การกำจัดฟีนอลออกจากน้ำเสียโดยอาศัยการแบ่งวัฏภาคของสารละลายผสมของสารลดแรงตึงผิว
ชนิดประจุบวกและประจุลบในถังผสม-ตกตะกอนแบบต่อเนื่อง

นายเศรษฐา อินทะสระ

PHENOL REMOVAL FROM WASTEWATER USING A PHASE SEPARATION OF CATIONIC-ANIONIC SURFACTANT MIXTURE SOLUTION IN CONTINUOUS MIXER-SETTLER

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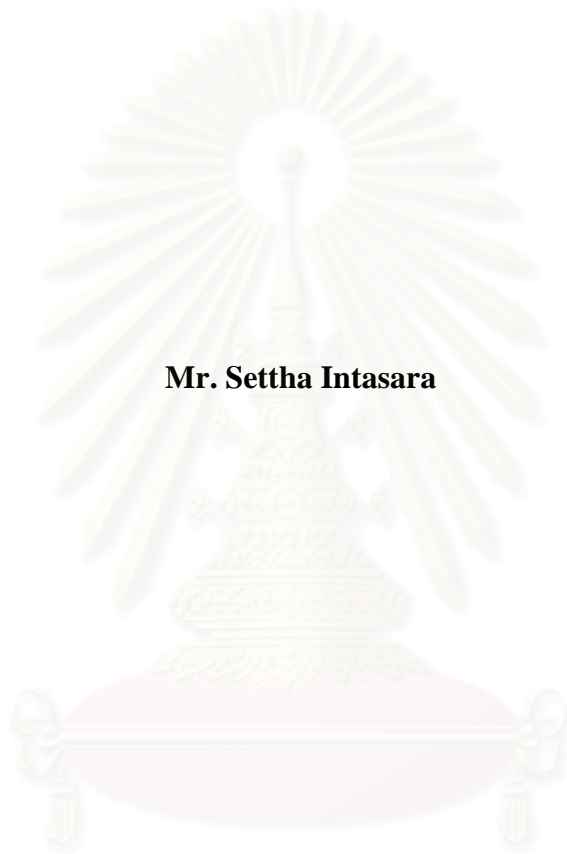
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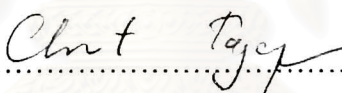Field of study Environmental Management
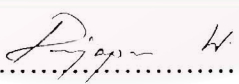Thesis Advisor Punjaporn Weschayanwiwat, Ph.D.
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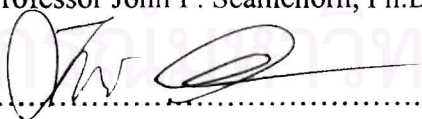
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ผสมของสารลดแรงตึงผิวชนิดประจุบวกและประจุลบในถังผสม-ตกตะกอนแบบต่อเนื่อง.
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สารละลายผสมที่ได้จากการผสมสารลดแรงตึงผิวชนิดประจุบวกและประจุลบเข้าด้วยกันนั้น
สามารถแยกออกเป็นสองวัฏภาคได้ด้วยตัวเอง เรียกว่าระบบสองวัฏภาคของสารละลายลดแรงตึงผิว
หรือเอเอสทีพี ระบบดังกล่าวถูกนำไปใช้ประโยชน์ในการสกัดสารเคมีที่ต้องการให้มีความบริสุทธ์
และความเข้มข้นสูงได้ หลังจากเกิดการแบ่งออกเป็นสองวัฏภาค ซึ่งประกอบไปด้วยวัฏภาคที่เข้มข้น
ไปด้วยสารลดแรงตึงผิวหรือวัฏภาคโคแอกเซอร์เวท ส่วนอีกวัฏภาคประกอบด้วยสารลดแรงตึงผิวซึ่งมี
ความเข้มข้นเจือจาง โดยวัฏภาคโคแอกเซอร์เวทมีปริมาตรน้อยมากเมื่อเปรียบเทียบกับอีกวัฏภาค ถ้า
ในระบบมีสารประกอบอินทรีย์ร่วมอยู่ด้วย จะพบว่า สารประกอบอินทรีย์ส่วนใหญ่จะละลายและถูก
ทำให้มีเข้มข้นสูงอยู่ในวัฏภาคโคแอกเซอร์เวท ในขณะที่วัฏภาคสารลดแรงตึงผิวความเข้มข้นเจือจาง
จะมีสารประกอบอินทรีย์ละลายอยู่ในความเข้มข้นต่ำมาก ในการศึกษาวิจัยได้ทำการประยุกต์ใช้ระบบ
เอเอสทีพีที่ได้จากการผสมระหว่างโดเดคซิลไตรเมททิลแอมโมเนียมโบรไมด์ (ดีแทบ) กับอัลคิลไดฟี
นิลออกไซด์ไดซัลโฟเนต (ดาวแฟ็ก) ซึ่งเป็นสารลดแรงตึงผิวชนิดประจุบวกและลบตามลำดับ ใน
อัตราส่วนผสมความเข้มข้น 2 ต่อ 1 เพื่อกำจัดฟีนอลในน้ำเสีย ณ อุณหภูมิห้อง โดยอาศัยระบบสกัด
แบบต่อเนื่องที่ประกอบด้วยถังผสมและตกตะกอน โดยทำการศึกษาถึงปัจจัยต่างๆ ที่มีผลต่อการสกัด
เช่น จำนวนรอบในการกวนผสม อัตราส่วนปริมาตรระหว่างสารละลายผสมของสารลดแรงตึงผิวต่อ
น้ำเสีย จำนวนถังตกตะกอนที่นำมาเชื่อมต่อในรูปแบบต่าง ๆ และความไม่ชอบน้ำของสารปนเปื้อน
จากการศึกษาโดยใช้จำนวนถังตกตะกอน 3 ถังต่อกันแบบผสมผสาน ใช้อัตราส่วนของอัตราการไหล
ระหว่างสารผสมลดแรงตึงผิวต่อน้ำเสีย 0.12 ซึ่งมีความเข้มข้นสารลดแรงตึงผิว 81.9 มิลลิโมลาร์ โดย
ให้จำนวนรอบในการกวนผสม 700 รอบต่อนาที ฟีนอลถูกกำจัดออกไป 74% มากกว่านั้นสาร
ปนเปื้อนที่ไม่ชอบน้ำมากจะยิ่งถูกสกัดอยู่ในวัฏภาคโคแอกเซอร์เวทจำนวนมาก ดังนี้ 4-คลอโรฟีนอล
>2-คลอโรฟีนอล > ฟีนอล

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KEY WORD: AQUEOUS SURFACTANT TWO-PHASE SYSTEM / PHENOL / WASTEWATER / MIXED SURFACTANT / MIXER-SETTLER

SETTHA INTASARA : PHENOL REMOVAL FROM WASTEWATER USING A PHASE SEPARATION OF CATIONIC-ANIONIC SURFACTANT MIXTURE SOLUTION IN CONTINUOUS MIXER-SETTLER. THESIS ADVISOR: PUNJAPORN WESCHAYANWIWAT, THESIS COADVISOR: JOHN F. SCAMEHORN, 104 pp.

Some cationic-anionic surfactant mixtures can spontaneously separate into two phases called aqueous surfactant two-phase system (ASTP). The separated phases are the micellar-rich phase and micellar-dilute phase. The organic compound present in the solution tend to solubilize and concentrate in the rich phase. The system is utilized as separation technique to remove phenol from wastewater in a continuous vessel at ambient temperature. Two moles of dodecyltrimethylammonium bromide (DTAB) and one mole of alkyldiphenyloxide disulfonate (ADPODS or trade name in DOWFAX 8390) were mixed and used as extracting agent. The mixer-settler was used as the continuous extractor in this study because it yields high throughput with less complication in term of vessel design and operation. The effects of degree of mixing in the mixer (via agitator speed), surfactant solution to wastewater flow rate ratio, and the number of settlers were investigated. The concentration of phenol in the effluence dilute phase decreases with increasing agitator speed, surfactant solution to wastewater flow rate ratio and number of settlers. It was found that the percentage of phenol removal achieved from this continuous extractor was approximately 74 % which was higher than that observed in a single stage, batch extraction at equilibrium condition at the same initial conditions. The optimal operation condition was 700 rpm of agitator speed, 81.9 mM of total surfactant concentration obtained by 0.12 surfactant to wastewater flow ratio and three settlers. Moreover, the higher degree of hydrophobicity of contaminant showed the greater potential of contaminant to be extracted in the surfactant-rich phase in the following order: 4-chlorophenol > 2-chlorphenol > phenol.

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

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                                       Co-advisor's signature...........................

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CHAPTER I

INTRODUCTION

Phenol is widely used as a raw material in petrochemical and paper industries, synthesis of plastics, chemicals and pharmaceuticals, etc. Phenolic compounds are among the most abundant organics impurities released into aquatic environment as a result of their use in many industries. The aqueous effluents from these industries are toxic and cause considerable damage and threat to the aqua system and human health (United States Environmental Protection Agency [U.S.EPA], 2000). Because of their toxicity, they are classified as high priority pollutant by the US Environmental Protection Agency (EPA) and other agencies in many countries (Puig and Barceló, 1996). In wastewater treatment, phenol can be removed by physical, chemical and biological processes. Phenol has high oxygen demand and low biodegradability. Therefore, the removal of phenol from wastewater is of environmental interest. At very high concentrations of phenol, the conventional biological oxidation processes are inapplicable, and this causes a need to develop the efficient and inexpensive water treatment processes (Fu and Ji, 2004).

Phase separation of the colloid systems has a great attention in the past decade (Schmitz and Bhuiyan, 2002). The liquid-liquid phase separation phenomenon is well established in mixed polymer solution (Lee et al., 2001) and polymer-colloid mixtures (Tuinier, Dhont, and Kruif, 2000), called aqueous two-phase systems (ATPs). A separation technique utilizing an environmentally friendly surface active agent called surfactant-based separation is an interesting technology gaining more attention. Surfactant-based separation processes represent one of the most promising new separation techniques over the past decades with potential for breakthrough improvements in industrial and analytical separation. The surfactant aggregates formed at interfaces (air-liquid, solid-liquid, and liquid-liquid) or in solution (spherical micelles, rod-like micelles, vesicles, etc.) can be used to cause or aid a separation. The examples of surfactant–based separation technique include micellar-enhanced ultrafiltration, cloud point extraction, froth flotation, foam fractionation, etc. Some environmental applications using surfactant-based separation techniques

include groundwater and wastewater clean-up, in-situ and ex-situ remediation of contaminated soil (Scamehorn and Harwell, 2000).

The phase separation of surfactant solution is known as an aqueous surfactant two-phase system (ASTP). The cloud point extraction (CPE) or micelle-mediated extraction (ME) of nonionic surfactant is one of ASTP exploited for extraction, purification and preconcentration of desired analytes. The CPE has shown to be an effective technique in environmental clean-up (Pramauro and Pelizzetti, 1990). Upon heating, aqueous solutions of nonionic surfactant become turbid at temperature known as cloud point, above that there is a separation of solution into two aqueous phases (Pramauro and Prevot, 1995), which are the surfactant-dilute phase and the surfactant-rich phase or the coacervate phase. In general, the surfactant-rich phase is small in volume and contains most of surfactant aggregates. Consequently, the analyte that solubilizes or bounds to micellar aggregates can be extracted and preconcentrated into a small volume of the surfactant-rich phase. The physical separation of the phases is caused by a difference in density between two phases. The phase separation process is reversible and thus, upon cooling the mixtures to temperature below cloud point, two phases again merge forming an isotropic, homogeneous solution (Attwood and Florence, 1983). CPE was firstly introduced by Hiroto Watanabe and co-workers to extract metal ions with an addition of metal chelate complexes (Tani, Kamidate, and Watanabe, 1997). Later on, CPE has been applied to extract and preconcentrate the organic compounds of environmental concern (Quina and Hinze, 1999; Kimchuwanit et al., 2000; Trakultamupatam, Schamehorn, and Osuwan, 2002; Santana, Ferrera, and Rodríguez, 2004).

In general, anionic and cationic surfactants are incompatible as manifested by precipitate formation. The precipitation phenomenon of mixtures of anionic and cationic surfactants in aqueous solutions has been extensively studied (Scamehorn and Harwell, 2005). However, soluble anionic-cationic surfactant complexes can be formed successfully if either an anionic surfactant or a cationic surfactant or both have a large hydrophilic group (Mehreteab and Loprest, 1988). The resulting neutralized water-soluble complexes exhibit similar properties to nonionic surfactants and thus, can be thought of a pseudo-nonionic surfactant. A mixture of anionic and cationic surfactants often exhibits different properties deviated from an individual surfactant, for example, increasing surface activity, exhibiting new properties (e.g., cloud point phenomenon similar to nonionic surfactants), and forming

different types of surfactant aggregates (e.g., vesicles instead of spherical micelles). In addition, they often show lower critical micelle concentrations (CMCs) than those of individual anionic and cationic surfactant (Mehreteab and Loprest, 1988). Therefore, it becomes topics of interest for numerous technical applications (Ruiz and Aguiar, 2003). However, to our knowledge, the investigations about vesicle formation in cationic and anionic mixed surfactant systems are mostly in aqueous solutions and rarely in ethanol (Huang, 1997).

Cationic-anionic surfactant mixtures can spontaneously separate into two phases, one is the surfactant-rich phase and the other is the surfactant-dilute phase. The phase separation is found to be strongly dependent on the mixing ratio of mixed surfactants, electrolyte concentration, and the presence of additives (Yin et al., 2002; Krutlert, 2004; Kunanupap, 2004; Khaolerk, 2006). A new ASTP has been used for an isolation and the separation of biomaterials (Zhao and Xiao, 1996; Xiao, Sivars, and Tjerneld 2000; Lu et al., 2005) and organic dye (Tong, Dong, and Li, 1999). When the surfactant-rich phase is diluted, the solution forms a new ASTP system. Therefore, a multi-step partitioning can be achieved and the selectivity of the system can also be enhanced (Xiao et al., 2000). It has been reported that the phase separation of a solution containing dodecyltrimethyl ammonium bromide (DTAB) and alkyldiphenyloxide disulfonate (DOWFAX 8390) occurs even at temperature closed to the freezing point of water (Kunanupap, 2004). It is beneficial in economic viewpoint because the phase separation can occur in a wide range of temperature and especially at ambient temperature. So, an addition of energy is not essentially required like the system of nonionic surfactant that the phase separation is induced only at temperature above cloud point which can be higher than the ambient temperature.

In addition, the organic pollutants such as phenol containing in the wastewater tend to solubilize into the surfactant aggregates due to its affinity to the surfactant aggregates. After the phase separation, surfactant and organic pollutants are concentrated in the surfactant-rich phase. The dilute phase, which contains a low concentration of organic pollutant and surfactant, can be discharged to the environmental as the effluent water if the concentration of pollutant is well below the regulation. The ASTP extraction technique does not only remove pollutants from wastewater but also preconcentrate the pollutants in the concentrated form in the surfactant-rich phase. Thus, it can reduce the amount of waste required for further treatment. Moreover, the surfactant in the surfactant-rich phase can be recovered for

reuse (Xiao et al., 2000). Especially, if it is applied to remove the volatile organic compounds (VOCs), the surfactant in the surfactant-rich phase solution can be recovery for reuse because the VOCs have high enough volatility to be separated from the concentrated surfactant solution by gas, steam or vacuum stripping (Hasegawa, Sabatini, and Harwell, 1997; Choori et al., 1998; Kibby, Pennell, and Hayes, 2001).

The pilot scale CPE using nonionic surfactant in continuous differential extractor was investigated to extract the aromatic compounds of environmental concern such as toluene and ethylbenzene (Trakultamupatam, Scamehorn, and Osuwan, 2004a, 2004b). They studied the factors, for example, rotating speed of mixing, flow rate ratio of surfactant solution and wastewater, and added electrolyte concentration, affecting the surfactant partition ratio, organic pollutant partition ratio, fraction of organic extracted in the surfactant-rich phase and mass transfer coefficient. Using ASTP extraction system formed by cationic and anionic surfactant mixtures to remove benzene from aqueous wastewater was studied in batch experiment (Kunaupap, 2004). However, it has never been investigated as a continuous, steady state operation to extract and preconcentrate the organic pollutants of environmental concern and the operating variables in a continuous vessel affecting the extraction efficiency in this novel cationic-anionic surfactant system. In addition, a simple, easy to design, fabricate and operate continuous device that is applicable for this ASTP extraction system should be introduced.

1.1 Objectives of the study

The main objective of this research was to study the ASTP extraction technique formed by mixtures of cationic and anionic surfactants as separating agents in a continuous, stage wise mixer-settler to remove phenol from a synthesis wastewater. The sub-objectives were as follows:

1. To design and fabricate a mixer-settler which can be operated in continuous mode.

2. To determine an optimal operating condition such as mixing speed in mixer; flow rate ratio of surfactant solution and wastewater; and settling time in settlers.

3. To compare the extraction efficiency between batch and continuous operation.

1.2 Scope of the study

The ASTP system formed by cationic-anionic surfactant mixture was utilized to remove phenol from synthetic wastewater at fixed initial phenol concentration of 100 ppm. Dodecyltrimethylammonium bromide (DTAB) and alkyldiphenyloxide disulfonate (DPDS or tradename of DOWFAX 8390) were used as cationic and anionic surfactants in this study, respectively at 2:1 molar ratio of DTAB:DOWFAX. The ASTP extraction system was continuously operated in a stagewise mixer-settler. The time for system to attain the steady state condition was determined. The optimal condition such as contact time and mixing speed in the mixer; flowrate ratio of surfactant solution to wastewater; and settling time in settler were examined. Removal of phenol from synthetic wastewater was done in batch experiment at equilibrium condition for comparison purpose on removal efficiency.

CHAPTER II

THEORECTICAL BACKGROUND AND LITERATURE REVIEW

2.1 Phenol

Phenol, empirical formula as C_6H_6O, is a weak acid which is normally in form of colorless to light pink crystalline solid. Pure phenol absorbs water easily from air and liquefies. It has high boiling point of 181.8°C at atmospheric pressure. The water solubility of phenol is 84 g/L at 20°C. Above 68.4°C, it is completely miscible with water. It has a strong odor that is sickeningly sweet and irritating. It evaporates slower than water. Phenol and especially most of its reaction products with chlorine have an unpleasant taste and odour. The occurrence of phenol in drinking water is unacceptable (European Chemicals Bureau [ECB], 2006). Therefore, notification of the Ministry of Industry of Thailand regulates the maximum acceptable concentration of 1 µg phenol per liter of drinking water (Pollution Control Department [PCD], 2006).

Phenol is produced through both natural and anthropogenic processes. It is naturally occurring in some foods, human and animal wastes, decomposing of organic materials, and is produced endogenously from the metabolism of protein. Phenol has been isolated from coal tar but it is now synthetically manufactured. Currently, the largest use of phenol is as an intermediate in the production of phenolic resins, which are used in the plywood, adhesive, construction, automotive, and appliance industries. Phenol is also used in the production of synthetic fibers, such as nylon, and as epoxy resin precursors such as bisphenol-A. Phenol is toxic to bacteria and fungi, and is used as a slimicide and disinfectant. Because of its anesthetic effects, phenol is used in medicines such as ointments, ear and nose drops, cold sore lotions, throat lozenges, and antiseptic lotions. People are also exposed to phenol from consumer products such as medicines and lotions, as well as from foods and tobacco smoke. Phenol has been found in drinking water (U.S.EPA, 2000).

Widespread of water contamination by phenol has been recognized as an important issue in recent years. The primary sources of phenol contamination in

environmental are automobile exhaust (direct emission and photochemical degradation of benzene), human and animal metabolism and combustion processes. From industrial sources, it enters the environment from production and processing of chemicals. Releases also occur due to the wastewater from cooking plants and low-temperature carbonization plants using hard coal and brown coal, from refineries, from pulp manufactures and landfill leachate (ECB, 2006).

Phenol is usually found in the environment below 100 parts per billion (ppb), although much higher levels have been reported. One ppb or less of phenol has been found in relatively unpolluted surface and ground waters. High concentration of phenol has been found in surface waters when phenol was released from industries. Phenol has been found in 184 out of 1177 hazardous waste sites as reported in the National Priorities List (NPL) in the United States.

Studies in humans and animals show that most of phenol entering human body through the skin by breathing contaminated air, or eating food and drinking water, or taking products that contain phenol, leave the body in the urine within 24 hours. From the available test results stated that phenol has only a low bioaccumulation potential. The serious effects usually increase when both the level and length of exposure increase. The effect caused by breathing phenol in the air is still unknown. The effects of exposure to phenol on human reproduction and the developing fetus are also unknown. There is not enough information to identify whether phenol can cause cancer in humans, but cancer occurs in mice when phenol is put on the skin. When phenol is combined with other chemicals that cause cancer and put on the skin, more chances of cancer can be found than when the other chemicals are put on alone. The US Environmental Protection Agency (EPA) regulates that waters (lakes, streams) should not contain more than 0.3 milligrams phenol per liter of water (0.3 mg/L) to protect human health from the possible harmful effects of exposure by drinking water and eating contaminated water plants and animals (United States Public Health Service [USPHS], 1989). Hence, the treatment of wastewater containing phenol is important.

The aqueous effluents from chemical, pharmaceutical and petrochemical often contains with high boiling point, such as phenol and its derivative that cannot be discharged into a sewage treatment plant without reprocessing and cleaning. The undesired pollutants in process water need to be removed prior

reclamation into the process or discharging to the environment. The destruction through burning is not an ecologically preferred method as well as energy intensive due to high water content. The separation of phenolic compounds from wastewater is rather difficult due to their relatively low volatility and tendency to form azeotropes and eutectics. Hence the distillation process is inapplicable. Alternative techniques such as electrochemical treatment using semiconductor electrodes reactor (Fu and Ji, 2004), extraction using supercritical CO_2 (Ghonasgi et al., 1991), oxidation in presence of enzymes, photo catalytic oxidation by TiO_2 particles, separation using liquid membranes and adsorption on activated carbon and clays are proposed. Adsorption is the most accepted choice among these techniques for water treatment mainly because of low operational costs. However, the recovery of activated carbon particles from treated water shows another separation problem. The application such liquid-liquid extraction using surfactant was developed for removing phenol from wastewater (López-Montilla et al., 2005). With the phenol content in the wastewater of less than 5 ppm, the water can be discharged into the biological sewage treatment plant. Then, the extraction offers the decisive advantage. The chosen extraction unit depends on the wastewater volume and type of solutes to be extracted. With greater volume streams, extraction should be performed continuously in serially connected mixer-settlers (QVF Engineering GmbH, 2006).

