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สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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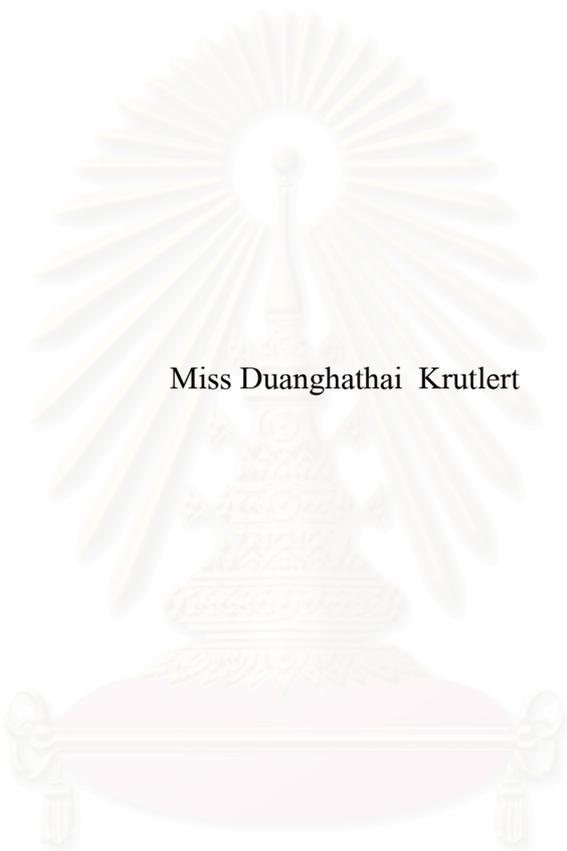
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

EFFECT OF ELECTROLYTE ON BTEX REMOVAL USING AQUEOUS
SURFACTANT TWO-PHASE SYSTEMS TECHNIQUE FORMED BY CATIONIC
AND ANIONIC SURFACTANT MIXTURES



Miss Duanghathai Krutlert

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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ดวงหทัย ครุฑเลิศ : ผลของอิเล็กโทรไลต์ต่อการกำจัดเบนซิน โทลูอีน เอธิลเบนซิน และไซลีนโดยใช้เทคนิคการแบ่งวัฏภาคของสารละลายผสมของสารลดแรงตึงผิวชนิดประจุบวกและประจุลบ. (EFFECT OF ELECTROLYTE ON BTEX REMOVAL USING AQUEOUS SURFACTANT TWO-PHASE SYSTEMS TECHNIQUE FORMED BY CATIONIC AND ANIONIC SURFACTANT MIXTURES) อ.ที่ปรึกษา : ดร. ปัญญาพร เวชยันตีวิวัฒน์, อ.ที่ปรึกษาร่วม : ศ.ดร. จอห์น สแกมมีย์ฮอห์น 73 หน้า. ISBN 974-17-7055-3.

การปนเปื้อนของเบนซิน โทลูอีน เอธิลเบนซินและไซลีนมักพบโดยทั่วไปในน้ำเสียอุตสาหกรรมซึ่งเป็นที่สาเหตุให้เกิดปัญหาที่ส่งผลกระทบต่อสุขภาพและสภาวะแวดล้อมอย่างมาก วิธีการสกัดแบบใหม่ที่ใช้กำจัดสารปนเปื้อนออกจากน้ำเสียเรียกว่าเทคนิคการแบ่งวัฏภาคของสารละลายผสมของสารลดแรงตึงผิวชนิดประจุบวกและประจุลบ(ASTP)การแบ่งวัฏภาคจะเกิดขึ้นที่อัตราส่วนโดยโมลและความเข้มข้นของสารลดแรงตึงผิวที่เหมาะสมซึ่งจะแบ่งออกเป็นสองวัฏภาค ประกอบด้วยวัฏภาคที่มีไมเซลล์จำนวนมากและวัฏภาคที่มีไมเซลล์จำนวนน้อย ซึ่งสารปนเปื้อนส่วนใหญ่ถูกสกัดได้อยู่ในวัฏภาคที่มีไมเซลล์จำนวนมากในขณะที่วัฏภาคที่มีไมเซลล์จำนวนน้อยจะถูกปล่อยออกเป็นน้ำที่ผ่านการบำบัดแล้ว ในงานวิจัยนี้จะศึกษาผลของการเติมอิเล็กโทรไลต์ต่อความเข้มข้นวิกฤตที่เกิดการรวมกลุ่มของสารลดแรงตึงผิวและประสิทธิภาพการสกัดของสารละลายผสมของสารลดแรงตึงผิวประจุบวก (dodecyltrimethylammonium bromide; DTAB) และประจุลบ (alkyl diphenyl oxide disulfonate; DOWFAX 8390) ผลของงานวิจัยพบว่าค่าความเข้มข้นวิกฤตที่เกิดการรวมกลุ่มของสารลดแรงตึงผิวลดลงเมื่อมีการเติมอิเล็กโทรไลต์โดยเรียงตามลำดับดังนี้ โซเดียมฟลูออไรด์ > โพแทสเซียมคลอไรด์ ~ โซเดียมคลอไรด์ > ลิเทียมคลอไรด์ > แมกนีเซียมคลอไรด์ ในทางกลับกันเมื่อเติมโซเดียมไฮดรอกไซด์พบว่าค่าความเข้มข้นวิกฤตที่เกิดการรวมกลุ่มของสารลดแรงตึงผิวมีค่าสูงขึ้น มากไปกว่านั้นการสกัดเบนซิน โทลูอีน เอธิลเบนซินและไซลีนออกจากน้ำเสียโดยใช้สารผสมของสารลดแรงตึงผิวประจุบวก (DTAB) และประจุลบ (DOWFAX) ที่ความเข้มข้นของสารลดแรงตึงผิวรวม 50 มิลลิโมลาร์และอัตราส่วนโดยโมลที่ 2:1 และมีการเติมอิเล็กโทรไลต์พบว่าดีขึ้นเมื่อเปรียบเทียบกับไม่เติมอิเล็กโทรไลต์ โดยเมื่อเติมโซเดียมคลอไรด์เข้มข้น 1 โมลาร์พบว่า 95% ของไซลีน, 92% ของเอธิลเบนซิน, 90% ของโทลูอีน และ 79% ของเบนซินสามารถถูกสกัดอยู่ในวัฏภาคที่มีไมเซลล์จำนวนมาก อย่างไรก็ตามอิเล็กโทรไลต์ที่มีประจุบวกที่แตกต่างกันสามารถเพิ่มประสิทธิภาพการสกัดสารระเหยง่ายได้เกือบเทียบเท่ากัน มากกว่านั้นพบว่ายิ่งสารปนเปื้อนมีระดับของความไม่ชอบน้ำมากก็ยิ่งสามารถถูกสกัดอยู่ในวัฏภาคที่มีไมเซลล์จำนวนมากตามลำดับดังนี้ ไซลีน > เอธิลเบนซิน > โทลูอีน > เบนซิน

สาขาวิชา การจัดการสิ่งแวดล้อม
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ลายมือชื่อนิสิต.....
ลายมือชื่ออาจารย์ที่ปรึกษา.....
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

4689426120 : MAJOR ENVIRONMENTAL MANAGEMENT

KEY WORD: AQUEOUS SURFACTANT TWO-PHASE SYSTEM(ASTP) / CATIONIC SURFACTANT / EXTRACTION / ELECTROLYTE/ CAC VALUE

DUANGHATHAI KRUTLERT : EFFECT OF ELECTROLYTE ON BTEX REMOVAL USING AQUEOUS SURFACTANT TWO-PHASE SYSTEMS TECHNIQUE FORMED BY CATIONIC AND ANIONIC SURFACTANT MIXTURES. THESIS ADVISOR: PUNJAPORN WESCHAYANWIWAT, Ph.D., THESIS COADVISOR : PROF. JOHN F. SCAMEHORN, Ph.D., 73 pp. ISBN 974-17-7055 -3.

Contamination of benzene, toluene, ethylbenzene, and xylene (BTEX) are commonly found in industrial wastewater causing several concerns including environmental problems and health effects to human. A new separation technique to remove BTEX from wastewater by using mixtures of cationic and anionic surfactants is called aqueous surfactant two-phase system (ASTP). A phase separation occurs at certain surfactant composition and concentration forming two immiscible phases. One is surfactant-rich and the other is surfactant-diluted. Most of contaminants concentrate in the surfactant-rich phase leaving the surfactant-depleted phase containing only small amount of contaminants as treated water. In this research, the effect of added electrolytes on the critical aggregation concentration (CAC) and the extraction efficiency of ASTP formed by mixtures of cationic (dodecyltrimethylammonium bromide; DTAB) and anionic (alkyl diphenyl oxide disulfonate; DOWFAX 8390) surfactants were investigated. The results show that the CAC value decreases with the addition of electrolyte in the following order; NaF > KCl ~ NaCl > LiCl > and MgCl₂. But the addition of NaI shows the opposite result in which the CAC value is enhanced upon added electrolyte. In addition, the extraction of BTEX from wastewater at total surfactant concentration of 50 mM with 2:1 molar ratio of DTAB:DOWFAX in the presence of electrolyte (LiCl, NaCl, KCl, and MgCl₂) is enhanced as compared with the absence of electrolyte. At 1.0 M NaCl, about 95 % of xylene, 92 % of ethylbenzene, 90% of toluene and 79% of benzene are extracted into the surfactant-rich phase, respectively. Nevertheless, different cation of inorganic electrolyte equally enhances the efficiency on VOC extraction. The higher degree of hydrophobicity shows the greater potential of contaminant to be extracted in the surfactant-rich phase in the following order: xylene > ethylbenzene > toluene > benzene.

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

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Co-advisor's signature.....

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ABBREVIATIONS

Abs	Absorbance
ADPODS	Alkyl Diphenyl Oxide Disulfonate
Al (NO ₃) ₂	Aluminium Nitrate
AMA	Sodium Dihexyl Sulfosuccinate
ASTP	Aqueous Surfactant Two-Phase System
BSA	Bovine Serum Albumin
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
CACs	Critical Aggregate Concentrations
CaCl ₂	Calcium Chloride
Ca (NO ₃) ₂	Calcium Nitrate
CMCs	Critical Micelle Concentrations
CTAB	Cetyltrimethylammonium Bromide
C ₉ APSO ₄	3-(nonyldimethylammonio) propylsulfate
C ₁₂ NE	Dodecyltriethylammonium Bromide
C _t	Total concentration
°C	Degree Centigrade
DEAB	Dodecyltriethylammonium Bromide
DOWFAX	Alkyl Diphenyl Oxide Disulfonate
DTAB	Dodecyltrimethylammonium Bromide
FID	Flame Ionized Detector
GC	Gas chromatograph
g/mole	Gram per mole
KCl	Potassium Chloride
KPa	Kilopascal
LiCl	Lithium Chloride
M	Molar
Mg ₂ Cl	Magnesium Chloride
mg/L	Milligram per Liter
mM	Millimole

mm Hg	Millimeters of mercury
NaBr	Sodium Bromide
NaCl	Sodium Chloride
NaF	Sodium Fluoride
NaI	Sodium Iodide
Ni	Nickel
Nm	Nanometer
Ppm	Parts per Million
SDS	Sodium Dodecyl Sulfate
SL	Sodium Laurate
SOS	Sodium Octyl Sulfate
SPFO	Sodium Perfluorooctanoate
TTAB	Tetradecyltrimethylammonium Bromide
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
VOCs	Volatile Organic Compounds
WWTFs	Wastewater Treatment Facilities

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CHAPTER I

INTRODUCTION

1.1 General

Benzene, toluene, ethylbenzene, and xylene (BTEX) are volatile organic compounds (VOCs) which are commonly found together in petroleum products such as gasoline, diesel fuel and crude oil. They are also produced on the scale of megatons per year as bulk chemicals for industrial use as solvents and starting materials for the manufacture of pesticides, plastics, and synthetic fibers (Harwood and Gibson, 1997). They are often a result from spillage of fuels, solvents or chemicals and are drained to wastewater treatment facilities (WWTFs) causing several concerns including a direct health threat to human and contribution to the formation of photochemical oxidants and ozone in the ambient air, etc. (Pitts and Filayson, 1986; Corsi and Card, 1991). A case study done by Worrall and Zuber in 1998 reported that benzene discharge can be as high as 54 tons/year if the refinery releases the wastewater containing benzene concentration of 50 ppm at the flow rate of 500 gallons/minute (<http://www..amcec.com/case3.html>). According to the U.S. Environmental Protection Agency (USEPA), there are sufficient evidences from both human and animal studies to believe that benzene is also a human carcinogen and is a risk factor for leukemia and lymphomas (Harwood and Gibson, 1997). Toluene has been proved to be a depressant of human central nervous system. Ethylbenzene causes a skin irritant, also long-term exposure to xylene has been correlated to aplastic anemia (Sittig, 1985). These concerns have led to U.S. State and Federal requirements to control VOC emission from industrial and at municipal wastewater treatment facilities.

In general, there are several procedures, which have been used to remove BTEX from wastewater such as carbon adsorption, stream/air stripping, and thermal destruction. Although these methods are highly effective, they are likely to be suffered from limitations with different degrees in terms of recovery efficiency,

volume of the chemicals required, processing time, energy consumption, safety and ease of use (Hinze, 1993; <http://www.amcec.com/case3.html>).

One promising process to remove and preconcentrate various substances including undesirable organic pollutants from wastewater is aqueous surfactant two-phase system (ASTP), which is a new separation technique formed by mixture of cationic and anionic surfactants (Zhao and Xiao, 1996). According to Xiao, Sivars, and Tjerneld (2000), ASTP is an alternative extraction technique, which is safe, rapid, convenient, mild and accurate. Moreover, Kang et al.(2001) reported that mixed surfactant systems exhibit attractive features in the viewpoint of economy and performance. They are less expensive than a pure, single surfactant. In addition, they often enhance the effectiveness of extraction (Khan and Marques, 2000).

Furthermore, the addition of electrolyte induces some advantages, which will improve the physicochemical properties and efficiency of extraction that cannot be seen in usual ASTP (Herrington, Brasher, and Kaler, 1995; Brasher and Kaler, 1996). This research has been conducted to study the effect of added electrolytes (LiCl, NaCl, KCl, NaF, NaI, and $MgCl_2$) on the removal of BTEX from wastewater by using ASTP technique formed by mixture of cationic-anionic surfactants (dodecyltrimethylammonium bromide; DTAB and Alkyl diphenyl oxide disulfonate; ADPODS or DOWFAX 8390). In addition, the effect of pollutant type on the extraction efficiency has been investigated.

1.2 Objectives

1. To study the physicochemical properties of the cationic-anionic surfactant mixtures with variation of pollutant types and added electrolytes, i.e. cloud point temperature and critical aggregate concentrations (CACs) and characteristic of phases after ASTP technique is applied, i.e. phase separation time, phase volume ratio, partition ratio.

2. To determine the effect of solute type and added electrolyte on the extraction efficiency of BTEX via ASTP technique formed by cationic-anionic surfactant mixtures.

1.3 Scope of work

The research has been conducted to investigate the efficiency of BTEX removal from wastewater using the ASTP technique formed by cationic-anionic surfactant mixtures, which can be divided into three phases as follows;

Phase 1: Preliminary study

- To find out a suitable system of cationic-anionic surfactant mixtures, which have the potential to extract BTEX from wastewater based on ASTP technique.

Phase 2: A study on the physicochemical properties of the system and phase behaviors of cationic-anionic surfactant mixtures

- To study phase behaviors of the system, i.e. phase separation time, phase volume ratio, partition ratio of the cationic-anionic surfactant mixtures with various surfactant compositions and total concentrations in the absence of electrolytes.
- To study phase behaviors and the physicochemical properties, i.e. cloud point temperature and critical aggregate concentrations (CACs) of cationic-anionic surfactant mixtures in the presence of electrolytes.

Phase 3: The extraction study of BTEX from wastewater via ASTP technique

- To apply the appropriate composition and total concentration of cationic-anionic surfactant mixtures obtained from phase 2 to extract the BTEX from wastewater and find out the extraction efficiency in the presence of electrolytes.

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 BTEX compounds

2.1.1 Characteristics of BTEX

BTEX are found naturally in many petroleum products such as crude oil, diesel fuel and gasoline. They are also used extensively in manufacturing processes. Benzene is used in the production of synthetic materials and consumer products, such as synthetic rubber, plastics, nylon, insecticides and paints. Toluene is used as a solvent for paints, coatings, gums, oil, and resins. Ethylbenzene may be presented in consumer products such as paints, ink and plastics. Xylenes are used as a solvent in printing, rubber, and leather industries (<http://www.envirottools.org/factsheets/btex.pdf>). These compounds are usually colorless, sweet-smelling liquid with aromatic odors. They have high volatility due to its relatively low molecular weight and high vapor pressure as shown in Table 2.1. Among the BTEX, benzene has the highest volatility with lowest boiling point.

