โซลูบิไลเซชันและแอดโซลูบิไลเซชันของฟีนิลเอทานอลและเอทิลไซโคลเฮกเซนด้วยสารลดแรงตึงผิวที่มีส่วนขยายบนพื้นผิวอะลูมินาออกไซด์

นางสาวจิรภัทร์ ลิ่วลมไพศาล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2552

SOLUBILIZATION AND ADSOLUBILIZATION OF PHENYLETHANOL AND ETHYLCYCLOHEXANE USING ANIONIC CARBOXYLATE EXTENDED SURFACTANTS ON AN ALUMINUM OXIDE SURFACE

Miss Jirapat Lewlomphaisan

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management
(Interdisciplinary Program)
Graduate School
Chulalongkorn University
Academic Year 2009

Thesis Title	SOLUBILIZATION AND ADSOLUBILIZATION OF PHENYLETHANOL AND ETHYLCYCLOHEXANE USING ANIONIC CARBOXYLATE EXTENDED SURFACTANTS ON AN ALUMINUM OXIDE SURFACE
By	Miss Jirapat Lewlomphaisan
Field of Study	Environmental Management
Thesis Advisor	Associate Professor Sutha Khaodhiar, Ph.D.
Thesis Co-Advisor	Professor David A. Sabatini, Ph.D.

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

.... Dean of the Graduate School

(Associate Professor Pornpote Piumsomboon,Ph.D.)

THESIS COMMITTEE

.... Chairman

(Chantra Tongcumpou, Ph.D.)

.... Thesis Advisor

(Associate Professor Sutha Khaodhiar, Ph.D.)

.... Thesis Co-Advisor

(Professor David A. Sabatini, Ph.D.)

.... Examiner

(Patiparn Punypalakul, Ph.D.)

.... External Examiner

(Aranya Fuangswasdi, Ph.D.)

จิรภัทร์ ลิ่วลมไพศาล : โซลูบิไลเซชันและแอดโซลูบิไลเซชันของฟีนิลเอทานอลและเอทิลไซโคลเฮกเซนด้วยสารลดแรงตึงผิวที่มีส่วนขยายบนพื้นผิวอะลูมินาออกไซด์ (SOLUBILIZATION AND ADSOLUBILIZATION OF PHENYLETHANOL AND ETHYLCYCLOHEXANE USING ANIONIC CARBOXYLATE EXTENDED SURFACTANTS ON AN ALUMINUM OXIDE SURFACE) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร. สุธา ขาวเธียร, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม : PROF. DAVID A. SABATINI, Ph.D., 142 หน้า.

เนื่องจากในปัจจุบันนี้การใช้สารลดแรงตึงผิวเพื่อเพิ่มประสิทธิภาพในการบำบัดสารอินทรีย์ที่ปนเปื้อนในชั้นกักเก็บน้ำใต้ดินกำลังได้รับความสนใจอย่างมาก และในการใช้สารลดแรงตึงผิวที่มีส่วนขยายของโพลีโพรไพรีนออกไซด์และ/หรือเอทิลีนออกไซด์ที่อยู่ในระหว่างไฮโดรคาร์บอนส่วนหางกับส่วนหัวที่ชอบน้ำสามารถช่วยเพิ่มประสิทธิภาพในการโซลูบิไลเซชันของสารลดแรงตึงผิว โดยในการศึกษานี้ได้ศึกษาเกี่ยวกับกระบวนการดูดซับและการไม่ดูดซับประสิทธิภาพในการโซลูบิไลเซชันและแอดโซลูบิไลเซชันของสารลดแรงตึงผิวที่มีส่วนขยายชนิดประจุลบ โดยเทียบกับสารลดแรงตึงผิวธรรมดาชนิดประจุลบ ผลการศึกษาพบว่ากระบวนการดูดซับของสารลดแรงตึงผิวที่มีส่วนขยายชนิดซัลเฟตแสดงประสิทธิภาพการดูดซับสูงสุดบนพื้นผิวอะลูมินาออกไซด์สูงที่สุด นอกจากนี้ยังพบว่าสารลดแรงตึงผิวที่มีส่วนขยายชนิดคาร์บอกซิเลตทั้งชนิด 16.5 คาร์บอน และ 17 คาร์บอน มีการดูดซับในรูปแบบแอดไมเซลที่แข็งแรงและสามารถลดการสูญเสียสารลดแรงตึงผิวจากพื้นผิวตัวกลาง สำหรับการศึกษาโซลูบิไลเซชันและแอดโซลูบิไลเซชันในครั้งนี้พบว่าสารลดแรงตึงผิวที่มีส่วนขยายแสดงประสิทธิภาพในการโซลูบิไลเซชันและแอดโซลูบิไลเซชันของฟีนิลเอทานอลและเอทิลไซโคลเฮกเซนดีกว่าสารลดแรงตึงผิวธรรมดา ทั้งนี้เนื่องจากสารลดแรงตึงผิวที่มีส่วนขยายมีจำนวนโมเลกุลของสารลดแรงตึงผิวสำหรับการรวมกลุ่มไมเซลและแอดไมเซลมากกว่าสารลดแรงตึงผิวธรรมดา ผลการศึกษาชี้ให้เห็นว่าตัวกลางสำหรับดูดซับที่เพิ่มประสิทธิภาพด้วยสารลดแรงตึงผิวที่มีส่วนขยายสามารถนำมาใช้พัฒนางานในด้านอุตสาหกรรมและสิ่งแวดล้อม

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต..

ปีการศึกษา 2552 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..............................

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม..............................

5187517020 : MAJOR ENVIRONMENTAL MANAGEMENT
KEYWORDS : EXTENDED SURFACTANT / ADMICELLE / SOLUBILIZATION / ADSOLUBILIZATION / ADSORPTION / DESORPTION

JIRAPAT LEWLOMPHAISAN : SOLUBILIZATION AND ADSOLUBILIZATION OF PHENYLETHANOL AND ETHYLCYCLOHEXANE USING ANIONIC CARBOXYLATE EXTENDED SURFACTANTS ON AN ALUMINUM OXIDE SURFACE. THESIS ADVISOR : ASSOC. PROF. SUTHA KHAODHIAR, Ph.D., THESIS CO-ADVISOR : PROF. DAVID A. SABATINI, Ph.D., 142 pp.

Surfactant enhanced aquifer remediation (SEAR) of organic contaminants has been receiving increased attention. It makes use of extended surfactants, within which groups of intermediate polarity such as polypropylene oxides (PO) and/or ethylene oxide (EO) have been inserted between the hydrocarbon tail and hydrophilic head groups, thereby enhancing the surfactants' solubilization capacity. In this study, the adsorption/desorption, solubilization, and adsolubilization capabilities of anionic extended surfactants are evaluated and compared to those of a conventional surfactant (C12S). The results of surfactant adsorption onto aluminum oxide surfaces showed that the sulfate extended surfactant (C16.5-4POS) has the highest maximum adsorption capacity. Moreover, the carboxylate extended surfactants (C16.5-4PO5EOC and C17-4PO5EOC) have strong packing (bilayer coverage) and reduce the surfactants' desorption from the surface. For solubilization and adsolubilization, the extended surfactant systems showed greater phenylethanol and ethylcyclohexane solubilization and adsolubilization compared to the C12S. This is because the extended surfactants have larger aggregation numbers than that of the C12S. These results provide insights into extended surfactant-based admicellar systems that can enhance the industrial and environmental applications of surfactant-modified materials.

Field of Study : Environmental Management
Academic Year : 2009

Student's Signature
Advisor's Signature
Co-Advisor's Signature

ACKNOWLEDGEMENTS

This work is based on financial supported by the National Center of Excellence for Environmental and Hazardous Waste Management (NCE-EHWM), Chulalongkorn University, Thailand and the CU.Graduate School Thesis Grant of Chulalongkorn University. Moreover, financial supported for this research was received from the industrial sponsors of the Institute for Apply Surfactant Research (IASR), University of Oklahoma, including Akzo Noble, Clorox, Conoco/Phillips, Church & Dwigth, Ecolab, Halliburton, Dow Chemical, Huntsman, Oxiteno, Procter & Gamble, Sasol and Shell. Finally, funds from the Sun Oil Company Chair (DAS) at the University of Oklahoma helped support this research. I would like to thank Ms. Victoria Stolarski from Sasol Company (Houston, Texas, USA) for providing me with the extended surfactants samples for this research.

I would like to express my sincere gratitude to my advisor, Assoc. Prof. Sutha Khaodhiar and Prof. David A. Sabatini for his invaluable guidance. They continuous encouragement and support has always been an inspiration and generosity for me. I would like to acknowledge the members of my committee, Dr. Chantra Tongcumpou, Dr. Patiparn Punypalakul, and Dr. Aranya Fuangswasdi. I would like to extend a special thanks to Dr. Ampira Charoensaeng, Miss Ramnaree Netvichian and Miss Noulkamol Arpornpong for their time, helpful suggestions, and discussions. I would like to thank my colleagues, Ms. Donyaporn Panswad. Furthermore, I would like to thank the officers and my friends at NCE-EHWM for their encouragement and help.

Lastly, I would like to especially thank all of my family members, my beloved parents, my brothers, and my relatives for their years of support, encouragement, and for making me what I am today.

CONTENTS

Page

Page

LIST OF TABLES

Page

Page

Page

LIST OF FIGURES

Page

CHAPTER I

INTRODUCTION

1.1 INTRODUCTION

The surfactant-enhanced aquifer remediation (SEAR) of organic contaminants has become of great interest (Nivas et al., 1996) because classical remediation techniques such as conventional pump-and treat technologies have been leaving much to be desired due to their high costs, unreliability, and longer time requirements (Sabatini et al., 1996; Harwell et al., 1999; Childs et al., 2006; Paria, 2008). Surfactant-enhanced aquifer remediation technology addresses the removal of immiscible-phase liquid contaminants, also termed *nonaqueous phase liquids* (NAPLs), from the saturated zone (NFESC, 2003). The use of surfactants can greatly increase the solubilization of organic contaminants and reduce the interfacial tension (IFT) between contaminants and the aqueous phase, thereby, substantially accelerating the remediation process (Cheng and Sabatini, 2002). By promoting the rapid removal of these non-aqueous phase contaminants, groundwater cleanup goals may be accomplished more quickly. Moreover, surfactants aggregates adsorbed at the solid-liquid interface are capable of solubilizing organic solutes due to the partitioning of organic solutes from the aqueous phase into hydrophobic regions, which is known as *adsolubilization*. SEAR is used in many applications, including admicellar-enhanced chromatography (AEC), fixed-bed separation using the adsorbed surfactants to induce the partitioning of organic solutes into admicelles (Harwell and O'Rear, 1989), admicellar polymerization, the adsolubilization of solid phase extraction (SPE) of pharmaceutical products, wastewater treatments, and soil remediation (Potjanee Asvapathanagul, 2005; Ampira Charoensaeng et al., 2008).

New classes of surfactants called extended surfactants are surfactants in which groups of intermediate polarity, such as polypropylene oxides (PO) or copolymers of propylene oxides and/or ethylene oxides (EO), are inserted between the hydrocarbon tail and hydrophilic head groups. They can enhance the solubilization capacity (Miñana-Perez et al., 1995; Anuradee Witthayapayanon et al., 2006) better than linker-based micelles and conventional surfactant systems (Ampira Charoensaeng et al., 2008). In addition to enhancing adsolubilization, only small amounts of extended-surfactants are needed to form admicelles. Noulkamol Arpornpong (2008), who has studied several extended sulfate and carboxylate surfactants (C_{16-17}-4PO-5EO-COONa, C_{16-18}-4PO-5EO-COONa, and C_{16-17}-4PO-SO_4Na), found that extended surfactants can enhance the solubilization and adsolubilization of styrene and phenanthrene. Although the physical properties (water solubility and dipole moment) of styrene and phenanthrene are significantly different, the results did not clearly illustrate a relationship between the physical properties of organic solutes and their locus in the micelle.

In this study, two organic solutes, phenylethanol and ethylcyclohexane, were used because of their comparable structure to styrene. Phenylethanol has relatively high dipole movement, while ethylcyclohexane has low dipole moment. These two solutes were used to evaluate the extent of solubilization and adsolubilization by carboxylate and sulfate extended surfactants. Sodium dodecyl sulfate (C12S), a conventional surfactant, was used in this study in order to compare its properties with those of the extended surfactants.

1.2 OBJECTIVES

The overall objectives of this study are to determine the effects of two anionic carboxylate extended surfactants and an anionic sulfate extended surfactant on the solubilization and adsolubilization of phenylethanol and ethylcyclohexane onto positively charged aluminum oxide in the forms of micelles and admicelles, respectively. The electrolyte concentration, temperature, and solution pH were controlled under constant conditions in batch systems. The specific objectives of this study are as follows:

1) To investigate the surfactant adsorption capacities of a conventional surfactant, two carboxylate extended surfactants, and a sulfate extended surfactant.
2) To study the alumina surface charge of the conventional and anionic extended surfactant systems.
3) To evaluate the desorption capacity of adsorbed admicelles onto an alumina oxide surface after the washing process.
4) To study the organic removal efficiency by surfactant modified materials with the conventional and extended surfactants.

1.3 SCOPES OF THE STUDY

This study aims to enhance the ability of adsorbent materials for organic contaminants removal through the surfactant-based adsorption process. The surfactants used in this study were sodium dodecyl sulfate (a conventional surfactant), two alkyl propoxylated ethoxylated carboxylate surfactants, and an alkyl propoxylated sulfate surfactant. The surfactant adsorption, solubilization, and adsolubilization isotherms of organic solutes were determined to evaluate the impact of the anionic extended surfactants on a positively charged aluminum oxide surface. Solubilization and adsolubilization experiments of phenylethanol and ethylcyclohexane, with high dipole moment and low dipole moment, were conducted to evaluate the solubilization capacity by determining the micellar and admicellar partition coefficients (K_{mic} and K_{adm}). The surface charge of aluminum oxide (zeta potential) and surfactant adsorption, and desorption capacity were studied to evaluate the surfactant formation and stability of surfactants adsorbed onto an aluminum oxide surface. Batch experiments were conducted at room temperature (25±2 °C), an electrolyte concentration of 0.001 M NaCl, and a solution pH of 8.0-8.5, which was maintained by the addition of NaOH and/or HCl.

1.4 HYPOTHESES

The extent and locus of organic solutes in admicelles and micelles depends on the properties of the extended surfactants and of the organic solutes. The more specific hypotheses of this work are as follows:

1) Extended-surfactant-based micellar and admicellar systems enhance solubilization and adsolubilization due to an increase of the micellar and admicellar interior.
2) Longer alkyl chain lengths of the surfactant improve the solubilization and adsolubilization of phenylethanol and ethylcyclohexane.

3) Charge repulsion of adjacent surfactants carrying the same charge is decreased by extended surfactants, which leads to increases in the adsorption density and adsolubilization capacity.

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 SURFACTANT PHENOMENA

Surfactants (derived from “surface active agents”) are typically ampiphilic molecules that contain both polar, hydrophilic groups (their "heads") and nonpolar, lipophilic or hydrophobic groups (their "tails"), as shown in Figure 2-1 (West and Harwell, 1992). Surfactants can be categorized by the ionic charge of their polar moiety (hydrophilic group): nonionic, anionic, cationic, and zwitterionic (containing both anionic and cationic charges) and the lipophilic group is usually a long-chain hydrocarbon residue, and less often a halogenated or oxygenated hydrocarbon or siloxane chain. The balance between the lipophilic and hydrophilic parts of the molecule gives these systems their unique properties, such as their accumulation at various interfaces and interactions within the solution (to form micelles). Surfactants tend to accumulate in interfacial regions (e.g., oil-water, air-water, and liquid-solid interfaces) and alter or reduce free energy states or interfacial tensions (free energy per unit area) (Rouse et al., 2001; Rosen, 2004; Tadros, 2005).

Figure 2-1 Schematic illustration of a surfactant molecule

Carboxylate and sulfate are the polar groups found in anionic surfactants. They are used in greater volume than any other surfactant class and used in most detergent formulations. The counterions most commonly used are sodium, potassium, ammonium, calcium and various protonated alkyl amines. Sodium and potassium impart water solubility, whereas calcium and magnesium promote oil solubility, and amine/alkanol amine salts give products with both oil and water solubility (Holmberg et al., 2002).

In an aqueous solution, surfactants have the ability to form many different types of aggregates depending on the nature of the surfactant and the solution's properties, such as solvent type, concentration, and temperature. At low surfactant concentrations in water, surfactants occur as *monomers* in the solution as well as at the interface. When the surfactant concentration increases until it exceeds a certain level, the surfactant monomers self-aggregate into cluster called *micelles* (West and Harwell, 1992; Matsson, 2005). In normal micelles, the hydrophobic tails are oriented toward the interior of the spherical micelles and the hydrophilic heads faces the water (Rosen, 2004). This phenomenon is called *micellization* or micelle formation. Micelles are formed when the surfactant concentrations exceeds the *critical micelle concentration (CMC)*, which depend on the type of surfactant, the temperature, and electrolyte concentration. If the surfactant concentration rises above the CMC, the number of micelles increases. The structure of a surfactant can transform when the solution conditions change (i.e., the electrolyte concentration, temperature, pressure, and solution pH). Possible structures are restricted by the forces acting to keep amphiphiles polar and nonpolar parts in favorable environments (Uppgård, 2002). The surfactant micellization process is shown in Figure 2-2.

When a solid phase is added to a surfactant solution, surfactant monomers will adsorb at the solid-liquid interface. At low concentrations, a surfactant begin to form *hemimicelles* and *admicelles*, depending on whether the aggregates have one surfactant layer (monolayer) or two (bilayer) (as shown in Figure 2-2). As the surfactant reaches its CMC, the amount of adsorbed surfactant does not increase but rather increases the concentration of micelles in the aqueous solution (West and Harwell, 1992). The surfactant adsorption at solid-liquid interface is described in next section.

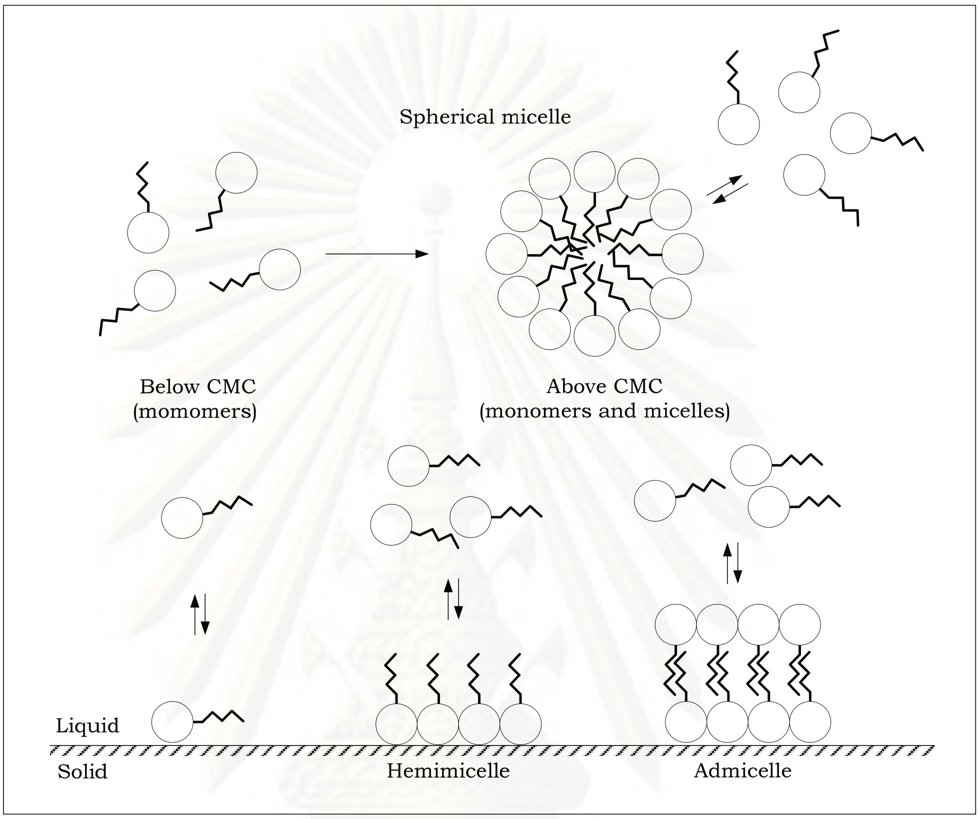


Figure 2-2 Example of surfactant micellization (West and Harwell, 1992)

2.2 ADSORPTION OF A SURFACTANT ONTO THE SOLID OXIDE SURFACE

2.2.1 Surfactant Adsorption Phenomena

Many interactions on interface occur when the adsorption of ionic surfactants take place on an oppositely charged surface (e.g., aluminum oxide); electrostatic, dispersion, hydrophobic forces, hydrogen bonding, and Lewis acid-base interactions are examples of these interactions. The adsorption at the solid/liquid interface most commonly characterized by the adsorption isotherm in typically an S-shaped isotherm, where the adsorbed amount at equilibrium is set in relation to the bulk solution concentration at equilibrium (Matsson, 2005; Zhang and Somasundaran, 2006). These isotherms are commonly divided into four regions, as shown in Figure 2-3.

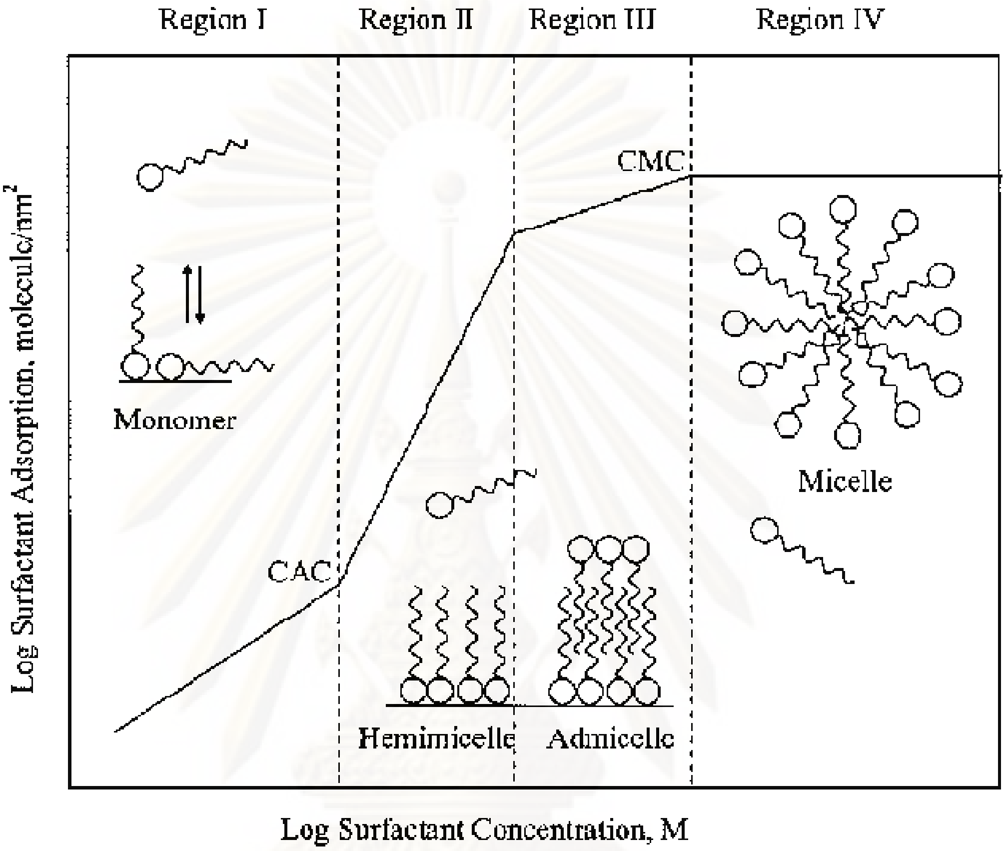


Figure 2-3 Adsorption isotherm of a surfactant onto a solid surface (Aranya Fuangswasdi et al., 2006 modified from Scamehorn et al., 1982)

Region I is a region of low adsorption densities and sometimes referred to as the Henry's law region. In this region, the surfactants are adsorbed as monomers in a linear manner and do not interact with one another. The adsorption in this zone results primarily from electrostatic forces between surfactant ions and the charged solid surface.

Region II is indicated by an increase in the isotherm slope. In this region, the adsorption is due to the electrostatic attraction between the ions and the charged solid surface and hemimicelles association of hydrocarbon chains, which have head groups that adsorb on the solid surface while the tail groups are in contact with the aqueous solution. When the surfactant molecules/ions are equivalent in number to the surface sites have been adsorbed, the contribution due to the electrostatic attraction disappears and the further increase in adsorption will be only due to the association between the hydrocarbon chains. Micelle-like aggregates form a monolayer structure that is called *hemimicelle* and a bilayerd structure that is called an *admicelle*, consisting of a lower layer of head groups that adsorb on the solid surface and an upper layer of head groups in contact with solution. The concentration at which the transition from region I to region II occurs is called the critical admicelles concentration (CAC) or hemimicelle concentration (HMC).

Region III is the region that has the slope of the isotherm decreasing from Region II. This decrease in slope is attributed to lateral electrostatic repulsions between adjacent surfactant molecules adsorbing on the surface and/or to the beginning of admicelle formation on lower energy surface patches. The transition from region II to region III is marked by a decrease in the slope of the isotherm.

Region IV is called the plateau adsorption region occurring above the CMC. In most systems, the transition point from region III to region IV occurs approximately at the CMC, representing the first formation of micelles that are formed after the interface is saturated by admicelles. While increases in the surfactant concentration contribute to the micellization in solution, it does not change the adsorption density. The adsorption in this region is mainly through lateral hydrophobic interactions between the hydrocarbon chains (Boonyarach Kitiyanan et al., 1996; Paria and Khilar, 2004; Rosen, 2004; Adak et al., 2005; Aranya Fuangswasdi et al., 2006; Zhang and Somasundaran, 2006; Ampira Charoensaeng et al., 2008).

2.2.2 Mechanisms of Surfactant Adsorption

In general, the adsorption of a surfactant is controlled by a number of forces, such as covalent bonding, electrostatic attraction, hydrogen bonding or non-polar interactions between the adsorbed species, lateral associative interaction, solvation, and desolvation. The total adsorption is usually the cumulative result of some or all of the above forces. The mechanisms of surfactant adsorption are reviewed in terms of various forces involved and factors controlling them (Fuerstenau, 1971; Somasundaran and Grieves, 1975; Zhang and Somasundaran, 2006).

Electrostatic interactions: When the ionic surfactants and the charge of solid particles are in a system. The charge on the particle surface could be due to either the result of the hydrolysis of surface species in the case of oxides or due to the preferential dissolution of the lattice ions and subsequent adsorption of the resulting complexes.

Chemical interactions: The chemical interaction is an important driving force for the adsorption of surfactants on solid particles. Compared to other driving forces, this interaction is specific to certain systems where covalent bonding can occur between the surfactant and the solid.

Hydrophobic lateral interactions: The driving force for adsorption results from the free energy from the transfer of the hydrocarbon chains from the aqueous environment to the hydrophobic interior of the aggregates.

Hydrophobic interactions between the hydrocarbon chains and hydrophobic sites on the solid: In this case, the surfactant molecules attach to the hydrophobic sites with the hydrocarbon chains aligning parallel to the surface at low concentrations and to the surface at higher concentrations. 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.

Hydrogen bonding: Hydrogen bonding between surfactant species and the solid surface species could occur in systems containing hydroxyl, phenolic, carboxylic and amine groups on the surfactant. For instance, the adsorption of a nonionic surfactant such as ethoxylated alcohol and sugar-based alkyl glucoside on oxides has been proposed to involve hydrogen bonding.

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

2.2.3 Aluminum Oxide Surface Structure

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

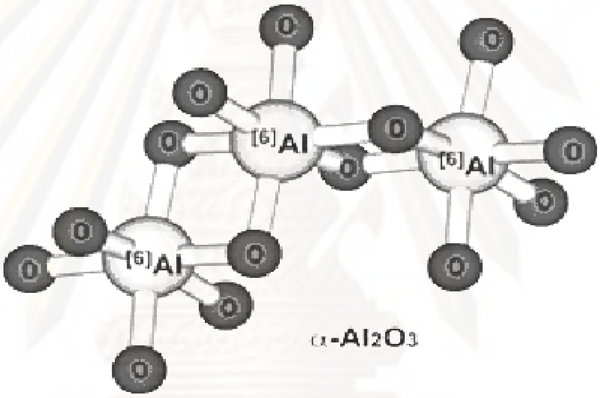


Figure 2-4 Schematic crystal structure of α-Al_2O_3

The crystal surface can form a layer of hydroxyl ions in contact with water by a two-step process involving the chemical adsorption of the monolayer of water and its dissociation. Since the alumina surface is covered with hydroxyl groups, hydrogen and hydroxyl ions are the potential determining ions for aluminum oxide. Moreover, there is also a physically adsorbed layer of water molecules on top of the layer of hydroxyl ions. Therefore, the solution pH is critical for the adsorption of ionic surfactants due to its capacity to control the charge of the alumina surface.

The solution pH of alumina has a net surface charge density equal zero, which is called the *point of zero charge* (PZC). The PZC of alumina at 25 °C has been reported to be pH 9.1 (Sun and Jaffe, 1996). When the solution pH is below the PZC (<9.1), the alumina surface is positively charged. On the other hand, when the solution pH is above the PZC (>9.1), the alumina surface is negatively charged. It must be noted that alumina has been widely studied in relation to the adsorption of anionic surfactants and mixed anionic and nonionic surfactants yet only on positively charged surfaces (Sun and Jaffe, 1996; Esumi et al., 2000; Esumi, 2004; Aranya Fuangswasdi et al., 2006; Noulkamol Arpornpong, 2008; Ampira Charoensaeng et al., 2008; Ampira Charoensaeng et al., 2009).