2.2 Surfactant

2.2.1 Introduction

The term "surfactant" is a contraction of "surface active agent". By its name, it has a tendency to adsorb or concentrate at interfaces between bulk phases such as at water-air surface or solid-liquid interface. A surfactant molecule is composed of two basic parts: a water-soluble (hydrophilic) head group and an oil-soluble (hydrophobic) tail group as shown in Figure 2.1. While the tail group is often a hydrocarbon chain, the head group can be charged or uncharged. Because of two dissimilar parts in one molecule, it is called an amphipathic structure (Scamehorn, Sabatini, and Harwell, 2004). This combination makes the surfactant ambivalent; the hydrophilic head group is attracted to polar environments, for example water, while

Figure 2.1 General representation of surfactant molecule (Scamehorn et al., 2004)

the hydrophobic tail is attracted to non-polar 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).

The surfactant under several names such as detergents, coagulants, dispersants, emulsifiers, de-emulsifiers, foaming agents and defoamers is one of the most widely used class of chemicals in industries. They used in various products such as pharmaceuticals, detergents, drilling muds and flotation agents. Of late, surfactants have applied in such high-technology areas such as electronic printing, magnetic recording, biotechnology, microelectronics and viral research (Rosen, 2004).

2.2.2 Types of surfactant

The vast majority of tailed group, used as commercial surfactants, have a hydrocarbon group. They can be fluorocarbon or silicon based to used for special application. The hydrocarbon tail is generally derived from natural sources like animal fat or vegetable oil, or synthetic sources like petroleum derivatives. The head group can be varying dramatically between surfactants. The surfactants are normally classified into four major types which depended on the charge of the hydrophilic group, as illustrated in Table 2.1.

Anionic surfactants are molecules possessed a negatively charged in the hydrophobic portion such as sulfonate, carboxylate, sulfate and phosphate which

Table 2.1 Classification of surfactant molecules

Hydrophilic group	Examples	Structure
Anionic	Linear Alkyl Sulfate	
Cationic	Quaternary Ammonium Cation	
Nonionic	Ethers of fatty alcohol	
Zwitterionic/ Amphoteric	Betaine	

(Source: http://www.scienceinthebox.com/en_UK/glossary/surfactants_en.html)

are the polar group found in this type. The most commonly used surfactants are including alkylbenzene sulfonates (detergents), soaps (fatty acid), lauryl sulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent), lignosulfonates (dispersants), etc. Anionic surfactants are the largest volume used in the commercial and household product. Anionic surfactants account for about 50% of the world production.

In contrast to anionic surfactant, cationic surfactants are molecule possessed a positively charge in the hydrophilic portion such as a quaternary ammonium salt, with one or several long chain of the alkyl group. They are often coming from natural fatty acids. Due to the positive charge on the head group giving the strong substantively on negatively charged fibers such as cotton and hair, they are used as fabric and hair conditioners. In general, this surfactant is more expensive than anionic because of the high –pressure hydrogenation reaction used during synthesis.

Nonionic surfactants are surfactant without charges in their hydrophilic part of molecule. They typically have a polymeric group or an uncharged hydrophilic group like poly(ethylene oxide) as the head group. A large proportion of nonionic surfactant used in industries has their hydrophilic portion as monoglyceride of long-chain fatty acid or polyethylene glycol chain, obtained by the polycondensation of ethylene oxide. Hence, they are called polyethoxylated nonionic surfactant.

Zwitterionic surfactant has both of positive and negative charges on the head group. This group is milder on the skin particular on eyes than anionic surfactants. They are used in toiletries and baby shampoos. Amphoteric surfactants have their head group which charges depending on pH. For example, they have got positive charge at low pH but they become negative charge at high pH. Because amphoteric are generally zwitterionic surfactant at some pH. Zwitterionic surfactants are often amphoteric. Then, the terms "zwitterionic" and "amphoteric" are used as synonyms. Both of surfactants are generally expensive. Then, their applications are limited such using in cosmetics (Rosen, 1989; Holmberg, 1998; Rosen, 2004; Scamehorn et al., 2004).

2.2.3 Surfactant aggregates and behavior

The surfactant is a molecule which alters the interfacial properties of any two immiscible phases by concentrating at the interface and changing the interfacial free energy of the interface (Rosen, 2004). In aqueous solution, the driving force for a surfactant's tendency to adsorb at interfaces and to form aggregates is the incompatibility of the tail group with water. Because of their hydrophobic nature, tail groups tend to insert themselves into a hydrophobic phase, or tend to self-assemble by forming aggregates in which the tails intertwine to form a hydrophobic environment from which water is largely excluded. Surfactant can aggregate in aqueous solution to form colloidal-sized clusters referred to as micelles (normal micelles). At low surfactant concentration in aqueous solution, surfactant presents as monomer in the solution as well as adsorbed at the interface. However, the surfactant monomers start to interact, self-assemble and aggregate forming at sufficiently high concentration in solution. The concentration at which this phenomenon occurs is called the critical

micelle concentration (CMC). However, depending upon the specific surfactant and solution conditions, micelles can adopt a variety of shapes, ranging from roughly spherical to ellipsoidal (oblate or prolate) as illustrated in Figure 2.2. In either case, the interior region of the micelle contains the hydrophobic moieties of the surfactant molecules and the outer surface consists of the hydrated hydrophilic groups along with any bound water molecules. In the case of the variation of aggregate formation, the certain value of surfactant called critical aggregation concentration (CAC) will be used. (Herrington and Kaler, 1997; Quina and Hinze, 1999; Scamehorn et al., 2004).

Micelle formation is an important phenomenon in detergency and solubilization. When surfactant monomers are dissolved in water at low concentration, the hydrophobic groups distort the structure of the water and increase the free energy of the system. Reorienting the surfactant monomers so that their hydrophobic groups directed away from the water is one way to minimize the system free energy. If the surfactant concentration is increased beyond a point at which the interface is completely covered with surfactant monomers, micelle formation is another way to reduce the free energy of the system (Rosen, 2004). The hydrophilic heads orient toward the water, while the attractive tail-tail hydrophobic interaction provides the driving force for the aggregation as the simplest new structure. The electrostatic repulsion between the polar head groups limits the size (Aswal, 2003).

When dissolved in non-polar organic solvents, surfactants form reversed micelles as seen in Figure 2.2. In the micelle, the hydrophobic tails flock to interior to minimize 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 interaction (Tanford, 1980; Israelachvili, 1991). There are fewer studies of reverse micelles compared to those on normal micelles, because the vast majority of surfactant applications are in aqueous solution.
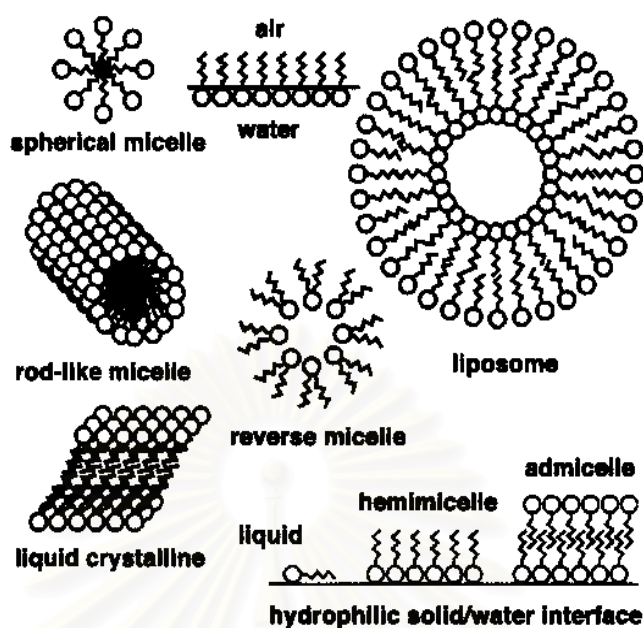
Figure 2.2 Typical surfactant aggregates (Scamehorn et al., 2004)

Surfactant molecule contributes differently to a given property when present as monomer versus in a micelle. The CMC value can be determined by plotting a physicochemical property of the solution, i.e. surface tension, conductivity, turbidity, osmotic pressure, fluorescence, and light scattering versus the surfactant concentration (Rosen, 1989; Hiemenz and Rajogopalan, 1997; Scamehorn et al., 2004).

In general, the critical micelle formation concentration (CMC) can be determined by carrying out surface tension measurements on a series of different surfactant concentrations. Surfactants exhibit a specific surface tension curve as a function of the concentration. Initially the surfactant molecules increasingly enrich themselves at the water surface. During this phase the surface tension decreases linearly with the logarithm of the surfactant concentration. When the CMC is reached, i.e. when the surface is saturated with surfactant molecules, a further increase in surfactant concentration no longer has any appreciable influence on the surface tension. At the CMC the water/air interface is saturated with surfactant monomers and the reduction of the surface tension strongly diminishes, as shown in Fig. 2.3. The value of the CMC is determined by the discontinuity in the plot. The magnitude of the CMC value is specific for each surfactant (Uppgård, 2002; KRÜSS GmbH, 2007).
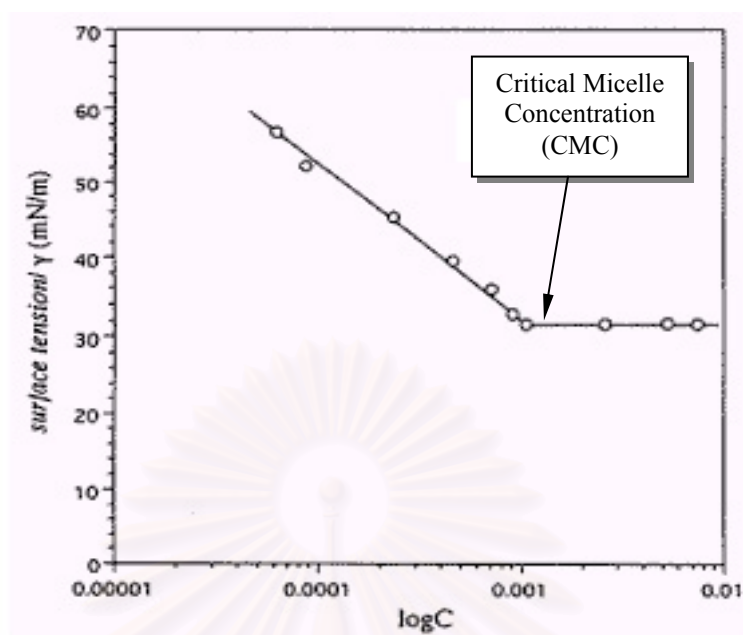
Figure 2.3 Determination of the critical micelle formation concentration
(KRŰSS GmbH, 2007)

Factor affecting the CMC and micellization are structure of surfactant (hydrophobic volume, chain length, head group area), temperature, additive, pH, surfactant concentration and surfactant composition (for surfactant mixtures) (Rio et al., 1994; Kang, Kim and Lim, 2001; Murphy and Taggart, 2002; Yin et al., 2003). In general, the CMC decreases strongly with increasing CH_2 group (Holmberg et al., 2003; Rosen, 2004). In addition, the CMC may vary depending on the variation in hydrophobicity, counterion, or electrolyte concentration (Hiemenz and Rajagopalan, 1997). The electrolytes which usually are used for the purpose such as NaCl, KCl, NaBr and $NaNO_3$ are capable of salting-out, while $Mg(NO_3)_2$ and $Al(NO_3)_3$ are capable of salting-in. The effect of adding electrolytes to nonionic and zwitterionic surfactants is more complex in describing by the salting-in and salting out effects which increasing and decreasing of CMC, respectively. The presence of electrolyte in aqueous solution of inonic surfactant, causes changing to the CMC. The reduction of the electrostatic repulsion, between head groups, will promote the micelle formation at lower concentration. Thus, the CMC is declined (Clint, 1992).

2.2.4 Geometrical aspects of the aggregation

The structure of aggregates formed from surfactant molecules varied widely. Possibilities include spherical, rod-like micelles, bilayers and inverted structure etc. (Fig. 2.2). The aggregation structures of surfactant in aqueous solution depend on the chemical structure of surfactant and solution condition such as concentration, temperature, pH and ionic strength. These structures can transform from one to another when solution are changed (Uppgård, 2002; Aswal, 2003). The single-phase systems can be divided into isotropic solutions, solid phases and liquid crystalline phases.

2.2.4.1 Micelles

(i) Spherical Micelles

Spherical micelles are clusters composing of surfactant tails in the inner core while the hydrophilic head group facing with water. In general, the unbranched single-tailed surfactant posses a conical shape which usually to form spherical micelles in aqueous solution above their CMC. Spherical micelles usually consist of 40-100 monomers and have got the radius of hydrocarbon which is close to the length of the extended alkyl chain (Holmberg et al., 2003; Rixt, 2001).

(ii) Rod-like or Cylindrical Micelles

The existing of rod-like micelles in aqueous solution is reflected by an increase in relative viscosity. The viscoelasticity indicates that an entangled network of rod-like micelles has been formed. Rod-like micelles are the form which that the surfactants elongate themselves into tube with the hydrophobic tail oriented into the inner and the hydrophilic head towards the water. Both theoretical and experimental studies show that rod-like micelles are long in scale of several tens of micrometers. Formation of rod-like micelles can often be induced by addition of strongly binding

counter ions to ionic surfactants in aqueous (Rixt, 2001; Holmberg et al., 2003; Ridell, 2003).

(iii) Vesicles or Liposome

Usually, surfactant molecules possessing one head group with two alkyl tails form vesicles in aqueous solution. Vesicle form curved bilayers similar to those of the lamellar phase. The hydrophobic tails are the inner core of the bilayer while the hydrophilic head are located at the bilayer-water interface. A vesicle is a shell which encapsulates an aqueous interior. Vesicle range in diameter from 20 mm to several micrometers (Persson, 2003; Rosen, 2004).

(iv) Lamellar Micelles

Lamellars are flat bilayer similar to cell membranes (Visscher, 2004). The comparable effects of unsaturation and branching on thermotropic phase behavior of bilayers have led to the suggestion that branched-fatty acyl chains perform similar functions in lipids of bacterial membranes as unsaturated hydrocarbon chains in lipids of eukaryotic cell membranes (Menger et al., 1988)

(v) Reverse Micelles

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

2.2.4.2 Liquid crystals

Many surfactants form solution in which the micelles are no longer randomly distributed but are organized into structure known as liquid crystal. The

structure will be formed, if the surfactant concentration increases above CMC. The four main types of liquid crystal are shown in Figure 2.4.
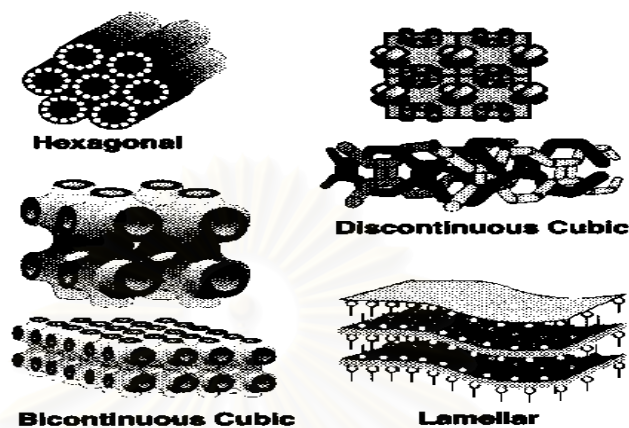
Figure 2.4 Types of surfactant liquid crystals (Scamehorn et al., 2004)

The surfactant structures transition as follow: spherical micelles, cylindrical micelles, discontinuous cubic liquid crystals, hexagonal liquid crystals, bicontinuous cubic liquid crystals and lamellar liquid crystals. Liquid crystal formation or transition of one type of liquid crystal to another can be induced by other factors, such as ionic strength and temperature. Liquid crystals have substantially longer lifetimes than micelles. Optical microscopy under polarized light is often used to detect liquid crystal (Scamehorn et al., 2004).

In order to understand the formation of aggregates, molecular packing constraints within the core of the aggregates. Aggregation into assemblies of definite size and shape is the result of the combined effect of opposing forces which complete mainly in the interfacial region (Evans, Mitchell, and Ninham, 1984). One factor tends to decrease the head group area (a) of the surfactant monomer in the surfactant aggregates: the interfacial tension. This tendency is counteracted by the (electrostatic) head group repulsion and chain packing constraints. Therefore, an optimal head group area (a_o) exists, which is the surface area for which both factors are balanced. Obviously, a_o is dependent on the nature of surfactant, concentration both of surfactant and added salt, temperature, pressure and solvent. In a first approximation, surfactant molecules will associate solely into types of aggregates for which their

head group area is closed to the optimal value. In addition, two other constraints are the volume (v) of the hydrocarbon chain of a surfactant monomer and the maximum length (l_c) that the alkyl chains of monomer can assume by calculation via number of carbon atom in unbranched and saturated alkyl chain. For a particular surfactant molecule, the ratio $v/a_o l_c$ will be used to determine the possible geometry of the aggregate. This dimensionless is called packing parameter (P). The schematic representation of the relationship between the shape of surfactant monomer, the packing parameter and the morphology of the aggregate is presented in Figure 2.5 (Israelachvili, Mitchel, and Ninham, 1976).

2.2.5 Solubilization by micelles

The shape of surfactant aggregates brings about interesting properties e.g. their ability to solubilize the solute molecules into inner core of the micelle, viscosity, cloud point phenomenon. Solubilization is an ability to dissolve the water-insoluble hydrophobic molecules (solubilizates) in micelle core which has the oil-like environment (Rosen, 2004). The use of surfactants to enhance subsurface remediation of organic pollutant has gained more attentions. Solubilizate is incorporated into micelles in different location according to their structure. The surfactant micelles can enhance the solubility of highly hydrophobic compounds via the hydrocarbon pseudo-phase in the micellar core. Moderately polar and ionic compounds can also be solubilized into outer palisade layer of micelle, which consists of polar moiety of amphipathic surfactant molecule. Both phenomena result in high concentration of hydrocarbons in solution beyond their expected solubility limits and thus contribute to enhance the product recoveries.

Tokiwa and Aigami (1971) studied on a solubilization of aromatic alcohols and phenol by a surfactant. Solubilization of aromatic alcohols varied the extended carbon from 1 to 3 and phenol by an anionic surfactant, sodium dodecyl sulfate, has been investigated by NMR measurements. They stated that these materials are probably solubilized near the surface of the micelle or at palisade layer, depending on their structures and the number of carbon on alcohol chain extended from benzene ring.
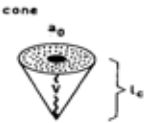
Critical packing shape of a surfactant monomer	Packing parameter	Morphology of the aggregate
cone	< 1/3	spherical micelles
truncated cone or wedge	1/3< > 1/2	rod-like micelles
cylinder	1/2< >1	bilayers
inverted truncated cone	>1	inverted structures

Figure 2.5 Schematic representation of the relationship between the shape of surfactant monomer, the packing parameter and the morphology of the aggregate.

Solubilization is one of the most important properties of surfactant that has been widely utilized in industries such as removal of oil. They usually are used as ingredient in household and agro applications such as detergents, pharmaceuticals, cosmetics, insecticides, etc. Solubilization potential (the ability of surfactant micelles to increase the hydrocarbon concentration in solution beyond the aqueous solubility component) is quantified by micelle-water partition coefficient, K_m, which is a partitioning of hydrocarbons between micellar and the aqueous pseudo-phase. To determine solubilization potentials for aqueous hydrocarbon concentration below the solubility limit, semi-equilibrium dialysis (SED) cells has been utilized (Rouse et al., 1995). The solubilization equilibrium constants of organic solutes in surfactant solution have been measured by other methods, for example, vapor pressure method, head-space gas chromatography, micellar-enhanced ultrafiltration and molecular sieve or gel filtration methods (Abe et al., 1993). If the solute is volatile, head-space chromatography is recommended.

The solubilization ability is influenced by the structure of surfactant and solubilizate, added electrolyte, organic additive, type of aggregate and temperature (Holmberg et al., 2003; Rosen, 2004). The factors affecting solubilization in surfactant aggregates were investigated. Highly hydrophobic solutes solubilize well but high molecular weight solutes such as highly-branched alkane yields a different result. Larger micelles or lower CMC value of surfactant bind more solublizate. It is known that the shape of the micelle is determined by critical packing parameter. As this value increases, the volume of the inner core increases. The amount of solubilizates can be increased in solubilization. Because of the solubilized positon of solubilizates, increasing in the chain length of the hydrophobic portion of the surfactant leads to increase the solubilization capacity for hydrocarbon solubilizates. Electrolytes can enhance solubilization on the ionic surfactant solution by decreasing CMC and increases in volume of the micelles due to reduction in the repulsion forces between the similar charged ionic surfactant head groups. The solubility of solutes can be enhanced by temperature raising in system of nonionic surfactant especially the polyoxyethylene type. Because of increasing in micelle size and aggregation number, the nonionic surfactant increases in the extent of solubilization for both polar and non-polar solubilizate (Clint, 1992; Dunaway, Christian, and Scamehorn, 1995; Rosen, 2004).

Abou et al. (2004) studied on the effect of phenol addition on the critical micelle concentration and molar enthalpy of micellisation of alkanediyl-α,ω-bis(dodecyldimethyl-ammonium bromide) geminis at 298 K. Depression of the critical micelle concentration and the enhanced thermal effect of micellisation in the presence of phenol were reported. The location of polarisable phenol molecules at the outer portion of the surfactant micelles is postulated.