Table 2.1 Physical and chemical properties of BTEX

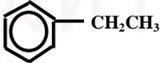
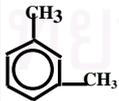
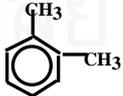
Properties	Benzene	Toluene	Ethyl benzene	m-Xylene	o-Xylene	p-Xylene
Chemical structure						
Chemical formula	C ₆ H ₆	C ₇ H ₈	C ₈ H ₁₀	C ₈ H ₁₀	C ₈ H ₁₀	C ₈ H ₁₀
Molecular weight [g/mole]	78	92	106	106	106	106
Boiling point (°C)	80.09	110.63	136.19	139.12	144	138.37
Water solubility[mg/L]	1700	515	152	-	175	198

Table 2.1 (cont.) Physical and chemical properties of BTEX

Properties	Benzene	Toluene	Ethyl benzene	m-Xylene	o-Xylene	p-Xylene
Vapor pressure(at 20 °C)[mm Hg]	95.2	28.4	9.5	-	6.6	-
Specific density (at 20 °C)	0.8787	0.8669	0.8670	0.8642	0.8802	0.8610
Henry's law constant (at 25 °C) [kPa·m ³ /mole]	0.55	0.67	0.80	0.70	0.50	0.71
Polarity	Non-polar	Non-polar	Non-polar	Non-polar	Non-polar	Non-polar

(Source: Jesper and Jason, 1996; Anne, 2000)

2.1.2 The effect of BTEX on environment

The main sources of BTEX emitted into the environment are the petroleum and chemical industries, mainly by a release from large bulk facilities, surface spills, and pipeline leaks and other combustion processes. They are also released when natural materials are burned. Trace amounts are found in cigarette smoke. Most releases of BTEX end up in the atmosphere, although some can be bound to soils and sediments. They react with other air pollutants and return to the earth or involve in the formation of photochemical smog. In general, environmental concentration of BTEX is unlikely to damage the environment, but high concentration resulting from a spillage is moderately toxic to aquatic life. However, bioaccumulation and concentration through the food chain is unlikely a significant concern. As VOCs, BTEX are involved in the formation of ground level ozone that can damage crops and materials. (http://www.sepa.org.uk/data/eper/contextual_info.aspx).

2.1.3 The effect of BTEX on human health

The exposure of BTEX to human can be occurred by inhalation of contaminated air containing BTEX vapors, ingestion of contaminated water or food containing BTEX, or by dermal contact with BTEX in liquid form. Acute exposure to high levels of BTEX will cause skin and sensory irritation, central nervous system

depression, and the respiratory system deficiency. Long-term exposure to these compounds has the effects on kidney, liver and blood systems (<http://www.envirottools.org/factsheets/btex.pdf>). Most studies have been concerned on benzene, which is the only proven carcinogen. Benzene is suspected to cause the leukemia. Strong evidence between long term benzene exposure and leukemia has been found. Upon exposure to benzene, it will move into the blood stream and get into fatty tissues where can undergo reactions producing phenol, which can cause a stronger carcinogenic effect than benzene. An inhalation of toluene and xylene at concentration of 0.4 mg/L causes headache, dizziness and irritation of the mucous membranes. At higher concentration, toluene and xylene can lead to a reduced ability of co-ordination. Long term exposure of toluene and xylene has been proven to cause brain damage, but neither toluene nor xylene is carcinogens (Jesper and Jason, 1996).

2.2 Surfactant

2.2.1 Characteristic of surfactants

Surfactant is a contraction of a term surface active agent. Sometime it is also called amphiphile or detergent. It is one of the most widely used classes of chemicals. They have applications in many areas, including industries, agricultures, and households. Surfactants consist of hydrophobic tail or water-insoluble long-chain hydrocarbon linked to hydrophilic head or water-soluble group as shown in Figure 2.1 (Olivier, 2003). This combination makes the surfactant ambivalent; the hydrophilic head group is attracted to polar environments, for example water, while the hydrophobic tail is attracted to nonpolar environments, such as oil. Thus, the surfactants can dissolve in either aqueous or oil phase and have the ability to solubilize water or oil to create homogeneous system (Uppgård, 2002).

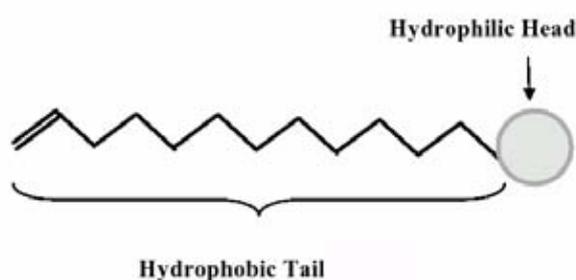


Figure 2.1 Surfactant molecule or monomer

2.2.1.1 Type of surfactants

The classification of surfactants is based on the charge of their hydrophilic head. They can be classified into four types as follows; (Milton, 1989; Salager, 2002).

- Anionic: surfactants with the negative charge at the head portion, which are the most commonly used surfactants including alkylbenzene sulfonates (detergents), soaps (fatty acid), lauryl sulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent), lignosulfonates (dispersants), etc. Anionic surfactants account for about 50 % of the world production.

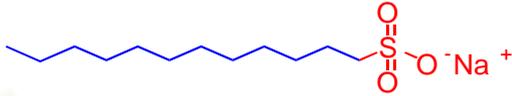
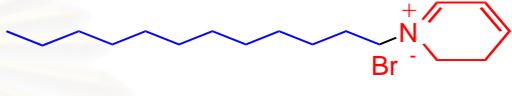
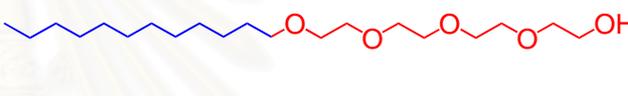
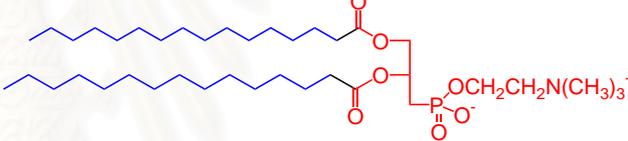
- Cationic: surfactants possess the positive charge at the head portion. A very large proportion of this class corresponds to nitrogen compounds such as fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type, often coming from natural fatty acids. In general, these surfactants are more expensive than anionic because of the high-pressure hydrogenation reaction used during synthesis.

- Nonionic: surfactants which hydrophilic group has no ionic charge. They account for about 45 % of the overall industrial production. They do not ionize in aqueous solution because their hydrophilic group is a non-dissociable type, such as alcohol, phenol, ether, ester, or amide. A large proportion of nonionic surfactants used in industries has their hydrophilic portion as a polyethylene glycol chain, obtained by the polycondensation of ethylene oxide. Hence, they are called polyethoxylated nonionic surfactant.

- Zwitterionic: surfactants which their charges depending on pH, i.e. they possess positively charged at low pH, negatively charged at high pH, and at neutral pH, have both negatively and positively charged. They are generally expensive and consequently, their use is limited to very special applications e.g. cosmetics.

Table 2.2 shows these four surfactant types along with the structures and examples.

Table 2.2 Classification of surfactant molecules

Hydrophilic group	Examples	Structure
Anionic	Sodium dodecylsulfate (SDS)	
Cationic	Cetylpyridinium bromide	
Nonionic	Polyoxyethylene(4) lauryl ether (Brij 30)	
Zwitterionic	Dipalmitoyl phosphatidylcholine (lecithin)	

(Source: Milton, 1989; Rixt, 2001)

With the continuous improving surfactant properties, a promising system of surfactant mixture comprising of cationic-anionic surfactant has been discovered. They can be in a neutral form at their stoichiometry ratio and often have a better performance than the individual components (Khan and Marques, 2000). In addition, many systems of cationic-anionic surfactant mixture exhibit interesting properties and molecular structures including bolaforms, gemini, polymeric and polymerisable surfactants as shown in Figure 2.2 and Table 2.3 (Rixt, 2001; Robb, 1997; Holmberg, 1998).

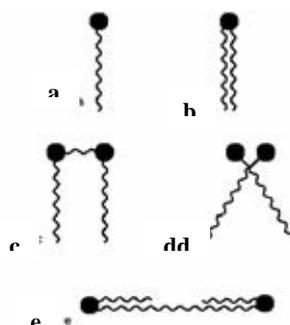
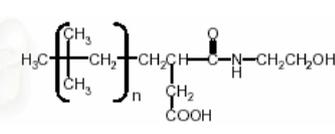
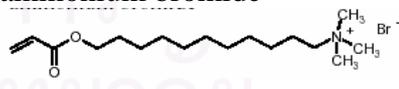


Figure 2.2 Schematic representation of different types of surfactants : (a) single-tailed, (b) double-tailed, (c) and (d)gemini, (e) bolaform

Table 2.3 Structural features and examples of new surfactant classes

Classes	Structural characteristics	Example
Catanionic	Equimolar mixture of cationic and anionic surfactants (no inorganic counterion)	<i>n</i> -dodecyltrimethylammonium <i>n</i> -dodecyl sulfate (DTADS) $C_{12}H_{25} (CH_3)_3 N^+ O_4 S C_{12}H_{25}$
Bolaform	Two charged headgroups connected by a long linear polymethylene chain	Hexadecanediyl-1,16-bis(trimethyl ammonium bromide) $Br^- (CH_3)_3 N^+ (CH_2)_{16} N^+ (CH_3)_3 Br^-$
Gemini (or dimeric)	Two identical surfactants connected by a spacer close to or at the level of the headgroup	Propane-1,3-bis(dodecyl dimethyl ammonium bromide) $C_3H_6 -1,3-bis[(CH_3)_2 N^+ C_{12}H_{25} Br^-$
Polymeric	Polymer with surface active properties	Copolymer of isobutylene and succinic anhydride 
Polymerisable	Surfactant that can undergo homopolymerisation or copolymerisation with other components of the system	11-(acryloyloxy)undecyltrimethyl ammonium bromide 

(Source, www.chm.bris.ac.uk/.../1%20Surfactant%20chemistry%20and%20general%20phase%20behaviour.pdf)

2.2.1.2 Aggregation behavior of surfactants

At low surfactant concentration in aqueous solution, surfactant presents as monomer in the solution as well as adsorbed at the interface. If the surfactant

concentration is increased, the monomers start to interact, self-assemble, and aggregate forming a new structure when the concentration of surfactant exceed a certain value called the critical micelle concentration (CMC) for micelle formation or the critical aggregation concentration (CAC) in the case of variation of aggregate formations (Herrington and Kaler, 1993; Uppgård, 2002; Rixt, 2001) as will be discussed below.

The simplest new structure formed by the aggregation of monomer is called micelle, where hydrophilic heads orient toward the water. The attractive tail-tail hydrophobic interaction provides the driving force for the aggregation, while the electrostatic repulsion between the polar head groups limits the size (Aswal, 2003). When dissolved in non-polar organic solvents, surfactants form reversed micelles where the hydrophilic portions are shielded from contacting with the surrounding solvent, as seen in Figure 2.3. In the micelle, the hydrophobic tails flock to the interior to minimize their contact with water and the hydrophilic heads remain on the outer to maximize their contact with water. The micellization process in aqueous solution results from a delicate balance of intermolecular forces, including hydrophobic, steric, electrostatic, hydrogen bonding, and van der Waals interactions (Israelachvili, 1991; Tanford, 1980).

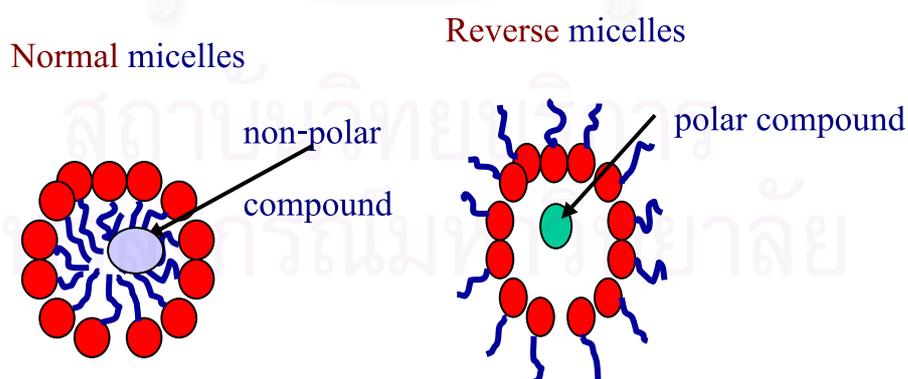


Figure 2.3 Micelle and reversed micelle

At surfactant concentration higher than the critical micelle concentration (CMC), molecular aggregates termed micelles are formed. The CMC value may be attained graphically by plotting a physicochemical property of the solution, i.e. surface tension, conductivity, turbidity, osmotic pressure, fluorescence, and light scattering, versus the surfactant concentration. The value of the CMC is determined by the discontinuity in the plot, or the sudden variation in the above relation as given in Figure 2.4 (Milton, 1989; Hiemenz and Rajagopalan, 1997).

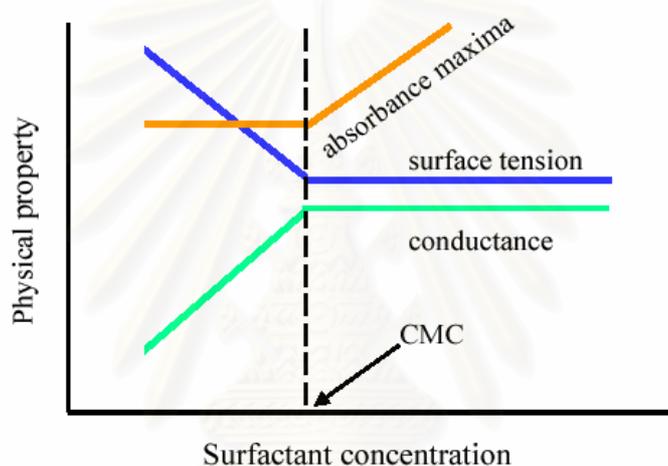


Figure 2.4 Measurement of CMC based on several solution parameters

In general, surface tension measurements can be used to determine the CMC value since the surfactant monomers disrupt the hydrogen bonding between water molecules at the surface and thus lower the surface tension. At the CMC the water/air interface is saturated with surfactant monomers and the reduction of the surface tension strongly diminishes. The magnitude of the CMC value is specific for each surfactant (Uppgård, 2002).

At lower concentration than the CMC, only monomers are presented. On the other hand at concentration above the CMC, there are micelles in equilibrium with monomers as shown in Figure 2.5. However, the CMC may vary depending on the

variation in hydrophobicity, counterion, or electrolyte concentration (Hiemenz and Rajagopalan, 1997).

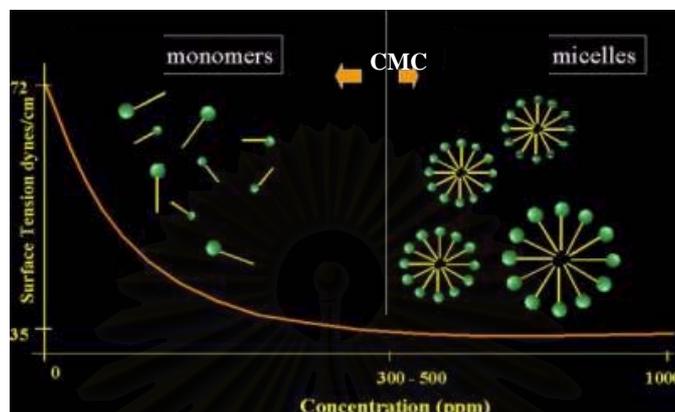


Figure 2.5 Graph shows monomer-micelle relationship

2.2.1.3 Aggregate Morphologies

The aggregation structures of surfactant in aqueous solution depend on the chemical structure of surfactants and solution condition such as concentration, temperature, pressure, pH and ionic strength. The structure can be in form of spherical micelles, worm-like micelles, vesicles, bilayer fragment, and reversed micelle, etc. (Figure 2.6). These structures can transform from one to another when solution conditions are changed (Aswal, 2003; Uppgård, 2002).

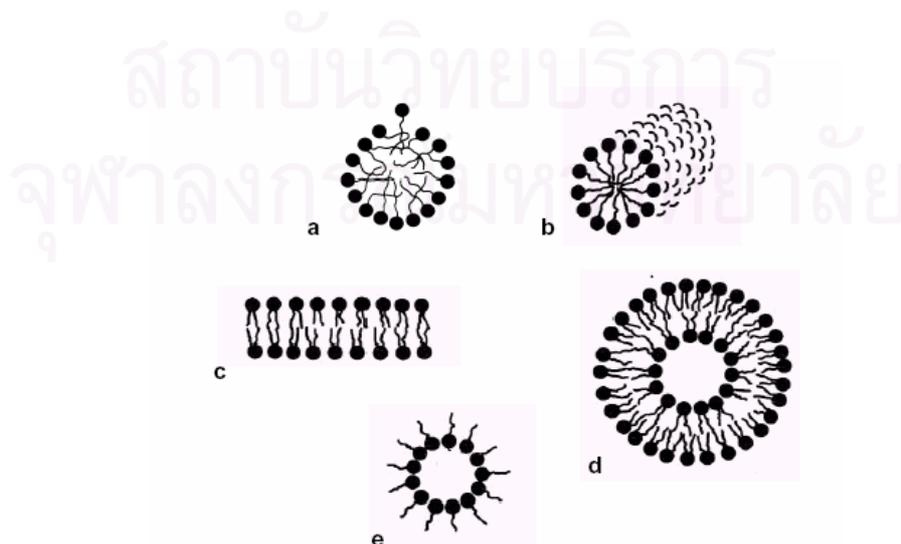


Figure 2.6 Typical aggregate morphologies into which surfactant self-assemble in aqueous solution : (a) spherical micelle (b) wormlike micelle (c) bilayer fragment (d) vesicle (e) reversed micelle

- Spherical micelles

Generally, 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 (Rixt, 2001).

- Wormlike micelles

Both theoretical and experimental studies show that wormlike micelles are long typically in scale of several tens of micrometers. 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 wormlike micelles can often be induced by addition of strongly binding counter ions to ionic surfactants in aqueous solution (Rixt, 2001).

- Vesicles

In general, surfactant molecules possessing one head group and two alkyl tails form vesicles in aqueous solution. A vesicle is a shell, consisting of a surfactant bilayer, which encapsulates an aqueous interior (Figure 2.7). A particle is also called an onion or a multilamellar vesicle. 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 (Rixt, 2001; Persson, 2003).