2.2.4 Parameters Affecting Surfactant Adsorption

The adsorption of surfactants at the solid–liquid interface is strongly influenced by a number of factors: (1) the nature of the structural groups on the solid surface, whether the surface contains highly charged sites or essentially nonpolar groupings, and the nature of the atoms of which these sites or groupings are constituted (i.e., alumina, silica, and zeolite); (2) the molecular structure of the surfactant being adsorbed (the adsorbate), whether it is ionic or nonionic, and whether the hydrophobic group is long or short, straight chain or branched, aliphatic or aromatic; and (3) the environment of the aqueous phase such as the pH, electrolyte concentration, presence of any additives with short chain polar solutes (e.g., alcohol and urea), and temperature. Together these factors determine the mechanisms by which adsorption occurs and the efficiency and effectiveness of adsorption (Rosen, 2004).

Surfactant aggregation at oppositely charged surfaces (a negatively charged aluminum oxide was used in this study) is thus a matter of a balance between the interaction of the surfactant head group with the surface and the interaction between the hydrophobic moieties of the surfactant. The parameters that controlled surfactant adsorption such as the type of surfactant molecule, the pH of the solution, the electrolyte concentration, and the temperature are described below (Boonyarach Kitiyanan et al., 1996; Holmberg et al., 2002; Rosen, 2004).

2.2.4.1 Type of Surfactant Molecule

For ionic surfactants, the effectiveness of adsorption (i.e., the amount adsorbed at surface saturation), may increase, decrease, or show no change with increases in the length of the hydrophobic group, depending on the orientation of the adsorbate at the adsorbent–solution interface. Moreover, the size of the hydrophilic group may be used to determine the effectiveness of adsorption when the cross-sectional area of that group is greater than that of the hydrophobic chain: the larger the hydrophilic group, the smaller the amount adsorbed at surface saturation.

2.2.4.2 Solution pH

The pH of the solution usually causes marked changes in the adsorption of ionic surfactants onto charged solid substrates. As the pH of the aqueous phase is lowered, a solid surface (alumina) will usually become more positive, or less negative, because of adsorption onto charged sites of protons from the solution, with consequent increases in the adsorption of anionic surfactants and decreases in the adsorption of cationic surfactants. When the pH of the aqueous phase increases, it may convert the surfactant from one containing an ionic group capable of strong adsorption onto oppositely charged sites on the adsorbent to a neutral molecule capable of adsorption only through hydrogen bonding or dispersion forces. This charge variability is caused by the release and uptake of protons or hydroxyls. Generally, the H^+ and OH^- are the potential determining ions (Paria and Khilar, 2004; Rosen, 2004). The equilibrium pH is usually higher than the initial solution pH due to the anionic surfactant ions exchange with the adsorbed counter ions and hydroxyl ions on the alumina. So, the equilibrium pH is closely related to surfactant adsorption.

2.2.4.3 Electrolyte Concentration

The addition of neutral electrolyte (such as NaCl or KBr) causes a decrease in the adsorption of ionic surfactants onto an oppositely charged adsorbent and an increase in the adsorption onto a similarly charged adsorbent. These effects are caused by the decreased attraction between oppositely charged species and the decreased repulsion between similarly charged species at higher ionic strengths. Admicelle patches with the complete bilayer are capable of a larger aggregation number of surfactant admicelles. In the aqueous solution, when the concentration of electrolyte increases, the maximum surfactant adsorption also increases (Rosen, 2004).

2.2.4.4 Temperature

Temperature increases generally cause a decrease in the efficiency and effectiveness of ionic surfactants adsorption (Paria and Khilar, 2004; Rosen, 2004; Wasan Saphanuchart et al., 2008). The effect of temperature is relatively small compared to that caused by solution pH. However, a rise in temperature usually results in an increase in the adsorption of non-ionic surfactants containing a polyelectrolyte chain as the hydrophobic group.

2.3 SOLUBILIZATION AND ADSOLUBILIZATION OF ORGANIC SOLUTION

Micelles are formed when the surfactant concentration exceeds the CMC. Above the CMC, surfactant monomers associate with one another to form micelles, which have a hydrophobic interior. When an organic solute comes in contact with an aqueous micellar solution, the organic solute partitions into the hydrophobic core of these micelles in a process known as *solubilization*. Upon the addition of a solid below the CMC, the surfactant bilayers are arranged as follows: the surfactant head group of the bottom layer is in contact with solid surfaces of the opposite charge and other head groups of the top layer is positioned towards the aqueous solution. The surfactant will adsorb on the solid surface and form “adsorbed micelles” or admicelles. The hydrophobic core of an admicelle is ideal for solubilizing organic solutes, a process known as *adsolubilization* (Boonyarach Kitiyanan et al., 1996; Rosen, 2004; Aranya Fuangswasdi et al., 2006; Ampira Charoensaeng et al., 2008). The phenomena of adsolubilization and solubilization are shown in Figure 2-5.

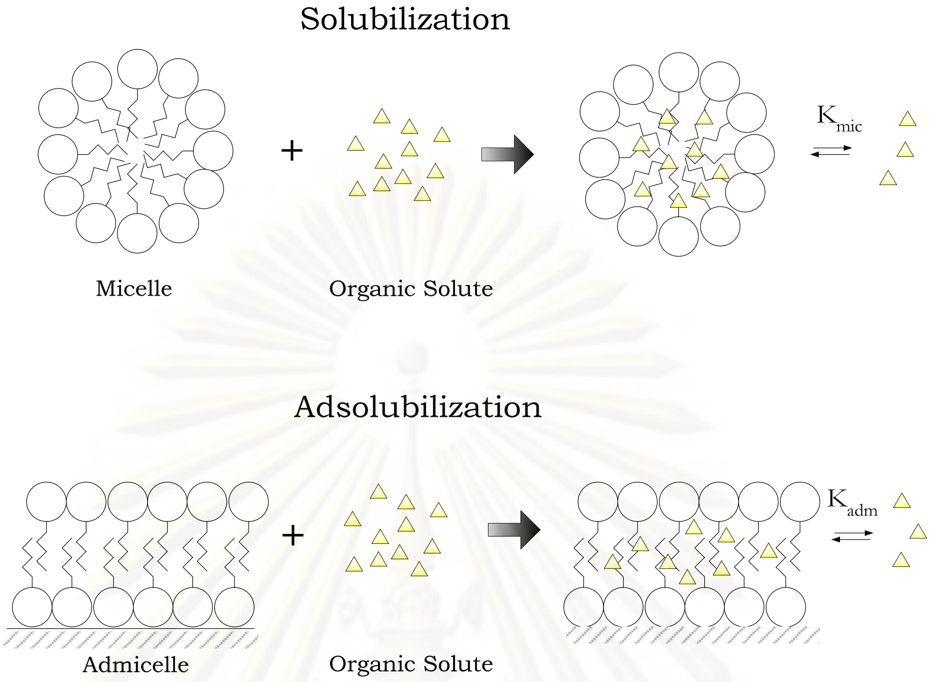


Figure 2-5 Phenomena of solubilization and adsolubilization (adapted from Boonyarach Kitiyanan et al., 1996)

Similar in nature to a micelle, the admicelle is characterized by three regions. The outer region is the most polar, because it consists of the surfactant head groups and forms the admicelle/water and admicelle/solid interfaces. The inner region is referred to as the core region. This region is nonpolar in nature because it consists of the hydrocarbon chains. Nonpolar solute is expected to partition primarily within the core region. The region between the head groups and the core is the palisade region. This region is intermediate in polarity, consists of the carbons near the head groups, and is also characterized by water molecules that have penetrated the admicelle. Polar solute is expected to preferentially adsolubilize in the palisade layer. The bilayer structure of an admicelle is shown in Figure 2-6 (Dickson and O’Haver, 2002; Aranya Fuangswasdi et al., 2006).

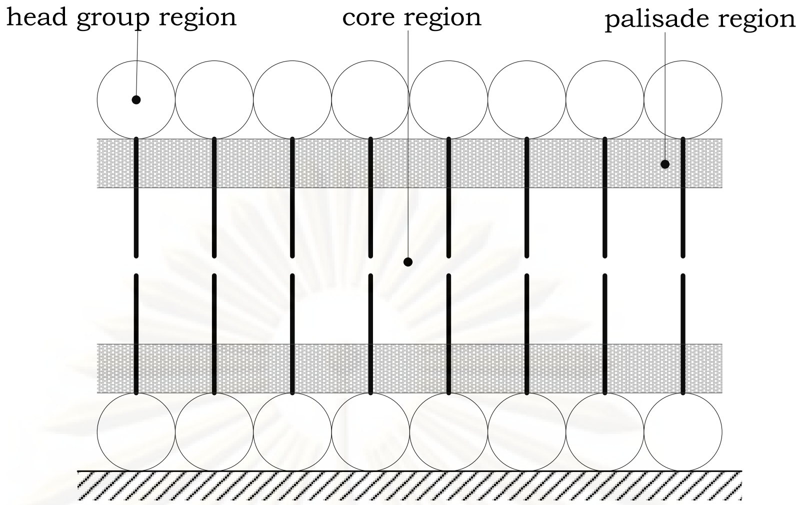


Figure 2-6 The bilayer structure of surfactant admicelles at the solid-liquid interface (Nayyar et al., 1994)

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

The solubilization capacity or solubilizing power of the micelle is defined as the molar solubilization ratio (MSR). The MSR is the moles of the solute solubilized per mole of surfactant in the micelles, and it is obtained from the slope of the graph of the surfactant concentration versus the organic solutes concentration in mol/L. MSR can be calculated as follows:

$$MSR = \frac{(C_{mic} - C_{cmc})}{(S_{surf} - S_{cmc})} \tag{2-1}$$

where C_{cmc} is the solubilization of the organic solute at the CMC (mol/l), C_{mic} is the total apparent solubility of the organic solute in the micelles (mol/l), and S_{surf} is the concentration of the surfactant above the CMC. Another measurement of solubilization is the micellar partition coefficient (K_{mic}). K_{mic} can be described as the partitioning of the various organic solutes between the surfactant micelle and the aqueous phase. The K_{mic} is used to quantity the solubilization capacity, shown in Equation 2-2:

$$K_{mic} = \frac{X_{mic}}{X_{aq}} \tag{2-2}$$

Here, X_{mic} is the mole fraction of the organic solute in the micelle pseudophase, X_{aq} is the mole fraction of the organic solute in the aqueous phase. X_{mic} and X_{aq} are calculated using Equations 2-3 and 2-4, respectively (Fuangswasdi et al., 2006).

$$X_{mic} = \frac{MSR}{[1+MSR]} \tag{2-3}$$

$$X_{aq} = \frac{C_{eq}}{C_{eq} + 55.55} \tag{2-4}$$

where C_{eq} is the molar solubility of the organic solute in the aqueous phase, and 55.55 is the inverse molar volume of water.

Additionally, the partitioning of organic solutes into admicelles can be described by the admicellar partitioning coefficient (K_{adm}). K_{adm} is used to quantify the adsolubilization capacity. It can be calculated from Equation 2-5 (Nayyar et al., 1994).

$$K_{adm} = \frac{X_{adm}}{X_{aq}} \tag{2-5}$$

where X_{adm} and X_{aq} represent the mole fraction of the organic solute in the admicelle and the aqueous phase, respectively. The X_{adm} value can be calculated from Equation 2-6.

$$X_{adm} = \frac{(C_0 - C_{eq})}{(C_0 - C_{eq}) + (S_0 - S_{eq})} \tag{2-6}$$

Here C_O and C_{eq} are the respective initial and equilibrium concentrations of the organic solute, and S_O and S_{eq} are the respective concentrations of the surfactant added and present as monomers. The value of X_{aq} can be calculated using Equation 2-7.

$$X_{aq} = \frac{C_{eq}}{C_{eq} + 55.55} \tag{2-7}$$

Many researchers have demonstrated that surfactants can greatly increase the solubilization and adsolubilization of organic contaminants in the subsurface (Childs et al., 2006; Cheng and Sabatini, 2002; Harwell et al., 1999; Sabatini et al., 1996). Solubilization and adsolubilization have been studied in many systems consisting of different combinations of surfactants and particles (Esumi et al., 2000).

Nayyar et al. (1994) have reported on the adsolubilization of nonpolar, polar, and ionizable organic compounds (naphthalene, naphthol, and 4-amino-1 naphthalene sulfonic acid, respectively) using sodium dodecyl sulfate and alumina particles. They have explained the variations in adsolubilization results on the basis of surfactant fundamentals and contaminant properties.

Boonyarach Kitiyanan et al. (1996) have studied adsolubilization of styrene, isoprene, and mixtures of styrene and isoprene into cetyltrimethylammonium bromide (CTAB) bilayers (admicelles) on precipitated silica. The results show that the admicellar partition coefficient of styrene in the CTAB bilayer remains almost constant as the styrene concentration increases, which suggests that styrene is adsolubilized into both the palisade layer and the core layer of the admicelle. For isoprene, the admicellar partition coefficient decreases when the isoprene mole fraction is increased. It believed to be adsolubilized into the palisade layer of the admicelle and in the co-monomer system. Styrene adsolubilization is slightly increased in the presence of isoprene but isoprene adsolubilization is significantly enhanced in the presence of styrene. This result is similar to that of Dickson and O’Haver (2002), who founded that partition coefficients can be used to elucidate the locus of solubilization in micelles. If the solute partitions primarily to the core, the partition coefficients will increase as the mole fraction of the solubilizate increases. If the solute partitions primarily to the palisade region, the partition coefficients will decrease as the mole fraction of the solubilizate increases. If the solute partitions to both the core and the palisade, the partition coefficient will remain constant as the mole fraction of the solubilizate increases. Furthermore, the factors that affect adsolubilization have been investigated such as the surfactant concentration, solution pH, ionic strength of the solution, and hydrocarbon chain structure.

Aranya Fuangswasdi et al. (2006) have investigated the mixtures of cationic and anionic surfactants with twin and single head groups used to solubilize styrene and ethylcyclohexane into mixed micelles and adsolubilize them into mixed admicelles on silica surfaces. The mixed cationic-anionic micelles show a higher solubilization capacity compared to that of single surfactant micelles, and mixtures of cationic-anionic surfactants produce larger adsolubilization of organic compounds than do single surfactant admicelles.

2.4 SURFACE TENSION AT THE LIQUID-AIR INTERFACE

The surfactant adsorbs at the liquid-air surface with their polar parts directed towards the aqueous solution and the hydrocarbon parts directed towards the air. This lowers the surface tension. Typically, surfactants show a gradual reduction in surface tension until the CMC is reached, above which the surface tension remains virtually constant (Matsson, 2005).

The surface tension is defined as the increase in Gibbs free energy per unit increment in area, or the amount of work it takes to form the interface area. It is intimately linked with the surfactant adsorption on the liquid-air interface, since surfactant adsorption reduces the surface tension. Both the surface tension and the surfactant adsorption exhibit a discontinuity in the slope as the concentration reaches the CMC of the surfactant. This corresponds to reaching an adsorption plateau just after the CMC. The reason for this plateau comes from solution thermodynamics. The surfactant adsorbing at the same time as the first micelle is formed has to have the same chemical potential as the surfactants in the micelle for the system to be at equilibrium. A surfactant molecule added to the system above the CMC must go into the formation of new micelles, since any new micelle has the same chemical potential as the first, while for a surfactant to adsorb at the interface above CMC, the chemical potential needs to be increased. When the plateau is reached, the surfactants on the liquid-air interface normally form monolayers (Holmberg et al., 2002).

For surface-active solutes the surface excess concentration, Γ, can be considered to be equal to the actual surface concentration without significant error. The concentration of the surfactant at the interface may therefore be calculated from the surface or interfacial tension data by use of the appropriate Gibbs equation. This following equation (Equation 2-8) is for a 1:1 ionic surfactant in the absence of any other solution (Rosen, 2004).

$$\Gamma = -\frac{1}{4.606\,RT}\left(\frac{\partial\gamma}{\partial \log C_1}\right)_T \tag{2-8}$$

where γ is the surface (interfacial) tension (N/m). R is equal to 8.314 $\mathrm{Jmol^{-1}K^{-1}}$, T is equal to 298 $^{\circ}$C at 25 $^{\circ}$C, and C_1 is the surfactant concentration (molar). The surface concentration can be obtained from the slope of a plot of γ versus log C_1 at constant temperature.

The area per molecule at the interface provides information for the degree of packing and the orientation of the adsorbed surfactant molecule when compared with the dimensions of the molecule as obtained by use of the molecular model. From the surface excess concentration, the area per molecule at the interface a^{s}_{1}, in square angstroms can be calculated from Equation 2-9 (Rosen, 2004).

$$a_1^{s} = \frac{10^{23}}{N\Gamma_1} \tag{2-9}$$

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

2.5 EXTENDED SURFACTANTS

Extended surfactants are surfactants in which groups of intermediate polarity, such as polypropylene oxides (PO) or copolymers of propylene oxides and ethylene oxide (EO), are inserted between the hydrocarbon tail and hydrophilic head group and thus have been referred to as internal linker systems as shown in Figure 2-7. Due to the resulting unique molecular structure, the surfactant is stretched out further into both the oil and water phases, providing a smoother transition between the hydrophilic and hydrophobic regions of the interface, which provides a more suitable environment for solubilizing hydrophilic and lipophilic molecules. The disadvantage of extended surfactants is that, as with any large surfactant molecule, they tend to form gels at moderate surfactant concentrations (Sabatini et al., 2003; Anuradee Witthayapayanon et al., 2006).

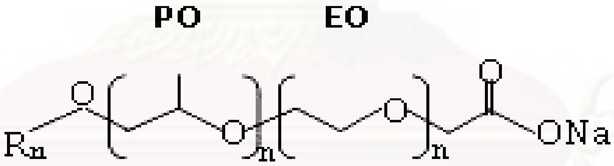


Figure 2-7 Extended surfactant structure

Anionic carboxylate or sulfate extended surfactants that exhibit a unique characteristic allow for the improved solubilization of oily materials in an aqueous medium by extending the interface. The advantages of carboxylate extended surfactants include their ready biodegradability, low toxicity, ability to increase water solubility, and enhancement of chemical stability (no hydrolysis) (Tadros, 2005). The applications of anionic extended surfactants can be used to enhance a wide variety of industrial processes and personal care products: oil recovery, soil remediation, drill cutting washing, oil/seed extraction, dry cleaning, industrial cleaning, personal care formulations, and a variety of other applications (Sasol North America Inc., 2007).

Recently, the extended surfactants containing the EO group and/or PO group have been showen to enhance the solubilization and adsolubilization of organic solutes onto positively charged surfaces (Miñana-Perez et al., 1995; Anuradee Witthayapayanon et al., 2006; Noulkamol Arpornpong, 2008; Ampira Charoensaeng et al., 2008; Ampira Charoensaeng et al., 2009). Miñana-Perez et al. (1995) found that the CMC decreases as the propylene oxide chain (PO) increases by using alkyl polypropylene oxide ether sulfates as extended surfactants, as expected from the fact that PO number is globally lipophilic. In their study, the solubilization of oil (hexadecane, ethyl oleate, myglyol 812, and soja oil) increased when the PO number increased. The presence of EO groups in the alcohol chain length of the extended surfactant structures gives outstanding solubilization parameters. The study of Tan and O'Haver (2004) reported that styrene adsolubilization at the water–silica interface decreases as the numbers of ethyoxylated (EO) units in the surfactant increases, especially at higher styrene loading levels while using Triton X surfactants on precipitated silica without a lipophilic linker. Moreover, the amount of adsorbed surfactant in the plateau region decreases significantly when the CMC increases slightly with the increasing numbers of EO units. At low levels of adsorption, the amount of adsorbed surfactant increased significantly with the increasing number of EO units due to the stronger interaction between silica and the larger head groups.

Ampira Charoensaeng et al. (2008 and 2009) studied the solubilization and adsolubilization of higher and lower polar organic solutes by linker molecules and extended surfactants. The results show that for phenylethanol, the solubilization capacities (K_{mic}) and adsolubilization capacities (K_{adm}) of the extended surfactants ($C_{12,13}$-3PO-SO_4 and $C_{14,15}$-3PO-SO_4) were higher than those of the conventional surfactants. Increasing the PO number for the C-14,15 and C-12,13 extended surfactants has relatively small effects on K_{mic} values. MSR and K_{adm} decreased as the PO number increased. Moreover, varying the carbon chain length in the surfactant tail

(C_{12}-C_{14}) with same PO number had no effect on solubilization and adsolubilization. For styrene and ethylcyclohexane, the extended surfactants produced higher K_{mic} and K_{adm} than the conventional surfactants alone and with a linker solute. As the number of PO groups and the tail length increased, the K_{mic} and K_{adm} of ethylcyclohexane also increased but the K_{mic} and K_{adm} of styrene only slightly increased.

Noulkamol Arpornpong (2008) studied the adsolubilization and solubilization of styrene (higher polarity) and phenanthrene (lower polarity) using a conventional (SDS) and three extended anionic surfactants (C_{16-17}-4PO-5EO-COONa, C_{16-18}-4PO-5EO-COONa, and C_{16-17}-4PO-SO_4Na) on an aluminum oxide surface. She founded that styrene adsolubilization by SDS was greater than that of the extended surfactants, but the extended sulfate surfactants showed the highest adsolubilization capacity on phenanthrene. For solubilization of styrene and phenanthrene, the extended surfactants had greater styrene and phenanthrene solubilization capacity than did SDS. The desorption capacity of the extended carboxylate surfactants showed a lower desorption capacity as compared to the conventional surfactant.

CHAPTER III

METHODOLOGY

3.1 MATERIALS

3.1.1 Surfactants

The surfactants used in this study are divided into two types: the conventional surfactant and extended surfactants.

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

Extended surfactants: The anionic extended surfactant used in this study was branched and contained a linear alkoxylated alcohol of the Alfoterra® series with distributions in carbon chain length of either 16 to 17 carbon atoms or 16 to 18 carbon atoms with different number of intermediate groups and hydrophilic head types. These anionic extended surfactants were donated from Sasol North America Inc. (LA, USA). The properties of the studied surfactants are shown in Table 3-1.

Each of the alkyl propoxylated ethoxylated carboxylate surfactants studied contained 4 moles of the propylene oxide (PO) group, 5 moles of the ethylene oxide (EO) group, and the carboxylated head group connected to a sodium carboxylate hydrophilic head. The linear alkyl chain varied between 16-17 carbon atoms (C16.5) and 16-18 carbon atoms (C17).

The alkyl propoxylated sulfate surfactant is an anionic sulfate extended surfactant of the Alfoterra® series and contains 4 moles of propylene oxide groups (PO).

It has an alkyl chain length of 16 to 17 carbon atoms (C16.5) and the sulfated head group is connected to a sodium sulfate hydrophilic head.

Table 3-1 The properties of the surfactants

Surfactant	Abb[a]	Type	Carbon	Formula	HLB[b] Number
Conventional surfactant					
Sodium dodecyl sulfate	C12S	Anionic conventional	12	$C_{12}H_{25}OSO_3Na$	40.00
Carboxylate surfactant					
Alkyl propoxylated ethoxylate carboxylate	C16.5-4PO5EOC	Anionic extended	16-17	$C_{16,17}$- $(PO)_4$-$(EO)_5$-COONa	19.31
Alkyl propoxylated ethoxylate carboxylate	C17-4PO5EOC	Anionic extended	16-18	$C_{16,18}$- $(PO)_4$-$(EO)_5$-COONa	19.08
Sulfate surfactant					
Alkyl propoxylated sulfate	C16.5-4POS	Anionic extended	16-17	$C_{16,17}$- $(PO)_4$-SO_4Na	37.26

[a] C# = the number of carbon, #PO = the number of PO groups, #EO = the number of EO groups, and S/C = the sulfate or carboxylate

[b] HLB is the hydrophilic - lipophilic balance (see in Appendix A)

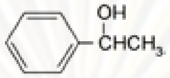
PO: Propylene oxide (C_3H_6O)

EO: Ethylene oxide (C_2H_4O)

3.1.2 Organic Solutes

Two organic solutes with different polarities were selected in this study. Phenylethanol was purchased from Fluka Chemical Company with a purity of 98%. Ethylcyclohexane was purchased from Arcos Chemical Company with a purity of 99%. Phenylethanol and ethylcyclohexane were selected as the organic solutes with a strong and weak polarity, respectively. The physical and chemical properties of the organic solutes are shown in Table 3-2.

Table 3-2 Properties of the organic solutes

Organic solute	Molecular formula		MW	Water solubility (mg/L)	Density 25 °C (g/mL)	log K_{ow}	Dipole moment
	Formula	Structure					
Phenylethanol	$C_6H_5CH(OH)CH_3$		122.16	1,950	1.01	1.42[a]	1.65
Ethylcyclohexane	$C_6H_{11}C_2H_5$		112.40	2.92	0.79	3.44[b]	0.00

[a] http://agrippina.bcs.deakin.edu.au/bcs_admin/msds/msds_docs/1-Phenylethanol.pdf

[b] For cyclohexane (adapted from Schwarzenbach, R.P.; Gschwend, P.M.; Imboden, D.M. (1993), Environmental organic chemistry. John Wiley & Son, Inc)

3.1.3 Solid Oxide Surface

Aluminum oxide or alumina (Al_2O_3), which was used as received, was used as the adsorbent and purchased from Aldrich Chemical Company. Alumina has a particle size of approximately 150 meshes. The specific surface area obtained from the product description of the manufacturer 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 were used as received and were of ACS analytical reagent grade. All solutions were prepared with deionized water with a resistance of 18.2 MΩ cm. Plastic and glassware were rinsed well with deionized water three times prior their use.

3.2 EXPERIMENTAL SECTION

The experimental setup in this study was divided into five sections: (1) the CMC measurements, (2) the adsorption study, (3) the surface charge of aluminum oxide (zeta potential) and surfactant adsorption, (4) the surfactant desorption studies, and (5) the solubilization and adsolubilization studies. All experiments were conducted in batch experiments using 40 mL vials at room temperature (25±2 °C), a constant solution pH of

8.0-8.5 adjusted by using sodium hydroxide (NaOH) and hydrochloric acid (HCl), and an electrolyte concentration of 0.001 M NaCl.

3.2.1 CMC Measurements

The CMCs of the surfactant systems used in this research were determined using a Wilhelmy plate tensiometer (DCAT 11, DataPhysics, Filderstadt, Germany) with a platinum plate. The CMC of each system was obtained from the graph of the surface tension plotted against the logarithm of the total concentration of the surfactant. The break point of the curve was determined to be the CMC of the surfactant.

3.2.2 Surfactant Adsorption Study

Surfactant adsorption was studied by adding 40 mL of a surfactant solution to different amounts of alumina. Equilibrium was reached by shaking the solutions at 150 rpm for at least 48 h; after 12 h, the solution pH was measured and adjusted to 8.0-8.5. After reaching equilibration, each solution was centrifuged to remove the alumina. The surfactant concentration in the supernatant was analyzed. Surfactant density adsorption was calculated by Equation 3-1. It is assumed that the adsorption of water or salt is negligible and the adsorptions of the surfactant had no effect on solution density (Lopata, 1988).

$$q_i = \frac{(C_{i,b} - C_{i,a})V}{W_g} \tag{3-1}$$

Where

q_i = Adsorption density of surfactant i (mole/g)
V = Volume of sample (L)
$C_{i,a}$ = Concentration of surfactant at equilibrium (Molar)
$C_{i,b}$ = Initial surfactant concentration (Molar)
W_g = Weight of aluminum oxide (g)

3.2.3 Surface Charge of Aluminum Oxide (Zeta Potential) and Surfactant Adsorption

The alumina surface charges (zeta potential) of the conventional and anionic extended surfactants on alumina were conducted to evaluate the adsorption of surfactant onto an alumina surface. Varying surfactant concentrations and amounts of alumina were added into 40 mL and demonstrated the surfactant formation from monolayer through bilayer above the CMC concentration. Equilibrium was reached by shaking the solutions at 150 rpm for at least 48 h; after 12 h, the solution pH was measured and adjusted to 8.0-8.5. After reaching the equilibrium, the zeta potential of the alumina particles were analyzed by using a zeta potential meter (Zeta-Meter System 3.0, Zeta-Meter Inc.) in an electric field. Each surfactant sample was placed into an electrophoretic cell before applying 75-100 mV to the apparatus. The measurement was repeated ten times per sample, with the average value reported as the zeta potential for each sample.

3.2.4 Surfactant Desorption Study

Desorption studies were performed to determine the amount of surfactants that desorbed from the alumina surface during the washing process. Varied surfactant concentrations and amounts of alumina were added into 40 mL. The surfactant concentrations for each surfactant were chosen to be below and above the CMC. The surfactant modified alumina was washed with deionized water. Then, the vials were equilibrated by shaking them at 150 rpm for 48 h. After reaching equilibrium, the solution was centrifuged to remove the supernatant from the alumina. The alumina was rinsed three times with deionized water to remove the excess surfactant. Deionized water (pH 8.0-8.5) was added into the vials as a blank solution. After shaking it at 150 rpm for 48 h for washing, the zeta potential of the alumina was determined by using a zeta potential meter (Zeta-Meter System 3.0, Zeta-Meter Inc.) to evaluate the charges of the alumina surface and measure the desorption potential.