2.3 Cloud Point Extraction (CPE)

Novel classes of separation processes known as surfactant-based separation have shown to be effective techniques in environmental clean-up (Scamehorn and Harwell, 2000). These techniques involve biodegradable, non-toxic separating agent and included technologies such as foam fractionation, froth floatation

and microemulsion. One surfactant-based separation of interest is cloud point extraction (CPE). The basis of the phase separation (or cloud point) extraction technique, was introduced and pioneered by Hiroto Watanabe and co-workers which utilized it for the effective extraction of metal ions as hydrophobic metal chelate complexes (Quina and Hinze, 1999). The well-known phase phenomenon is exhibited by some micellar surfactant solutions. The best known example of this technique is the separation of a nonionic micellar phase above the cloud point temperature of polyethylene surfactant solution (Kimchuwanit et al., 2000). When the micellar solution of nonionic surfactant is heated at a temperature higher than a certain temperature known as cloud point, the surfactant tends to be more soluble in oil than water. Above a certain temperature called the cloud point which solution become turbid, it loses its water solubility nearly completely; hence, the surfactant micelles separate out from the aqueous phase. As a result, the clear solution becomes turbid and phase separation occurs. For nonionic system, the temperature-induced dehydration of the polyoxyethylene head-groups promotes micellar growth and demixing. Above the cloud point temperature, the homogeneous surfactant solution separates into two phases. Phase separation results from the competition between entropy which favors miscibility of micelles in water and enthalpy which favors miscibility of micelles from water. Phase separation occurs over a narrow temperature range. One phase called the surfactant-rich phase (typically referred to as coacervate phase) contains most of surfactant aggregates and the other phase called the surfactant-dilute phase. It is important to note that the surfactant concentration in surfactant-dilute phase contains water with surfactant aggregates at concentration equals or exceeds as 3-20 times higher that it's CMC. So, those micelles or other surfactant aggregate species are also present. The actual physical separation of the phases is facilitated by the difference density between the two (dilute-aqueous and surfactant-rich) phases. The phase separation process is reversible and upon cooling the mixture to a temperature below the cloud point, the two phases again merge to form an isotropic, homogeneous solution. The hydrophobic compounds presented in the solution tend to solubilize into the surfactant aggregates and concentrate in the surfactant-rich phase, leaving only very small portion in the surfactant-dilute phase (Quina and Hinze, 1999; Kimchuwanit et al., 2000; Trakultamupatam et al., 2002). For homologous series of polyoxyethylated nonionic surfactants, the cloud point

increases with decreasing length of the hydrocarbon chain or increasing length of the oxyethylene moiety. The presence of other surfactants, acids or bases, salts and/or organic additives can alter the critical temperature of such aqueous surfactant solutions, sometimes dramatically (Quina and Hinze, 1999).

Marterna et al. (2001) studied on the removal of phenols, 4-methylphenol, and 4-nitrophenol from aqueous streams by cloud point extraction technique with oxyethylated methyl dodecanoates as surfactant with average degrees of oxyethylation (n) ranging between 5 and 14 (denoted OMD-n). The cloud point (CP) increases with the average degree of oxyethylation n but is independent of OMD-n concentration, except at low concentration (i.e., < 10 g.L^{-1}) but strongly decreases when electrolyte such as NaCl is presented. Many parameters influence the extraction of phenols in OMD-n-rich phase, including the characteristics of phenols (hydrophobicity, hydrogen-bond acidity, hydrogen-bond basicity, etc.), the average degree of oxyethylation of OMD-n, the concentration of electrolyte, the settling temperature (Tset), and overheating (delta T = Tset - CP). The distribution coefficients typically range between 20 and 100. Recovery of phenols changes in the following order: 4-nitrophenol > 4-methylphenol > phenol (Materna and Szymanowski, 2002). The kinetics of the separation process is limited by the slow coalescence of the fine droplets of surfactant-rich phase formed above CP.

The cloud point extraction (CPE) method, sometimes also called micellar or micelle-mediated, liquid-coacervate extraction is based upon this unique phase separation behavior exhibited by aqueous solution of certain neutral (non-ionic and zwitterionic) surfactant micelles. Consequently, any desired analyte that solubilized by or bound to the micellar aggregate entity can be separated and extracted (and preconcentrated) into the small volume element of the surfactant-rich phase as a conventional liquid-liquid extraction step (Quina and Hinze, 1999). CPE offers many advantages over traditional liquid–liquid extraction, for example, CPE is an aqueous-based extraction system that avoids using a large amount of toxic and flammable organic solvents as conventional solvent-extraction technique. In addition, CPE can lead to higher recovery efficiency and preconcentration factor because the presence of surfactant can minimize losses of analytes due to their adsorption onto the container and the surfactant-rich is generally small in volume (Li and Chen, 2003). Moreover, this technique serves in terms of experimental convenience, lower cost and

accrues with respect to sample/analyte storage and analyte detection (Quina and Hinze, 1999).

Haddou, Canselier and Gourdon (2003) studied the purification of effluents which contains phenol and benzyl alcohol by two-aqueous phase extraction via cloud point properties of nonionic surfactant as commercial alcohol ethoxylates. The soluble pollution was used at 0.15 wt %. They found that, the presence of phenol or benzyl alcohol lowers the cloud point of the nonionic surfactants. The extraction percentages close to 95 % for phenol and 90 % for benzyl alcohol, provided that the surfactant concentration is high enough. In addition, a significant temperature rise beyond the cloud point has negative effect on extraction percentage of benzyl alcohol, although less water-soluble than phenol, is less easy to extract. Thus, the aqueous solubility of the solute is not the only parameter controlling solubilization and extraction efficiency.

Trakultumupatam et al. (2004a, 2004b) studied on scaling up cloud point extraction of aromatic contaminants (toluene and ethyl benzene) from wastewater in a continuous rotating disk contactor by using nonionic surfactant, t-octylphenolpolyethoxylate as separating agent. The concentration of solutes in the surfactant-rich phase increases as agitator speed, wastewater to surfactant solution flow rate ratio and degree of alkylation of the aromatic solutes increase. In the pilot scale with multistage operation, the toluene partition ratio and concentration of toluene in the surfactant-rich phase is two times grater than that observed in a single stage, equilibrium batch experiment with the same initial condition. The addition of NaCl results in an increase in temperature gap between operating and cloud point temperature since NaCl can depress the cloud point. The overall volumetric mass transfer coefficient and the number of transfer unit increase, whereas the height of transfer unit decreases when temperature is raised or NaCl is added to solution.

2.4 Anionic-Cationic Surfactant Mixtures

Mixtures of surfactants exhibit different levels of synergism depending on the charge and molecular structure of the individual surfactant component (Rosen, 1989). When anionic and cationic surfactants are mixed, they neutralize each other.

The charge of complex is eliminated causing it to precipitate out of solution, especially surfactants which containing highly symmetric straight chain. However, soluble anionic-cationic surfactant complexes can be successfully without precipitation if either the anionic or cationic or both of surfactants have a large hydrophilic group or the bulky substitutes in the hydrophobic moiety (Mehreteab and Loprest, 1988). In addition, when either anionic or cationic surfactant is significantly in excess, the precipitation does not occur. In addition, 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 in mixed anionic/cationic surfactant systems (Yatcilla, 1996; Mehreteab, 1999).

The effect of chain-length asymmetry on the phase behavior and aggregate morphology of mixtures of anionic and cationic was explored using cryotransmission electron microscopy, quasielastic light scattering and surface tensionsiometry. When surfactants are branched and/or contain a bulky substitute (e.g., a benzene group) in the tail group, the precipitate-phase stability is reduced relative to that of micellar and vesicle phases. Because the charges are neutralized, the area occupied by a head group is less than the sum of two ionic surfactants because of less electrostatic repulsion. Estimation of the packing parameter suggests that the complexes will favorably form vesicles (Mehreteab, 1999). Studies on anionic/cationic mixtures have an important contribution to the fundamental issue of vesicle formation because of its stability or thermodynamically stable state in aqueous surfactant systems (Södermann et al., 1997). The morphology of cationic/anionic aggregate differs from the single surfactant. The individual surfactant forms micelles in aqueous solution, while the vesicle is formed spontaneously in aqueous solution of anionic/cationic surfactant as mentioned before (Herrington and Kaler, 1997). Moreover, the vesicle provides more available sites for solubilization than the micelles (Hinze and Armstrong, 1987).

Nan, Liu, and Hu (2006) studied on composition, microstructure and rheology of aqueous two-phase cationic/anionic surfactant systems. Aqueous systems containing 1,3-propanediyl bis(dodecyl dimethylammonium bromide) (12-3-12) and sodium dodecyl sulfonate (AS) can separate into a concentrated phase and a dilute phase at certain conditions. Microstructures of some concentrated phases in the phase-

separated systems were determined by negative stained TEM method indicating that vesicle aggregates are usually formed.

Ong et al. (1994) studied on the potential of mixed cationic/anionic surfactant system consisting of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) in the electrophoretic medium to improve the separation of nine phenylthiohydantoin amino acids (PTH amino acids) by micellar electrokinetic chromatography (MEKC). The mixed surfactant system was found to improve the separation of the PTH-amino acids compared to the use of CTAB or SDS alone. Complete separation of the PTH amino acids was achieved using a buffer solution containing 2.5 mM CTAB and 40 mM SDS.

The resulting neutralized water-soluble complexes exhibit properties that are similar to nonionic surfactant and can, therefore, be thought of as pseudononionic surfactants. The surfactant complex can exhibit cloud point phenomena like nonionic surfactant. As determined by surface tension, they have low critical micelle concentrations and are more efficient and more effective than their anionic and cationic surfactant components. The cloud point temperature of the anionic/cationic surfactant mixtures is affected by total surfactant concentration and by the relative concentration of the anionic and cationic surfactants. The cloud point temperature of the surfactant mixtures decreased with an increase in the hydrophobic of the surfactant portion. In the same manner, the cloud point temperature of the anionic and cationic mixtures increased with an increase in the hydrophilic moiety of the surfactant components (Mehreteab, 1999).

The CMC of surfactant mixture is much lower than that of either individual anionic or cationic surfactant. In addition, the pseudononionic complex has a lower attainable surface tension. A mixture can be considered more effective if the surface tension at its CMC is lower than those of its surfactant components at their CMC (Mehreteab, 1999). Moreover, the mixtures of anionic and cationic have self-assembly ability forming aggregates easier than individual component resulting from the reduction of polar interaction by charge neutralization. In the viewpoint of economy, the anionic/cationic surfactants form aggregate at the CAC which generally less than CMC, therefore the quantity of surfactant needed to form the aggregates is less than that needed for individual surfactant to form the normal micelle at the CMC (Holmberg et al., 2003).

2.5 Aqueous Surfactant Two-Phase (ASTP) Extraction Systems

An aqueous two-phase system was observed originally with polymer solution as aqueous polymer two-phase system consisting of an aqueous solution of two particular polymers. Above critical concentration of these components, spontaneous phase separation takes place. One phase is rich in one polymer and another is rich in another polymer. The two-phase separation of the surfactant solution known as an aqueous surfactant two-phase (ASTP) (Zhao and Xiao, 1996). The phase 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 Blankenschtein, 1996). Similarly, the surfactant mixtures can separate spontaneously into two immiscible aqueous phases with a clear interfacial boundary between them. In general, the nonionic surfactant is usually used to induce the phase separation due to its special characteristic. Upon heating above critical temperature called cloud point, aqueous solutions containing nonionic surfactant is separated into two isotropic phases. The phases consist of a surfactant-depleted (or dilute) phase and surfactant-rich aggregate (or concentrated) phase, sometime referred to as the coacervate phase. As a result, the organic pollutants of environmental concern which solubilized in the hydrophobic core of micelles can be extracted and accumulated into the surfactant-rich phase (Watanabe, Tani, and Kamidate, 1998; Quina and Hinze, 1999).

The ASTP system can be formed when cationic and anionic surfactant surfactants are mixed at certain concentrations (much higher than CMC but still very dilute) and compositions. The mixed surfactants solution separates spontaneously into two aqueous phases. One phase is rich and another phase is poor in surfactant with a clear interfacial boundary between them. It can be applied as extraction technique to extract and preconcentrate organic solutes by an ability of surfactant to solubilize solutes into the surfactant aggregates (Zhao and Xiao, 1996).

Cui and Canselier (2003) studies on the solubilization behavior of n-heptane, toluene and octan-1-ol in anionic/cationic surfactant binary mixtures. Triethanolammonium dodecylpolyoxyethylene sulfate (TADPS) was mixed with hexadecyltrimethylammonium bromide (CTABr), dodecylpyridinium chloride (DPCl)

or hexadecylpyridinium chloride (CPCl). The synergism for solubilization in those mixtures depended on the polarity of the solubilizate, involving its location in micelles. For n-heptane (non-polar), a practically positive synergistic effect was observed and the maximum additive concentration (MAC) was found in the TADPS/CTABr system. For toluene (slightly polarizable), solubilizes both in the core and palisade layer of the micelle. For octan-1-ol (amphipathic), it usually solubilizes in the palisade layer or forms mixed micelles with surfactants.

ASTP is also obtained at low temperature while a temperature-induced aqueous two-phase system of nonionic surfactant takes place only above a critical temperature called cloud point. The ASTP extraction system can be operated at desired temperatures, which is especially suitable for partitioning of thermo-sensitive substances such as biomaterials. Phase behavior, volume ratio and settling time are strongly influenced by total concentration; and molar ratio of mixed surfactants, thus it can be adjusted for a selective partitioning of target solutes. ASTP extraction technique show many advantages such as required low concentration of surfactants, low viscosity of surfactant-rich phase and fast in phase separation. Surfactants can be simply removed from the desired solutes after partitioning by dilution of surfactant-rich phase or by changing temperature. Multi-step partitioning can be achieved without an addition of new surfactants (Xiao et al., 2000).

All these attractive features make an aqueous surfactant two-phase systems become interesting. The systems are utilized as useful method for separation, purification and concentration of biomaterials. Their performance can be controlled and optimized by varying solution condition. In addition, these systems can also readily scaled up (Liu et al., 1996). Moreover, the two-phase extraction system is formed in aqueous media which avoided in using of large amounts of organic solvent unlike conventional liquid-liquid extraction. Therefore, the extraction system is economical and safe since most of organic solvents are toxic (Tong et al., 1998).

Factors affecting the ASTP system are surfactant composition and concentration, electrolytes, temperature and pH. There is found that the ASTP system occurs at certain surfactant composition and concentration. The regions that phase separation occurs are different for each mixture. Phase separation can be found in the region that anionic or cationic is in excess or even at equimolar. It is shown that the effect of molar ratio is quite strong (Zhao and Xiao, 1996; Xiao et al., 2000). The

temperature is one of the other factors which affect in the changes in the structure of aggregates such as the transition from micelle to vesicle which affect to the solubility of surfactant (Yin, Mao et al., 2002; Yin, Zhou et al., 2003). In addition, the added acid such as hydrochloric, acetic, sulfuric and nitric acid or adding base such hydroxide can cause changes in phase behavior by altering phase volume ratio and inducing precipitation (Tong et al., 1999).

Kunanupap (2004) studied on the effect of operating conditions on benzene removal using an aqueous surfactant two-phase (ASTP) system formed by mixed dodecyltrimethylammonium bromide (DTAB) and alkyldiphenyloxide disulfonate (trade name of DOWFAX) as cationic and anionic surfactant, respectively. The high surfactant and benzene partition ratio and extremely low fractional coacervate phase volume proved the ASTP technique could be applicable to extract or preconcentrate the pollutant of environmental concern from wastewater. As high as 72% of benzene was extracted and preconcentrated in surfactant-rich phase at ambient temperature of 30 °C with the total surfactant concentration of 50 mM at 2:1 molar ratio of DTAB:DOWFAX within a single stage.

This phenomenon can be enhanced by increasing electrolyte concentration. The phase behavior of these surfactant system change markedly when an electrolyte is added. There are many reports that the addition of electrolyte drastically affects the phase behavior of the anionic/cationic system. The addition of salts generally has effect on micellization by screening the electrostatic interaction such as repulsion between aggregates and promoting a large aggregate formation (Yin et al., 2002). The addition of NaI, $CaCl_2$, $Ca(NO_3)_2$ and $Al(NO_3)_2$ show the "salting in" effect which elevate the cloud point temperature. On the other hand, the addition of NaCl and NaBr show the "salting out" effect which decrease in cloud point temperature of the nonionic surfactant and anionic/cationic surfactant mixture (Arai, 1967; Zhang, Somasundaran, and Maltesh, 1996; Krutlert, 2004). In addition, the additives such as lipophilic linker (long chain alcohol) and nonionic surfactants can enhance the solubilization of organic pollutant into the surfactant aggregates in the system of cationic/anionic surfactant mixtures. The mixing composition of cationic surfactant (DTAB) to anionic surfactant (DPDS) was fixed at 2:1 molar ratio and the total surfactant concentration of 70 mM where 91.4 % of Tetrachloroethylene (PCE) can be extracted into the surfactant-rich phase in the absence of additives. An addition

of lipophilic linkers (*n*-octanol, *n*-dodecanol, and *n*-hexadecanol) and nonionic surfactants (POE surfactants; TX-114 and TX-100) was found to enhance the extraction efficiency. Dodecanol shows the greatest PCE extraction enhancement in which up to 98 % of PCE is removed within a single stage extraction with only 0.1 mM dodecanol addition. An addition of 2 mM nonionic surfactants can also increase the PCE removal to about 96 %. However, the concentration of nonionic surfactants and alcohols plays a minor role onto PCE removal efficiency (Khaolerk, 2006).

2.6 Extraction

2.6.1 Introduction

Extraction is a process whereby a mixture of several substances in the liquid phase is at least partially separated upon addition of a liquid solvent in which the original substances have different solubilities. The solvent-rich phase is called the extract and solvent-poor phase is called the raffinate. A high degree of separation may be achieved with several extraction stages in series, particularly in countercurrent flow. Extraction often is effective at near-ambient temperatures, a valuable feature in the separation of thermally unstable natural mixtures or pharmaceutical substances.

In mixer-separator, the contact times can be made long enough for any desired approach to equilibrium, but 80-90% efficiencies are economically justifiable. The simplest in concept are various kinds of tower arrangements. The relations between their dimensions, the operating conditions and the equivalent number of stages are the key information. The calculations of the relations between the input and output amounts and compositions and the number of extraction stages are based on material balances and equilibrium relations. Knowledge of efficiencies and capacities of the equipment then is applied to find its actual size and configuration (Laddha and Degaleesan, 1978; Walas, 1988).

2.6.2 Equipment for extraction

Equipment for extraction must be capable of providing intimate contact between two phases so as to affect transfer of solute between them and also of

ultimately effecting a complete separation of the phases. A very general classification of equipment, their main characteristics and industrial application is summarized in Table 2.2.

Table 2.2 Features and industrial application of liquid-liquid extractors

Type of extractor	General features	Field of industrial application
Unagitated columns	Low capital cost	Petrochemical
	Low operating and maintenance cost	Chemical
	Simplicity in construction	
	Handles corrosive material	
Mixer-settlers	High-stage efficiency	Petrochemical
	Handles wide solvent ratios	Nuclear
	High capacity	Fertilizer
	Good flexibility	Metallurgical
	Reliable scale-up	
	Handles liquids with high viscosity	
Pulsed columns	Low HETS	Nuclear
	No internal moving parts	Petrochemical
	Many stages possible	Metallurgical
Rotary-agitation columns	Reasonable capacity	Petrochemical
	Reasonable HETS	Metallurgical
	Many stage possible	Pharmaceutical
	Reasonable construction cost	Fertilizer
	Low operating and maintenance cost	
Reciprocating-plate columns	High throughput	Petrochemical
	Low HETS	Metallurgical
	Great versatility and flexibility	Pharmaceutical
	Simplicity in construction	Chemical
	Handles liquids containing suspended solids	
	Handles mixtures with emulsifying tendencies	
Centrifugal extractors	Short contacting time for unstable material	Pharmaceutical
	Limited space required	Nuclear
	Handles easily emulsified material	Petrochemical
	Handles systems with little liquid density difference	

The sizing of liquid-liquid extraction equipment always requires some pilot plant data or acquaintance with analogous cases. Literature data is almost entirely for small equipment whose capacity and efficiency cannot be scaled up to commercial sizes (Lo, Baird, and Hanson, 1983).

When a substantial difference in resistances of extract and raffinate films to mass transfer exists, the high phase resistance should be compensated for the increased surface by dispersion. From this point of view, Laddha and Degaleesan (1978) point out that water should be the dispersed phase in the system of water - diethylamine - toluene. The dispersed phase should be the one that does not well wet the material of construction. Since the holdup of continuous phase is usually greater, the phase that is less hazardous or less expensive should be continuous. In addition, it is best to disperse a highly viscous phase.

2.6.3 Mixer-Settlers

Liquid-liquid contacting equipment can be generally classified into two categories: stagewise and differential contactors. The function of a stage is to contact liquids, allow equilibrium to be approached, and to make a mechanical separation of liquids. The contacting and separating correspond to mixing the liquids, and settling the resulting dispersion. The device is called a mixer-settler. The simplest way of accomplishing extractions is to mix the two phases thoroughly in one vessel. A series of such operation performed with series or countercurrent flows of the phases can accomplish any desired degree of separation (Walas, 1988).

There are two types of mixer: flow or line mixers and agitated vessels. The settler is categorized into two types: non-mechanical and mechanical. The operation can be carried out in batch or continuous flow. If batch, it is likely that the same vessel will serve for both mixing and settling, whereas if continuous, separating vessels are usually but not always used. In principle, at least, any mixers may be coupled with any settlers to provide the complete stage. There are several combinations which are especially popular. Continuous operated devices usually, but not always, distinguish the mixing and settling parts in separate vessels. Batch-operated devices may use the same vessel alternately for separate functions. Insoluble

liquids will be brought into direct contact to cause a transfer of dissolved substances creating permanent emulsion, to allow transfer of heat and to promote chemical reaction. One of the four principal purposes of operations involving the direct contact of liquids is separation of component in solution due to an unequal distribution of that component between two insoluble liquids. Design of equipment is based on the quantities of liquids and the efficiency and operating characteristics of the selected equipment (Dahlstrom et al., 1997).

Over the past 20 years, mixer–settlers have been intensively used in chemical, pharmaceutical and hydrometallurgical industries. Mixer-settlers have several advantages and disadvantages. For instance of the advantages, the equipment are strong operational loads; easy operation and maintenance; and simple start-up. The stages are independent, can be added to or removed as needed which are easy to start-up and shut down. The equipment is not bothered by suspended solids and can be sized for high efficiencies. However, emulsions can be formed by severe mixing which are hard to break up. The other disadvantages are pumping of one or both phases between tanks may be required, independent agitation equipment, large floor space need are expensive, and high holdup of valuable or hazardous solvents exists particularly in the settlers (Walas, 1988).

Separation of the mixed phases is accomplished by gravity settling or less commonly by centrifugation. It can be enhanced by inducing coalescence with packing or electrically or by shortening the distance of fall to a coalesced phase (Laddha and Degaleesan, 1978). The rate of mass transfer across a phase boundary is a function of the drop size distribution and interfacial area between phases, in which the smaller the drop size, the greater the rate of mass transfer is achieved. As dispersion increasing, the coalescence time required is increased. Therefore, the settler size is a critical factor in mixer–settler design. The size is governed by throughput limitations imposed by the rate of coalescence of the dispersed phase. Due to the fact that settling problems related to solvent loss and/or entrainment, which have been shown to be the major cost factor in the design, attempts have been made to increase the settling rate, and therefore throughput, resulting in an increase in the overall economy. Finally, in order to achieve good settling ability together with good flexibility, many designs such as the Lurgi Multi-Tray Settler and the Segmental Circular Settler have been proposed with the general aim to decrease the area required

while maintaining high throughput and efficiency (Hadjiev and Paulo, 2005). A common basis for the design of settlers is an assumed droplet size of 150 μm, which is the basis of the standard API design method for oil-water separators. Stokes law is applied to find the settling time. In open vessels, residence times of 30-60 min commonly are provided (Walas, 1988).

