แอดโซลูบิไลเซชันและโซลูบิไลเซชันด้วยสารลดแรงตึงผิวประจุลบชนิดธรรมดาและชนิดที่มีส่วนขยายบนพื้นผิวอะลูมินาออกไซด์

นางสาวนวลกมล อาภรณ์พงษ์

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ADSOLUBILIZATION AND SOLUBILIZATION USING CONVENTIONAL AND EXTENDED ANIONIC SURFACTANTS ON AN ALUMINUM OXIDE SURFACE

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THESIS TITLE	ADSOLUBILIZATION AND SOLUBILIZATION USING CONVENTIONAL AND EXTENDED ANIONIC SURFACTANTS ON AN ALUMINUM OXIDE SURFACE
By	Miss Noulkamol Arpornpong
Field of Study	Environmental Management
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นวลกมล อาภรณ์พงษ์ : แอดโซลูบิไลเซชันและโซลูบิไลเซชันด้วยสารลดแรงตึงผิวประจุลบชนิดธรรมดาและชนิดที่มีส่วนขยายบนพื้นผิวอะลูมินาออกไซด์ (ADSOLUBILIZATION AND SOLUBILIZATION USING CONVENTIONAL AND EXTENDED ANIONIC SURFACTANTS ON AN ALUMINUM OXIDE SURFACE) **อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. สุธา ขาวเธียร, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม:** PROF. DAVID A. SABATINI, Ph.D., 142 **หน้า.**

แอดโซลูบิไลเซชันของสารอินทรีย์ด้วยสารลดแรงตึงผิวที่ดูดซับอยู่บนตัวกลางเป็นปรากฏการณ์ที่สำคัญสำหรับเทคโนโลยีทางด้านสิ่งแวดล้อมโดยใช้พื้นฐานของสารลดแรงตึงผิว แอดโซลูบิไลเซชันได้รับอิทธิพลอย่างมากจากปริมาณการดูดซับของสารลดแรงตึงผิว ซึ่งขึ้นอยู่กับความเป็นกรด-ด่าง ชนิดตัวกลาง และโครงสร้างสารลดแรงตึงผิว ในงานวิจัยนี้ กระบวนการดูดซับของสารลดแรงตึงผิวคาร์บอกซิเลทที่มีส่วนขยายชนิดประจุลบ 2 ชนิด (16-17 คาร์บอน กับ 16-18 คาร์บอน) สารลดแรงตึงผิวซัลเฟทที่มีส่วนขยายชนิดประจุลบ และสารลดแรงตึงผิวธรรมดาชนิดประจุลบ บนพื้นผิวอะลูมินาออกไซด์ได้ถูกศึกษา ผลการศึกษาพบว่ากระบวนการดูดซับของสารลดแรงตึงผิวทุกประเภทบนพื้นผิวอะลูมินาออกไซด์เพิ่มขึ้นเมื่อมีความเข้มข้นของสารลดแรงตึงผิวเพิ่มขึ้น นอกจากนี้ สารลดแรงตึงผิวชนิดซัลเฟทที่มีส่วนขยายแสดงประสิทธิภาพการดูดซับสูงสุดบนพื้นผิวอะลูมินาออกไซด์ที่สูงที่สุด ขณะที่สารลดแรงตึงผิวชนิดคาร์บอกซิเลทที่มีส่วนขยาย ชนิด 16-18 คาร์บอน มีการดูดซับสูงสุดที่ปริมาณความเข้มข้นของสารลดแรงตึงผิวต่ำที่สุด สารอินทรีย์ 2 ชนิดที่มีคุณสมบัติความมีขั้วที่แตกต่างกัน จากค่าความมีขั้วสูงถึงค่าความมีขั้วต่ำ ประกอบด้วยสไตรีนและฟีแนนทรีนซึ่งจะถูกนำมาใช้ในการศึกษาแอดโซลูบิไลเซชันและโซลูบิไลเซชันในครั้งนี้ จากการศึกษาแอดโซลูบิไลเซชันของสไตรีนพบว่า สารลดแรงตึงผิวธรรมดามีประสิทธิภาพในการแอดโซลูบิไลเซชันของสไตรีนดีกว่าสารลดแรงตึงผิวที่มีส่วนขยาย อย่างไรก็ตาม สารลดแรงตึงผิวที่มีส่วนขยายต้องการปริมาณสารลดแรงตึงผิวที่ต่ำกว่าในการสร้างแอดไมเซล สารลดแรงตึงผิวซัลเฟทที่มีส่วนขยายแสดงประสิทธิภาพแอดโซลูบิไลเซชันของฟีแนนทรีนสูงที่สุดเกี่ยวเนื่องกับประสิทธิภาพการดูดซับสูงสุด ประสิทธิภาพแอดโซลูบิไลเซชันของฟีแนนทรีนได้รับอิทธิพลสำคัญจากปริมาณของแอดไมเซลที่ดูดซับบริเวณที่มีการดูดซับเปลี่ยนแปลงเล็กน้อย จากการศึกษาโซลูบิไลเซชัน พบว่า สารลดแรงตึงผิวที่มีส่วนขยายแสดงประสิทธิภาพโซลูบิไลเซชันของสไตรีนและฟีแนนทรีนสูงกว่าสารลดแรงตึงผิวธรรมดา ปริมาณการละลายของสารอินทรีย์ด้วยสารลดแรงตึงผิวขึ้นอยู่กับความชอบน้ำและความไม่ชอบน้ำของทั้งสารลดแรงตึงผิวและสารอินทรีย์ การพิจารณาการสูญเสียสารลดแรงตึงผิวจากพื้นผิวตัวกลาง ปริมาณการไม่ดูดซับจะถูกทำนายเพื่อประเมินความมีเสถียรภาพของสารลดแรงตึงผิวที่ดูดซับบนพื้นผิว ผลการศึกษาชี้ให้เห็นว่าสารลดแรงตึงผิวชนิดคาร์บอกซิเลทที่มีส่วนขยายแสดงให้เห็นถึงปริมาณการไม่ดูดซับที่ต่ำกว่าสารลดแรงตึงผิวธรรมดาเกี่ยวเนื่องกับการทำปฏิกิริยาด้านข้างที่แน่นหนาระหว่างส่วนหางของสารลดแรงตึงผิว ดังนั้นการใช้สารลดแรงตึงผิวที่มีส่วนขยายดูดซับบนพื้นผิวสามารถลดการสูญเสียสารลดแรงตึงผิวจากพื้นผิวและปรับปรุงคุณลักษณะการทำงานของตัวกลางสำหรับการดูดซับที่เพิ่มประสิทธิภาพด้วยสารลดแรงตึงผิวสำหรับการบำบัดสารอินทรีย์

สาขาวิชา.....การจัดการสิ่งแวดล้อม......................ลายมือชื่อนิสิต.....นวลกมล.....
ปีการศึกษา 2551..ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..........
ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม..........

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KEYWORDS : ADMICELLE/ ADSOLUBILIZATION/ ADSOPTION/ DESORPTION/ EXTENDED SURFACTANT/ SOLUBILIZATION

NOULKAMOL ARPORNPONG : ADSOLUBILIZATION AND SOLUBILIZATION USING CONVENTIONAL AND EXTENDED ANIONIC SURFACTANTS ON AN ALUMINUM OXIDE SURFACE. ADVISOR : ASSOC. PROF. SUTHA KHAODHIAR, Ph.D., CO-ADVISOR : PROF. DAVID A. SABATINI, Ph.D., 142 pp.

Adsolubilization of organic solutes by media-sorbed surfactants is an important phenomenon for surfactant-based environmental technologies. Adsolubilization is strongly influenced by the amount of adsorbed surfactant, solution pH, surface type, and surfactant molecular structure. In this research, the adsorption of two anionic extended carboxylate surfactants ($C_{16\text{-}17}$-4PO-5EO-COONa and $C_{16\text{-}18}$-4PO-5EO-COONa), an anionic extended sulfate surfactant ($C_{16\text{-}17}$-4PO-SO_4Na) and an anionic conventional surfactant (SDS) on alumina oxide surface were investigated. The results showed that the adsorption of all surfactant types onto aluminum oxide surface increased with increasing surfactant concentration. Moreover, the extended sulfate surfactant exhibited the highest maximum adsorption capacity onto the aluminum oxide surface while the extended carboxylate surfactant with C16-18 reached maximum adsorption at the lowest surfactant concentration. Two organic solutes with different the degree of polarity, styrene and phenanthrene, were evaluated in adsolubilization and solubilization studies. For styrene adsolubilization study, SDS showed a greater styrene adsolubilization capacity than the extended surfactants; however, the extended surfactants required lower surfactant amounts to form admicelles. The extended sulfate surfactant showed the highest phenanthrene adsolubilization capacity due to the maximum adsorption capacity. The adsolubilization capacity of phenanthrene was significantly influenced by the amounts of adsorbed admicelles at the plateau region. For solubilization study, the extended surfactants exhibited the higher styrene and phenanthrene solubilization capacities than the conventional surfactant. The extent of solubility of organic solutes by surfactants depended on both hydrophilic and hydrophobic of surfactant and organic solutes. In consideration of surfactant loss from the solid surface, the desorption capacity was determined to evaluate the stability of the surfactants adsorbed onto the surface. The results indicated that the extended carboxylate surfactants showed the lower desorption capacity as compared to the conventional surfactant due to the stronger lateral interaction between surfactant tails. Therefore, the use of extended surfactant adsorbed onto solid surface can reduce the surfactant losses from the surface and improved the operating characteristics of the surfactant-modified adsorbent for removal of organic pollutants.

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Student's Signature : นวลกมล
Advisor's Signature :
Co-Advisor's Signature :

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CONTENTS

Page

LIST OF TABLES

Page

LIST OF FIGURES

Page

Page

CHAPTER I
INTRODUCTION

1.1 Introduction

Non-aqueous phase liquids (NAPLs) are hydrocarbons that exist as a separate, immiscible phase when in contact with water and/or air. NAPLs are a major environmental concern because they are commonly found in contaminated soil and groundwater due to unseemly disposals, accidental spills, and the leakage of petroleum hydrocarbons. These compounds are listed by the US Environmental Protection Agency (EPA) as priority environmental toxic pollutants due to their substantial toxicity and their carcinogenic potential even at low concentrations (US-EPA, 2008). Contamination with organic compounds is a complex process and difficult to treat due to many reasons such as the adsorption tendency of the contaminants onto the soil matrix, fate and transport, low water solubility, and the limited rate of mass transfer for biodegradation (Harwell et al., 1999; Paria and Khilar, 2004; Childs et al., 2006).

Generally, there are different remediation technologies available for subsurface soil and groundwater that has been contaminated with organic pollutants, such as pump and treat, soil flushing, and bioremediation. However, these methods have their limitations; they can be ineffective, expensive, unreliable, and they often require an extended time period to perform adequate clean ups (West and Harwell, 1992; Reddy et al., 1995). To solve these problems, surfactant-based processes may be used due to their low cost, low toxicity, low adsorption to soil, and low concentration requirements. Their low soil dispersion and low surface tension properties also make them an attractive alternative.

Furthermore, surfactants can be recovered and reused, making them an economical option (Mulligan et al., 2001).

According to the application, surfactant aggregates adsorbed onto a solid oxide surface are capable of acting as two-dimensional solvents attached to the solid surface. The nature of these aggregates is much like that of micelles and they have thus been termed admicelles (adsorbed micelles). Admicelles can solubilize various kinds of organic solutes; this process is called adsolubilization (O'Haver et al., 1995; Kitiyanan et al., 1996; Fuangsawasdi et al., 2006b; Saphanuchart et al., 2007; Charoensaeng et al., 2008). Adsolubilization can be applied in industrial and environmental applications; for instance, admicellar-enhanced chromatography (AEC) is a new fixed-bed separation process using adsorbed surfactants to induce the partitioning of organic solutes into admicelles (Harwell and O'Rear, 1989). Admicellar polymerization has been used to improve the physical properties of substrates such as increasing tear strength and improving elongation to break off rubber physical properties (Pongprayoon et al., 2002). Other applications, such as soil-slurry washing, wastewater treatment, landfill liners, or subsurface barriers, are used to eliminate the transportation of pollutants (Shaobai et al., 1996).

Extended surfactants are novel surfactants that have been recently produced to enhance the solubilization of organic solutes. The molecular structure of an extended surfactant consists of one or more intermediate-polarity groups between its hydrophilic head and hydrophobic tail. They also provide a more suitable region for solubilizing both hydrophilic and lipophilic solutes. Moreover, adsolubilization using extended-surfactant-based admicelles can enhance adsolubilization but it requires small amounts of surfactants to form admicelles (Charoensaeng et al., 2008).

Previous studies have indicated that anionic extended surfactants with a PO group could be effectively used to enhance the solubilization (Mińana-Perez et al., 1995; Witthayapanyanon et al., 2006; Aumpuch, 2007) and adsolubilization (Charoensaeng et al., 2008) capacities of organic solutes. Recently, a new class of anionic extended surfactants containing propylene oxide (PO) groups, ethylene oxide (EO) groups, and carboxylate head groups has been produced and developed. This novel class of anionic extended surfactants is expected to enhance the adsolubilization of organic solutes at levels similar to or greater than those of conventional surfactants and all prior extended surfactants. Additionally, the main benefits of these types of surfactant are its biodegradability and low toxicity.

This study aims to enhance the ability of surfactant adsorbent materials to remove organic contaminants during the surfactant-based adsorption process. In view of the fact that extended surfactant systems have shown improved solubilization in aqueous systems. However, the performance of extended carboxylate surfactant systems has not been systematically studied. Thus, the purpose of this study is to investigate the adsorption of anionic extended carboxylate surfactants onto a positively charged aluminum oxide surface and to determine the solubilization and adsolubilization of organic solutes into micelles and admicelles. To determine surfactant loss from the solid surface, the desorption capacity was obtained to evaluate the stability of the surfactants adsorbed onto the surface.

1.2 Objectives

The overall objectives of this study are to investigate the adsorption of anionic extended carboxylate surfactants onto a positively charged aluminum oxide surface, to determine the solubilization and adsolubilization of organic solutes into micelles and admicelles, and to evaluate the desorption capacity of adsorbed admicelles. The electrolyte concentration, solution pH, and temperature have been controlled under a constant condition in batch equilibrium systems. The specific objectives of this study are as follows:

1) To investigate the surfactant adsorption capacities of a conventional surfactant, two extended carboxylate surfactants, and an extended sulfate surfactant

2) To evaluate the effects of carbon chain length on the solubilization and adsolubilization of organic solutes

3) To evaluate the desorption capacity of the surfactants adsorbed onto an alumina oxide surface after the washing process

1.3 Hypotheses

To our knowledge, this is the first time that extended carboxylate surfactant-based admicelles have been evaluated. The specific structure of this surfactant system includes internal linkers, propylene oxide (PO) groups, ethylene oxide (EO) groups, and then carboxylated. The specific hypotheses of this research are as follows:

1) Extended-surfactant-based admicellar systems enhance adsolubilization due to the increased size of the admicelle interior.

2) The longer alkyl chain length of the surfactant increases the solubilization of organic solutes.

3) Reduced charge-repulsion between adjacent surfactants increases adsorption density and adsolubilization potential.

1.4 Scope of the study

This work aims to enhance the ability of surfactant modified adsorbent to remove organic contaminants during the surfactant-based adsorption process. Sodium dodecyl sulfate (SDS), alkyl propoxylated ethoxylated carboxylate surfactants (C_n-4PO-5EO-COONa), and alkyl propoxylated sulfate surfactant (C_{16-17}-4PO-SO_4Na) were used as the anionic conventional surfactant, anionic extended carboxylate surfactants, and anionic extended sulfate surfactant, respectively. Aluminum oxide or alumina (Al_2O_3) was used as the positively charged oxide surface. Styrene and phenanthrene were selected as the higher and lower polar organic solutes, respectively. All experiments were conducted in batch experiments at room temperature ($25\pm2^{o}C$), with an electrolyte concentration of 1 mM NaCl, and a solution pH of 8.0-8.5.

The surfactant adsorption, solubilization, and adsolubilization isotherms of organic solutes were used to evaluate the impact of extended surfactants onto the positively charged aluminum oxide surface. The solubilization and adsolubilization of styrene and phenenthrene were conducted to evaluate the solubilization capacity of higher and lower polar organic solutes in micelles and admicelles by using micellar and admicellar partition coefficients (K_{mic} and K_{adm}), respectively. The desorption capacity was determined to evaluate the stability of the surfactants adsorbed onto the surface by using the zeta potential measurement.

CHAPTER II

THEORETICAL BACKGROUNDS AND LITERATURE REVIEWS

2.1 Surfactant phenomena

Surfactants (surface active agents) are amphipathic molecules consisting of two dissimilar parts in the same molecule, a polar hydrophilic portion as the head group and a non-polar hydrophobic portion as the tail group as shown in Figure 2-1 (Rosen, 2004; Eftekhari, 2000; Tadros, 2005). The hydrophilic head group is attracted to polar environments (water-like), whereas the hydrophobic tail containing a long chain hydrocarbon is attracted to nonpolar environments (oil-like). Therefore, the surfactants can be dissolved either in water or oil and have the capability to solubilize water or oil to create a homogeneous system (Uppgård, 2002). Surfactants, moreover, can reduce the interfacial tension between two immiscible phases by decreasing the dissimilarity between two phases (e.g., air-water, oil-water, and solid-liquid interfaces). Surfactants are classified into four general classes dependent on the nature of the polar head group: anionic surfactants (negatively charged head groups), cationic surfactants (positively charged head groups), zwitterionic surfactants (negatively and positively charged head groups), and nonionic surfactants (non-charged head groups) (West and Harwell, 1992). In addition, the most commonly used hydrophilic groups of anionic surfactants are the carboxylate and sulfate head groups.

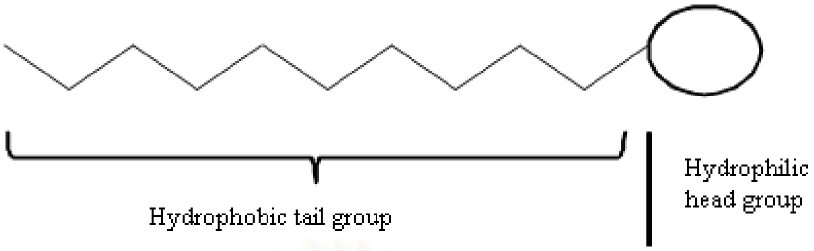


Figure 2-1 Schematic diagram of surfactant molecule (Eftekhari, 2000)

Carboxylate anionic surfactants are perhaps the earliest known surfactants used in early soaps, e.g., sodium or potassium stearate, $C_{17}H_{35}COONa$, derived from animal fats or vegetable oils (Tadros, 2005; Myers, 2006). The main benefits of employing this type of surfactant are its low cost, biodegradability, and low toxicity. To avoid precipitation in hard water the carboxylates are modified by introducing some hydrophilic chains (e.g., ethoxylated groups) into the general structure. The addition of the ethoxylated groups increases the water solubility and enhances the chemical stability; moreover, the solution pH of these carboxylate surfactants influences micelle formation. The carboxylated surfactants are relatively weak acids, and the free acid is liberated in acidic aqueous solutions. Since free acids are insoluble in water, they are only effective in alkaline aqueous solution (Perkins, 1998).

Sulfate surfactants, which are produced in the reaction of an alcohol with sulphuric acid, are the largest and most important class of synthetic surfactants. Since the sulfate group is a strong acid, the sulfate surfactants are soluble and effective in acidic as well as in alkaline media. However, due to their chemical instability (hydrolysis to the alcohol, particularly in acidic solutions), they are now replaced by the chemically stable sulphonates. The properties of sulfate surfactants depend on the nature of the alkyl chain and the sulfate group. Alkali metal salts show good solubility in water but tend to be affected by the presence of electrolytes. The most common sulfate surfactant is sodium dodecyl sulfate (SDS), which has been extensively used in both fundamental studies and many industrial applications. As with carboxylate, sulfate surfactants are also chemically modified to change their properties. The most common modification is to introduce polyethylene oxide units (PEO) into the chain. The presence of PEO confers improves solubility compared to straight alcohol sulfates (Perkins, 1998; Tadros, 2005).

Surfactants are able to form many different types of aggregates in aqueous solution dependent on the nature of the surfactant and the solution properties, such as the type of solvent, concentration, and temperature. At low surfactant concentrations, surfactants are present as monomers, which mainly adsorb onto the air-water interface. When the surfactant concentration increases above a certain point, the surfactant monomers self-aggregate into clusters called micelles (West and Harwell, 1992; Hill, 1999). In normal micelles, the hydrophobic tails is oriented towards the interior of the cluster, and the hydrophilic head is directed towards the water phase (Rosen, 2004). This phenomenon is called micellization or micelle formation. The first micelle is formed when the surfactant concentration exceeds the critical micelle concentration (CMC), which is different for each type of surfactant. If the surfactant concentration rises above the CMC, the number of micelles increases (West and Harwell, 1992). The surfactant micellization process is shown in Figure 2-2.

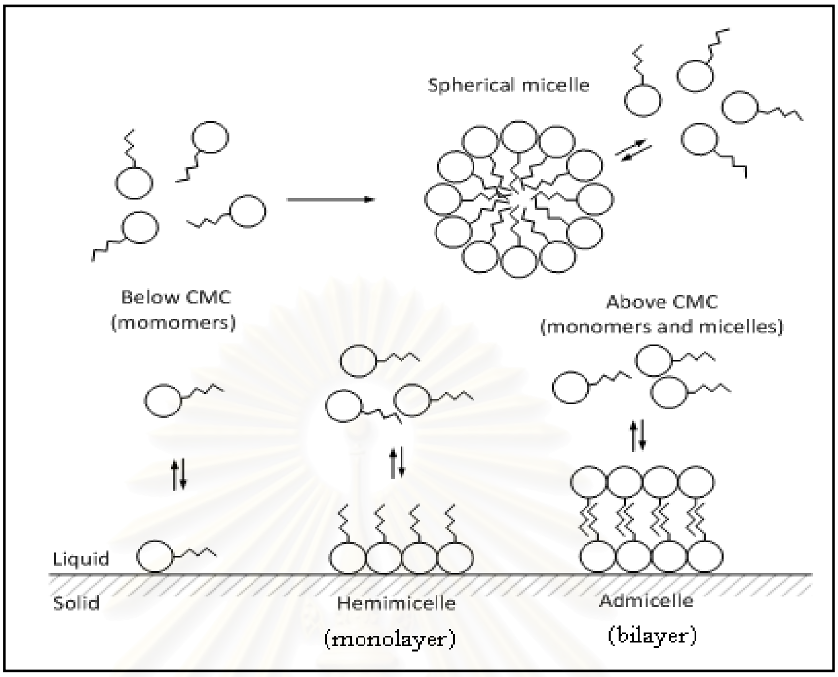


Figure 2-2 Example of surfactant micellization (adapted from West and Harwell, 1992)

When a solid phase is added to a surfactant solution, individual surfactants will adsorb onto the solid-liquid interface. At low surfactant concentrations, referred to as the critical hemimicelle concentration (CHC) or critical admicelle concentration (CAC), aggregates are formed. The hydrophobic group of the surfactant is directed towards the surface of the solid and the hydrophilic group towards the water phase. Lateral interactions occur between adjacent hydrophobic groups of other surfactants, and structures called hemimicelles (monolayer structure) and admicelles (bilayer structure) are formed. If the surfactant concentration exceeds the CMC, the surface concentration of the surfactant stays constant, but the micelle concentration in the water phase increases (West and Harwell, 1992).

2.2 Adsorption of ionic surfactants onto metal oxide surfaces

Surfactant adsorption onto metal oxide surfaces is a complex process that is strongly influenced by a number of parameters: (1) the nature of structural groups of the solid surface, i.e., alumina, silica, and zeolite; (2) the molecular structure of surfactants being adsorbed, i.e., type of surfactant head group and lengths of surfactant tail group; and (3) the environment of the aqueous solution, i.e., solution pH, electrolyte concentration, and temperature. These parameters determine the mechanism of adsorption and the efficiency and effectiveness of the surfactant adsorption (Rosen, 2004; Zhang and Somasundaran, 2006).

2.2.1 Driving forces for surfactant adsorption

In general, adsorption is governed by a number of forces such as electrostatic attraction, hydrogen bonding or non-polar interactions between the adsorbed species, and lateral associative interactions. Total adsorption is usually the cumulative result of some or all of the above mentioned forces. Mechanisms of surfactant adsorption are reviewed in terms of the forces involved and the factors controlling them (Zhang and Somasundaran, 2006).

1) *Electrostatic interactions*: They appear when the system contains ionic surfactants and charged solid particles. The charge on the particle surface is created either due to hydrolysis of surface species in the case of oxides or the preferential dissolution of the lattice ions and subsequent adsorption of the resulting complexes.

2) *Chemical interactions*: Chemical interactions are another important driving force for adsorption of surfactants onto solid particles. This interaction is specific to certain systems and can occur between the surfactant and the solid surface. For example, adsorption of fatty acids on fluorite and hematite has been attributed to chemical bonding between the surfactant and the mineral surface.

3) *Hydrophobic lateral interactions*: The driving force for adsorption results from the free energy of transferring the hydrocarbon chains from the aqueous solution into the hydrophobic interior of the aggregates.

4) *Hydrophobic interactions between the hydrocarbon chains and hydrophobic sites on the solid*: The hydrophobic interaction between the alkyl chain of a surfactant and the hydrophobic sites on the solid becomes a significant factor for surfactant adsorption on fully or partially hydrophobic surfaces.

5) *Hydrogen bonding*: Hydrogen bonding between surfactant species and solid surface species could occur in systems containing hydroxyl, carboxylic, and amine groups on the surfactant. For instance, adsorption of a nonionic surfactant such as ethoxylated alcohols on oxide surfaces has been proposed to involve hydrogen bonding.

6) *Desolvation energy*: When a hydrated head group of the surfactant transfers from the bulk to the mineral–solution interfacial region, the partial removal of water from the secondary solvation shell around the surfactant head groups can occur.

2.2.2 Surfactant adsorption phenomena

Surfactant adsorption onto metal oxide surfaces is a complex process that contains various adsorption mechanisms such as ion exchange, ion pairing, and hydrophobic bonding. In equilibrium studies of surfactant adsorption onto metal oxide surfaces (e.g., aluminum oxide) it is important to determine the maximum amount of surfactants adsorbed per unit area and the adsorption isotherm (Paria and Khilar, 2004). The adsorption of the surfactant onto the solid oxide surface can be calculated by using Equation 2-1. In this equation the adsorption of water or salt is neglected, and the adsorption of the surfactant has no effect on solution density (Lopata, 1988).

$$q_i = \frac{(C_f - C_i)V}{W_g} \tag{2-1}$$

Where

q_i = the adsorption density of surfactant i (mole/g)

V = the volume of the sample (liter)

C_i = the initial concentration of the surfactant (mole/liter)

C_f = the concentration of the surfactant at equilibrium (mole/liter)

W_g = the weight of aluminum oxide (g)

Adsorption of surfactants onto the solid-liquid interface is usually characterized by an adsorption isotherm. The adsorption isotherm is obtained by determining the “depletion of the surfactant due to adsorption onto a solid surface at constant temperature” (Zhang and Somasundaran, 2006) and is commonly seen for ionic surfactants adsorbed from aqueous solution onto oppositely charged metal oxide surfaces. It is typically an S-shaped isotherm, which can be divided into four regions. Figure 2-3 shows these four regions when the log of the surfactant adsorbed per unit area of the solid is plotted versus the log of the equilibrium concentration of surfactants (O’Haver et al., 1995; Paria, 2003; Adak et al., 2005; Paria and Khilar, 2004).

Region I can be observed at low surfactant and monomer concentrations where the surfactants are electrostatically adsorbed to the solid surface. This region is sometimes referred to as the Henry’s law region, where adsorption increases linearly with concentration. The slope of the curve may be less than one because the surfactants are adsorbed by ion exchange, with the hydrophilic surfactant head group adsorbing onto the solid surface without forming surfactant aggregates.

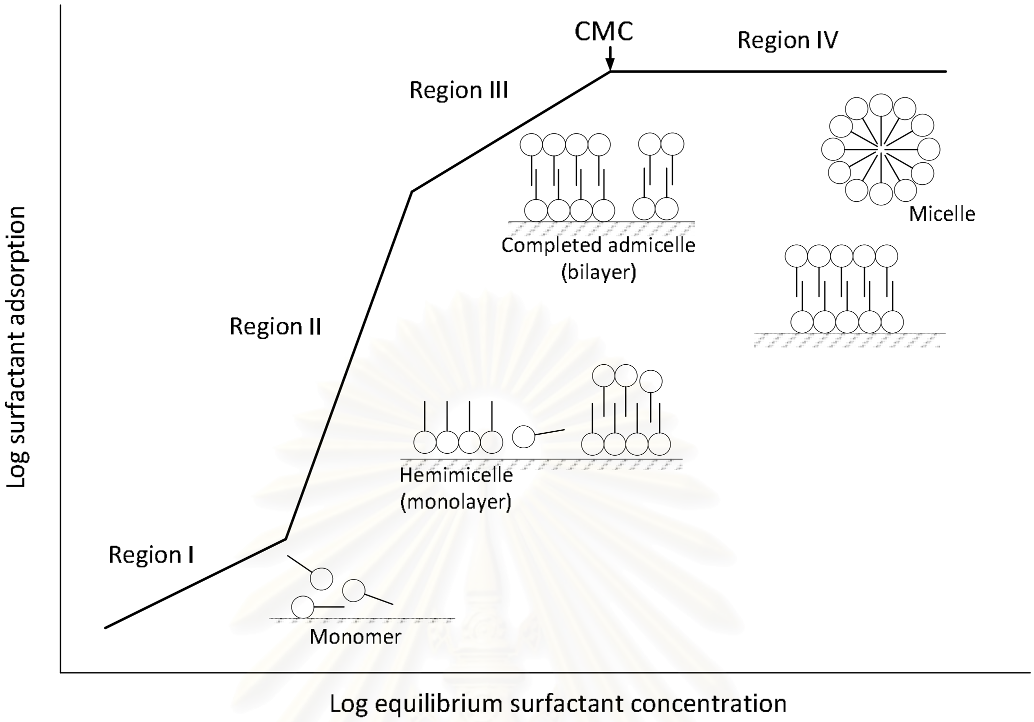


Figure 2-3 Schematic diagram of a typical surfactant adsorption isotherm (Adak et al., 2005)

Region II is indicated by the sharp increase of the slope of the isotherm, which indicates the beginning of lateral interactions between surfactant monomers resulting in surface aggregation of the surfactants. When the concentration of the surfactants is below the CMC, the adsorbed surfactants form hemimicelles or admicelles. A hemimicelle is a monolayer structure where the head groups of the surfactants adsorb to the solid surface, whereas the tail groups are directed towards the aqueous solution. Admicelles are considered as a bilayer structure that consists of a lower layer of head groups adsorbed onto the solid surface and an upper layer of head groups directed towards the aqueous solution. The change in slope indicates that a greater amount of surfactants adsorb for a small increment of surfactant concentration in the aqueous solution and signals that the critical admicelle concentration (CAC) or hemimicelle concentration (HMC) has been reached. In this adsorption region the original charge of the solid is neutralized by the adsorption of oppositely charged surfactant ions and eventually reversed.