3.2.5 Solubilization Study

Solubilization was studied by adding 40 mL of surfactant solution to different amounts of alumina. All vials were sealed with Teflon-lined screw caps (PTFE). The surfactant concentration was varied from below to above the CMC. The solution was equilibrated by shaking it at 150 rpm for 48 h. Organic solutes were allowed to phase-separate, and then the solution was analyzed for its surfactant concentration. The amounts of solubilized organic solutes were calculated by the mass balance of the organic solutes. The solubilization capacity was determined in terms of the molar solubilization ratio (MSR) and the micellar partition coefficient (K_{mic}).

3.2.6 Adsolubilization Study

The adsolubilization capacity of conventional and anionic extended surfactants in organic solutes was evaluated. The solutions with known surfactant concentrations was added to 40 mL vials that containing a known mass of alumina with varying phenylethanol and ethylcyclohexane concentrations. The vials were sealed with Teflon-lined screw caps (PTFE). The surfactant concentration and the amount of alumina were 90-95% of the CMC obtained from the adsorption isotherms in order to obtain maximum admicelle formation (bilayer coverage) and to avoid micelle formation. Pinacyanol chloride was used as the indicator to verify the absence of micelles. In the absence of micelles, pinacyanol chloride yields a violet color. At a surfactant concentration in aqueous solution above the CMC, a blue color is observed (Kittyanan et al., 1996; Charoensaeng et al., 2008). All solutions in vials were equilibrated by shaking them at 150 rpm for 48 h followed by centrifugation to remove the alumina. The surfactant concentration and organic solutes concentration in aqueous solution were analyzed during the initial and equilibrium stages to determine the admicellar partition coefficient (K_{adm}).

3.3 ANALYTICAL METHODS

The surfactant concentration was analyzed by using High Performance Liquid Chromatography, HPLC (LC 1100, Agilent), with acetonitrile and NH_4OAc (40:60) as the mobile phase and detected by an evaporative light scattering (ELSD) detector at the temperature of 70 °C. The natural complex was separated with a reverse phase column (Acclaim Surfactant Column, Dionex).

Phenylethanol was analyzed using HPLC (LC 1100, Agilent) with acetonitrile and NH_4OAc (40:60) as the mobile phase and detected by a diode array detector at 260 nm. Using reverse phase column (Acclaim Surfactant Column, Dionex) for measurement.

Ethylcyclohexane was analyzed using gas chromatography, GC (6890N, Agilent) with a HP-5 column (Agilent), at a temperature of 300°C and detected by a Flame Ionization Detector (FID).

CHAPTER IV

RESULTS AND DISCUSSION

4.1 CRITICAL MICELLE CONCENTRATION MEASUREMENT

The critical micelle concentration (CMC) of the surfactant systems in this research were determined by the surface tension measurements at room temperature (25±2°C), an electrolyte concentration of 0.001 M NaCl, and at a solution pH of 8.0-8.5. The breakpoint in the curve of the plot of the surface tension versus the logarithm of the total concentration of the surfactant is the CMC of the surfactant (see Figure 4-1). For carboxylate extended surfactants, the CMC of the C17-4PO5EOC surfactant was slightly lower than that of the C16.5-4PO5EOC surfactant, at 0.015 mM and 0.02 mM, respectively (see Figure 4-1 and Table 4-1). However, the CMC of the extended surfactants were two orders of magnitude lower than that of the conventional surfactant, C12S (0.015 to 0.02 mM and 7.00 mM, respectively; see Figure 4-1 and Table 4-1). The extended surfactants with longer hydrocarbon chain length had the lower CMC values (Anuradee Witthayapanyanon et al., 2006; Ampira Charoensaeng et al., 2008). These trends are consistent with previous results and indicate that an increase in the intermediate chain length or alkyl chain of the tail tends to reduce the CMC (Fernández et al., 2005; Noulkamol Arpornpong, 2008; Ampira Charoensaeng et al., 2008). Moreover, previous results advised that the more the extended surfactant lipophilic group affects the surfactant monomer, the less it has the need to form aggregates like micelles in an aqueous solution.

When comparing the CMCs of extended surfactant systems of carboxylate surfactants and a sulfate surfactant, it was found that the CMCs of carboxylate extended surfactants (C16.5-4PO5EOC and C17-4PO5EOC) were lower than that of the sulfate extended surfactant (C16.5-4POS), as shown in Table 4-1. These results are due to the carboxylate extended surfactants having lower HLB numbers or higher hydrophobicity than that of the sulfate extended surfactant. Therefore, since the surfactant with the lower HLB number has the lower CMC value, the carboxylate extended surfactants have lower CMC values than the sulfate extended surfactant does (Rosen, 2004). From Table 4-1, it can be seen that the HLB numbers were in the following pattern: C16.5-4POS > C16.5-4PO5EOC > C17-4PO5EOC. Therefore, C17-4PO5EOC had the lowest CMC value. Furthermore, Myers (2006) reported that in the more common ionic head groups, the order of decreasing CMC values for a given hydrocarbon chain was found to be carboxylates (containing one more carbon atom) > sulfonates > sulfates.

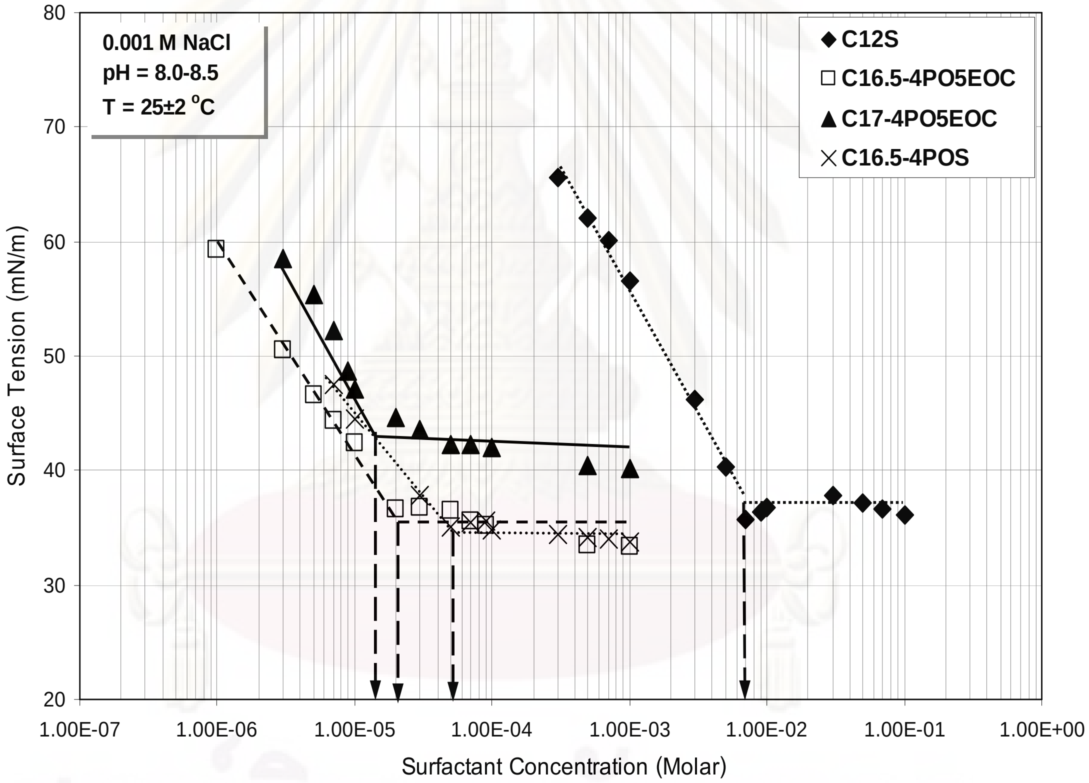


Figure 4-1 The surface tensions of the extended surfactant systems and conventional surfactant system, in 0.001 M NaCl, at equilibrium pH of 8.0-8.5 and, a temperature of 25±2°C

The surface concentration (Γ) and effective area per surfactant molecule at the liquid–air interface were calculated from the slope of the surface tension in Figure 4-1 using the Gibbs equation (Rosen, 2004; see Equations 2-8 and 2-9).The results are shown in Table 4-1. The effective areas per molecule of the carboxylate extended surfactant systems and the sulfate extended surfactant system were higher than that of the conventional surfactant (C12S), indicating that the extended surfactants have the lower amount of adsorbed surfactant aggregates at the liquid–air interface. These results may be due to the EO/PO groups of the extended surfactants forming coils and thus occupying a higher cross-sectional area per molecule at the liquid–air interface. In addition, the length of the hydrocarbon chain increased as the effective areas per molecule increased due to the larger lateral interaction and lower packing density of the extended surfactant tail, which is consistent with previous observations (Anuradee Witthayapanyanon et al., 2006; Ampira Charoensaeng et al., 2008).

Table 4-1 CMC values and effective areas per molecule for extended and conventional surfactant systems at 0.001 M NaCl, pH 8.0-8.5, and 25±2°C

Surfactant	HLB[a]	CMC (mM)	Slope[b]	r^2	Average plateau (mN/m)	Γ (mmol/1000 m^2)	Effective area per molecule ($Å^2$)
Conventional surfactant							
C12S	40.0	7.00	-9.52	0.99	36.69±0.7	0.83	199
Carboxylate extended surfactant							
C16.5-4PO5EOC	19.31	0.02	-7.47	0.99	35.12±1.5	0.65	254
C17-4PO5EOC	19.08	0.015	-7.24	0.99	42.22±1.9	0.63	262
Sulfate extended surfactant							
C16.5-4POS	37.26	0.05	-6.22	0.99	34.70±0.7	0.55	305

[a] HLB is the hydrophilic-lipophilic balance

[b] From Figure 4-1

The results of the effective area per molecule between the carboxylate extended surfactant systems and the sulfate extended surfactant system show that the carboxylate extended surfactants had a lower effective area per molecule than that of the sulfate extended surfactant. Due to the lower electrostatic repulsion between the polar head groups of the carboxylate head group, this surfactant's molecules packed more closely to another one than that of the surfactant with sulfate head groups (due to their higher electrostatic repulsion) (Golub et al., 2004).

4.2 SURFACTANT ADSORPTION STUDY

The study of the adsorption isotherms of the carboxylate extended surfactants (C16.5-4PO 5EOC and C17-4PO 5EOC), sulfate extended surfactant (C16.5-4POS), and conventional surfactant (C12S) onto the positively charged aluminum oxide surface was conducted at room temperature (25±2°C), an electrolyte concentration of 0.001 M NaCl, and solution pH 8.0-8.5 as shown in Figure 4-2.

For all surfactant systems, the adsorption increased when the surfactant concentration increased according to the S-shaped isotherm that was plotted using the logarithm of the adsorbed surfactant's density and the logarithm of the equilibrium surfactant concentration (Rosen, 2004). The CMC was determined by the transition point between Regions III and IV, and the maximum adsorption was evaluated as the mean value of the plateau region (Regions IV) of the isotherm (Rosen, 2004).

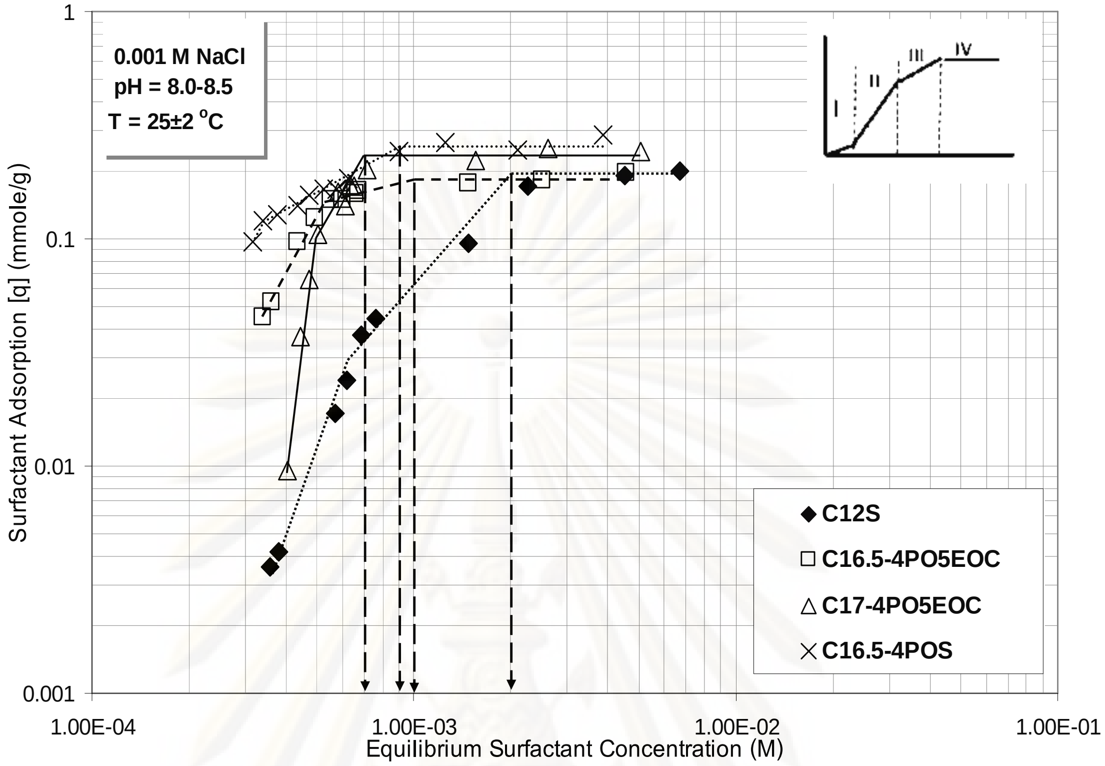


Figure 4-2 The adsorption isotherms of the extended surfactant systems and the conventional surfactant system onto alumina, in 0.001 M NaCl, at equilibrium pH of 8.0-8.5 and, a temperature of 25±2°C

In all surfactant systems, the isotherm demonstrated the characteristics of Regions II, III, and IV. However, the analytical detection limits measurement of the surfactant concentration did not allow for the measurement the low surfactant concentrations in Region I. From Figure 4-2, the adsorption isotherms of the extended surfactant systems in Region II had more sharp slopes when compared to those of the conventional surfactant system. Since increases due to longer hydrocarbon chains have a much greater driving force for the aggregation, the extended surfactants with longer hydrocarbon chain have greater lateral interactions between hydrocarbon chains than the conventional surfactant does (Paria and Khilar, 2004; Zhang and Somasundaran, 2006).

The CMC values from the adsorption isotherms of the carboxylate extended surfactants (C16.5-4PO5EOC and C17-4PO5EOC) and sulfate extended surfactant (C16.5-4POS) was 1.0, 0.7, and 0.9 mM, respectively (Figure 4-2, Table 4-2), which were an order of magnitude higher than the results of the CMC values from the surface tension measurement (0.02, 0.015, and 0.05 mM, respectively) (see Table 4-1). For the conventional surfactant systems (C12S), the CMC obtained from the adsorption isotherm (7.00 mM) at the solid-liquid interface was close to the CMC obtained from the surface tension measurement (2.00 mM) (see Table 4-1 and 4-2, respectively). These results are accordant with the results of previous researchers (Noulkamol Arpornpong, 2008; Ampira Charoensaeng et al., 2008). The study of Ampira Charoensaeng and co-worker (2008) reported that surfactant adsorption should plateau at the CMC of the surfactant since there is no driving force for additional adsorption above the CMC. Moreover, the extended surfactants require much lower equilibrium surfactant concentrations to reach the plateau adsorption region than the conventional surfactant does.

Table 4-2 CMC and maximum adsorption capacity from adsorption isotherms of the extended surfactant systems and conventional surfactant system at 0.001 M NaCl, pH 8.0-8.5, and 25±2°C

Surfactant	CMC[a]	Maximum adsorption (q_{max})			Effective area
	(mM)	mmole/g	Molecule/nm^2	Å^2/molecule[b]	per molecule[c] (Å^2)
Conventional surfactant					
C12S	2.0	0.19±0.01	0.72	139	199
Carboxylate extended surfactant					
C16.5-4PO5EOC	1.0	0.18±0.01	0.71	141	254
C17-4PO5EOC	0.7	0.23±0.02	0.89	112	203
Sulfate extended surfactant					
C16.5-4POS	0.9	0.26±0.02	1.02	98	305

[a] The CMC is obtained from the plateau adsorption level at a solid-liquid interface

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

[c] Calculated from surface tension measurement at a liquid-air interface (Rosen, 2004; see Table 4-1)

The results in Table 4-2 show how the carboxylate extended surfactant in C17-4PO5EOC has a higher maximum adsorption capacity than the carboxylate extended surfactant in C16.5-4PO5EOC. Since, the hydrophobic carbon chain length or tail groups of C17-4PO5EOC higher than C16.5-4PO5EOC, which increased the amounts of adsorbed surfactants in the plateau region (Paria and Khilar, 2004). Furthermore, the sulfate extended surfactant (C16.5-4POS) had a higher adsorption capacity than did the carboxylate extended surfactants. This could be due to the stronger ionic charge of SO_4^- , which allowed it to readily adsorb onto the positively charged aluminum oxide surface (increasing the effectiveness of adsorption). When the carboxylate extended surfactant in C16.5-4PO5EOC and the sulfate extended surfactant (C16.5-4POS) of the same carbon chain length were compared, the sulfate extended surfactant required much lower equilibrium surfactant concentrations to reach the plateau adsorption region. These results are in accord with the results of previous researchers (Paria and Khilar, 2004; Noulkamol Arpornpong, 2008).

When comparing the maximum adsorption capacity at the plateau region of the conventional surfactant (C12S) and extended surfactants, it was no observable tend (see Table 4-2). Since, both of the hydrophobicity of extended surfactants tail groups (i.e., PO and EO) and the surfactant head groups have affected to the adsorption behavior and adsorption densities. However, Myers (2006) reported that each additional EO group added to the heads of the carboxylate extended surfactants increases the total area required for adsorption, reducing the packing density of the hydrophobic groups at the interface. This therefore results in a smaller reduction in the surface tension of the system. Moreover, in previous a study, they reported that nonionic EO surfactants weakly adsorb on aluminum oxide surfaces (Zhang and Somasundaran, 2006).

According to the results of the maximum adsorption by normalizing with a specific area of alumina (155 m^2/g), the coverage on alumina of the conventional surfactant (C12S), carboxylate extended surfactants (C16.5-4PO5EOC and C17-4PO5EOC) and sulfate extended surfactant (C16.5-4POS) are 0.72, 0.71, 0.89, and 1.02

molecule/nm^2, respectively or 139, 141, 112, and 98 Å^2/molecule, respectively (see Table 4-2). The effective areas per molecule from the surface tension measurement were 199, 254, 203, and 305, respectively, based on the monolayer coverage at the liquid-air interface. If the admicelles provide complete bilayer coverage, the area per molecule should be half of these values. From these results it was found that the area of per molecule of surfactant aggregates at the solid- liquid interface was slightly larger than the area of per molecule calculated from the complete bilayer coverage at the liquid-air interface. It could be that the heads of the surfactants were too large to adsorb to the narrow pores provided by the metal oxide surface (Boonyarach Kitiyanan et al., 1996; Ampira Charoensaeng et al., 2008).

Furthermore, Golub and co-worker (2004) who studied the effect of the electrolyte concentration and pH of the solution in the adsorption isotherms of cationic surfactant (dodecylpyridinium chloride) on an Aerosil OX50 with 0.001 and 0.1 M KCl solution at pH 7 and 9 found that at high salt concentration, the slope in the region II is higher than unity, indicating a significant molecular association in the adsorption layer. The surfactant polar groups can be adsorbed rather close to one another, thus causing the lateral interactions between the hydrocarbon tails and the formation of hemimicelles. The adsorption isotherms obtained at pH 7 and 9 shows that at the same salt concentration, their forms are similar to one another, but the values of adsorption increase with pH over all four regions because of the increasing surface charge.

4.3 SURFACE CHARGE OF ALUMINUM OXIDE (ZETA POTENTIAL) AND SURFACTANT ADSORPTION

The alumina surface charge (zeta potential) of the conventional surfactant system (C12S), the carboxylate extended surfactant systems (C16.5-4PO5EOC and C17-4PO5EOC) and the sulfate extended surfactant system (C16.5-4POS) were conducted to evaluate the adsorption of surfactant onto an alumina surface. This experiment was conducted at room temperature (25±2°C), an electrolyte concentration of 0.001 M NaCl and solution pH 8.0-8.5. The zeta potential measurements were used to measure the concentration of charge (mV) on the alumina surface for the conventional surfactant system and the extended surfactant systems. The zeta potential of alumina with various concentrations of the anionic surfactants demonstrated the surfactant adsorption and the surfactant formation from monolayer through bilayer above the CMC concentration.

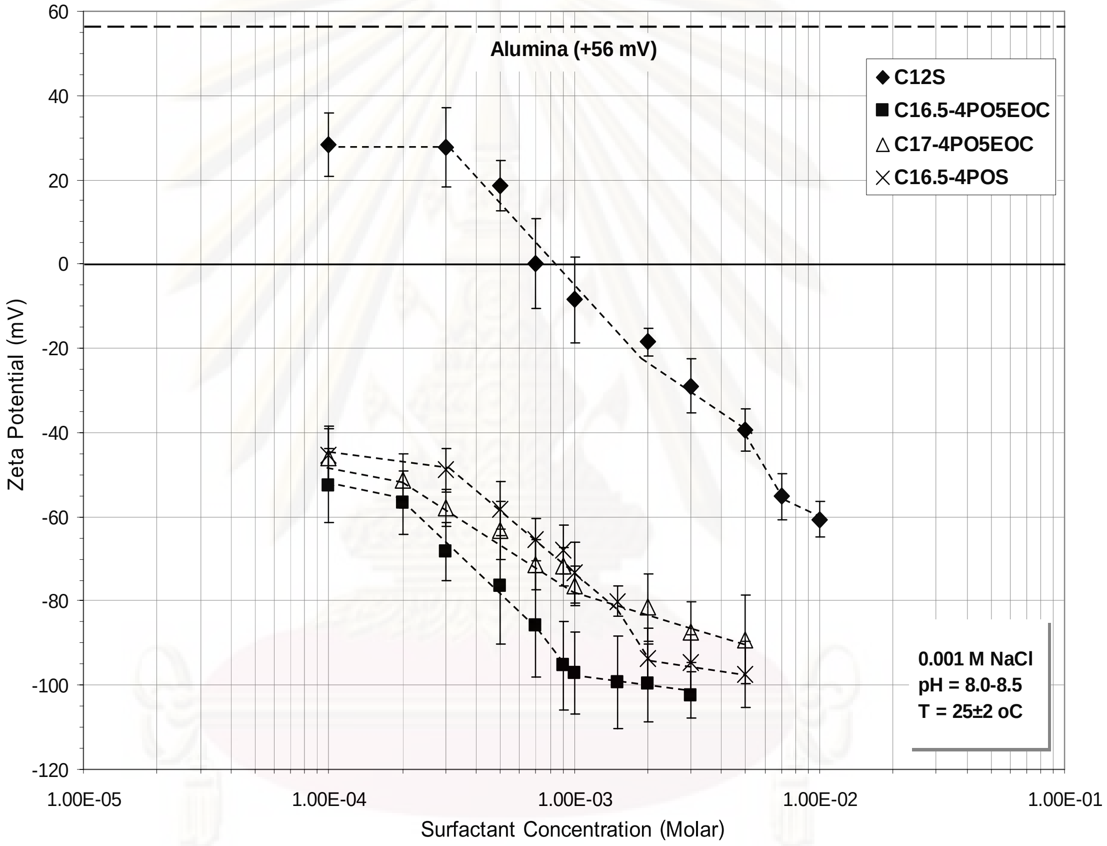


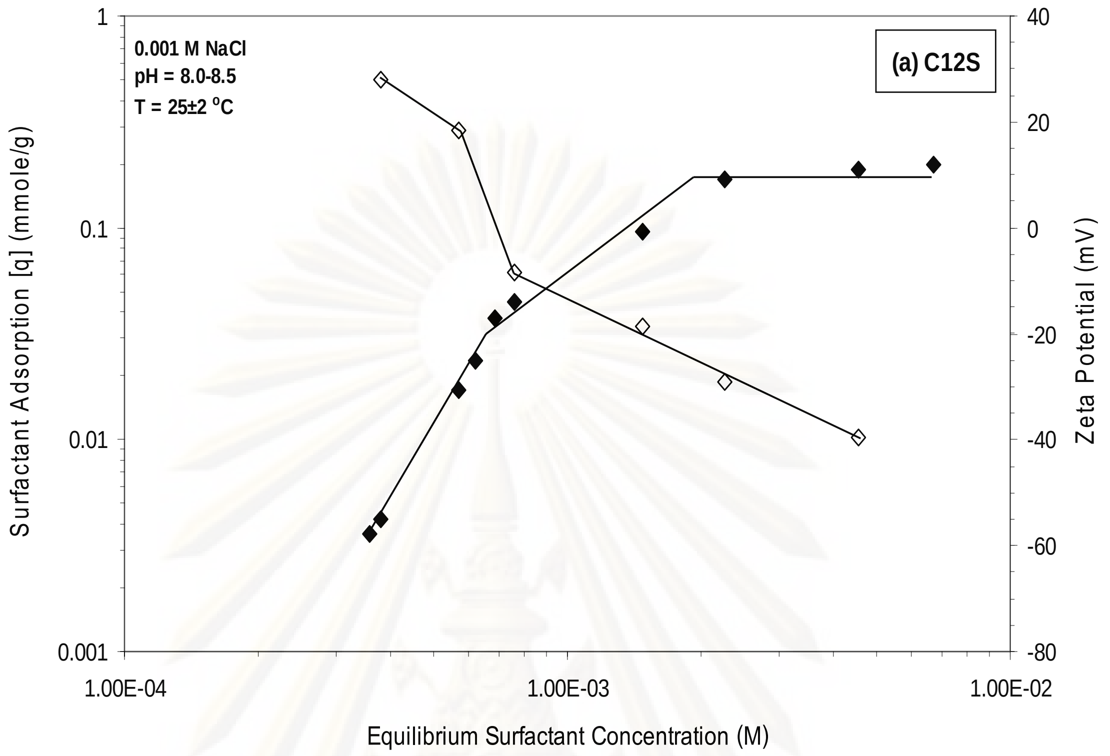
Figure 4-3 Zeta potential values of adsorption for the extended surfactant systems and the conventional surfactant system onto alumina, in 0.001 M NaCl, at equilibrium pH of 8.0-8.5 and, a temperature of 25±2°C

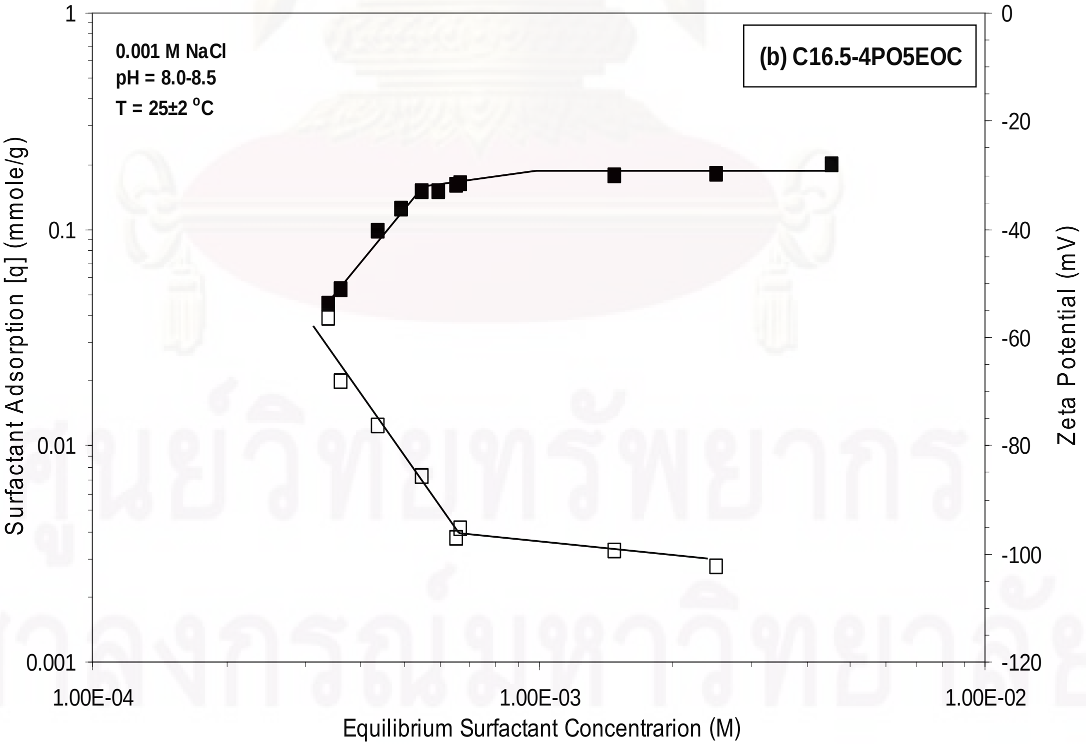
The zeta potentials of alumina with the conventional surfactant and the extended surfactants at an equilibrium pH of 8.0-8.5 are showed in Figure 4-3. The results showed that the zeta potential of the alumina surface without an adsorbed surfactant had a positively charged surface (+56 mV). The results for the conventional surfactant system

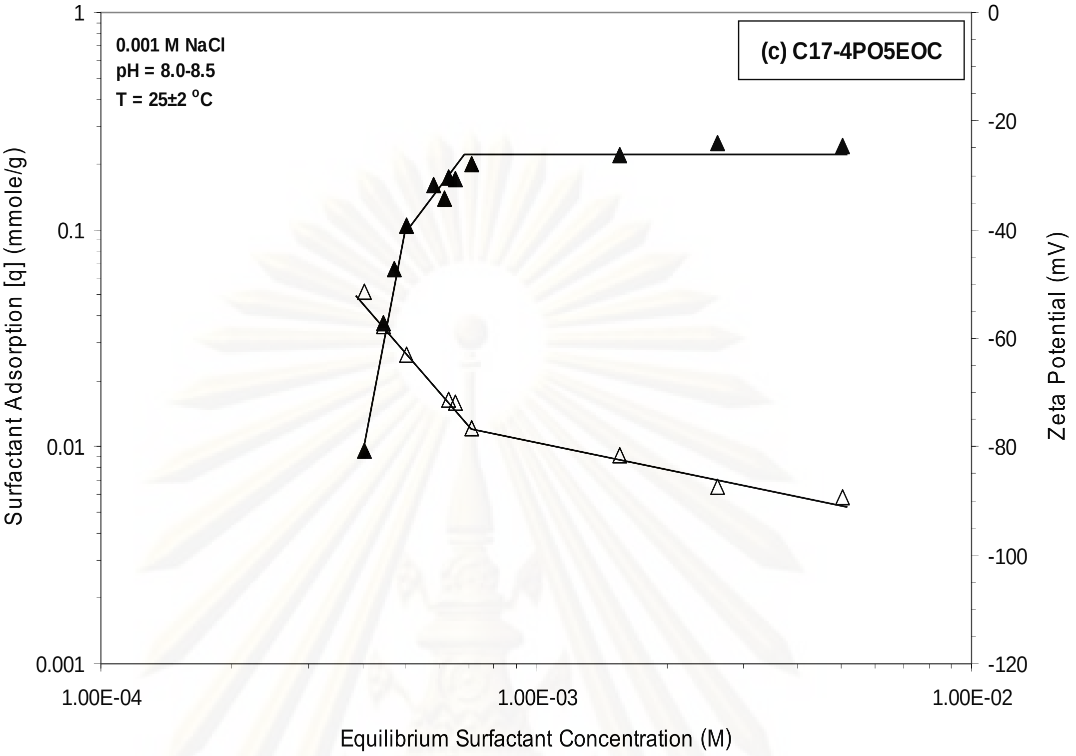
(C12S), whereas the zeta potential of alumina with adsorbed surfactant based showed gradually decreased to zero (charge neutralization), after which a negative value was obtained. This finding indicates that the surfactants form a bilayer on the alumina and achieve charge reversal by changing it from positive to negative values as the surfactant concentration attained the maximum bilayer coverage. For the extended surfactant systems, the results showed that the zeta potential of the surfactant-modified alumina increases from less negative to highly negative when the surfactant adsorption increased. These results are consistent with what was found in the study of Tadros (2005), who reported that the adsorption and zeta potential results show three distinct regions. The first region shows a gradual increase of adsorption as the concentration increases, with virtually no change in the zeta potential. The rapid increase slope in the second region was explained in terms of the hemimicelle formation. The hydrophobic moieties of the adsorbed surfactant chains are squeezed out from the aqueous solution by forming two-dimensional aggregates on the adsorbent surface. Here, the positive zeta potential gradually decreases to zero (charge neutralization) after which a negative value is obtained, which increases rapidly with increasing surfactant concentration. In third region, the slope of the adsorption isotherm is reduced. Since the adsorption is hindered by the electrostatic repulsion between the hemimicelles (reached maximum bilayer coverage) thus, the zeta potential of the alumina surface is a constant. Moreover, extended surfactants have always negatively charged surface because unable to measure in Region I or II where it would have still been positively charged surface.