Dekker et al. (1986) studied on recovery of α-amylase from aqueous phase to transport to another by liquid-liquid extraction by using reversed micelles of the cationic surfactant, trioctylmethylammonium chloride to solubilize α-amylase in isooctane. Reversed micelles are aggregates of surfactant molecules in a non-polar solvent, surrounding an inner core of water. A continuous forward and back extraction of the enzyme was performed in two mixer-settler units, with the reversed micellar phase circulating between the two units. During the forward extraction the conditions (pH, ionic strength) favoured the transfer of α-amylase from the aqueous phase towards the reversed micellar phase. The reversed micellar phase containing the α-amylase was subsequently extracted with a second aqueous phase, which favoured the transfer of the enzyme towards the aqueous phase. In this way, the concentration of active α-amylase in the second aqueous phase was eight times greater than that of the original solution. The forward and back extraction could be described in terms of the data on the distribution coefficients and the mass transfer rate constants.

Ali, Ahmad, and Daoud (2006) studied on extraction and recovery of Zn(II) from aqueous waste solution using a mixer-settler unit. Bis(2,4,4-trimethylpentyl) phosphinic acid, common name known as CYANEX 272, in kerosene was used for extraction the aqueous waste of zinc in media contained sulphate, chloride or nitrate. A continuous counter-current extraction flow sheet was developed and tested using a 15-stage horizontal type mixer-settler, contained eight extraction, two scrubbing and five stripping stages, for the recovery of Zn(II) from simulated and real industrial waste resulting from rayon industry. The loading capacity of CYANEX 272, as extractant agent, was found to be 0.105 M Zn(II) per mole extractant after four stages. The extraction was found to increase with CYANEX 272 concentration, pH of the aqueous phase and ammonium sulphate concentrations. Investigations on stripping units using different stripping agents indicated that HCl and HNO_3 are effective for stripping zinc. The extraction efficiencies were 97 % and 94 % for a simulated waste solution and real solution, respectively.

CHAPTER III
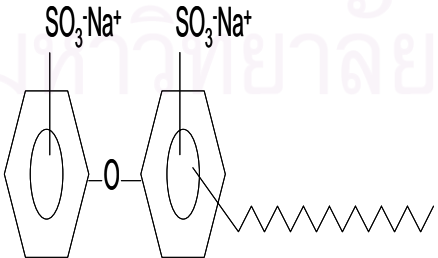
METHODOLOGY

3.1 Material

3.1.1 Surfactants

Dodecyltrimethylammonium bromide (DTAB), with 99 % purity, was used as a cationic surfactant which purchased from Robiot Co., Ltd. (Nanjing, China). The anionic surfactant used in the research was alkyldiphenyloxide disulfonates (ADPODS or trade name of DOWFAX 8390) with 35 % active which contributed from Dow Chemical Co., Ltd. (West Virginia, USA). Their properties were listed in Table 3.1.

Table 3.1 Physical properties of the studied surfactants
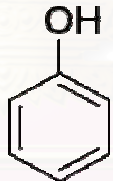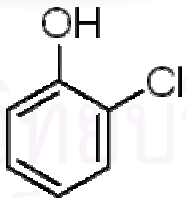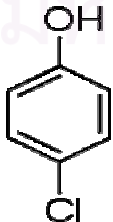
Surfactant	MW (g/mol)	Chemical Structure	CMC (mM)
Dodecyltrimethylamonium bromide, $C_{15}H_{34}BrN$	308.3		15.6 [1]
Alkyldiphenyloxide disulfonate, $C_{16}H_{33}C_{12}H_7O(SO_3Na)_2$	642		3.0 [2]

(1) Holmberg et al. (2003), (2) http://www.dow.com/surfactants/products/alkyl_sa.htm

3.1.2 Pollutants

The pollutants utilized in the research were phenolic compounds. Reagent grade phenol purchased from Panreac Quimica (Barcelona, Spain) with a purity of 99 % was used as a model pollutant. The other pollutants such *o*-chlorophenol (or 2-) and *p*-chlorophenol (or 4-) were used for studying the effect of hydrophobicity of solute in extraction via aqueous surfactant two-phase system which formed by the anionic/cationic surfactant mixture. They were purchased from Riedel-de Haën Sigma-Aldrich Laborchemikalien GmbH (Switzerland) which sold as Fluka and Riedel-de-Haën brand product, with the purity of ≥98 % and ≥99 %, respectively. Their physical and chemical properties were shown in Table 3.2.

Table 3.2 Physical and chemical properties of phenolic compounds

Phenolic Compound	MW (g/mol)	Chemical Structure	Log K_{ow}	Water solubility (g/100 mL)
Phenol, C_6H_5OH	94.11		1.46 [1]	11.3 [1]
2-Chlorophenol, ClC_6H_4OH	128.56		2.15 [2]	2.85 [2]
4-Chlorophenol, ClC_6H_4OH	128.56		2.39 [3]	2.7 [3]

(1) http:www.atsdr.cdc.gov/toxprofiles/tp115.html, (2) http://www.ilo.org/public/english/protection/safework/cis/products/icsc/dtasht/_icsc08/icsc0849.htm, (3) http://www.ilo.org/public/english/protection/safework/cis/products/icsc/dtasht/_icsc08/icsc0850.htm

3.2 Preliminary study on phase behavior of ASTP extraction system to remove phenol

The concentration of total surfactants was 70 mM, which was adopted from the optimum concentration to achieve the highest extraction efficiency for Tetrachloroethylene (PCE) (Khaolerk, 2006). The concentration of phenol was 100 ppm (mg/L), which was corresponded to the reported data from U.S. EPA that the acute and chronic toxicities of phenol to fresh water aquatic life occur at concentration as low as 102 ppm and it has been measured in effluents up to 53 ppm (U.S.EPA, 1986). In addition, the annual report of Lenntech Petrochemical Co. showed that the polluted wastewater released by petroleum refinery process contains phenol concentration ranged from 20 to 100 ppm. (Lenntech Petrochemical Company, 2006).

The ASTP extraction system was preliminary studied in batch experiment at equilibrium condition prior to study in the continuous mixer-settler. Cationic/anionic surfactants and phenol were prepared and mixed for 30 minutes in the volumetric flask and the solution was transferred to the volumetric calibrated vials. The solutions were equilibrated in a temperature controlled water bath at 30°C for 5 days to assure a complete phase separation. The concentration of surfactants and phenol in both separated phase were analyzed by the analytical instruments and techniques addressed in later section.

3.3 Mixer-Settler

The schematic diagram of the ASTP continuous extraction unit was illustrated in Figure 3.1. A 100 mL reagent glass bottle was used as a mixer placed on the magnetic agitator where the agitating speed can be adjusted. The settler was an empty glass column in which the overflowed solution from the mixer was entered at 25 cm above the bottom of the column. At the bottom of the settler, there was an adjustable stopcock to control the flow rate of the coacervate solution leaving the column. The settler has 4.8 cm. inside diameter with 2 mm thickness and 75 cm.in length.
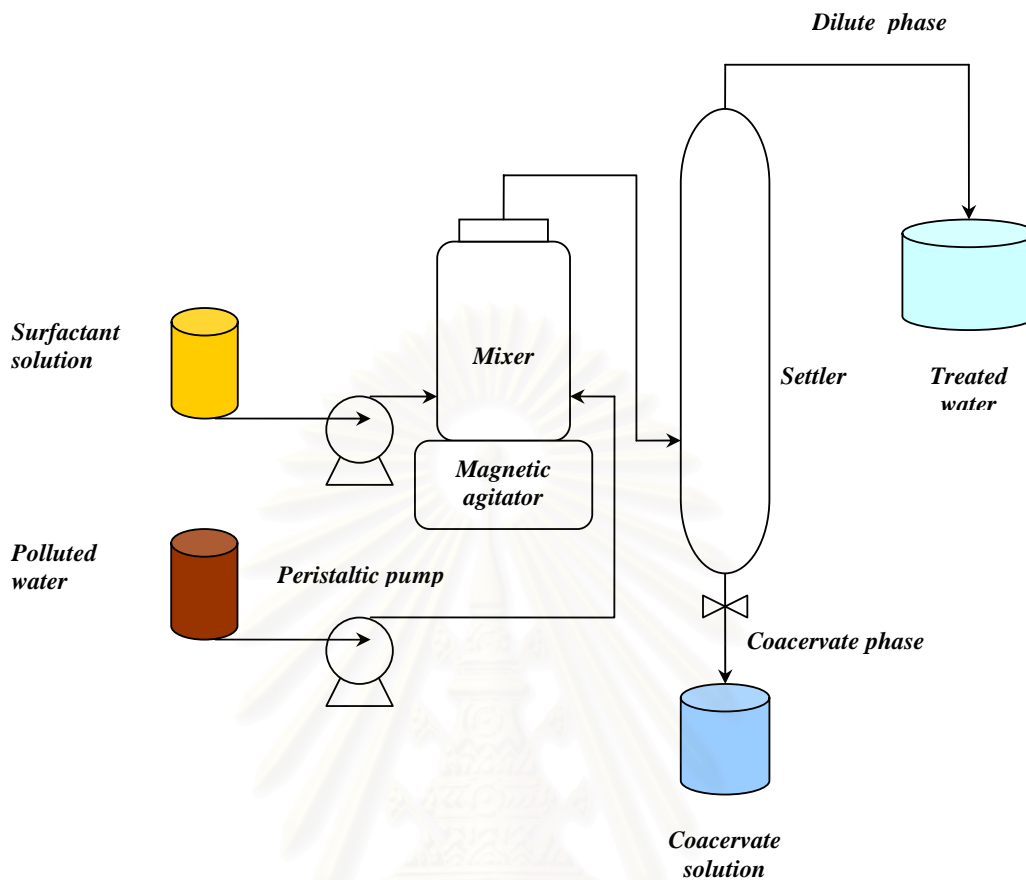
Figure 3.1 A schematic diagram of ASTP extraction unit using a mixer-settler

3.4 Experimental Procedures

3.4.1 Investigation of optimum operating condition

The extraction unit was operated at ambient temperature. After the unit was assembled and checked for leaks, the continuous phase (wastewater) and dispersed phase (surfactant solution) were fed at desired flow rate into the mixer by peristaltic pumps. They were entered to the mixer at 1.5 cm above the bottom of the mixer. The angle is 120° between lines of entered phase. While filling the unit, the surfactant solution was dispersed in the wastewater, containing phenol as pollutant, by magnetic stirrer in the mixer. The total flow rate obtained via summation of surfactant and wastewater flow rate was non-variable parameter controlling the residence time

of mixed-liquids retained in the mixer before overflowing at the top of the mixer to the settler. It was the same value for all of experiments.

The phase separation occurred in the settler. The surfactant-dilute phase is overflowed at the top of setter to a collecting tank as the treated water while the coacervate solution which is a heavy phase leaving the settler at the bottom to another collecting tank. When the system reached steady state, which was indicated by no changing in the surfactant and pollutant concentration in the surfactant-dilute phase with time, samples were collected from the effluent water (surfactant-dilute phase) and the coacervate phase to determine the concentrations of surfactant and pollutant. In addition, the flow rate of the coacervate and dilute phase solutions leaving from the settler were determined by measuring the volume of solution over time.

The operating conditions and variables were as follows: the concentrate of stock surfactant solution containing DTAB:DOWFAX at molar ratio 2:1 at total surfactant concentration of 770 mM; synthetic wastewater containing 100 ppm phenol compound; agitator speed in the mixer of 125 to 1100 rpm; and surfactant to wastewater flow rate ratio in range of 1:8 to 1:16.

In addition, the number of settler and types of connection were studied to get the best efficiency in the phenol removal from synthetic wastewater. After the optimum condition of agitator speed and surfactant to wastewater flow rate ratio were obtained, the extraction unit was modified by varying the connection with more settlers. The overflow of mixed liquid from mixer was entered to the two settlers which connected as series and parallel type. Moreover, the three setters were utilized in the experiment known as integrated connection. The overflow of mixed liquid from first settler was spitted into two parallel lines prior to enter to the settlers.

3.4.2 Effect of hydrophobic phenolic compound

2-chlorophenol and 4-chorophenol were used as the hydrophobic contaminant. Individual phenolic compound was studied at a time in the same extraction unit with one settler. The concentration of each phenolic compound was held constant at 100 ppm. The experiment was conducted using the same steady state

time which obtained by the phenol removal with single settler. The external standard quantitative calibration of each phenolic compound was conducted for the concentration analysis for both phases.

3.4.3 Extraction performance: batch extraction at equilibrium

The ASTP extraction system, conducted in vial, was studied in batch experiment at equilibrium condition. The cationic/anionic surfactants and phenol were prepared and mixed using the optimum agitator speed and total surfactant concentration obtained by continuous operation. They were mixed for 30 minutes in the volumetric flask and the solution was transferred to volumetric calibrated vials. The extraction system was equilibrated for 5 days for complete phase separation in temperature controlled water bath at 30 °C. Both phases were analyzed for the concentration of phenol and surfactant. The extraction performances were used to compare with the results obtained by continuous operation in mixer-settler using the optimum condition.

3.5 Analysis for surfactants and phenol concentration

The concentration of DOWFAX was measured by UV-Visible spectrophotometer (Thermo Spectronic, Model Helios Alpha) at 240 nm with no interference of phenol. The concentration of DTAB can be indirectly evaluated corresponded by the prepared molar ratio of DTAB and DOWFAX. The phenol concentration was determined by using UV-Visible spectrophotometer (Thermo Spectronic Model Helios Alpha) at 510 nm after oxidizing with coupling agent (4-aminoantipyrine) (Clesceri, Greenberg, and Eaton, 1998; Katsaounos et al., 2003). The external standard quantitative calibrations were conducted for the analysis of surfactant (DOWFAX) and phenol in both phases, where the absorptive value was controlled in range of 0 to 1 absorbance unit. Closure of the material balances of DOWFAX and phenol were taken as evidences to ascertain the reliability of experiments.

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Criteria for mixer-settler design

In common practice, at least following parameters: the purification of the effluent solution, composition, concentration, and flow rate of feed; and composition and concentration of solvent have to be known in order to design the extractor. As a result, the number of stages needed to achieve the target effluent concentration will be figured out based on material balances and equilibrium relations. However, a different approach was used to design a mixer-settler in this study due to the fact that the precise relationship among 4 components in this system (cationic surfactant, anionic surfactant, phenol, and water) has not yet known resulting in no phase diagram existing at present. In addition, this ASTP system is quite complex as compared to the conventional solvent extraction system because the characteristic of the separated phases, coacervate phase (extract) and surfactant-dilute phase (raffinate), depends on the surfactant composition and concentration, unlike the solvent extraction where the characteristic of extract and raffinate phase are rigid regarded to the physical and chemical properties of feed and solvent. Therefore, the criteria used in the mixer-settler design were based on practical point of view.

The size of mixer was simply calculated by the multiplication of total input flow rate (surfactant solution and wastewater) and desired mixing time. In this study, the assigned flow rate of surfactant solution was 0.5 mL/min while that of the wastewater was 5 mL/min. Consequently, the total input flow rate to the mixer was 5.5 mL/min. The desired mixing time in the mixer was approximately set as 30 minutes. Therefore, the required volume of the mixer was 165 mL. However, the 100 mL labeled reagent bottle with actual volume of 137 mL was used as mixer in which 25 minutes for mixing time was achieved which does not much differ from required value.

For settlers, the design was based on two important rationales. Firstly, the volume of settler has to be large enough to provide a suitable settling time of the

separated phases. In this study, the desired settling time was quite long because the settling rate of the droplet of the surfactant-rich phase is slow. Unlike the common extraction system where the separated phases was due to the immiscibility of the solution and the solvent, the phase separation of this ASTP of cationic/anionic surfactant mixture was caused by the special characteristic of this surfactant system. Secondly, the size of the settler should have suitable height with large enough diameter in order to reduce the velocity of surfactant-rich droplet which can be overflowed out of the settler with the effluence dilute phase. In addition, the height of surfactant-rich phase layer should be lower than the position where the mixed solution from mixer entered the settler in order to avoid the disturbance of the coming solution to the well settled coacervate phase.

In this study, the size of settlers was as follows: 4.8 cm inside diameter with 2 mm thickness and 75 cm in length. The settler size provides the residence time of 246.8 minutes based on the input flow rate to the settler of 5.5 mL/min. The upflow velocity was 0.3 cm/min. Thus, the settling rate of surfactant-rich phase droplet must be higher than the upflow velocity to exhibit the surfactant-rich phase settlement. The inlet position of the settlers was approximated from the volume of coacervate presence in batch experiment at equilibrium condition. Our base condition for mixer-settler design was 70 mM total surfactant concentration to extract phenol from wastewater at concentration of 100 ppm. The fractional coacervate volume from equilibrium condition was found to be 0.078. Since the total volume of our settler is 1357.17 mL, the volume of coacervate in the settler is 105.86 mL which corresponds to 5.85 cm in height.

However, this height was obtained from equilibrium condition, the higher value is expecting from the continuous operation because the coacervate phase has less time for settling and concentrating. Furthermore, from the engineering viewpoint, safety factor need to be associated in the design. Thus, suitable inlet position is 25 cm from the bottom of the settlers, which is approximately 4 times greater than that obtained from equilibrium condition, to make sure that the well settled coacervate phase is not disturbed by the coming solution. The approximated height was conformable with the estimated value obtained by the relationship of sedimentation rate and residence time in the settler. The schematic diagram of the mixer-settler extraction unit with one settler was shown in Figure 3.1.

4.2 Results of phase behavior on phenol removal via batch extraction at equilibrium condition

The ASTP system is formed by mixing 2 to 1 molar ratio of DTAB and DOWFAX at the total concentration of 70 mM. The study aimed to observe the phase behavior of the mixed surfactants for phenol removal prior to operate in continuous mixer-settler. The phase separation was observed suddenly after the agitator was stopped. Due to the density difference, the coacervate phase, which is the heavier phase, settles at the bottom of the calibrated vial while the lighter surfactant-dilute phase presents on top. The appearance of clear boundary between two phases was obtained when the ASTP system was equilibrated for 3.5 hours. The height of coacervate phase was then become constant. The system was left in a water bath at controlled temperature of 30 °C for 5 days to ensure that the system reached the equilibrium condition. There is no surfactant precipitation observed while forming the phase separation. The fractional coacervate phase volume obtained from the batch experiment was as low as 0.078. Most of surfactant aggregates present in the coacervate phase as evidenced by the fractional of surfactant in coacervate phase which was as high as 0.993 or more than 99 % of surfactant aggregates accumulates in the coacervate phase. The percentage of phenol removal was about 67. This percentage is not very high even this experiment was done in batch experiment at equilibrium condition due to the fact that phenol has high water solubility or in another words, phenol has low hydrophobicity and is considered as a polar compound. Thus, the affinity of phenol to solubilize into the surfactant aggregates is not very strong as compared to that of a non-polar compound. The locus of solubilization of polarisable phenol is located at the outer portion of the surfactant aggregate (Tokiwa and Aigami, 1971) which corresponded well with another report indicating that phenol is probably solubilized near the surface of surfactant aggregate or at palisade layer (Abou et al., 2004).

4.3 Steady state time analysis

Steady state time in the mixer-settler was determined by measuring the concentration of solute (phenol) in the effluent micellar-dilute phase as a function of time. The steady state time is achieved when there is no further change in solute concentration with respect to time. The initial phenol concentration in the wastewater was held constant at 100 ppm and the position of the interface between two separated phases in the settler were controlled to be constant throughout the experiment. The surfactant solution to wastewater flow rate ratio was 1 to 10 in this experiment. After the mixer-settler was completely filled which was approximately 4.5 hours, the system took 3.5 hours afterward to reach the steady state condition as shown in Figure 4.1. Therefore, 3.5 hours of operation was used for all experiments to ensure that the steady state condition was approached.
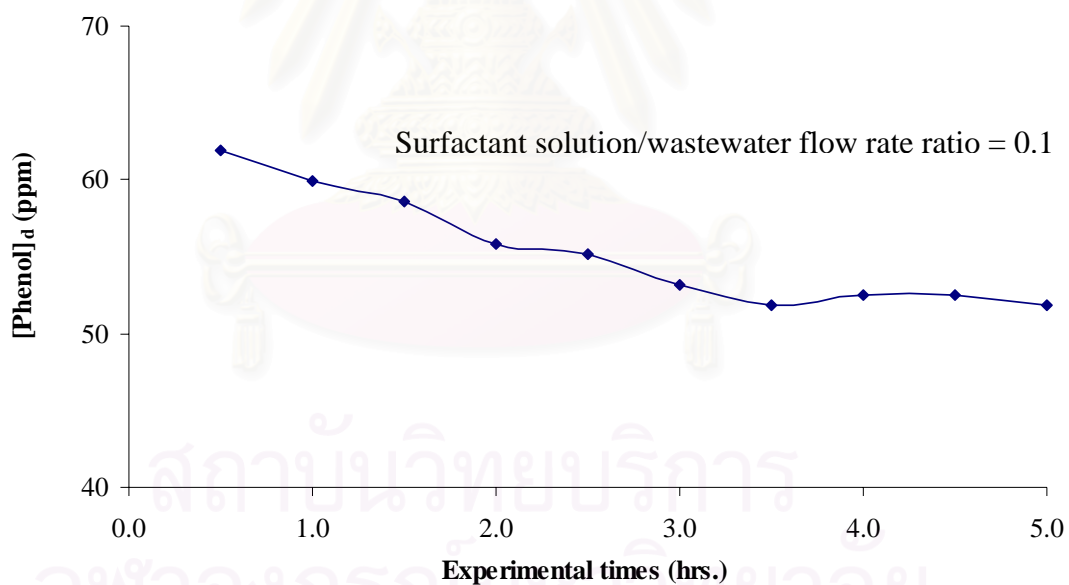
Figure 4.1 Phenol concentration in surfactant-dilute phase solution as a function of operating time (System: 100 ppm phenol and agitator speed of 700 rpm)

4.4 **Effect of agitator speed**

When the agitation speed increases, the dispersed drop size is smaller. The small drop size has higher interfacial area, which will influent the mass transfer of solute among phases. There was a studying on the effect of agitator speed in a multistage mixer-settler in the reversed micellar extraction of lysozome. The results reveal that the extraction efficiency depends on the agitator speed (Tong and Furusaki, 1995). The results showed that the agitator speed in the mixer did not have much effect on the surfactant concentrations in coacervate and dilute phase solutions as shown in Figure 4.2.
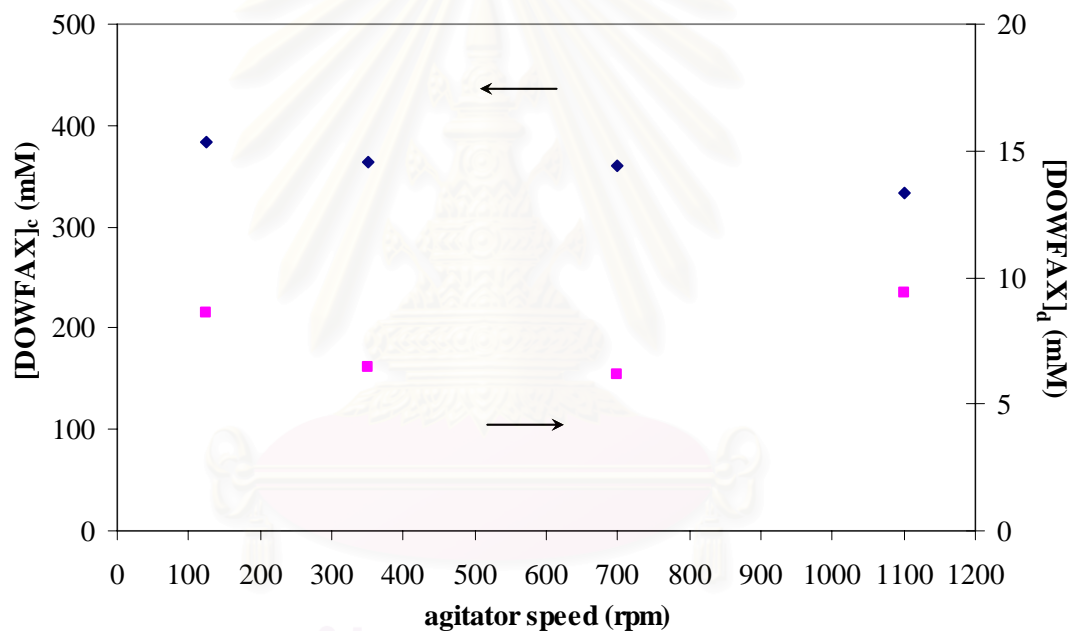
Figure 4.2   DOWFAX concentration in coacervate solution (c) and dilute
               phase solution (d) as a function of agitator speed (system: 100
               ppm phenol, 1/10 surfactant solution to wastewater flow rate
               ratio)

There are two possible reasons. Firstly, the characteristic of surfactant in the separated phases is governed by the concentration and composition of the mixed surfactant system. Secondly, the provided settling time in the settler was sufficient at certain point for settling the fine coacervate dispersed droplets

downward. Thus, the concentration of surfactant in the dilute phase was not much affected by the carried over coacervate dispersed droplets.