In region III the slope of the isotherm decreases again. This decrease in slope is attributed to lateral electrostatic repulsion between adjacent surfactants adsorbing on the surface and/or to the beginning of admicelle formation on lower energy surface patches.

Region IV is the plateau adsorption region usually occurring above the critical micelle concentration of the surfactant. The surfactant monomer activity becomes constant, while the surfactant concentration increases. This increase in surfactant concentration affects only the micellization in solution and does not change the adsorption density. The transition point from region III to region IV represents the first formation of micelles after the interface is saturated with admicelles. Due to lateral hydrophobic interactions between the hydrocarbon chains, surfactant molecules will adsorb with a reversed orientation, which results in a decrease of the hydrophobicity of the particles in this region (Harwell and O'Rear, 1989; Paria and Khilar, 2004; Adak et al., 2005; Zhang and Somasundaran, 2006; Charoensaeng et al., 2008).

2.2.3 Aluminum oxide surface structure

The crystal structure of alpha alumina oxide (α-Al_2O_3) or alumina comprises hexagonally packed oxygen atom layers stacked on top of each other in a balanced behavior, with aluminum ions packed between the oxygen layers as shown in Figure 2-4 (Lopata, 1988; Attaphong, 2006; Charoensaeng, 2008).

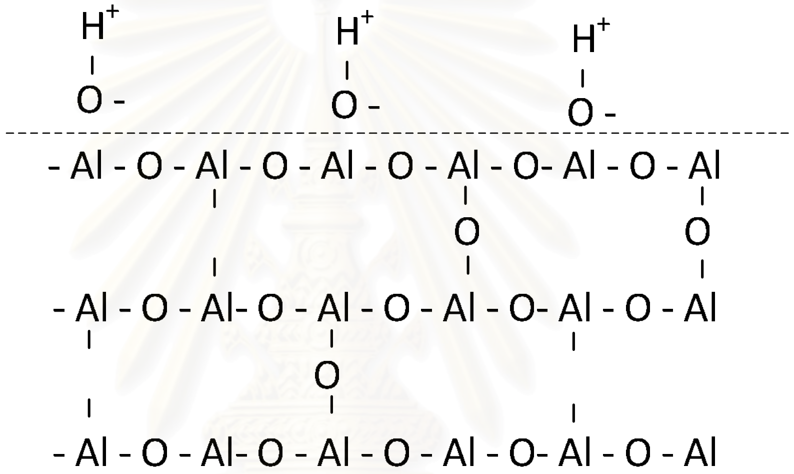


Figure 2-4 Schematics of the crystal structure and surface layer of alpha aluminum oxide

When in contact with water, the crystal surface can form a layer of hydroxyl ions by a two-step process involving the chemical adsorption of a monolayer of water and its dissociation. Since the alumina surface is covered with hydroxyl groups, hydrogen, and hydroxyl ions are potential defining ions for alumina. Additionally, there is a physically adsorbed monolayer of water molecules on top of the hydroxyl ions layer; therefore, the solution pH is significant for the adsorption of ionic surfactants since it controls the charge of the alumina surface.

The point of zero charge (PZC) of the alumina is the solution pH at which the net surface charge density is zero. The PZC of alumina at 25^{o}C has been reported to be pH 9.1 (Sun and Jaffe, 1996). If the solution pH is lower than the PZC of the alumina, the alumina surface is positively charged. On the other hand, at a solution pH higher than the PZC of alumina, the alumina surface is negatively charged.

Alumina is a good adsorbent to study the adsorption of anionic surfactants and mixed anionic and nonionic surfactants onto its positively charged surface (Park and Jaffe, 1993; Sun and Jaffe, 1996; Attaphong, 2006; Fuangswasdi et al., 2006a; Li et al., 2007; Charoensaeng, 2008; Charoensaeng et al., 2008). Many technical applications based on the adsorption of surfactants onto alumina have led to many theoretical studies. The information obtained was very useful for improving the efficiency of adsorbing organic solutes in environmental media. Additionally, the hydrophilic alumina surface has a low adsorption affinity for organic compounds (Sun and Jaffe, 1996; Esumi et al., 2000; Li et al., 2007).

2.2.4 Parameters affecting surfactant adsorption

The adsorption of surfactants on solid surfaces is controlled by the nature of structural groups of the solid surface and the molecular structure of surfactant adsorbed on the solid surfaces, which was already mentioned above (Section 2.2.2). The other parameters controlling surfactant adsorption are the environment of the aqueous solution, solution pH, electrolyte concentration, and temperature.

2.2.4.1 Solution pH

The pH of an aqueous solution is an important parameter for the adsorption of ionic surfactants onto charged solid surfaces. In an aqueous solution the protonation or deprotonation of chemically adsorbed water causes the solid surface to bear a charge, with a pH dependent sign and net charge (Harwell et al., 1989; Pradubmook et al., 2003). As the pH of the aqueous solution is decreased, the alumina surface becomes more positive or less negative due to the adsorption of additional protons from the solution: consequently, the adsorption of anionic surfactants increases and the adsorption of cationic surfactants decreases (Rosen, 2004). Conversely, raising the pH of the solution leads to an increased desorption of anionic surfactants and a decreased desorption of cationic surfactants. When anionic surfactants adsorb onto alumina, the equilibrium pH is usually greater than the initial pH of solution because the anionic surfactants exchange with the adsorbed counter ions and hydroxyl ions on the alumina surface. For this reason, the equilibrium pH is closely related to surfactant adsorption.

2.2.4.2 Electrolyte concentration

An addition of small amounts of a neutral electrolyte (e.g., NaCl) to the solution of ionic surfactant can affect the adsorbed surfactants by reducing the electrostatic repulsion between the similarly charged ionic surfactant head groups. When the electrolytes are present in the system, the admicelles are formed more easily due to the decreased repulsion between ionic surfactant head groups. Admicelle patches with a complete bilayer contain a larger aggregation number of surfactant admicelles. When the concentration of electrolytes in the aqueous solution increases, maximum surfactant adsorption also increases (Rosen, 2004).

2.2.4.3 Temperature

An increase in temperature leads to a considerable decrease in the efficiency and effectiveness of the maximum adsorption of ionic surfactants (Rosen, 2004; Paria and Khilar, 2004; Saphanuchart et al., 2008). The effect of temperature is relatively small compared to the effect of solution pH; however, a rise in temperature usually results in an increased adsorption of non-ionic surfactants containing a polyelectrolyte chain like a hydrophilic group.

2.3 Surface tension and the calculation of surface concentrations and area per molecule at the liquid-air interface using the Gibbs equation

Reduction of surface tension is one of the most commonly measured properties of surfactants in solution. It depends directly on the replacement of molecules of solvent at the interface by molecules of surfactant, and therefore on the surface excess concentration of the surfactant, as shown by the Gibbs equation (Rosen, 2004).

Surface tension, or surface excess free energy, is equivalent to a force per unit length or Gibbs (free) energy per unit area. The surface tension indicates the interaction forces between molecules in the surface region and its neighbors, and the magnitude of surface tension depends on the cohesive energy density of the molecules. The measurement of the surface tension can be done by using a tensiometer with either the DuNouy Ring or the Wilhelmy Plate. This technique is based on force measurements of the interaction of a probe with the surface of the interface of two fluids (Rosen, 2004; Attaphong, 2006).

For surface-active solutes, the surface excess concentration, Γ, can be considered to be equal to the actual surface concentration without significant error. Therefore, the concentration of surfactant at the interface may be calculated from surface or interfacial tension data using the appropriate Gibbs equation. This equation (Equation 2-2) is suitable for 1:1 ionic surfactants in the presence of a swamping amount of electrolyte.

$$\Gamma = -\frac{1}{2.303RT}\left(\frac{\partial \gamma}{\partial \log C_1}\right)_T \tag{2-2}$$

where γ is the surface (interfacial) tension in N/m, R is equal to 8.314 J mol^{-1} K^{-1}, T is equal to 298°K at 25°C, and C_1 is the surfactant concentration (molar). The surface concentration can be obtained from the slope of γ plotted against log C_1 at constant temperature.

The area per molecule at the interface gives information about the degree of packing and the orientation of the adsorbed surfactant molecules when compared with the dimensions of the molecules obtained by using molecular models. Using the surface excess concentration, the area per molecule at the interface a^S_1 (square angstroms) is calculated with Equation 2-3.

$$a_1^s = \frac{10^{23}}{N\Gamma_1} \qquad (2\text{-}3)$$

where N is Avogado's number (6.023 x 10^{23}) and Γ is the surfactant adsorption (mol/1000m^2).

2.4 Adsolubilization and solubilization of organic solutes

Surfactant aggregates adsorbed on the solid/liquid interface are an important phenomenon for surfactant-based environmental technologies such as admicellar polymerization process, admicellar chromatography, admicellar catalysis, as well as water and soil remediation (Tan and O'Haver, 2004). The hydrophobic core within admicelles provides sites capable of solubilizing organic solutes. This phenomenon is known as adsolubilization. These admicelles can be used to solubilize organic solutes into the interior of adsorbed surfactant aggregates. In the same manner organic solutes are solubilized into the interior of micelles. This phenomenon is also known as solubilization. The phenomena of adsolubilization and solubilization are shown in Figure 2-5. Generally, the amount of adsolubilization rises as surfactant adsorption increases (i.e., the extent of the admicellar phase) and the concentration of the adsolubilizate in the aqueous solution increases (Harwell and O' Rear, 1989).

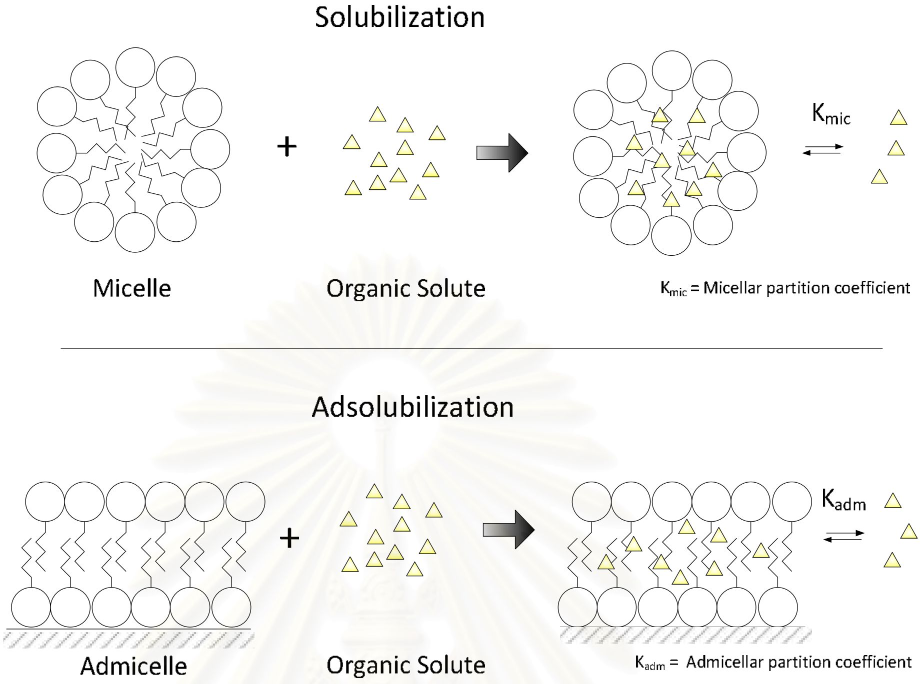


Figure 2-5 Phenomena of solubilization and adsolubilization (Charoensaeng et al., 2008)

Figure 2-6 shows that admicelles having a bilayer structure can be divided into three regions, similar to micelles. These regions consist of an outer region, an inner region, and a palisade region. The outer region is the most polar or ionic region because it consists of surfactant head groups and forms the liquid/solid interfaces. Thus, the inner region or the core region is a non-polar region because it consists of the surfactant tail groups' hydrocarbon chains, whereas the palisade region defines the transition region between the head group and the core. It has an intermediate polarity (Dickson and O'Haver, 2002).

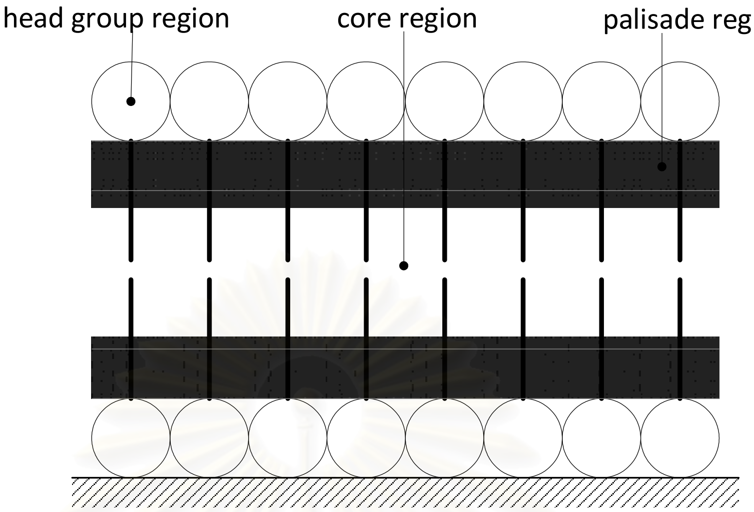


Figure 2-6 The bilayer structure of surfactant admicelles at the solid-liquid interface (Nayyar et al., 1994)

Many studies have elucidated the locus of solubilization in the surfactant micelle and admicelle. The solubilization and the partition coefficients have been derived observing the following trends: (1) If the solute partitions primarily into to the core, the partition coefficient increases with increasing solute mole fractions in the admicelle; (2) If the solute partitions into the palisade layer, the partition coefficient decreases with increasing solute mole fractions; and (3) If the solute partitions into both the core and palisade regions, the partition coefficient remains relatively constant with increasing mole fractions of solute solubilization (Rouse et al., 1995; Dickson and O'Haver, 2002). Previous studies have found that nonpolar organic solutes tend to partition into the core region of the admicells that have a similar polarity as the solute, whereas polar organic solutes partition into the palisade region (Nayyar, et al., 1994; Kitiyanan et al., 1996; Dickson and O' Haver, 2002; Tan and O' Haver, 2004; Fuangswasdi et al., 2006b; Saphanuchart et al., 2008).

2.4.1 Micellar and Admicellar Partition Coefficients (K_{mic} and K_{adm})

The partitioning of organic solutes into a micelle can be described by the micellar partition coefficient, K_{mic} (Nayyar et al., 1994; Fuangswasdi et al., 2006b). Similarly, the admicellar partition coefficient (K_{adm}) can be used to evaluate the solubilization of organic solutes into adsorbed admicelles (Kitiyanan et al., 1996; Dickson and O' Haver, 2002; Tan and O' Haver, 2004; Fuangswasdi et al., 2006b; Charoensaeng et al., 2008).

The effectiveness of a given surfactant in solubilizing a particular solute is known as the molar solubilization ratio (MSR). The MSR is the number of moles of organic solute solubilized per mole of micellar surfactant, and it was obtained from the slope of the curve of the solubilizate concentration as a function of the surfactant concentration. It can be calculated using Equation 2-4.

$$\mathrm{MSR} = \frac{(S_{mic} - S_{CMC})}{(C_{surf} - \mathrm{CMC})} \tag{2-4}$$

where S_{CMC} is the solubility of the organic solute at the CMC (mol/l), S_{mic} is the total apparent solubility of the organic solute in the micelle (mol/l), and C_{surf} is the concentration of the surfactant above the CMC. Another measurement of solubilization is the micellar partition coefficient (K_{mic}). K_{mic} represents the partitioning of the organic solute between the surfactant micelle and the aqueous phase. K_{mic} is the ratio of the mole fraction of the organic solute in the micellar phase to the mole fraction of the organic solute in the aqueous phase and is expressed as follows:

$$K_{mic} = \frac{X_{mic}}{X_{aq}} \quad (2\text{-}5)$$

$$X_{mic} = \frac{MSR}{(1+MSR)} \quad (2\text{-}6)$$

$$X_{aq} = \frac{C_{aq}}{C_{aq} + 55.55} \quad (2\text{-}7)$$

Here, X_{mic} and X_{aq} represent the mole fractions of the organic solute in the micelles and the aqueous phase, respectively. C_{aq} is the molar concentration of the organic solute at aqueous solubility and 55.55 represents 1/molar volume of water.

Due to an analogous structure between micelle and admicelle, the admicellar partition coefficient (K_{adm}) is defined analogous to the micellar partition coefficient (K_{mic}). K_{adm} is used to quantify the adsolubilization capacity and can be calculated from

$$K_{adm} = \frac{X_{adm}}{X_{aq}} \quad (2\text{-}8)$$

X_{adm} and X_{aq} are the mole fractions of the organic solute in the admicelle and the aqueous phase, respectively. In this study, X_{adm} values can be calculated as follows:

$$X_{adm} = \frac{(C_{i,s} - C_{f,s})}{(C_{i,s} - C_{f,s}) + (S_i - S_f)} \quad (2\text{-}9)$$

where $C_{i,s}$ and $C_{f,s}$ are the initial and final concentrations of the organic solute, and S_i and S_f are the initial and final concentrations of the surfactant that were added as monomers, respectively. All concentrations are expressed in moles per liter. The value of X_{aq} can be calculated using the following equation:

$$X_{aq} = \frac{C_{f,s}}{C_{f,s} + 55.55} \tag{2-10}$$

Kitiyanan and co-workers (1996) evaluated the adsolubilization of styrene and isoprene into cationic surfactant bilayers (admicelles) on silica. They calculated the admicellar partition coefficient of organic solutes in order to determine the locus of solubilization in the surfactant micelles. They found that the partition coefficient for styrene was nearly constant with increasing styrene mole fraction while the partition coefficient for isoprene decreased with increasing isoprene mole fraction in the admicelle. From these results, they concluded that styrene was partitioned into both the palisade layer and the core of the admicelles, while isoprene was partitioned only into the palisade layer.

There are many factors that affect admicelle formation and adsolubilization of organic solutes including surfactant concentration, solution pH, ionic strength of the solution, and the structure of the organic solute. Dickson and O'Haver (2002) investigated the effects of various factors on the maximum adsolubilization of an organic solute. By measuring the adsolubilization of organic solutes with varying polarities, the partition coefficients were calculated for each system to predict the locus of adsolubilization within the admicelles. The results showed that the level of solute adsolubilization depends on both the amount of surfactant present at the solid/liquid interface and the structure of the adsorbed layer.

Moreover, a mixed surfactants system is one way to improve the solubilization and adsolubilization capacity of a surfactant system because it can reduce the CMC and enhances solubilization when the surfactants are mixed together at an appropriate ratio. Fuangswasdi et al. (2006b) applied anionic and cationic surfactant mixtures with single and twin head groups to solubilize styrene and ethylcychlohexane into mixed micelles and to adsolubilize them into mixed admicelles on silica and alumina surfaces. They found that mixing anionic and cationic surfactants can improve the solubilization capacity of both organic solutes in micelles and admicelles depending on the molecular structure of the surfactant and the ratio of anionic and cationic surfactant used.

2.5 Extended surfactants

Extended surfactants are a new generation of surfactants that have been recently produced to enhance the solubilization of organic solutes (Sabatini et al., 2003; Witthayapanyanon et al., 2006). The advantage of an extended surfactant is the presence of one or more intermediate-polarity groups between the hydrophilic head and the hydrophobic tail. The hydrocarbon tail is “extended” by a number of ethoxylate groups (EO) and/or propoxylate groups (PO) as shown in Figure 2-7. Thus, the extended surfactants act as an internal linker system. Due to their unique molecular structure, the surfactants are stretched out further into both oil and water phases. As a result, they are able to provide a smoother transition between the hydrophilic and hydrophobic interface resulting in a more suitable environment for solubilizing both hydrophilic and lipophilic solutes (Witthayapanyanon et al., 2006).

The extended surfactants (e.g., Alfoterra®) can be used in a wide variety of industrial and personal care applications such as enhanced oil recovery, soil remediation, oil extraction, industrial cleaning, and personal care formulations. Moreover, they may be utilized in mining, textile processing, lubricants, metal working, leather processing, and a variety of other applications (Sasol North America Inc, 2007).

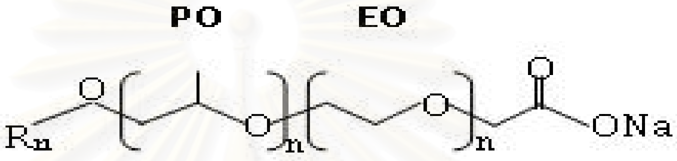


Figure 2-7 Extended surfactant structure

Witthayapanyanon et al. (2006) formulated ultra low interfacial tension (IFT) systems using extended surfactants. The results showed that extended surfactant systems have lower critical micelle concentrations (CMC) than conventional surfactants. Moreover, the extended surfactant provides ultra low IFT with highly hydrophobic oils. Additionally, Charoensaeng et al. (2008) investigated the impact of lipophilic linker and extended surfactant properties on styrene solubilization and adsolubilization. They found that the styrene solubilization capacity of extended-surfactant-based micelles is greater than that of linker-based micelles. They also found that the MSR of styrene for the C14,15 extended surfactant is slightly higher than that of the C12,13 extended surfactant. Additionally, they found that the PO groups in extended-surfactant-based systems improved the overall adsolubilization process because these systems required lower amounts of surfactant to reach maximum adsorption than conventional-surfactant-based systems and linker-based systems.

CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 Surfactants

The surfactants in this research were divided into two systems: the conventional surfactant system and extended surfactant system.

Conventional surfactant system: Sodium dodecyl sulfate, SDS (98% purity), was selected as the conventional anionic surfactant with a C12 alkyl chain length and purchased from Sigma Chemical Company (St. Louis, MO, USA).

Extended surfactant system: The anionic extended surfactants evaluated in this research were an extended carboxylate surfactant and extended sulfate surfactant (Alfoterra$^{®}$) with different number of carbon chain lengths, intermediate groups, and hydrophilic head types. These extended surfactants were received from Sasol North America Inc. (Texas, USA). The properties of the studied surfactants are shown in Table 3-1.

The alkyl propoxylated ethoxylated carboxylate surfactants in this research, which were used as the anionic extended carboxylate surfactant, are branched and linear alkoxylated alcohol of the Alfoterra$^{®}$ series with distributions in carbon chain length of either 16 to 17 or 16 to 18. They have 4 moles of the propylene oxide (PO) group, 5 moles of the ethylene oxide (EO) group, and the carboxylated head group.

The alkyl propoxylated sulfate surfactant, which was used as the anionic extended sulfate surfactant, is a mixture of linear and monobranched alcohols with alkyl chain lengths of 16 to 17, 4 moles of the propylene oxide (PO) group, and the sulfated group. (see above)

Table 3-1 The properties of surfactants

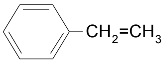
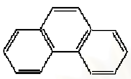
Surfactant	Type	Carbon	Formula	HLB[a] number
Conventional surfactant				
Sodium dodecyl sulfate, SDS	Anionic conventional	12	$C_{12}H_{25}SO_4Na$	40.0
Extended Carboxylate surfactant				
Alkyl propoxylated ethoxylated carboxylate, C16-17	Anionic extended	16-17	$C_{16,17}$- $(PO)_4$-$(EO)_5$-COONa	19.3
Alkyl propoxylated ethoxylated carboxylate, C16-18	Anionic extended	16-18	$C_{16,18}$- $(PO)_4$-$(EO)_5$-COONa	19.1
Extended Sulfate surfactant				
Alkyl propoxylated sulfate, C16-17	Anionic extended	16-17	$C_{16,17}$- $(PO)_4$-SO_4Na	37.3

[a] HLB is hydrophilic - lipophilic balance
PO: Propylene oxide (C_3H_6O)
EO: Ethylene oxide (C_2H_4O)

3.1.2 Organic Solutes

Two organic solutes with different polarities were selected in this study. Styrene with 99% purity was purchased from the Arcos Chemical Company. Phenanthrene with 98% purity was purchased from the Aldrich Chemical Company. Styrene and phenanthrene were selected as the higher and lower polar organic solutes, respectively. The physical and chemical properties of organic solutes are shown in Table 3-2.

Table 3-2 Properties of organic solutes

Organic solutes	Molecular formula	Molecular structure	MW	Water solubility (mg/l)	Density (g/mL) 25 °C	log K_{ow}	Dipole moment
Styrene	C_8H_8		104.15	312	0.909	2.95[a]	0.13
Phenanthrene	$C_{14}H_{10}$		178.23	1.6[b]	1.063	4.57[C]	0.00

[a] http://www.epa.gov/OGWDW/dwh/t-voc/styrene.html
[b] http://chemicalland21.com/industrialchem/organic/PHENANTHRENE.htm
[c] Zhu and Feng, 2003

3.1.3 Solid Oxide Surface

Aluminum oxide or alumina (Al_2O_3) was purchased from the Aldrich Chemical Company. Alumina has a particle size of about 150 meshes. The specific surface area according to the manufacturer's product description is 155 m^2/g and the point of zero charge (PZC) of aluminum oxide is 9.1 (Sun and Jaffe, 1996).

3.1.4 Chemicals

All chemicals in this study were used as they were received and were of ACS analytical reagent grade. All solutions were prepared with deionized water with a resistance of 18.2 MΩ cm. Plastics and glassware were rinsed well with deionized water three times prior to their use.

3.2 Experimental Section

The experimental setup in this study is divided into five sections: CMC measurements, and the surfactant adsorption, surfactant desorption, adsolubilization, and solubilization studies. All experiments were conducted in batch experiment under a constant temperature (25±2°C). The electrolyte concentration of the solution was adjusted to 1.0 mM by adding sodium chloride (NaCl) and the solution pH was adjusted to pH 8.0-8.5 by adding an HCl and/or NaOH solution.

3.2.1 CMC measurements

The experiments for determining the critical micelle concentration (CMC) of the surfactant systems were conducted at room temperature (25±2°C) using a Wilhelmy plate tensiometer (DCAT 11, DataPhysics, Filderstadt, Germany) with a platinum plate, an electrolyte concentration of 1.0 mM NaCl, and a solution pH of 8.0-8.5. The CMC of each system was obtained by plotting the surface tension versus the logarithm of the surfactant concentration. A sharp change in the plotted points indicated the CMC of the surfactant.

3.2.2 Surfactant adsorption study

The surfactant adsorption isotherm onto the positively charged surface of aluminum oxide was studied to evaluate the surfactant adsorption behavior at a solid/liquid interface. The surfactant adsorption study was conducted at room temperature (25±2°C) with an electrolyte concentration of 1.0 mM NaCl and a solution pH of 8.0-8.5. The solution pH of the surfactant stock solution was measured and adjusted to be 8.0-8.5 by adding NaOH and/or HCl. Different amounts of alumina were added into several vials containing 40 mL of surfactant solution. All solutions were subsequently equilibrated by shaking at 150 rpm for 48 hours. After twelve hours of shaking, the solution pH was measured and adjusted using a NaOH and/or HCl solution. This process was repeated, but with a minimum waiting time of 3 hours, until the solution pH remained constant at the desired level. After being equilibrated, the solutions were centrifuged to remove the alumina. The concentrations of the surfactants in the supernatant were then analyzed.

3.2.3 Adsolubilization study

The adsolubilization of organic solutes by the conventional and extended surfactants was studied in batch experiments. This study is divided into two sub-experiments. In general, the equilibrium aqueous surfactant concentration was selected at 90-95 percent of the CMC value from the adsorption isotherms to insure that the system equilibrated just slightly below the CMC which assured that no micelles were present in aqueous solution at equilibrium. This could be tested by adding the pinacyanol chloride dye to aqueous solution which was used as an indicator. In absence of micelles, pinacyanol chloride yields a violet color. At surfactant concentration in the solution above the CMC, the blue color is observed. Corresponding nature of micelle as admicelle, the blue color is observed in adsorbed admicelles on the surface of alumina (Kittyanan et al., 1996; Charoensaeng et al., 2008). At the end of this experiment, the amount of adsolubilization was calculated from the initial and equilibrium concentrations in term of the admicellar partition coefficient, K_{adm}.

3.2.3.1 Styrene adsolubilization

The adsolubilization isotherms of styrene were studied at room temperature (25±2°C) with an electrolyte concentration of 1.0 mM of NaCl and a solution pH of 8.0-8.5. In order to determine styrene adsolubilization, surfactant solutions with known concentrations were added to vials containing known masses of alumina with various styrene concentrations. The vials were subsequently sealed with Teflon-line screw caps (PTFE) and then the solutions were shaken at 150 rpm for 48 hours. The organic solute was allowed to phase separate, and then the solution was analyzed (Kittyanan et al., 1996; Charoensaeng et al., 2008).

3.2.3.2 Phenanthrene adsolubilization

The adsolubilization isotherms were also studied at the same condition as previously described in section 3.2.3.1. An aqueous solution of phenanthrene was prepared by dissolving the desired amount of phenanthrene in 100 mL of methanol and adjusting the volume to 1000 mL with deionized water. The concentration of methanol in the aqueous solution was 10% by volume. The phenanthrene stock solutions were then diluted to varying solute concentrations by adding a surfactant solution of the same surfactant concentration. The aqueous solutions were added to vials containing known masses of alumina. The vials were subsequently sealed with Teflon-line screw caps (PTFE) and then the solutions were equilibrated by shaking them at 150 rpm for 48 hours. The organic solute was allowed to phase separate and then the solution was analyzed (modified from Kibbey and Hayes, 1993; Saphanuchart et al., 2008).

3.2.4 Solubilization Study

This study is divided into two sub-experiments: styrene and phenanthrene solubilization. The solubilization of these organic solutes by various types and concentrations of surfactants was investigated in batch experiments. At the end of this experiment, the solubilization capacity was determined in terms of the molar solubilization ratio (MSR) and the micellar partition coefficient (K_{mic}) (Nayyar et al., 1994).

3.2.4.1 Styrene solubilization

Styrene solubilization by various types and concentrations of surfactants was studied at room temperature (25±2 °C) using an electrolyte concentration of 1.0 mM NaCl and a solution pH of 8.0-8.5with the maximum solubilization (adapted from Nayyar et al., 1994). Each system consisted of a 40 mL solution containing deionized water with 1.0 mM NaCl, styrene, and surfactant. The surfactant concentrations varied from below to above the CMC. An excess amount of styrene was added into the vials containing 40 mL of surfactant solution. All vials were sealed with Teflon-line screw caps (PTFE). The solutions were then equilibrated by shaking them at 150 rpm for 48 hours. The styrene was allowed to phase-separate, and then each solution was analyzed.