A comparison of the zeta potential at maximum adsorption of the conventional surfactant system (C12S) and the extended surfactant systems (C16.5-4PO5EOC, C17-4PO5EOC, and C16.5-4POS), it is found that the alumina with the extended surfactants had higher negatively charge surface (-100, -89, and -97 mV, respectively) than that with the conventional surfactant (-60 mV) (see Figure 4-3). Thus, this can imply that the extended surfactants formed bilayer coverage on to alumina oxide surface and surfactant molecule orient in denser packing than the conventional surfactant. Since the extended surfactants have more hydrophobicity than the conventional surfactant.

In Figure 4-4, shows the adsorption isotherm and zeta potential of alumina as a function of equilibrium surfactant concentration for the conventional surfactant system (C12S) and the extended surfactant systems (C16.5-4PO5EOC, C17-4PO5EOC, and C16.5-4POS). The results showed that the zeta potential of alumina surface with all surfactant systems decreases to negatively charge surface with increasing the surfactant concentration. Since, at low surfactant concentration, the anionic surfactant molecules adsorb onto the positively charged alumina surface by orienting hydrocarbon chains to the aqueous solution that the surface of the alumina becomes less positively charged. When the surfactant concentration increases, the bilayer is formed by the hydrophilic groups of surfactants oriented toward the aqueous solution, which according to the results of Tadros (2005) that mention above. These results support the idea that a complete bilayer is formed at CMC and above CMC of the adsorption isotherm. Moreover, these results are accordant with the results of previous studies (Esumi et al., 1991; Huang and Somasundaran, 1996; Esumi, 2001; Golub et al., 2004; Tadros, 2005). As comparing the zeta potential of alumina surface between the conventional surfactant and the extended surfactants, it demonstrated that the extended surfactants had higher negatively charge surface than that with the conventional surfactant at the plateau region from the adsorption isotherm (see Figure 4-4). It due to the extended surfactants could form upper layer of bilayer more than the conventional surfactant. Because the hydrophobic carbon chain length of the extended surfactants have longer than that of the conventional surfactant. For the results of carboxylate and sulfate extended surfactants, it found that the zeta potential of alumina of C16.5-4PO5EOC had higher negatively charge surface than that with C16.5-4POS at the plateau region. These results are unclear and should be further evaluated in future research.


0.001 M NaCl
pH = 8.0-8.5
T = 25±2 °C
(a) C12S
Surfactant Adsorption [q] (mmole/g)
Zeta Potential (mV)
1
0.1
0.01
0.001
40
20
0
-20
-40
-60
-80
1.00E-04
1.00E-03
1.00E-02
Equilibrium Surfactant Concentration (M)


0.001 M NaCl
pH = 8.0-8.5
T = 25±2 °C
(b) C16.5-4PO5EOC
Surfactant Adsorption [q] (mmole/g)
Zeta Potential (mV)
1
0.1
0.01
0.001
0
-20
-40
-60
-80
-100
-120
1.00E-04
1.00E-03
1.00E-02
Equilibrium Surfactant Concentrarion (M)



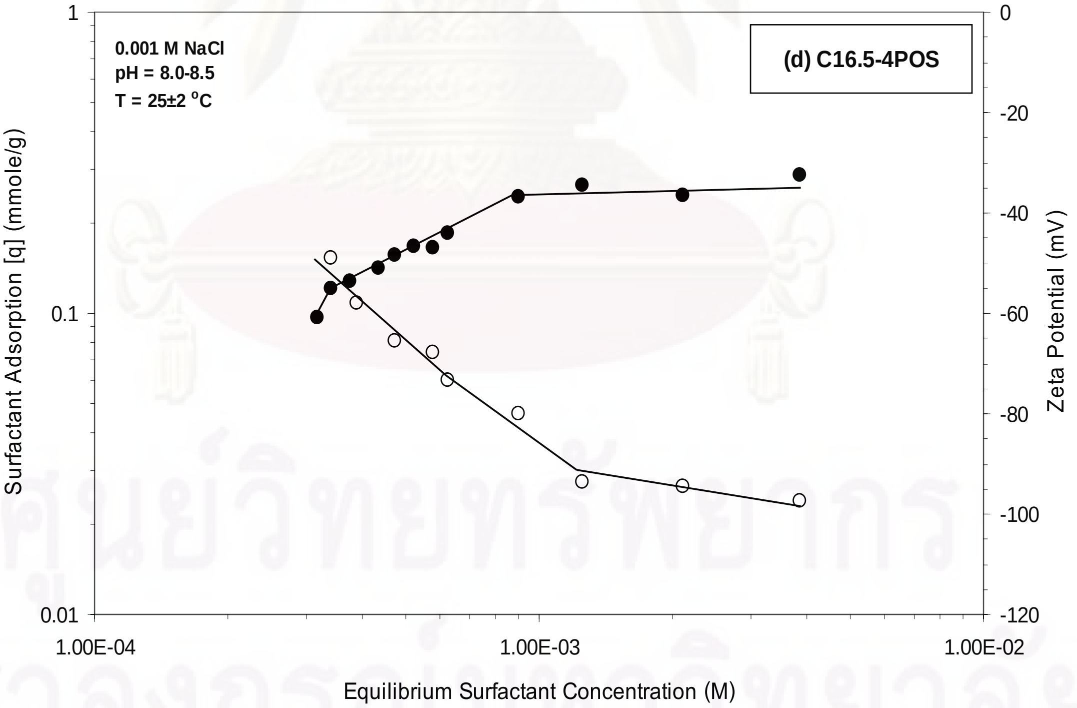


Figure 4-4 Adsorption isotherms (dark color) and zeta potential of alumina surface (light color) as a function of equilibrium surfactant concentration for (a) C12S, (b) C16.5-4PO5EOC, (c) C17-4PO5EOC, and (d) C16.5-4POS

4.4 SURFACTANT DESORPTION STUDY

The surfactant desorption study evaluate the amount of anionic surfactants that desorbed from the alumina surface after washing process. The surfactant concentrations for each surfactant type were selected from below to above the CMC from adsorption isotherms. The surfactant modified alumina was washed using deionized water. Due to the detection limit of the instrument, the surfactant concentration of the conventional and extended surfactants after the first wash could not be detected for use in the adsorption study. It can be assumed that the amount of surfactant desorbed was very low. To confirm this results, an indirect method to evaluate the surfactant desorption was conducted by using the zeta potential measurement. This method was applied to measure the concentration of charge (mV) on the modified alumina surface.

The results from zeta potential measurement in the desorption studies of the conventional surfactant system (C12S), the carboxylate extended surfactant systems (C16.5-4PO5EOC and C17-4PO5EOC), and the sulfate extended surfactant system (C16.5-4POS) onto an alumina surface are show in Figure 4-5. The zeta potential of the alumina surface at the electrolyte concentration of 0.001 M NaCl and pH 8.0-8.5 (PZC of alumina is 9.1) without the addition of a surfactant had a positive charge (+56 mV). The desorption potential was obtained by changing the concentration of the charge (mV) on the modified alumina surface.

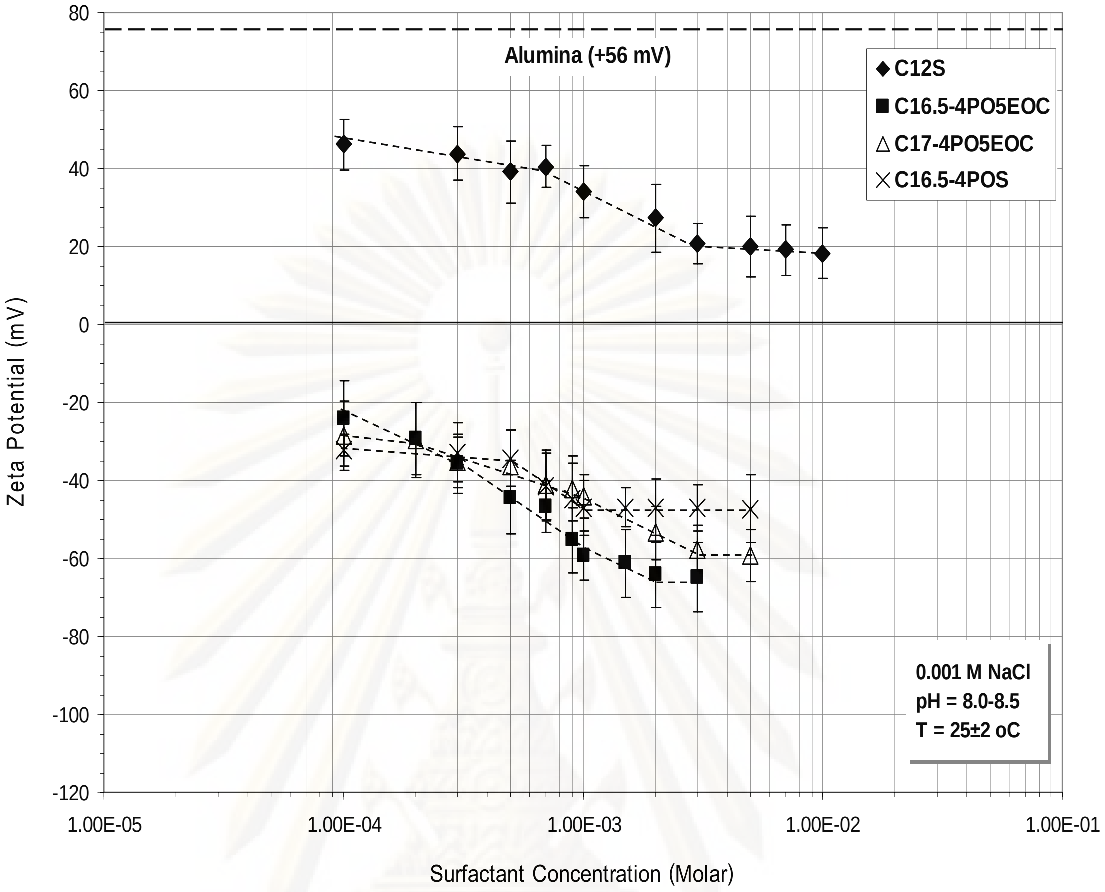


Figure 4-5 Zeta potentials of desorption for the extended surfactant systems and the conventional surfactant system onto alumina, in 0.001 M NaCl, at equilibrium pH of 8.0-8.5 and a temperature of 25±2°C

After the washing process, the zeta potential of alumina surface with the conventional surfactant and the extended surfactants increased at all surfactant concentrations (see Figure 4-5 and Figure 4-3). At the highest surfactant concentration, the conventional surfactant changed from negative to positive (from -60 mV to +20 mV, see Figure 4-3 and 4-5). This indicated that the surfactant bilayer of C12S was not observed or that the C12S had been washed off from the surface. The zeta potentials of the extended surfactant systems remained negatively charged. This demonstrated that the surfactant bilayer coverage was still present on the surface. Therefore, it can be concluded that the extended surfactants can enhance the stability of the adsorbed surfactant bilayer. Since the extended surfactants have higher lateral interaction of carbon chain length than the conventional surfactant. This result is in accord with those of previous studies (Noulkamol Arpornpong, 2008; Emma Asnachinda et al., 2009a).

Furthermore, when compared the zeta potential of the carboxylate extended surfactant systems (C16.5-4PO5EOC and C17-4PO5EOC) and the sulfate extended surfactant system (C16.5-4POS) onto an alumina surface, the zeta potential of alumina surface at the highest surfactant concentration of the sulfate extended surfactant was decreased negative values more than the carboxylate extended surfactants (see Figure 4-5 and Figure 4-3). From more -90 mV for all extended surfactants to -65 mV for C16.5-4PO5EOC, -60 mV for C17-4PO5EOC, and -47 mV for C16.5-4POS. This it could be explained by the fact that the sulfate head group of the sulfate extended surfactant was more hydrophilic than the carboxylate head group in the carboxylate extended surfactants. So, the sulfate extended surfactant can easier desorb by water than the carboxylate extended surfactants. In addition, the carboxylate extended surfactants have EO groups in molecule thus, the carboxylate extended surfactants have stronger lateral interaction than the sulfate extended surfactant. For comparison the zeta potential of alumina surface between C16.5 and C17 of the carboxylate extended surfactants, the results are not clear and it should be evaluated in future research.

According to these results, it could be concluded that the carboxylate extended surfactants have strong packing (bilayer coverage) and retain their negative charge more than the conventional surfactant and the sulfate extended surfactant. Therefore, the use of carboxylate extended surfactants could reduce surfactant desorption.

4.5 SOLUBILIZATION STUDY

The solubilization studies of phenylethanol and ethylcyclohexane by the conventional surfactant system (C12S), the carboxylate extended surfactant systems (C16.5-4PO5EOC and C17-4PO5EOC) and sulfate extended surfactant system (C16.5-4POS) were conducted using the maximum solubilization (Nayyar et al., 1994; Rouse et al., 1995; Ampira Charoensaeng et al., 2009) at room temperature (25±2°C), an electrolyte concentration of 0.001 M NaCl, and a solution pH 8.0-8.5. The solubilization capacity of a particular surfactant for a given solute can be measured by the molar solubilization ratio (MSR). The MSR is the number of moles of organic solute solubilized per mole of surfactant added to the solution, and it is obtained from the slope of the curve that plots between the solubilizate concentration and surfactant concentration. The MSR and the micellar partition coefficient (K_{mic}) were calculated using Equations 2-1 to 2-4 shown in Chapter 2.

4.5.1 Phenylethanol Solubilization

The solubilization isotherms were plotted using the aqueous phenylethanol concentrations and the aqueous surfactant concentrations. The transition point, where the solute concentration begins to increase, corresponds approximately to the CMC of the surfactant system, as shown in Figure 4-6. However, the CMC of the surfactant system can be affected by the presence of the solute. At low surfactant concentrations (below the CMC), phenylethanol solubility is constant and approximately equal to its aqueous solubility (Nayyar et al., 1994; Aranya Fuangswasdi et al., 2006; Ampira Charoensaeng et al., 2009). At higher surfactant concentrations (above the CMC), the solubility increases through phenylethanol solubilization in surfactant micelles. The slope of this region demonstrates the MSR indicating the moles of organic solute (solubilizate) per mole of the micellar surfactant (see Figure 4-7). The MSR is used to calculate the micellar partition coefficient (K_{mic}) using a X_{aq} value for phenylethanol of 2.87×10^{-4}, Table 4-3 provides the MSR and K_{mic} values.

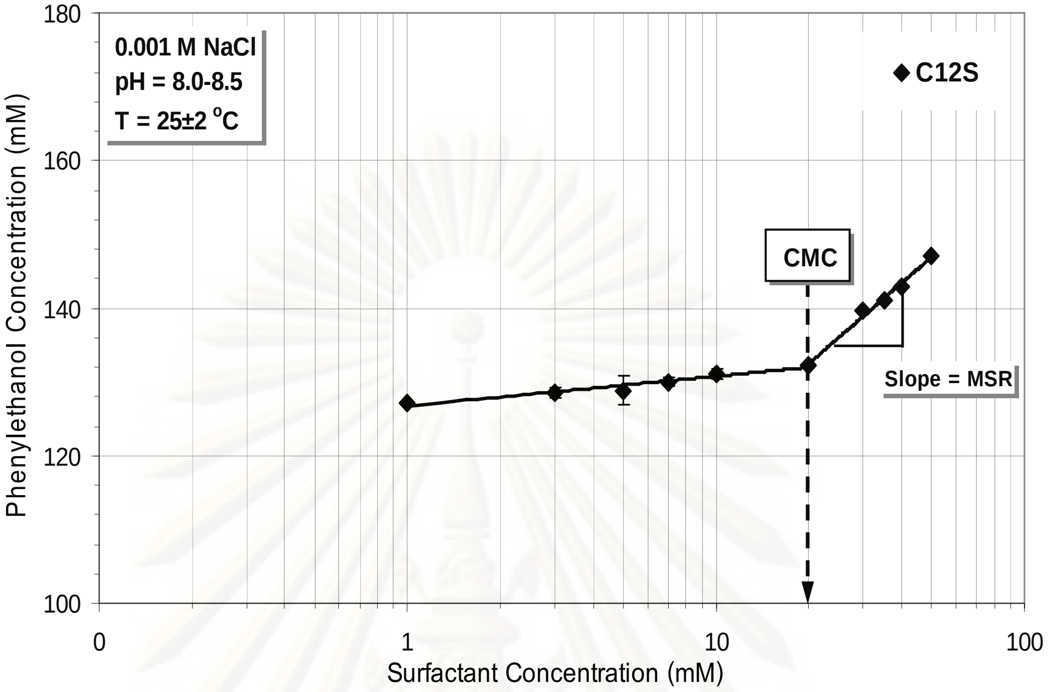


Figure 4-6 Solubilization isotherm of phenylethanol by the conventional surfactant system (C12S), in 0.001 M NaCl, at equilibrium pH of 8.0-8.5 and a temperature of 25±2°C

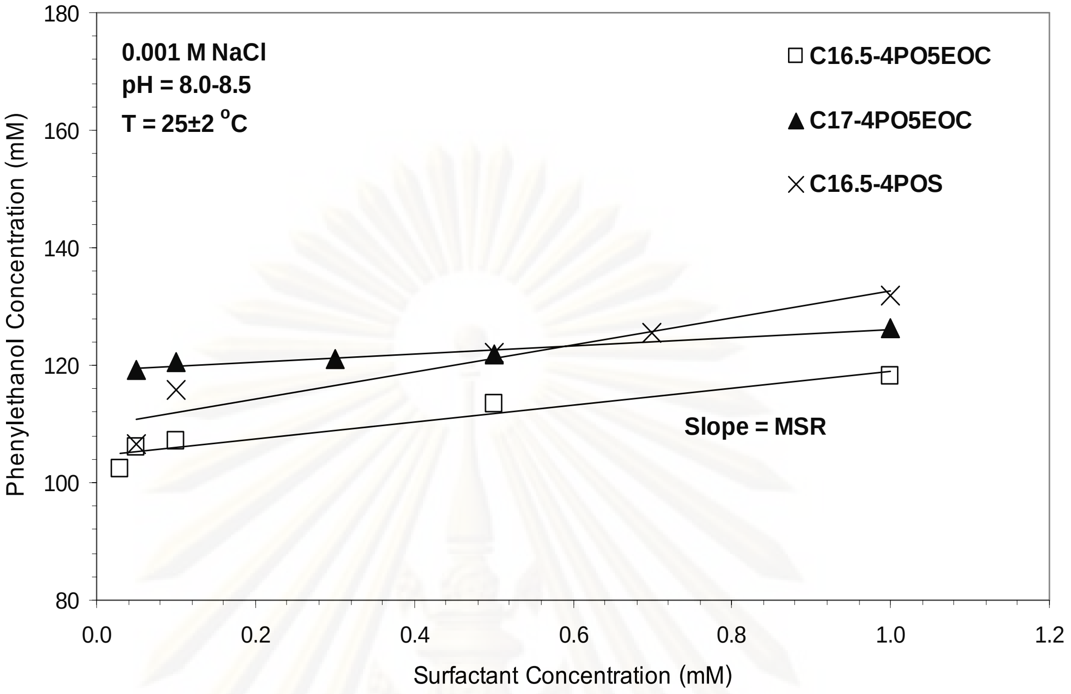


Figure 4-7 Solubilization capacity (MSR) of phenylethanol by the carboxylate extended surfactant systems and sulfate extended surfactant system, in 0.001 M NaCl, at equilibrium pH of 8.0-8.5 and a temperature of 25±2°C

Table 4-3 The phenylethanol micellar partition coefficient (K_{mic}) values of the conventional surfactant system and extended surfactant systems

Surfactant	HLB[a]	Phenylethanol solubilization				
		MSR	r^2	X_{mic}	K_{mic}	log K_{mic}
Conventional surfactant						
C12S	40.00	0.48	0.97	0.32	1124	3.05
Carboxylate extended surfactant						
C16.5-4PO5EOC	19.31	14.52	0.92	0.94	3260	3.51
C17-4PO5EOC	19.08	7.07	0.96	0.88	3052	3.48
Sulfate extended surfactant						
C16.5-4POS	37.26	23.00	0.91	0.96	3339	3.52

[a] HLB is the hydrophilic - lipophilic balance

The MSR and log K_{mic} values were calculated to evaluate the extent of phenylethanol solubilization in micelles, and the results are shown in Table 4-3. The results show that the phenylethanol solubilization capacity of the extended surfactants systems (C16.5-4PO5EOC, C17-4PO5EOC, and C16.5-4POS) was higher than that of conventional surfactant (C12S). Since phenylethanol is a polar organic solute, it was expected to partition primarily into the palisade region (Uchiyama et al., 1991; Kondo et al., 1993; Rosen, 2004; Ampira Charoensaeng et al., 2009). The extended surfactants with EO/PO groups have longer hydrophobic groups than do the conventional surfactant (C12S) without EO/PO groups; therefore, the extended surfactant micelles have larger aggregation numbers resulting in the larger palisade layer and greater phenylethanol solubilization capacity than the conventional surfactant (Rosen, 2004). These results are similar to those of Ampira Charoensaeng and co-workers (2009) who founded that the extended surfactant systems (C-14,15 and C-12,13) with increasing PO number (n = 3, 5, 8) have greater phenylethanol solubilization capacity (log K_{mic}) than that of the conventional surfactant (SDS) due to their higher hydrophobicity.

As the carbon chain length slightly increased from C16.5 to C17 for the carboxylate extended surfactants, the log K_{mic} values remained the same (3.51 and 3.48, respectively), indicating that the hydrophobicity of the core does not significantly impact the solubilization of phenylethanol. Since, phenylethanol is a polar organic solute, it was expected to partition primarily into the palisade region. This result is consistent with the result of a previous study (Ampira Charoensaeng et al., 2009) on extended surfactant systems and whether they increase the carbon chain length from C-12,13 to C-14,15 when solubilizing phenylethanol.

When comparing the phenylethanol solubilization of the carboxylate extended surfactants and the sulfate extended surfactant (C16.5-4POS), it shows that the sulfate extended surfactant has a higher K_{mic} value than the carboxylate extended surfactant does (see Table 4-3). However, the log K_{mic} values are not significantly different. It could be that the sulfate extended surfactant (C16.5-4POS) has higher HLB number than the carboxylate extended surfactants (see Table 4-3), which implies that the sulfate extended surfactant has higher hydrophilic site for phenylethanol solubilize into micelles (Noulkamol Arpornpong, 2008). In addition, due to the sulfate head group having a stronger charge, it caused increased repulsion between the head groups in the micelles, which consequently increased in the space available for solubilization between the surfactant molecules in the palisade layer. Moreover, the coiling EO in the carboxylate extended surfactants, it could have caused the reduction of the cavities in which phenylethanol likes to solubilize in the palisade layer, reducing the solubilization of phenylethanol (Rosen, 2004).

4.5.2 Ethylcyclohexane Solubilization

The solubilization isotherms of ethylcyclohexane by the conventional surfactant system (C12S) are shown in Figure 4-8. The surfactant concentration at which the solute concentration begins to increase corresponds to the CMC of the surfactant system. The solubilization capacities of ethylcyclohexane for the carboxylate extended surfactant systems (C16.5-4PO5EOC and C17-4PO5EOC) and sulfate extended surfactant system (C16.5-4POS) are illustrated in Figure 4-9. The solubilization of ethylcyclohexane increased linearly when the surfactant concentration was above its CMC in the conventional surfactant and extended surfactants. The MSR and solubilization capacity of ethylcyclohexane (log K_{mic}) are summarized in Table 4-4 (using a X_{aq} value for ethylcyclohexane of 4.68×10^{-7} to calculate the K_{mic} value).

