.76	3.71	1.42
	5.79	5.70	1.50
	7.86	7.72	1.74
	9.81	9.64	1.70
DTAB:DOWFAX at 1:1.5 molar ratio	1.79	1.76	1.68
	3.60	3.55	1.39
	5.47	5.40	1.28
	7.44	7.32	1.61
	9.17	9.04	1.42
DTAB:DOWFAX at 1:2 molar ratio	1.83	1.81	1.09
	3.58	3.54	1.12
	5.49	5.42	1.28
	7.51	7.40	1.46
	9.34	9.22	1.28
Average			1.58
STD			0.34

Note: C_{in} is the initial DTAB:DOWFAX concentration (mM)

C_{eq} is the equilibrium DTAB:DOWFAX concentration (mM)

Table D-19 The percentage of surfactant loss for adsorption of DTAB presented in DTAB:DOWFAX at all studied molar ratios onto silica sand

Surfactant system	C_{in} (mM)	C_{eq} (mM)	Surfactant loss (%) $[(C_{in} - C_{eq})/ C_{in}]*100$
DTAB in DTAB:DOWFAX at 1.5:1 molar ratio	1.08	1.00	7.41
	1.50	1.41	6.00
	2.51	2.34	6.77
	3.40	3.18	6.47
	4.72	4.43	6.14
DTAB in DTAB:DOWFAX at 1:1 molar ratio	0.97	0.94	3.09
	1.60	1.52	5.00
	2.61	2.48	4.98
	3.70	3.49	5.68
	4.63	4.33	6.48
DTAB in DTAB:DOWFAX at 1:1.5 molar ratio	0.78	0.71	8.97
	1.59	1.48	6.92
	2.50	2.37	5.20
	3.59	3.34	6.96
	4.25	4.02	5.41
DTAB in DTAB:DOWFAX at 1:2 molar ratio	0.68	0.63	7.35
	1.21	1.12	7.44
	2.03	1.88	7.39
	3.06	2.85	6.86
	3.75	3.51	6.40
Average			6.35
STD			1.25

Note: C_{in} is the initial DTAB concentration (mM) in DTAB:DOWFAX solution

C_{eq} is the equilibrium DTAB concentration (mM) in DTAB:DOWFAX solution

APPENDIX E

Results of pyrene solubilization study

Table E-1 Results of the equilibrium time determination for pyrene solubilization by DTAB:DOWFAX solution at 1:1.5 molar ratio, at 25ºC for 5 days

Time (days)	**Total surfactant concentration (mM)**	**Pyrene analysis (10 times dilution)**		**Average**	**STD**	**%RSD**
		Absorbance at 333.6 nm	**Solubility of pyrene (ppm)**			
1	1.0	0.120	6.43	6.43	0.17	2.66
		0.117	6.32			
		0.114	6.43			
2	1.0	0.117	6.43	6.39	0.06	0.94
		0.115	6.32			
		0.117	6.43			
3	1.0	0.118	6.48	6.43	0.06	0.93
		0.116	6.37			
		0.117	6.43			
4	1.0	0.119	6.54	6.41	0.12	1.87
		0.115	6.32			
		0.116	6.37			
5	1.0	0.116	6.37	6.41	0.12	1.87
		0.119	6.54			
		0.115	6.32			

Table E-2 Results of pyrene solubilization by the solution of DTAB at 25ºC

DTAB concentration (mM)	Pyrene analysis			Average	STD	%RSD
	Absorbance at 333.6 nm	Times dilution	Solubility of pyrene (ppm)			
0	0.002	10	0.11	0.13	0.03	23.1
	0.002		0.11			
	0.003		0.16			
1	0.002		0.11	0.13	0.03	23.1
	0.002		0.11			
	0.003		0.16			
2	0.002		0.11	0.15	0.06	40.0
	0.002		0.11			
	0.004		0.22			
5	0.002		0.11	0.15	0.06	40.0
	0.004		0.22			
	0.002		0.11			
10	0.015		0.82	0.86	0.06	6.98
	0.015		0.82			
	0.017		0.93			
20	0.841		46.21	46.48	0.43	0.93
	0.842		46.26			
	0.855		46.98			
30	0.256	100	140.66	139.56	1.10	0.79
	0.252		138.46			
	0.254		139.56			
40	0.429		235.71	232.78	2.59	1.11
	0.422		231.87			
	0.42		230.77			
50	0.587		322.53	323.63	1.45	0.45
	0.588		323.08			
	0.592		325.27			
60	0.722		396.70	396.70	1.10	0.28
	0.720		395.60			
	0.724		397.80			
100	0.236	500	648.35	652.01	4.20	0.64
	0.239		656.59			
	0.237		651.10			
200	0.318		873.63	868.13	5.50	0.63
	0.316		868.13			
	0.314		862.64			

Table E-3 Results of pyrene solubilization by the solution of DOWFAX at 25ºC

DOWFAX concentration (mM)	Pyrene analysis			Average	STD	%RSD
	Absorbance at 333.6 nm	Times dilution	Solubility of pyrene (ppm)			
0	0.002	10	0.11	0.13	0.03	23.1
	0.003		0.16			
	0.002		0.11			
0.02	0.005		0.27	0.33	0.06	18.2
	0.006		0.33			
	0.007		0.38			
0.05	0.008		0.44	0.46	0.03	6.98
	0.008		0.44			
	0.009		0.49			
0.1	0.011		0.60	0.58	0.03	5.17
	0.010		0.55			
	0.011		0.60			
0.2	0.019		1.04	1.10	0.06	5.45
	0.020		1.10			
	0.021		1.15			
0.5	0.027		1.48	1.52	0.03	1.97
	0.028		1.54			
	0.028		1.54			
1	0.057		3.13	3.15	0.08	2.54
	0.056		3.08			
	0.059		3.24			
2	0.152		8.35	8.32	0.03	0.36
	0.151		8.30			
	0.151		8.30			
5	0.456		25.05	24.83	0.33	1.33
	0.455		25.00			
	0.445		24.45			
10	0.110	100	60.44	59.89	0.55	0.92
	0.108		59.34			
	0.109		59.89			
20	0.222		121.98	126.01	3.53	2.80
	0.232		127.47			
	0.234		128.57			
50	0.573		314.84	316.12	1.14	0.36
	0.576		316.48			
	0.577		317.03			

Table E-4 Results of pyrene solubilization by the solution of DTAB:DOWFAX at 1.5:1 molar ratio, at 25^{o}C