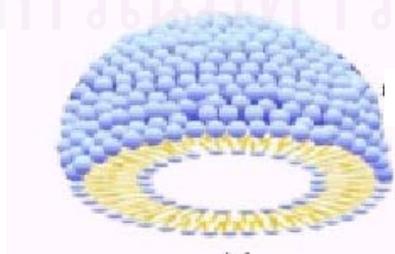


Figure 2.7 A schematic picture of a vesicle

2.2.1.4 Packing parameter

The relationship between the shape of the surfactant monomer and the aggregate morphology can be represented by the packing parameter approach. The packing parameter (P) is calculated from equation (1). 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.

$$P = V / a_0 l \quad (1)$$

However, the most difficult parameter to determine is the area per headgroup, a , especially for ionic surfactant which is sensitive for both electrolyte and surfactant concentration. An increase of P for a single chain ionic surfactant can be accomplished by i) increasing the length of the hydrocarbon chain, where V/l will be constant but a will decrease due to larger chain attraction ii) addition of salt in which a is reduced iii) increasing the branching of the chain, whereby reducing l for a given V iv) using surfactants with two hydrocarbon chains that increase V but have no effect on l v) addition of a surfactant with oppositely charge, that results in a reduction of a (Boschkova, 2002).

Surfactants where $0 < P < 1/3$, the relative bulkiness of the polar part dominates, the aggregates show a strongly curvature towards water, and spherical micelles are formed. If $1/3 < P < 1/2$, wormlike micelles are formed whereas surfactants with $1/2 < P < 1$ form vesicles. Inverted structures are formed when $P > 1$. Table 2.4 shows the relationship of the architecture of surfactant monomer and aggregate morphology (Israelachvili, Michel and Ninham, 1976).

Several authors have criticized this packing parameter for predicting the aggregate morphology.

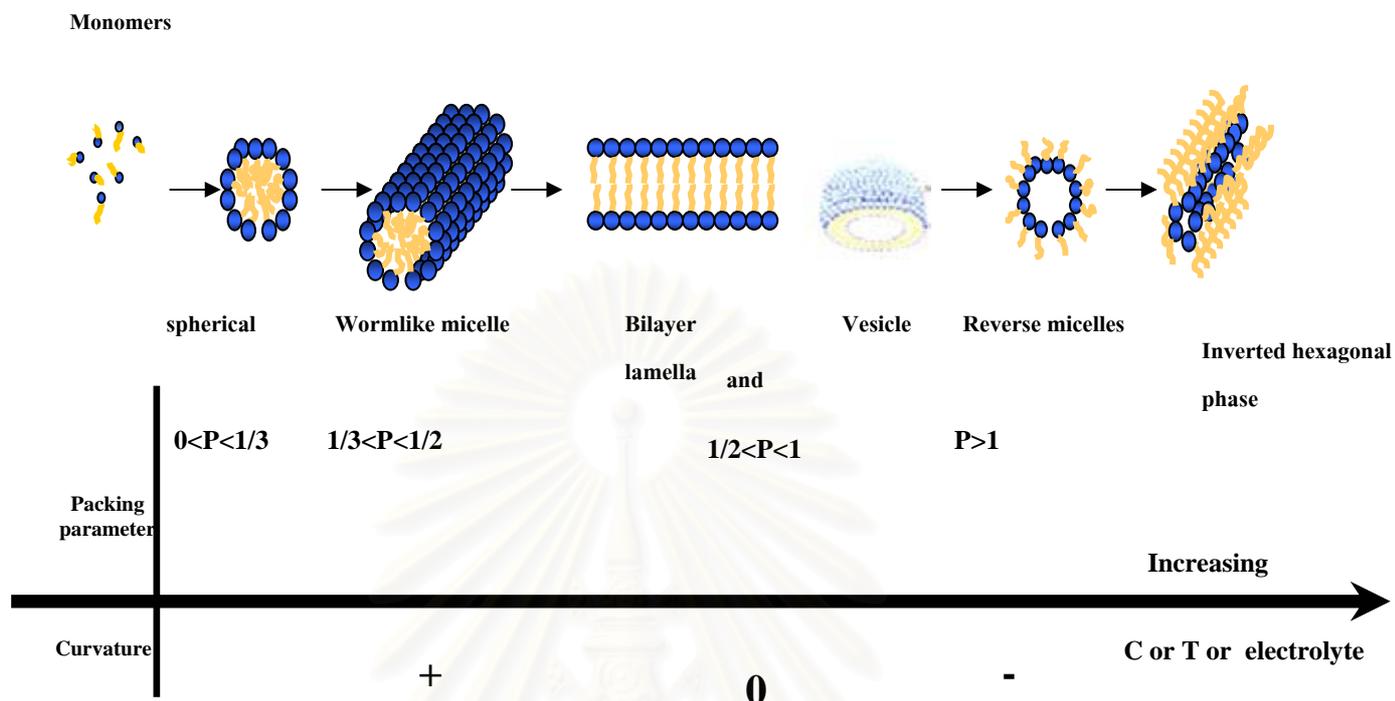


Figure 2.8 An idealized sequence of the structures found in surfactant systems as a function of surfactant concentration or temperature or electrolyte

Table 2.4 Relationship between the shape of surfactant monomers and preferred aggregate morphology

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

Table 2.4 (cont.) Relationship between the shape of surfactant monomers and preferred aggregate morphology

Effective shape of the surfactant molecule	Packing parameter	Aggregate morphology
 inverted (truncated cone)	> 1	Inverted micelles

(Source: Rixt, 2001)

2.2.1.5 Solubilization

The reason why surfactant monomers form aggregates is to minimize the free energy of the solution. As a result, the shape of surfactant aggregates brings about interesting properties e.g. their ability to solubilize the solute molecules into the inner core of the micelle, viscosity, cloud point phenomenon (Milton, 1989).

The micelles have the ability to dissolve hydrophobic substances into the core of their structure. This is known as micellar solubilization and the solubilized substance being termed the solute or the solubilizate. Solubilizates are incorporated into the micelles in different location according to their structure (Figure 2.9) (<http://hls.dmu.ac.uk/teaching/gsmith>).

- (a) Saturated solubilizates dissolve in the interior non-polar part of the micelle.
- (b) Solubilizates possessed weakly polar or polarizable groups (such as double bonds) locate nearer the micelle surface.
- (c) Amphiphillic solubilizates orient alongside with surfactant monomers.
- (d) Water-soluble solubilizates are thought to form complex with the polyoxyethylene chain, i.e. the pallisade layer surrounding the hydrocarbon core.



Figure 2. 9 Aggregate of surfactant monomers to form micelle and possible solubilization sites of the micelle

2.2.1.6 Surfactants utilization in extraction process

The two-phase separation of the surfactant solution known as aqueous surfactant two-phase system (ASTP) can be used as the extraction technique. The phase separation behavior results from the competition between internal energy and entropy. The internal energy promotes the separation of micelles from water but the entropy promotes the miscibility of micelles in water (Liu, Nikas, and Blankschtein, 1996). In general, the nonionic surfactant is frequently used to induce the phase separation due to its special characteristic. When the aqueous solution of nonionic surfactant is heated above a certain temperature so called the cloud point (Watanabe, Tani, and Kamidate, 1998), the phase separation occurs forming two isotropic phases. The two phases consist of a surfactant-depleted phase so called the diluted phase, where the concentration of surfactant in this phase is as low as a few times of their CMC and a surfactant-rich phase so called the coacervate phase, where most of surfactant aggregates present in this phase in a concentrated form as shown in Figure 2.10. As a result, the organic pollutants of environmental concern, which are

solubilized in the hydrophobic core of micelles, can be extracted and accumulated into the surfactant-rich phase (Watanabe, Tani, and Kamidate, 1998).

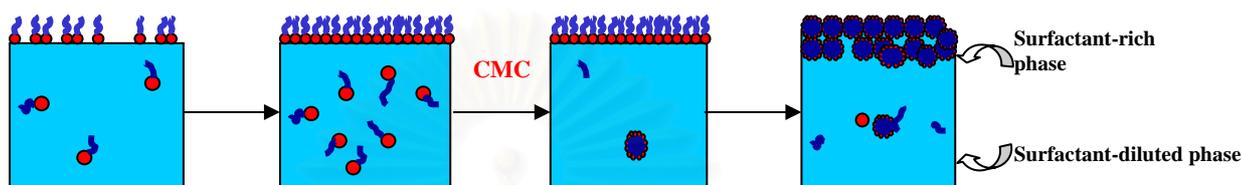


Figure 2.10 schematic illustration of phase separation in the aqueous solution

These systems are formed by environment friendly surfactants that can be used even with the biological materials, and their performance can be controlled and optimized by varying solution condition. In addition, these systems can also readily scaled up. All these attractive features make two-phase aqueous surfactant systems a convenient and potentially useful method for the separation, purification, and concentration of biomaterials. As mentioned in the introduction, although there are several techniques available to remove contaminants from wastewater, they have several limitations and concerns (Nikas, Liu, Srivastava, Abbott, and Blankschtein, 1992; Hinze, 1993; Liu, Nikas, and Blankschtein, 1995, <http://www.amcec.com/case3.html>). As compared with the conventional solvent extraction, the two-phase system is formed in aqueous solution and thus needs no handling of large amounts of organic solvent; therefore it is economical and safe since most of organic solvents are hazard (Tong, 1998). In addition, the contaminants in the surfactant-rich phase can be separated out of the surfactant aggregate leaving the contaminant-free surfactant for reuse by common procedures, i.e. precipitation for ionic surfactant or vacuum/gas stripping for nonionic surfactant if the contaminants have high enough volatility (Xiao et al., 2000; Trakultamupatum, 2002).

The ASTP technique was firstly applied by Watanabe, Ishii, and Junishiro in 1977 to separate and preconcentrate metal ions (Ni (II)) from aqueous solution by using a nonionic surfactant, Triton X-100 as the extractant and 1-(2-thiazolylazo)-2-naphthol (TAN) as a chelating agent. This technique was further studied by Bordier in 1981 to extract the hydrophobic membrane proteins by using Triton X-114. Trakaltamupatam, Scamehorn, and Osuwan (2002) applied this technique to remove benzene, toluene, and ethylbenzene from wastewater also by using Triton X-114. The results showed that the aromatic contaminants can be solubilized into the micelles and the extraction efficiency increased with increasing temperature, added electrolyte concentration, and degree of alkylation of the solutes.

Moreover, the zwitterionic surfactant was investigated for extraction of organic and biomaterial by Saitoh and Hinze in 1991. They extracted bacteriorhodopsin into the 3-(nonyldimethylammonio) propylsulfate (C_9 APSO₄) – rich phase with a yield of 90 %, while decyl analog (C_{10} APSO₄) system, biological compound such as steroidal hormones and vitamin E were effectively extracted.

Interestingly, Zhao and Xiao (1996) have introduced a novel ASTP technique formed by mixtures of a cationic-anionic surfactant. They reported the extraction condition when cationic surfactant; dodecyltriethylammonium bromide (C_{12} NE) or anionic surfactant; sodium dodecyl sulfate (SDS) is in excess. The ASTP system can be formed at specific surfactant concentration and composition.

Tong et al. (1998) applied this separation technique to extract several dyes from wastewater e.g. anthraquinone, methyl red, methylene blue, porphyrin compounds, and metalloporphyrins by using a mixture of C_{12} NE and SDS. It was found that anthraquinone and methyl red, which have higher hydrophobicity than methylene blue, were extracted into the surfactant-rich phase, while hydrophilic methylene blue distributed in the two phase almost uniformly. Moreover, porphyrins with sulfonic or carboxyl substituted groups as negatively charged species could be

extracted into the surfactant-rich phase effectively, while the extraction efficiency of positively charged groups substituted porphyrins are about 30% only.

In addition, Tong, Dong, and Li (1999) also investigated the system consisting of sodium perfluorooctanoate (SPFO) and $C_{12}NE$ to extract dyes and porphyrin compounds. The result showed that the positively charged porphyrins are extracted with high extraction efficiency into the surfactant-rich phase, but the results of negatively charged porphyrins are not satisfactory.

Another investigation has been done by Xiao et al. (2000) for separation and purification of biomaterials e.g. bovine serum albumin (BSA) and lysozyme in the ASTP system formed by $C_{12}NE$ and SDS. It was shown that when $C_{12}NE$ is in excess, negatively charged BSA and positively charged lysozyme are concentrated in the surfactant-rich phase and in the surfactant-diluted phase, respectively. In contrary, if SDS is in excess, BSA partitions to the surfactant-diluted phase and lysozyme partitions to the surfactant-rich phase.

2.3 Catanionic surfactant mixture system

The catanionic is a new type of surfactant system which can form ASTP at appropriate total concentration and composition of mixed surfactant (Zhao and Xiao, 1996; Herrington and Kaler, 1997). The catanionic surfactant mixtures can be applied to separate various compounds as previously mentioned. Some aqueous solutions of catanionic surfactant mixtures often form precipitate with water, especially those containing alkyl carboxylate as one of the surfactants and the highly symmetric straight chain. However, the precipitate can be redissolved to form mixed micelles on adding an excess amount of one of the two parent ionic surfactant. In some cases, they produce vesicles, when an excess amount of one of the two parent surfactant is added. However, increasing the asymmetry of the cationic and anionic surfactant alkyl tails can also widen the composition range over which vesicles appear and lessen the precipitation region in mixed cationic/anionic surfactant systems (Yatcilla, 1996). Studies on catanionic mixtures have an important contribution to the

fundamental issue of vesicle formation because of its stability or a thermodynamically stable state in aqueous surfactant systems (Kaler and Herrington, 1992; Huang and Zhao, 1995; Brasher and Kaler, 1996; Khan and Marques, 1997; Södermann, Herrington, and Kaler, 1997).

As cationic/anionic molar ratio (A^+/A^-) or the total concentration is varied, different aggregate shape transitions and phase equilibria can be found: (i) micelles/vesicles; (ii) vesicles/liquid crystals; (iii) vesicles/precipitate; and (iv) monomers/vesicles. A schematic diagram depicting the equilibria between the cationic vesicles and other phases is shown in Figure 2.11 (Robb, 1997).

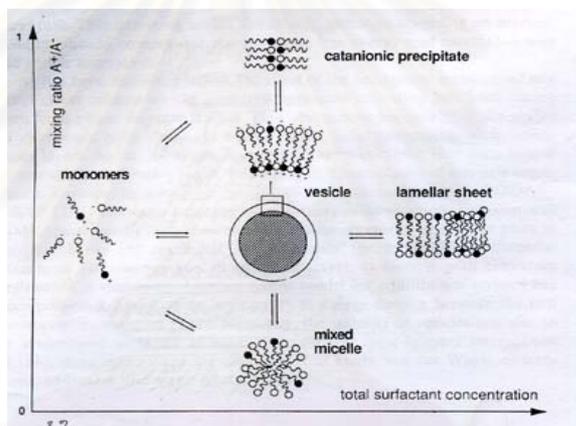


Figure 2.11 The difference phase equilibria for the cationic vesicles as a function of mixing ratio and total surfactant concentration.

Their aqueous mixtures also perform many superior properties as compared to a single surfactant system. These properties are both fundamental and commercial issues of interest since the cationic surfactant mixtures enhance the adsorption and have much lower CAC. In addition, the cationic surfactant aggregates are more tightly packed than the other types of aggregates due to the reduction in the repulsion force between oppositely charged head groups resulting in the smaller effective head group area. Moreover, the volume of the alkyl part of the surfactant increases owing to the presence of the second alkyl tail. Correspondingly, the increase in volume of the aggregation provides more capacity for solute molecules to solubilize therein. (Herrington and Kaler, 1997; Khan and Marques, 2000; Rixt, 2001).

Furthermore, the morphology of cationic aggregates differs from the single surfactant. The individual surfactant forms micelles in aqueous solution, while the vesicle is formed spontaneously in aqueous solution of cationic surfactant as mentioned before (Herrington and Kaler, 1997; Rixt, 2001). Moreover, the vesicle provides more available sites for solubilization than the micelles (Hinze and Armstrong, 1987).

In the viewpoint of economy, the cationic surfactant forms aggregate at the CAC which is generally less than CMC, therefore the quantity of surfactant needed to form the aggregates is less than that needed for pure surfactant to form the normal micelle at the CMC.

2.4 The effect of electrolyte on ASTP

Numerous investigators reported that the addition of electrolyte drastically affects the phase behavior of the ASTP system. The addition of NaCl and NaBr show the “salting out” effect and thus, decrease in cloud point temperature of the nonionic surfactant and this phenomenon can be enhanced by increasing electrolyte concentration. On the other hand, the addition of NaI, CaCl₂, Ca(NO₃)₂, and Al(NO₃)₃ show the “salting in” effect and elevate the cloud point temperature (Schick, Atlas, and Eirich, 1962; Arai, 1967).

Mukerjee (1967) explained that the addition of electrolyte has been presented mainly by the “salting out” or “salting in” effect of the hydrophobic groups. Salting in or salting out by an ion depends upon whether the ion is a water structure breaker or a water structure maker. Ions with a large ionic charge/radius ratio, such as F⁻, are highly hydrated and are water structure makers. They salt out the hydrophobic groups of the monomeric form of the surfactant and decrease the CMC. Ions with a small ionic charge/radius ratio, such as SCN⁻, are water structure breakers. They salt in the hydrophobic groups of the monomeric form of the surfactant and increase the CMC.

In 1988, Imae et al. reported that the liquid-liquid phase separation of surfactant solution with the presence of simple salts is induced by the destruction of the specific attractive interaction between the surfactant and water such as hydrogen bonding. So, the attractive interaction of surfactant is strengthened leading to micellar growth.