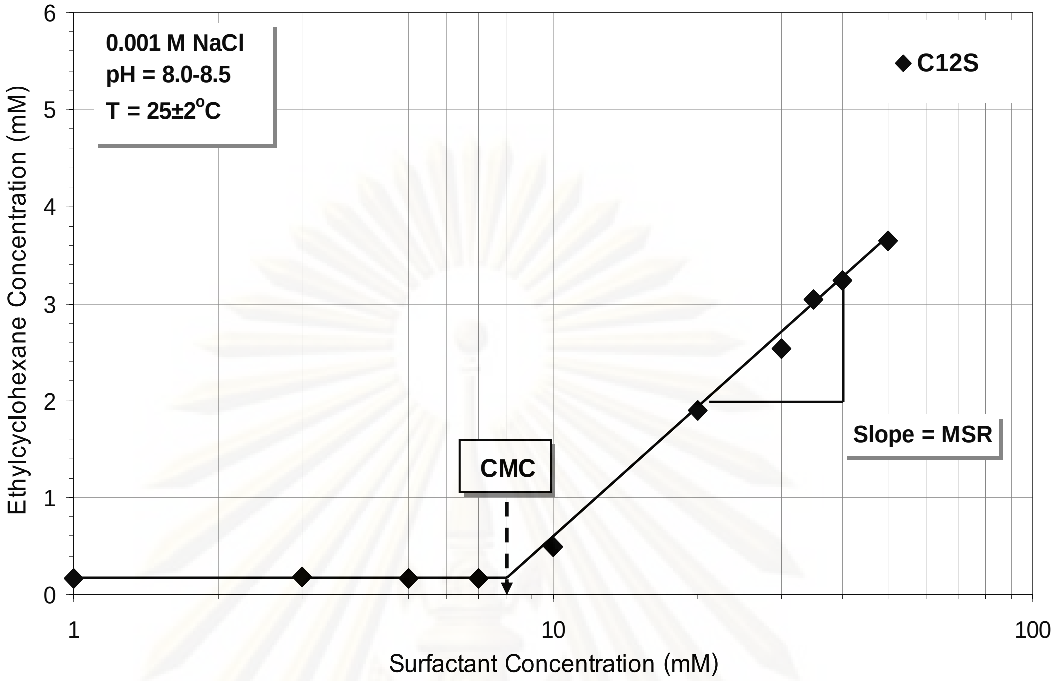


Figure 4-8 Solubilization isotherm of ethylcyclohexane by the conventional surfactant system (C12S), in 0.001 M NaCl, at equilibrium pH 8.0-8.5 and a temperature of 25±2°C

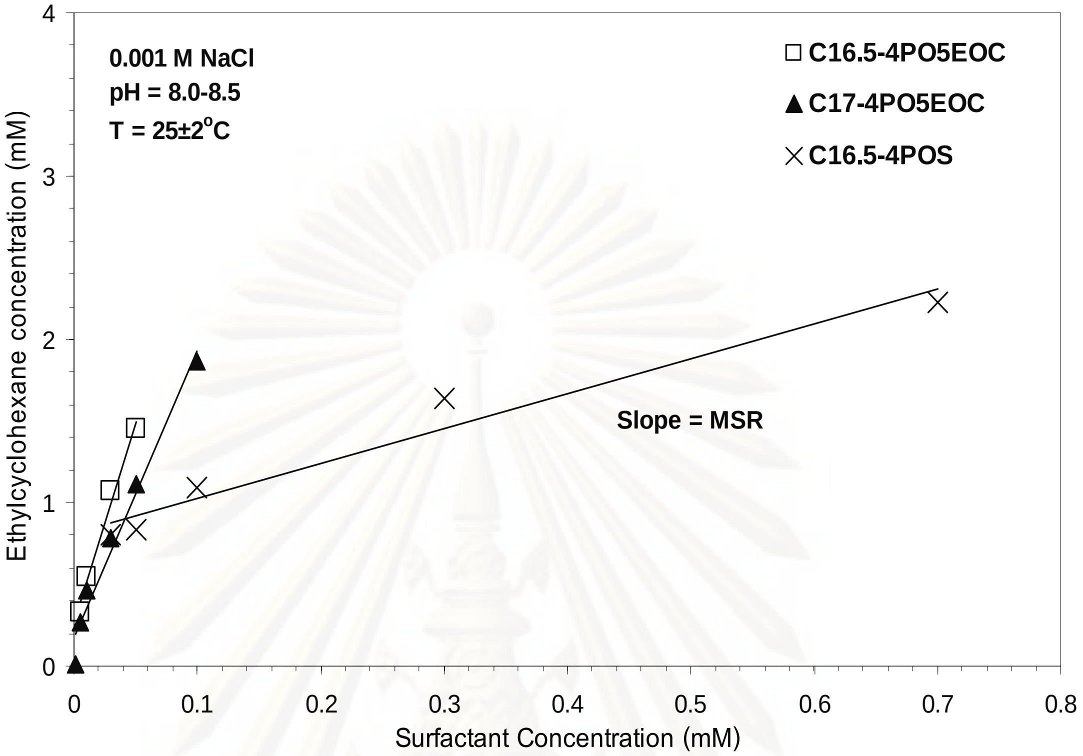


Figure 4-9 Solubilization capacity (MSR) of ethylcyclohexane by the carboxylate extended surfactant systems and sulfate extended surfactant system, in 0.001 M NaCl, at equilibrium pH 8.0-8.5 and a temperature of 25±2°C

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

Surfactant	HLB[a]	Ethylcyclohexane solubilization				
		MSR	r^2	X_{mic}	K_{mic}	log K_{mic}
Conventional surfactant						
C12S	40.00	0.09	0.97	0.08	176,916	5.25
Carboxylate extended surfactant						
C16.5-4PO5EOC	19.31	24.39	0.99	0.96	2,054,064	6.31
C17-4PO5EOC	19.08	17.54	0.97	0.94	2,022,955	6.31
Sulfate extended surfactant						
C16.5-4POS	37.26	2.13	0.96	0.68	1,455,527	6.16

[a] HLB is the hydrophilic - lipophilic balance

As seen in Table 4-4, the log K_{mic} values of the extended surfactant systems are higher than those of the conventional surfactant system, indicating that the extended surfactants enhance the solubilization capacity of ethylcyclohexane. Since ethylcyclohexane has low water solubility (low polarity solute), it prefer to solubilize in the miceller inner core (Rosen, 2004; Aranya Fuangswasdi et al., 2006; Ampira Charoensaeng et al., 2009). Because both of the carboxylate extended surfactants (C16.5-4PO5EOC and C17-4PO5EOC) and the sulfate extended surfactant (C16.5-4POS) have longer hydrophobic groups than the conventional surfactant (C12S), their extended surfactant micelles have larger aggregation numbers (increased micelle size) resulting in larger hydrophobic core regions; thus, their ethylcyclohexane solubilization capacities are higher than that of the conventional surfactant (Rosen, 2004). This result confirms those of Ampira Charoensaeng and co-worker (2009), who studied the solubilization of ethylcyclohexane by extended surfactants, and Noulkamol Arpornpong (2008), who studied the solubilization of phenanthrene as a non polar organic solute by using extended surfactants.

As the carbon chain lengths of the carboxylate extended surfactants slightly increased from C16.5 to C17, the ethylcyclohexane solubilization capacity (log K_{mic} values) remained the same (6.31 and 6.31, respectively) (see Table 4-4). It may have been that the number of carbon chain length of the carboxylate extended surfactants was not different enough to produce a visible result in the hydrophobic core region. Therefore, the carbon chain length of the carboxylate extended surfactants for the ethylcyclohexane solubilization will be evaluated in a future study.

The MSR and log K_{mic} values of the carboxylate extended surfactants and the sulfate extended surfactant (C16.5-4POS) from Table 4-4 show that the carboxylate extended surfactant provides higher ethylcyclohexane solubilization than the sulfate extended surfactant does. This is due to the carboxylate extended surfactants being more hydrophobic (having a lower HLB number) than the sulfate extended surfactant, which ethylcyclohexane prefers to solubilize with in the hydrophobic core region.

The results from Tables 4-3 and 4-4 show that all the surfactant systems have lower solubilization capacities (log K_{mic} values) for phenylethanol than they do for ethylcyclohexane. This can be explain by the different partitioning behavior of phenylethanol from that of ethylcyclohexane. Phenylethanol is highly soluble in water (highly polar) and prefers to solubilize in the aqueous phase rather than partition into the palisade layer of the micelles, while ethylcyclohexane (non polar) prefers to partition into the miceller inner core (see dipole moment in Table 3-2 from Chapter 3) (Rosen, 2004; Aranya Fuangswasdi et al., 2006; Ampira Charoensaeng et al., 2009). Moreover, the phenylethanol and ethylcyclohexane solubilization values (log K_{mic} values) of the extended surfactant systems were greater than those of the conventional surfactant system. This can be the cause of the increased hydrophobicity of the surfactants with additional EO/PO groups have larger micelles, and improved solubilization for longer (extended) surfactants.

4.6 ADSOLUBILIZATION STUDY

This study evaluated the phenylethanol and ethylcyclohexane adsolubilization capacities of a conventional surfactant system (C12S), two carboxylate extended surfactant systems (C16.5-4PO5EOC and C17-4PO5EOC), and one sulfate extended surfactant system (C16.5-4POS) onto an alumina surface at room temperature (25±2°C), an electrolyte concentration of 0.001 M NaCl, and a solution pH of 8.0-8.5. The surfactant concentration and the amount of alumina were 90-95% below the CMC in order that the surfactants could form admicelles (bilayer coverage) with the maximum and not have micelles in aqueous solution at equilibrium. The partitioning of organic solutes into admicelles can be measured by the admicellar partitioning coefficient (K_{adm}) (Nayyar et al., 1994). K_{adm} was used to determine the adsolubilization capacity and was calculated from Equations 2-5 to 2-7 (shown in Chapter 2).

4.6.1 Phenylethanol Adsolubilization

The phenylethanol admicellar partition coefficient (K_{adm}) of the conventional surfactant system (C12S), the carboxylate extended surfactant systems (C16.5-4PO5EOC and C17-4PO5EOC) and the sulfate extended surfactant system (C16.5-4POS) onto the alumina surface are show in Figure 4-10 and Table 4-5. The values of K_{adm} were obtained at the maximum of the mole fraction of phenylethanol in the aqueous phase (X_{aq}), which is the value that approaches the water solubility (maximum additivity) of the solute as adsolubilization sites become saturated. When the adsolubilization isotherms are nonlinear, this is the standard approach for demonstrating the K_{adm} values (Esumi, 2001; Emma Asnachinda et al., 2009b; Chodchanok Attaphong et al., 2010). In the absence of a surfactant, the adsorption of phenylethanol onto the aluminum oxide surface was negligible.

In Figure 4-10, the value of K_{adm} of all surfactant systems decreased as the aqueous molar fraction (X_{aq}) of the phenylethanol increased, implying that phenythanol prefers partitioning in the palisade layer of surfactant admicelles because it is a highly polar organic solute (dipole moment = 1.65). This result concurs with previous research that a polar solute will partition in the palisade region (Nayyar et al., 1994; Kitiyanan et al., 1996; Dickson and O'Haver, 2002).

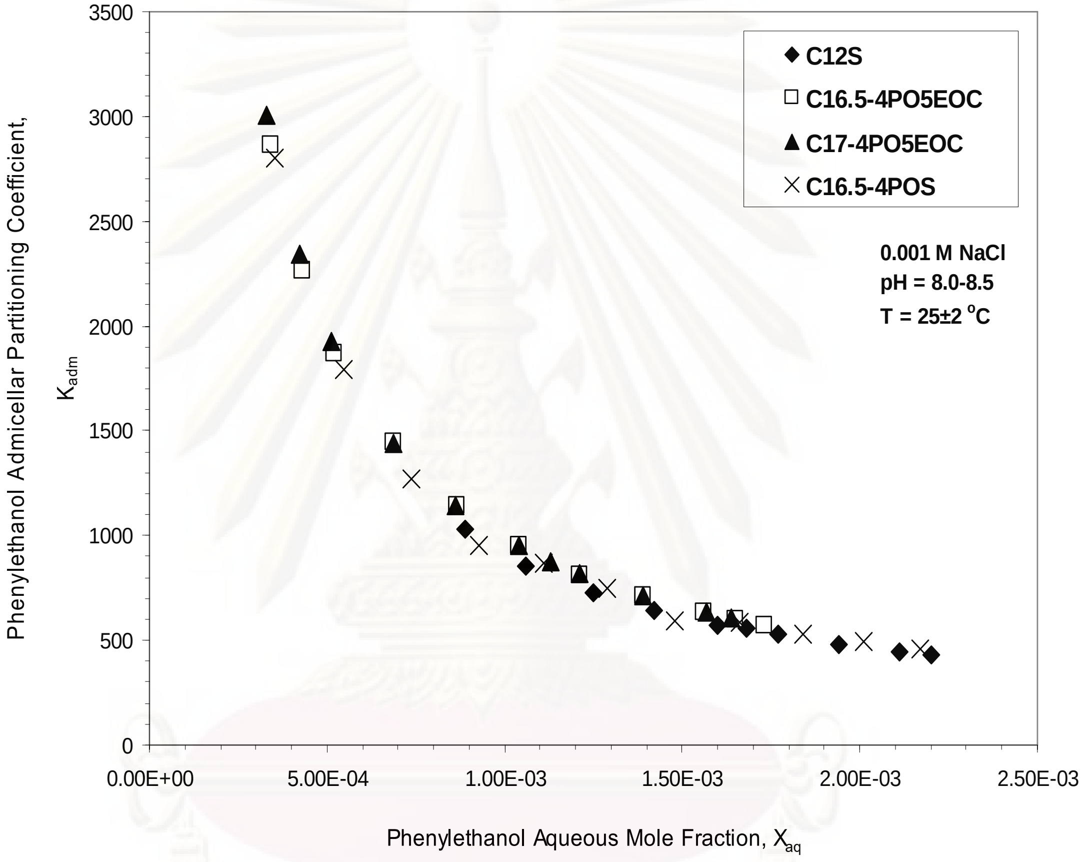


Figure 4-10 The phenylethanol admicellar partition coefficient (K_{adm}) of the extended surfactant systems and the conventional surfactant system onto alumina, in 0.001 M NaCl, at equilibrium pH 8.0-8.5 and a temperature of 25±2°C

Table 4-5 Adsolubilization capacities of the extended surfactant systems and the conventional surfactant system for phenylethanol

Surfactant	HLB[a]	Phenylethanol adsolubilization		
		Ads. q_{max} (mmole/g)	K_{adm}	log K_{adm}
Conventional surfactant				
C12S	40.00	0.19±0.01	454	2.66
Carboxylate extended surfactant				
C16.5-4PO5EOC	19.31	0.18±0.01	630	2.80
C17-4PO5EOC	19.08	0.23±0.02	652	2.81
Sulfate extended surfactant				
C16.5-4POS	37.26	0.26±0.02	531	2.73

[a] HLB is the hydrophilic - lipophilic balance

As can be seen in Table 4-5, the adsolubilization capacity values (log K_{adm}) of the extended surfactants (C16.5-4PO5EOC, C17-4PO5EOC, and C16.5-4POS) were higher than that of the conventional surfactant (C12S). This could be due to the extended surfactants containing PO/EO groups with longer hydrophobic groups, allowing the extended surfactants to have larger aggregation numbers, which resulted in them having larger palisade layers and more phenylethanol adsolubilization (Rosen, 2004). Since, phenylethanol is a polar organic solute, it was expected to partition primarily into the palisade region. This result is consistent with a finding in the study of Ampira Charoensaeng et al. (2009); they found that the K_{adm} values of phenylethanol for extended surfactants are greater than those for SDS alone and SDS with linker systems.

The carbon chain length of the carboxylate extended surfactants' tail didn't have much of an effect on the log K_{adm} values (2.80 and 2.81 for C16.5 and C17, respectively). Based on these results it could be said that the hydrophobicity of the core does not significantly impact to the adsolubilization of phenylethanol. Since, phenylethanol is a polar organic solute, it was expected to partition primarily into the palisade region. This result is similar to previous study (Ampira Charoensaeng et al., 2009).

When comparing the phenylethanol adsolubilization of the carboxylate extended surfactant (C16.5-4PO5EOC) and sulfate extended surfactant system (C16.5-4POS), it was found that the adsolubilization capacity (log K_{adm}) of the carboxylate extended surfactant was higher than that of the sulfate extended surfactant (see Table 4-5). Since, phenylethanol is a relatively polar organic solute, it was expected to partition primarily into the palisade region (Ampira Charoensaeng et al., 2009). The carboxylate extended surfactant containing PO/EO groups had a higher area per molecule value (Å^2/molecule) than the sulfate extended surfactant did (see Table 4-2), and the carboxylate extended surfactant had a larger aggregate size (loose packing arrangement), which resulted in it having a larger palisade layer, compared to that of the sulfate extended surfactant (Dickson and O'Haver, 2002; Rosen, 2004; Tan and O'Haver, 2004). For this reason, the phenylethanol adsolubilization capacitie of the carboxylate extended surfactant was greater than that of the sulfate extended surfactant.

4.6.2 Ethylcyclohexane Adsolubilization

The ethylcyclohexane admicellar partition coefficients (K_{adm}) of the conventional surfactant system (C12S), the carboxylate extended surfactant systems (C16.5-4PO5EOC and C17-4PO5EOC), and the sulfate extended surfactant system (C16.5-4POS) onto an alumina surface are summarized in Table 4-6. The values of K_{adm} were obtained at the maximum mole fraction of ethylcyclohexane in the aqueous phase (X_{aq}) (see Figure 4-11), which is the value that the solute approaches water solubility (maximum additivity) as adsolubilization sites become saturated. That also the same with the measurement of the phenylethanol admicellar partition coefficient. In the absence of an adsorbed surfactant, the adsorption of ethylcyclohexane onto aluminum oxide was negligible.

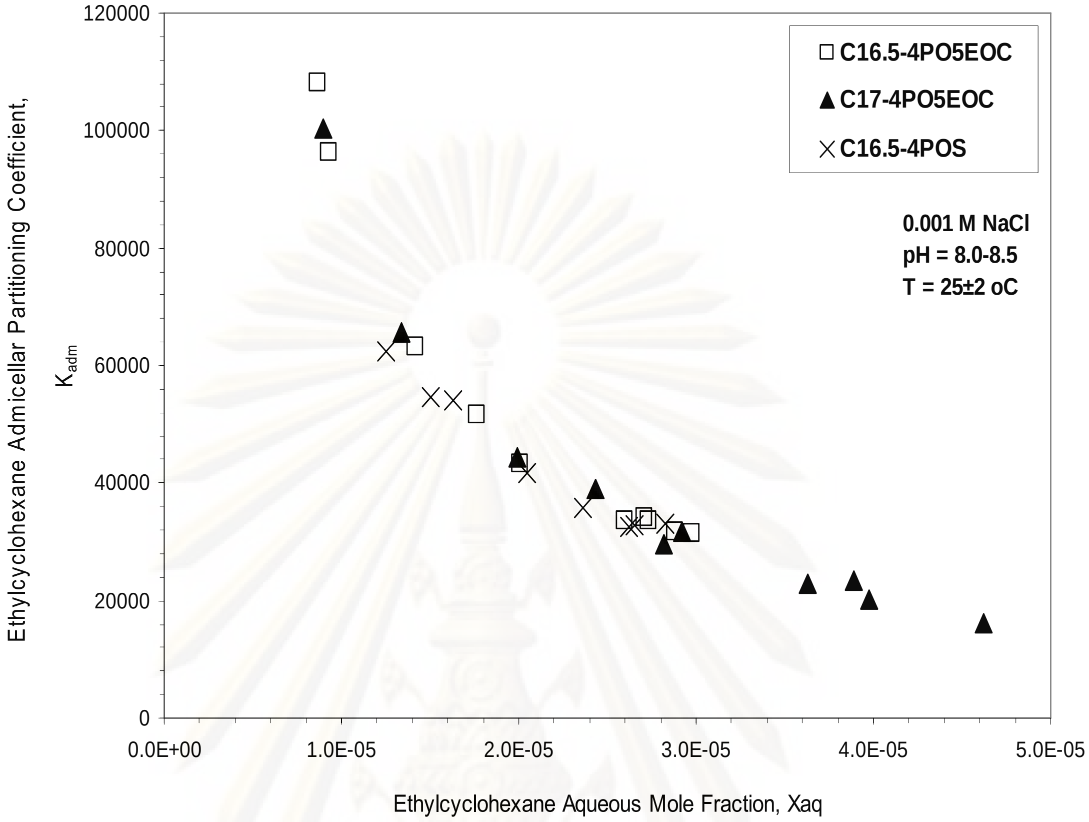


Figure 4-11 The ethylcyclohexane admicellar partition coefficient (K_{adm}) of the carboxylate extended surfactant systems and the sulfate extended surfactant system onto alumina, in 0.001 M NaCl, at equilibrium pH 8.0-8.5 and a temperature of 25±2°C

Table 4-6 Ethylcyclohexane adsolubilization capacities of the extended surfactant systems and the conventional surfactant system

Surfactant	HLB[a]	Ethylcyclohexane adsolubilization		
		Ads. q_{max} (mmole/g)	K_{adm}	log K_{adm}
Conventional surfactant				
C12S	40.00	0.19±0.01	NM	NM
Carboxylate extended surfactant				
C16.5-4PO5EOC	19.31	0.18±0.01	32,987	4.52
C17-4PO5EOC	19.08	0.23±0.02	20,676	4.32
Sulfate extended surfactant				
C16.5-4POS	37.26	0.26±0.02	33,950	4.53

[a] HLB is the hydrophilic-lipophilic balance
NM is not measurable

The reason why the partition coefficient (K_{adm}) of ethylcyclohexane of the conventional surfactant (C12S) was unmeasurable, as listed in Table 4-6, was because the amount of adsolubilization was too small to quantify. With regard to the carboxylate extended surfactant systems (C16.5-4PO5EOC and C17-4PO5EOC), the log K_{adm} value of C16.5-4PO5EOC was higher than that of C17-4PO5EOC (4.52 and 4.32, respectively--see Table 4-6). It was due to the fact that C16.5-4PO5EOC had a higher area per molecule ($Å^2$/molecule) (see Table 4-2), so it had a larger aggregate size (with a loose packing arrangement) that needed more ethylcyclohexane to saturate the admicelles. This result consistent with the studied of Dickson and O'Haver (2002) who found that the adsolubilization of naphthalene onto HiSil 233 is less favorable in C_{14}TAB admicelles than in C_{12}TAB and C_{16}TAB admicelles. Since, naphthalene being intermediate in polarity is expected to adsolubilize into both the palisade and core regions of the admicelle. C_{14}TAB adsorption on this silica has tighter packing arrangement (lowest area per molecule), which reduced adsolubilization of naphthalene into this region. When the log K_{adm} values of the carboxylate extended surfactant (C16.5-4PO5EOC) and the sulfate extended surfactant system (C16.5-4POS) were evaluated at the same carbon chain length, the log K_{adm} values remained the same (4.52 and 4.53, respectively).

The graph in Figure 4-11 that plots the K_{adm} values and the ethylcyclohexane aqueous mole fractions (X_{aq}) evaluates the locus of solubilization of ethylcyclohexane. The results show that the K_{adm} values of the extened surfactant systems decreased as the aqueous molar fraction (X_{aq}) of ethylcyclohexane increased. It was implied that ethylcyclohexane partitioned into the palisade layer of the surfactant admicelles. But that fact, ethylcyclohexane was expected to partition into the core region. Since ethylcyclohexane is a non polar organic solute (dipole moment = 0) (Nayyar et al., 1994; Dickson and O'Haver, 2002). However, ethylcyclohexane tended to partition into the palisade region in this study. This may have been due to the effect of the intermediate groups in the extended surfactant that consisted of EO/PO or PO groups, along with the structure and smaller molecular size of the solute, which may have allowed ethylcyclohexane to escape from the hydrophobic core regions. This finding is similar to that of a previous study (Ampira Charoensaeng et al., 2009).

When comparing the results from Tables 4-5 and 4-6, it can be seen that the surfactant systems' adsolubilization capacities (log K_{adm} values) for phenylethanol (range from 2.66-2.81) were lower than they were for ethylcyclohexane (range from 4.32-4.53). This result was consistent with the results from the solubilization study. This could have been due to the different partitioning behavior of phenylethanol, which has higher solubility in water (highly polar) and preference to solubilizing in the aqueous phase rather than partitioning into admicelles. Ethylcyclohexane (non polar), on the other hand, trends to adsolubilize in the admicelles of the surfactant (Rosen, 2004; Ampira Charoensaeng et al., 2009).

Comparing the partition coefficients in the solubilization and adsolubilization of both phenylethanol and ethylcyclohexane (log K_{mic} and log K_{adm} - in Tables 4-3 to 4-6, respectively) demonstrates that the admicellar systems (log K_{adm}) were less efficient at solubilizing organic solutes than the micellar system (log K_{mic}) was. This could be due to the fact that the extended surfactant aggregates pack more efficiently into three-dimensional micelles than they do into the more planar, two-dimensional admicelles. Moreover, the partitioning of organic solutes into extended surfactant micelles and admicelles depends on several factors, such as the degree of the organic solute's polarity, the carbon chain length of the surfactant, the hydrophilic head type of the surfactant, and the number of PO/EO groups inserted in the extended surfactant (Ampira Charoensaeng et al., 2009). This result is also consistent with what was found in the study of Noulkamol Arpornpong (2008), who researched the solubilization and adsolubilization of styrene (slightly polar) and phenanthrene (non polar) by using carboxylate extended surfactants, a sulfate extended surfactant, and a conventional surfactant (SDS). Furthermore, when comparing with the solubilization and adsolubilization of phenylethanol (highly polar) and ethylcyclohexane (non polar), it found that only the solubilization of ethylcyclohexane was higher than the results of the solubilization and adsolubilization of styrene and phenanthrene from Noulkamol Arpornpong (2008).

CHAPTER V

SUMMARY, CONCLUSION AND ENGINEERING SIGNIFICANCE

5.1 SUMMARY

This study evaluates the conventional surfactant (C12S), two anionic carboxylate extended surfactants (C16.5-4PO5EOC and C17-4PO5EOC), and an anionic sulfate extended surfactant (C16.5-4POS) to enhance adsorbent material's ability to remove an organic contaminant through a surfactant-based adsorption process. The surfactant adsorption, solubilization and adsolubilization isotherms of organic solutes were used to evaluate the impact of anionic extended surfactants on a positively charged aluminum oxide surface. The surface charge of aluminum oxide (zeta potential) and surfactant adsorption were used to determine the surfactant formation, and the surfactant desorption study was conducted to evaluate the desorption of surfactant and stability of surfactants adsorbed onto aluminum oxide surface. Each of the experiments was conducted in a batch system at room temperature (25 ± 2 °C), an electrolyte concentration of 0.001 M NaCl, and at a solution pH of 8.0-8.5. Two organic solutes--one with high dipole moment (phenylethanol) and one with low dipole moment (ethylcyclohexane)--were utilized to evaluate the solubilization capacity in the micelles and admicelles--through the micellar and admicellar partition coefficients (K_{mic} and K_{adm}), respectively.

The critical micelle concentration (CMC) of the surfactant systems in this research were determined by the surface tension measurements of the surfactant at the liquid–air interface. The CMCs of the extended surfactants were two orders of magnitude lower than that of the conventional surfactant, C12S. With regard to the carboxylate extended surfactants, the CMC of the C17-4PO5EOC surfactant was slightly lower than that of the C16.5-4PO5EOC surfactant. A comparison of the CMCs of the carboxylate extended surfactants and the sulfate extended surfactant revealed that the

CMCs of the carboxylate extended surfactants (C16.5-4PO5EOC and C17-4PO5EOC) were lower than that of the sulfate extended surfactant (C16.5-4POS).

The surfactant adsorption study on aluminum oxide determined that the adsorption of all surfactant systems increased when the surfactant concentration increased in accord with the S-shaped isotherm. The maximum adsorption capacity at the plateau region of the sulfate extended surfactant (C16.5-4POS) was higher than those of the conventional surfactant and the carboxylate extended surfactants. The carboxylate extended surfactant C17-4PO5EOC reached the maximum adsorption capacities at a lower equilibrium surfactant concentration than did the conventional surfactant, the sulfate extended surfactant, and the carboxylate extended surfactant C16.5-4PO5EOC.

In the alumina oxide surface charge study, the zeta potential of alumina with all surfactants decreases to negatively charge surface with an increases of the surfactant concentration. For the zeta potential of alumina at the plateau adsorption, it was observed that the zeta potential of alumina with all surfactants had the stability negatively charge surface. These results confirm the idea that a complete bilayer is s formed at CMC and above CMC of the adsorption isotherm. Additionally, at the maximum adsorption, the zeta potential of alumina indicated that the extended surfactant systems produced more negatively charged surfaces than the conventional surfactant system did. Thus, the extended surfactants formed bilayer coverage and surfactant molecule orient in denser packing more than the conventional surfactant.

The desorption studies determined the amount of anionic surfactants that desorbed from the alumina surface after the washing process by the zeta potential measurement. The zeta potential of alumina with the conventional surfactant and the extended surfactants increased at all surfactant concentrations, but the zeta potential of alumina with the extended surfactants remained negatively charged at all surfactant concentration. Since, the extended surfactants have greater lateral interactions due to their longer carbon chain length. Through studying the zeta potential of alumina with the carboxylate extended surfactant systems (C16.5-4PO5EOC and C17-4PO5EOC) and the sulfate extended surfactant system (C16.5-4POS), it was found that the zeta potential of alumina at the highest surfactant concentration of the sulfate extended surfactant was decreased to lower negative values than those produced by the carboxylate extended surfactants. This is because the carboxylate extended surfactants have stronger lateral interaction (bilayer coverage). Therefore, it could be concluded that the carboxylate extended surfactants can reduce the surfactant desorption and enhance the stability of adsorbed surfactant bilayer more than the conventional surfactant and the sulfate extended surfactant.

For solubilization study, the phenylethanol and ethylcyclohexane solubilization (log K_{mic} values) of the extended surfactant systems were greater than those of the conventional surfactant system. Since, the extended surfactant micelles have larger aggregation number resulting in greater the cavities in the micelle where the phenylethanol and ethylcyclohexane would segregate. As the carbon chain length slightly increased from C16.5 to C17 for the carboxylate extended surfactants, the log K_{mic} values remained the same. Moreover, when phenylethanol was solubilized by the extended surfactants, the sulfate extended surfactant produced a higher K_{mic} value than the carboxylate extended surfactants did. This result may have been due to the sulfate extended surfactant's higher HLB number. On the other hand, when ethylcyclohexane solubilization was studied, the carboxylate extended surfactants proved to provide higher ethylcyclohexane solubilization than the sulfate extended surfactant did. This was due to the impact of hydrophobicity of surfactant, thus, the ethylcyclohexane exhibits to solubilize in the extent of the carboxylate extended surfactants aggregates than that of the sulfate extended surfactant aggregates.

The results of the extended surfactants adsolubilization capacities (log K_{adm} values) of phenylethanol and ethylcyclohexane show that the extended surfactants (C16.5-4PO5EOC, C17-4PO5EOC, and C16.5-4POS) were better than the conventional surfactant (C12S) at adsolubilizing these two organic solutes. This could have been due to the extended surfactants having larger aggregation size, which resulted in them having more phenylethanol and ethylcyclohexane adsolubilization. For the carboxylate extended surfactant systems (C16.5-4PO5EOC and C17-4PO5EOC), the adsolubilization capacity of phenylethanol have the log K_{adm} values remain the same but the adsolubilization capacity of ethylcyclohexane have the log K_{adm} value of C16.5-4PO5EOC higher than C17-4PO5EOC. This was due to the fact that C16.5-4PO5EOC has a higher area per molecule ($Å^2$/molecule), so it had a larger aggregate size than the C17-4PO5EOC surfactant did. Moreover, the adsolubilization capacity of phenylethanol have log K_{adm} of the carboxylate extended surfactants higher than that of the sulfate extended surfactant, but the adsolubilization capacity of ethylcyclohexane have the log K_{adm} values of the carboxylate extended surfactant (C16.5-4PO5EOC) and the sulfate extended surfactant system (C16.5-4POS) remain as the same.