Although the concentration of surfactant in both phases is independent of agitator speed, the mass transfer of solute into the surfactant aggregates is influenced by the size of dispersed droplets. When the agitator speed increases, the size of coacervate dispersed droplets is smaller. Therefore, as illustrated in Figure 4.3, phenol concentration in the coacervate solution drastically increases with increasing agitator speed in the mixer.
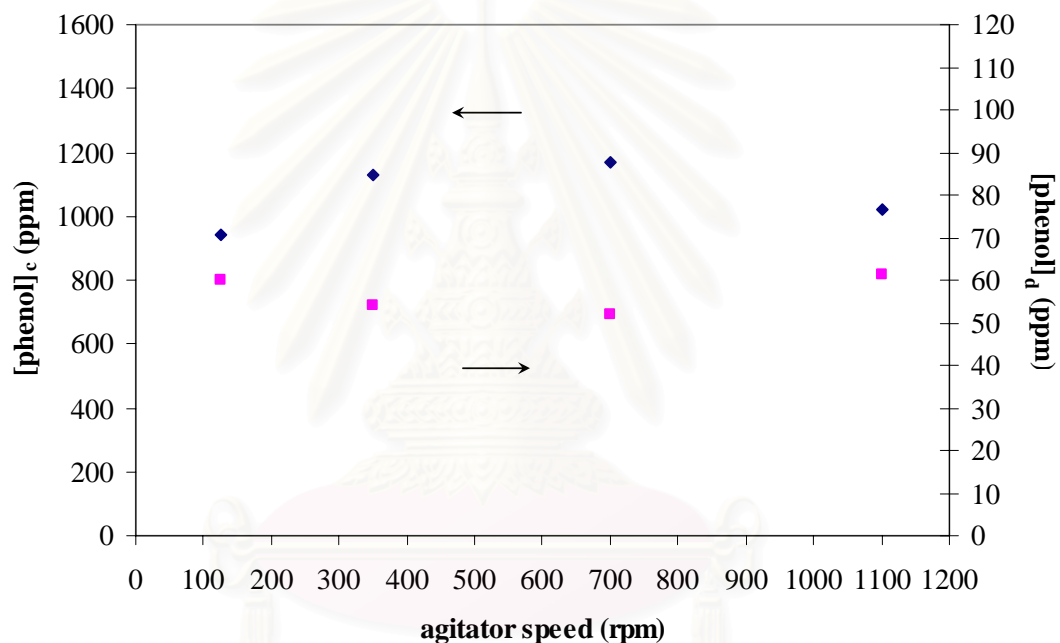
Figure 4.3 Phenol concentration in coacervate solution (c) and dilute phase solution (d) as a function of agitator speed (system: 100 ppm phenol, 1/10 surfactant solution to wastewater flow rate ratio)

The mechanical agitation can improve extraction performance by increasing the interfacial area between contacting phases and reducing the mass transfer resistance (McKetta, 1993). Thus, the smaller droplet size, the greater the rate of mass transfer can be achieved (Hadjiev and Paulo, 2005). The phenol concentration in the dilute phase decreased from 59.9 ppm with 125 rpm agitating speed to 51.8 ppm at an agitator speed of 700 rpm. However, at 1100 rpm, the phenol concentration

in the dilute phase should be the lowest but it turns out that it is higher than that obtained at 700 rpm. The result indicated that too high agitated speed leads to too fine dispersed coacervate droplets. Hence, the settling velocity of coacervate droplet was declined but the upflow velocity of the surfactant-dilute phase was constant. The settler did not accommodate all surfactant droplets, thus leading to an entrainment of some coacervate droplets with the surfactant-dilute phase solution. Thus, it should be noted that although an increase in agitation enhances the extraction efficiency but there is a limitation. Beyond a certain point, an excessive agitation can reduce the extraction efficiency.

In term of preconcentration ability, the partition ratio is considered. The surfactant partition ratio is the ratio of surfactant concentration in the coacervate phase to that of in the dilute phase. Likewise, the phenol partition ratio is the ratio of phenol concentration in the coacervate phase to that of in the dilute phase. The higher partition ratio indicates a better preconcentration and separation. The results show that an increase in agitator speed up to 700 rpm can enhance both surfactant and phenol partition ratios as shown in Figure 4.4.
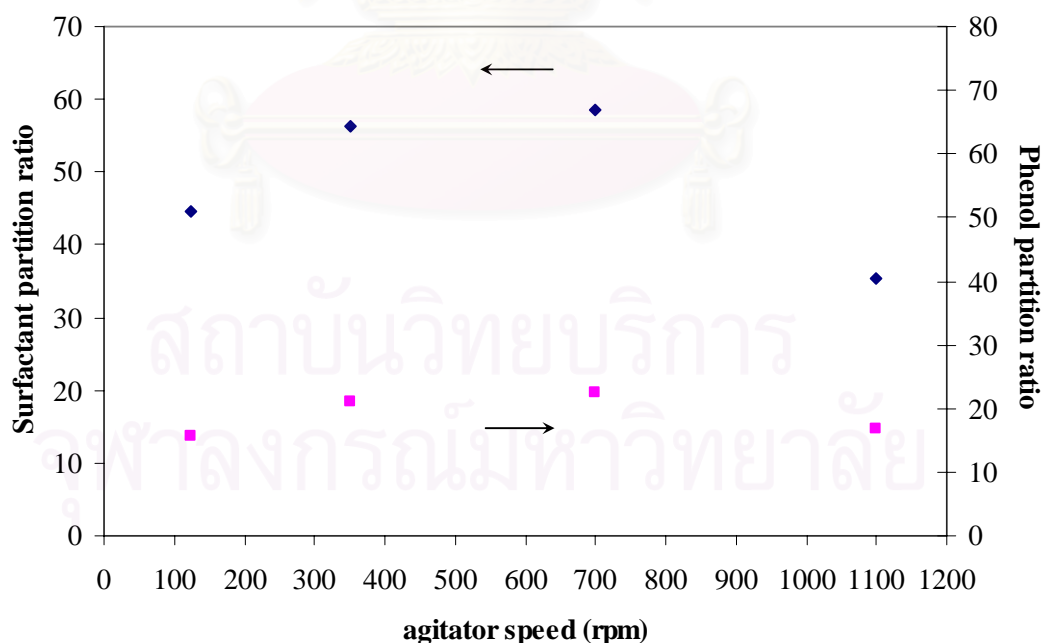
Figure 4.4   Surfactant and phenol partition ratio as a function of agitator speed (system: 100 ppm phenol, 1/10 surfactant solution to wastewater flow rate ratio)

However, these ratios decrease when the agitator speed was raised beyond 700 ppm due to the entrainment of the coacervate droplets as previously mentioned.

At an agitator speed of 700 rpm, the phenol partition ratio of 22.6 was observed indicating that phenol concentration in coacervate is 22.6 times higher than that of in the surfactant-dilute phase. The fraction of coacervate phase volume is relatively constant but the percentage of phenol removal increases about 8 % upon an increase in agitator speed when compared to the lowest agitator speed studied here (125 rpm) as shown in Figure 4.5. There is a 10 % reduction on phenol removal as the agitator speed further increases from 700 to 1100 rpm. At the agitator speed of 700 rpm, 48.2 % of phenol removal is observed.
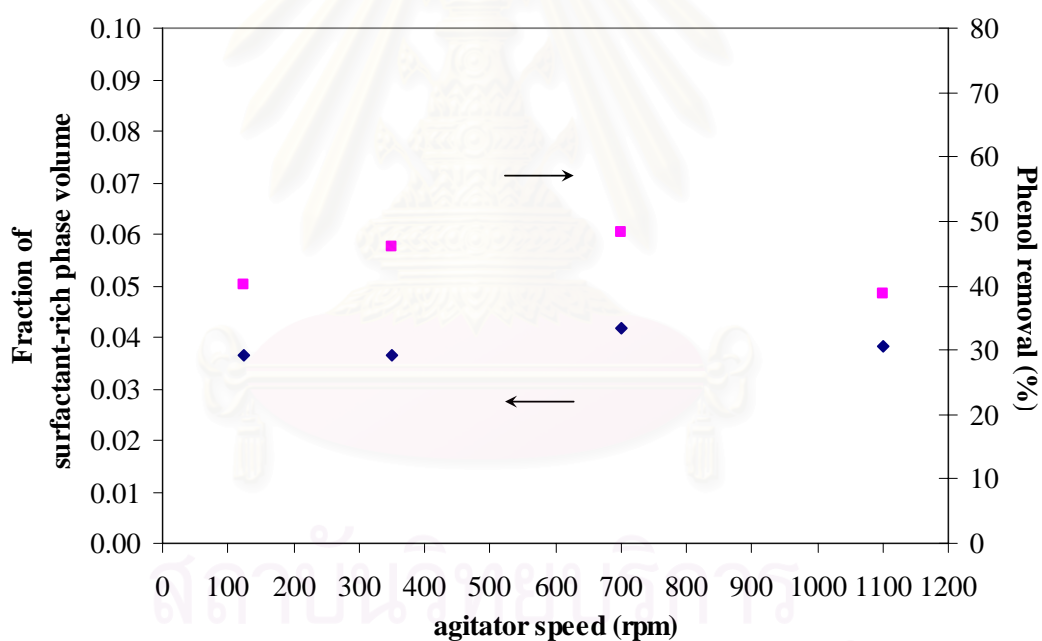
Figure 4.5 Fraction of coacervate phase volume and percentage of phenol removal as a function of agitator speed (system: 100 ppm phenol, 1/10 surfactant solution to wastewater flow rate ratio)

4.5 Effect of surfactant to wastewater flow rate ratio

In this study, the flow rates of surfactant solution and wastewater were varied to make a different in flow rate ratio in such a way that the total flow rate input into the system remains constant at 5.5 mL/min in order to maintain the same settling time in the settler for each condition. The results revealed that the surfactant concentrations in both coacervate phase and dilute phase do not much affected by the surfactant to wastewater flow ratio when the ratio was not more than 0.10 as shown in Figure 4.6 which well corresponds to the fraction of coacervate phase volume that increases with increasing the surfactant to wastewater flow rate ratio as required for material balance as shown in Figure 4.9.
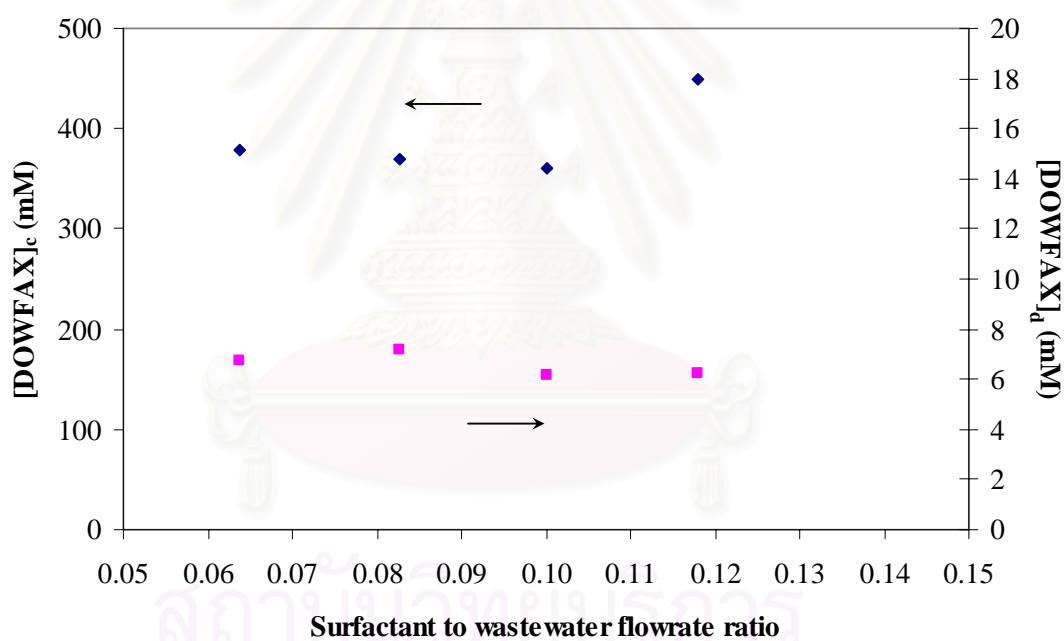
Figure 4.6   DOWFAX concentration in coacervate solution (c) and dilute

phase solution (d) as a function of surfactant to wastewater flow

rate ratio (system: 100 ppm phenol, 700 rpm agitator speed)

However, at the highest flow rate ratio studied here at 0.12 (total surfactant concentration of 81.88 mM in the system), the surfactant concentration in coacervate phases drastically increased. In addition, the behavior of the separated

phases changes if the surfactant to wastewater flow ratio is more than 0.12. The coacervate solution becomes a lighter phase and leaves the system on top of the settler as effluent. This phenomenon occurred at very high mixed cationic/anionic surfactants concentration, different types of surfactant aggregate tends to form. Typically, as the total concentration of mixed surfactants increased above certain concentration, transition from vesicle aggregates to other aggregates occurred (Mehreteab, 1999). Based on this phase inversion, this flow rate ratio is then become a constraint because the coacervate phase cannot settle down but tends to overflow out of the settler on top instead.

The lower phenol concentration in the dilute phase solution was observed when the surfactant to wastewater increased due to a higher surfactant concentration or in another words a higher amount of extractant to extract phenol in the system as shown in Figure 4.7. The average coacervate drop size with high flow rate ratio was visually larger than that observed with low flow rate ratio. However, the concentration of phenol in coacervate phase slightly decreases upon increasing flow rate ratio due to a greater volume of coacervate solution as previously mentioned.
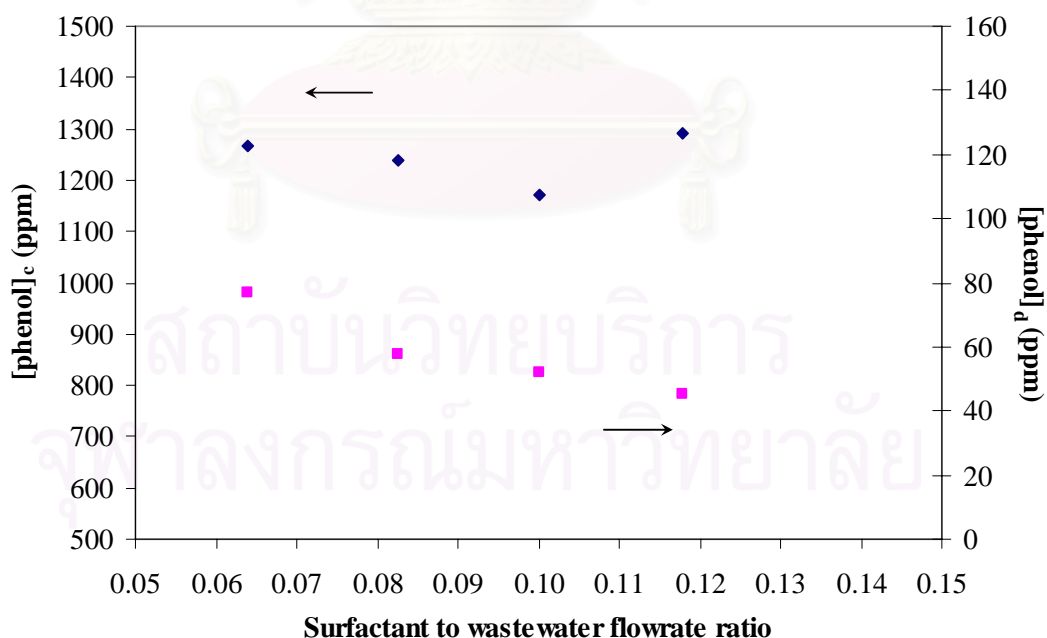
Figure 4.7 Phenol concentration in coacervate solution (c) and dilute phase solution (d) as a function of surfactant to wastewater flow rate ratio (system: 100 ppm phenol, 700 rpm agitator speed)

Thus, undoubtedly that both surfactant and phenol partition ratios; and percentage of phenol removal increase with increasing the surfactant to wastewater flow rate ratio as illustrated in Figure 4.8 and 4.9, respectively. These results correspond well with the results done by Kimchuwanit et al. (2000) and Trakultamupatum et al. (2002), which applied the cloud point technique to extract aromatic pollutants from wastewater by using nonionic surfactant.
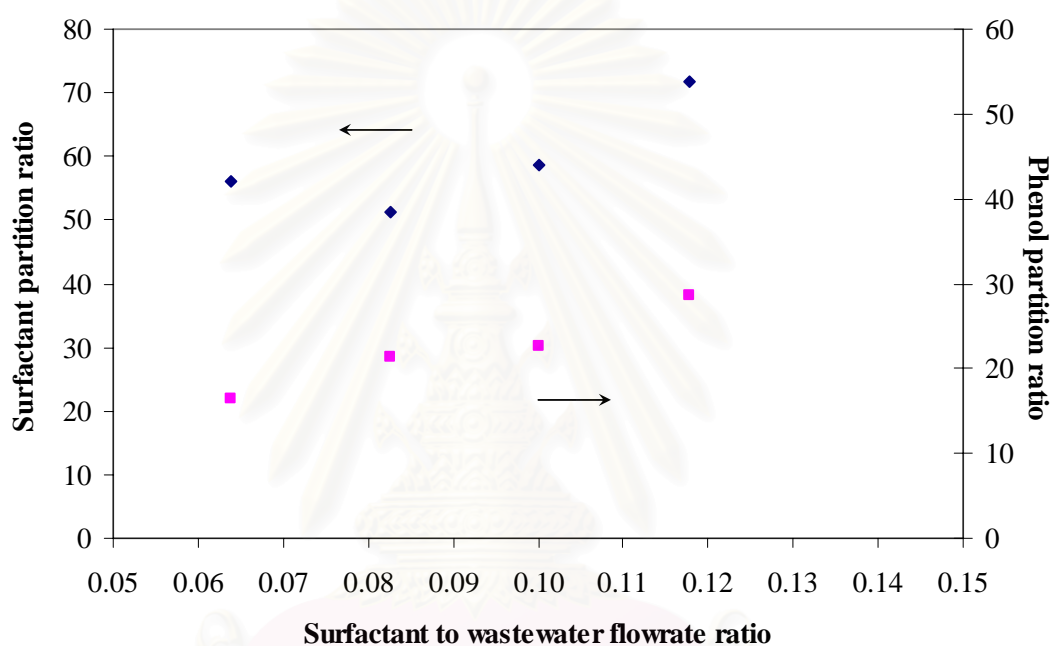
Figure 4.8   Surfactant and phenol partition ratio as a function of surfactant to wastewater flow rate ratio (system: 100 ppm phenol, 700 rpm agitator speed)

They also found that an increase in total surfactant concentration in the system can enhance the extraction efficiency. The best surfactant to wastewater flow rate ratio for this stage wise mixer-settler was found to be 0.12 where the surfactant and phenol partition ratio were 71.73 and 28.66, respectively and 54.90 % of phenol was continuously removed as shown in Figure 4.9.
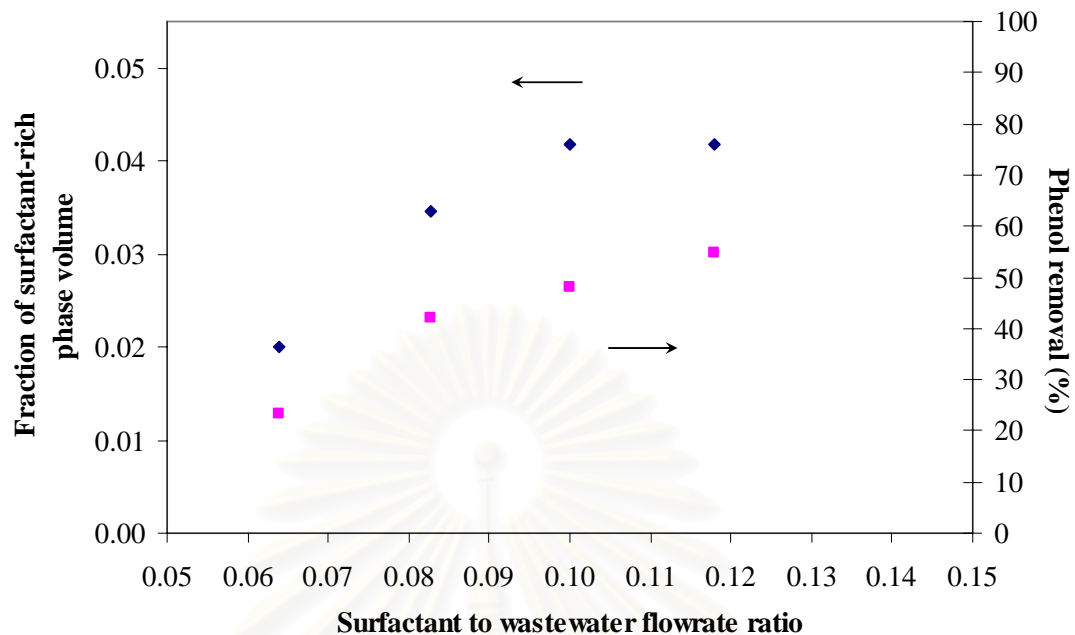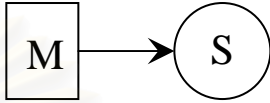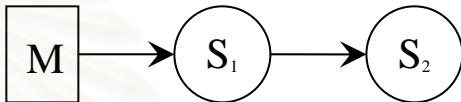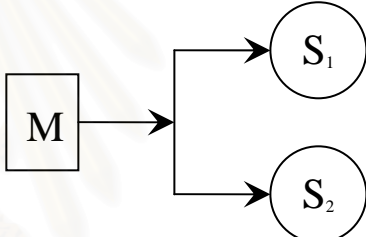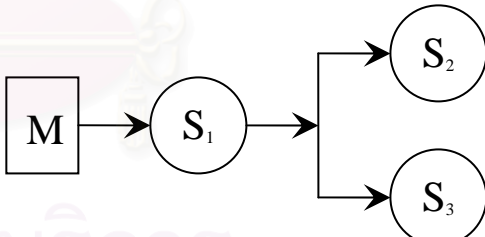
Figure 4.9 Fraction of coacervate phase volume and percentage of phenol
removal as a function of surfactant to wastewater flow rate ratio
(system: 100 ppm phenol, 700 rpm agitator speed)

4.6 Effect of the number of settlers and connection patterns

The results obtained from previous sections using only one settler
indicated that there was some coacervate droplets entrained with the surfactant-dilute
phase leading to a reduction of extraction efficiency. To solve this problem, more
settlers are recommended to provide a longer settling time for coacervate droplet.
Therefore, the number of settlers and type of settler connection were studied. The
optimum condition of agitator speed and surfactant to wastewater flow rate ratio
adopted from the previous experiments, which were 700 rpm of agitator speed and
0.12 of surfactant to wastewater flow rate ratio at the total input flow rate of 5.5
mL/min, were applied in this experiment. There were 4 patterns of mixer-settlers
including (A): mixer with one settler; (B): mixer with two settlers connected in series;
(C) mixer with two settlers connected in parallel; and (D) mixer with 3 settlers where
the first settler directly connected with the mixer and the other two settlers were

connected to the first settler in parallel. All types of pattern are illustrated in Table 4.1.