Furthermore, there are publications reporting salt effects on CMC values of nonionic surfactants. Ray and Nemethy (1971) described that the CMC is lowered by all inorganic salts except LiI, which raises the CMC of OPE₃₀ (p-tert-octylphenoxy (polyethoxy)-ethanols). The salting out effectiveness of the inorganic ions are as follows: $0.5\text{SO}_4^{2-} > \text{F}^- > \text{Cl}^- > \text{ClO}_4^- > \text{Br}^- > \text{NO}_3^- > \text{I}^-$, SCN^- and $\text{Na}^+ > \text{K}^+ > \text{Li}^+ > 0.5\text{Ca}^{2+}$. Likewise, Miyagishi et al. (2001) showed the similar result as; $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Cs}^+ > \text{Li}^+$ for cation and $\text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{SO}_3^{2-} > \text{HPO}_4^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^- > \text{SCN}^-$ for anion. In addition, even the CMC of nonionic surfactants are lowered by adding salt, but with less degree than those of ionic surfactants. (Shick et al., 1967).

For the same cation Na^+ , the effect of anions decreases depending on the charge/radius ratio in the order $\text{F}^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{PO}_4^{3-} > \text{Br}^- > \text{citrate}^- > \text{I}^- > \text{SCN}^-$. For the same anion Cl^- , the effect of cations follows the order $\text{K}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Li}^+ > \text{Ca}^{2+} > \text{Al}^{3+}$. The reason for the order of cations is not clear. Thus, the effectiveness of the salts is correlated with the charge/radius ratios of the ions, and it is clear that cations and anions have disparate effect. The results are discussed in terms of the structure-making and structure-breaking properties (Zhang, Somasundaran, Maltesh, 1996).

Klevens (1950) described about effect of electrolyte on solubilization, the small amounts of neutral electrolyte added to ionic surfactant solutions will increase the extent of solubilization of hydrocarbons that are solubilized in the hydrophobic region of the micelle. In addition, the neutral electrolyte added to solutions of nonionic POE surfactants increases the extent of solubilization and causes an increase in the aggregate number of the micelles. The order of increase in solubilization appear to the

same pattern mentioned above for depression of the cloud point: $K^+ > Na^+ > Li^+$; $Ca^{2+} > Al^{3+}$; $SO_4^{2-} > Cl^-$ (Saito, 1967).

For cationic surfactant systems, Israelachvili (1976) reported that a combination of counter ion of ionic surfactants leads to a decrease of the effective head group area. This result affects on an increase in packing parameter, volume of alkyl part of the surfactant and consequently the surfactants self-assemble into a less curved aggregate. This phenomenon corresponds to the microstructure transformation from spherical to wormlike micelles.

Herrington et al. (1995) revealed the effect of added electrolyte on the phase behavior of cetyltrimethylammonium bromide (CTAB) and sodium octyl sulfate (SOS) with added sodium bromide (NaBr). They summarized that addition of a monovalent salt alters the electrostatic contribution to the free energy of aggregation and thus changes the equilibrium phase behavior and aggregation properties. Owing to added salt, increased screening between charged head groups produces a smaller effective head groups area causing the phase transition to larger and flatter structures.

Yin et al. (2002) concluded that the addition of salt transforms the small micelles into large aggregates (the rodlike micelles and lamellar structure) and leads to the phase separation upon the addition of NaBr of dodecyltrimethylammonium bromide (DTAB) / Sodium laurate (SL) mixed system.

Despite many advantages in characteristic of cationic surfactant mixtures, there are very limited amounts of work devoted to investigate the ability of these surfactant systems to extract the organic compounds of environmental concerns such as BTEX, pesticides and toxic dyes. So, this research aims to study in the extraction aspect using ASTP technique to remove a various kind of pollutants from the wastewater. Moreover, the effect of added electrolytes on the extraction performance will be investigated.

CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 Surfactants

Two surfactants were studied in this work and their properties are listed in Table 3.1. Dodecyltrimethylammonium bromide (DTAB) is cationic surfactant purchased from Nanjing Robiot Co., Ltd. (China), with purity of 99% and Alkyl diphenyloxide disulfonate (ADPODS or DOWFAX 8390) is anionic surfactant contributed from DOW Chemical Co., Ltd. (USA) with 35% active.

Table 3.1 Physical and chemical properties of surfactant

Surfactant trade name	Ionic form	Chemical name	Chemical formula	MW (g/mol)	CMC(mM)
DTAB	cationic	Dodecyltrimethylammonium bromide	$C_{15}H_{34}BrN$	308.3	15 @ 20 °C ^a 14.6±0.3 @ 17 °C ^b 14.4±0.2 @ 25 °C ^c 14.2±0.1 @ 29 °C ^d
DOWFAX 8390	anionic	Alkyl diphenyloxide disulfonate	$C_{16}H_{33}C_{12}H_7O(SO_3Na)_2$	642	0.663 ^e 1.5 ^f 3.0 ^g

(Source: ^aJönsson et al., 1998; ^{b, c and d}Loh, Teixcira and Lee, 2004; ^eVane et al., 2000; ^fRouse, Hirata and Furukawa, 2001; ^gwww.dow.com/webapps/lit/literature.asp.filepath=surfactant/pdfs/noreg/119-01970.pdf&pdf=true.)

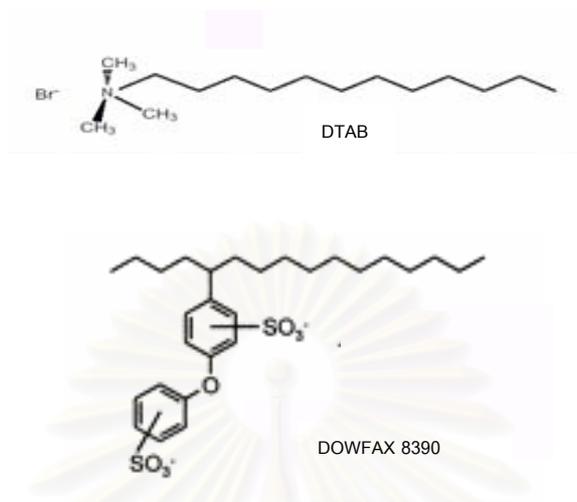


Figure 3.1 Structures of DTAB and DOWFAX 8390

Five types of cationic and anionic surfactants were used in the preliminary step to investigate if phase separation can occur as briefly described in Table 3.2.

Table 3.2 Physical and chemical properties of surfactant in preliminary study

Surfactant trade name	Ionic form	Chemical name	Chemical formula	MW (g/mol)
CTAB	cationic	Cetyltrimethylammonium bromide	$C_{19}H_{42}BrN$	364.5
TTAB	cationic	Tetradecyltrimethylammonium bromide	$C_{17}H_{38}BrN$	336.4
$C_{12}NE$ or DEAB	cationic	Dodecyltriethylammonium bromide	$C_{18}H_{41}BrN$	350
SDS	anionic	Sodium Dodecyl Sulphate	$C_{12}H_{25}OSO_2ONa$	288.4
AMA or Aerosol MA	anionic	Sodium Dihexyl Sulfosuccinate	$C_{16}H_{30}O_7SNa$	388

3.1.2 Volatile organic compounds (VOCs)

The VOCs included benzene, toluene, ethylbenzene, and xylene (mixture of isomers) with purity higher than 99% were purchased from Carlo Erba Reagent (Italy), Carlo Erba Reagent (Italy), Acros Organics (Belgium), and Scharlau (Spain), respectively.

3.1.3 Electrolytes

NaCl, KCl, LiCl, NaF, NaI, MgCl₂ of analytical grade with purity higher than 99% were used as the electrolytes. NaCl, KCl, and MgCl₂ were purchased from Ajax chemical (Australia). NaF and NaI were purchased from BDH (England). LiCl was a product of Fisher Scientific (England).

All chemicals were used as received. The water utilized in all studies was deionized and distilled.

3.2 Experimental procedure

The cationic surfactant aqueous solution were prepared at 50 mM, 2:1 molar ratio of DTAB and DOWFAX with 100 ppm of contaminant in the presence or absence of electrolyte into the volumetric flask. Each surfactant was prepared by precisely weighing the DTAB crystals and concentrated DOWFAX solution into the 50 mL volumetric flask. Electrolyte was then weighed and added into the flask. Later on, VOCs was pipetted carefully into the volumetric flask followed by adjusting the volume of solution by deionized water. The sample was mixed by vortex stirrer for 15 minutes and then transferred into the two 22 mL vial sealed with rubber septa. The samples must be prevented from headspace loss, so the samples must occupy almost all of vial volume to avoid the vapor volume. The samples were equilibrated in a water bath controlled at 30 °C for 4 days. When the equilibrium is approached, which is defined as the condition where no further change in the surfactant-rich phase

volume and concentration of surfactant in both phases are observed, the volume of each phase was measured by the solution height. Then the top and bottom phases were collected carefully. Calibration curves of the surfactant-rich phase and surfactant-diluted phases were made and the concentrations of surfactants and VOCs in both phases were analyzed. The schematic diagram of experimental procedure is illustrated in Figure 3.2.



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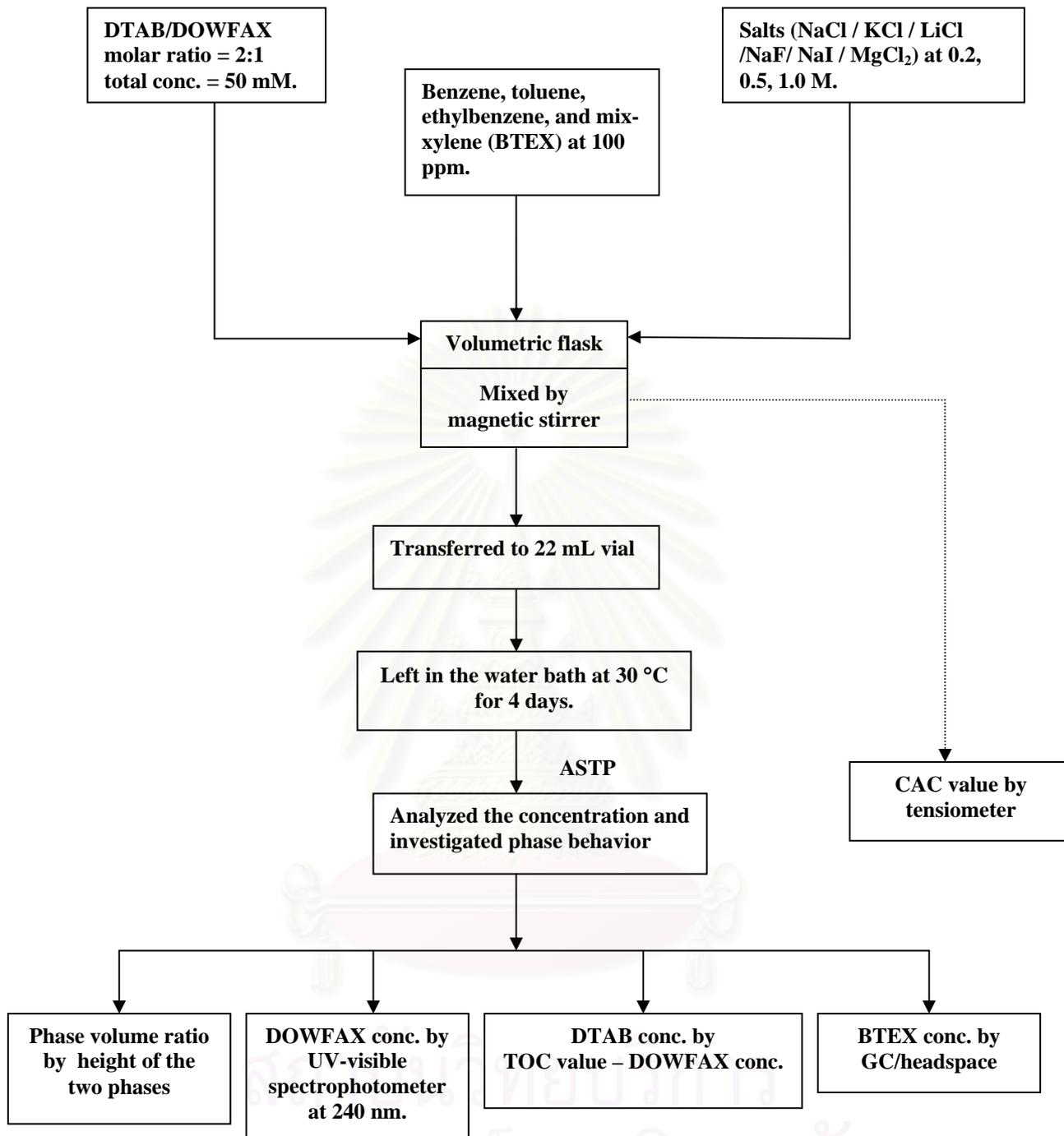


Figure 3.2 Schematic diagram of experimental procedure

3.3 Analytical instruments and method

3.3.1 Determinations of CAC

The CAC values are determined by the point of discontinuity in the plot between surface tension and surfactant concentrations. The surface tension can be measured by tensiometer with a Wilhelmy plate (DataPhysics; Model DCAT 11).

3.3.2 Determination of phase volume ratio

The ratio of the volume of the surfactant-rich phase to the surfactant-dilute phase was calculated by comparing the height of the two phases (the actual volume can be calculated from the solution height and radius of vial using the relationship $v = \pi r^2 h$)

3.3.3 Determination of equilibrium time for phase separation

The phase separation time was determined by no further change in the surfactant-rich phase or coacervate volume and stable value of DOWFAX concentration in both phases. In this study, the equilibrium time for phase separation is about 4 days.

3.3.4 Determination of surfactant concentration

The concentration of DOWFAX was examined using UV-Visible spectrophotometer at 240 nm. (Thermo Electron Corporation; Model Helios Alpha). The concentration of DTAB can be indirectly evaluated by measuring the total surfactant concentration of the mixture using Total Organic Carbon Analyzer (O.I. Analytical Model; 1010) prior deducting with the concentration of DOWFAX previously analyzed by UV-Visible spectrophotometer.

Throughout the experiment, DOWFAX concentration was used to be a representative of total surfactant concentration as it had already been proved that the ratio of DTAB and DOWFAX was 2: 1.

3.3.5 Determination of BTEX concentration

The concentration of BTEX in each phase was analyzed using gas chromatograph (Perkin-Elmer; Model Clarus 500GC) equipped with a flame ionized detector (FID); column: Elite-Wax with 30 m×0.32 mm ID, 0.25 µm film thickness; carrier gas: helium at 20 mL/min; oven temperature: 120 °C for 10 min; injector temperature: 120 °C for 10 min; injector temperature: 250 °C; and detector temperature: 250 °C. The static headspace sampling technique was applied using headspace autosampler (Perkin-Elmer TurboMetrix40). Experimental conditions of the headspace autosampler were as follows; thermostating time: 20 min; oven temperature: 85 °C; needle temperature: 100 °C; transfer line temperature: 110 °C; GC cycle time: 10 min; pressurization time: 2 min; injection time: 0.08 min; and withdrawal time: 0.2 min.

To assure the reliability and accuracy of the experiment, at least triplicate experiments were done and material balance of surfactant and VOCs were also carried out.

CHAPTER IV

Results and Discussion

The results and discussion are divided into three phases corresponded to the objectives of this study.

4.1 Preliminary study

This study aimed to find out a suitable system of cationic-anionic surfactant mixtures, which have the potential to extract BTEX from wastewater based on ASTP technique. The phase separation in aqueous solution of various mixed cationic and anionic surfactant with altering total concentrations, mixing ratios, temperatures and equilibrated time were investigated. The phase behavior of each mixed surfactant was compared by visual observation in order to select the system, which has the possibility to have a phase separation and ability to separate the substance of concern. Nevertheless, the analyses in details in terms of extraction ability to illustrate and confirm the potential are in the next step. Every system of cationic surfactant mixtures was equilibrated within 10-24 hr. Table A (APPENDIX A) shows phase separation behavior of eight cationic surfactant mixtures as follows; 1) CTAB/DOWFAX 2) CTAB/SDS 3) DTAB/SDS 4) TTAB/SDS 5) C₁₂NE/SDS 6) TTAB/DOWFAX 7) DTAB/AMA 8) DTAB/DOWFAX. These cationic aqueous solutions without added electrolyte were prepared with total concentration at 20, 50, and 80 mM, molar ratio at 1:2, 1:1.5, 1:1, 1.5:1 and 2:1, controlled temperature at 30, 40 and 50 °C and equilibrated times such as 10, 15, 17, 20, 21 and 24 hr. In first six systems i.e. CTAB/DOWFAX, CTAB/SDS, DTAB/SDS, TTAB/SDS, C₁₂NE/SDS and TTAB/DOWFAX, they can be solubilized in water to form a homogeneous solution at room temperature. After standing in the water bath, the results reveal that there is no phase separation phenomenon in many systems. In some circumstances, two phase separation could

occur but not in a good condition, for example, both phases are turbid solution or one phase is turbid with the other phase is a clear solution. The system of DTAB/AMA at 1:1 molar ratio and concentration of 20, 50, and 80 mM show separated phase of surfactant-rich as several droplets appearing at the top of the solution when heated at 40 °C. However, there is no phase separation at other molar ratio. For DTAB/DOWFAX system, it consists of two transparent solutions in which one phase is an oil-like phase of surfactant-rich solution while the other phase is water-like phase of surfactant-diluted solution. Thus, DTAB/DOWFAX system was selected for further study because they possess basically desirable features, which make it particularly suitable to be used in extraction work.

4.2 The physicochemical properties of DTAB/DOWFAX system and its phase behavior

4.2.1 Effect of equilibrium time and temperature

The equilibrium time of DTAB/DOWFAX was investigated to find the shortest time required for complete separation of the phases. The temperature was varied from 0 °C to 80 °C. The results show that temperature does not have any significant effect on the occurrence of phase separation. Therefore, the experiments were carried out at ambient temperature. For equilibrium time (Table B and Figure B in Appendix B), a stable aqueous two-phase system with a clear interface approaches in about 71.5 hr or 3 days considering by no longer altering in the surfactant-rich phase volume and concentration of surfactant in both phases. However, the equilibrium time at 4 days will be used in this experiment.