DTAB:DOWFAX (1.5:1) concentration (mM)	**Pyrene analysis**			**Average**	**STD**	**%RSD**
	Absorbance at 333.6 nm	**Times dilution**	**Solubility of pyrene (ppm)**			
0	0.002	10	0.11	0.14	0.03	21.4
	0.003		0.16			
	0.003		0.16			
0.001	0.002		0.11	0.13	0.03	23.1
	0.003		0.16			
	0.002		0.11			
0.005	0.002		0.11	0.13	0.03	23.1
	0.003		0.16			
	0.002		0.11			
0.01	0.009		0.49	0.56	0.06	10.7
	0.011		0.60			
	0.011		0.60			
0.05	0.011		0.60	0.57	0.03	5.26
	0.010		0.55			
	0.010		0.55			
0.1	0.028		1.54	1.46	0.09	6.16
	0.025		1.37			
	0.027		1.48			
0.5	0.081		4.45	4.60	0.25	5.43
	0.089		4.89			
	0.081		4.45			
1	0.193		10.60	10.46	0.21	2.01
	0.192		10.55			
	0.186		10.22			
2	0.413		22.69	22.91	0.25	1.09
	0.422		23.19			
	0.416		22.86			
5	0.223	50	61.26	62.00	0.69	1.11
	0.226		62.09			
	0.228		62.64			
10	0.366		100.55	101.01	1.56	1.54
	0.363		99.73			
	0.374		102.75			
20	0.487		133.79	132.60	1.04	0.78
	0.481		132.14			
	0.480		131.87			

Table E-5 Results of pyrene solubilization by the solution of DTAB:DOWFAX at 1:1 molar ratio, at 25ºC

DTAB:DOWFAX (1:1) concentration (mM)	Pyrene analysis			Average	STD	%RSD
	Absorbance at 333.6 nm	Times dilution	Solubility of pyrene (ppm)			
0	0.002	10	0.11	0.13	0.03	23.08
	0.003		0.16			
	0.002		0.11			
0.001	0.003		0.16	0.14	0.03	21.43
	0.002		0.11			
	0.003		0.16			
0.005	0.002		0.11	0.14	0.03	21.43
	0.003		0.16			
	0.003		0.16			
0.01	0.004		0.22	0.18	0.03	16.67
	0.003		0.16			
	0.003		0.16			
0.05	0.010		0.55	0.58	0.03	5.17
	0.011		0.60			
	0.011		0.60			
0.1	0.017		0.93	0.93	0.06	6.45
	0.016		0.88			
	0.018		0.99			
0.5	0.081		4.45	4.54	0.11	2.42
	0.082		4.51			
	0.085		4.67			
1	0.165		9.07	9.25	0.19	2.05
	0.172		9.45			
	0.168		9.23			
2	0.330		18.13	18.24	0.34	1.86
	0.339		18.63			
	0.327		17.97			
5	0.796		43.74	43.55	0.20	0.46
	0.793		43.57			
	0.789		43.35			
10	0.328	50	90.11	89.38	1.04	1.16
	0.327		89.84			
	0.321		88.19			
20	0.679		186.54	185.35	1.41	0.76
	0.676		185.71			
	0.669		183.79			

Table E-6 Results of pyrene solubilization by the solution of DTAB:DOWFAX at 1:1.5 molar ratio, at 25ºC

DTAB:DOWFAX (1:1.5) concentration (mM)	**Pyrene analysis**			**Average**	**STD**	**%RSD**
	Absorbance at 333.6 nm	**Times dilution**	**Solubility of pyrene (ppm)**			
0	0.002	10	0.11	0.13	0.03	23.1
	0.003		0.16			
	0.002		0.11			
0.001	0.002		0.11	0.13	0.03	23.1
	0.003		0.16			
	0.002		0.11			
0.005	0.002		0.11	0.15	0.06	40.0
	0.004		0.22			
	0.002		0.11			
0.01	0.002		0.11	0.13	0.03	23.1
	0.003		0.16			
	0.002		0.11			
0.05	0.008		0.44	0.37	0.06	16.2
	0.006		0.33			
	0.006		0.33			
0.1	0.008		0.44	0.46	0.03	6.52
	0.009		0.49			
	0.008		0.44			
0.5	0.047		2.58	2.88	0.31	10.8
	0.052		2.86			
	0.058		3.19			
1	0.118		6.48	6.39	0.08	1.25
	0.116		6.37			
	0.115		6.32			
2	0.255		14.01	13.92	0.12	0.86
	0.254		13.96			
	0.251		13.79			
5	0.703		38.63	38.68	0.30	0.78
	0.71		39.01			
	0.699		38.41			
10	0.294	50	80.77	83.88	2.75	3.28
	0.309		84.89			
	0.313		85.99			
20	0.569		156.32	155.86	1.30	0.83
	0.562		154.40			
	0.571		156.87			

Table E-7 Results of pyrene solubilization by the solution of DTAB:DOWFAX at 1:2 molar ratio, at 25°C

DTAB:DOWFAX (1:2) concentration (mM)	Pyrene analysis			Average	STD	%RSD
	Absorbance at 333.6 nm	Times dilution	Solubility of pyrene (ppm)			
0	0.003	10	0.16	0.14	0.03	21.4
	0.002		0.11			
	0.003		0.16			
0.001	0.003		0.16	0.18	0.03	16.7
	0.004		0.22			
	0.003		0.16			
0.005	0.004		0.22	0.24	0.03	12.5
	0.005		0.27			
	0.004		0.22			
0.01	0.009		0.49	0.53	0.03	5.66
	0.010		0.55			
	0.010		0.55			
0.05	0.009		0.49	0.51	0.03	5.88
	0.010		0.55			
	0.009		0.49			
0.1	0.008		0.44	0.51	0.08	15.7
	0.009		0.49			
	0.011		0.60			
0.5	0.057		3.13	3.15	0.08	2.54
	0.059		3.24			
	0.056		3.08			
1	0.118		6.48	6.30	0.17	2.70
	0.112		6.15			
	0.114		6.26			
2	0.238		13.08	12.80	0.24	1.88
	0.231		12.69			
	0.230		12.64			
5	0.692		38.02	38.28	0.28	0.73
	0.696		38.24			
	0.702		38.57			
10	0.280	50	76.92	78.57	1.46	1.86
	0.288		79.12			
	0.290		79.67			
20	0.595		163.46	162.45	1.99	1.22
	0.596		163.74			
	0.583		160.16			