Table 4.1 The connection patterns of mixer-settlers

Type	Number of settlers	Connection Pattern
A	1	
B	2	
C	2	
D	3	

Note: M = Mixer, S = Settler

However, it should be noted that when more than one settler was applied, the surfactant-dilute phase reported here was the one leaving the last settler as the effluent solution. On the other hands, the coacervate solution left the system at the bottom of each settler and the obtained surfactant and phenol concentrations from each stream was not equal. Therefore, only surfactant and phenol concentrations in the surfactant-dilute phase, the fractional surfactant-rich phase volume, and the percentage of phenol removal were reported and interpreted here since these

parameters are less complicate but good enough to elucidate the effect of number of settles and type of settler connection on the extraction efficiency. Furthermore, the surfactant and phenol partition ratios were not reported because their calculation was based on the concentration in the coacervate phase.

In overall appearance, an increase in the number of settlers can reduce the entrainment of coacervate droplets due to a longer residence time prior the droplets to leave the settlers. The higher residence time provided by more settlers can enhance the rate of droplet coalescence. Thus, the gravitational force was sufficiently to promote the settling of droplets. As shown in the Figure 4.10, the surfactant and phenol concentrations in dilute phase substantially decrease when the number of settler increases.
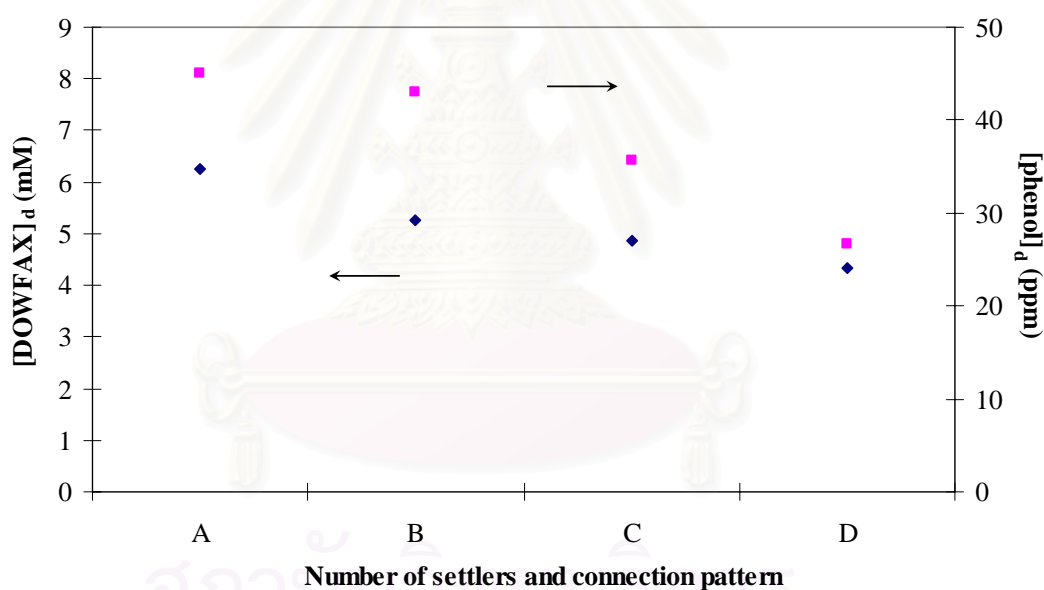
Figure 4.10 DOWFAX and phenol concentration in dilute phase solution (d) as a function of number settlers and connection patterns (system: 100 ppm phenol, 700 rpm agitator speed and 1/8.483 of surfactant to wastewater flow rate ratio).

As a result, the percentage of phenol removal can be enhanced from 54.9 using one settler to 74.4 using 3 settlers as shown in Figure 4.11. In addition, the fractional surfactant-rich phase volume also rises upon the addition with more settlers

indication that there are more surfactant aggregates accumulation in the system as illustrated in Figure 4.11. Thus, the process becomes more economical due to less surfactants loss.
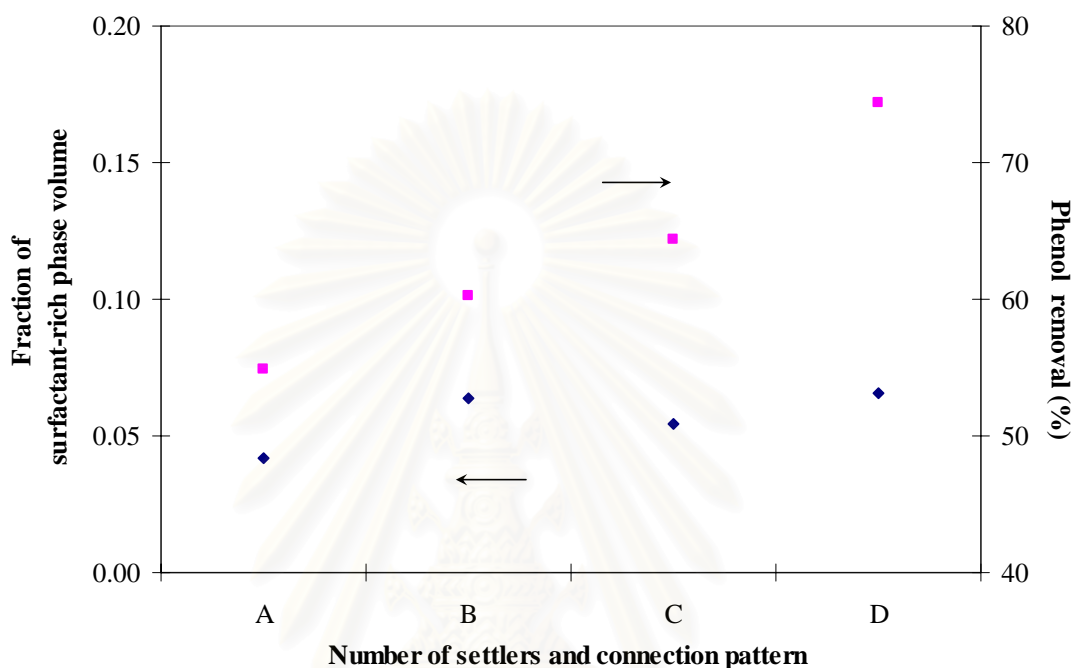
Figure 4.11 Fraction of coacervate phase volume and percentage of phenol removal as a function of number settlers and connection patterns (system: 100 ppm phenol, 700 rpm agitator speed and 1/8.483 of surfactant to wastewater flow rate ratio)

In order to investigate the effect of settling time on the extraction efficiency, two patterns were paired up as follows: (1) pattern A – B (one settler VS two settlers in series), (2) pattern B – C (two settlers in series VS two settlers in parallel). The first pattern A – B was studied because it is considered as the simplest case where one settler cannot provide enough settling time, one more unit is connected to the system in series. The results showed that for pattern A – B, the surfactant and phenol concentrations in the dilute phase slightly decrease upon the addition of second settler as shown in Figure 4.10. The phenol removal is also slightly enhanced by 5 % as shown in Figure 4.11. This is due to an increase in overall settling

time in the system. In pattern B (2 settlers in series), the overall settling time is 8 hours as compared to 4 hours in pattern A (one settler). However, if considered the settling time in individual settler in pattern B, it is only 4 hours because the flow rates of dilute phase solution entering both settlers connected in series are the same. Thus, this type of connection cannot drastically enhance the extraction efficiency of the system.

The second pattern B – C (two settlers in series VS two settlers in parallel) was studied because it can clearly elucidate the effect of settler connection type. In pattern B, the entire solution left from the mixer was fed into the first settler, however in pattern C, the solution left from the mixed was split into two equally portions before entering into two settlers connected in parallel. In this case, the flow rate in each settler was reduced by half resulting in a twofold greater in settling time. The overall settling time for both patterns is 8 hours but if considered individual pattern, the settling time is 4 hours and 8 hours for pattern B and C, respectively. The results showed that the concentrations of surfactant and phenol in dilute phase obtained from pattern C are lower that those from pattern B as shown in Figure 4.10. Accordingly, the percentage of phenol removal obtained from pattern C is 64.3 which is about 4 %greater than that from pattern B and 10% greater than that from pattern A as shown in Figure 4.11. It can be concluded the setters connected in parallel yields a better extraction performance rather than connected in series according to less flow rate present in the setter. As a consequent, the overall settling time plays less important role to the extraction efficiency as compared to the actual settling time in each settler.

The connecting scheme using 3 settlers (pattern D) was previously described. Although, the parallel-type connection is the most promising type, we cannot adapt the studied system to have 3 settlers connecting in parallel since we cannot find an appropriate connector to split the solution into 3 exactly equaled portions. However, within the existing connecting scheme of these 3 settlers, the highest extraction efficiency was obtained, where the percentage of phenol removal can be as high as 74.4 (which is 20 % greater than that using only one setter. This is because the overall settling time of the pattern D is approximately 12.5 hours which is the highest one among the 4 settlers connecting patterns studied here. It is worthwhile to note that, the obtained extraction efficiency from pattern D is comparable to that

observed in equilibrium extraction done in batch experiment. Thus, the mixer–settler operated at optimum condition and suitable number of settlers is proved to be an effective unit operation process unit for phenol removal from wastewater using the ASTP extraction technique.

4.7 Effect of hydrophobicity of phenolic compounds

Three phenolic compounds including phenol, 2- and 4-chlorophenol were used in this study to investigate the effect of hydrophobicity of solute on the extraction efficiency and to determine if this mixer-settler is applicable for other wastewater containing different contaminants. These phenolic compounds have difference degree of hydrophobicity as shown by differences in $logK_{ow}$ value as detailed in Table 3.2. A comparison of solute partition ratio, surfactant partition ratio and the percentage of solute removal among phenolic solutes were shown in Figure 4.12.
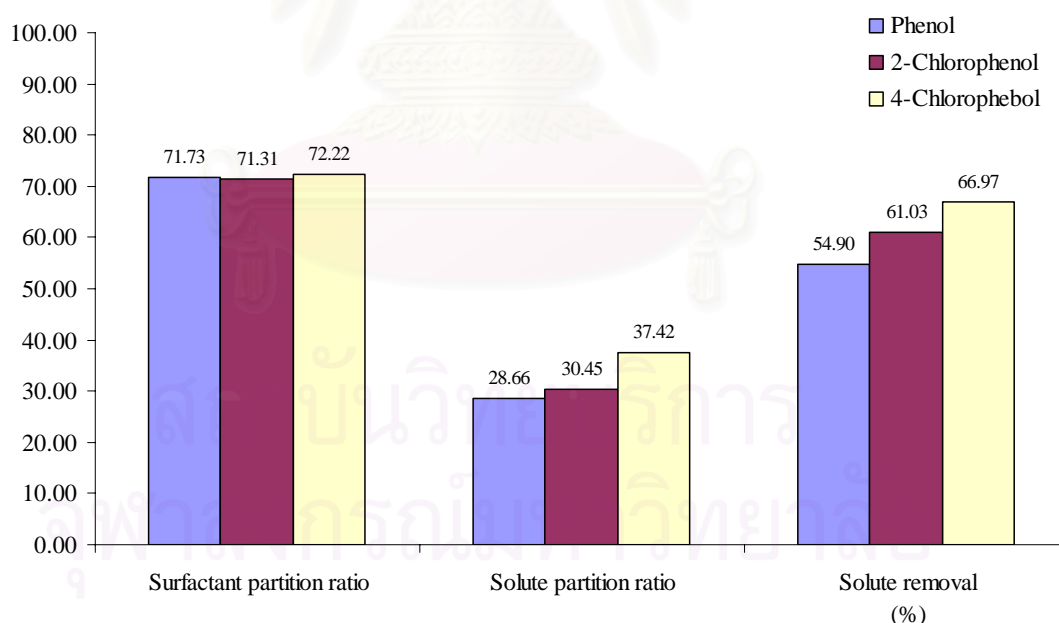
Figure 4.12 Comparison of surfactant and solute partition ratio and percentage of solute removal from wastewater between phenol, 2-chlorophenol and 4-chlorophenol (system: 100 ppm solute, 700 rpm agitator speed and 1/8.483 of surfactant to wastewater flow rate ratio using one settler)

The results showed that the surfactant concentrations in the coacervate and the dilute phase do not much affected by the type of solute as shown in Appendix F and G, due to the fact that the characteristic of the separated phase of cationic/anionic surfactants mixture is mainly governed by the surfactant composition and concentration (Kunanupap, 2004). As a consequent, the surfactant partition ratio is almost the same upon varying type of solute. On the other hands, the degree of hydrophobicity of solute has an effect on the solute partition ratio. 4-Chlorophenol shows the greatest ability in partitioning into the surfactant aggregates followed by 2-chlorophenol and phenol, respectively which corresponded well with their degree of hydrophobicity. Among these 3 phenolic solutes, the degree of hydrophobicity is in the following order: 4-chlorophenol (log Kow = 2.39) > 2-chlorophenol (log Kow = 2.15) > phenol (log Kow = 1.46). The solute partition ratio can be as high as 37.42 for 4-chlorophenol, 30.45 for 2-chlorophenol, and 28.66 for phenol. These results are in agreement with work done by Krutlert (2004) who applied ASTP extraction technique formed by mixtures of cationic/anionic surfactants to remove benzene, toluene, ethyl benzene and xylene from wastewater in batch experiment. She found that the degree of hydrophobicity of solute influents the partitioning of solutes into the surfactant aggregates and thus considered as a predominant factor affecting the ASTP extraction ability. Similar results were observed in the system of ASTP using nonionic surfactant as the extracting agent to extract benzene, toluene and ethyl benzene from contaminated water (Trakultamupatam et al., 2002).

In addition, a reduction of water solubility of hydrocarbon compounds with increasing degree of chlorination was reported (Nawakowska, White, and Guillet, 1989; Miyamoto and Klein, 1998). Thus, the chlorinated hydrocarbon tends to solubilize into the surfactant aggregates instead of dissolving in aqueous solution. This is in agreement with the solubilization study of organic solutes in aqueous solution of nonionic surfactant. The higher solubilization is achieved if the organic solutes have higher degree of chlorination (Frankewish and Hinze, 1994; Sakulwongyai et al., 2000).

From this study, up to 67 % of 4-chlorophenol, 61% of 2-chlorophenol, and 55% of phenol can be removed within this single stage mixer-settler. The extraction efficiency can be enhanced if appropriate number of settles is applied as previously discussed.

4.8 Comparison of extraction performance between batch and continuous operation

Figure 4.13 illustrated the surfactant and phenol concentrations in the coacervate solution, as well as the surfactant and phenol partition ratios obtained from a batch equilibrium extraction and continuous operation in mixer-settler using the same total surfactant concentration of 81.88 mM. Batch experiment was done in calibrated vial while the continuous operation was carried out using mixer-settler with three settlers which connected as integrated type (type D).
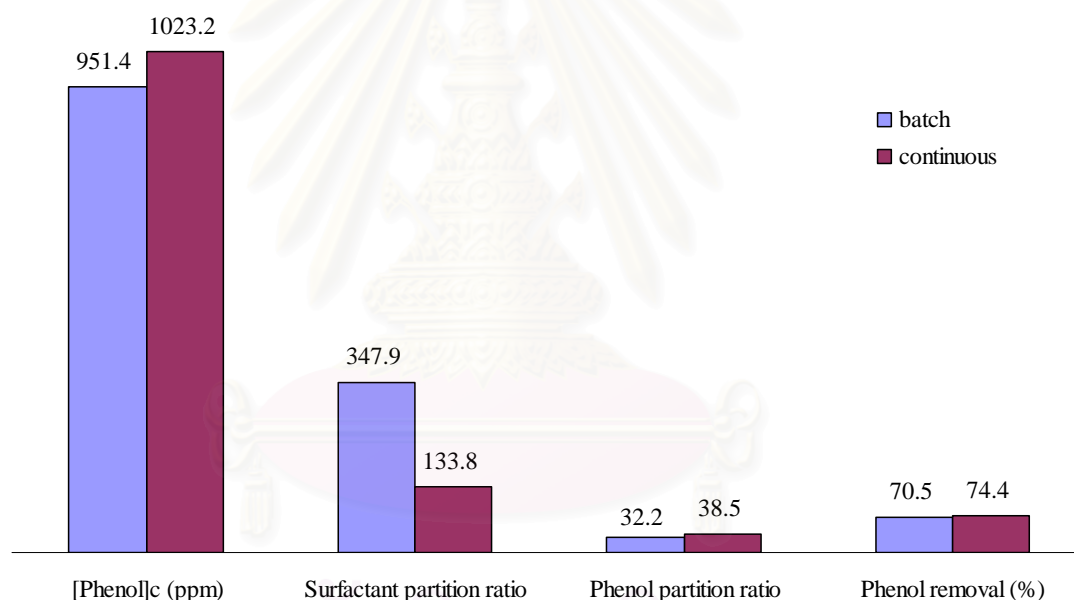
Figure 4.13 Comparison of phenol concentration in extracted coacervate (c), surfactant and phenol partition ratio, and percentage of phenol removal between equilibrium batch and continuous operation (System: batch, 81.88 mM total surfactant, 100 ppm phenol; continuous, 100 ppm phenol, 1/8.483 surfactant to wastewater flow rate ratio, 700 rpm agitator speed)

The concentration of phenol in coacervate phase, phenol partition ratio and percentage in phenol removal obtained from continuous extraction are

comparable to those obtained from batch experiment. However, the surfactant partition ratio obtained from continuous mixer-settler is more than two times lower than that obtained from batch experiment where there is no disturbing during the settlement mainly due to an overflow or unsettlement of fine coacervate droplets out of the settler with the dilute phase solution, resulting in an obviously high surfactant concentration in the dilute phase.

        To overcome this problem and hence, to enhance the surfactant partition ratio, more settlers are recommended to apply in this continuous mixer-settler unit where the connection type for settlers should be in parallel.
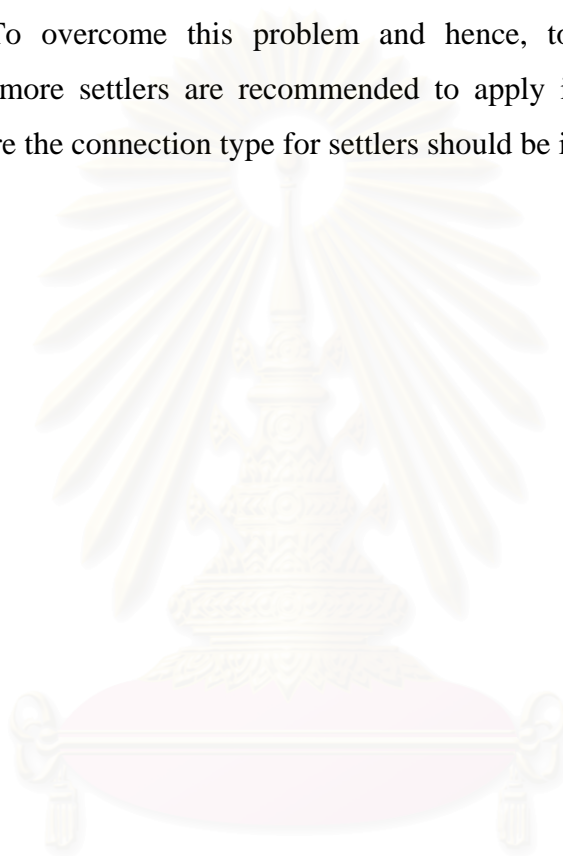
CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research demonstrates the feasibility of aqueous surfactant two-phase (ASTP) extraction system formed by mixtures of cationic (DTAB)/anionic (DOWFAX 8390) at 2 to 1 molar ratio to remove phenol from the synthesis wastewater in a continuous mixer-settler. The device used in the experiment is rather simple in term of design and operation; and defined as a single stage extractor. However, the achieved extraction yield in phenol removal is satisfaction and comparable to that observed in batch extraction carried out at equilibrium condition. So, this continuous mixer-settler is proven to be applicable for ASTP extraction technique. In continuous extraction, the coacervate drop size generated by agitator affects to extraction efficiency. High interfacial area of smaller drop size causes greater mass transfer of phenol into the surfactant aggregates. Although an increase in agitation enhances the extraction efficiency, there is a limitation. Beyond the agitator speed of 700 rpm, the tiny coacervate droplets need more settling time for coalescence in settler. Single settler cannot provide enough time for settling, thus some coacervate droplets overflow out of the settler leading to high surfactant and phenol in the surfactant-dilute phase (effluent stream) and low percentage of phenol removal.