3.2.4.2 Phenanthrene solubilization

The solubilization of phenenthrene by various types and concentrations of surfactants was studied at the same condition as previously described in section 3.2.4.1. The surfactant concentrations varied from below to above the CMC. 0.03 g of solid crystal phenenthrene was added into the vials and then 40 mL of surfactant solution at various concentrations was added. The amount of phenanthrene added (0.03 g) exceeded its apparent solubility, thus the crystalline phase of phenanthrene was observed at the end of experiment. The vials were subsequently sealed with Teflon-line screw caps (PTFE) and then the solutions were equilibrated by shaking them at 150 rpm for 48 hours. The samples were centrifuged at 3000 rpm for 20 min to separate the undissolved solute from the aqueous phase. An appropriate aliquot of the supernatant solution was carefully withdrawn. The supernatant was then diluted to 20 mL by adding 10 mL of methanol. The concentration of phenanthrene in each solution was analyzed (modified from Zhu and Feng, 2003).

3.2.5 Surfactant desorption study

The zeta potential of alumina was measured to determine the change in its surface charge density due to surfactant adsorption and thus provide indirect evidence of adsorption/desorption potential onto the alumina surface. In this study, the surfactant concentration for each surfactant type was chosen so as to approach bilayer coverage just below the CMC (95% below the CMC). The surfactant modified alumina was sequential washed with deionized water. The pH values and number of washings were varied in the batch experiment, which took place at room temperature (25±2°C). The adsorbent was shaken for least 48 hours in deionized water. The alumina in the solution before and after being washed were measured using an electrophoretic apparatus (Zeta-Meter System 3.0, Zeta-Meter Inc.) to determine the charged density of alumina in order to evaluate desorption potential. The zeta potential values of the adsorbed surfactants onto the alumina were compared by varying the solution pH and number of washings steps.

3.3 Analytical methods

The concentrations of the conventional surfactant and extended carboxylate surfactants in the supernatant were analyzed by HPLC (LC 1100, Agilent). The natural complex was separated with a reverse phase column (Acclaim Surfactant Column, Dionex). The complex was eluted from the column by the acetonitrile-NH_4OAc mobile phase (40:60) and finally detected by an evaporative light scattering detector (ELSD) with temperature of 40 °C.

In addition, ion chromatography, IC (ICS-2500, Dionex), was used to quantify the concentration of extended sulfate surfactant in the supernatant following a technique used by previous researchers (Doan et al., 2003; Fuangswasdi et al., 2006 a and b; Charoensaeng et al., 2008). The extended sulfate surfactant was analyzed using a coupling agent, tetrabutyle ammonium hydroxide (TBAOH). The natural complex was separated with a reverse phase column (NS1, Dionex) and the acetronitrile-water mobile phase; the complex was eluted from the column and de-coupled by anionic suppression (ASRS ultra II, Dionex) and finally detected by an electrical conductivity detector (ECD).

All organic solutes in this study were analyzed by HPLC (LC 1100, Agilent) with a reverse phase column (Acclaim Surfactant Column, Dionex) and detected by a diode array detector. Styrene was eluted from the column by the acetonitrile-NH_4OAc mobile phase (40:60) and detected by the diode array detector operating at 247 nm. Phenanthrene was eluted by the acetonitrile-water mobile phase (60:40) and detected at 254 nm with the diode array detector.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Critical micelle concentration measurement

The critical micelle concentrations (CMCs) of the various surfactant systems were determined by measuring the surface tension of the surfactant solution with 1.0 mM NaCl at room temperature (25±2°C). The break point in the plot of the surface tension versus surfactant concentration is the CMC of the surfactant system. Figure 4-1 shows the CMCs of the extended surfactant systems and conventional surfactant system. For extended carboxylate surfactants, the CMC of the higher carbon chain length, C16-18 surfactant was slightly lower than that of the C16-17 surfactant (0.01 mM and 0.02 mM, respectively; Table 4-1). The CMCs of the extended surfactants were two orders of magnitude lower than that of conventional surfactant, SDS (0.01 to 0.07 mM and 4.0 mM, respectively; as seen in Figure 4-1 and Table 4-1). As a rule of thumb, the longer the hydrocarbon chain is in length, the lower the resulting CMC (Witthayapanyanon et al., 2006; Aumpuch, 2007; Charoensaeng et al., 2008). The same trend was found in this study, suggesting that the higher the lipophilicity of the extended surfactant is, the less surfactant monomers are needed to form aggregates like micelles in an aqueous solution. These results are consistent with those of Charoensaeng et al. (2008), who found that the CMC of the surfactant decreased as an increase the alkyl chain of its tail. In their study, the CMCs of SDS, $C_{12\text{-}13}$-3PO-SO_4Na, and $C_{14\text{-}15}$-3PO-SO_4Na at a solution pH of 7.0±0.5 at room temperature were 5.0 mM, 0.2 mM, and 0.03 mM, respectively.

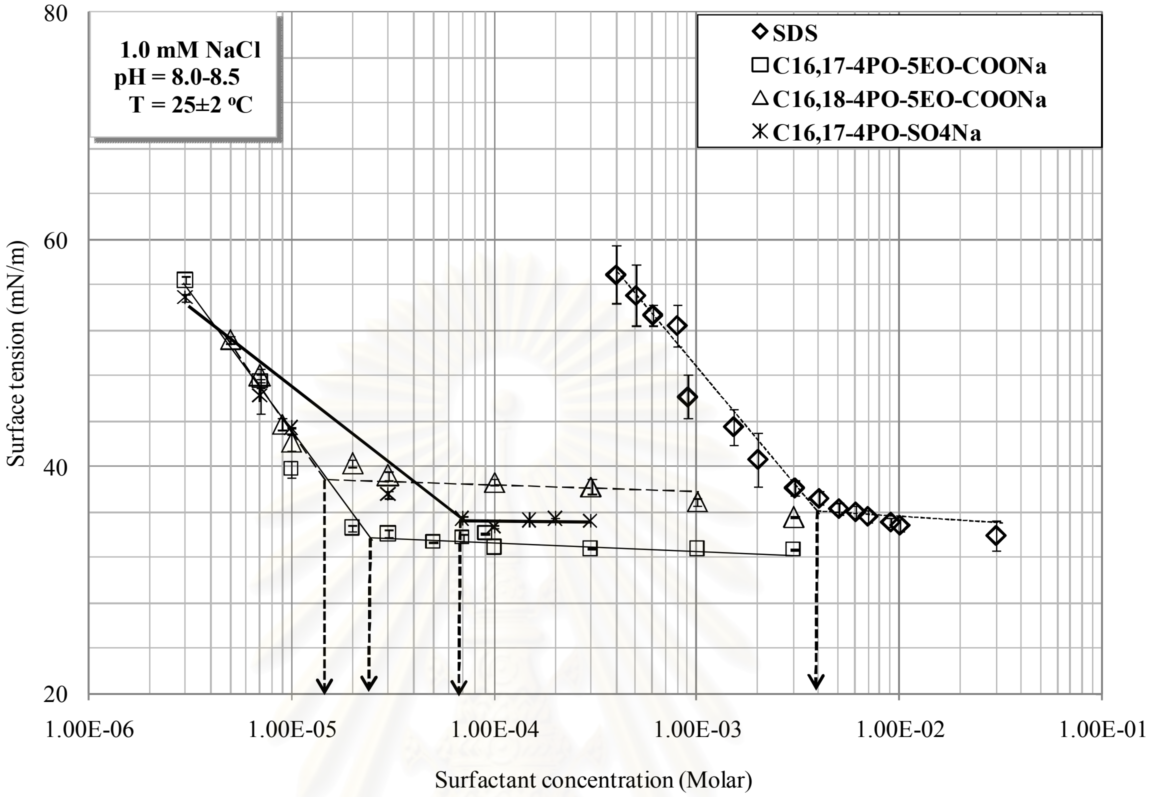


Figure 4-1 CMCs of the conventional surfactant system and extended surfactant systems in 1.0 mM NaCl, at pH 8.0-8.5, and a temperature of 25±2°C

When comparing the CMCs of two types of extended surfactant systems, namely carboxylate surfactants and sulfate surfactant, it was found that the CMC of the extended carboxylate surfactants (both C16-17 and C16-18) was lower than that of the extended sulfate surfactant (see Table 4-1). The extended carboxylate surfactants have the lower HLB values or higher hydrophobicity than the extended sulfate surfactant. The lower CMC values of the carboxylate surfactant are not surprising considering the fact that the surfactant with lower HLB values has the lower CMC values (Rosen, 2004). According to HLB value in Table 4-1, the hydrophobicity degree were $C_{16\text{-}18}$-4PO-5EO-COONa > $C_{16\text{-}17}$-4PO-5EO-COONa > $C_{16\text{-}17}$-4PO-SO_4Na. Therefore, the C16-18 extended carboxylate surfactant has the lowest CMC value. In addition, the findings in this study further support the observation of Myers (2006) who proposed that the order of decreasing CMC values of common ionic head groups within the same hydrocarbon chain is carboxylates (containing one more carbon atoms) > sulfonates > sulfates.

Table 4-1 CMC values obtained from surface tension measurement, the average plateau at minimum surface tension, surfactant adsorption, and effective areas per molecule for conventional and extended surfactant systems at 1.0 mM NaCl and pH 8.0-8.5

Surfactant	HLB[a] number	CMC (mM)	slope[b]	r^2	Average plateau[c] (mN/m)	Γ (mmol/1000 m^2)	Effective areas per molecule ($Å^2$)
Conventional surfactant							
$C_{12}H_{25}SO_4Na$, (SDS)	40.0	4.00	-13.09	0.99	37.5±1.9	1.15	145
Extended carboxylate surfactant							
$C_{16,17}$-4PO-5EO-COONa	19.3	0.02	-11.89	0.97	33.4±0.6	1.04	159
$C_{16,18}$-4PO-5EO-COONa	19.1	0.01	-10.39	0.99	38.7±1.2	0.91	182
Extended sulfate surfactant							
$C_{16,17}$-4PO-SO_4Na	37.3	0.07	-6.43	0.97	35.2±0.3	0.56	295

[a] HLB is the hydrophilic - lipophilic balance
[b] from Figure 4-1
[c] at minimum surface tension

From the slope of the surface tension, the effective area per surfactant molecule at the water-air interface was calculated from Figure 4-1 using the Gibbs equation (Rosen, 2004; see – Equation 2-2 and 2-3). The results are summarized in Table 4-1. Both extended surfactant systems, carboxylate and sulfate head group, had a larger effective areas per molecule than the conventional surfactant (SDS) due to a lower amount of adsorbed surfactant aggregates at the water-air interface. These results suggest that the EO/PO portions of the extended surfactants, which immersed in the form of a coil, and thus occupied a higher cross-sectional area per molecule on the liquid surface. Moreover, the length of the hydrocarbon chain increased as the effective areas per molecule increased due to the larger lateral interaction and a lower packing density of the extended surfactant tail. These findings are consistent with those in the literature (Witthayapanyanon et al., 2006; Charoensaeng et al., 2008).

As considered the effective areas per molecule of the extended carboxylate surfactants and the extended sulfate surfactant, the results show that the extended carboxylate surfactants had lower the effective areas per molecule than the extended sulfate surfactant. Due to the lower electrostatic repulsion between the polar head groups of carboxylate head groups , the surfactants pack more closely to one another than surfactant with sulfate head group (higher repulsion) (Golub et al., 2004).

4.2 Surfactant adsorption study

Adsorption isotherms allow us to study the surfactant adsorption behavior at solid-liquid interface. The adsorption isotherms of the conventional surfactant system (SDS), extended carboxylate surfactant systems ($C_{16\text{-}17}$-4PO-5EO-COONa, and $C_{16\text{-}18}$-4PO-EO-COONa), and extended sulfate surfactant system ($C_{16\text{-}17}$-4PO-SO_4Na) onto the positively charged aluminum oxide surface at room temperature (25±2°C), with 1.0 mM NaCl and a solution pH of 8.0-8.5 are shown in Figure 4-2. The logarithm of the adsorbed surfactant's density was plotted against the logarithm of the equilibrium surfactant concentration. The CMC was determined by identifying the transition point between Regions III and IV. The maximum adsorption was evaluated as the mean value of the plateau region (Region IV) of the isotherm. The results show that the adsorption of all surfactant systems increases when the surfactant concentration is increased in a manner that is consistent with the S-shaped isotherm (Rosen, 2004).

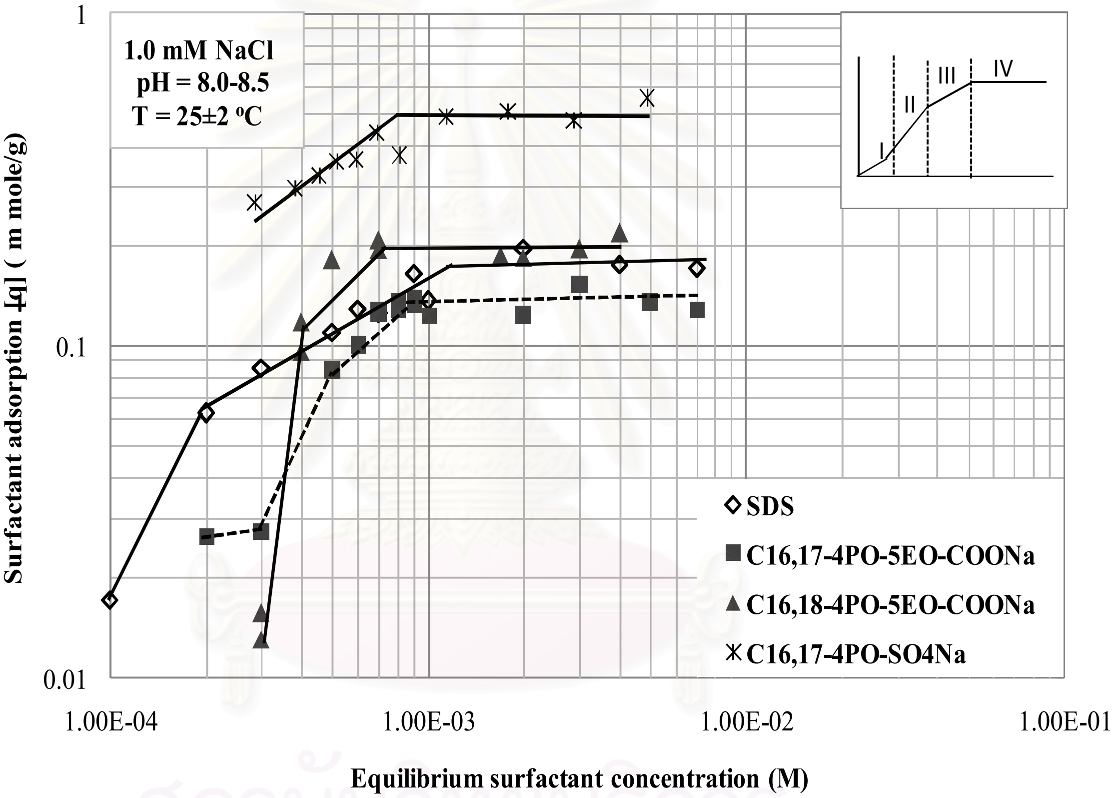


Figure 4-2 The adsorption isotherm of the conventional surfactant system and the extended surfactant systems onto alumina at 1.0 mM NaCl, an equilibrium pH of 8.0-8.5, and a temperature of 25±2°C

In the conventional surfactant system, SDS, the isotherm shows the characteristics of the Regions II, III, and IV; however, the detection limits of the analytical measurements did not allow the measurement of the low surfactant concentration in Region I. The CMC obtained from the adsorption isotherm at the solid-liquid interface was close to the CMC obtained from the surface tension measurement (see Tables 4-1 and 4-2, respectively).

For the extended surfactant systems, the results show that the CMCs of $C_{16\text{-}17}$-4PO-5EO-COONa, $C_{16\text{-}18}$-4PO-5EO-COONa, and $C_{16\text{-}17}$-4PO-SO_4Na obtained from the adsorption isotherms were 0.9, 0.7, and 0.8 mM, respectively (Figure 4-2, Table 4-2), which are an order of magnitude or more higher than the respective CMC values from surface tension measurement (0.02, 0.01, and 0.07 mM, respectively). This finding is consistent with the results of previous researchers (Charoensaeng et al., 2008), which reported that surfactant adsorption reaches a plateau at the CMC of a surfactant because there is no driving force for additional adsorption above the CMC.

Table 4-2 CMC and maximum adsorption values of the adsorption isotherms in the conventional and extended surfactant systems

Surfactant	CMC[a]	Maximum adsorption (q_{max})			Effective areas per molecule[c] (Å^2)
	(mM)	mmole/g	Molecule/nm^2	Å^2/molecule[b]	
Conventional surfactant					
$C_{12}H_{25}SO_4Na$, (SDS)	1.5	0.17 ± 0.02	0.66	151	145
Extended carboxylate surfactant					
$C_{16,17}$-4PO-5EO-COONa	0.9	0.14 ± 0.01	0.54	184	159
$C_{16,18}$-4PO-5EO-COONa	0.7	0.20 ± 0.01	0.78	129	182
Extended sulfate surfactant					
$C_{16,17}$-4PO-SO_4Na	0.8	0.47 ± 0.06	1.83	55	295

[a] the CMC obtained from the adsorption isotherm at a solid-liquid interface

[b] Calculated from the adsorption at the solid-liquid interface

[c] Calculated from the surface tension measurement at the liquid-air interface (Rosen et al., 2004)- see table 4-1

From Figure 4-2, it can be seen that the adsorption isotherms of all extended surfactants have a similar shape classifying as the s-shape isotherm. The isotherm showed the characteristics of Region II, III, and IV. However, analytical limits prevented measurement of surfactant concentrations in Region I. The adsorption isotherms of extended surfactant systems in Region II had more sharp slopes as compared with that of a conventional surfactant system because the extended surfactants have longer hydrocarbon chain lengths than conventional surfactant. Therefore, the lateral interaction between hydrocarbon chains of an extended surfactant system is greater than that of the conventional system (Paria and Khilar, 2004; Zhang and Somasundaran, 2006).

Table 4-2 summarizes the adsorption capacity of all surfactant systems. From Table 4-2, the results showed that the longer carbon chain length, C16-18-4PO-5EO-COONa was higher the maximum adsorption capacity than the shorter chain length, C16-17-4PO-5EO-COONa, due to the higher hydrophobicity of its carbon chain length in tail groups, which increased the amounts of adsorbed surfactants at the plateau region (Paria and Khilar, 2004). In addition, it was found that the extended sulfate surfactant had a higher adsorption capacity than the other extended carboxylate surfactants. It can be inferred that the stronger the charged ion of SO_4^{2-} readily adsorbs onto the positively charged alumina oxide surface, the higher the effectiveness of adsorption. It is well accepted that the extended carboxylate surfactants required much lower equilibrium surfactant concentrations to reach the plateau adsorption region than all surfactant systems.

At the plateau region there was no observable trend for the maximum adsorption capacity of the conventional surfactant system, SDS; extended carboxylate surfactant systems, $C_{16\text{-}17}$-4PO-5EO-COONa and $C_{16\text{-}18}$-4PO-5EO-COONa; and extended sulfate surfactant system, $C_{16\text{-}17}$-4PO-SO_4Na. The reason for this finding is rather complicated since both the hydrophobicity of the surfactant's extended tail groups (i.e., PO and EO) and the surfactant head type of in the surfactant structure influenced the adsorption behavior and with that affected the adsorption densities. Moreover, Zhang and co-workers (2006) studied nonionic EO surfactants adsorbed on aluminum oxide surface. They reported that EO surfactants are not strongly adsorbed on alumina. The EO groups are considered to be unable to disrupt the rigid water layer surrounding the aluminum oxide surface, and the EO-Al^{3+} complexes are relatively stable (Somasundaran and Krishnakumar, 1997).

Normalizing the maximum adsorption by the specific surface area of alumina (155 g/cm^3), the coverage on alumina of SDS, $C_{16\text{-}17}$-4PO-5EO-COONa, $C_{16\text{-}18}$-4PO-5EO-COONa, and $C_{16\text{-}17}$-4PO-SO_4Na are 0.66, 0.54, 0.78, and 1.83 molecule/nm^2 or 151, 184, 129, and 55 Å^2/molecule, respectively (Table 4-2). The area per molecule of SDS, $C_{16\text{-}17}$-4PO-5EO-COONa, $C_{16\text{-}18}$-4PO-5EO-COONa, and $C_{16\text{-}17}$-4PO-SO_4Na based on monolayer coverage at the water interface are 145, 159, 182, and 295 Å^2/molecule, respectively (see Table 4-2). If the admicelles had provided complete bilayer coverage, their area per molecule would have been half of these values. Thus, these results can be attributed to the fact that these surfactants were too large to adsorb into the narrow pores of alumina (69.70 Å by N_2 BET adsorption method). This finding is corroborated by the fact that the greatest deviations could be observed in molecules with the largest area per head group (Kitiyanan et al., 1996; Attaphong, 2006).

The pH of the solution is one of the prime factors that drastically influences the adsorption capacity of a surfactant system. When comparing the adsorption capacity of SDS onto alumina oxide surface from this study (pH 8.0-8.5) and a previous study (pH 7.0±0.5) done by Charoensaeng et al., 2008, the results showed that the maximum adsorption of SDS on alumina at pH 7±0.5 was higher than the adsorption at pH 8. It can be attributed to the fact that the alumina surface is positively charged when the pH value is below its PZC (9.1). As solution pH decreased (from pH 8 to 7), the positive charge of the alumina surface gradually increased when the pH was below its PZC; thus, SDS molecules adsorbed onto the alumina surface easily due to strong electrostatic interaction (Li et al., 2007).

4.3 Adsolubilization study

This study aimed to investigate the adsolubilization of styrene and phenanthrene by a conventional surfactant system (SDS), extended carboxylate surfactant systems (C_{16-17}-4PO-5EO-COONa, and C_{16-18}-4PO-5EO-COONa), and an extended sulfate surfactant system (C_{16-17}-4PO-SO_4Na) at 1.0 mM NaCl, an equilibrium pH of 8.0-8.5, and a temperature of 25±2 °C. The partitioning of organic solutes into an admicelle is described by the admicellar partition coefficient (K_{adm}), which was calculated using Equations 2-8 to 2-10. This experiment was carried out with the surfactant concentration at 90-95 percent of the CMC value to ensure that no micelles were formed in the aqueous solution at equilibrium.

4.3.1 Styrene adsolubilization

The adsolubilization isotherms for styrene in the conventional surfactant, extended carboxylate surfactant, and extended sulfate surfactant based-admicellar systems at 1.0 mM NaCl, an equilibrium pH of 8.0-8.5, and a temperature of 25±2 °C are shown in Figure 4-3, which shows the mole fractions of styrene in the admicelles (X_{adm}) and in the aqueous phase (X_{aq}). From Figure 4-3, the results show that as the equilibrium concentration of styrene increased, the amount of adsolubilized styrene in admicelles of all surfactant systems also increased. In addition, it is expected that the styrene adsolubilization reaches its maximum when water solubility of styrene is reached. The styrene admicellar partition coefficient values (K_{adm}) of the conventional surfactant system, extended carboxylate surfactant systems, and extended sulfate surfactant system are summarized in Table 4-3.

The locus of solubilization of styrene within surfactant admicelles was evaluated by the shape of the graph which plotted between the K_{adm} values of styrene versus the styrene aqueous mole fraction (X_{aq}) as shown in Figure 4-4. It was found that the K_{adm} of all surfactant systems decreased as the styrene equilibrium concentration increased due to the intermediate polarity of styrene. Styrene is an intermediate polar solute (dipole moment = 0.13). This figure shows the trend of the partitioning of styrene in surfactant-based admicelles consistent with the theory that polar and intermediate polar solute will partition to the palisade region. The results indicated that styrene mainly partitions in the palisade layer of the surfactant admicelles (Nayyar et al., 1994; Dickson and O'Haver, 2002; Attaphong, 2006).

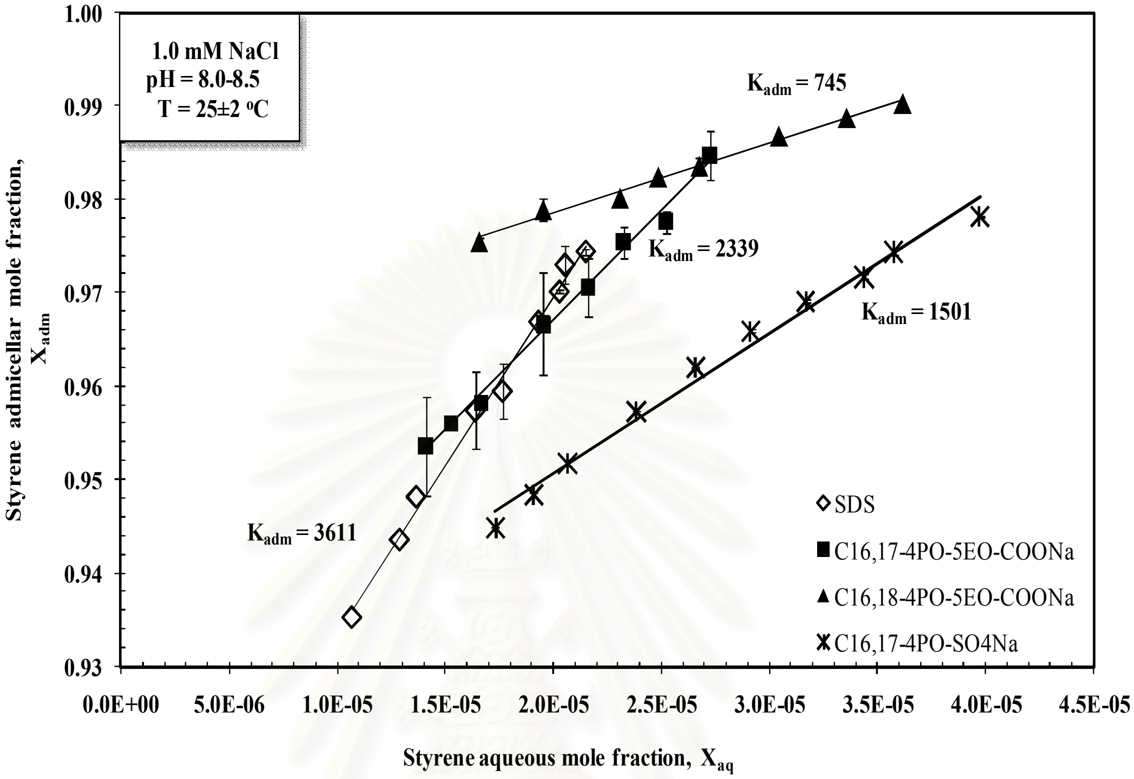


Figure 4-3 Adsolubilization capacities of styrene by the conventional surfactant system and the extended surfactant systems onto alumina at 1.0 mM NaCl, an equilibrium pH of 8.0-8.5, and a temperature of 25±2°C

From Figure 4-3 and Table 4-3, it is interesting to note that the K_{adm} value of SDS was higher than the K_{adm} values of $C_{16\text{-}17}$-4PO-5EO-COONa, $C_{16\text{-}17}$-4PO-SO_4Na, and $C_{16\text{-}18}$-4PO-5EO-COONa, respectively since those extended surfactants containing a PO groups causing less polarity in the palisade region (also see Table 4-3), it is likely that the cavities where styrene likes to adsolubilize in the palisade layer are filled by the coiling PO groups. This tends to "squeeze out" the cavities in the palisade layer where the polar solute would segregate, resulting in a reduction of the adsolubilized styrene. In addition, this finding is in close agreement with the previous work done by Charoensaeng (2008) who studied the adsolubilization of polar solute (phenylethanol) by the extended surfactants ($C_{14\text{-}15}$-PO_n-SO_4Na) with varying PO numbers. The results showed that the adsolubilization of phenylethanol decreases as the PO number increases. However, from the results of this study, the coiling effect seems to dominate over the effect of carbon chain length. This should be evaluated in future research.

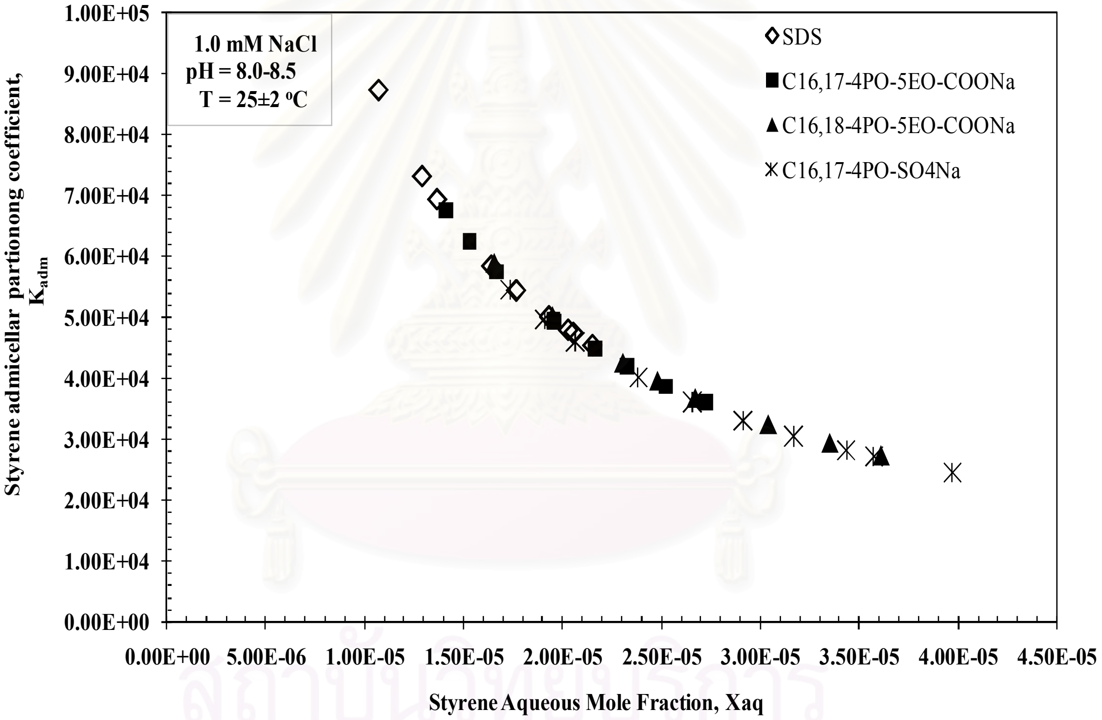


Figure 4-4 The styrene admicellar partitioning coefficient (K_{adm}) of the conventional surfactant system and the extended surfactant systems onto alumina at 1.0 mM NaCl, an equilibrium pH of 8.0-8.5, and a temperature of 25±2°C

In addition, Fuangswasdi and co-workers (2006b) proposed the styrene adsolubilization capacity of mixed surfactant systems (SHDPDS/DPCI) at ratio 3:1 and 10:1 adsorbed onto alumina were 0.35 and 0.40. As compared to this study, it could be conclude that the styrene adsolubilization capacities of the extended carboxylate surfactants have higher the adsolubilization efficiency than those of the mixed surfactant systems.