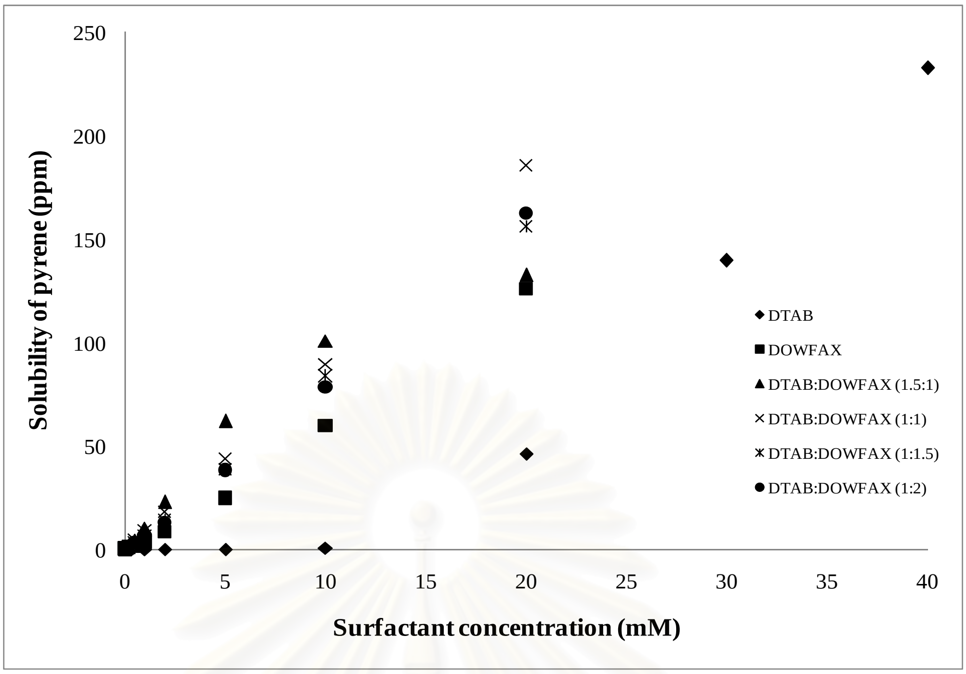


Figure E-1 Pyrene solubilization in the solution of DTAB, DOWFAX, and DTAB:DOWFAX mixtures at molar ratios of 1.5:1, 1:1, 1:1.5, and 1:2 at 25 ^oC

Table E-8 Molar solubilization ratio (MSR) and log micelle-water partitioning coefficient (log K_m) of pyrene for DTAB, DOWFAX, and DTAB:DOWFAX mixtures at various molar ratios

Surfactant system	Molar ratio	MSR	X_m	X_{aq}	K_m	Log K_m
DTAB	-	0.032	0.031	1.16E-08	2,678,819.04	6.43
DOWFAX	-	0.031	0.030	1.16E-08	2,597,623.02	6.41
DTAB:DOWFAX	1.5:1	0.060	0.057	1.16E-08	4,890,108.33	6.69
	1:1	0.045	0.043	1.16E-08	3,720,225.96	6.57
	1:1.5	0.039	0.038	1.16E-08	3,242,814.86	6.51
	1:2	0.040	0.038	1.16E-08	3,322,765.92	6.52

APPENDIX F

Results of the effects of additives in surfactant solution on pyrene solubilization

Table F-1 Results of the effects of $CaCl_2$ in DTAB:DOWFAX solution at 1:1 molar ratio on pyrene solubilization, at 25ºC (fixed $CaCl_2$ at concentration of 0.025% wt)

DTAB:DOWFAX (1:1) concentration (mM)	**Pyrene analysis**			**Average**	**STD**	**%RSD**
	Absorbance at 333.6 nm	**Times dilution**	**Solubility of pyrene (ppm)**			
0	0.003	10	0.16	0.14	0.03	21.4
	0.003		0.16			
	0.002		0.11			
0.001	0.003		0.16	0.18	0.03	16.7
	0.003		0.16			
	0.004		0.22			
0.005	0.004		0.22	0.20	0.03	15.0
	0.003		0.16			
	0.004		0.22			
0.01	0.003		0.16	0.20	0.03	15.0
	0.004		0.22			
	0.004		0.22			
0.05	0.010		0.55	0.59	0.06	10.2
	0.012		0.66			
	0.010		0.55			
0.1	0.023		1.26	1.24	0.03	2.42
	0.023		1.26			
	0.022		1.21			
0.5	0.127		6.98	7.11	0.11	1.55
	0.130		7.14			
	0.131		7.20			
1	0.243		13.35	13.46	0.11	0.82
	0.245		13.46			
	0.247		13.57			
2	0.479		26.32	26.04	0.24	0.92
	0.472		25.93			
	0.471		25.88			
5	0.223	50	61.26	61.72	0.42	0.68
	0.225		61.81			
	0.226		62.09			
10	0.409		112.36	113.19	0.73	0.64
	0.413		113.46			
	0.414		113.74			
20	0.759		208.52	209.25	1.51	0.72
	0.758		208.24			
	0.768		210.99			

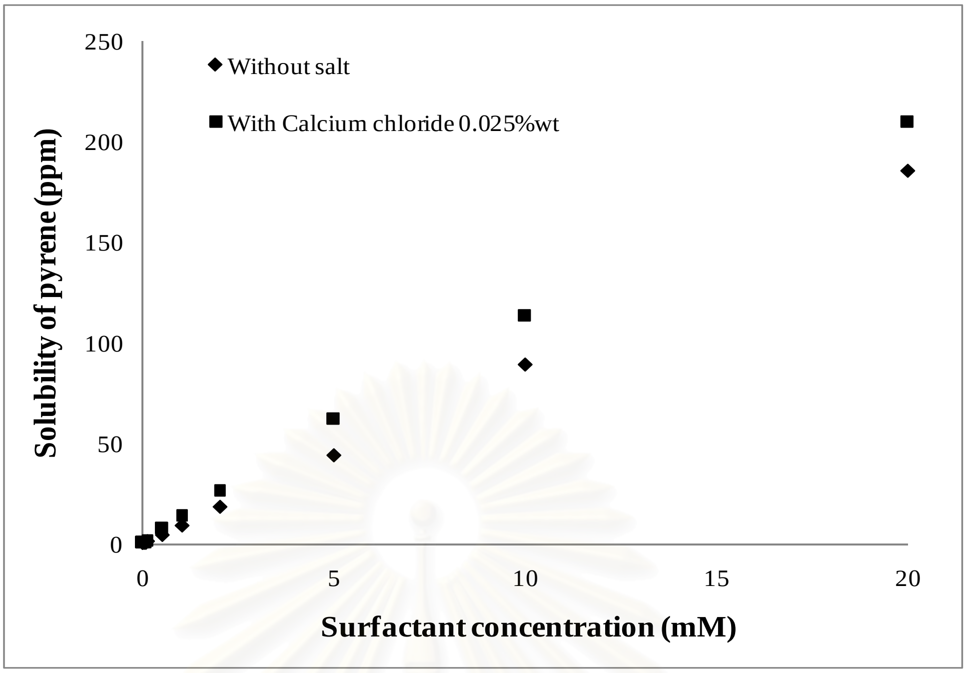


Figure F-1 Effects of $CaCl_2$ (0.025% wt) in DTAB:DOWFAX solution at 1:1 molar ratio on pyrene solubilization