In order to gain insight into locus of adsolubilization of organic solutes, it was observed that the phenylethanol prefers partitioning in the palisade layer of surfactant admicelles because it is a highly polar organic solute. As expected, the ethylcyclohexane should partition into the core region of admicelle. Since ethylcyclohexane is non polar organic solute. However, ethylcyclohexane tends to partition into palisade region in this study. This may be due to the effects of the intermediate groups in the extended surfactant consisting of EO/PO or PO groups and the structure and smaller molecular size of the solute, which may have allowed ethylcyclohexane to escape from the hydrophobic core regions.

Comparing the partition coefficients in the solubilization and adsolubilization of both phenylethanol and ethylcyclohexane (log K_{mic} and log K_{adm}) demonstrates that the admicellar systems (log K_{adm}) were less efficient at solubilizing organic solutes than the micellar systems (log K_{mic}) were. This could be due to the fact that the extended surfactant aggregates pack more efficiently into three-dimensional micelles than they do into the more planar, two-dimensional admicelles. Moreover, the partitioning of organic solutes into extended surfactant micelles and admicelles depends on several factors, such as the degree of the organic solute's polarity, the carbon chain length of the surfactant, the hydrophilic head type of the surfactant, and the number of PO/EO groups inserted in the extended surfactant.

5.2 CONCLUSION

The specific conclusions based on the results of this research are as follows:

1) The CMCs of the extended surfactant systems were lower than that of the conventional surfactant system. When the carbon chain length of carboxylate extended surfactants increased from C16.5 to C17, the CMCs decreased. In addition, the CMC of the carboxylate extended surfactant (C16.5-4PO5EOC) was lower than that of the sulfate extended surfactant (C16.5-4POS).

2) The surfactant adsorption of the sulfate extended surfactant showed higher maximum adsorption capacity but the carboxylate extended surfactant (C17-4PO5EOC) reached maximum adsorption at a lower equilibrium surfactant concentration. The hydrophilic head group type and the carbon chain length number can affect the adsorption capacity by increasing the interactions between the adsorbed surfactant molecules.

3) The extended surfactant systems had higher negatively charge surfaces than the conventional surfactant system did. The extended surfactants formed the bilayer coverage and surfactant molecule orient in denser packing more than the conventional surfactant. These results support the idea that a complete bilayer is formed at and above the CMC of the adsorption isotherm.

4) The carboxylate extended surfactants showed lower desorption capacities than the conventional surfactant and the sulfate extended surfactant did due to the strong packing (bilayer coverage) and higher lateral interaction of the carbon chain length.

5) The extended surfactant systems of the micellar and admicellar partition coefficients (log K_{mic} and log K_{adm}) exhibited higher phenylethanol and ethylcyclohexane enhancement as compare to the conventional surfactant system.

6) Relative to the effect of carbon chain length in the extended carboxylate surfactant systems, increasing the carbon chain length from C16.5 to C17 did not affect the solubilization and adsolubilization capacities of the high polarity organic solute, phenylethanol.

7) The solubilization capacity of the low polarity organic solute, ethylcyclohexane, by the carboxylate extended surfactants remained the same as the carbon chain length slighted increased from C16.5 to C17, but the adsolubilization capacity of ethylcyclohexane, with a log K_{adm} value of C16.5-4PO5EOC, was higher than that of C17-4PO5EOC. This was due to the fact that C16.5-4PO5EOC had a higher area per molecule ($Å^2$/molecule), so it had a larger aggregate size than that of C17-4PO5EOC.

8) The hydrophilic head groups of the surfactant had some effects on solubilization. Phenylethanol was able to better solubilize in the sulfate extended surfactant's micelles than in the carboxylate extended surfactants' micelles. It could be due to the sulfate extended surfactant C16.5-4POS having a higher HLB number and more hydrophilic sites for phenylethanol to solubilize into micelles. The carboxylate extended surfactants performed higher phenylethanol adsolubilization than the sulfate extended surfactant did. This is because the carboxylate extended surfactants contained PO/EO groups that had a higher area per molecule value ($Å^2$/molecule) and a larger palisade layer than the sulfate extended surfactant did.

9) The adsolubilization capacity (K_{adm}) was lower than solubilization capacity (K_{mic}) for both phenylethanol and ethylcyclohexane due to the fact that the extended surfactant aggregates pack more efficiently into three-dimensional micelles than they do into the more planar, two-dimensional admicelles.

5.3 ENGINEERING SIGNIFICANCE

Surfactant modified adsorbents have been used for the removal of organic contaminants from the aqueous phase in a wide range of industrial and environmental applications. The unique characteristics of an extended surfactant includes the PO/EO groups and carbon chain length, and organic solute properties such as structure and degree of polarity that all factors have effect the efficiency of admicelle formation, solubilization, and adsolubilization enhancement. Moreover, selecting an appropriate surfactant for a specific solute is important to enhance the efficiency of adsolubilization. The extended surfactants enhanced the solubilization, adsolubilization, and stability of the extended surfactant adsorbed onto the aluminum oxide surface. Therefore, surface modification using extended surfactants shows particular promise for the treatment of groundwater and wastewater contaminated with organic solutes. It could have admicellar-enhanced chromatography (AEC) and solid phase extraction (SPE) applications, for example.

In a surfactant-enhanced remediation process, surfactants are used as potential agents for the enhanced solubilization and removal of contaminants from soil and sediments. In a field application, a surfactant modified adsorbent using adsolubilization could be used for removing organic solutes in filter or packed-bed reactors. For in-situ applications, surfactant modified adsorbents could be used in passive permeable barriers for mitigating groundwater contaminated in the subsurface. In the case of the biodegradation of organic hydrocarbons, the rate is very slow due to low water solubility and dissolution rates, but the presence of surfactants may increase the bioavailability of hydrophobic compounds by solubilization and, hence, increase the degradation rate (Paria, 2008).

5.4 RECOMMENDATIONS AND FUTURE WORKS

The extended-surfactant modified adsorbents show promise in their ability to effectively remove organic contaminants in aqueous solution. From this research, some aspects should be carefully considered and studied further:

1) ***Surfactant structure:*** In this study, sodium dodecyl sulfate was used to represent a conventional anionic surfactant with a C12 alkyl chain length, so in the future a conventional surfactant with an alkyl chain length similar to that of the extended surfactants should be used for a more comparable comparison of their efficiencies. For the extended surfactants, the carboxylate extended surfactants (C16.5-4PO5EOC and C17-4PO5EOC) were used to evaluate the effect of the alkyl chain length on the efficiency of extended surfactants. Due to the water solubility limitations of C16.5-4PO2EOC and C17-4PO2EOC, we could not investigate the effect of the EO groups in the hydrophilic heads of the surfactants. To clarify the effect of the hydrophilic head groups of the sulfate extended surfactant (C16.5-4POS) and the carboxylate extended surfactant, the C16.5-4PO5EOS have been produced and should be evaluated in a future study.

2) ***Muti-component systems:*** In the environment, an aqueous solution usually contains more than a single organic solute. The organic solutes in this study (phenylethanol and ethylcyclohexane) have similar molecular structures but different water solubility and degrees of polarity. Therefore, a mixture of organic solutes or real wastewater contaminants should be used in future studies. Moreover, a mix surfactant system is interesting to study because the efficiency of a mix surfactant may be higher than that of a single surfactant system such as investigate mixed anionic carboxylate surfactant with cationic conventional surfactant.

3) ***Surfactant desorption:*** The surfactants adsorbed onto aluminum oxide surface in the extended surfactant based systems were more stable than the surfactant adsorbed in the conventional surfactant system. However, there are some limiting factors when using a surfactant modified adsorbent; for example, there are adsorbed surfactant aggregates losses from solid surface to aqueous solution, another factors are pH and salt concentration in aqueous solution.

4) *Surface characterization:* Enhancing the adsolubilization of organic solutes is dependent on the surfactant structure, organic solutes properties, and solid surface. Atomic force microscopy (AFM) to study the admicelles morphology at solid-liquid interface is a helpful technique for understanding the admicelle formation and adsolubilization mechanisms of extended surfactants onto a solid oxide surface.

REFERENCES

Adak, A., Bandyopadhyay, M., and Pal, A. Adsorption of Anionic Surfactant on Alumina and Reuse of the Surfactant-Modified Alumina for the Removal of Crystal Violet from Aquatic Environment. J. Environ. Sci. Health., Part A 40 (2005): 167-182.

Arpornpong, N. Adsolubilization and solubilization using conventional and extended anionic surfactants on an aluminum oxide surface. Master's Thesis, Environmental Management Program, Graduate School, Chulalongkorn University, 2008.

Asnachinda, E., Khaodhiar, S., and Sabatini, D. A. Effect of Ionic Head Group on Admicelle Formation by Polymerizable Surfactants. J. Surfactants Deterg. 12 (2009a.): 379-386.

Asnachinda, E., Khaodhiar, S., and Sabatini, D. A. Styrene and Phenylethanol Adsolubilization of a Polymerizable Gemini Surfactant. J. Surfactants Deterg. (2009b.): 143-148.

Asvapathanagul, P., Malakul, P., and O'Haver, J.H. Adsolubilization of toluene and acetophenone as a function of surfactant adsorption. J. Colloid Interface Sci. 292 (2005): 305–311.

Attaphong, C., Asnachinda, E., Charoensaeng, A., Sabatini, D. A., and Khaodhiar, S. Adsorption and adsolubilization of polymerizable surfactants on aluminum oxide. J. Colloid Interface Sci. 344 (2010): 126–131.

Charoensaeng, A., Sabatini, D.A., and Khaodhiar, S. Solubilization and Adsolubilization of Polar and Nonpolar Organic Solutes by Linker Molecules and Extended Surfactants. J. Surfactants Deterg. 12,3 (2009): 209-217.

Charoensaeng, A., Sabatini, D.A., and Khaodhiar, S. Styrene Solubilization and Adsolubilization on an Aluminum Oxide Surface Using Linker Molecules and Extended Surfactants. J. Surfactants Deterg. 11,1 (2008): 61-71.

Childs, J., Acosta, E., Annable, M.D., Brooks, M.C., Enfield, C.G., Harwell, J.H., Hasegawa, M., Knox, R.C., Rao, P. Suresh C., Sabatini, D.A., Shiau, B., Szekeres, E., and Wood, A.L. Field demonstration of surfactant-enhanced solubilization of DNAPL at Dover Air Force Base, Delaware. J. Contam. Hydrol. 82 (2006): 1– 22.

Cheng, H., and Sabatini, D.A. Phase–behavior-based surfactant–contaminant separation of middle phase microemulsions. Separation Science and Technology 37, 1 (2002): 127-146.

Dickson, J., and O' Haver, J. Adsolubilization of naphthalene and naphthol in C_nTAB admicelles. Langmuir. 18 (2002): 9171-9176.

Esumi, K. Adsolubilization by mixtures of ionic and non-ionic surfactants. Progr. Colloid Polym. Sci. 123 (2004): 44–47.

Esumi, K. Interactions between Surfactants and Particles: Dispersion, Surface Modification, and Adsolubilization. J. Colloid Interface Sci. 241, 1 (September 2001): 1-17.

Esumi, K., Maedomari, N., and Torigoe, K. Mixed Surfactant Adsolubilization of 2-Naphthol on Alumina. Langmuir. 16 (2000): 9217-9220.

Esumi, K., Watanabe, N., and Meguro, K. Polymerization of styrene adsolubilization in polymerizable surfactant bilayer on alumina. Langmuir. 7 (1991): 1775-1778.

Fernández, A., Scorzza, C., Usubillaga, A., and Salager, J. L. Synthesis of New Extended Surfactants Containing a Carboxylate or Sulfate Polar Group. J. Surfactants Deterg. 8 (April 2005): 187–191.

Fuangsawasdi, A., Charoensaeng, A., Sabatini, D.A., Scamehorn, J.F., Acosta, J.E., Osathaphan, K., and Khaodhiar, S. Mixtures of anionic and cationic surfactants with single and twin head groups: solubilization and adsolubilization of styrene and ethylcyclohexane. J. Surfactants Deterg. 9 (2006): 29-37.

Fuerstenau, D. W. The Adsorption of Surfactants at Solid-Water Interfaces. In the Chemistry of Bio-Surfaces, Vol. 1 Ch. 4 pp. 143-176. New York: Marcel Dekker, 1971.

Golub, T. P., Koopal, L. K., and Sidorova, M. P. Adsorption of Cationic Surfactants on Silica Surface: 1. Adsorption Isotherms and Surface Charge. Colloid J. 66, 1 (2004): 43-48.

Harwell, J.H., and O'Rear, E.A. Adsorbed surfactant bilayers as two-dimensional solvents. In Scamehorn, J.F., Harwell, J.H. (eds) Admicellar-enhanced chromatography. New York: Marcel Dekker, Chap 7 (1989): 155.

Harwell, J.H., Sabatini, D.A., and Knox, R.C. Surfactants for ground water remediation. Colloids Surf., A 151 (1999): 255–268.

Holmberg, K., Jönsson, B., Kronberg, B., and Lindman, B. Surfactants and Polymers in Aqueous Solution. 2nd ed. West Sussex: John Wiley & Sons, 2002.

Huang, L., and Somasundaran, P. The change in structure of surfactant aggregates during adsorption/desorption processes and its effect on the stability of alumina suspension. Colloids Surf., A 117 (1996): 235-244.

Kitiyanan, B., O'Haver, J.H., Harwell, J.H., and Osuwan, S. Absolubilization of Styrene and Isoprene in Cetyltrimethylammonium Bromide Admicelle on Precipitated Silica. Langmuir. 12 (1996): 2162-2168.

Kondo, Y., Abe, M., Ogino, K., Uchiyama, H., Scamehorn, J. F., Tucker, E. E., and Christian, S. D. Solubilization of 2-Phenylethanol in Surfactant Vesicles and Micelles. Langmuir. 9 (1993): 899-902.

Lopata, J. J. A study of the adsorption of binary anionic surfactant mixtures on alpa alumina oxide. Master's Thesis, Department of chemical engineering, University of Oklahoma, 1988.

Matsson, M.K. Adsorption of polyhydroxyl based surfactants. Doctoral thesis, the Royal Institute of Technology, Stockholm, 2005.

Myers, D. Surfactant science and technology. 3^{rd} ed. New Jersey: John Wiley & Sons, 2006.

Miñana-Perez, M., Graciaa, A., Lachaise, J., Salager, J. Solubilization of polar oils with extended Surfactants. Colloids Surf., A 100 (1995): 217-224.

Nayyar, S.P., Sabatini, D.A., and Harwell, J.H. Surfactant adsolubilization and modified admicellar sorption of nonpolar, polar, and ionizable organic contaminants. Environ. Sci. Technol. 28 (1994): 1874-1881.

NFES, Naval Facilities Engineering Service Center. Surfactant-Enhanced Aquifer Remediation (SEAR) Implementation Manual. NFES Technical Report TR-2219-ENV (April 2003).

Nivas, B.T., Sabatini, D.A, Shlau, B.J., and Harwell, J.H. Surfactant enhenced eemediation of subsurface chromium contamination. Wat. Res. 30 (1996): 511-520.

Paria, S. Surfactant-enhanced remediation of organic contaminated soil and water. Adv. Colloid Interface Sci. 138 (2008): 24–58.

Paria, S., and Khilar, K.C. A review on experimental studies of surfactant adsorption at the hydrophilic solid–water interface. Adv. Colloid Interface Sci. 110 (2004): 75-95.

Rosen, M. J. Surfactant and interfacial phenomena. 3^{rd} ed. New Jersey: John Wiley & Sons, 2004.

Rouse, J.D., Hirata, O. S., and Furukawa, K. Influence of Diphenyloxide Disulonate Surfactants on Biodegradation of Hydrocarbons. Global Nest: the Int. J. 3, 1 (2001): 23-36.

Rouse, J.D., Sabatini, D. A., Deeds, N. E., Brown, R. E., and Harwell, J. H. Micellar Solubilization of Unsaturated Hydrocarlron Concentration As Evaluated by Semiequilibrium Dialysis. Environ. Sci. Technol. 29 (1995): 2484-2489.

Sabatini, D.A., Knox, R.C., and Harwell, J.H. Surfactant-enhanced DNAPL remediation: surfactant selection, hydraulic efficiency, and economic factors. EPA: Environmental Research Brief. (August 1996).

Sabatini, D.A, Acosta, E.J., and Harwell, J.H. Linker molecules in surfactant mixtures. J. Colloid Interface Sci. 8 (2003): 316–326.

Saphanuchart, W., Saiwan, C., and O'Haver, J. H. Temperature effects on adsolubilization of aromatic solutes partitioning to different regions in cationic admicelles. Colloids Surf., A 317 (2008): 303–308.

Sasol North America Inc. Alfoterra [online]. Louisiana: Sasol North America Inc., 2007. Available from: http:// www.sasoltechdata.com/tds/ALFOTERRA.pdf [2008, April 25].

Scamehorn, J. F., Schechter, R. S., and Wade, W. H. Adsorption of surfactant on mineral oxide surfaces from aqueous solutions: I: Isomerically pure anionic surfactants. J. Colloid Interface Sci. 85 (1982): 463.

Somasundaran P., and Grieves, R.B. Advances in Interfacial Phenomena of Particulate Solution-Gas Systems: Application to Flotation Research. AIChE Symp. 71 (1975): 124-133.

Sun, S., and Jaffe, P. R. Sorption of Phenanthrene from Water onto Alumina Coated with Dianionic Surfactants. Environ. Sci. Technol. 30 (1996): 2906-2913.

Tadros, T.F. Applied Surfactants: Principles and applications. Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA, 2005.

Tan, Y., and O'Haver, J.H. Lipophilic linker impact on adsorption of and styrene adsolubilization in Polyethoxylated octylphenols. Colloids Surf., A 232 (2004):101-111.

Uchiyama, H., Christian, S. D., Scamehorn, J. F., Abe, M., and Ogino, K. Solubilization of 2-Phenylethanol by Dodecyldimethylamine Oxide in Aqueous Solution. Langmuir. 7 (1991): 95-100.

Uppgård, L. L. Nonionic surfactants: A multivariate study. 2nd ed. Sweden: Umeå University Press, 2002.

West, C.C., and Harwell, J. H. Surfactants and Subsurface Remediation. Environ. Sci. Technol. 26 (1992): 2324.

Witthayapanyanon, A., Acosta, E.J., Harwell, J.H., and Sabatini, D.A. Formulation of ultralow interfacial tension systems using extended surfactants. J. Surfactants Deterg. 9 (2006): 331-339.

Zhang, R., and Somasundaran, P. Advances in adsorption of surfactants and their mixtures at solid/solution interfaces. Adv. Colloid Interface Sci. 123 (2006): 213-229.

APPENDICES

APPENDIX A

Calculation: Hydrophilic-Lipophilic Balance (HLB)

$$\mathrm{HLB} = 7 + \Sigma(\text{hydrophilic group numbers}) + \Sigma(\text{lipophilic group numbers})$$

Table A-1 HLB values for calculations

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

Condition for GC:

Each sample in 2.0 µL sample solution was injected into GC (6890N, Agilent) at the following conditions: injector temperature was 80°C, a column type HP-5 (Agilent) with 30 m x 0.32 mm ID was used with a film thickness of 0.25 µm, an oven temperature of 50-300°C was applied, a flame ionization detector (FID) was used, and a pressure of 6.07 psi utilized.

APPENDIX B

EXPERIMENTAL RAW DATA

Table B-1 Surface tension measurement of conventional surfactant (C12S) at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Conc. (M)	Surface tension (mN/m)			Average	SD
	[1]	[2]	[3]		
3.0E-04	67.454	66.021	63.487	65.6540	2.0088
5.0E-04	62.254	63.542	60.228	62.0080	1.6706
7.0E-04	60.496	62.328	57.548	60.1240	2.4116
1.0E-03	56.408	55.963	57.222	56.5310	0.6384
3.0E-03	46.622	45.778	46.299	46.2330	0.4259
5.0E-03	40.320	40.281	40.296	40.2990	0.0197
7.0E-03	36.763	35.571	35.002	35.7787	0.8987
9.0E-03	35.766	36.746	36.749	36.4203	0.5667
1.0E-02	36.418	37.080	37.002	36.8333	0.3618
3.0E-02	37.801	37.912	37.840	37.8510	0.0563
5.0E-02	37.459	37.178	37.023	37.2200	0.2210
7.0E-02	36.739	36.556	36.645	36.6467	0.0915
1.0E-01	36.382	35.775	36.173	36.1100	0.3084

Table B-2 Surface tension measurement of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Conc. (M)	Surface tension (mN/m)			Average	SD
	[1]	[2]	[3]		
1.0E-06	59.3060	59.3850	59.2380	59.3097	0.0736
3.0E-06	50.3520	50.4250	50.6760	50.4843	0.1700
5.0E-06	46.9620	45.7730	46.8940	46.5430	0.6677
7.0E-06	44.1680	44.5710	44.3580	44.3657	0.2016
1.0E-05	42.1430	42.9420	42.1000	42.3950	0.4742
2.0E-05	36.7120	36.4190	36.6840	36.6050	0.1617
3.0E-05	36.9580	36.6870	36.4780	36.7077	0.2407
5.0E-05	37.0210	36.4380	36.0600	36.5063	0.4841
7.0E-05	35.4400	35.6590	35.6620	35.5870	0.1273
9.0E-05	36.0440	34.9480	34.4320	35.1413	0.8232
5.0E-04	32.7590	34.1130	33.7890	33.5537	0.7070
1.0E-03	33.4410	33.2910	33.3280	33.3533	0.0781

Table B-3 Surface tension measurement of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Conc. (M)	Surface tension (mN/m)			Average	SD
	[1]	[2]	[3]		
1.0E-06	61.290	61.581	61.936	61.6023	0.3235
3.0E-06	58.510	58.442	58.443	58.4650	0.0390
5.0E-06	55.315	55.277	55.357	55.3163	0.0400
7.0E-06	52.250	52.257	52.249	52.2520	0.0044
9.0E-06	48.800	49.118	48.332	48.7500	0.3954
1.0E-05	47.400	47.835	46.268	47.1677	0.8089
2.0E-05	44.163	44.774	45.030	44.6557	0.4454
3.0E-05	43.425	42.982	44.286	43.5643	0.6631
5.0E-05	42.590	42.008	42.349	42.3157	0.2924
7.0E-05	42.753	42.054	42.101	42.3027	0.3907
1.0E-04	42.434	41.904	41.884	42.0740	0.3119
5.0E-04	40.601	40.375	40.256	40.4107	0.1752
1.0E-03	40.074	40.640	39.860	40.1913	0.4030
3.0E-03	38.411	38.920	39.361	38.8973	0.4754

Table B-4 Surface tension measurement of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Conc. (M)	Surface tension (mN/m)			Average	SD
	[1]	[2]	[3]		
7.0E-06	47.659	48.206	46.549	47.4713	0.8443
1.0E-05	44.280	44.297	44.907	44.4947	0.3572
3.0E-05	37.828	37.927	37.738	37.8310	0.0945
5.0E-05	35.148	35.188	34.980	35.1053	0.1104
7.0E-05	35.787	35.543	35.155	35.4950	0.3187
9.0E-05	35.724	35.221	36.012	35.6523	0.4003
1.0E-04	35.182	34.587	34.797	34.8553	0.3018
3.0E-04	34.474	34.250	34.648	34.4573	0.1995
5.0E-04	34.358	34.103	34.176	34.2123	0.1313
7.0E-04	34.185	33.912	34.013	34.0367	0.1380
1.0E-03	33.732	33.807	33.750	33.7630	0.0392

Table B-5 Adsorption of C12S at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Conc. (M)	Solution (ml)	Initial		Equilibrium		C_{in}-C_{eq} (M)	Alumina (g)	q (mmole/g)	[q] (molecule/nm^2)	pH (eq.)
		Area	Conc. (M)	Area	Conc. (M)					
2.00E-04	40	89.3	3.61E-04	85.8	3.57E-04	4.65E-06	0.0512	0.0036	0.0141	8.00
3.00E-04	40	107.0	3.85E-04	102.9	3.79E-04	5.45E-06	0.0516	0.0042	0.0164	8.00
6.00E-04	40	263.2	5.92E-04	245.2	5.68E-04	2.39E-05	0.0559	0.0171	0.0665	8.10
7.00E-04	40	307.6	6.51E-04	283.1	6.19E-04	3.26E-05	0.0547	0.0238	0.0925	8.02
8.00E-04	40	370.2	7.35E-04	332.1	6.84E-04	5.06E-05	0.0538	0.0376	0.1463	8.00
1.00E-03	40	472.3	8.70E-04	387.9	7.58E-04	1.12E-04	0.1001	0.0448	0.1741	8.06
2.00E-03	40	1112.5	1.72E-03	932.1	1.48E-03	2.40E-04	0.1002	0.0957	0.3718	8.15
3.00E-03	40	1833.8	2.68E-03	1514.8	2.26E-03	4.24E-04	0.0999	0.1697	0.6595	8.40
5.00E-03	40	3587.8	5.01E-03	3230.2	4.53E-03	4.75E-04	0.1003	0.1895	0.7364	8.38
7.00E-03	40	5265.5	7.24E-03	4883.2	6.73E-03	5.08E-04	0.1030	0.1973	0.7666	8.40

Table B-6 Adsorption of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Conc. (M)	Solution	Initial		Equilibrium			C_{in}-C_{eq}	Alumina	q	Avg. q	[q]	pH
	(ml)	Area	Conc. (M)	Area	Conc. (M)	Avg. Conc.	(M)	(g)	(mmole/g)	(mmole/g)	(molecule/nm^2)	(eq.)
2.00E-04	40	85.9	3.45E-04	74.6	3.40E-04	3.40E-04	5.65E-06	0.0050	0.0452	0.0452	0.1756	8.25
3.00E-04	40	150.2	3.78E-04	115.2	3.60E-04	3.60E-04	1.75E-05	0.0133	0.0526	0.0526	0.2045	8.37
5.00E-04	40	318.0	4.61E-04	267.3	4.36E-04	4.36E-04	2.54E-05	0.0104	0.0975	0.0975	0.3789	8.43
6.00E-04	40	444.4	5.25E-04	382.4	4.94E-04	4.94E-04	3.10E-05	0.0100	0.1240	0.1240	0.4818	8.33
7.00E-04	40	570.5	5.88E-04	494.9	5.50E-04	5.50E-04	3.78E-05	0.0102	0.1482	0.1482	0.5760	8.43
8.00E-04	40	671.2	6.38E-04	587.3	5.96E-04	5.97E-04	4.20E-05	0.0109	0.1539	0.1481	0.5982	8.44
8.00E-04	40	671.2	6.38E-04	592.2	5.99E-04		3.95E-05	0.0111	0.1423		0.5531	8.30
9.00E-04	40	824.0	7.14E-04	734.4	6.70E-04	6.71E-04	4.48E-05	0.0108	0.1659	0.1623	0.6448	8.29
9.00E-04	40	824.0	7.14E-04	739.1	6.72E-04		4.25E-05	0.0107	0.1587		0.6166	8.33
1.00E-03	40	960.6	7.83E-04	710.7	6.58E-04	6.57E-04	1.25E-04	0.0330	0.1515	0.1589	0.5885	8.39
1.00E-03	40	960.6	7.83E-04	707.0	6.56E-04		1.27E-04	0.0305	0.1663		0.6462	8.47
2.00E-03	40	2644.3	1.62E-03	2365.2	1.49E-03	1.48E-03	1.40E-04	0.0306	0.1824	0.1767	0.7088	8.41
2.00E-03	40	2644.3	1.62E-03	2360.5	1.48E-03		1.42E-04	0.0332	0.1710		0.6643	8.06
3.00E-03	40	4668.9	2.64E-03	4397.9	2.50E-03	2.50E-03	1.36E-04	0.0301	0.1801	0.1801	0.6997	8.29
5.00E-03	40	8819.8	4.71E-03	8499.7	4.55E-03	4.55E-03	1.60E-04	0.0325	0.1970	0.1970	0.7654	8.07

Table B-7 Adsorption of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Conc. (M)	Solution	Initial		Equilibrium			C_{in}-C_{eq}	Alumina	q	Avg. q	[q]	pH
	(ml)	Area	Conc. (M)	Area	Conc. (M)	Avg. Conc.	(M)	(g)	(mmole/g)		(molecule/nm^2)	(eq.)
2.00E-04	40	82.7	4.06E-04	80.2	4.04E-04	4.04E-04	1.25E-06	0.0052	0.0096	0.0096	0.0374	8.00
3.00E-04	40	173.1	4.51E-04	163.5	4.46E-04	4.46E-04	4.80E-06	0.0052	0.0369	0.0369	0.1435	8.05
4.00E-04	40	255.9	4.92E-04	217.9	4.73E-04	4.73E-04	1.90E-05	0.0115	0.0661	0.0661	0.2568	8.01
5.00E-04	40	335.9	5.32E-04	278.7	5.04E-04	5.04E-04	2.86E-05	0.0110	0.1040	0.1040	0.4041	8.26
6.00E-04	40	525.6	6.27E-04	434.5	5.81E-04	5.81E-04	4.56E-05	0.0113	0.1612	0.1612	0.6265	8.24
7.00E-04	40	623.4	6.76E-04	521.7	6.25E-04	6.31E-04	5.09E-05	0.0105	0.1937	0.1742	0.7527	8.00
7.00E-04	40	623.4	6.76E-04	545.3	6.37E-04		3.91E-05	0.0101	0.1547		0.6010	8.08
8.00E-04	40	710.8	7.20E-04	500.5	6.14E-04	6.14E-04	1.05E-04	0.0301	0.1397	0.1397	0.5430	8.01
9.00E-04	40	854.2	7.91E-04	575.8	6.52E-04	6.52E-04	1.39E-04	0.0327	0.1703	0.1703	0.6617	8.00
1.00E-03	40	1013.1	8.71E-04	698.5	7.13E-04	7.13E-04	1.57E-04	0.0313	0.2010	0.2010	0.7811	8.02
2.00E-03	40	2709.4	1.72E-03	2375.7	1.55E-03	1.55E-03	1.67E-04	0.0301	0.2217	0.2217	0.8616	8.02
3.00E-03	40	4882.9	2.81E-03	4491.4	2.61E-03	2.61E-03	1.96E-04	0.0313	0.2502	0.2502	0.9721	8.00
5.00E-03	40	9717.9	5.22E-03	9350.7	5.04E-03	5.04E-03	1.84E-04	0.0305	0.2408	0.2408	0.9357	8.03