An increment of surfactant to wastewater flow rate ratio, which corresponds to an increase in total surfactant concentration in the system, was found to improve the extraction efficiency. Because of the higher surfactant aggregates presented in the system as extracting agent when the surfactant to wastewater flow rate ratio increases, more phenol is removed from wastewater. However, there is also a limitation in increasing the flow rate ratio of surfactant to wastewater. If the flow rate ratio is too high resulting in too high total surfactant concentration in the system, there will be a phase inversion which probably due to a transition of surfactant aggregates from vesicles to other kinds of surfactant aggregates at very high surfactant concentrations. Thus, the coacervate phase becomes the lighter phase and

cannot settle at the bottom of settlers. Thus, in this study the total surfactant concentration should not exceed 82 mM.

The higher degree of hydrophobicity of contaminant shows the greater potential to be extracted in the coacervate phase in the following order; p-chlorophenol > o-chlorophenol > phenol, which is in agreement to the log Kow value of these contaminants where p-chlorophenol has the highest log Kow followed by o-chlorophenol, and phenol, respectively. The percentages of contaminant removal are 64% for p-chlorophenol, 61% for o-chlorophenol, and 55% for phenol. These extraction efficiencies are obtained from the system operated using optimum condition with only one settler.

The number of settlers and the connection type were also studied. In overall expression, an increase in the number of settlers can reduce the entrainment of coacervate droplets due to a longer residence time prior the droplets to leave the settlers. The process consequently becomes more economical owing to less surfactants loss. The percentage of phenol removal can be enhanced from 55 % using one settler to 74.4 % using 3 settlers. The type of settler connection is also important. The setters connected in parallel yields a better extraction performance rather than those of connected in series according to less upflow velocity present in the settler.

The comparison on process efficiency between extraction in batch at equilibrium condition and in continuous mixer-settle at steady state condition was also investigated. The phenol partition ratio and percentage of phenol removal obtained from continuous mixer-settler are comparable to those obtained in batch extraction. However, the surfactant partition ratio obtained from continuous mixer-settler is more than twofold lower than that obtained from batch experiment due to an entrained or unsettlement of fine coacervate droplets out of the settler with the dilute phase solution.

In summary, the ASTP extraction technique operated in continuous mixer-settler is applicable to extract and preconcentrate the contaminants of environmental concern from wastewater. As high as 74 % of phenol removal and 38.5 of phenol partition ratio were achieved using 2:1 molar ratio of DTAB:DOWFAX with 0.12 surfactant to wastewater flow rate ratio (equivalent to the total surfactant concentration of 82 mM) at 700 rpm agitator speed with three settlers.

5.2 Recommendations

The problem about an entrainment of fine coacervate droplets in the settler should be solved in order to improve the extraction performance. To reduce this problem, more settlers are recommended to provide a longer settling time for coacervate droplets or the size of settler should be adjusted to permit a good phase separation. In addition, the cross-sectional area at the top of settler may be enlarging to reduce the terminal velocity of coacervate droplets which entrain to the top of the settler with the surfactant-dilute phase. Thus, the gravitation forces are sufficient to promote the settling of coacervate droplets. Moreover, the continuous multi-stage extraction device such as rotating disk contactor (RDC) may be used as an extractor to get the better extraction performance.

If this ASTP system from by mixtures of cationic/anionic surfactants operated in continuous extractor is applied to remove organic pollutants with high volatility in the closed system, it will be a promising technique as regarded to its preconcentration ability and being less energy intensive which are very beneficial in an economic viewpoint since the phase separation is governed by surfactant composition and concentration not by the operating temperature like nonionic surfactants. Furthermore, the coacervate or surfactant-rich phase can be recovered for reuse by passing through gas, air, or vacuum stripper to strip the low boiling point compounds out of the surfactant aggregates leaving the solute-free surfactant solution for reuse (Hasegawa et al., 1997; Choori et al., 1998). Otherwise, the surfactant mixture may be recovered by precipitation upon altering the surfactant composition. Unlike other structures of aggregates, the precipitate cannot solubilize the organic pollutants. This, the pollutants will separate out of the surfactant aggregates as an another immiscible phase (Xiao et al., 2000).

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APPENDICES

APPENDIX A

Terms Notification

To investigate the extraction performance, these following terms are introduced.

    (i) Percentage of phenol removal

$$\% \text{Phenol removal} = \left[\frac{[P]_{initial} - [P]_{dilute}}{[P]_{initial}} \right] \times 100$$

    where $[P]_{initial}$ is the initial concentration of phenol in wastewater

                  $[P]_{dilute}$ is the initial concentration of phenol in surfactant-dilute phase

    (ii) Surfactant Partition Ratio

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

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

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

    (iii)Phenol Partition Ratio

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

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

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

(iv)Fractional Surfactant-Rich Phase Volume

$$\text{Fractional surfactant rich phase volume} = \frac{\text{Surfactant - rich phase volume}}{\text{Total volume}}$$

(v) Fractional of Surfactant in Surfactant-Rich Phase

$$\text{Fraction of surfactant in surfactant rich phase} = \frac{(F_c)([S]_{rich})}{(F_c)([S]_{rich}) + (1 - F_c)([S]_{dilute})}$$

where F_c is the fractional surfactant-rich phase volume

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

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

phase

APPENDIX B

Table B-1 Standard curve of DOWFAX and total surfactant concentration at 2:1 of DTAB:DOWFAX

DTAB:DOWFAX	Total surfactant concentration (mM)	DOWFAX(mM)	Absorbance at 240 nm
2:1	0.010	0.003	0.063
	0.020	0.007	0.116
	0.040	0.013	0.251
	0.060	0.020	0.357
	0.080	0.027	0.477
	0.100	0.033	0.597
	0.120	0.040	0.725
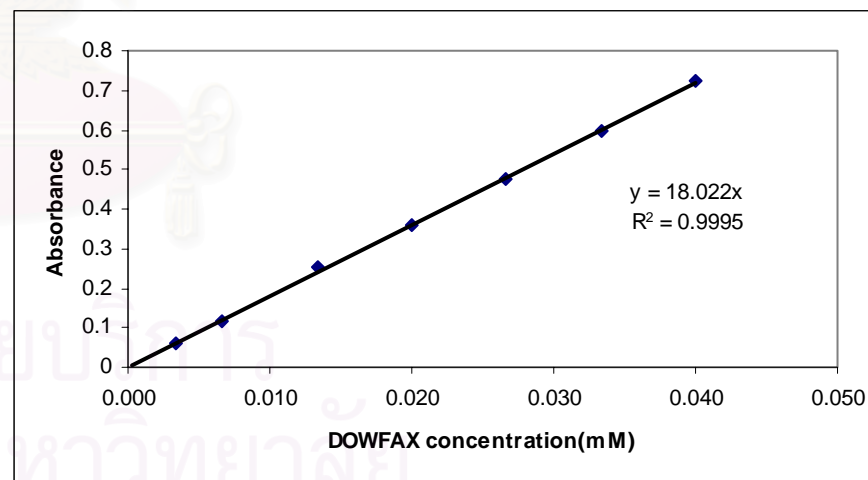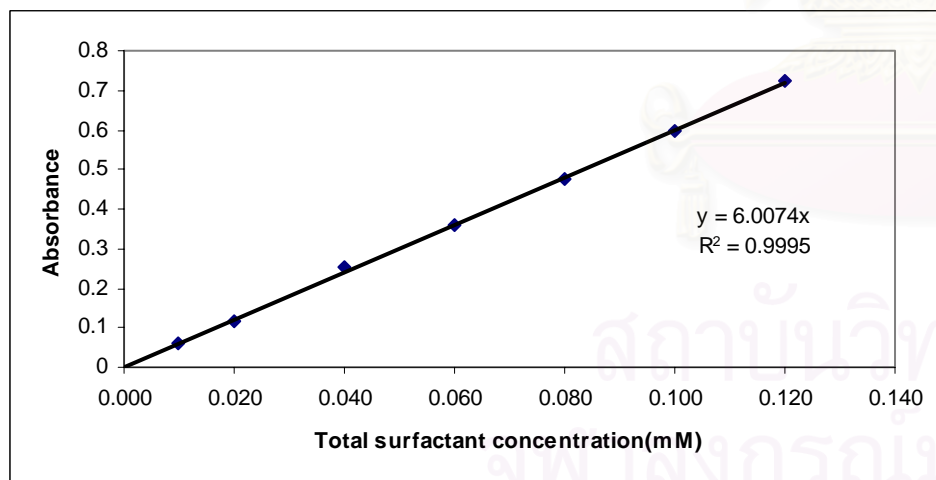
Table B-2 Standard curve of phenol

Phenol concentration (ppm)	Absorbance at 510 nm
0.050	0.004
0.100	0.012
0.200	0.026
0.500	0.062
0.800	0.096
1.000	0.126
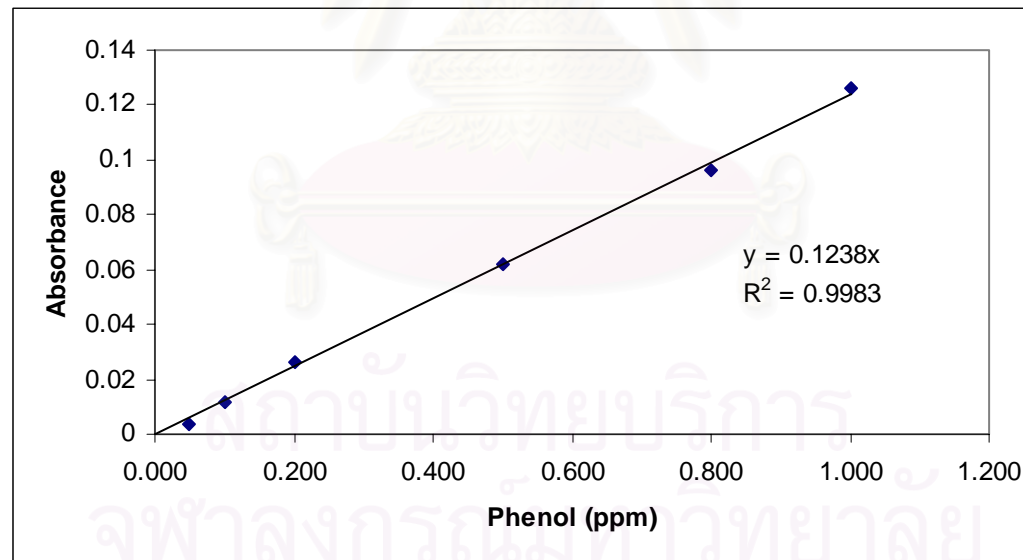
Table B-3   Standard curve of 2-chlorophenol

2-Chlorophenol concentration (ppm)	Absorbance at 510 nm
0.05	0.003
0.10	0.008
0.20	0.018
0.50	0.048
0.80	0.079
1.00	0.091

$y = 0.0941x$

$R^2 = 0.9958$
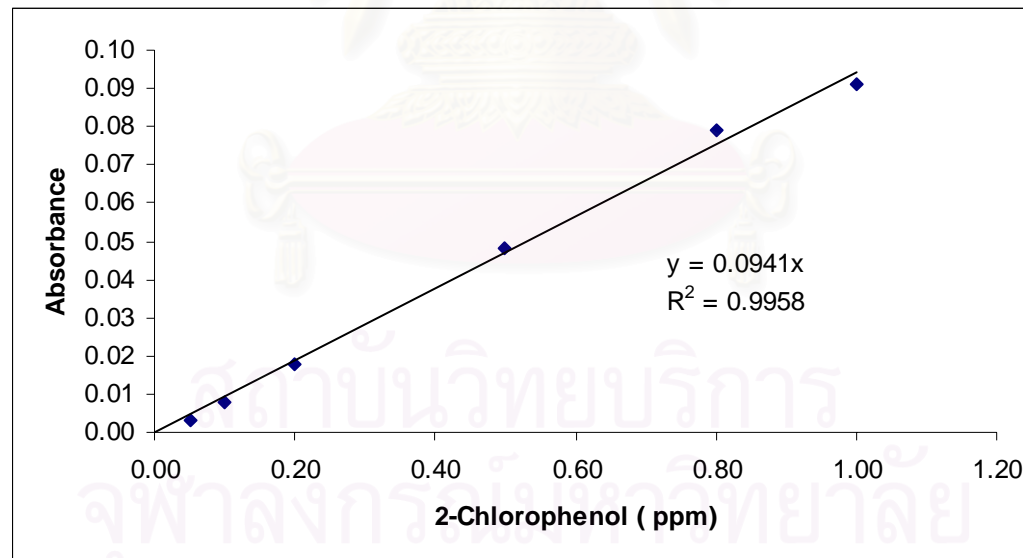
Table B-4   Standard curve of 4-chlorophenol

4-Chlorophenol concentration (ppm)	Absorbance at 510 nm
0.05	0.003
0.10	0.006
0.20	0.014
0.50	0.038
0.80	0.063
1.00	0.079
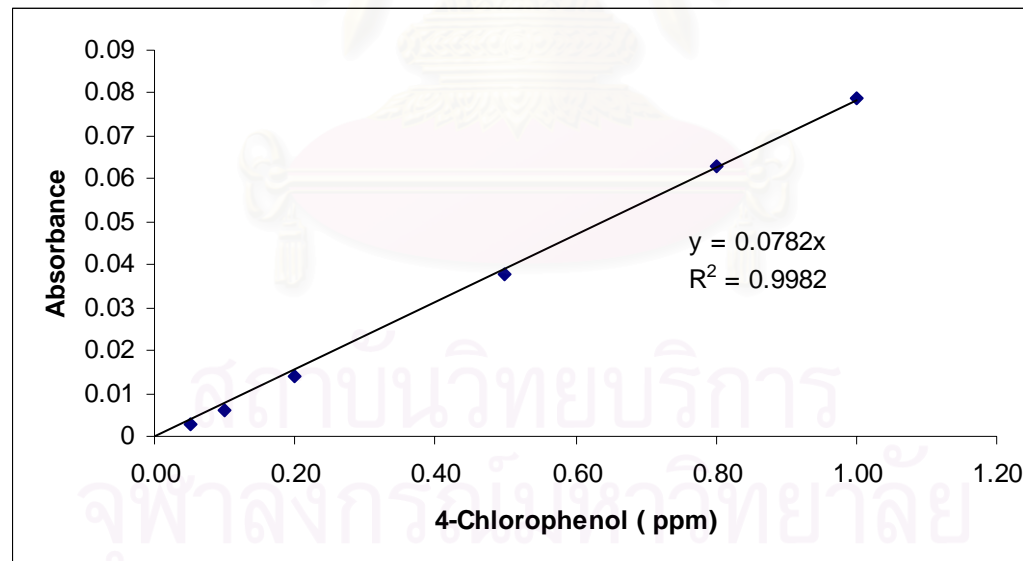
APPENDIX C

Table C-1 Results of preliminary study in phase behavior of Aqueous Surfactant Two-Phase (ASTP) system in calibrated volumetric vial at temperature 30 ^{o}C: Initial [DTAB+DOWFAX] = 70 mM, initial [phenol] = 100 ppm.

		Surfactant-dilute phase					
		DOWFAX analysis (20 times dilution)			Phenol analysis (50 times dilution)		
		Abs. at 240 nm		Concentration (mM)	Abs. at 510 nm		Concentration (ppm)
Vial No.	Volume (mL)	1	2		1	2	
1	19.83	0.154	0.155	0.171	0.080	0.078	31.906
2	20.00	0.168	0.185	0.196	0.079	0.084	32.916
3	19.67	0.147	0.169	0.175	0.082	0.080	32.714
average	19.83			0.181			32.512
STDEV	0.17			0.013			0.534

		Surfactant-rich phase					
		DOWFAX analysis (10000 times dilution)			Phenol analysis (2500 times dilution)		
		Abs. at 240 nm		Concentration (mM)	Abs. at 510 nm		Concentration (ppm)
Vial No.	Volume (mL)	1	2		1	2	
1	1.67	0.515	0.487	277.994	0.045	0.045	908.724
2	1.50	0.596	0.584	327.378	0.056	0.055	1120.759
3	1.83	0.477	0.482	266.064	0.046	0.047	939.015
average	1.67			290.478			989.499
STDEV	0.17			32.508			114.679

Table C-2 Summary of data obtained from preliminary study in phase behavior of Aqueous Surfactant Two-Phase (ASTP) system in calibrated volumetric vial at temperature 30 ^{o}C: Initial [DTAB+DOWFAX] = 70 mM, initial [phenol] = 100 ppm

DOWFAX (mM)		Phenol (ppm)		Surfactant Partition Ratio	Phenol Partition Ratio	Fractional Surfactant-Rich Phase Volume	Fraction of Surfactant in Rich Phase	Phenol Removal (%)	Mass Balance (%)	
Dilute	Rich	Dilute	Rich						DOWFAX	Phenol
0.181	290.478	32.512	989.499	1605.828	30.435	0.078	0.993	67.488	97.220	106.697

APPENDIX D

Results of effect of agitator speed used one settler: Initial [DTAB+DOWFAX] = 770 mM, initial [phenol] = 100 ppm, surfactant flow rate = 0.5 mL/min, wastewater flow rate = 5 mL/min

Table D-1   Agitator speed: 125 rpm

Time (hrs.)	Flow out (mL/min)	Surfactant-dilute phase									
		DOWFAX analysis (250 times dilution)					Phenol analysis (250 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
1	5.29	0.525	0.357	0.467	6.238	1.184	0.031	0.031	0.031	62.601	0.000
2	5.27	0.621	0.607	0.596	8.434	0.174	0.032	0.030	0.031	62.601	2.019
2.5	5.27	0.707	0.687	0.734	9.840	0.327	0.031	0.030	0.030	61.255	1.166
3	5.28	0.557	0.601	0.637	8.300	0.556	0.030	0.030	0.030	60.582	0.000
3.5	5.30	0.542	0.763	0.561	8.628	1.699	0.029	0.030	0.030	59.908	1.166
4	5.29	0.568	0.573	0.588	7.995	0.144	0.029	0.030	0.030	59.908	1.166
4.5	5.28	0.546	0.524	0.547	7.477	0.180	0.029	0.030	0.029	59.235	1.166

Time (hrs.)	Flow out (mL/min)	Surfactant-rich phase									
		DOWFAX analysis (10000 times dilution)					Phenol analysis (5000 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
3.5	0.20	0.693	0.696	0.686	383.790	2.847	0.024	0.023	0.023	942.380	23.318

Table D-2 Agitator speed: 350 rpm

Time (hrs.)	Flow out (mL/min)	Surfactant-dilute phase									
		DOWFAX analysis (250 times dilution)					Phenol analysis (250 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
1	5.29	0.508	0.533	0.510	7.172	0.193	0.027	0.028	0.028	55.870	1.166
2	5.29	0.491	0.490	0.492	6.811	0.014	0.027	0.027	0.028	55.197	1.166
2.5	5.30	0.473	0.484	0.469	6.594	0.108	0.027	0.027	0.028	55.197	1.166
3	5.29	0.468	0.468	0.487	6.580	0.152	0.027	0.027	0.027	54.523	0.000
3.5	5.27	0.465	0.465	0.464	6.446	0.008	0.026	0.027	0.027	53.850	1.166
4	5.29	0.462	0.455	0.465	6.390	0.071	0.026	0.026	0.027	53.177	1.166
4.5	5.30	0.408	0.406	0.412	5.669	0.042	0.025	0.025	0.026	51.158	1.166

Time (hrs.)	Flow out (mL/min)	Surfactant-rich phase									
		DOWFAX analysis (10000 times dilution)					Phenol analysis (5000 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
3.5	0.23	0.655	0.655	0.656	363.630	0.320	0.028	0.028	0.028	1130.856	0.000

Table D-3 Agitator speed: 700 rpm

Time (hrs.)	Flow out (mL/min)	Surfactant-dilute phase									
		DOWFAX analysis (250 times dilution)					Phenol analysis (250 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
1	5.29	0.528	0.529	0.529	7.334	0.008	0.030	0.030	0.029	59.908	1.166
2	5.29	0.467	0.465	0.468	6.474	0.021	0.028	0.027	0.028	55.870	1.166
2.5	5.28	0.462	0.464	0.464	6.427	0.016	0.028	0.027	0.027	55.197	1.166
3	5.29	0.446	0.448	0.449	6.210	0.021	0.026	0.026	0.027	53.177	1.166
3.5	5.27	0.442	0.446	0.445	6.164	0.029	0.025	0.026	0.026	51.831	1.166
4	5.28	0.428	0.427	0.429	5.937	0.014	0.026	0.026	0.026	52.504	0.000
4.5	5.28	0.426	0.424	0.427	5.905	0.021	0.026	0.026	0.026	52.504	0.000

Time (hrs.)	Flow out (mL/min)	Surfactant-rich phase									
		DOWFAX analysis (10000 times dilution)					Phenol analysis (5000 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
3.5	0.23	0.651	0.651	0.650	361.040	0.320	0.029	0.028	0.03	1171.244	40.388

Table D-4   Agitator speed: 1100 rpm

Time (hrs.)	Flow out (mL/min)	Surfactant-dilute phase									
		DOWFAX analysis (250 times dilution)					Phenol analysis (250 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
1	5.30	0.802	0.800	0.804	11.125	0.028	0.034	0.034	0.036	70.005	2.332
2	5.29	0.786	0.784	0.788	10.903	0.028	0.032	0.036	0.034	68.659	4.039
2.5	5.30	0.686	0.685	0.687	9.516	0.014	0.030	0.032	0.032	63.274	2.332
3	5.29	0.676	0.679	0.679	9.405	0.024	0.032	0.031	0.031	63.274	1.166
3.5	5.29	0.672	0.685	0.677	9.405	0.091	0.030	0.030	0.031	61.255	1.166
4	5.29	0.663	0.657	0.660	9.155	0.042	0.029	0.029	0.028	57.889	1.166
4.5	5.29	0.590	0.589	0.587	8.166	0.021	0.029	0.028	0.029	57.889	1.166