Table F-2 Molar solubilization ratio (MSR) and log micelle-water partitioning coefficient (log K_m) of pyrene for DTAB:DOWFAX at 1:1 molar ratio with and without $CaCl_2$

Surfactant system	**DTAB:DOWFAX at 1:1 molar ratio**	**DTAB:DOWFAX at 1:1 molar ratio with 0.025%wt $CaCl_2$**
MSR	0.045	0.053
X_m	0.043	0.050
X_{aq}	1.16E-08	1.16E-08
K_m	3,720,225.96	4,348,310.96
Log K_m	6.57	6.64

Table F-3 Results of the effects of octanol in DTAB:DOWFAX solution at 1:1 molar ratio on pyrene solubilization, at 25ºC (the total mole of surfactants to total mole of alcohol at 10:1)

DTAB:DOWFAX (1:1) concentration (mM)	Pyrene analysis			Average	STD	%RSD
	Absorbance at 333.6 nm	Times dilution	Solubility of pyrene (ppm)			
0	0.002	10	0.11	0.14	0.03	21.4
	0.003		0.16			
	0.003		0.16			
0.001	0.003		0.16	0.18	0.03	16.7
	0.003		0.16			
	0.004		0.22			
0.005	0.003		0.16	0.18	0.03	16.7
	0.003		0.16			
	0.004		0.22			
0.01	0.007		0.38	0.38	0.06	15.8
	0.008		0.44			
	0.006		0.33			
0.05	0.008		0.44	0.47	0.03	6.38
	0.009		0.49			
	0.009		0.49			
0.1	0.019		1.04	1.08	0.12	11.1
	0.018		0.99			
	0.022		1.21			
0.5	0.097		5.33	5.35	0.14	2.62
	0.095		5.22			
	0.100		5.49			
1	0.178		9.78	10.02	0.21	2.10
	0.185		10.16			
	0.184		10.11			
2	0.350		19.23	19.12	0.11	0.58
	0.346		19.01			
	0.348		19.12			
5	0.832		45.71	45.38	0.33	0.73
	0.820		45.05			
	0.826		45.38			
10	0.354	50	97.25	95.97	1.14	1.19
	0.346		95.05			
	0.348		95.60			
20	0.733		201.37	201.10	0.28	0.14
	0.732		201.10			
	0.731		200.82			

Table F-4 Results of the effects of dodecanol in DTAB:DOWFAX solution at 1:1 molar ratio on pyrene solubilization, at 25ºC (the total mole of surfactants to total mole of alcohol at 10:1)

DTAB:DOWFAX (1:1) concentration (mM)	**Pyrene analysis**			**Average**	**STD**	**%RSD**
	Absorbance at 333.6 nm	**Times dilution**	**Solubility of pyrene (ppm)**			
0	0.002	10	0.11	0.14	0.03	21.4
	0.003		0.16			
	0.003		0.16			
0.001	0.004		0.22	0.24	0.03	12.5
	0.005		0.27			
	0.004		0.22			
0.005	0.005		0.27	0.25	0.03	12.0
	0.004		0.22			
	0.005		0.27			
0.01	0.007		0.38	0.36	0.03	8.33
	0.007		0.38			
	0.006		0.33			
0.05	0.012		0.66	0.64	0.03	4.69
	0.011		0.60			
	0.012		0.66			
0.1	0.028		1.54	1.48	0.10	6.76
	0.028		1.54			
	0.025		1.37			
0.5	0.127		6.98	6.96	0.14	2.01
	0.129		7.09			
	0.124		6.81			
1	0.226		12.42	12.36	0.06	0.49
	0.225		12.36			
	0.224		12.31			
2	0.434		23.85	23.70	0.14	0.59
	0.431		23.68			
	0.429		23.57			
5	0.231	50	63.46	63.37	0.42	0.66
	0.232		63.74			
	0.229		62.91			
10	0.440		120.88	121.34	0.57	0.47
	0.441		121.15			
	0.444		121.98			
20	0.850		233.52	234.43	1.14	0.49
	0.852		234.07			
	0.858		235.71			

Table F-5 Results of the effects of hexadecanol in DTAB:DOWFAX solution at 1:1 molar ratio on pyrene solubilization, at 25ºC (the total mole of surfactants to total mole of alcohol at 10:5.53 x 10^{-8})

DTAB:DOWFAX (1:1) concentration (mM)	Pyrene analysis			Average	STD	%RSD
	Absorbance at 333.6 nm	Times dilution	Solubility of pyrene (ppm)			
0	0.002	10	0.11	0.14	0.03	21.4
	0.003		0.16			
	0.003		0.16			
0.001	0.003		0.16	0.18	0.03	16.7
	0.003		0.16			
	0.004		0.22			
0.005	0.003		0.16	0.18	0.03	16.7
	0.003		0.16			
	0.004		0.22			
0.01	0.004		0.22	0.22	0.00	0.00
	0.004		0.22			
	0.004		0.22			
0.05	0.012		0.66	0.59	0.06	10.2
	0.010		0.55			
	0.010		0.55			
0.1	0.021		1.15	1.23	0.09	7.32
	0.022		1.21			
	0.024		1.32			
0.5	0.089		4.89	4.87	0.09	1.85
	0.087		4.78			
	0.090		4.95			
1	0.172		9.45	9.42	0.03	0.32
	0.171		9.40			
	0.171		9.40			
2	0.342		18.79	18.81	0.03	0.16
	0.342		18.79			
	0.343		18.85			
5	0.804		44.18	43.94	0.25	0.57
	0.795		43.68			
	0.800		43.96			
10	0.336	50	92.31	92.49	0.32	0.35
	0.336		92.31			
	0.338		92.86			
20	0.694		190.66	188.92	1.51	0.80
	0.685		188.19			
	0.684		187.91			