4.2.2 Phase behavior of DTAB/DOWFAX system with various surfactant composition and total concentration in the absence of electrolyte

Aqueous mixtures of DTAB and DOWFAX display many interesting appearances. In this aqueous system, DTAB has one cationic head and one alkyl tail,

while DOWFAX has two anionic heads and one or two alkyl. So, DTAB and DOWFAX system has a balance in stoichiometry at 2:1 molar ratio behaving as pseudo-nonionic surfactant. There are a number of criteria used to consider the suitable systems for the ASTP technique, i.e., the separated phases should be stable with clear interfacial boundary in between, one phase should be less in volume and exists in a concentrated form with high viscosity while the other phase is a bulk aqueous phase which has density similar to water, two phases should be isotropic and transparent. From Table C (APPENDIX C), surfactant precipitation occurs at almost every concentration ($C_t = 50, 80, \text{ and } 110 \text{ mM}$), particularly at 1:2, 1:1.5 and 1:1 molar ratio of DTAB to DOWFAX, which is anionic in excess except at very low concentration ($C_t = 20 \text{ mM}$) which forms a clear solution. Increasing concentration in those mixtures relates to higher quantity of solid crystalline phase.

At concentration of 50, 80, and 110 mM, solutions of anionic in excess (1.5:1), equimolar mixing ratio (2:1) and cationic in excess (2.5:1 and 3:1), separate into two phases; with a drastic difference in concentration between phases. From observation, at 1.5:1 molar ratio of every concentration, the upper phase is turbid while the lower phase is clear solution. For 2:1 molar ratio, the top phase is surfactant-diluted or water-like phase, and the bottom phase is surfactant-rich or oil-like phase. The surfactant-rich phase, volume ratio increases with increasing total concentration except at 110 mM. However, the surfactant partition ratio or the concentration ratio surfactant-rich to surfactant-diluted phase of 2:1 molar ratio at 50 mM is higher than that of 80 mM. For 2.5:1 molar ratio, the top phase is surfactant-diluted and the bottom phase is surfactant-rich phase. However, the bottom phase is not the isotropic solution because there are many oil-like droplets dispersed in the solution. Finally, at 3:1 molar ratio it shows phase separation with unstable interfacial boundary between phases.

In general, catanionic system at equimolar mixing ratio results in a strongly insoluble precipitate such as in the sodium dodecyl sulphate (SDS) / dodecylpyridinium chloride aqueous system where the equimolar mixture produces a crystalline precipitate in equilibrium with solution with monomers. Interestingly, the

neutralization ratio of DTAB/DOWFAX is 2:1, at this ratio the precipitation does not occur but instead forming the two-phase separation or ASTP system. This phenomenon corresponds with Herrington et al.'s report in 1993. They found that the asymmetry of the cationic and anionic surfactant alkyl tails can reduce the precipitation region resulting in less ability to form precipitates.

Moreover, Zhao and Xiao (1996) shows a similar phenomenon of the aqueous mixtures of cationic-anionic surfactants to form ASTP system when cationic or anionic surfactant is in excess. The ASTP systems are formed in the concentration range between the high concentration region and the precipitate-formed region and in very narrow molar ratio around equimolar.

To summary, DTAB/DOWFAX at 2:1 molar ratio, total concentration of 50 mM, the equilibrium at 4 days and 30 °C were chosen as the appropriate condition used throughout the experiment since the surfactant partition ratio is the highest. Moreover, there is a stable and clear interfacial boundary between two isotropic phases.

4.2.3 Effect of added electrolyte on CAC

The critical micelle concentration (CMC) values are generally determined as a point where the first micelle is formed. If the other aggregates are formed, the critical aggregation concentration or CAC is used. The CAC is taken from the point of discontinuity or break point in plots of surface tension versus surfactant concentration. As shown in Table D (Appendix D) and Figure 4.1, DTAB has CMC at about 10 mM ($\log C_t = 1$) and DOWFAX at 0.43 mM ($\log C_t = -0.37$). There are minimum drops in a curve of the surface tension versus surfactant concentration, not a sharp break, which can be happened in the commercial grade chemicals containing some impurities.

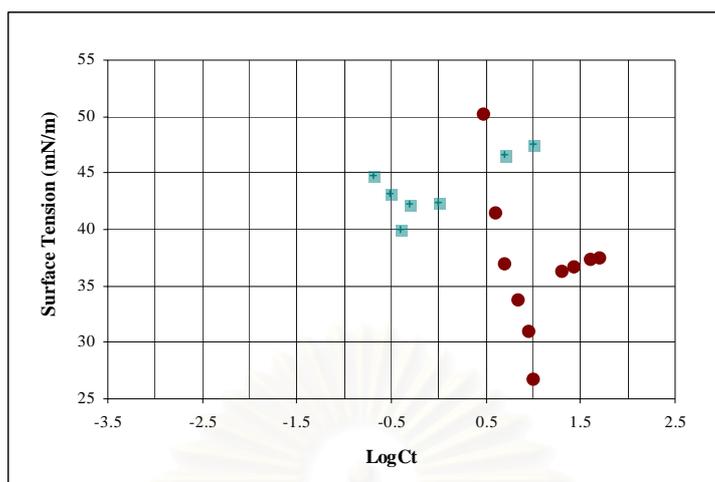


Figure 4.1 CAC determination of DTAB and DOWFAX (●DTAB; ■ DOWFAX)

The surface tension of surfactant solution at various types and concentrations of electrolytes are shown in Table E (Appendix E) and Figure F-1 to F-6 (Appendix F). The CAC values were determined as shown in Table 4.1 and Figure 4.2. The CAC of DTAB/DOWFAX at 2:1 molar ratio is about 0.024 mM, which is obviously lower as compared with pure single surfactant system (DTAB at 10 mM and DOWFAX at 0.43 mM). It is consistent with literature reviews, which report that the cationic surfactant mixtures have much lower CAC as compared to a single surfactant system. It is due to the reduction in the repulsion force between surfactant head group (Herrington and Kaler, 1997; Khan and Marques, 2000).

Table 4.1 CAC for various electrolyte types and concentrations of DTAB and DOWFAX at 2:1 molar ratio, 30 °C

Electrolyte concentration (M)	CACs (mM)					
	NaCl	KCl	NaF	LiCl	NaI	MgCl ₂
0	0.024	0.024	0.024	0.024	0.024	0.024
0.1	0.0224	0.0248	0.021	0.0248	0.0668	0.0286
0.2	0.0214	0.0204	0.0190	0.0240	0.0483	0.0275
0.5	0.020	0.0191	0.0140	0.0215	0.0395	0.0248
1	0.0166	0.0183	0.1230	0.0215	0.0329	0.0234

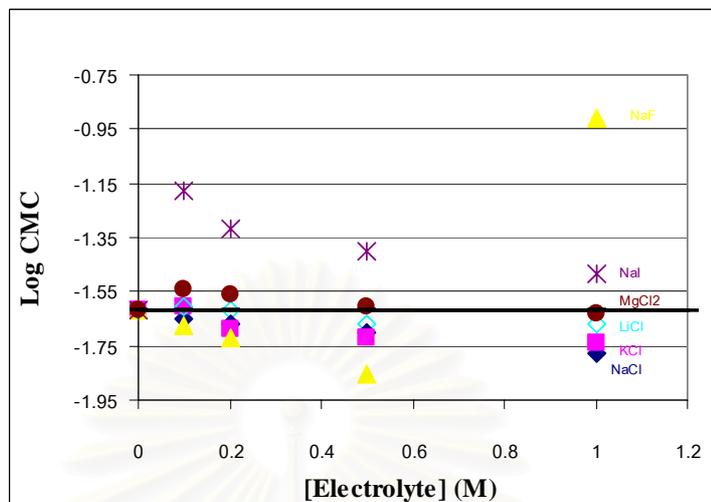


Figure 4.2 CAC of DTAB/DOWFAX at total concentration of 50 mM, 2:1 molar ratio and 30 °C at the presence of electrolytes at various concentration (♦ NaCl; ■ KCl; ▲ NaF; ◇ LiCl; * NaI; ● MgCl₂; — no salt)

Moreover, this figure shows that most of electrolytes slightly depress the CAC of DTAB and DOWFAX system except MgCl₂ and NaI. The order of CAC depression is as follow: NaF > KCl ~ NaCl > LiCl. However, the CAC is surprisingly raised with the addition of NaF at concentration of 1.0 M. The observed effect of electrolyte on the CAC of cationic system is similar to that happened to the nonionic system in which the CAC can be altered by the salting-in and salting-out effects. As has been reported previously, for the same Na⁺ cation, the effect of anion (F⁻ and Cl⁻) on the CMC follows the order F⁻ > Cl⁻ > I⁻ (Zhang et al., 1996). The ions of F⁻ and Cl⁻ are water structure makers (salting out effects) have large ionic charge/radius ratio. They can induce more coherent structure of water, i.e., the destruction of the attractive interaction between the surfactant and water. So, the electrolyte will contact with free water molecules instead of surfactant molecules leading to an increase in the effective concentration of surfactant, thus decrease the CAC. While NaI shows the salting in effect because I⁻ is a water structure breaker with small ionic charge/radius ratio. It promotes the amount of free water molecules resulting in a reduction of the effective concentration of the surfactant. Thus, it raises

the CAC value (Shick et al., 1967; mukerjee, 1967; Ray and Nemethy, 1971; Zhang et al., 1996 and Miyagishi et al., 2001).

Similarly, for the same Cl^- anion, the effect of cation in the CAC reduction is in the order $\text{K}^+ > \text{Na}^+ > \text{Li}^+ > \text{Mg}^{2+}$ in which the obtained results were corresponded. Ions with high ionic charge/radius ratio e.g. Li^+ are called structure making ions or water structure makers. In converse, ions with low ionic charge/radius ratio e.g. Mg^{2+} are water structure breakers. The publication reports that for anion effect, the electrolyte is correlated with the charge to radius ratio of the ions. But the reason for the order of cation has not been clear yet (Ray and Nemethy, 1971; Zhang et al., 1996 and Miyagishi et al., 2001).

4.3 BTEX removal via ASTP technique

The formation of the ASTP in this catanionic surfactant system has a two-phase region. In the absence of electrolyte, the surfactant-rich phase or coacervate is the bottom phase and the surfactant-diluted phase is the upper phase. Both phases are transparent and isotropic. In the presence of electrolyte, the two phases reverse upside down. The upper phase is the surfactant-rich phase and the bottom phase is the surfactant-diluted phase as can be seen in Figure 4.3 and 4.4. In addition, the phase separation phenomenon of catanionic surfactant is reversible. If the upper and bottom phases are mixed together, it will become a homogeneous, clear solution. The phase separation will occur once again after standing for a period of time. The effect of four inorganic electrolytes (NaCl , KCl , LiCl , and MgCl_2) on surfactant and VOCs partition ratio, fractional coacervate volume and percentage of VOCs extracted in the surfactant-rich phase of DTAB/DOWFAX system at 30 °C, total concentration of 50 mM, 2:1 molar ratio of DTAB/DOWFAX with 100 ppm initial concentration of VOCs has been investigated. It may be noted that the four electrolytes used in this research have the same anion (Cl^-) with different cation.

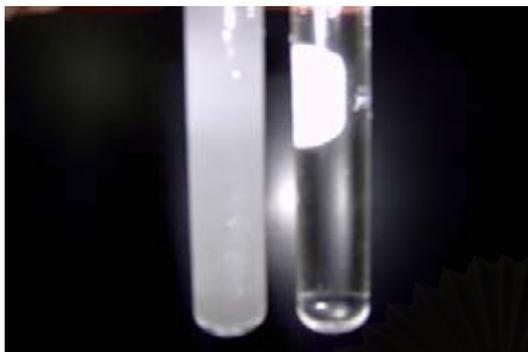


Figure 4.3 Effect of various electrolytes on VOC partition ratio at total concentration of 50 mM, 2:1 molar ratio of DTAB and DOWFAX and 30 °C at the absence of electrolyte

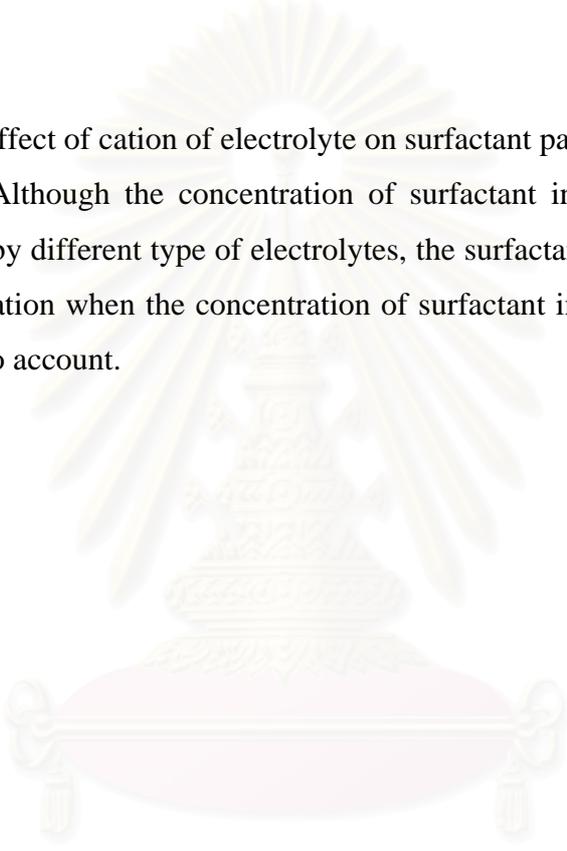


Figure 4.4 Effect of various electrolytes on VOC partition ratio at total concentration of 50 mM, 2:1 molar ratio of DTAB and DOWFAX and 30 °C at the presence of electrolyte

The fractional coacervate volume decreases with the addition of electrolyte as shown in Table 4.2 that leads to an increase in the surfactant concentration in the surfactant-rich phase if the concentration of NaCl increases as shown in Figure 4.5. Figure 4.6 demonstrates that all inorganic electrolytes studied here can slightly increase the surfactant concentration in the surfactant-rich phase which corresponds well with the CAC depression by these electrolytes except MgCl_2 , which raises the CAC resulting in less pronounced surfactant concentration enhancement. The ratio of surfactant concentration in the coacervate phase to that of in the diluted phase called surfactant partition ratio is affected by added electrolyte as shown in Figure 4.7. With the addition of NaCl, the surfactant partition ratio declines particularly at the lowest concentration studied here (0.2 M). As mentioned previously, the position of phases alters upside down when the electrolyte presents causing by a changing in density of the two-phases. It is possible that when the small amount of electrolyte is added into the system, the dissimilarity of density between phases is not strong enough to promote the disassociation of surfactant into the surfactant-rich phase. Therefore, the surfactant concentration in the surfactant-diluted phase is obviously high resulting in less surfactant partition ratio. When the concentration of added electrolyte is increased, it is believed that the degree of dissimilarity of density is enhanced as shown by a reduction in surfactant concentration in the diluted phase, thus an increase in surfactant partition ratio as can be seen in Table 4.2 and Figure

4.7. These results differ from that obtained in the system of typical nonionic surfactant in which the presence of electrolyte does not alter the position of phases. The partition ratio of surfactant obviously increases as the concentration of NaCl increases due to a dramatic increase in the surfactant concentration in the coacervate phase and a reduction of surfactant in the surfactant-depleted phase (Trakultamupatam et al., 2002).

The effect of cation of electrolyte on surfactant partition ratio is shown in Figure 4.8. Although the concentration of surfactant in surfactant-rich phase is slightly altered by different type of electrolytes, the surfactant partition ratio is almost unaffected by cation when the concentration of surfactant in surfactant-diluted phase is also taken into account.