Table B-8 Adsorption of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Conc. (M)	Solution (ml)	Initial		Equilibrium			C_{in}-C_{eq} (M)	Alumina (g)	q (mmole/g)	Avg. q	[q] (molecule/nm^2)	pH (eq.)
		Area	Conc. (M)	Area	Conc. (M)	Avg. Conc.						
2.00E-04	40	101.2	3.29E-04	77.1	3.17E-04	3.17E-04	1.21E-05	0.0050	0.0964	0.0964	0.3746	8.00
3.00E-04	40	155.0	3.56E-04	124.3	3.41E-04	3.41E-04	1.54E-05	0.0051	0.1204	0.1204	0.4678	8.00
4.00E-04	40	228.0	3.93E-04	192.8	3.75E-04	3.75E-04	1.76E-05	0.0055	0.1280	0.1280	0.4974	8.01
5.00E-04	40	301.1	4.29E-04	219.8	3.89E-04	3.89E-04	4.06E-05	0.0100	0.1626	0.1564	0.6318	8.05
5.00E-04	40	301.1	4.29E-04	221.5	3.90E-04		3.98E-05	0.0106	0.1502		0.5836	8.02
6.00E-04	40	396.7	4.77E-04	321.6	4.40E-04	4.37E-04	3.76E-05	0.0106	0.1417	0.1408	0.5506	8.03
6.00E-04	40	396.7	4.77E-04	312.7	4.35E-04		4.20E-05	0.0120	0.1400		0.5440	8.01
7.00E-04	40	494.9	5.26E-04	387.5	4.73E-04	4.73E-04	5.37E-05	0.0134	0.1603	0.1553	0.6229	8.09
7.00E-04	40	494.9	5.26E-04	390.4	4.74E-04		5.23E-05	0.0139	0.1504		0.5843	8.15
8.00E-04	40	579.6	5.69E-04	490.4	5.24E-04	5.23E-04	4.46E-05	0.0108	0.1652	0.1664	0.6419	8.07
8.00E-04	40	579.6	5.69E-04	487.4	5.23E-04		4.61E-05	0.0110	0.1676		0.6514	8.11

Table B-8a Adsorption of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Conc. (M)	Solution (ml)	Initial		Equilibrium			C_{in}-C_{eq} (M)	Alumina (g)	q (mmole/g)	Avg. q	[q] (molecule/nm^2)	pH (eq.)
		Area	Conc. (M)	Area	Conc. (M)	Avg. Conc.						
9.00E-04	40	685.9	6.22E-04	598.7	5.78E-04	5.76E-04	4.36E-05	0.0107	0.1630	0.1646	0.6334	8.04
9.00E-04	40	685.9	6.22E-04	590.3	5.74E-04		4.78E-05	0.0115	0.1663		0.6461	8.07
1.00E-03	40	809.2	6.83E-04	700.1	6.29E-04	6.26E-04	5.46E-05	0.0125	0.1746	0.1842	0.6783	8.02
1.00E-03	40	809.2	6.83E-04	688.1	6.23E-04		6.06E-05	0.0125	0.1938		0.7529	8.05
1.50E-03	40	1389.7	9.74E-04	1246.3	9.02E-04	9.02E-04	7.17E-05	0.0118	0.2431	0.2431	0.9444	8.13
2.00E-03	40	2099.4	1.33E-03	1948.3	1.25E-03	1.25E-03	7.56E-05	0.0116	0.2605	0.2659	1.0123	8.06
2.00E-03	40	2099.4	1.33E-03	1955.6	1.26E-03		7.19E-05	0.0106	0.2713		1.0543	8.04
3.00E-03	40	3786.8	2.17E-03	3660.4	2.11E-03	2.11E-03	6.32E-05	0.0103	0.2454	0.2454	0.9537	8.00
5.00E-03	40	7325.5	3.94E-03	7158.7	3.86E-03	3.86E-03	8.34E-05	0.0116	0.2876	0.2876	1.1175	8.08

Table B-9 The alumina surface charges (zeta potential) of C12S at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Conc. (M)	pH_{eq}	Zeta potential (mV)											
		1	2	3	4	5	6	7	8	9	10	Avg.	SD
1.00E-04	8.10	31.43	17.85	21.74	30.79	35.39	34.88	27.74	16.45	30.58	22.93	28.28	7.56
1.00E-04	8.11	28.01	47.18	26.07	16.26	31.92	20.59	34.11	33.58	31.14	26.96		
3.00E-04	8.01	26.95	25.89	20.00	17.52	23.57	30.58	31.92	12.96	19.63	16.57	27.83	9.39
3.00E-04	8.05	20.43	35.67	39.84	40.85	41.03	25.76	38.34	31.94	16.11	40.94		
5.00E-04	8.15	18.77	13.11	17.00	6.468	11.12	14.62	14.99	24.96	23.11	23.06	18.49	5.92
5.00E-04	8.14	22.42	25.25	27.03	15.07	25.80	15.40	12.14	18.30	14.79	26.39		
7.00E-04	8.03	5.804	6.703	4.007	4.171	10.71	-4.55	-12.1	9.171	-3.16	-15.3	0.07	10.72
7.00E-04	8.00	8.124	9.070	-8.12	-12.4	-27.4	6.874	6.226	10.01	10.46	-6.92		
1.00E-03	8.05	-7.55	8.281	-9.57	-14.5	-19.5	-14.0	-13.8	-10.9	-13.9	-14.1	-8.47	10.09
1.00E-03	8.09	-19.1	-16.9	-17.7	-10.5	-9.87	13.41	9.718	8.281	-9.43	-7.67		
2.00E-03	8.13	-12.9	-18.1	-17.5	-13.6	-21.2	-18.8	-18.9	-17.2	-18.6	-19.1	-18.52	3.20
2.00E-03	8.15	-24.4	-14.2	-21.3	-21.8	-19.8	-18.4	-16.0	-24.6	-15.1	-18.8		
3.00E-03	8.05	-28.6	-23.5	-23.3	-21.7	-35.4	-24.8	-22.6	-25.1	-23.4	-39.1	-28.96	6.34
3.00E-03	8.01	-27.2	-25.0	-26.4	-37.7	-25.1	-38.6	-23.2	-35.1	-36.9	-36.5		
5.00E-03	8.22	-39.3	-39.6	-46.9	-30.9	-32.1	-41.5	-36.4	-36.6	-32.5	-34.4	-39.45	4.99
5.00E-03	8.14	-40.6	-43.5	-42.9	-46.5	-38.4	-37.4	-46.5	-35.0	-43.8	-44.1		
7.00E-03	8.07	-56.7	-57.8	-46.7	-59.7	-61.0	-63.4	-47.7	-43.4	-53.5	-50.9	-55.12	5.47
7.00E-03	8.04	-52.7	-53.0	-63.1	-50.9	-57.2	-57.1	-57.4	-60.9	-57.1	-52.2		
1.00E-02	8.00	-66.5	-61.9	-57.9	-62.4	-51.9	-64.3	-61.7	-61.7	-60.1	-57.1	-60.58	4.27
1.00E-02	8.01	-64.0	-55.2	-66.2	-57.3	-62.7	-51.9	-60.1	-65.7	-60.0	-62.9		

Table B-10 The alumina surface charges (zeta potential) of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Conc. (M)	pH_{eq}	Zeta potential (mV)											
		1	2	3	4	5	6	7	8	9	10	Avg.	SD
1.00E-04	8.02	-49.7	-47.8	-49.6	-44.9	-57.7	-48.6	-43.3	-43.8	-61.5	-50.6	-52.48	8.76
1.00E-04	8.00	-55.9	-60.0	-67.8	-47.8	-40.1	-41.6	-67.1	-66.4	-58.7	-46.7		
2.00E-04	8.18	-53.5	-55.9	-62.0	-53.5	-77.7	-55.8	-59.3	-54.0	-50.0	-47.8	-56.61	7.46
2.00E-04	8.05	-68.6	-58.2	-47.5	-55.7	-59.3	-64.1	-53.2	-52.3	-57.4	-46.4		
3.00E-04	8.01	-69.1	-66.8	-70.6	-81.8	-80.8	-69.5	-68.7	-58.8	-70.6	-58.2	-68.22	6.86
3.00E-04	8.02	-76.3	-61.1	-77.6	-63.0	-63.9	-64.7	-69.9	-68.8	-64.0	-60.2		
5.00E-04	8.09	-91.9	-84.8	-93.3	-88.0	-90.8	-65.0	-66.9	-94.2	-61.6	-63.3	-76.50	13.64
5.00E-04	8.10	-84.8	-63.5	-86.7	-58.3	-79.9	-87.4	-58.0	-60.0	-64.5	-87.1		
7.00E-04	8.07	-70.6	-94.5	-93.0	-69.6	-79.2	-87.9	-95.6	-64.0	-93.1	-90.3	-85.69	12.40
7.00E-04	8.05	-62.7	-96.0	-87.8	-98.6	-99.9	-90.5	-88.3	-81.5	-68.6	-102		
9.00E-04	8.03	-95.1	-73.4	-81.5	-101	-92.9	-93.0	-104	-71.6	-98.0	-102	-95.36	10.44
9.00E-04	8.01	-86.0	-102	-98.3	-102	-112	-97.8	-93.3	-93.3	-104	-106		
1.00E-03	8.15	-103	-83.4	-97.1	-90.6	-100	-109	-85.2	-103	-111	-80.3	-97.07	9.75
1.00E-03	8.17	-98.1	-101	-111	-100	-86.6	-88.4	-86.5	-97.6	-97.5	-112		
1.50E-03	8.06	-105	-91.7	-103	-86.9	-83.6	-106	-94.3	-102	-109	-105	-99.32	10.98
1.50E-03	8.11	-75.7	-107	-105	-113	-113	-99.5	-109	-107	-82.6	-88.1		
2.00E-03	8.00	-81.0	-105	-86.1	-101	-113	-89.3	-105	-107	-102	-108	-99.50	9.34
2.00E-03	8.02	-111	-99.0	-102	-98.5	-106	-89.6	-104	-93.6	-82.9	-106		
3.00E-03	8.21	-107	-95.7	-109	-107	-90.6	-112	-99.9	-103	-109	-100	-102.33	5.53
3.00E-03	8.12	-104	-104	-103	-98.3	-104	-99.0	-95.7	-95.3	-108	-102		

Table B-11 The alumina surface charges (zeta potential) of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Conc. (M)	pH_{eq}	Zeta potential (mV)											
		1	2	3	4	5	6	7	8	9	10	Avg.	SD
1.00E-04	8.02	-38.9	-57.4	-45.6	-55.3	-49.0	-61.7	-43.4	-44.3	-53.1	-38.0	-45.86	6.64
1.00E-04	8.00	-41.7	-39.3	-49.6	-42.1	-42.7	-47.6	-45.5	-40.1	-40.3	-41.5		
2.00E-04	8.15	-48.7	-42.0	-42.6	-49.5	-58.4	-51.9	-58.4	-51.9	-59.2	-56.6	-51.45	6.49
2.00E-04	8.16	-54.8	-35.3	-56.6	-59.5	-49.5	-51.7	-51.4	-54.9	-52.1	-43.9		
3.00E-04	8.11	-57.5	-53.7	-64.4	-51.9	-63.1	-52.6	-54.5	-57.8	-60.9	-60.6	-57.90	4.28
3.00E-04	8.20	-61.8	-57.3	-55.9	-53.2	-65.2	-60.9	-54.8	-56.8	-52.3	-62.7		
5.00E-04	8.03	-54.6	-63.9	-67.3	-54.3	-61.2	-72.7	-63.6	-62.0	-59.2	-60.7	-63.14	6.89
5.00E-04	8.10	-53.2	-62.6	-55.7	-55.8	-73.0	-71.1	-70.4	-67.3	-58.5	-75.6		
7.00E-04	8.01	-69.7	-66.9	-68.1	-64.7	-65.5	-68.2	-80.5	-80.3	-71.5	-80.1	-71.44	5.99
7.00E-04	8.10	-61.6	-70.5	-67.3	-67.5	-75.0	-79.5	-68.0	-73.6	-69.3	-81.0		
9.00E-04	8.00	-72.3	-68.5	-67.3	-65.5	-69.7	-70.2	-67.5	-78.3	-76.1	-76.1	-71.82	4.47
9.00E-04	8.02	-78.2	-73.8	-68.7	-77.8	-71.3	-74.5	-67.1	-78.4	-68.9	-66.1		
1.00E-03	8.13	-78.2	-70.2	-86.1	-77.7	-80.5	-70.6	-74.0	-82.6	-73.8	-79.5	-76.48	4.66
1.00E-03	8.15	-70.6	-70.5	-80.5	-79.0	-74.7	-74.4	-71.2	-74.6	-81.4	-79.5		
2.00E-03	8.05	-91.5	-80.7	-83.4	-73.0	-80.8	-101	-74.8	-74.3	-100	-80.6	-81.52	8.07
2.00E-03	8.01	-84.8	-78.0	-72.8	-82.0	-73.1	-76.1	-76.5	-84.0	-79.3	-83.6		
3.00E-03	8.00	-95.9	-83.8	-80.8	-76.8	-90.5	-82.5	-92.9	-92.9	-85.4	-89.9	-87.39	7.26
3.00E-03	8.01	-95.0	-100.0	-95.7	-80.3	-78.4	-83.9	-79.1	-97.5	-86.5	-80.0		
5.00E-03	8.11	-87.9	-79.1	-91.3	-108	-106	-87.4	-104	-93.6	-81.4	-103	-89.20	10.52
5.00E-03	8.25	-100	-84.7	-82.7	-90.3	-81.9	-86.5	-81.5	-67.1	-86.8	-80.8		

Table B-12 The alumina surface charges (zeta potential) of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Conc. (M)	pH_{eq}	Zeta potential (mV)											
		1	2	3	4	5	6	7	8	9	10	Avg.	SD
1.00E-04	8.00	-44.3	-37.3	-49.8	-35.6	-42.0	-45.3	-40.5	-55.7	-39.3	-48.4	-45.46	6.97
1.00E-04	8.02	-36.3	-53.0	-60.6	-49.9	-45.7	-55.2	-40.3	-47.4	-40.7	-41.9		
3.00E-04	8.15	-55.0	-55.3	-49.9	-57.6	-52.9	-47.9	-52.8	-52.7	-54.3	-42.0	-48.92	5.18
3.00E-04	8.05	-48.3	-48.5	-52.4	-42.3	-48.1	-40.5	-43.6	-45.4	-41.0	-47.9		
5.00E-04	8.20	-53.5	-50.2	-65.3	-55.3	-62.7	-54.6	-46.9	-58.5	-58.7	-44.2	-58.07	6.52
5.00E-04	8.09	-55.4	-57.6	-56.6	-58.5	-61.2	-61.5	-60.4	-60.9	-69.2	-70.1		
7.00E-04	8.01	-71.3	-70.7	-64.0	-61.2	-67.5	-69.5	-64.7	-66.6	-69.4	-65.2	-65.39	5.12
7.00E-04	8.11	-51.5	-69.1	-55.8	-70.5	-62.4	-69.0	-69.1	-64.5	-62.1	-63.6		
9.00E-04	8.05	-60.7	-64.5	-72.0	-69.3	-62.3	-67.8	-63.6	-71.7	-61.1	-75.1	-67.84	5.71
9.00E-04	8.09	-63.3	-78.2	-62.1	-67.0	-62.1	-73.2	-70.8	-78.7	-63.2	-70.0		
1.00E-03	8.03	-76.2	-73.9	-60.6	-81.7	-61.8	-65.0	-82.2	-78.9	-82.7	-84.3	-73.29	7.31
1.00E-03	8.05	-71.8	-80.1	-76.6	-64.0	-76.8	-70.1	-70.4	-67.8	-66.6	-74.2		
1.50E-03	8.60	-80.3	-85.7	-79.5	-75.8	-78.1	-85.3	-73.7	-76.8	-81.0	-80.3	-80.04	3.55
1.50E-03	8.12	-81.6	-83.2	-85.3	-74.1	-78.7	-79.5	-84.4	-77.5	-78.7	-81.3		
2.00E-03	8.09	-87.4	-82.8	-98.1	-98.7	-89.9	-92.4	-86.4	-108	-85.4	-97.4	-93.52	7.06
2.00E-03	8.11	-93.4	-93.9	-85.5	-92.4	-99.7	-105	-96.8	-102	-88.4	-86.7		
3.00E-03	8.01	-95.6	-96.6	-106	-94.5	-103	-105	-89.7	-91.5	-96.2	-91.1	-94.62	6.50
3.00E-03	8.00	-88.6	-104	-89.1	-94.9	-87.5	-88.9	-91.1	-88.9	-104	-86.2		
5.00E-03	8.05	-93.5	-96.9	-115	-93.0	-97.6	-90.3	-84.4	-102	-92.8	-106	-97.42	7.78
5.00E-03	8.02	-113	-95.1	-101	-91.4	-105	-101	-91.7	-95.0	-91.5	-92.1		

Table B-13 The alumina surface charges of C12S after the washing process

Conc. (M)	Zeta potential (mV)											
	1	2	3	4	5	6	7	8	9	10	Avg.	SD
1.00E-04	39.04	46.49	49.87	46.21	41.15	39.96	39.25	42.56	41.22	55.85	46.18	6.50
1.00E-04	57.89	48.11	44.39	44.95	50.29	32.72	50.3	53.24	55.21	44.81		
3.00E-04	42.21	50.29	33.35	39.18	45.44	32.76	36.86	42.49	41.01	44.10	43.73	6.84
3.00E-04	52.40	43.12	47.69	31.52	44.53	54.02	42.91	44.03	52.33	54.37		
5.00E-04	27.93	47.69	30.46	38.13	38.41	44.60	31.03	33.07	23.86	29.46	39.14	7.91
5.00E-04	44.03	44.60	49.03	39.67	45.02	40.80	37.07	49.87	51.00	37.07		
7.00E-04	39.67	31.59	31.67	34.06	33.23	34.69	42.89	42.79	42.6	36.92	40.43	5.43
7.00E-04	41.01	45.86	46.99	36.58	44.17	45.65	50.01	45.51	42.28	40.52		
1.00E-03	23.86	29.27	35.67	41.92	38.62	41.78	44.95	33.91	33.57	35.32	34.14	6.77
1.00E-03	22.03	40.87	33.42	38.27	29.77	38.34	31.94	34.2	19.07	35.95		
2.00E-03	16.94	30.9	28.42	29.89	29.52	29.0	18.75	22.59	12.18	14.52	27.27	8.59
2.00E-03	15.47	32.72	27.45	39.52	21.50	38.27	37.92	32.78	40.08	26.88		
3.00E-03	16.96	26.95	25.34	23.36	28.67	19.49	20.74	16.01	26.79	13.17	20.74	5.34
3.00E-03	17.01	18.39	13.39	16.87	21.33	12.69	29.49	24.69	25.73	17.78		
5.00E-03	11.26	5.312	12.75	19.63	18.15	14.25	26.49	11.14	28.76	25.58	20.03	7.66
5.00E-03	29.24	12.12	18.74	27.18	24.96	23.85	30.10	22.51	28.06	10.47		
7.00E-03	25.97	16.41	16.89	12.57	26.41	30.1	27.42	20.16	23.44	25.8	19.08	6.38
7.00E-03	16.89	26.23	18.32	15.02	12.65	15.81	13.11	10.59	7.734	20.16		
1.00E-02	13.46	15.42	13.31	23.78	15.01	13.41	12.90	24.90	14.72	13.9	18.26	6.44
1.00E-02	31.54	12.07	20.91	16.59	27.63	28.68	12.40	26.57	15.28	12.79		

Table B-14 The alumina surface charges of C16.5-4PO5EOC after the washing process

Conc. (M)	Zeta potential (mV)											
	1	2	3	4	5	6	7	8	9	10	Avg.	SD
1.00E-04	-12.8	-23.5	-33.6	-26.8	-19.8	-41.0	-13.8	-28.8	-12.7	-39.2	-24.13	9.69
1.00E-04	-19.7	-20.2	-41.6	-18.8	-33.5	-20.9	-15.4	-15.8	-31.0	-13.7		
2.00E-04	-19.4	-37.3	-31.5	-35.7	-30.9	-26.6	-17.6	-20.9	-21.5	-34.9	-29.38	9.30
2.00E-04	-28.5	-12.1	-19.2	-25.1	-34.4	-45.9	-44.1	-41.1	-25.5	-35.4		
3.00E-04	-28.8	-50.9	-34.5	-47.9	-32.3	-42.4	-48.1	-21.7	-34.3	-23.6	-35.70	7.68
3.00E-04	-29.5	-31.0	-35.0	-34.6	-37.9	-41.0	-32.0	-40.4	-33.8	-34.3		
5.00E-04	-51.9	-40.0	-47.2	-35.5	-58.3	-20.5	-50.7	-54.0	-24.6	-37.5	-44.31	9.57
5.00E-04	-50.3	-51.7	-52.2	-40.9	-46.4	-46.9	-38.6	-48.7	-48.1	-42.1		
7.00E-04	-44.3	-45.3	-43.4	-55.5	-40.0	-50.3	-35.0	-45.6	-44.9	-37.0	-46.72	6.72
7.00E-04	-48.2	-54.0	-34.7	-55.0	-55.4	-46.0	-50.7	-50.5	-55.6	-42.9		
9.00E-04	-66.2	-52.9	-57.5	-42.2	-42.3	-45.3	-61.0	-46.6	-59.8	-46.7	-55.34	8.27
9.00E-04	-57.1	-56.4	-58.2	-61.6	-60.9	-48.5	-68.2	-65.6	-62.8	-47.0		
1.00E-03	-52.6	-55.5	-69.9	-67.2	-66.3	-61.5	-64.1	-53.8	-55.5	-60.8	-59.22	6.31
1.00E-03	-64.7	-65.6	-58.6	-57.6	-52.9	-55.0	-54.8	-67.3	-53.5	-47.1		
1.50E-03	-54.3	-61.8	-53.0	-66.6	-59.3	-72.5	-52.7	-68.4	-53.6	-54.5	-61.18	8.74
1.50E-03	-53.6	-64.7	-71.1	-57.8	-67.6	-55.7	-73.2	-52.4	-80.2	-50.5		
2.00E-03	-67.1	-62.6	-74.6	-77.2	-53.6	-57.8	-55.7	-64.2	-68.0	-62.0	-64.21	8.37
2.00E-03	-59.8	-54.1	-67.2	-69.9	-79.3	-53.6	-73.2	-55.9	-72.7	-55.6		
3.00E-03	-57.6	-66.6	-67.1	-58.5	-73.7	-69.0	-59.0	-84.1	-70.2	-53.8	-64.73	8.84
3.00E-03	-81.7	-53.7	-66.7	-57.7	-53.5	-65.5	-69.2	-63.7	-68.7	-54.6		

Table B-15 The alumina surface charges of C17-4PO5EOC after the washing process

Conc. (M)	Zeta potential (mV)										Avg.	SD
	1	2	3	4	5	6	7	8	9	10		
1.00E-04	-21.2	-20.9	-45.6	-16.1	-32.3	-35.2	-26.1	-27.8	-30.2	-24.7	-28.38	8.87
1.00E-04	-18.2	-46.7	-39.1	-22.4	-37.9	-29.5	-22.6	-30.4	-18.7	-21.9		
2.00E-04	-23.6	-41.7	-32.8	-17.5	-43.1	-37.9	-30.8	-39.8	-37.2	-14.9	-29.54	9.56
2.00E-04	-14.4	-36.2	-17.4	-24.9	-42.3	-31.2	-33.4	-22.9	-29.0	-19.7		
3.00E-04	-32.4	-46.1	-33.5	-22.4	-41.7	-41.6	-30.9	-31.3	-45.3	-40.2	-35.36	6.63
3.00E-04	-26.2	-33.4	-33.7	-25.2	-33.8	-45.0	-38.6	-36.3	-35.4	-34.2		
5.00E-04	-41.4	-29.3	-24.9	-40.2	-26.9	-29.1	-51.8	-42.0	-42.5	-47.3	-36.24	9.29
5.00E-04	-36.5	-38.5	-30.9	-20.7	-43.4	-24.3	-23.5	-40.8	-41.8	-49.0		
7.00E-04	-34.3	-34.5	-44.4	-56.5	-34.3	-35.9	-52.4	-51.6	-37.6	-31.7	-41.26	8.98
7.00E-04	-52.8	-43.4	-39.0	-51.4	-36.1	-56.1	-28.7	-32.8	-36.5	-35.2		
9.00E-04	-49.0	-34.1	-46.0	-36.1	-38.7	-38.5	-38.6	-55.1	-50.7	-49.3	-42.08	8.25
9.00E-04	-31.3	-39.4	-35.5	-34.7	-46.0	-30.6	-45.1	-32.8	-54.7	-55.3		
1.00E-03	-43.7	-50.1	-40.0	-37.3	-37.5	-39.0	-51.0	-48.9	-49.7	-42.7	-44.19	5.51
1.00E-03	-51.3	-53.4	-42.5	-47.4	-50.3	-41.3	-40.5	-41.7	-39.5	-35.9		
2.00E-03	-48.0	-55.2	-51.6	-50.2	-64.5	-36.3	-49.7	-53.6	-51.7	-54.5	-53.46	6.84
2.00E-03	-54.2	-59.2	-54.7	-46.0	-53.2	-66.9	-63.1	-57.1	-49.2	-50.2		
3.00E-03	-62.9	-53.6	-42.0	-53.7	-65.6	-65.0	-60.9	-61.6	-60.0	-58.4	-57.92	6.36
3.00E-03	-48.8	-53.7	-55.9	-61.9	-64.4	-56.0	-64.8	-48.4	-61.0	-59.7		
5.00E-03	-62.8	-51.9	-67.1	-54.6	-64.9	-56.6	-62.6	-66.3	-56.4	-55.2	-59.31	6.71
5.00E-03	-62.8	-71.6	-60.2	-45.7	-64.9	-54.9	-62.2	-56.6	-46.7	-62.1		

Table B-16 The alumina surface charges of C16.5-4POS after the washing process

Conc. (M)	Zeta potential (mV)											
	1	2	3	4	5	6	7	8	9	10	Avg.	SD
1.00E-04	-32.4	-34.1	-31.6	-34.7	-27.0	-28.0	-37.3	-29.1	-36.0	-34.4	-32.25	4.02
1.00E-04	-37.4	-30.3	-33.6	-25.1	-25.6	-32.4	-37.4	-30.0	-30.4	-38.2		
3.00E-04	-47.7	-31.2	-22.4	-30.5	-38.9	-30.3	-28.3	-23.9	-27.0	-29.2	-32.88	7.56
3.00E-04	-24.3	-36.1	-33.7	-37.1	-45.2	-42.1	-40.9	-33.5	-34.5	-20.7		
5.00E-04	-40.0	-45.3	-20.7	-33.6	-40.3	-37.5	-29.4	-32.1	-50.7	-30.5	-34.34	7.15
5.00E-04	-22.0	-31.1	-33.4	-31.4	-39.3	-28.7	-40.7	-33.0	-34.5	-32.6		
7.00E-04	-31.6	-41.2	-41.2	-55.1	-25.4	-33.0	-39.7	-45.4	-57.4	-36.9	-41.45	8.66
7.00E-04	-31.0	-42.5	-48.1	-40.1	-30.6	-52.4	-48.1	-43.0	-37.2	-49.1		
9.00E-04	-59.0	-49.8	-45.6	-33.8	-37.6	-43.4	-33.8	-52.4	-55.4	-31.6	-44.79	9.24
9.00E-04	-32.6	-34.6	-58.4	-42.7	-48.1	-56.5	-45.6	-34.8	-47.6	-52.4		
1.00E-03	-49.0	-50.9	-60.7	-58.3	-39.6	-41.1	-39.0	-36.6	-60.0	-47.0	-47.16	6.99
1.00E-03	-47.1	-42.0	-47.1	-48.4	-47.8	-39.8	-44.6	-42.1	-47.7	-54.4		
1.50E-03	-48.8	-54.0	-45.0	-54.3	-49.1	-43.9	-48.1	-51.3	-40.6	-46.4	-46.87	5.06
1.50E-03	-47.7	-54.1	-42.3	-39.3	-52.0	-48.7	-45.2	-48.2	-41.9	-36.4		
2.00E-03	-42.9	-41.3	-57.5	-59.5	-45.2	-52.6	-48.1	-50.0	-46.3	-51.1	-46.88	7.27
2.00E-03	-35.3	-46.6	-38.4	-40.3	-50.4	-55.9	-55.4	-47.1	-35.9	-37.7		
3.00E-03	-56.9	-42.8	-49.2	-44.6	-54.3	-40.4	-45.1	-53.6	-50.4	-38.3	-46.90	5.97
3.00E-03	-40.4	-45.1	-54.9	-55.9	-40.5	-46.6	-49.1	-39.7	-41.7	-48.4		
5.00E-03	-48.6	-59.8	-62.9	-47.4	-43.2	-38.4	-53.3	-37.3	-40.5	-41.7	-47.34	8.73
5.00E-03	-42.1	-44.0	-35.0	-60.6	-43.3	-46.8	-58.1	-55.2	-53.2	-35.4		