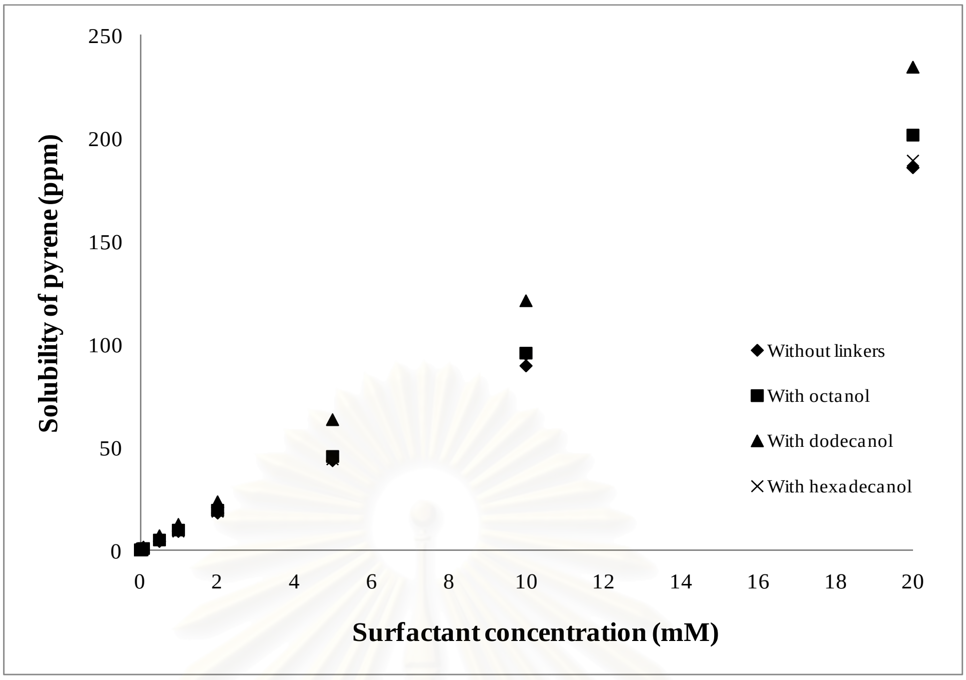


Figure F-2 Effects of lipophilic linkers type on pyrene solubilization (System: DTAB:DOWFAX solution at 1:1 molar ratio and the total mole of surfactants to total mole of alcohol at 10:1 for octanol and dodecanol, and at 10:5.53 x 10^{-8} for hexadecanol)

Table F-6 Molar solubilization ratio (MSR) and log micelle-water partitioning coefficient (log K_m) of pyrene for DTAB:DOWFAX at 1:1 molar ratio with and without lipophilic linkers at total mole of surfactants to total mole of alcohol at 10:1 for octanol and dodecanol, and at 10:5.53 x 10^{-8} for hexadecanol

Surfactant system	**DTAB:DOWFAX at 1:1 molar ratio**			
	Without linkers	**With Octanol**	**With dodecanol**	**With hexadecanol**
MSR	0.045	0.049	0.059	0.046
X_m	0.043	0.047	0.056	0.044
X_{aq}	1.16E-08	1.16E-08	1.16E-08	1.16E-08
K_m	3,720,225.96	4,035,465.95	4,813,147.23	3,799,261.99
Log K_m	6.57	6.61	6.68	6.58

Table F-7 Results of the effects of octanol concentration in DTAB:DOWFAX solution at 1:1 molar ratio with constant total surfactants concentration of 20 mM on pyrene solubilization

DTAB:DOWFAX (1:1) concentration (mM)	Octanol concentration (mM)	Pyrene analysis		Average	STD	%RSD
		Abs at 333.6 nM	Solubility of pyrene (ppm) 50 times dilution			
20	1	0.697	191.48	190.66	0.82	0.43
		0.691	189.84			
		0.694	190.66			
20	2	0.733	201.37	201.10	0.28	0.14
		0.732	201.10			
		0.731	200.82			
20	4	0.813	223.35	223.26	1.52	0.68
		0.807	221.70			
		0.818	224.73			

Table F-8 Results of the effects of dodecanol concentration in DTAB:DOWFAX solution at 1:1 molar ratio with constant total surfactants concentration of 20 mM on pyrene solubilization

DTAB:DOWFAX (1:1) concentration (mM)	Octanol concentration (mM)	Pyrene analysis			Average	STD	%RSD
		Abs at 333.6 nM	Times dilution	Solubility of pyrene (ppm)			
20	1	0.750	50	206.04	207.32	1.14	0.55
		0.756		207.69			
		0.758		208.24			
20	2	0.850		233.52	234.43	1.14	0.49
		0.852		234.07			
		0.858		235.71			
20	4	0.498	100	273.63	273.63	0.55	0.20
		0.497		273.08			
		0.499		274.18			

APPENDIX G

Results of the effects of total surfactant concentration and additives on pyrene removal and of the effect of the optimal surfactant formulation on pyrene removal

Table G-1 Results of the back extraction of pyrene from contaminated soil

Initial concentration of pyrene contaminated soil (mg/kg)	Mass of pyrene (mg) before extraction	Pyrene analysis			% Extraction
		Abs at 333.6 nm	Concentration (mg/L) 20 times dilution	Mass of pyrene (mg) after extraction	
200	0.500	0.445	48.90	0.489	97.80
		0.447	49.12	0.491	98.24
		0.425	46.70	0.467	93.41
		0.439	48.24	0.482	96.48
		0.452	49.67	0.497	99.34
		0.485	53.30	0.533	106.59
Average					98.64
STD					4.40
%RSD					4.46

Note: 2.5 g of pyrene contaminated soil was used in this experiment.

10 mL of 50% methanol was used as extractant.

Table G-2 Results of the effects of total surfactant concentration on pyrene removal from contaminated soil (System: DTAB:DOWFAX at 1:1 molar ratio without additives)

DTAB:DOWFAX (1:1) concentration (mM)	**Pyrene analysis**			**Pyrene Removal (%)**	**Average**	**STD**	**%RSD**
	Abs at 333.6 nm	**Concentration (mg/L) 50 times dilution**	**Mass of pyrene (mg)**				
5	0.209	57.42	0.144	28.71	28.80	0.16	0.56
	0.209	57.42	0.144	28.71			
	0.211	57.97	0.145	28.98			
10	0.344	94.51	0.236	47.25	47.76	0.44	0.92
	0.350	96.15	0.240	48.08			
	0.349	95.88	0.240	47.94			
20	0.510	140.11	0.350	70.05	69.09	0.84	1.22
	0.499	137.09	0.343	68.54			
	0.500	137.36	0.343	68.68			
30	0.633	173.90	0.435	86.95	86.72	0.21	0.24
	0.631	173.35	0.433	86.68			
	0.630	173.08	0.433	86.54			
40	0.629	172.80	0.432	86.40	86.45	0.35	0.40
	0.627	172.25	0.431	86.13			
	0.632	173.63	0.434	86.81			
50	0.666	182.97	0.457	91.48	91.67	0.21	0.23
	0.669	183.79	0.459	91.90			
	0.667	183.24	0.458	91.62			

Note: The initial concentration of pyrene contaminated soil was 200 mg/kg (mass of pyrene = 0.500 mg).