When the admicellization capacity of the two extended caboxylate surfactants was compared, it was clear that the K_{adm} of $C_{16\text{-}17}$-4PO-5EO-COONa was higher than that of $C_{16\text{-}18}$-4PO-5EO-COONa. This is due to the fact that $C_{16\text{-}17}$ has a higher degree of hydrophilicity than $C_{16\text{-}18}$ does. Styrene, which is an intermediate polar molecule, can adsolubilize more in the palisade layer of the $C_{16\text{-}17}$ admicelles than in the palisade layer of the $C_{16\text{-}18}$ admicelles.

Table 4-3 The styrene admicellar partition coefficient (K_{adm}) values of the conventional and extended surfactant systems

Surfactant (1 mM NaCl)	HLB[a] number	Styrene adsolubilization			
		ads q_{max} (mmole/g)	K_{adm}	r^2	log K_{adm}
Conventional surfactant					
$C_{12}H_{25}SO_4Na$, (SDS)	40.0	0.17	3611	0.99	3.56
Extended carboxylate surfactant					
$C_{16,17}$-4PO-5EO-COONa	19.3	0.14	2339	0.99	3.37
$C_{16,18}$-4PO-5EO-COONa	19.1	0.2	745	0.99	2.87
Extended sulfate surfactant					
$C_{16,17}$-4PO-SO_4Na	37.3	0.47	1501	0.99	3.18

[a] HLB is hydrophilic - lipophilic balance

One final observation related to Table 4-3 is that styrene adsolubilization is greatly increased in $C_{16,17}$-4PO-5EO-COONa above $C_{16,17}$-4PO-SO_4Na. It was expected that the K_{adm} values of $C_{16,17}$-4PO-SO_4Na should have been higher than the K_{adm} values of $C_{16,17}$-4PO-5EO-COONa due to the hydrophilicity of the surfactants (see HLB number in Table 4-3). In this case, the results were the opposite of this expectation. The reason for this finding is rather complicated. The two types of the extended surfactants used in this study, $C_{16,17}$-4PO-5EO-COONa and $C_{16,17}$-4PO-SO_4Na, were quite different in terms of their molecular structure, HLB values, and molecular weight. The main difference between these surfactants was the additional PO and EO groups in $C_{16,17}$-4PO-5EO-COONa. However, the carbon chain length and number of PO groups were equal. Thus, these reasons for these results are unclear and will have to be further evaluated in future research.

4.3.2 Phenanthrene adsolubilization

The adsolubilization capacities (K_{adm} values) of phenanthrene in the conventional surfactant, the extended carboxylate surfactant, and the extended sulfate surfactant based-admicellar systems at 1.0 mM NaCl, an equilibrium pH of 8.0-8.5, and a temperature of 25±2 °C are summarized in Table 4-4. Figure 4-5 shows the adsolubilization of phenanthrene in each of the surfactant admicelles versus the aqueous phenanthrene concentration. In all the surfactant systems, as the equilibrium concentration of phenanthrene increased, the amount adsolubilized phenanthrene also increased. Phenanthrene adsolubilization also attained its maximum level when the concentration of phenanthrene attained its water solubility, as expected for styrene. In the absence of the adsorbed surfactant, the adsorption of phenanthrene onto alumina was negligible.

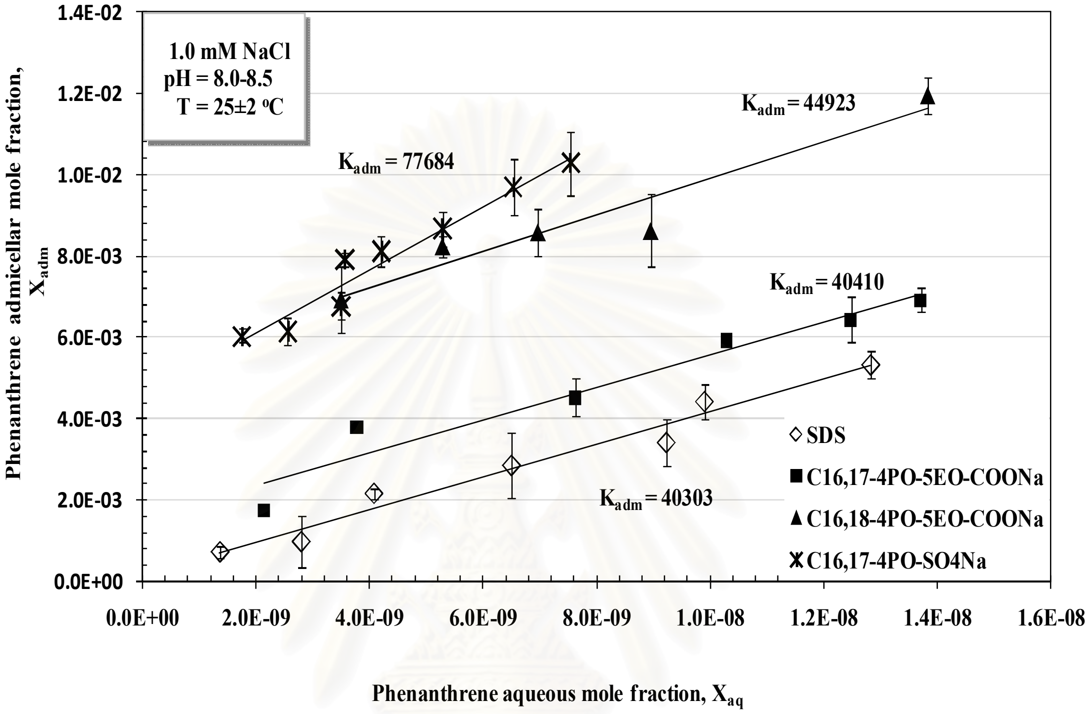


Figure 4-5 Adsolubilization capacities of phenanthrene by the conventional surfactant system and the extended surfactant systems onto alumina at 1.0 mM NaCl, an equilibrium pH of 8.0-8.5, and a temperature of 25±2°C

According to the results shown in Table 4-4, the partition coefficient values (K_{adm}) of phenanthrene were higher for $C_{16,17}$-4PO-SO_4Na, $C_{16,18}$-4PO-5EO-COONa, $C_{16,17}$-4PO-5EO-COONa, and SDS, respectively. This finding is very close to the results of the adsorption study. As mention above, the maximum adsorption capacity of surfactant admicelles is in the order of $C_{16,17}$-4PO-SO_4Na > $C_{16,18}$-4PO-5EO-COONa > SDS> $C_{16,17}$-4PO-5EO-COONa. Thus, it is interesting to note that the adsolubilization capacity of phenanthrene was significantly influenced by the amount of adsorbed admicelles at the plateau region. Additionally, this finding is in close agreement with the previous work of Asvapathanagul et al. (2005). It was found that the adsolubilization of toluene is related to the amounts of adsorbed CTAB on precipitated silica and arrangement of the adsorbed CTAB aggregates. This was found especially in region III of the adsorption isotherm; the adsolubilization of toluene seems to depend mainly on the amount of adsorbed CTAB on the silica.

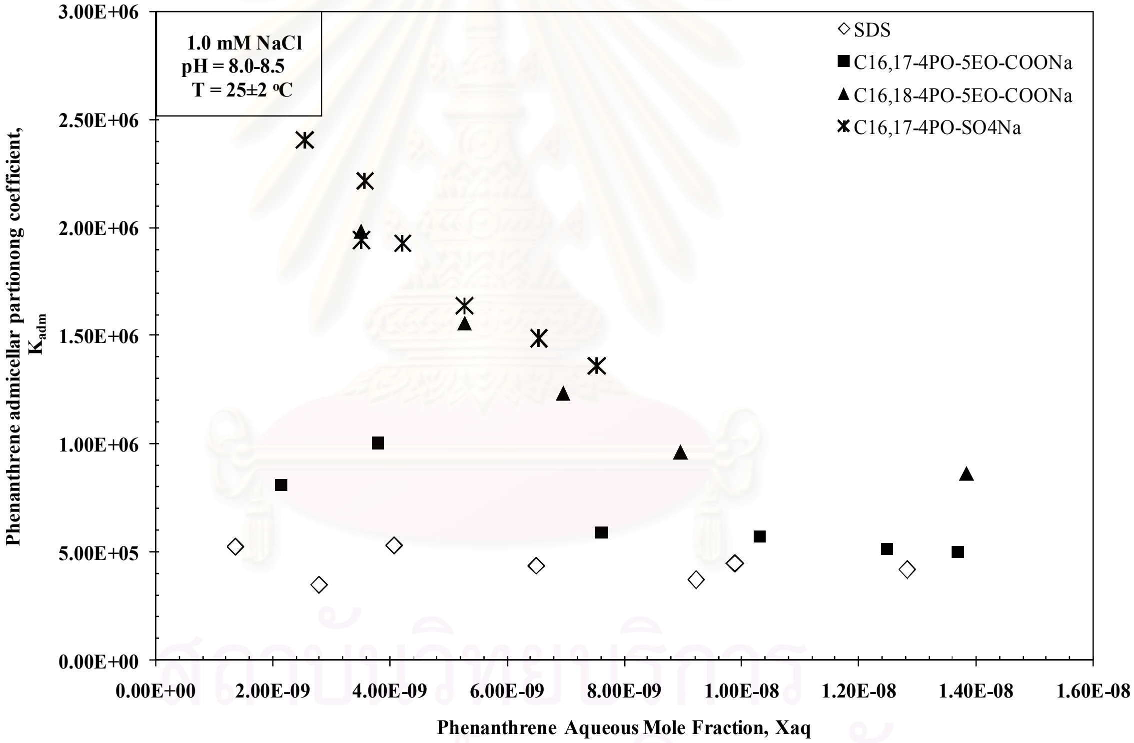


Figure 4-6 The phenanthrene admicellar partitioning coefficient (K_{adm}) of the conventional surfactant system and the extended surfactant systems onto alumina at 1.0 mM NaCl, an equilibrium pH of 8.0-8.5, and a temperature of 25±2°C

In order to gain insight into the locus of adsolubilization of phenanthrene, the K_{adm} values of phenanthrene were plotted as the function of the phenanthrene aqueous mole fraction (X_{aq}), shown in Figure 4-6. For $C_{16,17}$-4PO-SO_4Na and $C_{16,18}$-4PO-5EO-COONa, K_{adm} gradually decreased when the phenanthrene aqueous mole fraction increased. This indicates that phenanthrene partitions in the palisade region. In contrast, for SDS and $C_{16,17}$-4PO-5EO-COONa, the K_{adm} remained constant when the phenanthrene aqueous mole fraction increased, indicating that phenanthrene partitions in both the palisade and core region. The different partitioning behavior into admicelles is due to the effect of the intermediate groups in the extended surfactants and the short carbon chain length of the conventional surfactant. Since the extended surfactants consist of EO/PO or PO groups, a smoother transition is provided for solubilizing non-polar phenanthrene. Thus, phenanthrene could be accumulated in the palisade or the core region of the admicelle due to its favor. Moreover, phenanthrene, which is a non-polar solute, is expected to partition into the core of the admicelle. Phenanthrene, additionally, tends to accumulate in the palisade region because the space in the SDS core that is available for organic solutes is insufficient.

Table 4-4 The phenanthrene admicellar partition coefficient (K_{adm}) values of the conventional and extended surfactant systems

Surfactant (1 mM NaCl)	HLB[a] number	Phenanthrene adsolubilization			
		ads q_{max} (mmole/g)	K_{adm}	r^2	log K_{adm}
Conventional surfactant					
$C_{12}H_{25}SO_4Na$, (SDS)	40.0	0.17	40303	0.97	4.61
Extended carboxylate surfactant					
$C_{16,17}$-4PO-5EO-COONa	19.3	0.14	40410	0.94	4.61
$C_{16,18}$-4PO-5EO-COONa	19.1	0.20	44923	0.93	4.65
Extended sulfate surfactant					
$C_{16,17}$-4PO-SO_4Na	37.3	0.47	77684	0.95	4.89

[a] HLB is hydrophilic - lipophilic balance

Due to the water solubility of organic solutes, styrene (which is higher polar organic solute) has higher solubility in water ($X_{aq} = 5.36x10^{-5}$) than lower polar phenanthrene ($X_{aq} = 1.62x10^{-7}$). Therefore, styrene tends to solubilize both in the aqueous phase and the surfactant admicelles whereas lower polar phenanthrene trys to separate itself from the aqueous phase and tends to adsolubilize in surfactant admicelles. For this reason, the log K_{adm} values of styrene (which ranged from 2.87-3.56) were lower than those of phenanthrene (which ranged from 4.61-4.91). This trend was consistent with the results from the solubilization study

4.4 Solubilization study

In this study, the solubilization of styrene and phenanthrene by the conventional surfactant system (SDS), extended carboxylate surfactant systems (C_{16-17}-4PO-5EO-COONa, and C_{16-18}-4PO-5EO-COONa), and extended sulfate surfactant system (C_{16-17}-4PO-SO_4Na) were investigated at 1.0 mM NaCl, at pH 8.0-8.5 and a temperature of 25±2 °C. The solubilization capacity of a particular surfactant for a given solute was measured by determining the molar solubilization ratio (MSR) from the variation of solute solubility within the surfactant concentration. The MSR values were obtained from the slope of the curve along with the solubility of the solute. The MSR and micellar partition coefficient (K_{mic}) values were calculated using Equations 2-4 to 2-7 shown in Chapter 2.

4.4.1 Styrene solubilization

In this study, the styrene solubilization by the extended carboxylate surfactants and extended sulfate surfactant was investigated as shown in Figure 4-7, where the apparent solubility of styrene was plotted as a function of surfactant concentration. The transition point where the solute concentration begins to increase corresponds approximately to the CMC of the surfactant system (Fuangswasdi et al., 2006b). It was found that the solubility of styrene increased linearly with the surfactant concentration beyond its CMC in both the conventional surfactant and extended surfactants. The slope of the plot in Figure 4-7 represents the MSR and thus, the K_{adm} value can be calculated, Table 4-5 illustrates the MSR and K_{adm} value.

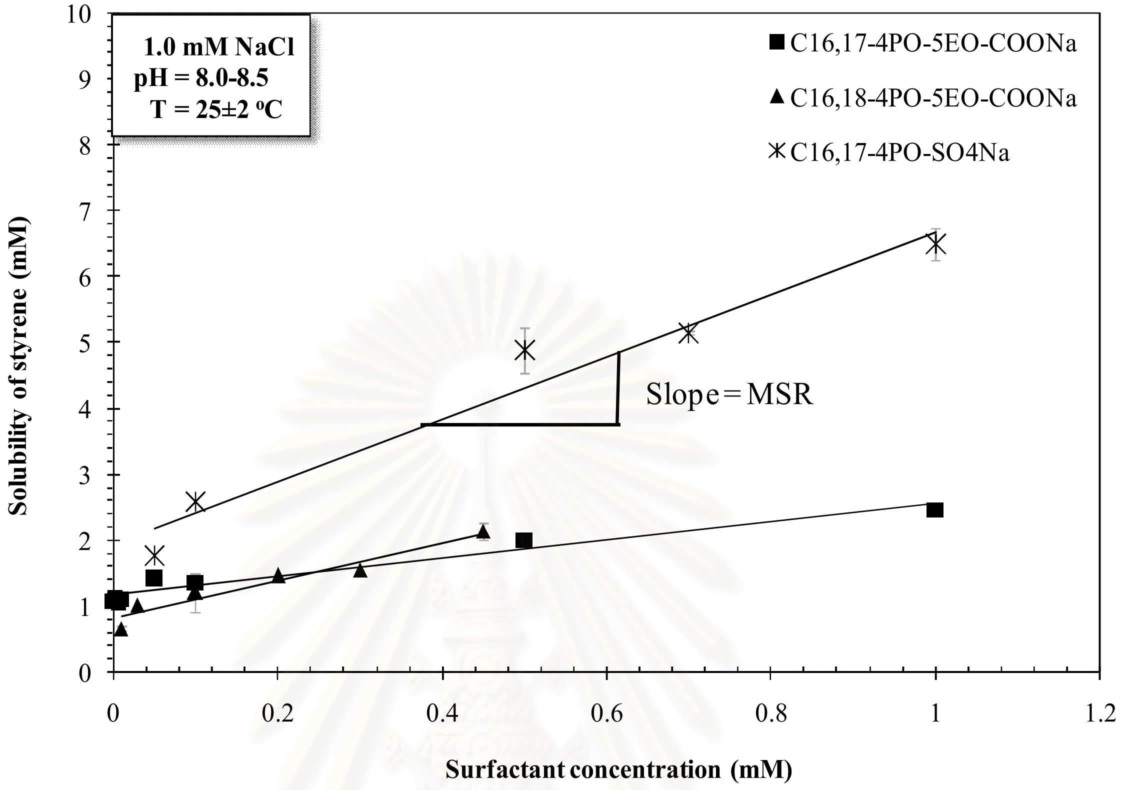


Figure 4-7 Solubilization capacities of styrene by the extended carboxylate surfactant systems and extended sulfate surfactant system at 1.0 mM NaCl, an equilibrium pH of 8.0-8.5, and a temperature of 25±2°C

Table 4-5 The styrene micellar partition coefficient (K_{mic}) values of the conventional surfactant system and extended surfactant systems

Surfactant (1 mM NaCl)	HLB[a] number	Styrene solubilization				
		MSR	r^2	X_{mic}	K_{mic}	log K_{mic}
Conventional surfactant						
$C_{12}H_{25}SO_4Na$, (SDS)	40.00	0.25	0.92	0.20	3,733	3.57
Extended carboxylate surfactant						
$C_{16,17}$-4PO-5EO-COONa	19.31	1.39	0.95	0.58	10,855	4.04
$C_{16,18}$-4PO-5EO-COONa	19.08	2.87	0.94	0.74	13,841	4.14
Extended sulfate surfactant						
$C_{16,17}$-4PO-SO_4Na	37.26	4.87	0.97	0.83	15,484	4.19

[a] HLB is hydrophilic - lipophilic balance

From Table 4-5, it was found that the MSR and K_{mic} values of the extended surfactant-based micelles were higher than those of the conventional surfactant-based micelles. Thus, it should be noted that the extended surfactants demonstrate the higher styrene solubilization capacities over the conventional surfactant. Since styrene is an intermediate polar solute, it tends to solubilize into palisade region of surfactant aggregate. The extended surfactant with EO/PO groups has a longer hydrophobic group than the conventional surfactant without EO/PO groups; therefore, the extended surfactant has a larger aggregate size and diameter (larger aggregation number) resulting in a larger palisade layer as compare to the conventional surfactant (Rosen, 2004). For this reason, the extended surfactant micelles show the higher styrene solubilization capacities than SDS. This finding is consistent with Charoensaeng et al. (2008) who reported the K_{mic} values of SDS and the extended surfactant ($C_{12\text{-}13}$-8PO-SO_4Na) for the solubilization of styrene were 4400 and 7480. The results show that styrene has higher solubilization capacity in the extended surfactants than SDS due to the greater hydrophobic length.

In addition, it was obvious that the MSR and K_{mic} values of the C_{16-18} extended carboxylate surfactant were higher than those of the C_{16-17} extended carboxylate surfactant. Thus, the same extended surfactant type with different alkyl chain length gave the different solubilization of solute. The extended surfactant with longer alkyl chains showed a greater capacity for solubilizing styrene. As mentioned above, the increase in the chain length of the hydrophobic portion of surfactant generally results in increased solubilization capacity of styrene in the palisade region of the micelle. In addition, Aumpuch (2007) studied the solubilization capacity of PCE in the systems consisting of AMA mixed with the extended surfactant series (C_n-$(PO)_n$-SO_4Na). The data shows that the increasing alkyl chain length gives the higher the K_{adm} value; the greater PCE solubilization.

When comparing the MSR and K_{mic} values of the extended carboxylate and sulfate surfactants from Table 4-5, the data show that the extended sulfate surfactant had higher MSR and K_{mic} values than the extended carboxylate surfactants. Nevertheless, log K_{mic} values were not significantly different. Besides, since styrene is an intermediate polar organic solute, it was expected to partition mainly in the palisade region. Thus, a possible explanation is that the extended sulfate surfactant, C_{16-17}-4PO-SO_4Na, has the highest HLB values (see Table 4-3), which implies that it is the highest hydrophilic site for styrene to solubilize into its micelles.

Additionally, this finding is due to the fact that the amount of the polar or intermediate polar solute are solubilized in the palisade layer generally increasing with increase in the size of the micelle (Rosen, 2004). For this study, the introduction of the sulfate group into the molecule was greater solubilization capacity of the styrene than the introduction of the carboxylate group. Since the sulfate group has stronger charged repulsion between the head groups in the micelles, with consequent the higher space available for solubilization between the surfactant molecules in the palisade layer. Thus, the greater repulsion between the head groups of the extended sulfate surfactant over the extended carboxylate surfactants result in the higher solubilization of polar molecules. Moreover, the presence of the coiling EO in the extended carboxylate surfactants might reduce the cavities where styrene likes to solubilize in the palisade layer, resulting in a reduction of the styrene solubilization (Rosen, 2004).

4.4.2 Phenanthrene solubilization

The solubilization of phenanthrene for the extended carboxylate surfactant systems (C_{16-17}-4PO-5EO-COONa, and C_{16-18}-4PO-5EO-COONa) and extended sulfate surfactant system (C_{16-17}-4PO-SO_4Na) are illustrated in Figure 4-8, where the apparent solubility of phenanthrene was plotted against the surfactant concentration. The result showed that the solubility of phenanthrene increased linearly with the surfactant concentration beyond its CMC in both the conventional surfactant and extended surfactants. The phenanthrene solubilization capacity in terms of MSR and K_{mic} values was summarized in Table 4-6.

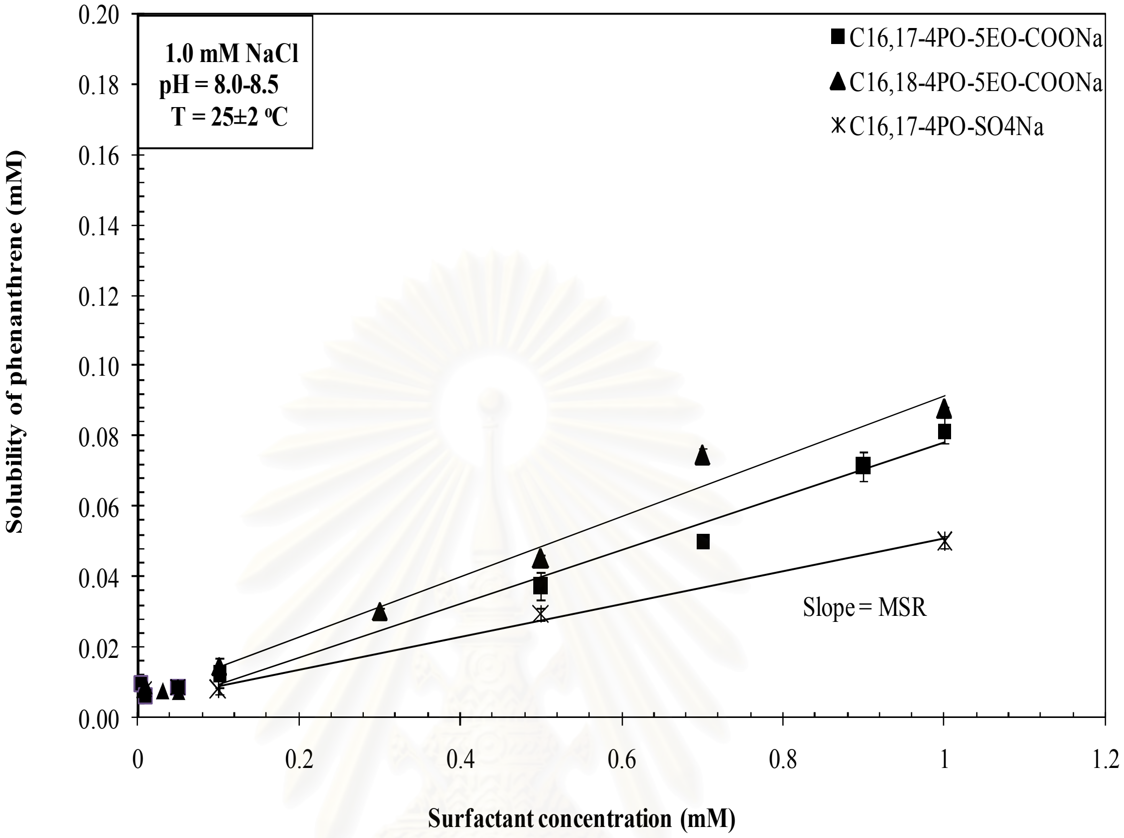


Figure 4-8 Solubilization capacities of phenanthrene by the extended carboxylate surfactant systems and extended sulfate surfactant system at 1.0 mM NaCl, an equilibrium pH of 8.0-8.5, and a temperature of 25±2°C

Table 4-6 The phenanthrene micellar partition coefficient (K_{mic}) values of the conventional surfactant system and extended surfactant systems

Surfactant (1 mM NaCl)	HLB[a] number	Phenanthrene solubilization				
		MSR	r^2	X_{mic}	K_{mic}	log K_{mic}
Conventional surfactant						
$C_{12}H_{25}SO_4Na$, (SDS)	40.0	0.01	0.99	0.01	61,247	4.79
Extended carboxylate surfactant						
$C_{16,17}$-4PO-5EO-COONa	19.3	0.07	0.99	0.07	410,088	5.61
$C_{16,18}$-4PO-5EO-COONa	19.1	0.08	0.98	0.08	479,356	5.68
Extended sulfate surfactant						
$C_{16,17}$-4PO-SO_4Na	37.3	0.04	0.99	0.04	260,711	5.42

[a] HLB is hydrophilic - lipophilic balance

Table 4-6 summarizes the MSR, K_{mic}, and log K_{mic} values. The log K_{mic} values of the extended carboxylate surfactant systems were higher than those of the extended sulfate surfactant system and the conventional surfactant system. Therefore, the extended surfactants exhibit a higher phenanthrene solubilization capacity as compared to the conventional surfactant. Phenanthrene has low water solubility due to its high degree of hydrophobicity (log K_{ow} = 4.46) and, therefore, it tends to solubilize in the hydrophobic core of the surfactant aggregates (Zhu and Feng, 2003; Mohamed and Mahfoodh, 2006). It was expected that the extended surfactants both carboxylate and sulfate have a longer alkyl chain length than the conventional surfactant; therefore, these extended surfactants have a larger aggregation number resulting in greater interactions between their hydrophobic chains and a larger hydrophobic core region than the conventional surfactant. For these reasons, the extended surfactant micelles yield a higher phenanthrene solubilization capacity than SDS.

As compared the phenanthrene solubilization capacity between the extended carboxylate surfactants with different hydrophobic chain length, (Table 4-6), it was found that the MSR and K_{adm} values of the C16-18 extended carboxylate surfactant were higher than those of the C16-17 extended carboxylate surfactant. Since the C16-18 extended carboxylate surfactant has a more hydrophobic core and a larger core region as compared with the C16-17 extended carboxylate surfactant. Therefore, it can be conclude that for the same extended surfactant type, the extended surfactant with longer alkyl chain length show a higher phenanthrene solubilization.

From Table 4-6, the results showed that the MSR and K_{adm} values of the extended carboxylate surfactants were higher than those of the extended sulfate surfactant. Thus, the extended carboxylate surfactants exhibit the greater phenanthrene solubilization capacity over the extended sulfate surfactant.

A Previous study (Zhu and Feng, 2003) on phenanthrene solubilization by three types of nonionic surfactants including TX100, Brij35, and TX305 reported the log K_{mic} values were 5.57, 5.60, and 5.09, respectively. It was observed that the log K_{mic} values of the both extended carboxylate surfactants used in this study were higher than those observed in nonionic surfactants.

The solubilization capacity (log K_{mic}) of phenanthrene is primarily higher than that of styrene (for dipole moments see Table 3-2). The different partition behavior between phenanthrene and styrene can be explained by the fact that non polar phenanthrene tends to be solubilized in the hydrophobic core of the micelles (Mohamed and Mahfoodh, 2006; Swe et al., 2006). In contrast, the slightly polar styrene tends to be accumulated in the palisade layer of micelles (Nayyar et al., 1994; Attaphong, 2006; Fuangswasdi et al., 2006b; Charoensaeng, 2008).

Furthermore, Luning Prakm and Pritchard (2002) evaluated the solubilization of phenanthrene in solutions of the nonionic surfactants. It is clear why the solubility enhancement of surfactants followed the order Tween 80 > Tween 20 and Brij 58 > Brij 35. Tween 20 and Brij 35 are more hydrophilic, which led to a lower solubility enhancement of phenanthrene as compared to Tween 80 and Brij 58. Their findings are consistent with those in this study. The solubilization of phenanthrene slightly increased as the hydrophobicity of all surfactants increased due to non-polarity of phenanthrene.

From the partition coefficient values in the solubilization and adsolubilization studies, it was observed that the log K_{adm} values of the admicellar systems are lower than the log K_{mic} of the micellar systems (see Table 4-3 and Table 4-4). This could be due to the fact that the adsolubilization of organic solute into extended surfactant aggregates is strongly influenced by several parameters: the polarity of the organic solute, the carbon chain length of the surfactant, the hydrophilic head type of the surfactant, and the PO/EO groups inserted in the surfactant structure. A recent study obtained nearly identical micellar and admicellar partitioning for organic solute by extended surfactants. It was mention that the coiling of PO groups in these surfactant aggregates was more efficient in three-dimensional micelles than into two-dimensional admicelles (Charoensaeng, 2008).

4.5 Desorption study

A surfactant desorption study was conducted to evaluate the desorption of surfactants from the alumina surface. The coated adsorbent was washed with DI water as a sequence of washing steps from 1-10 times, and then the supernatant of each batch was analyzed. From the analytical technique, there was no evidence of residual surfactant in the solution. Due to the detection limit of the instrument, the concentration of surfactant in an aqueous solution after the first-wash could not be detected as it was used in the adsorption study. It can be implied that the amount of desorbed surfactant was very low. To confirm this result, an indirect method to evaluate the surfactant desorption was conducted using the zeta-potential measurement. This method was applied to measure the concentration of charges (mV) on the modified alumina surface.

The zeta potentials of alumina with the conventional surfactant system (SDS), extended carboxylate surfactant systems (C_{16-17}-4PO-5EO-COONa, and C_{16-18}-4PO-5EO-COONa), and extended sulfate surfactant system (C_{16-17}-4PO-SO_4Na) as functions of the number of washing (desorption) steps at a solution pH of 5, 7, and 8 are shown in Figure 4-9. The results revealed that the zeta potential of alumina without an adsorbed surfactant bore a positively charged surface (+57 mV), whereas the zeta potential of alumina with an adsorbed surfactant produced a negatively charged surface. This finding indicates that surfactants form a bilayer on alumina and achieve charge reversal by changing it from positive to negative values as the surfactant concentration attained the maximum bilayer coverage.