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Table 4.2 Extraction data at 50 mM, 2:1molar ratio of DTAB and DOWFAX with 100 ppm VOC initial concentration(30 C)

additives	VOCs	[salt] (M)	Surfactant										VOC				
			Coacervate Phase				Diluted Phase				Fractional coacervate volume	Fraction of surfactant in coacervate	Surfactant Partition Ratio	Coacervate Phase	Diluted Phase	VOC	%Extraction
			Volume (ml)	Abs at 240 nm	DOWFAX conc (mM)	Total conc. (mM)	Volume (ml)	Abs at 240 nm	DOWFAX conc (mM)	Total conc. (mM)				Conc (ppm)	Conc (ppm)	Partition Ratio	
no added salt	Benzene	0	1.25	1.041	309.3795	928.1384	21.15	0.232	0.2758	0.8274	0.0558	0.9851	1121.77	1289.98	29.67	43.48	71.99
	Toluene		1.3	1.001	297.4917	892.4750	21.10	0.222	0.2639	0.7917	0.0580	0.9858	1127.25	1464.85	15.91	92.07	85.01
	Ethylbenzene		1.3	1.065	316.5121	949.5364	21.10	0.215	0.2556	0.7668	0.0580	0.9871	1238.37	1503.64	13.52	111.22	87.26
	Xylene		1.3	1.014	301.3552	904.0656	21.10	0.196	0.2330	0.6990	0.0580	0.9876	1293.37	1579.76	8.83	178.91	91.68
NaCl	Benzene	0.2	1.0	1.222	363.1717	1089.5150	21.40	0.525	0.6241	1.8723	0.0446	0.9645	581.90	1660.70	27.07	61.35	74.14
	Toluene		1.0	1.202	357.2278	1071.6833	21.40	0.543	0.6455	1.9365	0.0446	0.9628	553.41	1878.98	16.87	111.38	83.88
	Ethylbenzene		1.0	1.126	334.6410	1003.9230	21.40	0.543	0.6455	1.9365	0.0446	0.9604	518.42	1967.36	12.74	154.42	87.83
	Xylene		1.0	1.265	375.9510	1127.8531	21.40	0.553	0.6574	1.9722	0.0446	0.9639	571.88	2028.57	9.88	205.32	90.56
	Benzene	0.5	1.0	1.204	357.8222	1073.4665	21.40	0.281	0.3340	1.0021	0.0446	0.9804	1071.17	1610.84	29.40	54.79	71.91
	Toluene		1.0	1.252	372.0875	1116.2625	21.40	0.327	0.3887	1.1662	0.0446	0.9781	957.19	1950.24	13.54	144.04	87.06
	Ethylbenzene		1.0	1.117	331.9662	995.8987	21.40	0.225	0.2675	0.8024	0.0446	0.9830	1241.11	2042.91	9.21	221.81	91.20
	Xylene		1.0	1.214	360.7941	1082.3823	21.40	0.336	0.3994	1.1983	0.0446	0.9769	903.27	2031.35	9.75	208.34	90.69
	Benzene	1	0.95	1.172	348.3119	1044.9358	21.45	0.225	0.2675	0.8024	0.0424	0.9830	1302.22	1858.00	22.14	83.92	78.80
	Toluene		0.95	1.268	376.8426	1130.5278	21.45	0.239	0.2841	0.8524	0.0424	0.9833	1326.36	2124.88	10.32	205.90	90.12
	Ethylbenzene		0.95	1.192	354.2558	1062.7675	21.45	0.236	0.2806	0.8417	0.0424	0.9824	1262.71	2177.94	7.97	273.27	92.37
	Xylene		0.95	1.139	338.5045	1015.5136	21.45	0.214	0.2544	0.7632	0.0424	0.9833	1330.61	2230.55	5.64	395.49	94.60
KCl	Benzene	1	1.0	1.246	370.3043	1110.9130	21.40	0.261	0.3103	0.9308	0.0446	0.9824	1193.49	1771.34	21.90	80.88	79.08
	Toluene		1.0	1.268	376.8426	1130.5278	21.40	0.250	0.2972	0.8916	0.0446	0.9834	1268.00	2015.09	10.51	191.73	89.96
	Ethylbenzene		1.0	1.285	381.8949	1145.6847	21.40	0.236	0.2806	0.8417	0.0446	0.9845	1361.23	2076.08	7.66	271.03	92.68
	Xylene		1.0	1.303	387.2444	1161.7332	21.40	0.262	0.3115	0.9344	0.0446	0.9831	1243.32	2116.74	5.76	367.49	94.50
LiCl	Benzene	1	0.95	1.286	382.1921	1146.5763	21.45	0.266	0.3162	0.9486	0.0424	0.9817	1208.65	1904.74	20.07	94.90	80.78
	Toluene		0.95	1.359	403.8873	1211.6619	21.45	0.303	0.3602	1.0806	0.0424	0.9803	1121.29	2123.07	10.40	204.14	90.04
	Ethylbenzene		0.95	1.362	404.7789	1214.3367	21.45	0.246	0.2924	0.8773	0.0424	0.9839	1384.15	2190.13	7.43	294.77	92.89
	Xylene		0.95	1.329	394.9715	1184.9144	21.45	0.285	0.3388	1.0164	0.0424	0.9810	1165.79	2233.26	5.52	404.58	94.71
MgCl2	Benzene	1	1.15	1.150	341.7737	1025.3210	21.25	0.221	0.2627	0.7882	0.0513	0.9860	1300.90	1626.67	17.38	93.59	83.51
	Toluene		1.15	1.150	341.7737	1025.3210	21.25	0.210	0.2496	0.7489	0.0513	0.9867	1369.05	1785.22	8.80	202.87	91.65
	Ethylbenzene		1.15	1.165	346.2316	1038.6947	21.25	0.199	0.2366	0.7097	0.0513	0.9875	1463.57	1848.97	5.35	345.60	94.92
	Xylene		1.15	1.118	332.2634	996.7903	21.25	0.204	0.2425	0.7275	0.0513	0.9867	1370.10	1847.49	5.43	340.24	94.85

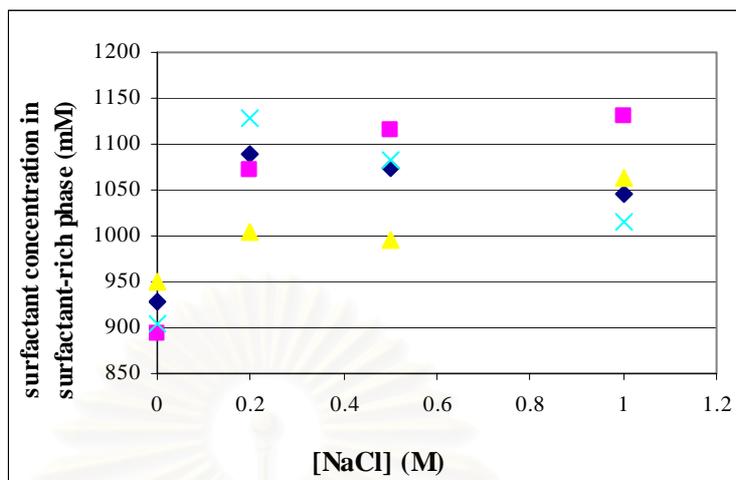


Figure 4.5 Effect of NaCl concentration on surfactant concentration in coacervate phase at total concentration of 50 mM, 2:1 molar ratio of DTAB and DOWFAX and 30 °C (◆ benzene; ■ toluene; ▲ ethylbenzene; × xylene)

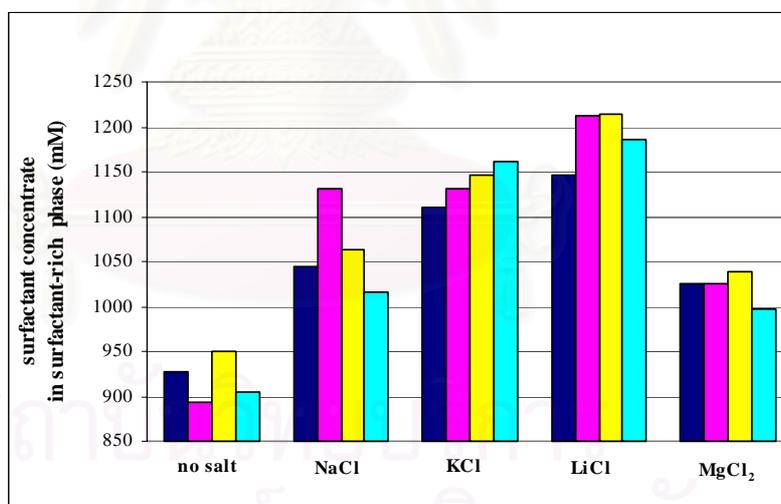


Figure 4.6 Effect of various electrolytes at 1 M on surfactant concentration in surfactant-rich phase at total concentration of 50 mM, 2:1 molar ratio of DTAB and DOWFAX and 30 °C (■ benzene; ■ toluene; ■ ethylbenzene; ■ xylene)

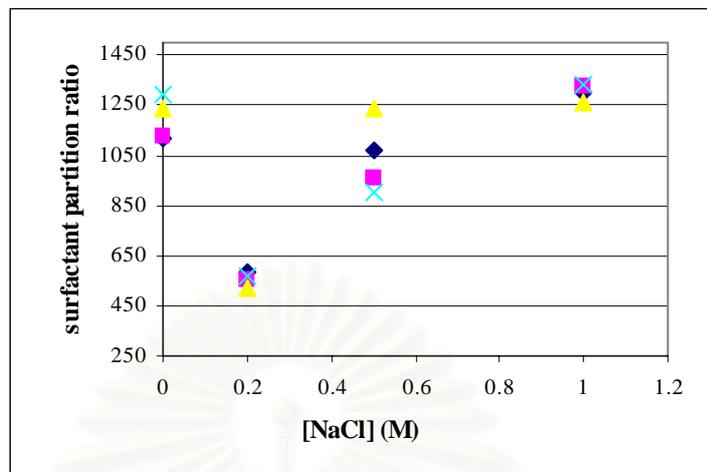


Figure 4.7 Effect of NaCl concentration on surfactant partition ratio at total concentration of 50 mM, 2:1 molar ratio of DTAB and DOWFAX and 30 °C (◆ benzene; ■ toluene; ▲ ethylbenzene; × xylene)

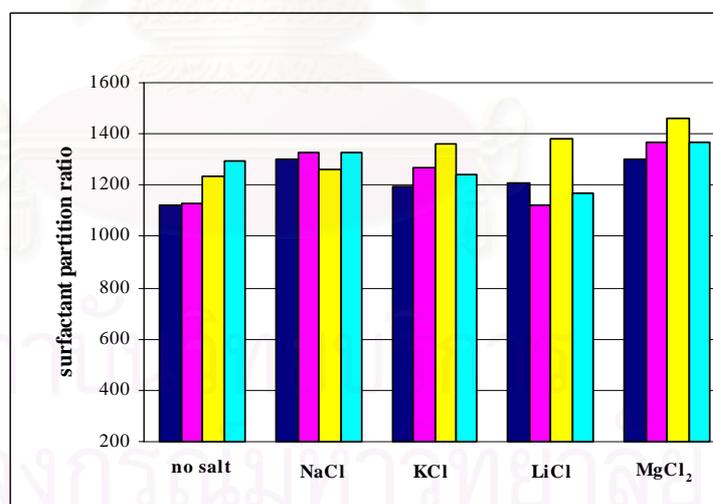


Figure 4.8 Effect of various electrolytes at 1 M on surfactant partition ratio at total concentration of 50 mM, 2:1 molar ratio of DTAB and DOWFAX and 30 °C (■ benzene; ■ toluene; ■ ethylbenzene; ■ xylene)

It has been reported that the addition of salt alters the equilibrium phase behavior due to an increase in the aggregation number causing a transformation of small micelles into larger and flatter structure leading to an extension in solubilization (Saito, 1967; Yin et al., 2002). In addition, the added electrolyte can cause the salting out effect in which the electrolyte interacts with water molecule resulting in less free water molecules in the system. Thus, the solubilization of VOCs into the aggregates which provide the hydrophobic environment is enhanced (Mukerjee, 1967).

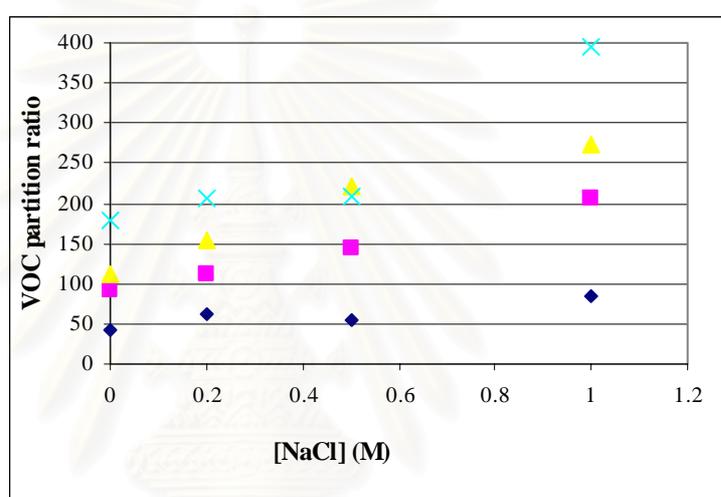


Figure 4.9 Effect of NaCl concentration on VOC partition ratio at total concentration of 50 mM, 2:1 molar ratio of DTAB and DOWFAX and 30 °C (♦ benzene; ■ toluene; ▲ ethylbenzene; × xylene)

The addition of NaCl enhances the VOC partition ratio in the sense that the higher the electrolyte concentration, the greater the VOC partition ratio. At NaCl concentration of 1.0 M, the partition ratio can be as high as 395 for xylene, 273 for ethylbenzene, 206 for toluene, and 84 for benzene as shown in Figure 4.9. It is worthwhile to note that the VOC partition ratio is doubled with the addition of 1.0 M of NaCl. Only 22 ppm of benzene, 10 ppm of toluene, 8 ppm of ethylbenzene and 6 ppm of xylene present in the surfactant-diluted phase after the extraction from the initial concentration of 100 ppm as shown in Table 4.2. Xylene shows the greatest ability in partitioning into the surfactant aggregates followed by ethylbenzene, toluene, and benzene, respectively as regarded to their hydrophobicity which is

concurrent to that reported by Trakultamupatam et. al., 2002. Xylene and ethylbenzene have the highest hydrophobicity or least water solubility, thus prefer dissolving in the surfactant aggregates to aqueous solution. However, ethylbenzene has a larger molecular structure as compared to xylene resulting in less ability in partitioning through the tightly packed zone at surfactant head outer region.

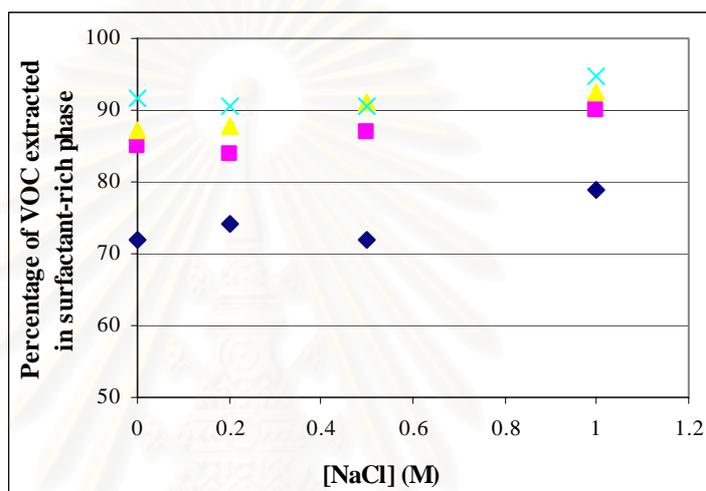


Figure 4.10 Effect of NaCl concentration on percentage of VOC extracted in surfactant-rich phase at total concentration of 50 mM, 2:1 molar ratio of DTAB and DOWFAX and 30 °C (◆ benzene; ■ toluene; ▲ ethylbenzene; × xylene)

From Figure 4.10, an increase of NaCl concentration from 0.2 to 0.5 M does not have significant effect on the percentage of VOC extracted. At 1.0 M NaCl, about 95 % of xylene, 92 % of ethylbenzene, 90% of toluene and 79% of benzene are extracted into the coacervate phase, respectively.

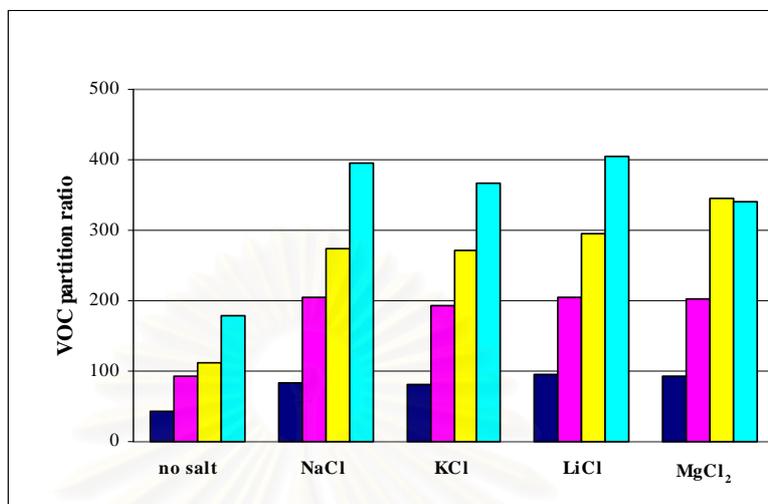


Figure 4.11 Effect of various electrolytes at 1 M on VOC partition ratio at total concentration of 50 mM, 2:1 molar ratio of DTAB and DOWFAX and 30 °C (■ benzene; ■ toluene; ■ ethylbenzene; ■ xylene)

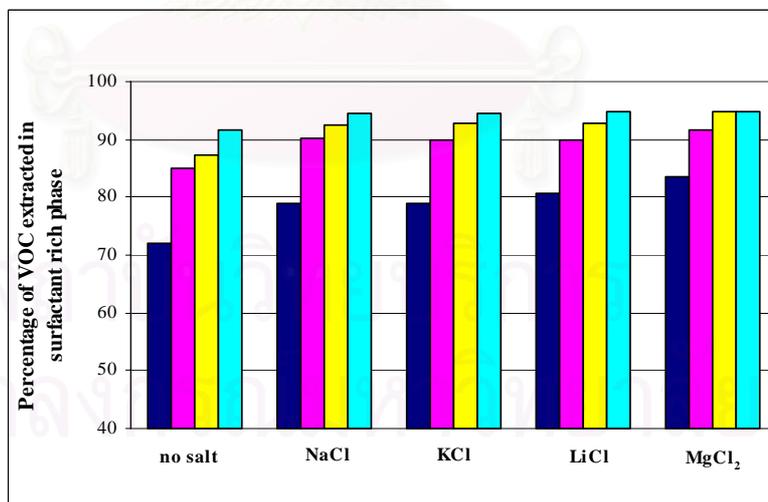


Figure 4.12 Effect of various electrolytes at 1 M on percentage of VOC extracted in surfactant-rich phase at total concentration of 50 mM, 2:1 molar ratio of DTAB and DOWFAX and 30 °C (■ benzene; ■ toluene; ■ ethylbenzene; ■ xylene)

The addition of different type of electrolytes at concentration of 1.0 M on VOC extraction via ASTP technique has been investigated. As shown previously that the presence of electrolyte can enhance the extraction efficiency but the type of cation (Na, K, Li, and Mg) in inorganic electrolyte does not have significant effect on the extraction of VOC both on the VOC partition ratio and the percentage of VOC extracted in the surfactant-rich phase as shown in Figure 4.11 and 4.12. Therefore, the appearance of any kind of cations of inorganic electrolyte in the wastewater can equally improve the extraction efficiency of VOC.