2.5 g of pyrene contaminated soil and 2.5 g of surfactant solution were used in this experiment.

Table G-3 Results of the effects of $CaCl_2$ concentration on pyrene removal from contaminated soil (System: DTAB:DOWFAX at 1:1 molar ratio with 20 mM of total surfactants concentration)

$CaCl_2$ concentration (%wt)	**Pyrene analysis**			**Pyrene Removal (%)**	**Average**	**STD**	**%RSD**
	Abs at 333.6 nm	**Concentration (mg/L) 50 times dilution**	**Mass of pyrene (mg)**				
0.005	0.527	144.78	0.362	72.39	72.99	0.70	0.96
	0.530	145.60	0.364	72.80			
	0.537	147.53	0.369	73.76			
0.010	0.564	154.95	0.387	77.47	77.15	0.29	0.38
	0.560	153.85	0.385	76.92			
	0.561	154.12	0.385	77.06			
0.025	0.607	166.76	0.417	83.38	83.52	1.17	1.40
	0.600	164.84	0.412	82.42			
	0.617	169.51	0.424	84.75			
0.040	0.552	151.65	0.379	75.82	75.87	0.48	0.63
	0.556	152.75	0.382	76.37			
	0.549	150.82	0.377	75.41			
0.050	0.444	121.98	0.305	60.99	60.39	0.91	1.51
	0.443	121.70	0.304	60.85			
	0.432	118.68	0.297	59.34			

Note: The initial concentration of pyrene contaminated soil was 200 mg/kg (mass of pyrene = 0.500 mg).

2.5 g of pyrene contaminated soil and 2.5 g of surfactant solution with various $CaCl_2$ concentrations were used in this experiment.

Table G-4 Results of the effects of octanol concentration on pyrene removal from contaminated soil (System: DTAB:DOWFAX at 1:1 molar ratio with 20 mM of total surfactants concentration)

Octanol concentration (mM)	**Pyrene analysis**			**Pyrene Removal (%)**	**Average**	**STD**	**%RSD**
	Abs at 333.6 nm	**Concentration (mg/L) 50 times dilution**	**Mass of pyrene (mg)**				
1	0.552	151.65	0.379	75.82	75.87	0.48	0.63
	0.549	150.82	0.377	75.41			
	0.556	152.75	0.382	76.37			
2	0.578	158.79	0.397	79.40	79.44	0.48	0.60
	0.582	159.89	0.400	79.95			
	0.575	157.97	0.395	78.98			
4	0.603	165.66	0.414	82.83	82.69	1.17	1.41
	0.593	162.91	0.407	81.46			
	0.610	167.58	0.419	83.79			

Note: The initial concentration of pyrene contaminated soil was 200 mg/kg (mass of pyrene = 0.500 mg).

2.5 g of pyrene contaminated soil and 2.5 g of surfactant solution with various octanol concentrations were used in this experiment.

Table G-5 Results of the effects of dodecanol concentration on pyrene removal from contaminated soil (System: DTAB:DOWFAX at 1:1 molar ratio with 20 mM of total surfactants concentration)

Dodecanol concentration (mM)	**Pyrene analysis**			**Pyrene Removal (%)**	**Average**	**STD**	**%RSD**
	Abs at 333.6 nm	**Concentration (mg/L) 50 times dilution**	**Mass of pyrene (mg)**				
1	0.578	158.79	0.397	79.40	79.62	0.78	0.98
	0.575	157.97	0.395	78.98			
	0.586	160.99	0.402	80.49			
2	0.593	162.91	0.407	81.46	83.06	1.58	1.90
	0.616	169.23	0.423	84.62			
	0.605	166.21	0.416	83.10			
4	0.635	174.45	0.436	87.23	86.72	0.44	0.51
	0.630	173.08	0.433	86.54			
	0.629	172.80	0.432	86.40			

Note: The initial concentration of pyrene contaminated soil was 200 mg/kg (mass of pyrene = 0.500 mg).

2.5 g of pyrene contaminated soil and 2.5 g of surfactant solution with various dodecanol concentrations were used in this experiment.

Table G-6 Results of the effect of the optimal surfactant formulation on pyrene removal from contaminated soil (System: DTAB:DOWFAX at 1:1 molar ratio with 20 mM total surfactants concentration, 0.025%wt $CaCl_2$, and 1 mM dodecanol)

Surfactant system	**Pyrene analysis**			**Pyrene Removal (%)**	**Average**	**STD**	**%RSD**
	Abs at 333.6 nm	**Concentration (mg/L) 50 times dilution**	**Mass of pyrene (mg)**				
The optimal surfactant formulation	0.637	175.00	0.438	87.50	87.50	0.27	0.31
	0.639	175.55	0.439	87.77			
	0.635	174.45	0.436	87.23			

Note: The initial concentration of pyrene contaminated soil was 200 mg/kg (mass of pyrene = 0.500 mg).

2.5 g of pyrene contaminated soil and 2.5 g of the optimal surfactant formulation were used in this experiment.

APPENDIX H

Table H-1 Results of aqueous surfactant two-phase (ASTP) system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration without additive at ambient temperature of 30 ºC

Sample No.	**Total volume (mL)**	**Rich-phase height (cm)**	**Rich-phase volume (mL)**	**Surfactant-dilute phase**				**Surfactant-rich phase**			
				DOWFAX analysis (20 times dilution)		**Pyrene analysis (50 times dilution)**		**DOWFAX analysis (10,000 times dilution)**		**Pyrene analysis (2,500 times dilution)**	
				Abs at 240 nm	**Conc. (mM)**	**Abs at 333.6 nm**	**Conc. (ppm)**	**Abs at 240 nm**	**Conc. (mM)**	**Abs at 333.6 nm**	**Conc. (ppm)**
1	9.26	0.20	0.29	0.113	0.11	0.004	1.10	0.651	330.96	0.306	4,203.30
		0.20	0.29	0.103	0.10	0.005	1.37	0.660	335.54	0.306	4,203.30
		0.20	0.29	0.104	0.11	0.007	1.92	0.650	330.45	0.307	4,217.03
2	9.31	0.20	0.29	0.105	0.11	0.006	1.65	0.662	336.55	0.304	4,175.82
		0.20	0.29	0.105	0.11	0.005	1.37	0.652	331.47	0.299	4,107.14
		0.20	0.29	0.102	0.10	0.005	1.37	0.650	330.45	0.305	4,189.56
Average	9.29		0.29		0.11		1.47		332.57		4,182.69
STD	0.04		-		0.01		0.30		2.74		39.58
%RSD	0.43		-		9.09		20.41		0.82		0.95