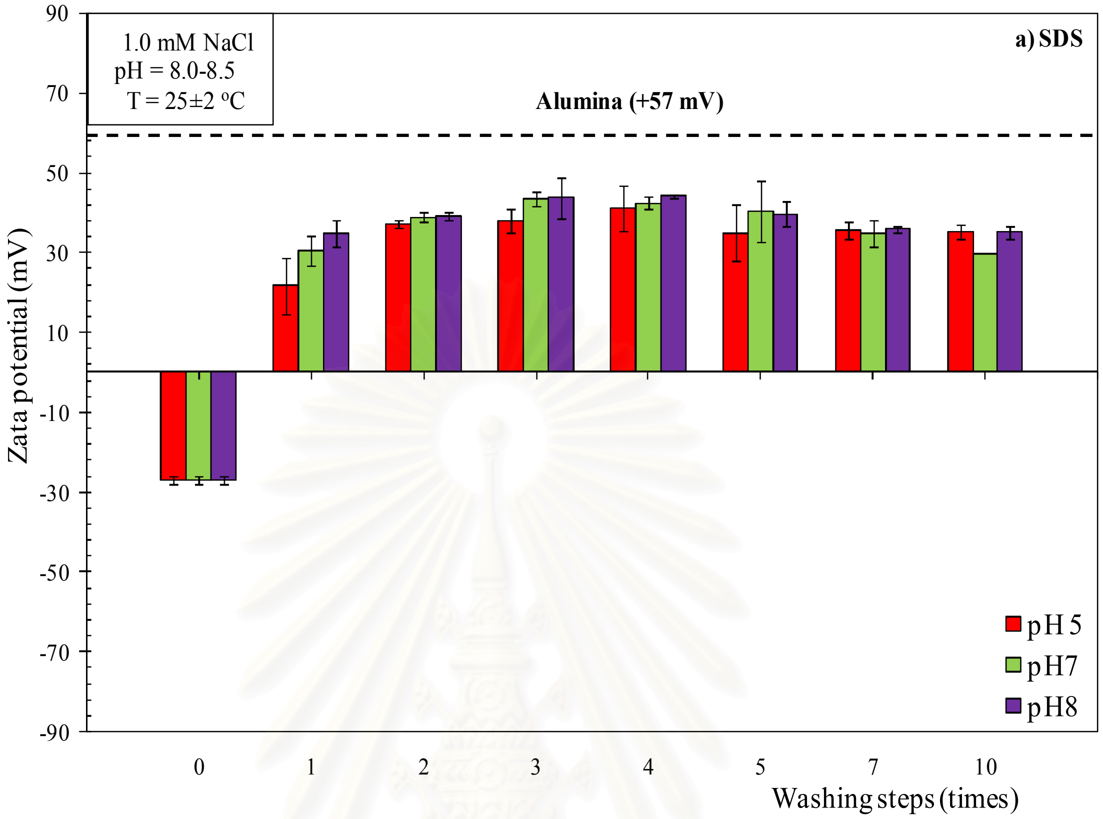
Figure 4-9 illustrates the zeta potential values for all surfactant systems (prior to the washing steps). The results show that the zeta potential values of all extended surfactant systems were lower (range from -71 mV to -88 mV) compared to those of the conventional surfactant system (-27 mV). This implies that the surfactant molecules of all extended surfactant systems had a denser packing orientation than those of the conventional surfactant system.

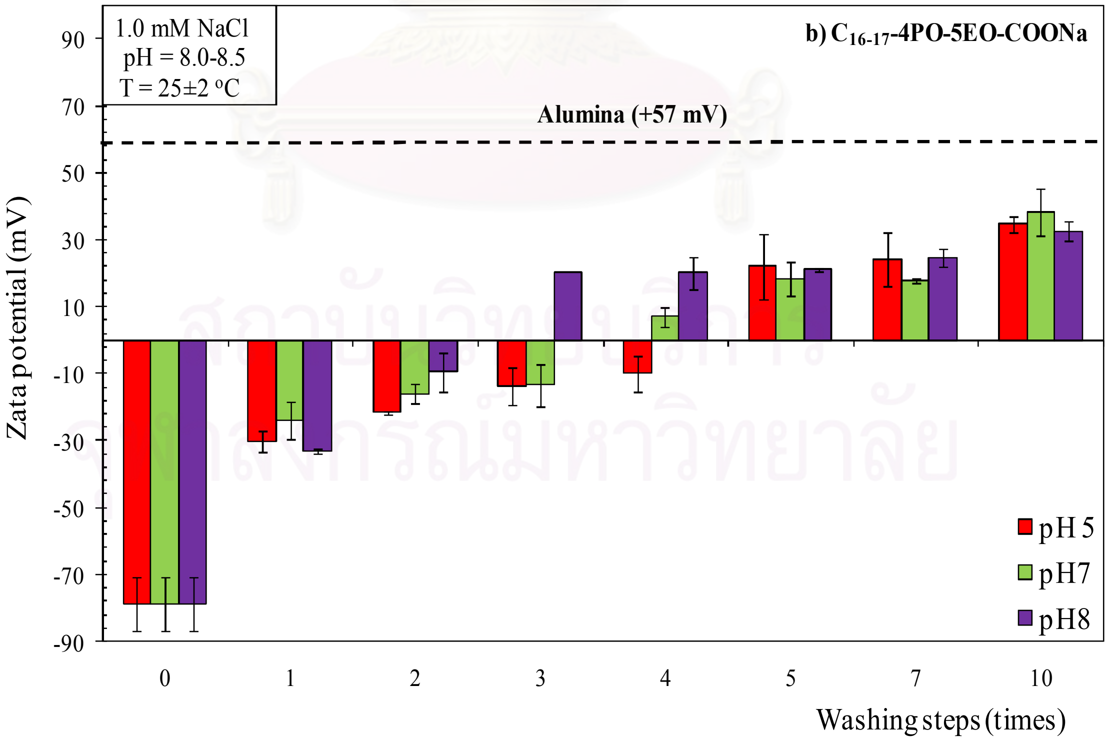
The zeta potential of alumina adsorbed by SDS, the extended carboxylate surfactant with C16-17 and C16-18, and the extended sulfate surfactant increased as the number of washing steps increased. This change in the zeta potential was caused by the desorption of the adsorbed surfactant monomer onto a solid interface to the aqueous phase due to equilibrium concentrations. As seen in Figure 4-9 (a) and (d), the zeta potential of alumina adsorbed by SDS and the extended sulfate surfactant increased as the number of washings progressed even when the pH levels of the aqueous solution were varied. Therefore, the effects of pH on the desorption potential of SDS and the extended sulfate surfactant adsorbed onto alumina were negligible.

As expected, the zeta potential increases of alumina due to the extended carboxylate surfactants should be greater than the increases produced by SDS and the extended sulfate surfactant at the same washing-step time increments. This is because the carboxylate head group of the extended surfactants is less hydrophilic than the sulfate head group of SDS and the extended sulfate surfactant. Moreover, the carboxylate group of the extended carboxylate surfactants has a higher pKa (~ 4 to 5) than the sulfate group of SDS and the extended sulfate surfactant (~1 to 2) (Douglas et al., 1999), so the extended carboxylate surfactant should be more protonated and, thus, less hydrophilic at pH 5 and capable of desorbing more readily. For these reasons, the zeta potential increases of alumina with the C16-17 extended carboxylate surfactant was greater than those of the C16-17 extended sulfate surfactant at the same washing-step time increments (see Figure 4-9 (b) and (d)). However, the results also showed that the zeta potential increases of alumina with SDS was greater than the increases of the extended carboxylate surfactants (C16-17 and C16-18) and the extended sulfate surfactant at the same washing-step time increments (Figure 4-9 (a) to (c)). In addition, the extended carboxylate surfactant C16-17's zeta potential increase was greater than that of C16-18's (see Figure 4-9 (b) and (c)). The surfactant washing results are interesting, as the reasons for these observations are not clear and should be further evaluated in future research. On the other hand, a possible explanation could be that the extended surfactants have longer hydrophobic tails than those of the conventional surfactant (SDS), and the hydrophobic tails of the C16-18 extended carboxylate surfactant are longer than those of both the C16-17 extended carboxylate and the sulfate surfactant. It can be concluded that surfactants with longer carbon chains have lower desorption potentials resulting from their stronger lateral interactions between the adsorbed surfactants (Paria and Khilar, 2004; Zhang and Somasundaran, 2006). For these reasons, the desorption potentials of the C16-18 extended carboxylate surfactant adsorbed onto alumina were lower than those of SDS and the C16-17 extended carboxylate surfactant adsorbed onto alumina.

With regard to the effects of pH on the desorption capacities of the extended carboxylate surfactant (C16-17 and C16-18) with alumina, it was observed that when the pH of the washing solution increased, the desorption capacity in terms of the zeta potential increased, as shown in Figure 4-9 (b) and (c). This is corroborated by the fact that the alumina surface is negatively charged when the solution pH is noticeably lower than the PZC of alumina (9.1). Hence, an anionic surfactant can strongly adsorb on the aluminum's surface (Kosmulski, 2003; Fuangswasdi et al., 2006a). When the solution pH is close to the PZC of alumina, the surfactant will be weakly adsorbed on the surface. For this reason, the adsorption of the surfactants onto alumina surface was maximum and the desorption capacity of adsorbed admicelle was minimal when the pH of the washing solution was lowest (pH 5). Furthermore, the pH value significantly affected the desorption capacities until the fourth to fifth steps of the washing process. After that, the desorption capacity remained equal even when the pH of washing solution was varied.

Overall, the extended carboxylate surfactant systems retained a negative charge (bilayer coverage) after sequential washing much better than the conventional surfactant system. This finding could be due to the characteristics of the extended carboxylate surfactant, which produced strong lateral interaction. This means that these extended carboxylate surfactants could reduce surfactant desorption.


1.0 mM NaCl
pH = 8.0-8.5
T = 25±2 °C
a) SDS
Alumina (+57 mV)
90
70
50
30
10
-10
-30
-50
-70
-90
Zata potential (mV)
0
1
2
3
4
5
7
10
Washing steps (times)
🟥 pH 5
🟩 pH7
🟪 pH8


1.0 mM NaCl
pH = 8.0-8.5
T = 25±2 °C
b) C_{16-17}-4PO-5EO-COONa
Alumina (+57 mV)
90
70
50
30
10
-10
-30
-50
-70
-90
Zata potential (mV)
0
1
2
3
4
5
7
10
Washing steps (times)
🟥 pH 5
🟩 pH7
🟪 pH8

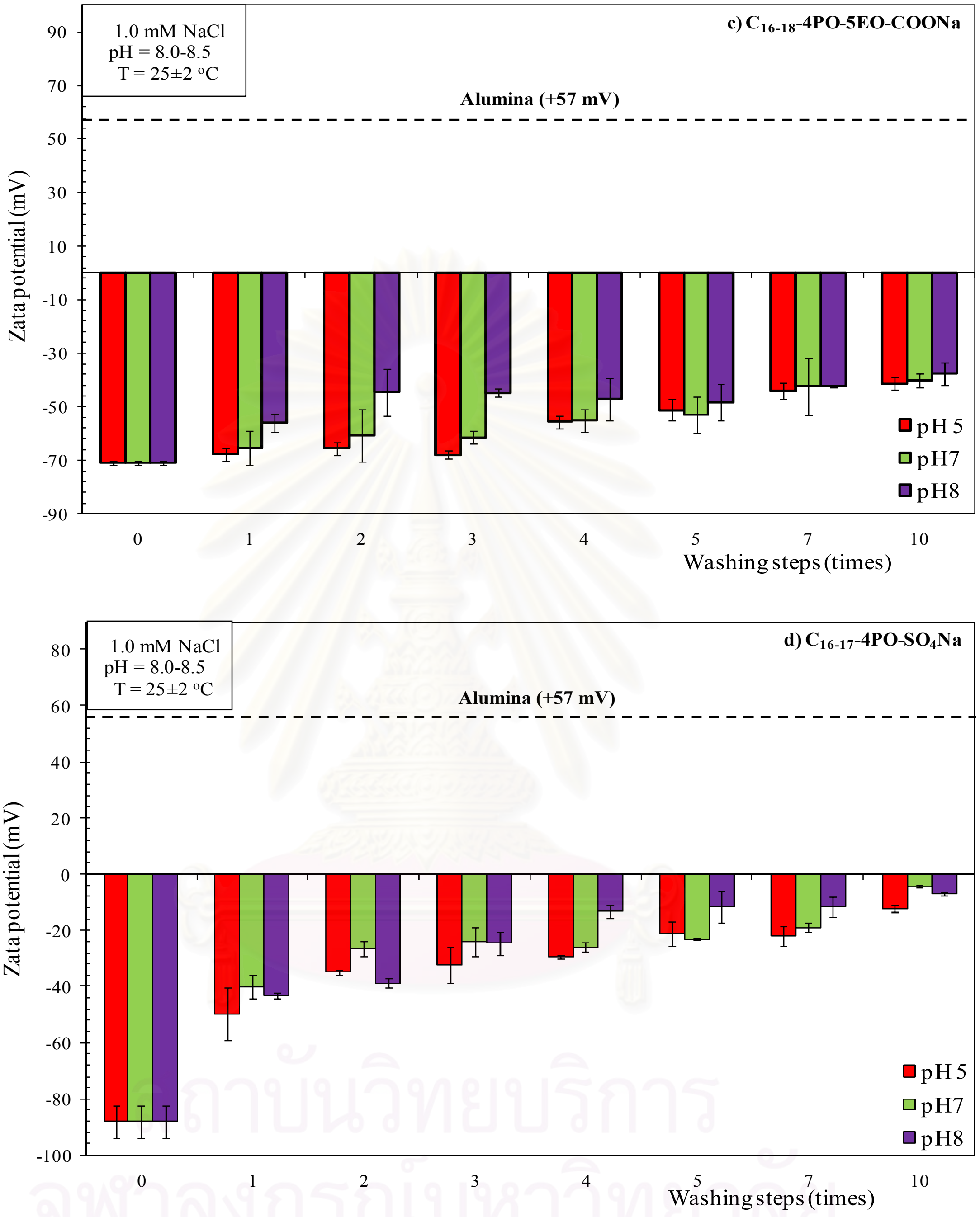


Figure 4-9 The zeta potentials of alumina with the conventional surfactant system and the extended surfactant systems for (a) SDS, (b) C_{16-17}-4PO-5EO-COONa, (c) C_{16-18}-4PO-5EO-COONa, and (d) C_{16-17}-4PO-SO_4Na

CHAPTER V

SUMMARIES, CONCLUSIONS AND ENGINEERING SIGNIFICANCE

5.1 Summaries

This study evaluated a novel class of anionic extended surfactants, alkyl propoxylated ethoxylated carboxylate surfactants (extended carboxylate surfactants), to enhance the organic solutes removal from aqueous solution. In this study, the conventional surfactant (SDS), extended carboxylate surfactants (C_{16-17}-4PO-5EO-COONa, and C_{16-18}-4PO-5EO-COONa), and extended sulfate surfactant (C_{16-17}-4PO-SO_4Na) were investigated. All experiments were conducted in batch at 1.0 mM NaCl, an equilibrium solution pH of 8.0-8.5, and a temperature of 25±2 °C. Two organic solutes, styrene and phenanthrene, were selected as a higher and lower polar organic solutes, respectively.

For the critical micelle concentration (CMC) study, the data illustrated that the CMC of the extended surfactants were two orders of magnitude lower than that of conventional surfactant, SDS. In addition, for extended carboxylate surfactants, the CMC of the surfactant with higher carbon chain length, C16-18, surfactant was slightly lower than that of the C16-17 surfactant. The CMC comparison between two types of the extended surfactant systems indicated that the extended carboxylate surfactants had slightly smaller CMC than the extended sulfate surfactant.

In the adsorption study, the adsorption of the conventional surfactant and extended surfactants onto an aluminum oxide surface increased with increasing surfactant concentration below CMC consistent with the S-shaped isotherm. Although the adsorption capacity of the extended sulfate surfactant was higher than that of the conventional surfactant and those of the extended carboxylate surfactants, the extended carboxylate surfactant with C16-18 required much lower equilibrium surfactant concentrations to reach the maximum adsorption capacities than the extended sulfate surfactant and conventional surfactant system.

Based on the adsolubilization study of styrene, it was found that the admicellar partition coefficient values (K_{adm}) of the conventional surfactant was higher than the K_{adm} of the extended surfactants. It should be noted that the PO groups in the extended surfactants tend to “squeeze out” the cavities in the palisade layer where the polar solute would segregate, resulting in a reduction of the adsolubilized styrene. The comparison of the adsolubilization capacity of two extended carboxylate surfactants indicated that the K_{adm} of C_{16-17}-4PO-5EO-COONa was higher than that of C_{16-18}-4PO-5EO-COONa. This is due to the fact that the C_{16-17} surfactant has a higher degree of hydrophilicity than the C_{16-18} surfactant. Thus, the intermediate polar styrene can adsolubilize in the palisade layer of the C_{16-17} admicelles than in the palisade layer of the C_{16-18} admicelles. For adsolubilization of phenanthrene, the K_{adm} values of phenanthrene was higher for $C_{16,17}$-4PO-SO_4Na, $C_{16,18}$-4PO-5EO-COONa, $C_{16,17}$-4PO-5EO-COONa, and SDS, respectively. This finding was very close to the results of adsorption study. Thus, it is interesting to note that the adsolubilization capacity of phenanthrene was significantly influenced by the amounts of adsorbed admicelles at the plateau region. In order to gain insight into locus of adsolubilization of styrene and phenanthrene, it was found that styrene mainly partitions into the palisade region while phenanthrene partitions into both the palisade and core region. Due to the effect of intermediate groups in the extended surfactants and the short carbon chain length of conventional surfactant, phenanthrene could also partition in palisade region.

In the styrene solubilization study, the extended surfactants had greater styrene solubilization capacities over the conventional surfactant. In addition, as the carbon chain length increased from C16-17 to C16-18 in the extended carboxylate surfactants, the log K_{mic} values also increased similar to the log K_{mic} values primarily increased from the changing hydrophilic carboxylate head group to sulfate head group in the extended surfactant system. This indicates that the hydrophobicity and hydrophilicity in the extended surfactant system also impact on the solubilization of styrene. In the phenanthrene solubilization study, the log K_{mic} values of the extended carboxylate surfactant systems were higher than the extended sulfate surfactant system, and the conventional surfactant system. Since these extended carboxylate surfactants have a larger aggregation number resulting in greater interactions between their hydrophobic chains and have a larger hydrophobic core region than the conventional surfactant. Relative to the impact of the hydrophilic head groups of surfactant, thus, phenanthrene exhibits to solubilize in the extent of the carboxylate surfactant aggregates than those of the sulfate surfactant aggregates.

As compared the micellar and admicellar partition coefficient values (log K_{mic} and log K_{adm}), it was observed that the log K_{adm} values of the admicellar systems were lower than the log K_{mic} of the micellar systems. This could be due to the fact that the adsolubilization of organic solutes into extended surfactant aggregate are strongly influenced by several parameters: polarity of organic solute, carbon chain length of surfactant, hydrophilic head type of surfactant, and PO/EO groups inserted in the surfactant structure.

In order to consider the stability of a surfactant onto an aluminum oxide surface, all of the adsorbed surfactants became more desorbed from aluminum oxide surface when the number of washing steps increased. However, the increase of the zeta potential of alumina with SDS was greater than the increases of the extended carboxylate surfactants and the extended sulfate surfactant at the same washing-step time increments. In addition, the extended carboxylate surfactant C16-17 zeta potential increase was greater than that of the C16-18. It could be concluded that surfactants with longer carbon chains have lower desorption potentials resulting from their stronger lateral interactions between the adsorbed surfactants. Due to the hydrophilic head group of surfactant, the increase of the zeta potential of alumina with the C16-17 extended carboxylate surfactant was greater than that of the C16-17 extended sulfate surfactant at the same washing-step time increments. Moreover, the effects of pH in solution on the desorption capacity of SDS and the extended sulfate surfactant from the aluminum oxide surface were negligible, whereas the desorption capacity of the extended carboxylate surfactants from the aluminum oxide surface increased by increasing the pH in the washing solution through the fourth to fifth times of washing steps. After that, the effects of pH in the solution were negligible.

5.2 Conclusions

Based on this research results, the specific conclusion are made as follow:

1) The CMCs of the extended surfactant systems was lower than the conventional surfactant system. As the carbon chain length increased, the CMCs of all surfactant systems also decreased. In addition, the extended carboxylate surfactant with C16-17 had slightly smaller CMC than the extended sulfate surfactant.

2) The adsorption of the extended sulfate surfactant showed higher maximum adsorption capacity while the extended carboxylate surfactant with C16-18 required much lower equilibrium surfactant concentrations to reach the maximum adsorption. The type of hydrophilic head group and the length of carbon chain both affect the amounts of adsorbed surfactants at the plateau region by increase interaction between adsorbed surfactant molecules.

3) The adsolubilization capacity of intermediate polar styrene decreased as the PO groups in the surfactant molecule presented since the surfactant with PO groups caused less polarity in the palisade region and tended to "squeeze out" the cavities where styrene would segregate.

4) Relative to the effect of carbon chain length in the extended carboxylate surfactants, the shorter carbon chain length (C16-17) exhibited the higher styrene adsolubilization enhancement as compare to the longer chain length (C16-18) due to the higher degree of hydrophilicity of surfactant.

5) The adsolubilization capacities of the non polar phenanthrene are significantly influenced by the amounts of adsorbed admicelle at the plateau region.

6) The adsolubilization enhancement of phenanthrene increased when the carbon chain length increased due to the larger hydrophobic core of surfactant where the non-polar phenanthrene was solubilized. Relative to the impact of hydrophilic head groups of surfactant, the non-polar phenanthrene exhibited to solubilize in the carboxylate surfactant aggregates than those of the sulfate surfactant aggregates.

7) The extended surfactants demonstrated the greater styrene solubilization capacities over the conventional surfactant. For the extended surfactants, both of hydrophilicity and hydrophobicity of surfactant had also impact on the solubilization of styrene.

8) The extended carboxylate surfactants exhibited higher phenanthrene solubilization enhancement because they have a larger aggregation number resulting in greater interactions between their hydrophobic chains and larger hydrophobic core region than the conventional surfactant.

9) Adsolubilization capacity (K_{adm}) was lower than solubilization capacity (K_{mic}). This could be due to the fact that the adsolubilization of organic solute into surfactant admicells is strongly influenced by several parameters: polarity of organic solute, carbon chain length of surfactant, hydrophilic head type of surfactant, and PO/EO groups inserted in the surfactant structure, and two-dimensional versus three-dimensional structure of micelles versus admicelles.

10) The extended surfactant systems showed lower desorption capacity than the conventional surfactant system. Due to the greater electrostatic attraction of adsorbed admicelles, the sulfate surfactant demonstrated the adsorption stability than the carboxylate surfactant at the same carbon chain lengths. The surfactant with longer carbon chains could reduce the surfactant desorption from un-equilibrium system resulting from their stronger lateral interactions between the adsorbed surfactants.

5.3 Engineering significance

Surfactant-modified materials have been widely used for industrial and environmental applications. Conceivable advantages of these modified materials include flexibility of design are given the large variety of known surfactant molecules as well as relative ease of future process modification by simply switching the surfactant rather than the process equipment. Due to unique characteristics of extended surfactant, the extended-based surfactant system showed the efficiency of admicelle formation, solubilization, and adsolubilization enhancement. Moreover, the extended surfactants demonstrated the stability of the surfactants adsorbed onto the surface.

The modified adsorbent can be applied in many technology and industrial application such as detergency, flotation, corrosion inhibition, dispersion of solids, and enhance oil recovery. In field applications, the surface modification by surfactants appears particularly promise for treatment of groundwater and wastewater contaminated with organic solutes by phenomenon called adsolubilization process. For ex-situ applications, the surfactant-modified adsorbent could be used for removal of organic solutes in filters or packed-bed reactors. For in-situ applications, the modified adsorbents could be used in subsurface barriers as passive permeable barrier for retard the movement of contaminants in the subsurface.

5.4 Recommendations and future works

Surfactant-modified adsorbents have been successfully used for removal of organic pollutants from aqueous environment (Fuangswasdi et al., 2006b; Fuangswasdi et al., 2007; Charoensaeng et al., 2008). From this research, some aspects should be carefully considered and some specific area should be evaluated in the future work.

1) ***Surfactant structure*****:** In this research, a novel class of the extended surfactants, alkyl propoxylated ethoxylated carboxylate surfactants (C_n-$(PO)_4$-$(EO)_n$-COONa) was evaluated their performance by comparing with the alkyl propoxylated sulfate surfactant (C_{16-17}-4PO-SO_4Na) and the conventional surfactant (SDS). Due to the limitation of the water solubility of C_n-$(PO)_4$-$(EO)_3$-COONa, we cannot use these series to investigate the effect of EO groups in hydrophilic head surfactant. To clear understand the effect of hydrophilic head groups of surfactant relevant to the adsorption/desorption capacities and adsolubilization enhancement, in the more detail, a new type of the extended surfactants, alkyl propoxylated ethoxylated sulfate surfactants (C_{16-17}-4PO-5EO-SO_4Na), which have been produced, are necessary and should be further investigated.

2) ***Surfactant desorption*:** Although the extended surfactant based system showed higher stability of adsorbed admicelle onto alumina oxide surface than the conventional surfactant system. One limitation of using surfactant-modified materials is surfactant loss from the solid surface to aqueous solution. Moreover, another factor which affect on the desorption of these surfactant is pH in the aqueous solution.

3) ***Surface characterization***: Adsolubilization of organic solutes into interior of surfactant admicelle is strongly influenced by the combination of surfactant structure, solute properties, and nature of solid surface. Understanding the admicelle formation and adsolubilization mechanism of the extended carboxylate surfactant onto solid oxide surface, the direct visualization of the morphology of admicelles using atomic force microscopy (AFM) is necessary.

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APPENDICES

APPENDIX A

FIGURES

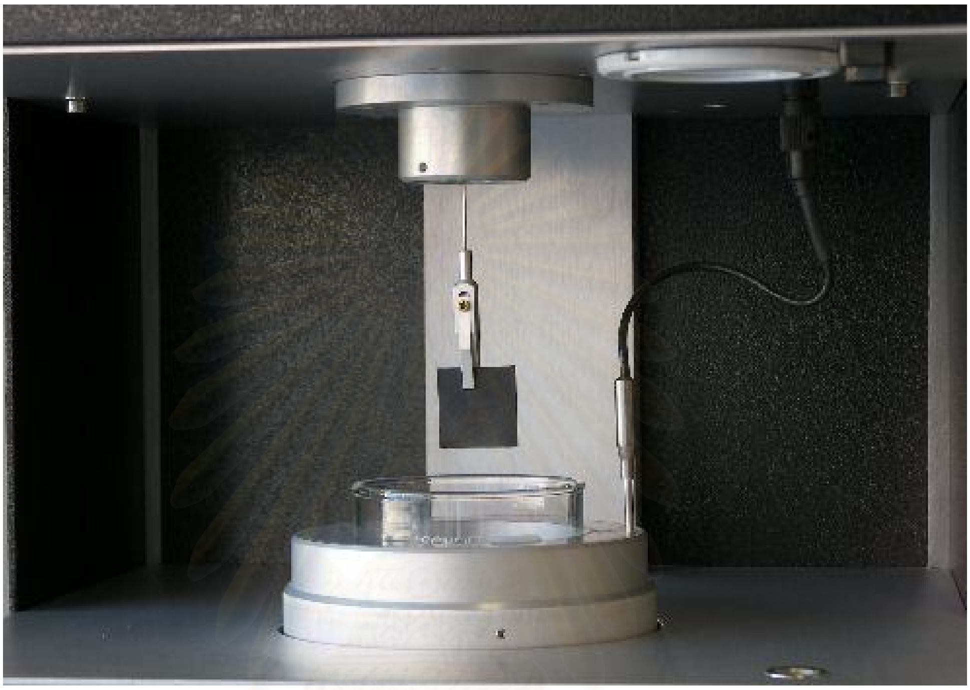

Figure A-1 Tensiometer

Figure A-2 pH meter (Model 215, Denver Instrument)

Figure A-3 The High Performance Liquid Chromatography (HPLC 1100, Agilent) with ELSD and UV detector

Figure A-4 Ion chromatography (ICS-2500, Dionex) with ECD detector

Figure A-5 UV/Visible spectrophotometer (Helios-Alpha, Thermo Electron Corporation)

Figure A-6 Centrifuge (Boeco C-28, Germany)

APPENDIX B

CALCULATION

Hydrophilic/Lipophilic Balance (HLB)

The hydrophilic/Lipophilic Balance (HLB) Method is the most frequently used method for selecting surfactant for solubilization of organic solutes (Sabatini, 2006)

$$HLB = 7 + \sum(\text{ hydrophilic group numbers}) + \sum(\text{ hydrophobic group numbers}) \qquad (2.1)$$

Table B-1 Some Calculated HLB Values for this study

	Group	HLB number
Hydrophilic	- SO_4Na	38.70
	- COONa	19.10
	- EO	0.33
Hydrophobic	- CH_2	-0.475
	- PO	-0.15

APPENDIX C

EXPERIMENTAL RAW DATA

Table C-1 Surface tension measurement of SDS at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Concentration (M)	Surface tension (mN/m)				SD
	Tube 1	Tube 2	Tube 3	Avg.	
3E-05	68.91	64.03	67.56	66.83	2.52
1E-04	63.58	67.19	68.91	66.56	2.72
4E-04	57.01	56.02	57.84	56.96	0.91
5E-04	54.94	57.01	53.40	55.11	1.81
6E-04	51.23	53.57	55.12	53.30	1.96
8E-04	50.90	52.40	53.98	52.43	1.54
9E-04	43.74	46.29	48.54	46.19	2.40
4E-03	35.80	37.07	37.88	36.92	1.05
5E-03	35.75	36.34	36.82	36.30	0.53
6E-03	35.63	36.08	36.30	36.00	0.34
7E-03	35.22	36.01	-	35.62	0.56
9E-03	34.82	33.95	36.55	35.11	1.32
1E-02	34.82	34.81	-	34.81	0.01
3E-02	33.95	33.80	-	33.88	0.11

Table C-2 Surface tension measurement of C_{16-17}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Concentration (M)	Surface tension (mN/m)				SD
	Tube 1	Tube 2	Tube 3	Avg.	
3E-03	32.78	32.64	32.71	32.71	0.07
1E-03	32.71	32.74	32.76	32.74	0.02
3E-04	32.79	32.69	32.78	32.76	0.05
1E-04	32.90	32.93	32.88	32.90	0.02
9E-05	34.22	34.08	34.01	34.10	0.11
7E-05	34.04	33.31	33.77	33.70	0.37
5E-05	33.35	33.39	33.24	33.33	0.08
3E-05	34.25	33.70	34.26	34.07	0.32
2E-05	34.68	34.80	34.26	34.58	0.28
1E-05	38.93	40.12	40.25	39.77	0.73
7E-06	47.19	48.19	47.12	47.50	0.60
3E-06	56.64	56.06	56.53	56.41	0.31
3E-03	32.78	32.64	32.71	32.71	0.07
1E-03	32.71	32.74	32.76	32.74	0.02