From the results, the ASTP technique of cationic surfactant shows high performance in extraction of VOCs from wastewater. In the system of the conventional ASTP formed by nonionic surfactant (t-octylphenolpolyethoxylate) at the same operating condition, i.e., 50 mM of surfactant, 100 ppm of benzene initial concentration at 30 °C, the benzene partition ratio is about 10 only with 70% of the extracted benzene into the surfactant-rich phase (Trakultamupatam et al., 2002) as compared to about 40 of benzene partition ratio and 74% of the extracted benzene in this study. These results are in agreement with literatures reported for the nonionic surfactant in the presence of electrolyte as previously mentioned (Saito, 1967; Yin et al., 2002).

CHAPTER V

CONCLUSION

A novel aqueous surfactant two-phase system (ASTP) of cationic and anionic surfactant mixtures is a promising technique. Its ability is not only removal but also preconcentration of BTEX from wastewater in the surfactant-rich phase, thus reduces the amount of waste for further treatment. The phase separation can occur at 2:1 molar ratio of DTAB:DOWFAX, total concentration of 50 mM at 30 °C, in which two aqueous phases of the surfactant-rich and surfactant-depleted phase are formed. The higher degree of hydrophobicity of contaminant shows the greater potential to be extracted in the surfactant-rich phase in the following order; xylene > ethylbenzene > toluene > benzene, where the extraction efficiencies can be as high as 92%, 87%, 85% and 72%, respectively without added electrolyte.

In addition, the presence of electrolytes has a synergistic effect to the cationic-anionic surfactant system since it can obviously improve the extraction efficiency. From this study, the type of electrolyte does not have significant effects on the extraction since the partition ratio and percentage of VOCs extracted are almost alike. Moreover, the added electrolyte screens the electrostatic repulsion forces between the surfactant head groups causing a decrease in CAC of the cationic surfactant system. Thus, the quantity of surfactant needed to form the aggregates is less than of needed for single surfactant. In addition, electrolytes can facilitate the phase separation process since it reverses the surfactant-rich phase into the top region making it is easier to handle. In summary, it is beneficial if the electrolyte appears in the wastewater because it can improve the VOC partition ratio and percentage of VOCs extracted.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE WORK

Based on the results of this research, some recommendations for further studies are proposed as follows;

1. The fundamental studies on phase behavior and the molecular structures of mixed cationic-anionic surfactant aggregates should be studied in detail before and after phase separation.
2. The ASTP technique may be applied to extract and pre-concentrate various kinds of environmental concerned materials, not only organic contaminants but also heavy metals.
3. The ASTP system should be scaled up to operate continuously in multi-stage extractor instead of being a single stage, batch extraction.
4. The direct analytical method determining the concentration of DTAB should be used rather than the indirect method that is currently used.

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APPENDICES

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Table A Phase separation of various cationic surfactant mixtures with altering conditions

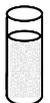
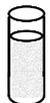
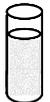
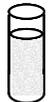
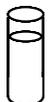
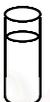
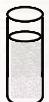
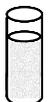
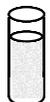
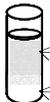
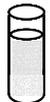
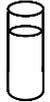
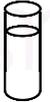
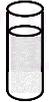
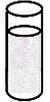
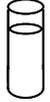
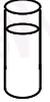
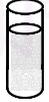
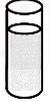
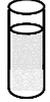
Molar ratio Temp(C)	Solution appearance				
	1:2	1:1.5	1:1	1.5:1	2:1
1. CTAB:DOWFAX					
At $C_T = 20$ mM					
30,40(15 hr)	 clear solution, no phase separation	 clear solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation
50(10 hr)	 clear solution, no phase separation	 clear solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation
At $C_T = 50$ mM					
30,40(15 hr)	 clear solution, no phase separation	 clear solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation
50(10 hr)	 clear solution, no phase separation	 clear solution, no phase separation	 Turbid solution clear solution	 Turbid solution clear solution	 Turbid solution, no phase separation
At $C_T = 80$ mM					
30,40(15 hr)	 clear solution, no phase separation	 clear solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation
50(10 hr)	 clear solution, no phase separation	 clear solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation

Table A (cont.) Phase separation of various cationic surfactant mixtures with altering conditions

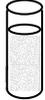
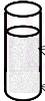
Molar ratio Temp(C)	Solution appearance				
	1:2	1:1.5	1:1	1.5:1	2:1
2. CTAB:SDS					
At $C_T = 20$ mM					
30(20 hr)	no phase separation				
40(21 hr)	no phase separation				
At $C_T = 50$ mM					
30(20 hr)	 clear solution, no phase separation	 Opalescent solution like a pearl Turbid solution	 Opalescent solution like a pearl Turbid solution	 Opalescent solution like a pearl Turbid solution	 Turbid solution, no phase separation
40(21 hr)	 clear solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation
At $C_T = 80$ mM					
30(20 hr)	 clear solution, no phase separation	 Opalescent solution Turbid solution, no phase separation Turbid solution	 Opalescent solution Turbid solution, no phase separation Turbid solution	 Opalescent solution like a pearl Turbid solution	 Opalescent solution like a pearl Turbid solution
40(21 hr)	 clear solution, no phase separation	 Opalescent solution like a pearl Turbid solution	 Opalescent solution like a pearl Turbid solution	 Opalescent solution like a pearl Turbid solution	 Opalescent solution like a pearl Turbid solution

Table A (cont.) Phase separation of various cationic surfactant mixtures with altering conditions

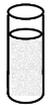
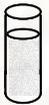
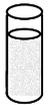
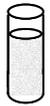
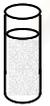
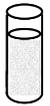
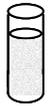
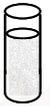
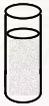
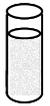
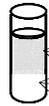
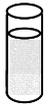
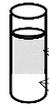
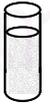
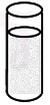
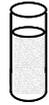
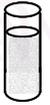
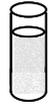
Molar ratio Temp(C)	Solution appearance				
	1:2	1:1.5	1:1	1.5:1	2:1
3.DTAB:SDS					
At $C_T = 20$ mM					
30(15 hr)	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution clear solution
40(20 hr)	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution clear solution
At $C_T = 50$ mM					
30(15 hr)	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution clear solution
40(20 hr)	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution clear solution
At $C_T = 80$ mM					
30(15 hr)	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation
40(20 hr)	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 Turbid solution, no phase separation

Table A (cont.) Phase separation of various cationic surfactant mixtures with altering conditions

Molar ratio Temp(C)	Solution appearance				
	1:2	1:1.5	1:1	1.5:1	2:1
4.TTAB:SDS					
no phase separation					
5.C₁₂NE:SDS					
no phase separation					
6.TTAB:DOWFAX					
no phase separation					

Table A-1 (cont.) Phase separation of various cationic surfactant mixtures with altering conditions

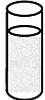
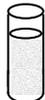
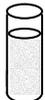
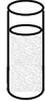
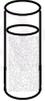
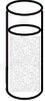
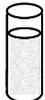
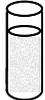
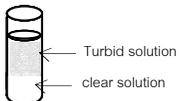
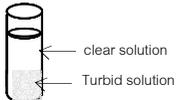
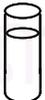
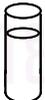
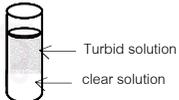
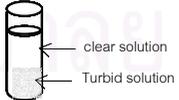
Molar ratio Temp(C)	Solution appearance				
	1:2	1:1.5	1:1	1.5:1	2:1
7.DTAB:AMA					
At $C_T = 20$ mM					
30	no experiment				
40(20 hr)	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 oil droplet a lot of oil droplets 'suspend in the solution the tube	 Turbid solution, no phase separation	 Turbid solution, no phase separation
At $C_T = 50$ mM					
30	no experiment				
40(20 hr)	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 oil droplet at the top Opalescent solution like ← a pearl	 Turbid solution, no phase separation	 Turbid solution, no phase separation
At $C_T = 80$ mM					
30	no experiment				
40(20 hr)	 Turbid solution, no phase separation	 Turbid solution, no phase separation	 oil like phase transparent solution, oil dust stick at the wall of the tube	 Turbid solution, no phase separation	 Turbid solution, no phase separation

Table A (cont.) Phase separation of various cationic surfactant mixtures with altering conditions

Molar ratio Temp(C)	Solution appearance				
	1:2	1:1.5	1:1	1.5:1	2:1
8.DTAB:DOWFAX					
At $C_T = 20$ mM					
30(17 hr)	 clear solution, no phase separation	 clear solution, no phase separation	 clear solution, no phase separation	 Turbid solution, no phase separation	 (water-like phase) transparent solution, oil dust stick at the oil droplet at the bottom
40(24 hr)	 clear solution, no phase separation	 clear solution, no phase separation	 clear solution, no phase separation	 Turbid solution, no phase separation	 (water-like phase) transparent solution, oil dust stick at the oil droplet at the bottom
At $C_T = 50$ mM					
30(17 hr)	 clear solution, no phase separation	 clear solution, no phase separation	 clear solution, no phase separation	 Turbid solution clear solution	 (water-like phase) transparent solution, oil dust stick at the oil droplet at the bottom
40(24 hr)	 clear solution, no phase separation	 clear solution, no phase separation	 clear solution, no phase separation	 clear solution Turbid solution	 transparent solution, oil dust stick at the wall of the tube oil droplet at the bottom
At $C_T = 80$ mM					
30(17 hr)	 clear solution, no phase separation	 clear solution, no phase separation	 clear solution, no phase separation	 Turbid solution clear solution	 (water-like phase) transparent solution, oil dust stick at the oil droplet at the bottom
40(24 hr)	 clear solution, no phase separation	 clear solution, no phase separation	 clear solution, no phase separation	 clear solution Turbid solution	 clear solution Turbid solution

APPENDIX B

Table B DOWFAX concentration in each phase at various time of DTAB and DOWFAX at total concentration of 80 mM and 2:1 molar ratio

Time(hr.)	Coacervate Phase			Diluted Phase			Surfactant Partition Ratio
	Hbottom (cm.)	Abs at 240 nm	Conc (mM)	Hupper (cm.)	Abs at 240 nm	Conc (mM)	
3	0.54	0.917	273.6823	7.05	3.303	3.9432	69.41
6	0.57	0.975	290.9927	6.95	2.582	3.0824	94.40
22	0.65	1.095	326.8071	6.65	1.403	1.6749	195.12
24	0.65	0.959	286.2174	6.80	1.432	1.7095	167.42
26	0.61	1.039	310.0937	6.70	1.287	1.5364	201.83
28	0.61	1.062	316.9582	6.80	0.646	0.7712	410.99
29	0.65	0.917	273.6823	6.65	0.764	0.9121	300.07
31	0.61	1.032	308.0045	6.80	0.887	1.0589	290.87
45	0.65	1.031	307.7061	6.65	0.609	0.7270	423.23
49	0.65	0.919	274.2792	6.60	0.493	0.5886	466.02
52	0.61	0.928	276.9653	6.80	0.420	0.5014	552.38
69	0.65	1.146	342.0283	6.75	0.377	0.4501	759.95
71.5	0.61	1.102	328.8963	6.73	0.306	0.3653	900.33
74.5	0.59	1.283	382.9165	6.70	0.277	0.3307	1157.94
141.5	0.59	1.027	306.5123	6.78	0.253	0.3020	1014.82
147.5	0.61	1.163	347.1020	6.60	0.257	0.3068	1131.32
SD(71.5-147.5 hr.)			32.2987			0.0289	
AVG(71.5-147.5hr.)			341.3568			0.3262	
%SD			9.4619			8.8660	

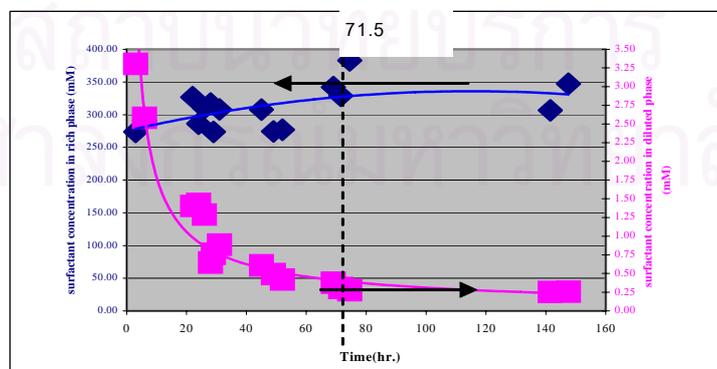


Figure B DOWFAX concentration in surfactant-rich and surfactant-diluted phase at various time

Table C Phase separation data of DTAB and DOWFAX at various total concentrations and molar ratios, 30 C

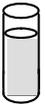
Ratio	Conc (mM)	Appearance Side View	Coacervate Phase			Diluted Phase			Surfactant Partition Ratio
			Volume (ml)	Abs at 240 nm	DOWFAX Conc (mM)	Volume (ml)	Abs at 240 nm	DOWFAX Conc (mM)	
At $C_T = 20$ mM									
1:2	6.67:13.33	 clear solution, no phase separation	no phase separation						
1:1.5	8.0:12.0	 clear solution, no phase separation	no phase separation						
1:1	10.0:10.0	 clear solution, no phase separation	no phase separation						
1.5:1	12.0:8.0	 Turbid solution, no phase separation	no phase separation						
2:1	13.33:6.67	 (water-like phase) transparent solution, oil dust stick at the wall of the tube oil droplet at the bottom		0.765	227.3538		0.111	0.1320	
2.5:1	14.29:5.71	 a lot of oil droplets suspend in the solution (oil-like phase) clear, viscous	0.59	0.445	132.2515	10.41	0.069	0.0820	1612.32
3:1	15.0:5.0	 a lot of oil droplets suspend in the solution (oil-like phase) clear, viscous	0.94	0.338	100.4517	10.06	0.058	0.0689	1456.90

Table C (cont.) Phase separation data of DTAB and DOWFAX at various total concentrations and molar ratios, 30 C

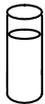
Ratio	Conc (mM)	Appearance Side View	Coacervate Phase			Diluted Phase			Surfactant Partition Ratio
			Volume (ml)	Abs at 240 nm	DOWFAX Conc (mM)	Volume (ml)	Abs at 240 nm	DOWFAX Conc (mM)	
At $C_T = 50$ mM									
1:2	16.67:33.33	 clear solution, no phase separation	no phase separation						
1:1.5	20.0:30.0	 clear solution precipitation	no phase separation						
1:1	25.0:25.0	 clear solution precipitation > 1:1.5	no phase separation						
1.5:1	30.0:20.0	 Turbid solution clear solution	not good phase separation						
2:1	33.33:16.67	 transparent solution, oil dust stick at the wall of the tube oil droplet at the bottom > 2:1 at 20 mM	0.88	0.821	243.9967	10.12	0.146	0.1736	1405.82
2.5:1	35.71:14.29	 a lot of oil droplets suspend in the solution (oil-like phase) not isotropic solution	0.90	0.309	91.8331	10.10	0.068	0.0808	1136.03
3:1	37.50:12.50	 clear solution turbid solution	not good phase separation						

Table C (cont.) Phase separation data of DTAB and DOWFAX at various total concentrations and molar ratios, 30 C

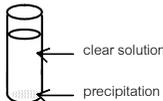
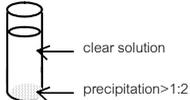
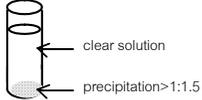
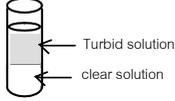
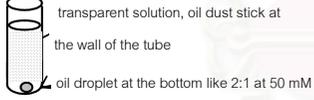
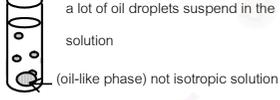
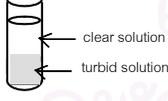
Ratio	Conc (mM)	Appearance Side View	Coacervate Phase			Diluted Phase			Surfactant Partition Ratio
			Volume (ml)	Abs at 240 nm	DOWFAX Conc (mM)	Volume (ml)	Abs at 240 nm	DOWFAX Conc (mM)	
At $C_T = 80$ mM									
1:2	26.67:53.33	 clear solution precipitation	no phase separation						
1:1.5	32.0:48.0	 clear solution precipitation>1:2	no phase separation						
1:1	40.0:40.0	 clear solution precipitation>1:1.5	no phase separation						
1.5:1	48.0:32.0	 Turbid solution clear solution	not good phase separation						
2:1	53.33:26.67	 transparent solution, oil dust stick at the wall of the tube oil droplet at the bottom like 2:1 at 50 mM	1.0	1.114	331.0747	10.00	0.295	0.3507	944.07
2.5:1	57.14:22.86	 a lot of oil droplets suspend in the solution (oil-like phase) not isotropic solution	1.18	0.310	92.1303	9.82	0.089	0.1058	870.79
3:1	60.0:20.0	 clear solution turbid solution	not good phase separation						

Table C (cont.) Phase separation data of DTAB and DOWFAX at various total concentrations and molar ratios, 30 C