Table H-2 Summary data obtained from aqueous surfactant two-phase (ASTP) system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration without additive at ambient temperature of 30 ºC

Fractional rich-phase volume	DOWFAX concentration (mM)		Pyrene concentration (ppm)		Partition ratio		Pyrene accumulated in the surfactant-rich phase (%)	Mass balance		Mass loss (%)	
	Rich phase	Dilute phase	Rich phase	Dilute phase	DOWFAX	Pyrene		DOWFAX (mM)	Pyrene (ppm)	DOWFAX	Pyrene
0.031	332.57	0.11	4,182.69	1.47	3,023.36	2,845.37	98.94	10.42	131.09	-4.2	5.14

Note: The average concentration of pyrene in the extracted surfactant solution before phase separation was 138.19 mg/L (ppm).

The concentration of DOWFAX in the extracted surfactant solution before phase separation was 10 mM.

Table H-3 Results of aqueous surfactant two-phase (ASTP) system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration and 0.025%wt $CaCl_2$ at ambient temperature of 30 °C

Sample No.	Total volume (mL)	Rich-phase height (cm)	Rich-phase volume (mL)	Surfactant-dilute phase				Surfactant-rich phase			
				DOWFAX analysis (20 times dilution)		Pyrene analysis (20 times dilution)		DOWFAX analysis (10,000 times dilution)		Pyrene analysis (2,500 times dilution)	
				Abs at 240 nm	Conc. (mM)	Abs at 333.6 nm	Conc. (ppm)	Abs at 240 nm	Conc. (mM)	Abs at 333.6 nm	Conc. (ppm)
1	9.34	0.20	0.29	0.099	0.10	0.015	1.65	0.661	336.04	0.396	5,439.56
		0.20	0.29	0.098	0.10	0.016	1.76	0.664	337.57	0.395	5,425.82
		0.20	0.29	0.098	0.10	0.015	1.65	0.662	336.55	0.399	5,480.77
2	9.32	0.20	0.29	0.102	0.10	0.014	1.54	0.660	335.54	0.391	5,370.88
		0.20	0.29	0.098	0.10	0.015	1.65	0.659	335.03	0.392	5,384.62
		0.20	0.29	0.097	0.10	0.016	1.76	0.653	331.98	0.400	5,494.51
Average	9.33		0.29		0.10		1.67		335.45		5,432.69
STD	0.01		-		-		0.08		1.91		49.72
%RSD	0.11		-		-		4.79		0.57		0.92

Table H-4 Summary data obtained from aqueous surfactant two-phase (ASTP) system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration and 0.025%wt $CaCl_2$ at ambient temperature of 30 ºC

Fractional rich-phase volume	**DOWFAX concentration (mM)**		**Pyrene concentration (ppm)**		**Partition ratio**		**Pyrene accumulated in the surfactant-rich phase (%)**	**Mass balance**		**Mass loss (%)**	
	Rich phase	**Dilute phase**	**Rich phase**	**Dilute phase**	**DOWFAX**	**Pyrene**		**DOWFAX (mM)**	**Pyrene (ppm)**	**DOWFAX**	**Pyrene**
0.031	335.45	0.1	5,432.69	1.67	3,354.50	3,253.11	99.00	10.50	170.03	-5.00	-1.79

Note: The average concentration of pyrene in the extracted surfactant solution before phase separation was 167.03 mg/L (ppm).

The concentration of DOWFAX in the extracted surfactant solution before phase separation was 10 mM.

Table H-5 Results of aqueous surfactant two-phase (ASTP) system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration and 1 mM dodecanol at ambient temperature of 30 °C

Sample No.	**Total volume (mL)**	**Rich-phase height (cm)**	**Rich-phase volume (mL)**	**Surfactant-dilute phase**				**Surfactant-rich phase**			
				DOWFAX analysis (100 times dilution)		**Pyrene analysis (50 times dilution)**		**DOWFAX analysis (10,000 times dilution)**		**Pyrene analysis (2,500 times dilution)**	
				Abs at 240 nm	**Conc. (mM)**	**Abs at 333.6 nm**	**Conc. (ppm)**	**Abs at 240 nm**	**Conc. (mM)**	**Abs at 333.6 nm**	**Conc. (ppm)**
1	9.37	0.14	0.21	0.624	3.17	0.238	65.38	0.622	316.22	0.330	4,532.97
		0.14	0.21	0.623	3.17	0.239	65.66	0.618	314.18	0.335	4,601.65
		0.14	0.21	0.622	3.16	0.244	67.03	0.620	315.20	0.334	4,587.91
2	9.36	0.14	0.21	0.639	3.25	0.247	67.86	0.622	316.22	0.328	4,505.49
		0.14	0.21	0.639	3.25	0.247	67.86	0.616	313.17	0.327	4,491.76
		0.14	0.21	0.638	3.24	0.248	68.13	0.626	318.25	0.341	4,684.07
Average	9.37		0.21		3.21		66.99		315.54		4,567.31
STD	0.01		-		0.04		1.20		1.78		72.04
%RSD	0.11		-		1.25		1.79		0.56		1.58

Table H-6 Summary data obtained from aqueous surfactant two-phase (ASTP) system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration and 1 mM dodecanol at ambient temperature of 30 ºC

Fractional rich-phase volume	**DOWFAX concentration (mM)**		**Pyrene concentration (ppm)**		**Partition ratio**		**Pyrene accumulated in the surfactant-rich phase (%)**	**Mass balance**		**Mass loss (%)**	
	Rich phase	**Dilute phase**	**Rich phase**	**Dilute phase**	**DOWFAX**	**Pyrene**		**DOWFAX (mM)**	**Pyrene (ppm)**	**DOWFAX**	**Pyrene**
0.022	315.54	3.21	4,567.31	66.99	98.30	68.18	57.93	10.08	166.00	-0.80	-4.24

Note: The average concentration of pyrene in the extracted surfactant solution before phase separation was 159.25 mg/L (ppm).