Table C-3 Surface tension measurement of C_{16-18}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Concentration (M)	Surface tension (mN/m)				SD
	Tube 1	Tube 2	Tube 3	Avg.	
3E-03	35.64	35.47	35.50	35.54	0.09
1E-03	37.10	36.61	-	36.86	0.35
3E-04	38.72	37.77	-	38.25	0.67
1E-04	38.86	38.41	-	38.64	0.32
3E-05	39.66	38.84	39.01	39.17	0.43
2E-05	40.02	40.50	-	40.26	0.34
1E-05	42.66	41.66	-	42.16	0.70
9E-06	43.24	43.85	44.19	43.76	0.48
7E-06	48.56	48.07	47.37	48.00	0.60
5E-06	51.55	51.24	50.90	51.23	0.32
3E-03	35.64	35.47	35.50	35.54	0.09
1E-03	37.10	36.61	-	36.86	0.35

Table C-4 Surface tension measurement of C_{16-17}-4PO-SO_4Na at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Concentration (M)	Surface tension (mN/m)				SD
	Tube 1	Tube 2	Tube 3	Avg.	
1E-06	58.27	61.41	64.36	61.35	3.05
3E-06	53.83	55.16	55.73	54.91	0.98
7E-06	45.99	46.45	47.05	46.49	0.54
1E-05	42.07	43.13	45.02	43.40	1.49
3E-05	37.59	37.59	37.45	37.55	0.08
7E-05	35.15	35.63	-	35.39	0.34
1E-04	34.86	34.55	-	34.70	0.22
2E-04	35.13	35.36	-	35.24	0.16
2E-04	35.40	35.34	-	35.37	0.04
3E-04	35.28	35.08	-	35.18	0.14
7E-04	34.33	34.20	-	34.26	0.09
1E-06	58.27	61.41	64.36	61.35	3.05

Table C-5 Adsorption of SDS at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Concentration (M)	Solution (ml)	Initial		Equilibrium		C_{in}-C_{eq} (M)	Mass (g)	q (mmloe/g)	pH equilibrium
		Area	Conc. (M)	Area	Conc. (M)				
7.00E-03	40	6493.01400	6.55E-03	6063.01400	6.12E-03	4.30E-04	0.1005	0.1711	8.05
4.00E-03	40	3463.01400	3.52E-03	3023.01400	3.08E-03	4.40E-04	0.1000	0.1760	8.03
2.00E-03	40	2918.33862	2.98E-03	2426.87671	2.48E-03	4.91E-04	0.1001	0.1964	8.12
1.00E-03	40	1323.74927	1.38E-03	981.42126	1.04E-03	3.42E-04	0.1000	0.1369	8.17
9.00E-04	40	1088.36462	1.15E-03	881.05109	9.38E-04	2.07E-04	0.0500	0.1659	8.11
7.00E-04	40	771.99890	8.29E-04	614.80713	6.72E-04	1.57E-04	0.0500	0.1258	8.10
6.00E-04	40	686.13202	7.43E-04	524.42731	5.81E-04	1.62E-04	0.0501	0.1291	8.09
5.00E-04	40	488.66336	5.46E-04	350.83542	4.08E-04	1.38E-04	0.0501	0.1100	8.15
3.00E-04	40	267.21317	3.24E-04	159.69017	2.17E-04	1.08E-04	0.0500	0.0860	8.15
2.00E-04	40	148.42099	2.05E-04	69.77895	1.27E-04	7.86E-05	0.0502	0.0627	8.20
1.00E-04	40	45.70126	1.03E-04	24.06188	8.10E-05	2.16E-05	0.0500	0.0173	8.01

Table C-6 Adsorption of $C_{16\text{-}17}$-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Concentration (M)	Solution (ml)	Initial		Equilibrium		C_{in}-C_{eq} (M)	Mass (g)	q (mmloe/g)	pH equilibrium
		Area	Conc. (M)	Area	Conc. (M)				
2.00E-04	40	65.6797	1.80E-04	58.9524	1.76E-04	3.36E-06	0.0050	0.0269	8.10
3.00E-04	40	204.3160	2.49E-04	189.7949	2.42E-04	7.26E-06	0.0104	0.0279	8.16
5.00E-04	40	516.9114	4.05E-04	473.0195	3.83E-04	2.19E-05	0.0104	0.0844	8.30
6.00E-04	40	723.1046	5.08E-04	673.9742	4.84E-04	2.46E-05	0.0098	0.1003	8.05
7.00E-04	40	926.4890	6.10E-04	862.1132	5.78E-04	3.22E-05	0.0100	0.1288	8.03
7.00E-04	40	927.4890	6.11E-04	862.7093	5.78E-04	3.24E-05	0.0103	0.1258	8.12
8.00E-04	40	1045.4346	6.70E-04	979.0328	6.36E-04	3.32E-05	0.0103	0.1289	8.16
8.00E-04	40	1045.4346	6.70E-04	977.2834	6.36E-04	3.41E-05	0.0101	0.1350	8.23
9.00E-04	40	1259.9856	7.77E-04	1189.4002	7.42E-04	3.53E-05	0.0100	0.1412	8.09
9.00E-04	40	1259.9856	7.77E-04	1190.9325	7.42E-04	3.45E-05	0.0103	0.1341	8.23
1.00E-03	40	763.4207	1.16E-03	575.1430	1.07E-03	9.41E-05	0.0302	0.1247	8.24
2.00E-03	40	2069.0037	1.81E-03	1882.9015	1.72E-03	9.31E-05	0.0300	0.1241	8.15
2.00E-03	40	2070.0037	1.81E-03	1880.0826	1.72E-03	9.50E-05	0.0302	0.1258	8.24
3.00E-03	40	3757.4692	2.66E-03	3528.2517	2.54E-03	1.15E-04	0.0299	0.1533	8.20
3.00E-03	40	3757.4692	2.66E-03	3520.8501	2.54E-03	1.18E-04	0.0303	0.1562	8.30
5.00E-03	40	7434.5503	4.50E-03	7232.6143	4.40E-03	1.01E-04	0.0299	0.1351	8.27
7.00E-03	40	11435.3000	6.50E-03	11240.6000	6.40E-03	9.73E-05	0.0300	0.1298	8.24

Table C-7 Adsorption of C_{16-18}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Concentration (M)	Solution (ml)	Initial		Equilibrium		C_{in}-C_{eq} (M)	Mass (g)	q (mmloe/g)	pH equilibrium
		Area	Conc. (M)	Area	Conc. (M)				
3.00E-04	40	249.89449	3.06E-04	246.5298	3.05E-04	1.68E-06	0.0051	0.013195	8.02
3.00E-04	40	255.36494	3.09E-04	251.4941	3.07E-04	1.94E-06	0.0049	0.015799	8.07
4.00E-04	40	408.59293	3.86E-04	350.6281	3.57E-04	2.90E-05	0.0098	0.118295	8.11
4.00E-04	40	403.99594	3.84E-04	356.849	3.60E-04	2.36E-05	0.0098	0.096218	8.15
5.00E-04	40	627.44708	4.95E-04	536.1216	4.50E-04	4.57E-05	0.0100	0.182651	8.20
7.00E-04	40	999.84210	6.81E-04	902.6213	6.33E-04	4.86E-05	0.0100	0.194442	8.27
7.00E-04	40	992.20825	6.78E-04	888.1114	6.26E-04	5.20E-05	0.0100	0.208194	8.25
1.70E-03	40	1740.37866	1.53E-03	1460.714	1.39E-03	1.40E-04	0.0301	0.185824	8.30
2.00E-03	40	2304.14282	1.81E-03	2024.712	1.67E-03	1.40E-04	0.0301	0.185668	8.33
3.00E-03	40	4042.77246	2.68E-03	3745.228	2.54E-03	1.49E-04	0.0303	0.196399	8.34
4.00E-03	40	5967.60840	3.65E-03	5415.294	3.37E-03	2.76E-04	0.0504	0.219172	8.33

Table C-8 Adsorption of C_{16-17}-4PO-SO_4Na at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Concentration (M)	Solution (ml)	Initial		Equilibrium		C_{in}-C_{eq} (M)	Mass (g)	q (mmloe/g)	Avg. q (mmloe/g)	pH equilibrium
		Area	Conc. (M)	Area	Conc. (M)					
3.00E-04	40	4.1906	3.15E-04	3.6052	2.87E-04	2.83E-05	0.0055	0.20559	0.2686	8.11
3.00E-04	40	4.4900	3.30E-04	3.7281	2.93E-04	3.68E-05	0.0051	0.28857		8.12
3.00E-04	40	4.6194	3.36E-04	3.7804	2.95E-04	4.05E-05	0.0052	0.31166		8.20
4.00E-04	40	6.4495	4.24E-04	5.5974	3.83E-04	4.11E-05	0.0049	0.33590	0.2984	8.33
4.00E-04	40	6.5003	4.27E-04	5.8009	3.93E-04	3.38E-05	0.0054	0.25018		8.23
4.00E-04	40	6.6810	4.36E-04	5.8808	3.97E-04	3.86E-05	0.0050	0.30914		8.23
5.00E-04	40	8.8766	5.42E-04	7.0890	4.55E-04	8.63E-05	0.0110	0.31391	0.3240	8.12
5.00E-04	40	8.8202	5.39E-04	6.9527	4.49E-04	9.02E-05	0.0108	0.33401		8.23
6.00E-04	40	10.7946	6.34E-04	8.3558	5.16E-04	1.18E-04	0.0134	0.35155	0.3581	8.34
6.00E-04	40	10.6114	6.25E-04	8.3458	5.16E-04	1.09E-04	0.0120	0.36469		8.23
7.00E-04	40	12.6005	7.21E-04	9.9889	5.95E-04	1.26E-04	0.0115	0.43866	0.3619	8.22
7.00E-04	40	11.9515	6.90E-04	9.9889	5.95E-04	9.48E-05	0.0133	0.28504		8.24
8.00E-04	40	14.5495	8.16E-04	11.9548	6.90E-04	1.25E-04	0.0107	0.46841	0.4355	8.30
8.00E-04	40	14.9747	8.36E-04	12.5130	7.17E-04	1.19E-04	0.0109	0.43625		8.12
8.00E-04	40	14.9159	8.33E-04	12.8348	7.33E-04	1.00E-04	0.0100	0.40199		8.13
9.00E-04	40	15.9712	8.84E-04	14.0700	7.92E-04	9.18E-05	0.0098	0.37473	0.3747	8.24
1.50E-03	40	23.9224	1.27E-03	21.2385	1.14E-03	1.30E-04	0.0106	0.48908	0.4891	8.22
2.00E-03	40	36.8068	1.89E-03	34.6362	1.79E-03	1.05E-04	0.0119	0.35233	0.5079	8.34
2.00E-03	40	37.5705	1.93E-03	34.6362	1.79E-03	1.42E-04	0.0115	0.49287		8.30
2.00E-03	40	38.3249	1.96E-03	34.6362	1.79E-03	1.78E-04	0.0105	0.67859		8.34
3.00E-03	40	60.4242	3.03E-03	57.2329	2.88E-03	1.54E-04	0.0120	0.51370	0.4778	8.23
3.00E-03	40	60.0391	3.01E-03	57.2329	2.88E-03	1.36E-04	0.0118	0.45937		8.34
3.00E-03	40	59.8298	3.00E-03	57.2329	2.88E-03	1.25E-04	0.0109	0.46020		8.23
5.00E-03	40	101.9768	5.04E-03	98.6348	4.88E-03	1.61E-04	0.0116	0.55651	0.5565	8.22

Table C-9 Styrene adsolubilization of SDS at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Styrene	Surf_initial		Surf_equilibrium		$Sur_{(in-eq)}$ (M)	Styrene_initial	Styrene_equilibrium		$Styrene_{(in-eq)}$
	(uL)	Area	Conc. (M)	Area	Conc. (M)		Conc. (M)	Area	Conc. (M)	(M)
1	5	903.73446	1.31E-03	807.72644	1.21E-03	9.60E-05	2.15E-03	1.44E+04	5.84E-04	1.57E-03
2	5	903.73446	1.31E-03	784.47192	1.19E-03	1.19E-04	2.15E-03	1.49E+04	6.06E-04	1.55E-03
3	6	903.73446	1.31E-03	815.96661	1.22E-03	8.78E-05	2.58E-03	1.67E+04	6.96E-04	1.89E-03
4	6	903.73446	1.31E-03	768.56879	1.17E-03	1.35E-04	2.58E-03	1.75E+04	7.39E-04	1.84E-03
5	7	903.73446	1.31E-03	793.82526	1.20E-03	1.10E-04	3.01E-03	1.86E+04	7.91E-04	2.22E-03
6	7	903.73446	1.31E-03	767.17236	1.17E-03	1.37E-04	3.01E-03	1.73E+04	7.29E-04	2.29E-03
7	8	903.73446	1.31E-03	797.45013	1.20E-03	1.06E-04	3.44E-03	2.02E+04	8.72E-04	2.57E-03
8	8	903.73446	1.31E-03	784.98706	1.19E-03	1.19E-04	3.44E-03	2.18E+04	9.51E-04	2.49E-03
9	9	903.73446	1.31E-03	785.98506	1.19E-03	1.18E-04	3.88E-03	2.13E+04	9.27E-04	2.95E-03
10	9	903.73446	1.31E-03	777.45227	1.18E-03	1.26E-04	3.88E-03	2.35E+04	1.04E-03	2.84E-03
11	12	903.73446	1.31E-03	764.69293	1.17E-03	1.39E-04	5.17E-03	2.36E+04	1.04E-03	4.13E-03
12	12	903.73446	1.31E-03	762.94427	1.17E-03	1.41E-04	5.17E-03	2.49E+04	1.11E-03	4.06E-03
13	13	903.73446	1.31E-03	763.27466	1.17E-03	1.40E-04	5.60E-03	2.37E+04	1.04E-03	4.55E-03
14	13	903.73446	1.31E-03	769.11313	1.17E-03	1.35E-04	5.60E-03	2.69E+04	1.21E-03	4.39E-03
15	15	903.73446	1.31E-03	762.94427	1.17E-03	1.41E-04	6.46E-03	2.45E+04	1.09E-03	5.37E-03
16	15	903.73446	1.31E-03	749.80939	1.16E-03	1.54E-04	6.46E-03	2.66E+04	1.19E-03	5.26E-03
17	17	903.73446	1.31E-03	743.11047	1.15E-03	1.61E-04	7.32E-03	2.55E+04	1.14E-03	6.18E-03
18	17	903.73446	1.31E-03	743.15991	1.15E-03	1.61E-04	7.32E-03	2.78E+04	1.25E-03	6.07E-03

Table C-9a Styrene adsolubilization of SDS at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	$Sur_{(in-eq)}$ (M)	$Styrene_{(in-eq)}$ (M)	X_{aq}	X_{adm}	Styrene equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	X_{adm} (stdev)	K_{adm}	log K_{adm}
1	0.0497	9.60E-05	1.57E-03	1.05E-05	0.94	5.95E-04	1.07E-05	0.9354	0.0098	87285.11	4.94
2	0.0496	1.19E-04	1.55E-03	1.09E-05	0.93						
3	0.0497	8.78E-05	1.89E-03	1.25E-05	0.96	7.17E-04	1.29E-05	0.9437	0.0169	73097.64	4.86
4	0.0497	1.35E-04	1.84E-03	1.33E-05	0.93						
5	0.0498	1.10E-04	2.22E-03	1.42E-05	0.95	7.60E-04	1.37E-05	0.9483	0.0066	69307.15	4.84
6	0.0498	1.37E-04	2.29E-03	1.31E-05	0.94						
7	0.0500	1.06E-04	2.57E-03	1.57E-05	0.96	9.12E-04	1.64E-05	0.9574	0.0041	58349.75	4.77
8	0.0500	1.19E-04	2.49E-03	1.71E-05	0.95						
9	0.0501	1.18E-04	2.95E-03	1.67E-05	0.96	9.81E-04	1.77E-05	0.9595	0.0030	54339.96	4.74
10	0.0501	1.26E-04	2.84E-03	1.86E-05	0.96						
11	0.0503	1.39E-04	4.13E-03	1.87E-05	0.97	1.07E-03	1.93E-05	0.9669	0.0007	50031.84	4.70
12	0.0503	1.41E-04	4.06E-03	1.99E-05	0.97						
13	0.0502	1.40E-04	4.55E-03	1.88E-05	0.97	1.13E-03	2.03E-05	0.9702	0.0001	47840.62	4.68
14	0.0502	1.35E-04	4.39E-03	2.18E-05	0.97						
15	0.0503	1.41E-04	5.37E-03	1.96E-05	0.97	1.14E-03	2.05E-05	0.9730	0.0020	47364.84	4.68
16	0.0503	1.54E-04	5.26E-03	2.15E-05	0.97						
17	0.0504	1.61E-04	6.18E-03	2.05E-05	0.97	1.19E-03	2.15E-05	0.9745	0.0003	45316.18	4.66
18	0.0504	1.61E-04	6.07E-03	2.25E-05	0.97						

K_{adm} from slope of isotherm = 3611.0

log K_{adm} = 3.56

Table C-10 Styrene adsolubilization of C_{16-17}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Styrene (uL)	Surf_initial		Surf_equilibrium		$Sur_{(in-eq)}$ (M)	Styrene_initial	Styrene_equilibrium		$Styrene_{(in-eq)}$ (M)
		Area	Conc. (M)	Area	Conc. (M)		Conc. (M)	Area	Conc. (M)	
1	6	962.77846	6.28E-04	796.32281	5.45E-04	8.32E-05	2.58E-03	1.84E+04	7.81E-04	1.80E-03
2	6	962.77846	6.28E-04	802.51837	5.48E-04	8.01E-05	2.58E-03	1.84E+04	7.84E-04	1.80E-03
3	6	962.77846	6.28E-04	763.91382	5.29E-04	9.94E-05	2.58E-03	1.85E+04	7.87E-04	1.80E-03
4	6.5	962.77846	6.28E-04	810.34180	5.52E-04	7.62E-05	2.80E-03	2.00E+04	8.63E-04	1.94E-03
5	6.5	962.77846	6.28E-04	810.96533	5.52E-04	7.59E-05	2.80E-03	1.93E+04	8.25E-04	1.97E-03
6	6.5	962.77846	6.28E-04	728.68530	5.11E-04	1.17E-04	2.80E-03	2.00E+04	8.62E-04	1.94E-03
7	7	962.77846	6.28E-04	743.96362	5.19E-04	1.09E-04	3.01E-03	2.05E+04	8.86E-04	2.13E-03
8	7	962.77846	6.28E-04	806.78546	5.50E-04	7.80E-05	3.01E-03	2.16E+04	9.42E-04	2.07E-03
9	7	962.77846	6.28E-04	790.44458	5.42E-04	8.62E-05	3.01E-03	2.18E+04	9.52E-04	2.06E-03
10	8	962.77846	6.28E-04	824.56116	5.59E-04	6.91E-05	3.44E-03	2.44E+04	1.08E-03	2.36E-03
11	8	962.77846	6.28E-04	761.66504	5.28E-04	1.01E-04	3.44E-03	2.44E+04	1.08E-03	2.36E-03
12	8	962.77846	6.28E-04	811.78497	5.53E-04	7.55E-05	3.44E-03	2.48E+04	1.10E-03	2.34E-03
13	9	962.77846	6.28E-04	800.26904	5.47E-04	8.13E-05	3.88E-03	2.67E+04	1.20E-03	2.68E-03
14	9	962.77846	6.28E-04	818.94910	5.56E-04	7.19E-05	3.88E-03	2.68E+04	1.20E-03	2.67E-03
15	9	962.77846	6.28E-04	783.35669	5.39E-04	8.97E-05	3.88E-03	2.69E+04	1.21E-03	2.67E-03

Table C-10a Styrene adsolubilization of C_{16-17}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Styrene (uL)	Surf_initial		Surf_equilibrium		$Sur_{(in-eq)}$ (M)	Styrene_initial	Styrene_equilibrium		$Styrene_{(in-eq)}$ (M)
		Area	Conc. (M)	Area	Conc. (M)		Conc. (M)	Area	Conc. (M)	
16	10	962.77846	6.28E-04	766.68805	5.30E-04	9.80E-05	4.31E-03	2.41E+04	1.07E-03	3.24E-03
17	10	962.77846	6.28E-04	715.54645	5.05E-04	1.24E-04	4.31E-03	2.47E+04	1.10E-03	3.21E-03
18	11	962.77846	6.28E-04	673.74878	4.84E-04	1.45E-04	4.74E-03	2.51E+04	1.11E-03	3.62E-03
19	11	962.77846	6.28E-04	728.30878	5.11E-04	1.17E-04	4.74E-03	2.59E+04	1.16E-03	3.58E-03
20	11	962.77846	6.28E-04	812.03662	5.53E-04	7.54E-05	4.74E-03	2.46E+04	1.09E-03	3.64E-03
21	12	962.77846	6.28E-04	750.56342	5.22E-04	1.06E-04	5.17E-03	2.81E+04	1.27E-03	3.90E-03
22	12	962.77846	6.28E-04	778.74817	5.36E-04	9.20E-05	5.17E-03	2.85E+04	1.29E-03	3.88E-03
23	12	962.77846	6.28E-04	773.08502	5.33E-04	9.48E-05	5.17E-03	2.91E+04	1.32E-03	3.85E-03
24	13	962.77846	6.28E-04	777.92426	5.36E-04	9.24E-05	5.60E-03	3.07E+04	1.40E-03	4.20E-03
25	13	962.77846	6.28E-04	765.16809	5.30E-04	9.88E-05	5.60E-03	3.14E+04	1.43E-03	4.17E-03
26	15	962.77846	6.28E-04	827.75153	5.61E-04	6.75E-05	6.46E-03	3.30E+04	1.51E-03	4.94E-03
27	15	962.77846	6.28E-04	791.14709	5.43E-04	8.58E-05	6.46E-03	3.30E+04	1.51E-03	4.95E-03

Table C-10b Styrene adsolubilization of C_{16-17}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	$Sur_{(in-eq)}$ (M)	$Styrene_{(in-eq)}$ (M)	X_{aq}	X_{adm}	Styrene equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	X_{adm} (stdev)	K_{adm}	log K_{adm}
1	0.0099	8.32E-05	1.80E-03	1.41E-05	0.96	7.84E-04	1.41E-05	0.954	0.005	67567.2	4.83
2	0.0110	8.01E-05	1.80E-03	1.41E-05	0.96						
3	0.0101	9.94E-05	1.80E-03	1.42E-05	0.95						
4	0.0102	7.62E-05	1.94E-03	1.55E-05	0.96	8.50E-04	1.53E-05	0.956	0.011	62491.1	4.80
5	0.0102	7.59E-05	1.97E-03	1.48E-05	0.96						
6	0.0102	1.17E-04	1.94E-03	1.55E-05	0.94						
7	0.0104	1.09E-04	2.13E-03	1.6E-05	0.95	9.27E-04	1.67E-05	0.958	0.006	57443.4	4.76
8	0.0102	7.80E-05	2.07E-03	1.7E-05	0.96						
9	0.0103	8.62E-05	2.06E-03	1.71E-05	0.96						
10	0.0104	6.91E-05	2.36E-03	1.95E-05	0.97	1.09E-03	1.96E-05	0.967	0.007	49346.4	4.69
11	0.0104	1.01E-04	2.36E-03	1.95E-05	0.96						
12	0.0104	7.55E-05	2.34E-03	1.98E-05	0.97						
13	0.0105	8.13E-05	2.68E-03	2.15E-05	0.97	1.20E-03	2.16E-05	0.971	0.003	44870.4	4.65
14	0.0104	7.19E-05	2.67E-03	2.16E-05	0.97						
15	0.0104	8.97E-05	2.67E-03	2.17E-05	0.97						

Table C-10c Styrene adsolubilization of C_{16-17}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	Sur$_{(in-eq)}$ (M)	Styrene$_{(in-eq)}$ (M)	X_{aq}	X_{adm}	Styrene equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	X_{adm} (stdev)	K_{adm}	log K_{adm}
16	0.0100	9.80E-05	3.24E-03	1.92E-05	0.97	1.08E-03	1.95E-05	0.967	0.005	49651.3	4.70
17	0.0101	1.24E-04	3.21E-03	1.97E-05	0.96						
18	0.0101	1.45E-04	3.62E-03	2.01E-05	0.96	1.12E-03	2.02E-05	0.970	0.009	48023.2	4.68
19	0.0101	1.17E-04	3.58E-03	2.09E-05	0.97						
20	0.0102	7.54E-05	3.64E-03	1.97E-05	0.98						
21	0.0103	1.06E-04	3.90E-03	2.28E-05	0.97	1.29E-03	2.33E-05	0.975	0.002	41941.0	4.62
22	0.0103	9.20E-05	3.88E-03	2.32E-05	0.98						
23	0.0103	9.48E-05	3.85E-03	2.37E-05	0.98						
24	0.0103	9.24E-05	4.20E-03	2.51E-05	0.98	1.41E-03	2.55E-05	0.978	0.001	38390.3	4.58
25	0.0103	9.88E-05	4.17E-03	2.58E-05	0.98						
26	0.0104	6.75E-05	4.94E-03	2.73E-05	0.99	1.51E-03	2.72E-05	0.985	0.003	36143.6	4.56
27	0.0103	8.58E-05	4.95E-03	2.72E-05	0.98						

K_{adm} from slope of isotherm = 2339.2

log K_{adm} = 3.37

Table C-11 Styrene adsolubilization of C_{16-18}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Styrene (uL)	Surf_initial		Surf_equilirium		$Sur_{(in-eq)}$ (M)	Styrene_initial	Styrene_equilibrium		$Styrene_{(in-eq)}$ (M)
		Area	Conc. (M)	Area	Conc. (M)		Conc. (M)	Area	Conc. (M)	
1	7	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	3.01E-03	2.16E+04	9.44E-04	2.07E-03
2	7	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	3.01E-03	2.12E+04	9.21E-04	2.09E-03
3	7	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	3.01E-03	2.07E+04	8.97E-04	2.12E-03
4	8	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	3.44E-03	1.94E+04	8.34E-04	2.61E-03
5	8	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	3.44E-03	2.45E+04	1.08E-03	2.36E-03
6	8	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	3.44E-03	2.45E+04	1.09E-03	2.36E-03
7	9	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	3.88E-03	2.85E+04	1.29E-03	2.59E-03
8	9	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	3.88E-03	2.88E+04	1.30E-03	2.58E-03
9	9	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	3.88E-03	2.79E+04	1.26E-03	2.62E-03
10	10	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	4.31E-03	3.02E+04	1.37E-03	2.93E-03
11	10	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	4.31E-03	2.99E+04	1.36E-03	2.95E-03
12	10	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	4.31E-03	3.10E+04	1.41E-03	2.90E-03

Table C-11a Styrene adsolubilization of C_{16-18}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Styrene (uL)	Surf_initial		Surf_equilibrium		$Sur_{(in-eq)}$ (M)	Styrene_initial	Styrene_equilibrium		$Styrene_{(in-eq)}$ (M)
		Area	Conc. (M)	Area	Conc. (M)		Conc. (M)	Area	Conc. (M)	
13	11	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	4.74E-03	3.20E+04	1.46E-03	3.28E-03
14	11	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	4.74E-03	3.88E+04	1.80E-03	2.93E-03
15	11	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	4.74E-03	3.30E+04	1.51E-03	3.23E-03
16	12	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	5.17E-03	3.36E+04	1.54E-03	3.62E-03
17	12	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	5.17E-03	3.25E+04	1.49E-03	3.68E-03
18	12	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	5.17E-03	3.38E+04	1.55E-03	3.61E-03
19	13	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	5.60E-03	3.68E+04	1.70E-03	3.89E-03
20	13	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	5.60E-03	3.63E+04	1.68E-03	3.92E-03
21	13	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	5.60E-03	3.65E+04	1.69E-03	3.91E-03
22	15	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	6.46E-03	4.00E+04	1.86E-03	4.60E-03
23	15	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	6.46E-03	4.00E+04	1.86E-03	4.60E-03
24	15	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	6.46E-03	4.01E+04	1.87E-03	4.59E-03
25	17	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	7.32E-03	4.30E+04	2.01E-03	5.31E-03
26	17	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	7.32E-03	4.34E+04	2.03E-03	5.29E-03
27	17	621.04177	4.92E-04	516.2206	4.40E-04	5.24E-05	7.32E-03	4.24E+04	1.98E-03	5.34E-03

Table C-11b Styrene adsolubilization of C_{16-18}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	$Sur_{(in-eq)}$ (M)	$Styrene_{(in-eq)}$ (M)	X_{aq}	X_{adm}	Styrene equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	X_{adm} (stdev)	K_{adm}	log K_{adm}
1	0.0116	5.24E-05	2.07E-03	1.70E-05	0.98	9.21E-04	1.66E-05	0.98	0.00026	5.89E+04	4.77
2	0.0122	5.24E-05	2.09E-03	1.66E-05	0.98						
3	0.0127	5.24E-05	2.12E-03	1.62E-05	0.98						
4	0.0122	5.24E-05	2.61E-03	-	0.98	1.00E-03	1.95E-05	0.98	0.00118	5.01E+04	4.70
5	0.0117	5.24E-05	2.36E-03	1.95E-05	0.98						
6	0.0117	5.24E-05	2.36E-03	1.95E-05	0.98						
7	0.0116	5.24E-05	2.59E-03	2.32E-05	0.98	1.28E-03	2.31E-05	0.98	0.00017	4.25E+04	4.63
8	0.0121	5.24E-05	2.58E-03	2.34E-05	0.98						
9	0.0117	5.24E-05	2.62E-03	2.26E-05	0.98						
10	0.0119	5.24E-05	2.93E-03	2.47E-05	0.98	1.38E-03	2.48E-05	0.98	0.00016	3.96E+04	4.60
11	0.0117	5.24E-05	2.95E-03	2.44E-05	0.98						
12	0.0121	5.24E-05	2.90E-03	2.54E-05	0.98						

Table C-11c Styrene adsolubilization of C_{16-18}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	$Sur_{(in-eq)}$ (M)	$Styrene_{(in-eq)}$ (M)	X_{aq}	X_{adm}	Styrene equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	SD	K_{adm}	log K_{adm}
13	0.0121	5.24E-05	3.28E-03	2.63E-05	0.98	1.59E-03	2.67E-05	0.98	0.00098	3.68E+04	4.57
14	0.0115	5.24E-05	2.93E-03	-	0.98						
15	0.0116	5.24E-05	3.23E-03	2.72E-05	0.98						
16	0.0124	5.24E-05	3.62E-03	2.78E-05	0.99	1.53E-03	2.75E-05	0.99	0.00014	3.59E+04	4.55
17	0.0117	5.24E-05	3.68E-03	2.67E-05	0.99						
18	0.0125	5.24E-05	3.61E-03	2.79E-05	0.99						
19	0.012	5.24E-05	3.89E-03	3.07E-05	0.99	1.69E-03	3.04E-05	0.99	0.00005	3.25E+04	4.51
20	0.0122	5.24E-05	3.92E-03	3.02E-05	0.99						
21	0.0107	5.24E-05	3.91E-03	3.04E-05	0.99						
22	0.0111	5.24E-05	4.60E-03	3.35E-05	0.99	1.86E-03	3.35E-05	0.99	0.00001	2.95E+04	4.47
23	0.0114	5.24E-05	4.60E-03	3.35E-05	0.99						
24	0.0109	5.24E-05	4.59E-03	3.36E-05	0.99						
25	0.0117	5.24E-05	5.31E-03	3.62E-05	0.99	2.01E-03	3.61E-05	0.99	0.00005	2.74E+04	4.44
26	0.0118	5.24E-05	5.29E-03	3.65E-05	0.99						
27	0.0121	5.24E-05	5.34E-03	3.56E-05	0.99						