Time (hrs.)	Flow out (mL/min)	Surfactant-rich phase									
		DOWFAX analysis (10000 times dilution)					Phenol analysis (5000 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
3.5	0.21	0.599	0.601	0.602	333.296	0.848	0.025	0.026	0.025	1023.156	23.318

Table D-5   Summary of data obtained from effect of agitator speed used one settler: Initial [DTAB+DOWFAX] = 770 mM, initial [phenol] = 100 ppm, surfactant flow rate = 0.5 mL/min, wastewater flow rate = 5 mL/min

Agitator Speed (rpm)	DOWFAX (mM)		Phenol (ppm)		Surfactant Partition Ratio	Phenol Partition Ratio	Fractional Surfactant-Rich Phase Volume	Fraction of Surfactant in Rich Phase	Phenol Removal (%)	Mass Balance (%)	
	Dilute	Rich	Dilute	Rich						DOWFAX	Phenol
125	8.628	383.790	59.908	942.380	44.480	15.730	0.036	0.627	40.092	95.445	101.198
350	6.446	363.630	53.850	1130.856	56.413	21.000	0.036	0.680	46.150	91.640	108.778
700	6.164	361.040	51.831	1171.244	58.575	22.597	0.042	0.719	48.169	90.017	108.507
1100	9.405	333.296	61.255	1023.156	35.438	16.703	0.038	0.585	38.745	93.308	107.780

APPENDIX E

Results of effect of surfactant to wastewater flow rate ratio used one settler: Initial [DTAB+DOWFAX] = 770 mM, initial [phenol] = 100 ppm, agitator speed 700 rpm, total flow rate [surfactant flow rate + wastewater flow rate] = 5.5 mL/min

Table E-1   Surfactant to wastewater flow ratio: 0.118

		Surfactant-dilute phase									
		DOWFAX analysis (250 times dilution)					Phenol analysis (250 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
Time (hrs.)	Flow out (mL/min)	1	2	3			1	2	3		
1	5.28	0.609	0.596	0.608	8.383	0.100	0.026	0.026	0.026	52.504	0.000
2	5.27	0.566	0.539	0.534	7.579	0.239	0.024	0.023	0.023	47.119	1.166
2.5	5.27	0.479	0.470	0.472	6.571	0.066	0.024	0.023	0.023	47.119	1.166
3	5.28	0.465	0.463	0.464	6.437	0.014	0.023	0.023	0.023	46.446	0.000
3.5	5.27	0.453	0.456	0.445	6.261	0.079	0.023	0.022	0.022	45.100	1.166
4	5.29	0.421	0.435	0.416	5.882	0.137	0.022	0.021	0.021	43.080	1.166
4.5	5.28	0.407	0.393	0.396	5.530	0.102	0.022	0.021	0.021	43.080	1.166

		Surfactant-rich phase									
		DOWFAX analysis (10000 times dilution)					Phenol analysis (5000 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
Time (hrs.)	Flow out (mL/min)	1	2	3			1	2	3		
3.5	0.23	0.813	0.805	0.810	449.081	2.243	0.032	0.032	0.032	1292.407	0.000

Table E-2   Surfactant to wastewater flow ratio: 0.100

		Surfactant-dilute phase									
		DOWFAX analysis (250 times dilution)					Phenol analysis (250 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
Time (hrs.)	Flow out (mL/min)	1	2	3			1	2	3		
1	5.29	0.528	0.529	0.529	7.334	0.008	0.030	0.030	0.029	59.908	1.166
2	5.29	0.467	0.465	0.468	6.474	0.021	0.028	0.027	0.028	55.870	1.166
2.5	5.28	0.462	0.464	0.464	6.427	0.016	0.028	0.027	0.027	55.197	1.166
3	5.29	0.446	0.448	0.449	6.210	0.021	0.026	0.026	0.027	53.177	1.166
3.5	5.27	0.442	0.446	0.445	6.164	0.029	0.025	0.026	0.026	51.831	1.166
4	5.28	0.428	0.427	0.429	5.937	0.014	0.026	0.026	0.026	52.504	0.000
4.5	5.28	0.426	0.424	0.427	5.905	0.021	0.026	0.026	0.026	52.504	0.000

		Surfactant-rich phase									
		DOWFAX analysis (10000 times dilution)					Phenol analysis (5000 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
Time (hrs.)	Flow out (mL/min)	1	2	3			1	2	3		
3.5	0.23	0.651	0.651	0.650	361.040	0.320	0.029	0.028	0.030	1171.244	40.388

Table E-3   Surfactant to wastewater flow ratio: 0.083

Time (hrs.)	Flow out (mL/min)	Surfactant-dilute phase									
		DOWFAX analysis (250 times dilution)					Phenol analysis (250 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
1	5.30	0.569	0.581	0.593	8.060	0.166	0.029	0.030	0.030	59.908	1.166
2	5.31	0.542	0.543	0.550	7.560	0.060	0.029	0.029	0.030	59.235	1.166
2.5	5.31	0.533	0.509	0.538	7.306	0.215	0.029	0.029	0.030	59.235	1.166
3	5.30	0.517	0.519	0.524	7.213	0.050	0.029	0.029	0.028	57.889	1.166
3.5	5.31	0.536	0.503	0.518	7.200	0.229	0.028	0.029	0.029	57.889	1.166
4	5.30	0.495	0.506	0.512	6.996	0.120	0.028	0.028	0.027	55.870	1.166
4.5	5.31	0.484	0.466	0.485	6.635	0.148	0.027	0.027	0.028	55.197	1.166

Time (hrs.)	Flow out (mL/min)	Surfactant-rich phase									
		DOWFAX analysis (10000 times dilution)					Phenol analysis (5000 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
3.5	0.19	0.657	0.665	0.674	369.178	4.719	0.031	0.031	0.030	1238.557	23.318

Table E-4   Surfactant to wastewater flow ratio: 0.064

Time (hrs.)	Flow out (mL/min)	Surfactant-dilute phase									
		DOWFAX analysis (250 times dilution)					Phenol analysis (250 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
1	5.38	0.614	0.610	0.618	8.517	0.055	0.040	0.040	0.041	81.449	1.166
2	5.39	0.579	0.533	0.522	7.556	0.419	0.040	0.040	0.040	80.775	0.000
2.5	5.38	0.504	0.510	0.514	7.065	0.070	0.041	0.039	0.040	80.775	2.019
3	5.39	0.490	0.485	0.495	6.797	0.069	0.040	0.039	0.040	80.102	1.166
3.5	5.39	0.480	0.487	0.494	6.756	0.097	0.038	0.038	0.038	76.737	0.000
4	5.39	0.471	0.452	0.460	6.395	0.132	0.038	0.037	0.038	76.064	1.166
4.5	5.39	0.435	0.433	0.448	6.085	0.113	0.037	0.037	0.037	74.717	0.000

Time (hrs.)	Flow out (mL/min)	Surfactant-rich phase									
		DOWFAX analysis (10000 times dilution)					Phenol analysis (5000 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
3.5	0.11	0.679	0.688	0.677	378.056	3.251	0.031	0.032	0.031	1265.482	23.318

Table E-5 Summary of data obtained from effect of surfactant to wastewater flow rate ratio used one settler: Initial [DTAB+DOWFAX] = 770 mM, initial [phenol] = 100 ppm, agitator speed 700 rpm, total flow rate [surfactant flow rate + wastewater flow rate] = 5.5 mL/min

Surf./Ww Flow Ratio	DOWFAX (mM)		Phenol (ppm)		Surfactant Partition Ratio	Phenol Partition Ratio	Fractional Surfactant-Rich Phase Volume	Fraction of Surfactant in Rich Phase	Phenol Removal (%)	Mass Balance (%)	
	Dilute	Rich	Dilute	Rich						DOWFAX	Phenol
0.118	6.261	449.081	45.100	1292.407	71.728	28.657	0.042	0.758	54.900	90.788	108.833
0.100	6.164	361.040	51.831	1171.244	58.575	22.597	0.042	0.719	48.169	90.017	108.507
0.083	7.200	369.178	57.889	1238.557	51.278	21.395	0.035	0.647	42.111	101.073	106.787
0.064	6.756	378.056	76.737	1265.482	55.962	16.491	0.020	0.533	23.263	90.931	107.014

APPENDIX F

Effect of number of settlers and connection pattern: Initial [DTAB+DOWFAX] = 770 mM, initial [phenol] = 100 ppm, agitator speed 700 rpm, surfactant to wastewater flow rate ratio = 0.118, total flow rate [surfactant flow rate + wastewater flow rate] = 5.5 mL/min

Table F-1   The connection pattern of mixer-settlers: Type A

		Surfactant-dilute phase									
		DOWFAX analysis (250 times dilution)					Phenol analysis (250 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
Time (hrs.)	Flow out (mL/min)	1	2	3			1	2	3		
1	5.28	0.609	0.596	0.608	8.383	0.100	0.026	0.026	0.026	52.504	0.000
2	5.27	0.566	0.539	0.534	7.579	0.239	0.024	0.023	0.023	47.119	1.166
2.5	5.27	0.479	0.470	0.472	6.571	0.066	0.024	0.023	0.023	47.119	1.166
3	5.28	0.465	0.463	0.464	6.437	0.014	0.023	0.023	0.023	46.446	0.000
3.5	5.27	0.453	0.456	0.445	6.261	0.079	0.023	0.022	0.022	45.100	1.166
4	5.29	0.421	0.435	0.416	5.882	0.137	0.022	0.021	0.021	43.080	1.166
4.5	5.28	0.407	0.393	0.396	5.530	0.102	0.022	0.021	0.021	43.080	1.166

Table F-2　　The connection pattern of mixer-settlers: Type B

Time overflow out S_2 (hrs)	Flow out (mL/min)	Surfactant-dilute phase									
		DOWFAX analysis (250 times dilution)					Phenol analysis (250 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
8.23	5.15	0.371	0.396	0.370	5.257	0.204	0.021	0.021	0.022	43.080	1.166

Table F-3   The connection pattern of mixer-settlers: Type C

Time overflow out S_n (hrs)	Flow out (mL/min)	Surfactant-dilute phase									
		DOWFAX analysis (250 times dilution)					Phenol analysis (250 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
S_1; 8.23	2.60	0.346	0.318	0.331	4.601	0.194	0.018	0.018	0.018	36.349	0.000
S_2; 8.23	2.60	0.390	0.327	0.385	5.096	0.486	0.017	0.017	0.018	35.003	1.166

Table F-4   The connection pattern of mixer-settlers: Type D

Time overflow out S_n (hrs)	Flow out (mL/min)	Surfactant-dilute phase									
		DOWFAX analysis (250 times dilution)					Phenol analysis (250 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
		1	2	3			1	2	3		
S_2; 12.34	2.55	0.323	0.319	0.313	4.416	0.070	0.013	0.014	0.014	27.598	1.166
S_3; 12.34	2.60	0.303	0.309	0.312	4.273	0.064	0.012	0.013	0.013	25.579	1.166

Table F-5 Summary of data obtained from effect of number of settlers and connection pattern: Initial [DTAB+DOWFAX] = 770 mM, initial

[phenol] = 100 ppm, agitator speed 700 rpm, surfactant to wastewater flow rate ratio = 0.118,

total flow rate [surfactant flow rate + wastewater flow rate] = 5.5 mL/min

Number of Settlers	Connection Pattern	Overall Settling Time (hrs.)	[DOWFAX]$_d$ (mM)	[Phenol]$_d$ (ppm)	Fractional Surfactant-Rich Phase Volume	Phenol Removal (%)	Mass Balance (%)	
							DOWFAX	Phenol
1	A	4.11	6.261	45.100	0.042	54.900	90.788	108.833
2	B	8.23	5.257	43.080	0.064	60.258	96.701	106.174
2	C	8.23	4.848	35.676	0.055	64.324	93.773	98.271
3	D	12.34	4.344	26.589	0.065	74.421	90.011	90.145

Note: M = Mixer, S = Settler

Pattern A   Pattern B   Pattern C   Pattern D
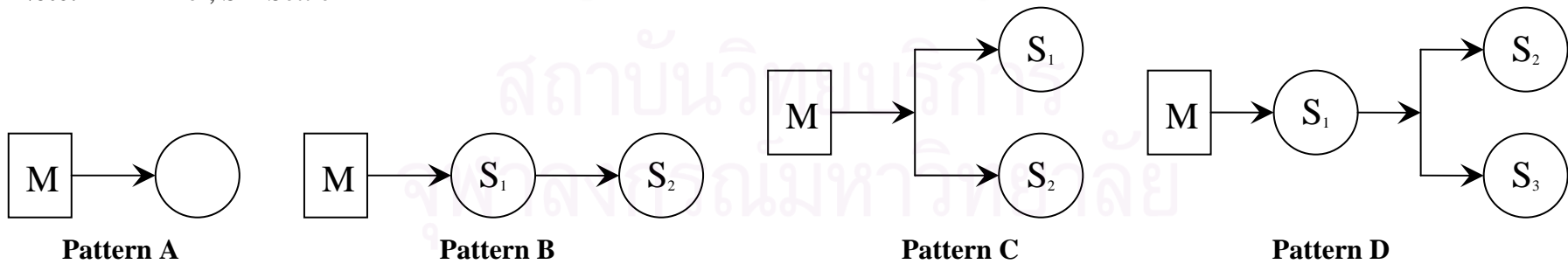
APPENDIX G

Table G-1 Results of phase behavior and extraction performance of Aqueous Surfactant Two-Phase (ASTP) system in calibrated volumetric vial at temperature 30 ^{o}C using same initial condition as obtained by optimal continuous operation: Initial [DTAB+DOWFAX] = 81.879 mM, initial [phenol] = 100 ppm

		Surfactant-dilute phase							
		DOWFAX analysis (50 times dilution)				Phenol analysis (50 times dilution)			
		Abs. at 240 nm			Concentration	Abs. at 510 nm			Concentration
Vial No.	Volume (mL)	1	2	3	(mM)	1	2	3	(ppm)
1	19.83	0.311	0.308	0.306	0.855	0.074	0.073	0.072	29.483
2	19.83	0.365	0.370	0.368	1.020	0.074	0.073	0.073	29.618
3	19.83	0.376	0.376	0.373	1.040	0.073	0.073	0.073	29.483
average	19.83				0.972				29.528
SD	0.00				0.101				0.078

		Surfactant-rich phase							
		DOWFAX analysis (10000 times dilution)				Phenol analysis (2500 times dilution)			
		Abs. at 240 nm			Concentration	Abs. at 510 nm			Concentration
Vial No.	Volume (mL)	1	2	3	(mM)	1	2	3	(ppm)
1	1.67	0.618	0.605	0.599	336.996	0.046	0.047	0.048	949.111
2	1.67	0.613	0.589	0.591	331.632	0.048	0.048	0.047	962.574
3	1.67	0.631	0.619	0.62	345.874	0.046	0.047	0.047	942.380
average	1.67				338.167				951.355
SD	0.00				7.193				10.282

Table G-2 Summary of data obtained from phase behavior and extraction performance of Aqueous Surfactant Two-Phase (ASTP) system in calibrated volumetric vial at temperature 30 $^{\circ}$C using same initial condition as obtained by optimal continuous operation: Initial [DTAB+DOWFAX] = 81.879 mM, initial [phenol] = 100 ppm

[DOWFAX] (mM)		[Phenol] (ppm)		Surfactant Partition Ratio	Phenol Partition Ratio	Fractional Surfactant-Rich Phase Volume	Fraction of Surfactant in Rich Phase	Phenol Removal (%)	Mass Balance (%)	
Dilute	Rich	Dilute	Rich						DOWFAX	Phenol
0.972	338.167	29.528	951.355	347.923	32.219	0.078	0.967	70.472	99.334	100.987

APPENDIX H

Table H Comparison on extraction performance between batch and continuous operation: Batch, [DTAB+DOWFAX] = 81.88 mM, [phenol] = 100 ppm; Continuous, initial [DTAB+DOWFAX] = 770 mM, initial [phenol] = 100 ppm, agitator speed 700 rpm, surfactant to wastewater flow rate ratio = 0.118, total flow rate [surfactant flow rate + wastewater flow rate] = 5.5 mL/min

	Batch Operation	**Continuous Operation**
[Phenol]$_c$ (ppm)	951.355	1023.156
Surfactant Partition Ratio	347.923	133.773
Phenol Partition Ratio	32.219	38.481
Phenol Removal (%)	70.472	74.421

APPENDIX I

Effect of hydrophobic solute used one settler: Initial [DTAB+DOWFAX] = 770 mM, initial [2-Chlorophenol or 2-CP] = 100 ppm, agitator speed 700 rpm, surfactant to wastewater flow rate ratio = 0.118, total flow rate [surfactant flow rate + wastewater flow rate] = 5.5 mL/min

Table I-1   Results of effect of hydrophobic solute**:** 2-Chlorophenol or 2-CP

		Surfactant-dilute phase										
		DOWFAX analysis (250 times dilution)					2-Chlorophenol analysis (250 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
Time (hrs.)	Flow out (mL/min)	1	2	3			1	2	3		
1	5.26	0.608	0.615	0.604	8.448	0.077	0.019	0.019	0.020	51.364	1.534
2	5.26	0.575	0.577	0.577	7.995	0.016	0.016	0.016	0.016	42.508	0.000
2.5	5.25	0.566	0.564	0.565	7.838	0.014	0.016	0.016	0.016	42.508	0.000
3	5.26	0.491	0.492	0.490	6.811	0.014	0.015	0.015	0.014	38.966	1.534
3.5	5.26	0.485	0.485	0.485	6.728	0.000	0.014	0.015	0.015	38.966	1.534
4	5.26	0.466	0.467	0.467	6.474	0.008	0.013	0.014	0.013	35.423	1.534
4.5	5.26	0.620	0.620	0.620	8.601	0.000	0.012	0.013	0.013	33.652	1.534

		Surfactant-rich phase										
		DOWFAX analysis (10000 times dilution)					2-Chlorophenol analysis (5000 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
Time (hrs.)	Flow out (mL/min)	1	2	3			1	2	3		
3.5	0.24	0.865	0.863	0.866	479.784	0.848	0.022	0.022	0.023	1186.681	30.677

Table I-2   Summary of data obtained from effect of hydrophobic solute**:** 2-Chlorophenol or 2-CP

[DOWFAX] (mM)		[2-Chlorophenol] (ppm)		Surfactant Partition Ratio	2-CP Partition ratio	Fractional Surfactant-Rich Phase Volume	Fraction of Surfactant in Rich Phase	2-CP Removal (%)	Mass Balance (%)	
Dilute	Rich	Dilute	Rich						DOWFAX	2-CP
6.728	479.784	38.966	1186.681	71.313	30.455	0.044	0.765	61.034	100.283	99.643

APPENDIX J

Effect of hydrophobic solute used one settler: Initial [DTAB+DOWFAX] = 770 mM, initial [4-Chlorophenol or 4-CP] = 100 ppm, agitator speed 700 rpm, surfactant to wastewater flow rate ratio = 0.118, total flow rate [surfactant flow rate + wastewater flow rate] = 5.5 mL/min

Table J-1 Results of effect of hydrophobic solute**:** 4-Chlorophenol or 4-CP

		Surfactant-dilute phase									
		DOWFAX analysis (250 times dilution)					4-Chlorophenol analysis (250 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
Time (hrs.)	Flow out (mL/min)	1	2	3			1	2	3		
1	5.27	0.678	0.677	0.679	9.405	0.014	0.017	0.017	0.018	55.413	1.846
2	5.27	0.625	0.625	0.626	8.675	0.008	0.015	0.015	0.015	47.954	0.000
2.5	5.26	0.521	0.519	0.520	7.213	0.014	0.014	0.014	0.015	45.823	1.846
3	5.27	0.495	0.497	0.498	6.890	0.021	0.012	0.013	0.012	39.429	1.846
3.5	5.26	0.480	0.482	0.482	6.677	0.016	0.010	0.011	0.010	33.035	1.846
4	5.26	0.448	0.448	0.450	6.224	0.016	0.010	0.010	0.010	31.969	0.000
4.5	5.26	0.445	0.448	0.452	6.219	0.049	0.010	0.010	0.009	30.904	1.846

		Surfactant-rich phase									
		DOWFAX analysis (10000 times dilution)					4-Chlorophenol analysis (5000 times dilution)				
		Abs. at 240 nm			Concentration (mM)	STDEV	Abs. at 510 nm			Concentration (ppm)	STDEV
Time (hrs.)	Flow out (mL/min)	1	2	3			1	2	3		
3.5	0.24	0.868	0.869	0.870	482.188	0.555	0.019	0.020	0.019	1236.147	36.915

Table J-2   Summary of data obtained from effect of hydrophobic solute**:** 4-Chlorophenol or 4-CP

[DOWFAX] (mM)		[4-Chlorophenol] (ppm)		Surfactant Partition Ratio	4-CP Partition ratio	Fractional Surfactant-Rich Phase Volume	Fraction of Surfactant in Rich Phase	4-CP Removal (%)	Mass Balance (%)	
Dilute	Rich	Dilute	Rich						DOWFAX	4-CP
6.677	482.188	33.035	1236.147	72.216	37.419	0.044	0.767	66.965	100.490	95.712

APPENDIX K

Comparison of surfactant and solute partition ratios, and percentage of solute removal from wastewater between phenol, 2-chlorophenol and 4-chlorophenol obtained by studying in effect of hydrophobic solute used one settler: Initial [DTAB+DOWFAX] = 770 mM, initial [solute] = 100 ppm, agitator speed 700 rpm, surfactant to wastewater flow rate ratio = 0.118, total flow rate [surfactant flow rate + wastewater flow rate] = 5.5 mL/min

Solute	[DOWFAX] (mM)		[Solute] (ppm)		Surfactant Partition Ratio	Solute Partition ratio	Fractional Surfactant-Rich Phase Volume	Fraction of Surfactant in Rich Phase	Solute Removal (%)
	Dilute	Rich	Dilute	Rich					
Phenol	6.261	449.081	45.100	1292.407	71.728	28.657	0.042	0.758	54.900
2-Chlorophenol	6.728	479.784	38.966	1186.681	71.313	30.455	0.044	0.765	61.034
4-Chlorophenol	6.677	482.188	33.035	1236.147	72.216	37.419	0.044	0.767	66.965

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