The concentration of DOWFAX in the extracted surfactant solution before phase separation was 10 mM.

Table H-7 Results of aqueous surfactant two-phase (ASTP) system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration, 0.025%wt $CaCl_2$, and 1 mM dodecanol at ambient temperature of 30 ºC

Sample No.	Total volume (mL)	Rich-phase height (cm)	Rich-phase volume (mL)	Surfactant-dilute phase				Surfactant-rich phase			
				DOWFAX analysis (100 times dilution)		Pyrene analysis (50 times dilution)		DOWFAX analysis (10,000 times dilution)		Pyrene analysis (2,500 times dilution)	
				Abs at 240 nm	**Conc. (mM)**	**Abs at 333.6 nm**	**Conc. (ppm)**	**Abs at 240 nm**	**Conc. (mM)**	**Abs at 333.6 nm**	**Conc. (ppm)**
1	9.39	0.13	0.19	0.603	3.07	0.252	69.23	0.673	342.15	0.397	5,453.30
		0.13	0.19	0.628	3.19	0.251	68.96	0.675	343.16	0.390	5,357.14
		0.14	0.21	0.602	3.06	0.258	70.88	0.674	342.65	0.392	5,384.62
2	9.39	0.13	0.19	0.599	3.05	0.256	70.33	0.667	339.10	0.396	5,439.56
		0.14	0.21	0.626	3.18	0.255	70.05	0.669	340.11	0.394	5,412.09
		0.14	0.21	0.602	3.06	0.259	71.15	0.678	344.69	0.395	5,425.82
Average	9.39		0.20		3.10		70.10		341.98		5,412.09
STD	-		1.10E-02		0.06		0.87		2.05		35.82
%RSD	-		5.00		1.94		1.24		0.60		0.66

Table H-8 Summary data obtained from aqueous surfactant two-phase (ASTP) system formed by DTAB:DOWFAX at 2:1 molar ratio with 30 mM total surfactants concentration, 0.025%wt $CaCl_2$, and 1 mM dodecanol at ambient temperature of 30 ºC

Fractional rich-phase volume	**DOWFAX concentration (mM)**		**Pyrene concentration (ppm)**		**Partition ratio**		**Pyrene accumulated in the surfactant-rich phase (%)**	**Mass balance**		**Mass loss (%)**	
	Rich phase	**Dilute phase**	**Rich phase**	**Dilute phase**	**DOWFAX**	**Pyrene**		**DOWFAX (mM)**	**Pyrene (ppm)**	**DOWFAX**	**Pyrene**
0.021	341.98	3.10	5,412.09	70.1	110.32	77.21	59.94	10.22	182.28	-2.20	-4.16

Note: The average concentration of pyrene in the extracted surfactant solution before phase separation was 175.00 mg/L (ppm).

The concentration of DOWFAX in the extracted surfactant solution before phase separation was 10 mM.

Table H-9 Results of aqueous surfactant two-phase (ASTP) system formed by DTAB:DOWFAX at 1:1 molar ratio with 20 mM total surfactants concentration and 0.2%wt $CaCl_2$ (Induced by the addition of 0.2%wt $CaCl_2$) at ambient temperature of 30 ºC

Sample No.	**Total volume (mL)**	**Rich-phase height (cm)**	**Rich-phase volume (mL)**	**Surfactant-dilute phase**				**Surfactant-rich phase**			
				DOWFAX analysis (100 times dilution)		**Pyrene analysis (50 times dilution)**		**DOWFAX analysis (10,000 times dilution)**		**Pyrene analysis (2,500 times dilution)**	
				Abs at 240 nm	**Conc. (mM)**	**Abs at 333.6 nm**	**Conc. (ppm)**	**Abs at 240 nm**	**Conc. (mM)**	**Abs at 333.6 nm**	**Conc. (ppm)**
1	9.26	0.25	0.37	0.201	1.02	0.063	17.31	0.458	232.84	0.231	3,173.08
		0.26	0.38	0.205	1.04	0.070	19.23	0.459	233.35	0.230	3,159.34
		0.25	0.37	0.213	1.08	0.064	17.58	0.462	234.88	0.232	3,186.81
2	9.33	0.25	0.37	0.212	1.08	0.062	17.03	0.451	229.28	0.229	3,145.60
		0.25	0.37	0.214	1.09	0.065	17.86	0.459	233.35	0.230	3,159.34
		0.25	0.37	0.216	1.10	0.069	18.96	0.457	232.33	0.231	3,173.08
Average	9.30		0.37		1.07		18.00		232.67		3,166.21
STDEV	0.05		4.08E-03		0.03		0.90		1.87		14.41
%RSD	0.54		1.10		2.80		5.00		0.80		0.46

Table H-10 Summary data obtained from aqueous surfactant two-phase (ASTP) system formed by DTAB:DOWFAX at 1:1 molar ratio with 20 mM total surfactants concentration and 0.2%wt $CaCl_2$ (Induced by the addition of 0.2%wt $CaCl_2$) at ambient temperature of 30 ºC

Fractional rich-phase volume	**DOWFAX concentration (mM)**		**Pyrene concentration (ppm)**		**Partition ratio**		**Pyrene accumulated in the surfactant-rich phase (%)**	**Mass balance**		**Mass loss (%)**	
	Rich phase	**Dilute phase**	**Rich phase**	**Dilute phase**	**DOWFAX**	**Pyrene**		**DOWFAX (mM)**	**Pyrene (ppm)**	**DOWFAX**	**Pyrene**
0.040	232.67	1.07	3,166.21	18.00	217.45	175.90	86.97	10.33	143.93	-3.3	-4.15

Note: The average concentration of pyrene in the extracted surfactant solution before phase separation was 138.19 mg/L (ppm).

The concentration of DOWFAX in the extracted surfactant solution before phase separation was 10 mM.

BIOGRAPHY

Name: Mr. Putchaya Thunhapran

Date of Birth: January 14, 1984

Nationality: Thai

University Education: 2002-2005 Bachelor Degree of Science in Environmental Science and Technology, Faculty of Environment and Resource Studies, Mahidol University, Bangkok, Thailand

Presentation:

Putchaya Thunhapran and Punjaporn Weschayanwiwat. *Removal and Concentration of Pyrene from Contaminated Soil using A Phase Separation of Mixed Cationic and Anionic Surfactants Solution*. 1st The Proceedings of Pure and Applied Chemistry International Conference (PACCON) 2008, Bangkok, Thailand, January 30 - February 1, 2008. Organized by Kasetsart University, Chemical Society of Thailand, and The Thailand Research Fund