K_{adm} from slope of isotherm = 745.31

log K_{adm} = 2.87

Table C-12 Styrene adsolubilization of C_{16-17}-4PO-SO_4Na at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Styrene (uL)	Surf_initial		Surf_equilibrium		$Sur_{(in-eq)}$ (M)	Styrene_initial	Styrene_equilibrium		$Styrene_{(in-eq)}$ (M)
		Area	Conc. (M)	Area	Conc. (M)		Conc. (M)	Area	Conc. (M)	
1	6	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	2.58E-03	2.21E+04	9.67E-04	1.62E-03
2	6	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	2.58E-03	2.19E+04	9.58E-04	1.63E-03
3	6.5	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	2.80E-03	2.41E+04	1.07E-03	1.73E-03
4	6.5	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	2.80E-03	2.38E+04	1.05E-03	1.75E-03
5	7	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	3.01E-03	2.59E+04	1.16E-03	1.86E-03
6	7	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	3.01E-03	2.55E+04	1.14E-03	1.88E-03
7	8	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	3.44E-03	2.91E+04	1.32E-03	2.13E-03
8	8	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	3.44E-03	2.93E+04	1.33E-03	2.12E-03
9	9	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	3.88E-03	3.22E+04	1.47E-03	2.40E-03
10	9	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	3.88E-03	3.24E+04	1.48E-03	2.39E-03
11	10	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	4.31E-03	3.54E+04	1.63E-03	2.68E-03
12	10	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	4.31E-03	3.49E+04	1.61E-03	2.70E-03
13	11	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	4.74E-03	3.77E+04	1.75E-03	2.99E-03
14	11	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	4.74E-03	3.83E+04	1.78E-03	2.96E-03
15	12	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	5.17E-03	4.06E+04	1.89E-03	3.28E-03
16	12	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	5.17E-03	4.13E+04	1.93E-03	3.24E-03
17	13	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	5.60E-03	4.18E+04	1.95E-03	3.65E-03
18	13	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	5.60E-03	4.32E+04	2.02E-03	3.58E-03
19	15	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	6.46E-03	4.71E+04	2.22E-03	4.24E-03
20	15	12.7117	7.27E-04	10.751	6.32E-04	9.47E-05	6.46E-03	4.67E+04	2.20E-03	4.26E-03

Table C-12a Styrene adsolubilization of C_{16-17}-4PO-SO_4Na at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	$Sur_{(in-eq)}$ (M)	$Styrene_{(in-eq)}$ (M)	X_{aq}	X_{adm}	Styrene equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	SD	K_{adm}	log K_{adm}
1	0.0123	9.47E-05	1.62E-03	1.74E-05	0.94	9.62E-04	1.73E-05	0.9448	0.00020	5.45E+04	4.74
2	0.0130	9.47E-05	1.63E-03	1.72E-05	0.94						
3	0.0119	9.47E-05	1.73E-03	1.92E-05	0.95	1.06E-03	1.91E-05	0.9484	0.00030	4.97E+04	4.70
4	0.0104	9.47E-05	1.75E-03	1.89E-05	0.95						
5	0.0106	9.47E-05	1.86E-03	2.08E-05	0.95	1.15E-03	2.06E-05	0.9517	0.00031	4.61E+04	4.66
6	0.0115	9.47E-05	1.88E-03	2.05E-05	0.95						
7	0.0114	9.47E-05	2.13E-03	2.37E-05	0.96	1.32E-03	2.38E-05	0.9573	0.00015	4.02E+04	4.60
8	0.0112	9.47E-05	2.12E-03	2.39E-05	0.96						
9	0.0129	9.47E-05	2.40E-03	2.65E-05	0.96	1.48E-03	2.66E-05	0.9620	0.00011	3.62E+04	4.56
10	0.0119	9.47E-05	2.39E-03	2.67E-05	0.96						
11	0.0134	9.47E-05	2.68E-03	2.93E-05	0.97	1.62E-03	2.91E-05	0.9660	0.00021	3.32E+04	4.52
12	0.0136	9.47E-05	2.70E-03	2.89E-05	0.97						
13	0.0118	9.47E-05	2.99E-03	3.14E-05	0.97	1.76E-03	3.17E-05	0.9692	0.00021	3.06E+04	4.49
14	0.0110	9.47E-05	2.96E-03	3.20E-05	0.97						
15	0.0114	9.47E-05	3.28E-03	3.40E-05	0.97	1.91E-03	3.44E-05	0.9718	0.00022	2.83E+04	4.45
16	0.0117	9.47E-05	3.24E-03	3.47E-05	0.97						
17	0.0114	9.47E-05	3.65E-03	3.51E-05	0.97	1.99E-03	3.57E-05	0.9745	0.00034	2.73E+04	4.44
18	0.0119	9.47E-05	3.58E-03	3.64E-05	0.97						
19	0.0125	9.47E-05	4.24E-03	3.99E-05	0.98	2.21E-03	3.97E-05	0.9782	0.00007	2.46E+04	4.39
20	0.0117	9.47E-05	4.26E-03	3.95E-05	0.98						

K_{adm} from slope of isotherm = 1501.00

log K_{adm} = 3.18

Table C-13 Phenanthrene adsolubilization of SDS at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Surf_initial		Surf_equilibrium		Sur$_{\text{(in-eq)}}$ (M)	Phenan_initial (M)	Phenen_equilibrium (M)	phenan$_{\text{(in-eq)}}$ (M)
	Area	Conc. (M)	Area	Conc. (M)				
1	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	1.68E-07	8.98E-08	7.86E-08
2	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	1.68E-07	6.17E-08	1.07E-07
3	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	1.68E-07	-	-
4	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	2.81E-07	2.47E-07	3.37E-08
5	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	2.81E-07	1.29E-07	1.51E-07
6	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	2.81E-07	8.98E-08	1.91E-07
7	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	5.05E-07	2.41E-07	2.64E-07
8	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	5.05E-07	2.08E-07	2.97E-07
9	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	5.05E-07	2.30E-07	2.75E-07
13	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	7.29E-07	2.47E-07	4.83E-07
14	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	7.29E-07	3.93E-07	3.37E-07
15	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	7.29E-07	4.43E-07	2.86E-07
19	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	9.54E-07	5.95E-07	3.59E-07
20	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	9.54E-07	4.43E-07	5.11E-07
21	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	9.54E-07	4.99E-07	4.54E-07
22	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	1.12E-06	5.95E-07	5.27E-07
23	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	1.12E-06	4.88E-07	6.34E-07
24	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	1.12E-06	5.67E-07	5.55E-07
28	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	1.40E-06	7.63E-07	6.40E-07
29	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	1.40E-06	6.79E-07	7.24E-07
30	903.73446	1.31E-03	777.4523	1.18E-03	1.29E-04	1.40E-06	6.96E-07	7.07E-07

Table C-13a Phenanthrene adsolubilization of SDS at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Sur$_{(in-eq)}$ (M)	phenan$_{(in-eq)}$ (M)	Alumina (g)	X$_{aq}$	X$_{adm}$	Phenan eq. (M)	Avg. X$_{aq}$	Avg. X$_{adm}$	X$_{adm}$ (stdev)	K$_{adm}$	log K$_{adm}$
1	1.29E-04	7.86E-08	0.0512	1.62E-09	6.10E-04	7.57E-08	1.36E-09	7.19E-04	1.54E-04	5.28E+05	5.72
2	1.29E-04	1.07E-07	0.0510	1.11E-09	8.28E-04						
3	1.29E-04	-	-	-	-						
4	1.29E-04	3.37E-08	0.0517	4.44E-09	2.62E-04	1.55E-07	2.79E-09	9.73E-04	6.35E-04	3.48E+05	5.54
5	1.29E-04	1.51E-07	0.0518	2.32E-09	1.18E-03						
6	1.29E-04	1.91E-07	-	1.62E-09	1.48E-03						
7	1.29E-04	2.64E-07	0.0507	4.34E-09	2.05E-03	2.26E-07	4.07E-09	2.16E-03	1.33E-04	5.31E+05	5.72
8	1.29E-04	2.97E-07	0.0528	3.74E-09	2.31E-03						
9	1.29E-04	2.75E-07	0.0511	4.14E-09	2.13E-03						
13	1.29E-04	4.83E-07	0.0516	4.44E-09	3.74E-03	3.61E-07	6.50E-09	2.86E-03	7.88E-04	4.40E+05	5.64
14	1.29E-04	3.37E-07	0.0530	7.07E-09	2.61E-03						
15	1.29E-04	2.86E-07	0.0529	7.98E-09	2.22E-03						
19	1.29E-04	3.59E-07	0.0520	1.07E-08	2.78E-03	5.12E-07	9.22E-09	3.42E-03	5.92E-04	3.71E+05	5.57
20	1.29E-04	5.11E-07	0.0530	7.98E-09	3.95E-03						
21	1.29E-04	4.54E-07	0.0525	8.99E-09	3.52E-03						
22	1.29E-04	5.27E-07	0.0511	1.07E-08	4.08E-03	5.50E-07	9.90E-09	4.43E-03	4.26E-04	4.48E+05	5.65
23	1.29E-04	6.34E-07	0.0524	8.79E-09	4.91E-03						
24	1.29E-04	5.55E-07	0.0521	1.02E-08	4.30E-03						
28	1.29E-04	6.40E-07	0.0509	1.37E-08	4.95E-03	7.13E-07	1.28E-08	5.34E-03	3.43E-04	4.16E+05	5.62
29	1.29E-04	7.24E-07	0.0500	1.22E-08	5.60E-03						
30	1.29E-04	7.07E-07	0.0521	1.25E-08	5.48E-03						

K$_{adm}$ from slope of isotherm = 40303
log K$_{adm}$ = 4.61

Table C-14 Phenanthrene adsolubilization of C_{16-17}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Surf_initial		Surf_equilibrium		$Sur_{(in-eq)}$ (M)	Phenan_initial	Phenan_equilibrium	$Phenan_{(in-eq)}$ (M)
	Area	Conc. (M)	Area	Conc. (M)		conc. (M)	conc. (M)	
1	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	2.81E-07	1.18E-07	1.63E-07
2	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	2.81E-07	1.23E-07	1.57E-07
3	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	2.81E-07	1.18E-07	1.63E-07
4	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	5.61E-07	2.13E-07	3.48E-07
5	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	5.61E-07	2.08E-07	3.53E-07
6	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	5.61E-07	-	-
7	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	8.42E-07	-	-
8	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	8.42E-07	3.93E-07	4.49E-07
9	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	8.42E-07	4.54E-07	3.87E-07
10	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	1.12E-06	5.78E-07	5.44E-07
11	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	1.12E-06	5.67E-07	5.55E-07
12	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	1.12E-06	-	-
13	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	1.29E-06	7.29E-07	5.61E-07
14	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	1.29E-06	6.56E-07	6.34E-07
15	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	1.29E-06	-	-
16	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	1.40E-06	7.29E-07	6.73E-07
17	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	1.40E-06	7.74E-07	6.28E-07
18	962.77846	6.28E-04	777.9243	5.36E-04	9.20E-05	1.40E-06	7.80E-07	6.23E-07

Table C-14a Phenanthrene adsolubilization of C_{16-17}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Sur$_{(in-final)}$ (M)	Phenan$_{(in-final)}$ (M)	Alumina (g)	X_{aq}	X_{adm}	Phenan eq. (M)	Avg. X_{aq}	Avg. X_{adm}	X_{adm} (stdev)	K_{adm}	log K_{adm}
1	9.20E-05	1.63E-07	0.0117	2.12E-09	1.77E-03	1.20E-07	2.15E-09	1.75E-03	3.51E-05	8.10E+05	5.91
2	9.20E-05	1.57E-07	0.0116	2.22E-09	1.70E-03						
3	9.20E-05	1.63E-07	0.0120	2.12E-09	1.77E-03						
4	9.20E-05	3.48E-07	0.0131	3.84E-09	3.77E-03	2.10E-07	3.79E-09	3.80E-03	4.28E-05	1.00E+06	6.00
5	9.20E-05	3.53E-07	0.0108	3.74E-09	3.83E-03						
6	9.20E-05	-	0.0136	-	-						
7	9.20E-05	-	0.0113	-	-	4.24E-07	7.63E-09	4.52E-03	4.70E-04	5.93E+05	5.77
8	9.20E-05	4.49E-07	0.0108	7.07E-09	4.86E-03						
9	9.20E-05	3.87E-07	0.0100	8.18E-09	4.19E-03						
10	9.20E-05	5.44E-07	0.0105	1.04E-08	5.89E-03	5.72E-07	1.03E-08	5.94E-03	8.52E-05	5.77E+05	5.76
11	9.20E-05	5.55E-07	0.0105	1.02E-08	6.00E-03						
12	9.20E-05	-	0.0101	-	-						
13	9.20E-05	5.61E-07	0.0125	1.31E-08	6.06E-03	6.93E-07	1.25E-08	6.45E-03	5.53E-04	5.17E+05	5.71
14	9.20E-05	6.34E-07	0.0106	1.18E-08	6.84E-03						
15	9.20E-05	-	0.0127	-	-						
16	9.20E-05	6.73E-07	0.0130	1.31E-08	7.27E-03	7.61E-07	1.37E-08	6.92E-03	2.97E-04	5.05E+05	5.70
17	9.20E-05	6.28E-07	0.0111	1.39E-08	6.78E-03						
18	9.20E-05	6.23E-07	0.0128	1.40E-08	6.72E-03						

K_{adm} from slope of isotherm = 40410

log K_{adm} = 4.61

Table C-15 Phenanthrene adsolubilization of C_{16-18}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Surf_initial		Surf_equilibrium		$Sur_{(in-eq)}$ (M)	Phenan_initial	Phenan_equilibrium	$Phenan_{(in-eq)}$ (M)
	Area	Conc. (M)	Area	Conc. (M)		conc. (M)	conc. (M)	
1	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	5.61E-07	1.29E-07	4.32E-07
2	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	5.61E-07	1.96E-07	3.65E-07
3	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	5.61E-07	2.58E-07	3.03E-07
4	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	7.29E-07	3.09E-07	4.21E-07
5	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	7.29E-07	2.81E-07	4.49E-07
6	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	7.29E-07	2.92E-07	4.38E-07
7	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	8.42E-07	3.53E-07	4.88E-07
8	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	8.42E-07	4.15E-07	4.26E-07
9	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	8.42E-07	3.93E-07	4.49E-07
10	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	9.54E-07	5.72E-07	3.82E-07
11	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	9.54E-07	4.26E-07	5.27E-07
12	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	9.54E-07	4.94E-07	4.60E-07
19	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	1.40E-06	7.57E-07	6.45E-07
20	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	1.40E-06	7.52E-07	6.51E-07
21	632.54177	4.92E-04	516.2206	4.40E-04	5.24E-05	1.40E-06	7.97E-07	6.06E-07

Table C-15a Phenanthrene adsolubilization of C_{16-18}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	$Sur_{(in-final)}$ (M)	$Phenan_{(in-final)}$ (M)	Alumina (g)	Phenan eq. (M)	Avg. X_{aq}	Avg. X_{adm}	X_{adm} (stdev)	K_{adm}	log K_{adm}
1	5.24E-05	4.32E-07	0.0131	1.95E-07	3.50E-09	0.00694	0.0008	1.98E+06	6.30
2	5.24E-05	3.65E-07	0.0127						
3	5.24E-05	3.03E-07	0.0125						
4	5.24E-05	4.21E-07	0.0098	2.94E-07	5.29E-09	0.00825	0.0003	1.56E+06	6.19
5	5.24E-05	4.49E-07	0.0115						
6	5.24E-05	4.38E-07	0.0134						
7	5.24E-05	4.88E-07	0.0105	3.87E-07	6.97E-09	0.00860	0.0006	1.23E+06	6.09
8	5.24E-05	4.26E-07	0.0118						
9	5.24E-05	4.49E-07	0.0135						
10	5.24E-05	3.82E-07	0.0116	4.97E-07	8.96E-09	0.00863	0.0009	9.64E+05	5.98
11	5.24E-05	5.27E-07	0.0112						
12	5.24E-05	4.60E-07	0.0125						
19	5.24E-05	6.45E-07	0.0109	7.69E-07	1.38E-08	0.01195	0.0005	8.64E+05	5.94
20	5.24E-05	6.51E-07	0.0106						
21	5.24E-05	6.06E-07	0.0127						

K_{adm} from slope of isotherm = 44923

log K_{adm} = 4.65

Table C-16 Phenanthrene adsolubilization of $C_{16\text{-}17}$-4PO-SO_4Na at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Surf_initial		Surf_eq		Sur$_{(in\text{-}eq)}$ (M)	Phenan_initial	Phenan_eq.	Phenan$_{(in\text{-}eq)}$ (M)
	Area	Conc. (M)	Area	Conc.(M)		Conc. (M)	Conc. (M)	
1	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	6.73E-07	-	-
2	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	6.73E-07	1.35E-07	5.39E-07
3	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	6.73E-07	1.57E-07	5.16E-07
4	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	7.29E-07	1.91E-07	5.39E-07
5	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	7.29E-07	-	-
6	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	7.29E-07	2.36E-07	4.94E-07
7	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	8.42E-07	2.30E-07	6.12E-07
8	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	8.42E-07	1.68E-07	6.73E-07
9	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	8.42E-07	1.85E-07	6.56E-07
10	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	9.54E-07	3.09E-07	6.45E-07
11	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	9.54E-07	-	-
12	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	9.54E-07	2.86E-07	6.68E-07
13	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	1.01E-06	3.25E-07	6.85E-07
14	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	1.01E-06	3.76E-07	6.34E-07
15	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	1.01E-06	-	-
16	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	1.12E-06	2.47E-07	8.75E-07
17	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	1.12E-06	3.25E-07	7.97E-07
18	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	1.12E-06	3.09E-07	8.14E-07
19	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	1.29E-06	2.86E-07	1.00E-06
20	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	1.29E-06	4.10E-07	8.81E-07
21	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	1.29E-06	3.93E-07	8.98E-07
22	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	1.40E-06	4.15E-07	9.87E-07
23	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	1.40E-06	5.33E-07	8.70E-07
24	12.71170	7.27E-04	10.751	6.32E-04	9.47E-05	1.40E-06	3.09E-07	1.09E-06

Table C-16a Phenanthrene adsolubilization of C_{16-17}-4PO-SO_4Na at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	$Sur_{(in-eq)}$ (M)	$Phenan_{(in-eq)}$ (M)	Alumina (g)	Phenan eq. (M)	Avg. X_{aq}	Avg. X_{adm}	X_{adm} (stdev)	K_{adm}	log K_{adm}
1	9.47E-05	6.73E-07	0.0110	9.73E-08	1.75E-09	6.05E-03	1.66E-04	3.45E+06	6.54
2	9.47E-05	5.39E-07	0.0105						
3	9.47E-05	5.16E-07	0.0100						
4	9.47E-05	5.39E-07	0.0113	1.42E-07	2.56E-09	6.16E-03	3.32E-04	2.41E+06	6.38
5	9.47E-05	7.29E-07	0.0110						
6	9.47E-05	4.94E-07	0.0110						
7	9.47E-05	6.12E-07	0.0101	1.95E-07	3.50E-09	6.79E-03	3.32E-04	1.94E+06	6.29
8	9.47E-05	6.73E-07	0.0109						
9	9.47E-05	6.56E-07	0.0114						
10	9.47E-05	6.45E-07	0.0106	1.98E-07	3.57E-09	7.91E-03	1.65E-04	2.22E+06	6.35
11	9.47E-05	9.54E-07	0.0123						
12	9.47E-05	6.68E-07	0.0104						
13	9.47E-05	6.85E-07	0.0119	2.34E-07	4.21E-09	8.13E-03	3.72E-04	1.93E+06	6.29
14	9.47E-05	6.34E-07	0.0137						
15	9.47E-05	1.01E-06	0.0104						

Table C-16b Phenanthrene adsolubilization of C_{16-17}-4PO-SO_4Na at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	$Sur_{(in-eq)}$ (M)	$Phenan_{(in-eq)}$ (M)	Alumina (g)	Phenan eq. (M)	Avg. X_{aq}	Avg. X_{adm}	X_{adm} (stdev)	K_{adm}	log K_{adm}
16	9.47E-05	8.75E-07	0.0122	2.94E-07	5.29E-09	8.67E-03	4.29E-04	1.64E+06	6.22
17	9.47E-05	7.97E-07	0.0099						
18	9.47E-05	8.14E-07	0.0113						
19	9.47E-05	1.00E-06	0.0106	3.63E-07	6.53E-09	9.70E-03	6.93E-04	1.49E+06	6.17
20	9.47E-05	8.81E-07	0.0106						
21	9.47E-05	8.98E-07	0.0099						
22	9.47E-05	9.87E-07	0.0107	4.19E-07	7.54E-09	1.03E-02	1.64E-03	1.36E+06	6.13
23	9.47E-05	8.70E-07	0.0133						
24	9.47E-05	1.09E-06	0.0105						

K_{adm} from slope of isotherm = 80618
log K_{adm} = 4.91

Table C-17 Styrene solubilization of SDS at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Styrene (uL)	Surfactant concentration (M)	Styrene initial (M)	Styrene equilibrium			
				Area	Conc. (M)	Conc.$_{avg}$ (M)	SD
1	20	1.00E-03	8.61E-03	2.58E+04	4.56E-04	2.26	1.56
2	20		8.61E-03	3.68E+04	3.19E-03		
3	20		8.61E-03	3.65E+04	3.13E-03		
4	20	2.00E-03	8.61E-03	-	-	2.57	0.53
5	20		8.61E-03	3.58E+04	2.95E-03		
6	20		8.61E-03	3.51E+04	2.77E-03		
7	20	3.00E-03	8.61E-03	3.71E+04	3.28E-03	2.62	0.43
8	20		8.61E-03	3.63E+04	3.06E-03		
9	20		8.61E-03	3.44E+04	2.59E-03		
10	20	4.00E-03	8.61E-03	3.64E+04	3.09E-03	3.08	0.211
11	20		8.61E-03	3.72E+04	3.29E-03		
12	20		8.61E-03	3.55E+04	2.87E-03		
13	20	5.00E-03	8.61E-03	3.60E+04	3.00E-03	3.00	0.005
14	20		8.61E-03	3.60E+04	3.00E-03		
15	20		8.61E-03	-	-		
16	20	6.00E-03	8.61E-03	3.70E+04	3.25E-03	3.26	0.013
17	20		8.61E-03	3.71E+04	3.27E-03		
18	20		8.61E-03	-	-		

Table C-17a Styrene solubilization of C_{16-17}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Styrene (uL)	Surfactant concentration (M)	Styrene initial (M)	Styrene equilibrium			
				Area	Conc. (M)	$Conc._{avg}$ (M)	SD
1	8	1.00E-07	3.44E-03	2.53E+04	1.13E-03	1.09	0.05
2	8		3.44E-03	2.39E+04	1.06E-03		
3	8	5.00E-07	3.44E-03	2.40E+04	1.06E-03	1.09	0.04
4	8		3.44E-03	2.51E+04	1.12E-03		
5	8	1.00E-06	3.44E-03	2.62E+04	1.17E-03	1.15	0.03
6	8		3.44E-03	2.53E+04	1.13E-03		
7	8	5.00E-06	3.44E-03	2.50E+04	1.11E-03	1.07	0.06
8	8		3.44E-03	2.34E+04	1.03E-03		
9	8	1.00E-05	3.44E-03	2.55E+04	1.14E-03	1.13	0.01
10	8		3.44E-03	2.50E+04	1.11E-03		
11	8		3.44E-03	2.54E+04	1.13E-03		
12	10	5.00E-05	4.31E-03	3.12E+04	1.42E-03	1.42	0.01
13	10		4.31E-03	3.10E+04	1.41E-03		
14	10		4.31E-03	-	-		
15	10	1.00E-04	4.31E-03	2.99E+04	1.36E-03	1.38	0.03
16	10		4.31E-03	3.08E+04	1.40E-03		
17	10		4.31E-03	-	-		
18	15	5.00E-04	6.46E-03	4.35E+04	2.04E-03	2.02	0.029
19	15		6.46E-03	4.35E+04	2.04E-03		
20	15		6.46E-03	4.25E+04	1.99E-03		
21	20	1.00E-03	8.61E-03	5.24E+04	2.48E-03	2.48	0.003
22	20		8.61E-03	5.25E+04	2.48E-03		
23	20		8.61E-03	5.23E+04	2.48E-03		

Table C-17b Styrene solubilization of C_{16-18}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	styrene (uL)	Surfactant concentration (M)	Styrene initial (M)	Styrene equilibrium			
				Area	Conc. (M)	Conc.$_{avg}$ (M)	SD
1	5	1.00E-07	2.15E-03	1.65E+04	6.85E-04	0.69	0.007
2	5		2.15E-03	1.67E+04	6.95E-04		
3	5	5.00E-07	2.15E-03	1.55E+04	6.35E-04	0.63	0.001
4	5		2.15E-03	1.54E+04	6.33E-04		
5	5	1.00E-06	2.15E-03	1.56E+04	6.42E-04	0.65	0.004
6	5		2.15E-03	1.57E+04	6.48E-04		
7	5	5.00E-06	2.15E-03	1.53E+04	6.26E-04	0.69	0.060
8	5		2.15E-03	1.68E+04	7.00E-04		
9	5		2.15E-03	1.77E+04	7.46E-04		
10	5	1.00E-05	2.15E-03	1.69E+04	7.09E-04	0.68	0.027
11	5		2.15E-03	1.65E+04	6.85E-04		
12	5		2.15E-03	1.59E+04	6.56E-04		
13	7	3.00E-05	3.01E-03	2.30E+04	1.01E-03	1.02	0.007
14	7		3.01E-03	2.31E+04	1.02E-03		
15	7		3.01E-03	2.33E+04	1.03E-03		
16	7	1.00E-04	3.01E-03	3.39E+04	1.56E-03	1.21	0.299
17	7		3.01E-03	2.37E+04	1.05E-03		
18	7		3.01E-03	2.35E+04	1.03E-03		
19	10	2.00E-04	4.31E-03	3.21E+04	1.47E-03	1.46	0.002
20	10		4.31E-03	3.20E+04	1.46E-03		
21	10	4.50E-04	4.31E-03	3.29E+04	2.23E-03	2.14	0.116
22	10		4.31E-03	3.23E+04	2.06E-03		

Table C-17c Styrene solubilization of C_{16-17}-4PO-SO_4Na at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Styrene (uL)	Surfactant concentration (M)	Styrene initial (M)	Styrene equilibrium			
				Area	Conc. (M)	Conc.$_{avg}$ (M)	SD
1	10	1.00E-05	4.31E-03	2.64E+04	5.88E-04	1.70	1.02
2	10		4.31E-03	3.44E+04	2.59E-03		
3	10		4.31E-03	3.17E+04	1.93E-03		
4	10	5.00E-05	4.31E-03	3.39E+04	2.48E-03	1.77	0.99
5	10		4.31E-03	2.66E+04	6.36E-04		
6	10		4.31E-03	3.34E+04	2.36E-03		
7	10	1.00E-04	4.31E-03	3.27E+04	2.18E-03	2.59	0.34
8	10		4.31E-03	3.52E+04	2.81E-03		
9	10		4.31E-03	3.51E+04	2.77E-03		
10	15	5.00E-04	6.46E-03	4.36E+04	4.90E-03	4.88	0.028
11	15		6.46E-03	4.52E+04	5.29E-03		
12	15		6.46E-03	4.35E+04	4.86E-03		
13	15	7.00E-04	6.46E-03	4.37E+04	4.92E-03	5.15	0.240
14	15		6.46E-03	4.45E+04	5.11E-03		
15	15		6.46E-03	4.56E+04	5.40E-03		
16	20	1.00E-03	8.61E-03	4.85E+04	6.12E-03	6.49	0.471
17	20		8.61E-03	4.94E+04	6.34E-03		
18	20		8.61E-03	5.21E+04	7.02E-03		
19	20	2.00E-03	8.61E-03	4.77E+04	5.93E-03	6.61	0.607
20	20		8.61E-03	5.13E+04	6.83E-03		
21	20		8.61E-03	5.23E+04	7.08E-03		

Table C-18 Phenanthrene solubilization of SDS at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Surfactant concentration (mM)	Phenanthrene equilibrium		
		Area	Conc. (M)	Conc. (mM)
1	1.00	669.3632	2.32E-06	2.32E-03
2	3.00	633.9309	2.21E-06	2.21E-03
3	5.00	693.1178	2.40E-06	2.40E-03
4	6.00	715.4978	2.48E-06	2.48E-03
5	7.00	783.8469	2.71E-06	2.71E-03
6	8.00	2259.9680	7.63E-06	7.63E-03
7	15.00	24667.7400	8.23E-05	8.23E-02
8	20.00	40637.3000	1.36E-04	1.36E-01
9	25.00	57857.8300	1.93E-04	1.93E-01
10	30.00	74518.8600	2.48E-04	2.48E-01
11	35.00	89095.6600	2.97E-04	2.97E-01
12	40.00	109624.0000	3.66E-04	3.66E-01
13	45.00	126599.0000	4.22E-04	4.22E-01
14	50.00	142099.0000	4.74E-04	4.74E-01

Table C-18a Phenanthrene solubilization of C_{16-17}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Surfactant concentration (mM)	Phenanthrene equilibrium			
		Area	Conc.(mM)	Conc._{avg} (mM)	SD
1	0.001	177.92871	6.87E-03	7.00E-03	2.34E-04
2		177.60173	6.86E-03		
3		189.93376	7.27E-03		
4	0.005	259.1134	9.57E-03	9.59E-03	2.39E-05
5		259.29889	9.58E-03		
6		260.43518	9.62E-03		
7	0.010	168.00209	6.54E-03	6.25E-03	4.89E-04
8		142.59782	5.69E-03		
9		168.00209	6.54E-03		
10	0.050	303.68915	-	8.51E-03	8.29E-04
11		244.71457	9.09E-03		
12		209.54352	7.92E-03		
13	0.100	305.29266	1.11E-02	1.25E-02	1.23E-03
14		366.86832	1.32E-02		
15		370.97641	1.33E-02		
16	0.500	1090.6499	3.73E-02	3.75E-02	3.91E-03
17		1215.2937	4.14E-02		
18		981.09155	3.36E-02		
19	0.700	103.10491	-	5.04E-02	2.20E-04
20		123.73875	5.06E-02		
21		122.8071	5.03E-02		
22	0.900	188.05167	7.20E-02	7.16E-02	4.17E-03
23		173.72081	6.73E-02		
24		198.65227	7.56E-02		