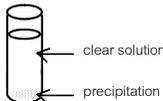
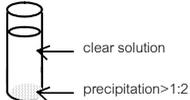
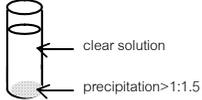
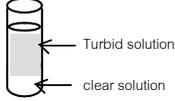
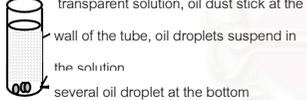
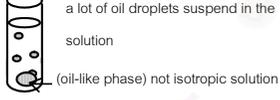
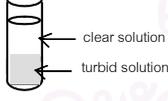
Ratio	Conc (mM)	Appearance Side View	Coacervate Phase			Diluted Phase			Surfactant Partition Ratio
			Volume (ml)	Abs at 240 nm	DOWFAX Conc (mM)	Volume (ml)	Abs at 240 nm	DOWFAX Conc (mM)	
At $C_T = 110$ mM									
1:2	36.67:73.33	 clear solution precipitation	no phase separation						
1:1.5	44.0:66.0	 clear solution precipitation > 1:2	no phase separation						
1:1	55.0:55.0	 clear solution precipitation > 1:1.5	no phase separation						
1.5:1	66.0:44.0	 Turbid solution clear solution	not good phase separation						
2:1	73.33:36.67	 transparent solution, oil dust stick at the wall of the tube, oil droplets suspend in the solution several oil droplet at the bottom	0.71	0.931	276.6881	10.29	0.636	0.7561	365.96
2.5:1	78.57:31.43	 a lot of oil droplets suspend in the solution (oil-like phase) not isotropic solution	0.38	0.445	132.2515	10.62	0.147	0.1748	756.80
3:1	82.5:27.5	 clear solution turbid solution	not good phase separation						

Table D Surface tension and concentration data of pure DTAB and pure DOWFAX for CAC value, 30 C

	Ct	50	40	26.667	20	10	9	7	5	4	3	2.028	1	0.5	0.1	0.010															
		(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)															
	LogCt	1.699	1.602	1.426	1.301	1.000	0.954	0.845	0.699	0.602	0.477	0.301	0.000	-0.301	-1.000	-2.000															
DTAB	ST	37.408	37.465	37.362	37.447	36.465	36.983	36.210	36.242	26.884	26.599	31.585	30.436	33.598	33.887	36.661	37.303	41.667	41.220	49.716	50.687	54.207	58.532	66.516	66.930	67.729	68.793	70.351	70.273	71.133	71.229
	ST avg	37.437	37.405	36.724	36.226	26.742	31.011	33.743	36.982	41.444	50.202	56.370	66.723	68.261	70.312	71.181															
	Ct	10	5	1	0.5	0.4	0.3	0.2	0.1	0.01	0.005	0.001																			
		(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)																			
	LogCt	1.000	0.699	0.000	-0.301	-0.398	-0.523	-0.699	-1.000	-2.000	-2.301	-3.000																			
DOWFAX	ST	47.601	47.559	45.952	47.277	43.231	41.652	42.298	42.340	40.382	39.517	41.851	44.543	45.578	43.958	70.188	70.372	70.975	70.819	70.930	70.662	69.580	70.993								
	ST avg	47.580	46.615	42.442	42.319	39.950	43.197	44.768	70.280	70.897	70.796	70.287																			

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Table E Surface tension and surfactant concentration data for different electrolytes of series of DTAB and DOWFAX at 2:1 molar ratio, 30 C

DTAB:DOW (2:1)	Surface Tension(mN/m)										
		5 (mM)	1 (mM)	0.1 (mM)	0.05 (mM)	0.02 (mM)	0.01 (mM)	0.008 (mM)	0.006 (mM)	0.004 (mM)	0.003 (mM)
Log Ct		0.6990	0.0000	-1.0000	-1.3010	-1.6990	-2.0000	-2.0969	-2.2218	-2.3979	-2.5229
no salt	ST	30.029	30.723	31.434	31.982	33.578	38.162	39.579	42.848	47.344	50.097
NaCl 0.1 M	ST	29.417	30.660	31.575	31.941	33.788	39.854	37.308	43.301	44.361	71.769
NaCl 0.2 M	ST	30.308	30.819	32.154	31.859	32.872	40.194	42.143	72.096	72.293	72.292
NaCl 0.5 M	ST	31.564	31.379	32.287	32.587	34.554	37.377	38.865	72.447	72.795	72.814
NaCl 1.0 M	ST	29.381	30.271	33.377	32.881	34.407	37.471	38.504	72.884	73.173	73.081
KCl 0.1 M	ST	30.161	31.039	32.085	32.690	34.830	40.075	41.373	43.282	72.615	70.686
KCl 0.2 M	ST		31.479	36.752	33.383	33.560	40.297	41.711	35.163	72.343	
KCl 0.5 M	ST	30.483	32.285	32.007	33.727	36.112	38.712	41.377	72.514	73.050	73.027
KCl 1.0 M	ST	31.645	31.789	32.410	33.685	35.579	37.871	39.965	41.616	73.760	73.975
NaF 0.1 M	ST		30.813	36.234	32.086	32.056	38.831	39.498	41.546	47.874	47.708
NaF 0.2 M	ST	29.195	29.920	31.497	32.393	35.760	39.427	40.641	40.300	71.317	
NaF 0.5 M	ST	29.369	33.770	35.066	33.091	33.716	36.683	38.812	40.475	56.383	
NaF 1.0 M	ST	28.815	29.901	32.912	40.303	71.201	71.385	72.032	72.318	72.521	
LiCl 0.1 M	ST	30.005	30.721	32.514	33.180	34.783	38.608	39.510	41.629	44.756	68.265
LiCl 0.2 M	ST	30.605	29.874	33.025	33.546	35.685	38.438	39.421	41.376	45.198	
LiCl 0.5 M	ST	31.394	31.065	36.552	32.978	33.592	39.948	41.358	72.069	72.307	
LiCl 1.0 M	ST	30.702	30.763	30.801	32.011	35.717	39.216	41.404	72.881	71.991	
NaI 0.1 M	ST	30.641	31.123	32.077	33.397	37.789	40.954	41.310	44.398	73.022	72.290
NaI 0.2 M	ST	30.711	31.362	32.668	33.720	36.727	39.652	41.601	41.788	43.783	
NaI 0.5 M	ST	31.320	32.006	32.868	34.379	36.884	40.230	41.226	43.661	64.157	
NaI 1.0 M	ST	31.530	32.135	33.347	34.772	36.915	40.500	40.542	42.529	45.159	
MgCl ₂ 0.1 M	ST	30.673	30.779	31.162	33.799	34.745	37.878	38.528	42.241	42.640	71.461
MgCl ₂ 0.2 M	ST	30.455	29.990	30.807	36.073	36.860	39.065	41.377	69.802	72.449	72.485
MgCl ₂ 0.5 M	ST	29.449	29.446	30.614	39.071	35.363	37.493	39.276	72.927	73.449	71.613
MgCl ₂ 1.0 M	ST	31.695	31.101	32.321	32.484	35.290	47.414	69.420	71.448	74.903	75.162

APPENDIX F

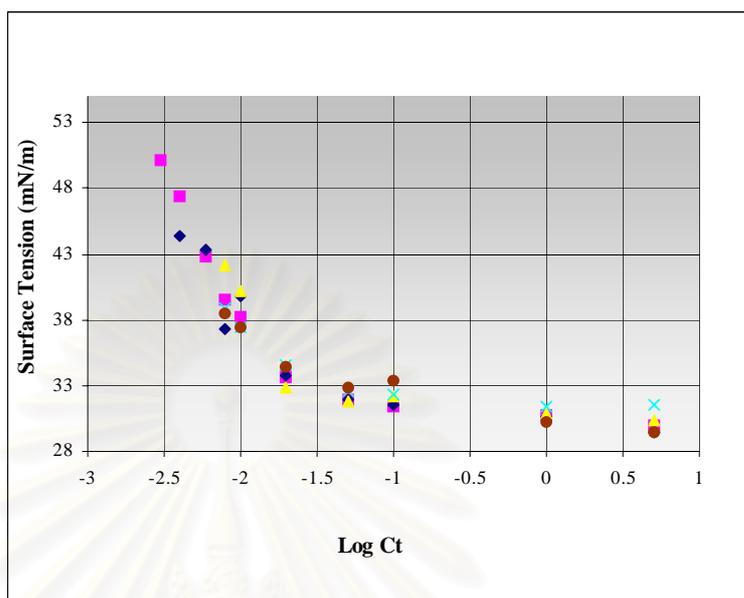


Figure F-1 CAC of DTAB and DOWFAX in NaCl solution at 2:1 molar ratio, 30 °C (\blacksquare no salt; \blacklozenge 0.1 M NaCl; \blacktriangle 0.2 M NaCl; \times 0.5 M NaCl; \bullet 1.0 M NaCl)

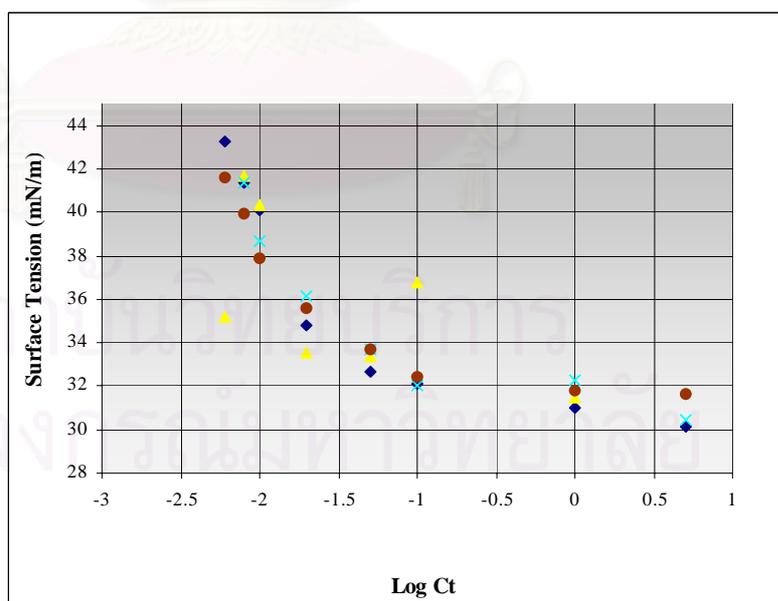


Figure F-2 CAC of DTAB and DOWFAX in KCl solution at 2:1 molar ratio, 30 °C (\blacklozenge 0.1 M KCl; \blacktriangle 0.2 M KCl; \times 0.5 M KCl; \bullet 1.0 M KCl)

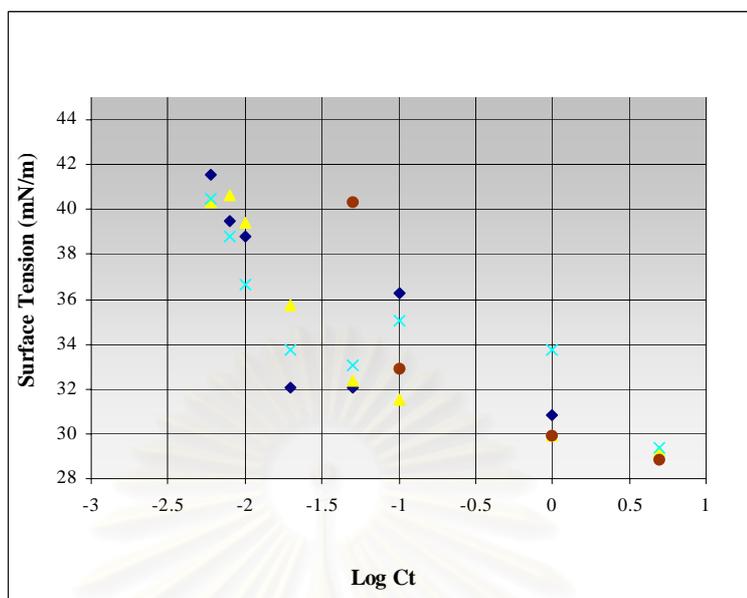


Figure F-3 CAC of DTAB and DOWFAX in NaF solution at 2:1 molar ratio, 30 °C (◆ 0.1 M NaF; ▲ 0.2 M NaF; × 0.5 M NaF; ● 1.0 M NaF)

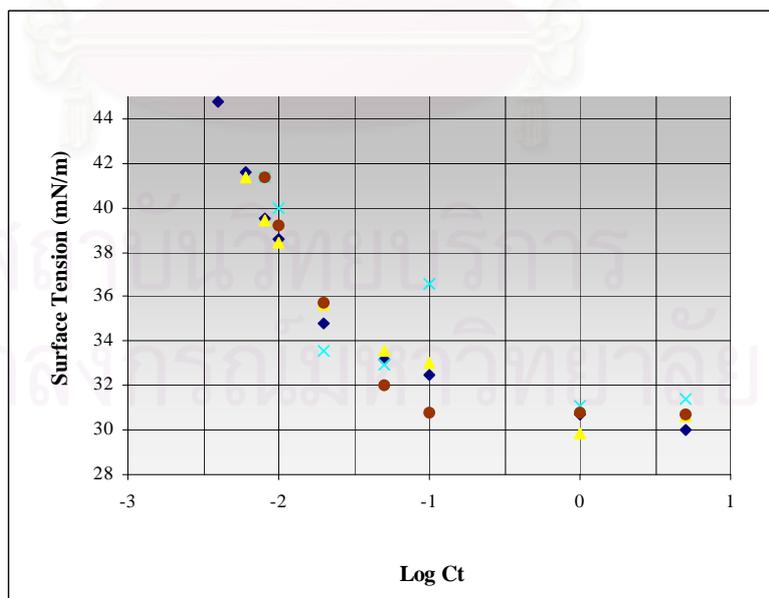


Figure F-4 CAC of DTAB and DOWFAX in LiCl solution at 2:1 molar ratio, 30 °C (◆ 0.1 M LiCl; ▲ 0.2 M LiCl; × 0.5 M LiCl; ● 1.0 M LiCl)

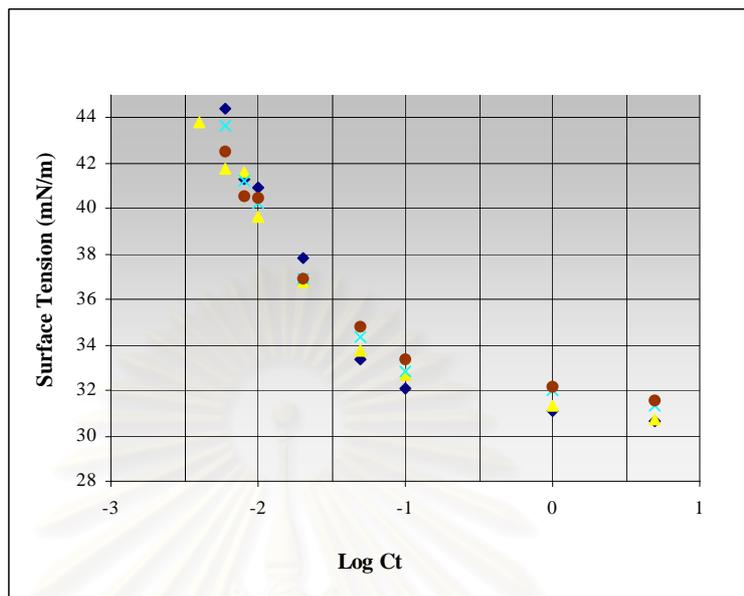


Figure F-5 CAC of DTAB and DOWFAX in NaI solution at 2:1 molar ratio, 30 °C (\blacklozenge 0.1 M NaI; \blacktriangle 0.2 M NaI; \times 0.5 M NaI; \bullet 1.0 M NaI)

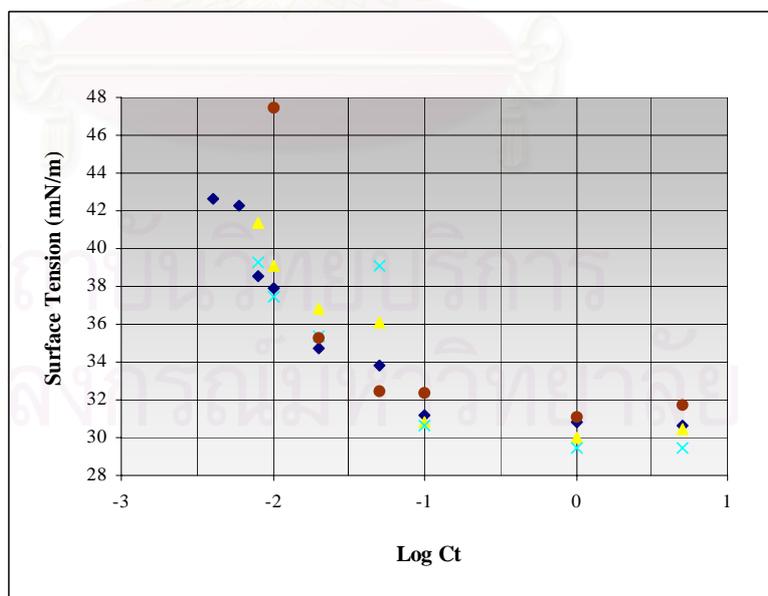


Figure F-6 CAC of DTAB and DOWFAX in MgCl₂ solution at 2:1 molar ratio, 30 °C (\blacklozenge 0.1 M MgCl₂; \blacktriangle 0.2 M MgCl₂; \times 0.5 M MgCl₂; \bullet 1.0 M MgCl₂)

BIOGRAPHY

Miss Duanghathai Krutlert was born on November 14, 1975 in Bangkok , Thailand. She graduated in Bachelor of Environmental Engineering from King Mongkut's Institute of Technology Thonburi in 1997. Firstly, she had work experiences at International Quality Assurance Laboratory Co., Ltd. After that from the end of 1997 to 2002, she had worked in Environmental Engineering Division, Bureau of Environmental Health, Department of Health, Ministry of Public Health as environmental engineer. From 2002 to present, she has been working in Appropriate Technology Division, Bureau Public Participation promotion, Department of Environmental Quality Promotion, Ministry of Natural Resources and Environment as environmental engineer as well. Later, she pursued her Master Degree study in the International Postgraduate Programs in Environmental management, Inter-Department of Environmental Management, Chulalongkorn University in May 2003 . She received Master Degree of Science in Environmental Management in May 2005 with outstanding reward as the winner for best paper at 4th National Environmental Conference of the Environmental Engineering Association of Thailand (EEAT).

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