Table C-18b Phenanthrene solubilization of C_{16-18}-4PO-5EO-COONa at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Surfactant concentration (mM)	Phenanthrene equilibrium				
		Area	Conc. (M)	Conc. (mM)	$\text{Conc.}_{\text{Avg}}$ (mM)	SD
1	0.001	201.83682	7.66E-06	7.66E-03	8.73E-03	2.32E-03
2		185.84192	7.13E-06	7.13E-03		
3		313.7363	1.14E-05	1.14E-02		
4	0.005	181.11185	6.97E-06	6.97E-03	7.71E-03	8.85E-04
5		196.17001	7.47E-06	7.47E-03		
6		232.73875	8.69E-06	8.69E-03		
7	0.010	263.21875	9.71E-06	9.71E-03	8.99E-03	8.54E-04
8		213.40019	8.05E-06	8.05E-03		
9		248.61844	9.22E-06	9.22E-03		
10	0.030	151.79538	5.99E-06	5.99E-03	7.63E-03	1.93E-03
11		186.48529	7.15E-06	7.15E-03		
12		264.55545	9.75E-06	9.75E-03		
13	0.050	215.4521	8.12E-06	8.12E-03	7.48E-03	9.05E-04
14		-	-	-		
15		177.03523	6.84E-06	6.84E-03		
16	0.100	406.64944	1.45E-05	1.45E-02	1.45E-02	1.37E-03
17		449.74792	1.59E-05	1.59E-02		
18		367.49973	1.32E-05	1.32E-02		
19	0.300	755.79602	2.61E-05	2.61E-02	3.03E-02	5.50E-03
20		818.00616	2.82E-05	2.82E-02		
21		1067.33508	3.65E-05	3.65E-02		
22	0.500	1479.62976	5.03E-05	5.03E-02	4.53E-02	4.44E-03
23		1224.49951	4.18E-05	4.18E-02		
24		1285.13489	4.38E-05	4.38E-02		

Table C-18c Phenanthrene solubilization of $C_{16\text{-}17}$-4PO-SO_4Na at 1.0 mM NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Surfactant concentration (mM)	Phenanthrene equilibrium				
		Area	Conc. (M)	Conc. (mM)	Conc. $_{avg.}$ (mM)	SD
1	0.010	233.34944	8.71E-06	8.71E-03	8.04E-03	9.57E-04
2		192.76318	7.36E-06	7.36E-03		
3	0.050	268.41953	9.88E-06	9.88E-03	8.61E-03	1.79E-03
4		192.29909	7.35E-06	7.35E-03		
5	0.100	269.82562	9.93E-06	9.93E-03	7.88E-03	1.81E-03
6		188.40048	7.22E-06	7.22E-03		
7		166.5889	6.49E-06	6.49E-03		
8	0.500	748.36407	2.59E-05	2.59E-02	2.96E-02	5.02E-03
9		1031.45813	3.53E-05	3.53E-02		
10		800.51538	2.76E-05	2.76E-02		
11	1.000	116.45409	4.82E-05	4.82E-02	4.99E-02	3.21E-03
12		132.75053	5.36E-05	5.36E-02		
13		115.75603	4.79E-05	4.79E-02		
14	2.000	225.68060	8.46E-05	8.46E-02	9.57E-02	1.11E-02
15		258.86172	9.56E-05	9.56E-02		
16		292.53873	1.07E-04	1.07E-01		
17	3.000	365.52417	1.31E-04	1.31E-01	1.29E-01	3.12E-03
18		352.30807	1.27E-04	1.27E-01		
19		279.70322	-	-		
20	5.000	834.57892	2.88E-04	2.88E-01	2.71E-01	2.16E-02
21		807.61908	2.79E-04	2.79E-01		
22		711.08124	2.46E-04	2.46E-01		

Table C-19 Zeta potential measurement of SDS at pH 5 of the washing solution

pH eq	Wash (times)	Zeta potential (mV)											
		1	2	3	4	5	6	7	8	9	10	Avg.	SD
8.05	0	-28.00	-19.10	-20.40	-24.60	-32.60	-26.30	-21.80	-32.70	-34.30	-24.20	-27.07	0.95
8.07		-30.00	-27.90	-26.80	-27.80	-23.90	-35.30	-23.50	-31.50	-31.30	-19.40		
8.05	1	16.85	20.76	17.67	21.81	18.42	14.78	-	-	-	-	21.74	8.05
8.12		11.42	25.46	13.71	9.87	15.67	16.74	18.53	-	-	-		
8.17		34.75	39.82	37.07	38.83	31.52	16.27	24.63	23.44	31.94	-		
8.11	2	26.95	43.89	36.09	46.78	40.31	33.49	24.84	44.24	36.51	-	37.15	2.52
8.01		47.97	53.81	49.94	53.74	33.35	33.57	31.67	33.70	31.24	28.35		
8.11		38.41	35.53	38.27	49.94	37.85	31.31	40.94	17.74	22.31	-		
8.10	3	34.62	39.04	42.98	44.95	42.21	42.63	38.76	36.79	36.65	-	37.44	3.79
8.11		27.51	42.14	30.53	41.43	36.86	48.46	43.33	45.23	39.60	38.97		
8.09		28.00	26.53	43.96	25.82	34.88	45.93	44.53	25.40	22.66	-		
8.09	4	26.74	35.04	44.10	42.28	39.04	34.12	33.28	32.93	32.85	-	37.55	2.16
8.15		27.30	32.43	41.57	42.00	24.92	46.92	41.01	41.22	-	-		
8.15		38.48	37.49	47.55	35.95	-	-	-	-	-	-		
8.15	5	30.14	44.79	40.00	35.25	-	-	-	-	-	-	37.86	0.72
8.05		38.73	41.42	41.68	32.93	-	-	-	-	-	-		
8.20		36.46	30.33	43.79	38.84	-	-	-	-	-	-		
8.15	7	39.00	39.95	45.15	33.19	35.27	38.3	37.1	45.15	-	-	37.83	1.16
8.10		40.12	30.71	37.91	34.85	41.11	-	-	-	-	-		
8.07		30.24	45.13	34.39	39.46	42.38	32.85	-	-	-	-		
8.11	10	38.64	34.88	-	-	-	-	-	-	-	-	37.71	1.00
8.01		39.23	37.28	37.23	36.71	-	-	-	-	-	-		
8.11		36.4	45.11	34.74	-	-	-	-	-	-	-		

Table C-19a Zeta potential measurement of SDS at pH 7 of the washing solution

pH $_{eq}$	Wash (times)	Zeta potential (mV)											
		1	2	3	4	5	6	7	8	9	10	Avg.	SD
8.05	0	-28.00	-19.10	-20.40	-24.60	-32.60	-26.30	-21.80	-32.70	-34.30	-24.20	-27.07	0.95
8.07		-30.00	-27.90	-26.80	-27.80	-23.90	-35.30	-23.50	-31.50	-31.30	-19.40		
8.05	1	37.14	19.17	25.80	25.25	18.87	17.28	29.90	26.24	35.46	36.79	30.35	3.93
8.15		34.75	31.88	30.89	45.16	43.96	23.65	37.78	44.95	21.60	32.93		
8.14		49.31	46.71	44.67	28.64	27.51	24.33	27.45	21.42	10.68	10.38		
8.03	2	58.10	39.32	37.00	42.07	30.40	50.71	24.42	34.42	28.89	-	38.82	1.31
8.00		49.17	44.67	33.21	35.81	39.32	27.79	44.24	27.66	45.93	30.19		
8.00		51.35	50.92	25.40	44.03	54.65	55.64	27.37	35.39	21.04	37.14		
8.00	3	49.59	51.91	42.14	43.68	39.04	41.50	48.46	48.60	46.64	-	42.01	3.27
8.00		57.53	48.96	49.45	20.83	31.10	39.46	41.15	35.10	32.72	-		
8.01		30.74	44.53	24.56	53.60	47.90	36.86	46.78	-	-	-		
8.05	4	55.00	30.25	36.72	51.91	36.02	47.76	-	-	-	-	42.33	2.06
8.09		43.68	53.53	31.52	44.03	43.12	31.03	42.21	31.10	-	-		
8.09		30.53	52.65	50.86	55.61	46.11	49.49	30.56	36.25	-	-		
8.13	5	45.21	47.01	42.01	48.43	-	-	-	-	-	-	40.43	4.65
8.14		38.42	35.46	36.41	-	-	-	-	-	-	-		
8.07		41.00	36.73	-	-	-	-	-	-	-	-		
8.03	7	40.21	37.49	39.23	38.64	40.79	34.24	-	-	-	-	38.67	0.91
8.05		39.85	40.23	32.42	37.95	36.01	40.96	-	-	-	-		
8.03		38.23	40.34	40.45	-	-	-	-	-	-	-		
8.06	10	40.34	34.39	38.79	36.85	-	-	-	-	-	-	42.93	4.91
8.04		42.23	45.68	-	-	-	-	-	-	-	-		
8.04		45.23	49.27	-	-	-	-	-	-	-	-		

Table C-19b Zeta potential measurement of SDS at pH 8 of the washing solution

pH $_{eq}$	Wash (times)	Zeta potential (mV)											
		1	2	3	4	5	6	7	8	9	10	Avg.	SD
8.05	0	-28.00	-19.10	-20.40	-24.60	-32.60	-26.30	-21.80	-32.70	-34.30	-24.20	-27.07	0.95
8.07		-30.00	-27.90	-26.80	-27.80	-23.90	-35.30	-23.50	-31.50	-31.30	-19.40		
8.00	1	41.84	31.77	51.86	22.01	52.17	23.07	24.01	44.42	45.11	-	34.75	3.37
8.00		36.67	50.70	43.06	29.92	34.20	29.39	36.04	26.44	37.10	-		
8.00		32.67	41.68	36.52	40.05	26.39	25.64	24.17	21.69	29.77	-		
8.00	2	29.98	36.52	36.73	37.52	49.01	33.09	44.90	42.74	35.57	-	38.82	1.87
8.03		32.61	42.16	29.03	41.16	31.82	36.46	44.74	39.36	-	-		
8.01		42.32	44.48	36.67	43.06	41.74	47.07	40.10	35.78	36.41	-		
8.04	3	38.73	44.90	-	35.41	39.21	38.10	49.49	45.38	-	-	42.85	4.85
8.19		36.10	41.42	39.15	38.31	-	-	-	-	-	-		
8.22		44.06	52.34	-	-	-	-	-	-	-	-		
8.17	4	30.24	47.64	-	48.80	42.10	34.20	36.99	37.73	-	-	42.47	2.97
8.22		58.93	47.43	48.01	43.21	30.66	30.40	64.63	41.47	-	-		
8.24		35.09	-	49.60	39.15	42.00		44.90		-	-		
8.02	5	36.64	37.93	47.64	-	-	-	-	-	-	-	39.52	1.66
8.00		41.21	31.45	47.17	30.66	-	-	-	-	-	-		
8.02		37.23	37.98	40.34	45.23	-	-	-	-	-	-		
8.02	7	38.45	26.55	39.99	36.43	37.67	47.56	-	-	-	-	39.89	2.55
8.31		38.45	30.87	41.89	40.23	44.37	-	-	-	-	-		
8.16		40.12	39.25	39.89	42.24	52.13	-	-	-	-	-		
8.08	10	39.48	36.57	37.14	46.48	44.85	-	-	-	-	-	42.09	1.11
8.11		36.11	40.23	41.12	43.45	50.33	-	-	-	-	-		
8.07		39.67	39.89	41.45	41.23	53.28	-	-	-	-	-		

Table C-19c Summarize zeta potential measurement of SDS at pH 5, 7, and 8 of the washing solution

Wash (times)	Zeta potential (mV)					
	pH 5	SD	pH7	SD	pH8	SD
0	-27.07	0.95	-27.07	0.95	-27.07	0.95
1	21.74	7.06	30.35	3.78	34.75	3.37
2	37.15	0.97	38.82	1.31	39.11	0.90
3	37.87	3.04	43.56	1.77	43.64	4.97
4	41.07	5.74	42.33	1.54	44.07	0.32
5	34.84	7.06	40.25	7.66	39.56	3.23
7	35.62	2.27	34.66	3.43	35.77	0.86
10	35.09	1.65	29.76	3.43	35.04	1.52

Table C-20 Zeta potential measurement of C_{16-17}-4PO-5EO-COONa at pH 5 of the washing solution

pH $_{eq}$	Wash (times)	Zeta potential (mV)											
		1	2	3	4	5	6	7	8	9	10	Avg.	SD
8.02	0	-67.30	-77.30	-61.50	-32.60	-92.10	-79.80	-97.70	-96.40	-102.00	-103.00	-89.87	8.32
8.00		-76.50	-92.40	-87.40	-92.00	-115.00	-106.00	-98.50	-92.80	-98.00	-116.00		
8.38		-73.90	-91.70	-95.20	-97.40	-96.90	-83.60	-90.50	-87.60	-89.10	-106.00		
8.03	1	-30.10	-25.40	-30.20	-27.70	-31.70	-52.80	-37.20	-36.50	-33.23	-	-30.16	3.30
8.00		-27.60	-28.30	-24.50	-25.60	-30.90	-36.00	-25.40	-25.70	-	-		
8.06		-24.40	-25.00	-16.30	-40.80	-21.20	-43.40	-	-	-	-		
8.01	2	-25.60	-23.10	-13.80	-22.20	-21.10	-20.10	-22.50	-23.40	-22.10	-	-21.57	1.86
8.02		-10.90	-11.30	-28.20	-21.90	-20.20	-14.00	-14.20	-25.50	-31.30	-		
8.01		-26.20	-33.40	-37.20	-30.80	-15.80	-12.00	-19.10	-18.80	-17.60	-		
8.01	3	-30.70	-22.20	-15.90	-16.60	-16.10	-32.80	-16.20	-15.00	-25.10	-	-13.52	8.51
8.09		-16.10	-18.50	-19.60	-16.80	-7.62	-8.99	-22.10	-9.02	-16.50	-		
8.11		-8.71	-	-	-	-	-	-	-	-	-		
8.07	4	-26.60	-19.30	-15.40	-11.20	-23.30	-19.70	-20.80	-19.80	-	-	-14.82	6.64
8.01		-3.04	-8.99	-21.50	-14.50	-19.60	0.00	-6.58	-6.77	-	-		
8.03	5	38.01	15.81	42.44	-	-	-	-	-	-	-	21.97	9.79
8.05		13.03	23.73	15.49	28.63	23.66	23.10	-	-	-	-		
8.06		13.52	10.60	14.28	11.55	12.73	-	-	-	-	-		
8.18	7	30.27	31.50	25.39	35.39	25.39	31.50	-	-	-	-	23.92	8.00
8.17		31.40	25.11	27.31	16.16	29.92	32.17	-	-	-	-		
8.03		12.33	14.21	16.07	10.35	18.85	14.72	17.29	-	-	-		
8.05	10	31.71	36.32	30.42	34.35	27.57	27.36	-	-	-	-	30.75	4.03
8.06		33.61	35.17	34.64	-	-	-	-	-	-	-		
8.15		23.21	22.16	29.68	36.29	21.03	-	-	-	-	-		

Table C-20a Zeta potential measurement of C_{16-17}-4PO-5EO-COONa at pH 7 of the washing solution

pH eq	Wash (times)	Zeta potential (mV)											
		1	2	3	4	5	6	7	8	9	10	Avg.	SD
8.02	0	-67.30	-77.30	-61.50	-32.60	-92.10	-79.80	-97.70	-96.40	-102.00	-103.00	89.87	8.32
8.00		-76.50	-92.40	-87.40	-92.00	-115.00	-106.00	-98.50	-92.80	-98.00	-116.00		
8.38		-73.90	-91.70	-95.20	-97.40	-96.90	-83.60	-90.50	-87.60	-89.10	-106.00		
8.15	1	-10.80	-15.30	-30.20	-	-	-	-	-	-	-	23.91	5.51
8.16		-24.34	-10.50	-28.56	-29.48	-	-	-	-	-	-		
8.15		-41.00	-51.30	-36.30	-36.20	-23.00	-12.50	-22.00	-22.60	-17.20	-35.20		
8.13	2	-16.40	-18.60	-10.20	-8.81	-14.00	-20.00	-26.10	-18.00	-	-	16.07	2.92
8.17		-28.90	-1.65	-8.31						-	-		
8.20		-16.60	-24.90	-10.53	-20.70	-21.00				-	-		
8.10	3	-22.40	-17.70	-12.30	-14.20	-14.60	-7.48	-19.30	-21.60	-	-	13.40	8.10
8.11		-16.40	-29.70	-17.20	-12.80	-19.90	-24.00	-28.50	-9.32	-	-		
8.03		11.53	-20.40	-15.00	-18.30	-15.00	6.87	19.36	-3.28	-	-		
8.25	4	-34.80	-32.60	33.30	34.20	24.38	37.46	0.00	-20.10	-10.40	-10.00	6.97	3.05
8.15		-16.60	-36.00	25.93	26.24	-27.70	21.32	10.92	28.15	14.35			
8.15		28.34	23.61	13.51	0.00	-11.70	-17.10	16.49	8.23	20.37	23.11		
8.00	5	23.14	25.17	23.16	-	-	-	-	-	-	-	18.43	5.09
8.02		13.93	12.82	28.71	15.59	-	-	-	-	-	-		
8.05		15.73	8.63	9.29	10.55	20.53	13.72	17.57	-	-	-		
8.16	7	14.25	23.60	21.51	11.07	20.05	21.21	19.79	-	-	-	18.47	0.38
8.15		23.39	13.34	12.49	20.21	23.39	-	-	-	-	-		
8.13		18.47	19.46	17.74	16.53	-	-	-	-	-	-		
8.17	10	42.94	46.32	53.31	53.70	54.54	38.79	33.13	32.03	32.82	-	38.12	7.00
8.20		4.78	42.94	36.57	30.49	34.50	33.45	46.84	35.80	-	-		

Table C-20b Zeta potential measurement of C_{16-17}-4PO-5EO-COONa at pH 8 of the washing solution

pH eq	Wash (times)	Zeta potential (mV)											
		1	2	3	4	5	6	7	8	9	10	Avg.	SD
8.02	0	-67.30	-77.30	-61.50	-32.60	-92.10	-79.80	-97.70	-96.40	-102.00	-103.00	-89.8733	8.32
8.00		-76.50	-92.40	-87.40	-92.00	-115.00	-106.00	-98.50	-92.80	-98.00	-116.00		
8.38		-73.90	-91.70	-95.20	-97.40	-96.90	-83.60	-90.50	-87.60	-89.10	-106.00		
8.15	1	-24.50	-36.80	-36.80	-36.60	-	-	-	-	-	-	-33.0375	0.76
8.05		-35.80	-30.70	-36.90	-33.70	-29.70	-24.60	-45.20	-29.30	-	-		
8.00		-29.40	-15.80	-29.70	-27.80	-40.60	-41.30	-40.80	-	-	-		
8.00	2	-29.80	-22.90	-23.40	-23.00	-22.10	-22.20	-26.70	-25.30	-29.50	-20.00	-9.5124	15.96
8.20		-8.64	-10.30	-10.90	-12.40	-14.80	-16.90	-11.30	-5.35	-	-		
8.09		-10.60	18.82	19.53	-27.60	-32.70	26.44	28.31	21.88	21.41	-		
8.01	3	14.67	18.21	21.67	20.85	31.37	-	-	-	-	-	20.3996	1.35
8.15		13.08	26.38	24.90	20.05	22.48	9.78	-	-	-	-		
8.05	4	16.00	27.28	23.85	37.42	37.88	19.59	23.07	20.96	-	-	20.2254	6.14
8.09		18.36	6.61	9.96	9.57	23.60	-	-	-	-	-		
8.00		11.89	22.27	23.99	26.23	22.12	-	-	-	-	-		
8.05	5	13.27	22.39	26.46	20.26	23.37	20.45	-	-	-	-	21.1266	0.57
8.03		12.90	26.24	24.77	23.03	-	-	-	-	-	-		
8.05		18.47	18.42	18.73	24.58	23.03	10.21	30.84	-	-	-		
8.03	7	14.89	34.27	14.23	20.61	19.34	22.07	20.89	23.54	28.14	19.89	24.5955	2.72
8.06		33.53	25.67	25.53	20.02	25.17	24.81	24.97	21.04	22.86	24.21		
8.15		30.37	27.15	24.81	38.89	21.55	19.79	27.97	-	-	-		
8.09	10	30.27	35.39	34.53	22.13	25.82	25.89	-	-	-	-	32.6152	3.13
8.22		27.97	32.28	42.58	-	-	-	-	-	-	-		
8.11		38.57	31.40	32.80	34.66	35.39	-	-	-	-	-		

Table C-20c Summarize zeta potential measurement of $C_{16\text{-}17}$-4PO-5EO-COONa at pH 5, 7, and 8 of the washing solution

Wash (times)	Zeta potential (mV)						
	pH 5	SD	pH7	SD	pH8	SD	alumina
0	-78.65	7.95	-78.65	7.95	-78.65	7.95	57.24
1	-30.16	3.30	-23.91	5.51	-33.04	0.76	57.24
2	-21.57	0.47	-16.07	2.92	-9.51	5.96	57.24
3	-13.52	5.53	-13.40	6.28	20.40	0.02	57.24
4	-9.88	5.35	6.97	2.76	20.23	4.83	57.24
5	21.97	9.79	18.43	5.09	21.13	0.57	57.24
7	23.92	8.00	18.06	0.71	24.60	2.72	57.24
10	34.61	2.47	38.12	7.00	32.62	3.13	57.24

Table C-21 Summarize zeta potential measurement of $C_{16\text{-}18}$-4PO-5EO-COONa at pH 5, 7, and 8 of the washing solution

Wash (times)	Zeta potential (mV)						
	pH 5	SD	pH7	SD	pH8	SD	alumina
0	-71.15	0.88	-71.15	0.88	-71.15	0.88	57.24
1	-67.78	2.42	-65.57	6.35	-56.03	3.33	57.24
2	-65.60	2.40	-60.71	9.94	-44.70	8.65	57.24
3	-67.80	1.41	-61.41	2.47	-44.81	1.60	57.24
4	-55.83	2.41	-55.18	4.10	-47.19	7.86	57.24
5	-51.33	4.05	-53.17	6.93	-48.27	6.93	57.24
7	-44.22	2.95	-42.53	10.68	-42.42	0.59	57.24
10	-41.35	2.47	-40.15	2.62	-37.73	4.35	57.24

Table C-22 Zeta potential measurement of C_{16-17}-4PO-SO_4Na at pH 5 of the washing solution

pH_{eq}	Wash (times)	Zeta potential (mV)										
		1	2	3	4	5	6	7	8	9	Avg.	SD
8.05	0	-67.30	-77.30	-61.50	-96.40	-92.10	-79.80	-97.70	-	-	-88.07	5.75
8.07		-76.50	-92.40	-87.40	-92.00	-98.00	-106.00	-98.50	-92.80	-		
8.00		-73.90	-91.70	-95.20	-97.40	-96.90	-83.60	-90.50	-87.60	-89.10		
8.00	1	-32.70	-34.40	-40.30	-38.80	-44.90	-39.30	-43.10	-47.10	-	-49.70	9.24
8.00		-34.80	-73.70	-75.70	-51.40	-58.60	-56.40	-54.00	-60.70	-60.90		
8.00		-43.40	-43.90	-53.70	-56.70	-55.00	-57.20	-44.20	-	-		
8.03	2		-36.00	-32.00	-31.30	-26.00	-40.80	-37.30	-34.30	-	-34.85	0.89
8.01		-26.80	-16.00	-39.60	-55.50	-30.20	-39.80	-42.20	-	-		
8.04		-24.40	-39.60	-42.30	-32.90	-37.40	-32.50	-	-	-		
8.19	3	-31.40	-33.50	-32.30	-32.00	-29.10	-47.20	-45.90	-39.60	-	-32.21	6.35
8.22		-22.10	-23.50	-26.50	-25.60	-43.40	-44.10	-41.10	-45.50	-46.50		
8.17		-24.50	-25.30	-31.00	-30.00	-27.30	-	-	-	-		
8.22	4	-41.10	-20.10	-27.80	-	-	-	-	-	-	-29.25	0.59
8.24		-15.80	-32.20	-38.50	-	-	-	-	-	-		
8.00	5	-23.79	-22.92	-	-	-	-	-	-	-	-21.11	4.47
8.02		-22.18	-25.85	-	-	-	-	-	-	-		
8.02		-15.20	-16.73	-	-	-	-	-	-	-		
8.31	7	-28.39	-17.21	-	-	-	-	-	-	-	-21.97	3.53
8.16		-18.11	-18.07	-	-	-	-	-	-	-		
8.08		-25.01	-	-	-	-	-	-	-	-		
8.11	10	-14.46	-12.36	-	-	-	-	-	-	-	-12.17	1.28
8.07		-10.58	-13.92	-	-	-	-	-	-	-		
8.03		-12.64	-9.05	-	-	-	-	-	-	-		

Table C-22a Zeta potential measurement of $C_{16\text{-}17}$-4PO-SO_4Na at pH 7 of the washing solution

pH $_{eq}$	Wash (times)	Zeta potential (mV)											
		1	2	3	4	5	6	7	8	9	10	Avg.	SD
8.05	0	-67.30	-77.30	-61.50	-96.40	-92.10	-79.80	-97.70	-	-	-	-88.07	5.75
8.07		-76.50	-92.40	-87.40	-92.00	-98.00	-106.00	-98.50	-92.80	-	-		
8.00		-73.90	-91.70	-95.20	-97.40	-96.90	-83.60	-90.50	-87.60	-89.10	-		
8.00	1	-35.60	-31.60	-34.10	-40.20	-35.90	-42.70	-	-	-	-	-39.99	4.18
8.00		-41.80	-42.10	-43.40	-35.90	-26.80	-41.60	-	-	-	-		
8.00		-47.80	-53.80	-49.30	-33.40	-39.10	-	-	-	-	-		
8.03	2	-20.10	-25.80	-28.00	-28.80	-	-	-	-	-	-	-26.37	2.77
8.01		-14.20	-27.80	-24.00	-26.30	-27.80	-	-	-	-	-		
8.04		-26.20	-27.10	-39.70	-31.30	-22.80	-	-	-	-	-		
8.19	3	-28.60	-21.80	-16.40	-15.30	-17.60	-24.20	-17.80	-	-	-	-23.98	5.29
8.22		-28.80	-26.40	-25.80	-26.90	-30.70	-	-	-	-	-		
8.22	4	-20.90	-33.60	-21.90	-20.20	-27.00	-	-	-	-	-	-25.85	1.59
8.24		-18.60	-32.50	-32.40	-24.40	-	-	-	-	-	-		
8.00	5	-22.30	-24.60	-	-	-	-	-	-	-	-	-23.02	0.40
8.02		-24.30	-21.00	-	-	-	-	-	-	-	-		
8.02		-22.30	-23.60	-	-	-	-	-	-	-	-		
8.31	7	-23.60	-24.30	-11.30	-	-	-	-	-	-	-	-18.84	1.59
8.16		-21.00	-16.60	-27.40	-14.10	-	-	-	-	-	-		
8.08		-10.80	-19.20	-21.00	-	-	-	-	-	-	-		
8.11	10	-4.60	-4.42	-5.45	-2.92	-2.59	-	-	-	-	-	-4.42	0.41
8.07		-4.60	-4.42	-5.45	-	-	-	-	-	-	-		
8.03		-9.11	-2.92	-1.28	-	-	-	-	-	-	-		

Table C-22b Zeta potential measurement of $C_{16\text{-}17}$-4PO-SO_4Na at pH 8 of the washing solution

pH eq	Wash (times)	Zeta potential (mV)										
		1	2	3	4	5	6	7	8	9	Avg.	SD
8.05	0	-67.30	-77.30	-61.50	-96.40	-92.10	-79.80	-97.70	-	-	-88.07	5.75
8.07		-76.50	-92.40	-87.40	-92.00	-98.00	-106.00	-98.50	-92.80	-		
8.00		-73.90	-91.70	-95.20	-97.40	-96.90	-83.60	-90.50	-87.60	-89.10		
8.00	1	-58.90	-42.00	-44.10	-38.00	-33.60	-49.50	-	-	-	-43.16	1.04
8.00		-45.80	-41.30	-42.70	-38.50	-38.90	-47.90	-	-	-		
8.00		-41.20	-47.90	-44.50	-44.70	-34.70	-	-	-	-		
8.03	2	-42.70	-34.20	-31.80	-35.20	-41.60	-	-	-	-	-38.79	1.74
8.01		-51.00	-41.60	-31.50	-38.30	-40.50	-	-	-	-		
8.04		-35.30	-34.80	-46.00	-	-	-	-	-	-		
8.19	3	-17.90	-22.70	-20.60	-18.40	-20.00	-21.30	-	-	-	-24.53	4.10
8.22		-34.40	-26.10	-20.20	-22.80	-26.40	-21.00	-	-	-		
8.22		-28.20	-28.40	-23.80	-32.70	-	-	-	-	-		
8.24	4	-10.00	-6.64	-6.47	-15.20	-15.90	-	-	-	-	-13.05	2.27
8.00		-8.76	-9.35	-19.90	-12.90	-12.70	-14.30	-12.70	-	-		
8.02		-17.50	-9.18	-17.20	-22.50	-10.50	-	-	-	-		
8.02	5	-19.10	-16.20	-	-	-	-	-	-	-	-11.37	5.59
8.31		-9.03	-5.60	-6.21	-	-	-	-	-	-		
8.16		-9.51	-7.59	-11.40	-	-	-	-	-	-		
8.08	7	-10.10	-	-	-	-	-	-	-	-	-11.53	3.34
8.11		-17.20	-13.50	-	-	-	-	-	-	-		
8.07		-9.14	-	-	-	-	-	-	-	-		
8.03	10	-7.07	-5.72	-5.98	-	-	-	-	-	-	-6.85	0.57
8.22		-9.11	-5.66	-	-	-	-	-	-	-		
8.24		-7.49	-6.30	-	-	-	-	-	-	-		

Table C-22c Summarize zeta potential measurement of $C_{16\text{-}17}$-4PO-SO_4Na at pH 5, 7, and 8 of the washing solution

Wash (times)	Zeta potential (mV)						
	pH 5	SD	pH7	SD	pH8	SD	alumina
0	-88.07	5.75	-88.07	5.75	-88.07	5.75	57.24
1	-49.70	9.24	-39.99	4.18	-43.16	1.04	57.24
2	-34.85	0.89	-26.37	2.77	-38.79	1.74	57.24
3	-32.21	6.35	-23.98	5.29	-24.53	4.10	57.24
4	-29.25	0.59	-25.85	1.59	-13.05	2.27	57.24
5	-21.11	4.47	-23.02	0.40	-11.37	5.59	57.24
7	-21.97	3.53	-18.84	1.59	-11.53	3.34	57.24
10	-12.17	1.28	-4.42	0.41	-6.85	0.57	57.24

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