Table B-17 Phenylethanol solubilization of C12S at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			Phe_Initial				Phe_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
1	1.0E-03	1.00	1.00	625	0.1292	129.20	129.20	32952.7	0.1273	127.30	127.11
2	1.0E-03	1.00		625	0.1292	129.20		32859.2	0.1269	126.93	
3	1.0E-03	1.00		625	0.1292	129.20		32905.1	0.1271	127.11	
4	3.0E-03	3.00	3.00	625	0.1292	129.20	129.20	33128.8	0.1280	127.98	128.50
5	3.0E-03	3.00		625	0.1292	129.20		33459.8	0.1293	129.26	
6	3.0E-03	3.00		625	0.1292	129.20		33202.7	0.1283	128.27	
7	5.0E-03	5.00	5.00	625	0.1292	129.20	129.20	33229.7	0.1284	128.37	128.85
8	5.0E-03	5.00		625	0.1292	129.20		32924.0	0.1272	127.19	
9	5.0E-03	5.00		625	0.1292	129.20		33909.8	0.1310	131.01	
10	7.0E-03	7.00	7.00	625	0.1292	129.20	129.20	33620.3	0.1299	129.88	129.99
11	7.0E-03	7.00		625	0.1292	129.20		33499.8	0.1294	129.42	
12	7.0E-03	7.00		625	0.1292	129.20		33823.2	0.1307	130.67	
13	1.0E-02	10.00	10.00	650	0.1344	134.40	134.40	33983.0	0.1313	131.29	131.03
14	1.0E-02	10.00		650	0.1344	134.40		33726.1	0.1303	130.29	
15	1.0E-02	10.00		650	0.1344	134.40		34041.4	0.1315	131.52	

Table B-17a Phenylethanol solubilization of C12S at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			Phe_Initial				Phe_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
16	2.0E-02	20.00	20.00	650	0.1344	134.40	134.40	34188.6	0.1321	132.09	132.30
17	2.0E-02	20.00		650	0.1344	134.40		34292.8	0.1325	132.49	
18	2.0E-02	20.00		650	0.1344	134.40		34253.5	0.1323	132.34	
19	3.0E-02	30.00	30.00	700	0.1447	144.70	144.70	36094.3	0.1395	139.47	139.63
20	3.0E-02	30.00		700	0.1447	144.70		36151.6	0.1397	139.69	
21	3.0E-02	30.00		700	0.1447	144.70		36161.1	0.1397	139.73	
22	3.5E-02	35.00	35.00	700	0.1447	144.70	144.70	36488.4	0.1410	141.00	141.10
23	3.5E-02	35.00		700	0.1447	144.70		36516.5	0.1411	141.10	
24	3.5E-02	35.00		700	0.1447	144.70		36541.1	0.1412	141.20	
25	4.0E-02	40.00	40.00	700	0.1447	144.70	144.70	37064.5	0.1432	143.23	142.86
26	4.0E-02	40.00		700	0.1447	144.70		36876.1	0.1425	142.50	
27	4.0E-02	40.00		700	0.1447	144.70		36970.0	0.1429	142.86	
28	5.0E-02	50.00	50.00	725	0.1499	149.90	149.90	38166.5	0.1475	147.50	147.09
29	5.0E-02	50.00		725	0.1499	149.90		38030.9	0.1470	146.97	
30	5.0E-02	50.00		725	0.1499	149.90		37987.9	0.1468	146.81	

Table B-18 Phenylethanol solubilization of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			Phe_Intial				Phe_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
1	1.0E-07	0.0001	0.0001	450	0.0930	93.00	93.00	24574.9	0.0948	94.84	95.11
2	1.0E-07	0.0001		450	0.0930	93.00		24713.4	0.0954	95.37	
3	5.0E-07	0.0005	0.0005	450	0.0930	93.00	93.00	24712.6	0.0954	95.37	95.89
4	5.0E-07	0.0005		450	0.0930	93.00		24978.5	0.0964	96.40	
5	1.0E-06	0.001	0.001	450	0.0930	93.00	93.00	24877.8	0.0960	96.01	96.14
6	1.0E-06	0.001		450	0.0930	93.00		24941.9	0.0963	96.26	
7	5.0E-06	0.005	0.005	450	0.0930	93.00	93.00	24759.8	0.0956	95.55	95.49
8	5.0E-06	0.005		450	0.0930	93.00		24728.0	0.0954	95.43	
9	1.0E-05	0.01	0.01	450	0.0930	93.00	93.00	24790.5	0.0957	95.67	95.74
10	1.0E-05	0.01		450	0.0930	93.00		24777.2	0.0956	95.62	
11	1.0E-05	0.01		450	0.0930	93.00		24853.7	0.0959	95.92	
12	3.0E-05	0.03	0.03	475	0.0982	98.20	98.20	26404.5	0.1019	101.93	102.28
13	3.0E-05	0.03		475	0.0982	98.20		26479.9	0.1022	102.22	
14	3.0E-05	0.03		475	0.0982	98.20		26600.2	0.1027	102.68	

Table B-18a Phenylethanol solubilization of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			Phe_Intial				Phe_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
15	5.0E-05	0.05	0.05	500	0.1033	103.30	103.30	27480.1	0.1061	106.09	106.18
16	5.0E-05	0.05		500	0.1033	103.30		27469.6	0.1061	106.05	
17	5.0E-05	0.05		500	0.1033	103.30		27556.3	0.1064	106.39	
18	1.0E-04	0.10	0.10	500	0.1033	103.30	103.30	27698.1	0.1069	106.94	107.01
19	1.0E-04	0.10		500	0.1033	103.30		27686.4	0.1069	106.89	
20	1.0E-04	0.10		500	0.1033	103.30		27765.6	0.1072	107.20	
21	5.0E-04	0.50	0.50	525	0.1085	108.50	108.50	29425.1	0.1136	113.63	113.47
22	5.0E-04	0.50		525	0.1085	108.50		29401.3	0.1135	113.54	
23	5.0E-04	0.50		525	0.1085	108.50		29325.7	0.1132	113.24	
24	1.0E-03	1.00	1.00	550	0.1137	113.70	113.70	30599.4	0.1182	118.18	118.15
25	1.0E-03	1.00		550	0.1137	113.70		30601.5	0.1182	118.19	
26	1.0E-03	1.00		550	0.1137	113.70		30578.2	0.1181	118.10	

Table B-19 Phenylethanol solubilization of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			Phe_Intial				Phe_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
1	5.0E-07	0.0005	0.0005	450	0.0930	93.00	93.00	24876.1	0.0960	96.00	95.35
2	5.0E-07	0.0005		450	0.0930	93.00		24537.2	0.0947	94.69	
3	1.0E-06	0.001	0.001	450	0.0930	93.00	93.00	25419.3	0.0981	98.11	98.08
4	1.0E-06	0.001		450	0.0930	93.00		25404.1	0.0981	98.05	
5	5.0E-06	0.005	0.005	450	0.0930	93.00	93.00	25157.3	0.0971	97.09	97.52
6	5.0E-06	0.005		450	0.0930	93.00		25311.0	0.0977	97.69	
7	5.0E-06	0.005		450	0.0930	93.00		25331.8	0.0978	97.77	
8	1.0E-05	0.01	0.01	500	0.1033	103.30	103.30	27949.5	0.1079	107.91	108.34
9	1.0E-05	0.01		500	0.1033	103.30		28201.2	0.1089	108.89	
10	1.0E-05	0.01		500	0.1033	103.30		28032.7	0.1082	108.23	
11	3.0E-05	0.03	0.03	525	0.1085	108.50	108.50	29757.0	0.1149	114.92	114.88
12	3.0E-05	0.03		525	0.1085	108.50		29819.5	0.1152	115.16	
13	3.0E-05	0.03		525	0.1085	108.50		29665.5	0.1146	114.56	
14	5.0E-05	0.05	0.05	550	0.1137	113.70	113.70	30753.9	0.1188	118.78	119.12
15	5.0E-05	0.05		550	0.1137	113.70		30925.5	0.1194	119.44	
16	5.0E-05	0.05		550	0.1137	113.70		30851.1	0.1192	119.15	

Table B-19a Phenylethanol solubilization of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			Phe_Intial				Phe_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
17	1.0E-04	0.10	0.10	550	0.1137	113.70	113.70	31294.5	0.1209	120.87	120.49
18	1.0E-04	0.10		550	0.1137	113.70		31112.4	0.1202	120.17	
19	1.0E-04	0.10		550	0.1137	113.70		31182.6	0.1204	120.44	
20	3.0E-04	0.30	0.30	575	0.1189	118.90	118.90	31385.6	0.1212	121.23	121.18
21	3.0E-04	0.30		575	0.1189	118.90		31361.5	0.1211	121.13	
22	5.0E-04	0.50	0.50	575	0.1189	118.90	118.90	31563.8	0.1219	121.92	121.88
23	5.0E-04	0.50		575	0.1189	118.90		31544.3	0.1218	121.84	
24	1.0E-03	1.00	1.00	600	0.1240	124.00	124.00	32674.9	0.1262	126.22	126.44
25	1.0E-03	1.00		600	0.1240	124.00		32788.6	0.1267	126.66	

Table B-20 Phenylethanol solubilization of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			Phe_Intial				Phe_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
1	1.0E-06	0.001	0.001	450	0.0930	93.00	93.00	24577.2	0.0948	94.85	94.88
2	1.0E-06	0.001		450	0.0930	93.00		24596.5	0.0949	94.92	
3	5.0E-06	0.005	0.005	450	0.0930	93.00	93.00	24639.7	0.0951	95.09	95.66
4	5.0E-06	0.005		450	0.0930	93.00		24936.7	0.0962	96.24	
5	1.0E-05	0.01	0.01	450	0.0930	93.00	93.00	24786.7	0.0957	95.66	95.87
6	1.0E-05	0.01		450	0.0930	93.00		24895.6	0.0961	96.08	
7	1.0E-05	0.01		450	0.0930	93.00		24843.6	0.0959	95.88	
8	3.0E-05	0.03	0.03	450	0.0930	93.00	93.00	24777.7	0.0956	95.62	95.74
9	3.0E-05	0.03		450	0.0930	93.00		24875.0	0.0960	96.00	
10	3.0E-05	0.03		450	0.0930	93.00		24768.9	0.0956	95.59	
11	5.0E-05	0.05	0.05	500	0.1033	103.30	103.30	27578.0	0.1065	106.47	106.55
12	5.0E-05	0.05		500	0.1033	103.30		27607.2	0.1066	106.59	
13	5.0E-05	0.05		500	0.1033	103.30		27611.3	0.1066	106.60	
14	1.0E-04	0.10	0.10	550	0.1137	113.70	113.70	29877.6	0.1154	115.38	115.66
15	1.0E-04	0.10		550	0.1137	113.70		29990.5	0.1158	115.82	
16	1.0E-04	0.10		550	0.1137	113.70		29976.1	0.1158	115.76	

Table B-20a Phenylethanol solubilization of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			Phe_Intial				Phe_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
17	5.0E-04	0.50	0.50	575	0.1189	118.90	118.90	31575.7	0.1220	121.96	121.99
18	5.0E-04	0.50		575	0.1189	118.90		31616.3	0.1221	122.12	
19	5.0E-04	0.50		575	0.1189	118.90		31559.7	0.1219	121.90	
20	7.0E-04	0.70	0.70	600	0.1240	124.00	124.00	32549.5	0.1257	125.73	125.64
21	7.0E-04	0.70		600	0.1240	124.00		32501.9	0.1256	125.55	
22	1.0E-03	1.00	1.00	625	0.1292	129.20	129.20	34183.5	0.1321	132.07	131.87
23	1.0E-03	1.00		625	0.1292	129.20		34081.8	0.1317	131.67	
24	2.0E-03	2.00	2.00	625	0.1292	129.20	129.20	35086.5	0.1356	135.56	135.10
25	2.0E-03	2.00		625	0.1292	129.20		34848.6	0.1346	134.64	

Table B-21 Ethylcyclohexane solubilization of C12S at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			ECH_Intial				ECH_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
1	1.0E-03	1.00	1.00	9	1.58E-03	1.58	1.58	3.4	1.62E-04	0.16	0.16
2	1.0E-03	1.00		9	1.58E-03	1.58		3.1	1.58E-04	0.16	
3	1.0E-03	1.00		9	1.58E-03	1.58		3.0	1.57E-04	0.16	
4	3.0E-03	3.00	3.00	10	1.76E-03	1.76	1.76	4.6	1.77E-04	0.18	0.18
5	3.0E-03	3.00		10	1.76E-03	1.76		4.8	1.79E-04	0.18	
6	3.0E-03	3.00		10	1.76E-03	1.76		5.2	1.84E-04	0.18	
7	5.0E-03	5.00	5.00	11	1.93E-03	1.93	1.93	3.8	1.67E-04	0.17	0.17
8	5.0E-03	5.00		11	1.93E-03	1.93		3.5	1.63E-04	0.16	
9	5.0E-03	5.00		11	1.93E-03	1.93		4.0	1.69E-04	0.17	
10	7.0E-03	7.00	7.00	12	2.11E-03	2.11	2.11	3.7	1.65E-04	0.17	0.16
11	7.0E-03	7.00		12	2.11E-03	2.11		3.5	1.63E-04	0.16	
12	7.0E-03	7.00		12	2.11E-03	2.11		3.4	1.62E-04	0.16	
13	1.0E-02	10.00	10.00	14	2.46E-03	2.46	2.46	31.2	5.08E-04	0.51	0.50
14	1.0E-02	10.00		14	2.46E-03	2.46		30.8	5.03E-04	0.50	
15	1.0E-02	10.00		14	2.46E-03	2.46		29.2	4.84E-04	0.48	

Table B-21a Ethylcyclohexane solubilization of C12S at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2^{o}C

Tube	Conc. Surf.			ECH_Intial				ECH_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
16	2.0E-02	20.00	20.00	16	2.81E-03	2.81	2.81	131.2	1.76E-03	1.76	1.89
17	2.0E-02	20.00		16	2.81E-03	2.81		145.3	1.93E-03	1.93	
18	2.0E-02	20.00		16	2.81E-03	2.81		150.3	1.99E-03	1.99	
19	3.0E-02	30.00	30.00	18	3.16E-03	3.16	3.16	183.9	2.41E-03	2.41	2.53
20	3.0E-02	30.00		18	3.16E-03	3.16		204.9	2.68E-03	2.68	
21	3.0E-02	30.00		18	3.16E-03	3.16		191.8	2.51E-03	2.51	
22	3.5E-02	35.00	35.00	20	3.51E-03	3.51	3.51	242.8	3.15E-03	3.15	3.04
23	3.5E-02	35.00		20	3.51E-03	3.51		203.0	2.65E-03	2.65	
24	3.5E-02	35.00		20	3.51E-03	3.51		255.4	3.31E-03	3.31	
25	4.0E-02	40.00	40.00	22	3.87E-03	3.87	3.87	252.6	3.27E-03	3.27	3.24
26	4.0E-02	40.00		22	3.87E-03	3.87		231.4	3.01E-03	3.01	
27	4.0E-02	40.00		22	3.87E-03	3.87		267.0	3.45E-03	3.45	
28	5.0E-02	50.00	50.00	24	4.22E-03	4.22	4.22	285.5	3.68E-03	3.68	3.65
29	5.0E-02	50.00		24	4.22E-03	4.22		285.6	3.68E-03	3.68	
30	5.0E-02	50.00		24	4.22E-03	4.22		277.3	3.58E-03	3.58	

Table B-22 Ethylcyclohexane solubilization of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			ECH_Intial				ECH_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
1	1.0E-07	0.0001	0.0001	8	1.41E-03	1.41	1.41	4.4	-1.57E-04	-0.16	-0.16
2	1.0E-07	0.0001		8	1.41E-03	1.41		4.2	-1.60E-04	-0.16	
3	1.0E-07	0.0001		8	1.41E-03	1.41		4.4	-1.57E-04	-0.16	
4	5.0E-07	0.0005	0.0005	8	1.41E-03	1.41	1.41	6.7	-1.20E-04	-0.12	-0.12
5	5.0E-07	0.0005		8	1.41E-03	1.41		6.3	-1.26E-04	-0.13	
6	5.0E-07	0.0005		8	1.41E-03	1.41		6.3	-1.26E-04	-0.13	
7	1.0E-06	0.0010	0.0010	9	1.58E-03	1.58	1.58	10.6	-5.80E-05	-0.06	-0.08
8	1.0E-06	0.0010		9	1.58E-03	1.58		11.5	-4.37E-05	-0.04	
9	1.0E-06	0.0010		9	1.58E-03	1.58		5.7	-1.36E-04	-0.14	
10	5.0E-06	0.0050	0.0050	9	1.58E-03	1.58	1.58	33.5	3.06E-04	0.31	0.33
11	5.0E-06	0.0050		9	1.58E-03	1.58		32.6	2.92E-04	0.29	
12	5.0E-06	0.0050		9	1.58E-03	1.58		38.9	3.92E-04	0.39	
13	1.0E-05	0.010	0.010	10	1.76E-03	1.76	1.76	50.0	5.69E-04	0.57	0.55
14	1.0E-05	0.010		10	1.76E-03	1.76		54.2	6.36E-04	0.64	
15	1.0E-05	0.010		10	1.76E-03	1.76		43.0	4.58E-04	0.46	

Table B-22a Ethylcyclohexane solubilization of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			ECH_Intial				ECH_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
16	3.0E-05	0.030	0.030	11	1.93E-03	1.93	1.93	78.9	1.03E-03	1.03	1.07
17	3.0E-05	0.030		11	1.93E-03	1.93		79.7	1.04E-03	1.04	
18	3.0E-05	0.030		11	1.93E-03	1.93		85.5	1.13E-03	1.13	
19	5.0E-05	0.050	0.050	12	2.11E-03	2.11	2.11	111.8	1.55E-03	1.55	1.45
20	5.0E-05	0.050		12	2.11E-03	2.11		88.4	1.18E-03	1.18	
21	5.0E-05	0.050		12	2.11E-03	2.11		116.0	1.62E-03	1.62	
22	1.0E-04	0.10	0.10	13	2.28E-03	2.28	2.28	116.5	1.63E-03	1.63	1.64
23	1.0E-04	0.10		13	2.28E-03	2.28		115.8	1.62E-03	1.62	
24	1.0E-04	0.10		13	2.28E-03	2.28		119.6	1.68E-03	1.68	
25	5.0E-04	0.50	0.50	14	2.46E-03	2.46	2.46	129.5	1.83E-03	1.83	1.87
26	5.0E-04	0.50		14	2.46E-03	2.46		159.3	2.31E-03	2.31	
27	5.0E-04	0.50		14	2.46E-03	2.46		105.7	1.46E-03	1.46	
28	1.0E-03	1.00	1.00	15	2.64E-03	2.64	2.64	148.9	2.14E-03	2.14	2.14
29	1.0E-03	1.00		15	2.64E-03	2.64		148.1	2.13E-03	2.13	
30	1.0E-03	1.00		15	2.64E-03	2.64		148.9	2.14E-03	2.14	

Table B-23 Ethylcyclohexane solubilization of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			ECH_Intial				ECH_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
1	5.0E-07	0.0005	0.0005	10	1.76E-03	1.76	1.76	11.0	-5.17E-05	-0.05	-0.05
2	5.0E-07	0.0005		10	1.76E-03	1.76		9.5	-7.55E-05	-0.08	
3	5.0E-07	0.0005		10	1.76E-03	1.76		13.4	-1.35E-05	-0.01	
4	1.0E-06	0.0010	0.0010	10	1.76E-03	1.76	1.76	11.1	-5.01E-05	-0.05	0.01
5	1.0E-06	0.0010		10	1.76E-03	1.76		16.7	3.90E-05	0.04	
6	1.0E-06	0.0010		10	1.76E-03	1.76		16.3	3.27E-05	0.03	
7	5.0E-06	0.0050	0.0050	11	1.93E-03	1.93	1.93	25.6	1.81E-04	0.18	0.27
8	5.0E-06	0.0050		11	1.93E-03	1.93		44.1	4.75E-04	0.48	
9	5.0E-06	0.0050		11	1.93E-03	1.93		23.5	1.47E-04	0.15	
10	1.0E-05	0.0100	0.010	11	1.93E-03	1.93	1.93	43.8	4.70E-04	0.47	0.46
11	1.0E-05	0.0100		11	1.93E-03	1.93		44.9	4.88E-04	0.49	
12	1.0E-05	0.0100		11	1.93E-03	1.93		41.4	4.32E-04	0.43	
13	3.0E-05	0.030	0.030	12	2.11E-03	2.11	2.11	52.3	6.06E-04	0.61	0.78
14	3.0E-05	0.030		12	2.11E-03	2.11		70.8	9.00E-04	0.90	
15	3.0E-05	0.030		12	2.11E-03	2.11		66.3	8.28E-04	0.83	

Table B-23a Ethylcyclohexane solubilization of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			ECH_Intial				ECH_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
16	5.0E-05	0.050	0.050	13	2.28E-03	2.28	2.28	85.9	1.14E-03	1.14	1.11
17	5.0E-05	0.050		13	2.28E-03	2.28		84.1	1.11E-03	1.11	
18	5.0E-05	0.050		13	2.28E-03	2.28		81.5	1.07E-03	1.07	
19	1.0E-04	0.100	0.10	14	2.46E-03	2.46	2.46	130.7	1.85E-03	1.85	1.87
20	1.0E-04	0.100		14	2.46E-03	2.46		135.4	1.93E-03	1.93	
21	1.0E-04	0.100		14	2.46E-03	2.46		129.3	1.83E-03	1.83	
22	3.0E-04	0.30	0.30	15	2.64E-03	2.64	2.64	160.1	2.32E-03	2.32	2.09
23	3.0E-04	0.30		15	2.64E-03	2.64		137.2	1.96E-03	1.96	
24	3.0E-04	0.30		15	2.64E-03	2.64		139.6	1.99E-03	1.99	
25	5.0E-04	0.50	0.50	16	2.81E-03	2.81	2.81	185.4	2.72E-03	2.72	2.62
26	5.0E-04	0.50		16	2.81E-03	2.81		174.4	2.55E-03	2.55	
27	5.0E-04	0.50		16	2.81E-03	2.81		177.3	2.59E-03	2.59	
28	1.0E-03	1.00	1.00	18	3.16E-03	3.16	3.16	198.9	2.94E-03	2.94	3.06
29	1.0E-03	1.00		18	3.16E-03	3.16		214.1	3.18E-03	3.18	
30	1.0E-03	1.00		18	3.16E-03	3.16		205.7	3.05E-03	3.05	

Table B-24 Ethylcyclohexane solubilization of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			ECH_Intial				ECH_equilibrium			
	(M)	(mM)	Average	µl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
1	1.0E-06	0.0010	0.0010	8	1.41E-03	1.41	1.41	10.2	4.01E-04	0.40	0.40
2	1.0E-06	0.0010		8	1.41E-03	1.41		10.0	3.99E-04	0.40	
3	1.0E-06	0.0010		8	1.41E-03	1.41		9.5	3.92E-04	0.39	
4	5.0E-06	0.0050	0.0050	8	1.41E-03	1.41	1.41	22.7	5.66E-04	0.57	0.59
5	5.0E-06	0.0050		8	1.41E-03	1.41		26.0	6.10E-04	0.61	
6	5.0E-06	0.0050		8	1.41E-03	1.41		24.4	5.89E-04	0.59	
7	1.0E-05	0.0100	0.0100	9	1.58E-03	1.58	1.58	20.5	5.37E-04	0.54	0.58
8	1.0E-05	0.0100		9	1.58E-03	1.58		30.1	6.64E-04	0.66	
9	1.0E-05	0.0100		9	1.58E-03	1.58		20.3	5.35E-04	0.53	
10	3.0E-05	0.0300	0.030	10	1.76E-03	1.76	1.76	38.3	7.72E-04	0.77	0.80
11	3.0E-05	0.0300		10	1.76E-03	1.76		41.5	8.14E-04	0.81	
12	3.0E-05	0.0300		10	1.76E-03	1.76		40.9	8.06E-04	0.81	
13	5.0E-05	0.050	0.050	11	1.93E-03	1.93	1.93	36.3	7.46E-04	0.75	0.83
14	5.0E-05	0.050		11	1.93E-03	1.93		54.6	9.87E-04	0.99	
15	5.0E-05	0.050		11	1.93E-03	1.93		38.0	7.68E-04	0.77	

Table B-24a Ethylcyclohexane solubilization of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Conc. Surf.			ECH_Intial				ECH_equilibrium			
	(M)	(mM)	Average	μl	Conc. (M)	Conc. (mM)	Average	Area	Conc. (M)	Conc. (mM)	Average
16	1.0E-04	0.100	0.10	12	2.11E-03	2.11	2.11	67.2	1.15E-03	1.15	1.09
17	1.0E-04	0.100		12	2.11E-03	2.11		50.1	9.27E-04	0.93	
18	1.0E-04	0.100		12	2.11E-03	2.11		69.0	1.18E-03	1.18	
19	3.0E-04	0.300	0.30	13	2.28E-03	2.28	2.28	104.7	1.65E-03	1.65	1.64
20	3.0E-04	0.300		13	2.28E-03	2.28		101.2	1.60E-03	1.60	
21	3.0E-04	0.300		13	2.28E-03	2.28		106.7	1.67E-03	1.67	
22	7.0E-04	0.70	0.70	14	2.46E-03	2.46	2.46	147.0	2.20E-03	2.20	2.23
23	7.0E-04	0.70		14	2.46E-03	2.46		148.2	2.22E-03	2.22	
24	7.0E-04	0.70		14	2.46E-03	2.46		150.8	2.26E-03	2.26	
25	1.0E-03	1.00	1.00	15	2.64E-03	2.64	2.64	158.2	2.35E-03	2.35	2.20
26	1.0E-03	1.00		15	2.64E-03	2.64		146.7	2.20E-03	2.20	
27	1.0E-03	1.00		15	2.64E-03	2.64		135.6	2.05E-03	2.05	
28	2.0E-03	2.00	2.00	16	2.81E-03	2.81	2.81	181.2	2.66E-03	2.66	2.55
29	2.0E-03	2.00		16	2.81E-03	2.81		159.3	2.37E-03	2.37	
30	2.0E-03	2.00		16	2.81E-03	2.81		178.7	2.62E-03	2.62	

Table B-25 Phenylethanol adsolubilization of C12S at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Phe	Surf_initial		Surf_equilibrium		Surf $_{(in-eq)}$	Phe_initial	Phe_equilibrium		Phe $_{(in-eq)}$
	(μl)	Area	Conc. (M)	Area	Conc. (M)	(M)	Conc. (M)	Area	Conc. (M)	(M)
1	250	989.0	1.56E-03	815.1	1.33E-03	2.31E-04	0.0517	12994.7	0.0492	0.0025
2	250	989.0	1.56E-03	833.5	1.35E-03	2.07E-04	0.0517	13079.4	0.0495	0.0022
3	300	989.0	1.56E-03	779.1	1.28E-03	2.79E-04	0.0620	15510.6	0.0590	0.0030
4	300	989.0	1.56E-03	789.3	1.29E-03	2.65E-04	0.0620	15598.6	0.0594	0.0026
5	350	989.0	1.56E-03	745.4	1.23E-03	3.24E-04	0.0723	18134.1	0.0693	0.0030
6	350	989.0	1.56E-03	754.7	1.25E-03	3.11E-04	0.0723	18150.5	0.0693	0.0030
7	400	989.0	1.56E-03	733.6	1.22E-03	3.39E-04	0.0827	20623.6	0.0790	0.0037
8	400	989.0	1.56E-03	733.9	1.22E-03	3.39E-04	0.0827	20736.3	0.0794	0.0033
9	450	989.0	1.56E-03	707.7	1.18E-03	3.74E-04	0.0930	23254.0	0.0892	0.0038
10	450	989.0	1.56E-03	748.2	1.24E-03	3.20E-04	0.0930	23273.7	0.0893	0.0037
11	475	989.0	1.56E-03	775.4	1.27E-03	2.84E-04	0.0982	24434.6	0.0938	0.0044
12	475	989.0	1.56E-03	760.8	1.25E-03	3.03E-04	0.0982	24355.7	0.0935	0.0047
13	500	989.0	1.56E-03	752.6	1.24E-03	3.14E-04	0.1033	25568.4	0.0983	0.0050
14	500	989.0	1.56E-03	732.4	1.22E-03	3.41E-04	0.1033	25602.5	0.0984	0.0049
15	550	989.0	1.56E-03	714.6	1.19E-03	3.65E-04	0.1137	28196.6	0.1085	0.0052
16	550	989.0	1.56E-03	715.1	1.19E-03	3.64E-04	0.1137	28003.8	0.1078	0.0059
17	600	989.0	1.56E-03	659.5	1.12E-03	4.38E-04	0.1240	30409.4	0.1172	0.0068
18	600	989.0	1.56E-03	699.9	1.17E-03	3.84E-04	0.1240	30473.5	0.1174	0.0066
19	625	989.0	1.56E-03	712.1	1.19E-03	3.68E-04	0.1292	31766.4	0.1225	0.0067
20	625	989.0	1.56E-03	704.8	1.18E-03	3.78E-04	0.1292	31671.8	0.1221	0.0071

Table B-25a Phenylethanol adsolubilization of C12S at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	pH (eq.)	Surf $_{(in-eq)}$ (M)	Phe $_{(in-eq)}$ (M)	X_{adm}	X_{aq}	Phe_equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	K_{adm}	log K_{adm}
1	0.1030	8.36	2.31E-04	0.0025	0.92	8.85E-04	0.0494	8.88E-04	0.915	1029.5	3.01
2	0.1016	8.46	2.07E-04	0.0022	0.91	8.91E-04					
3	0.1000	8.05	2.79E-04	0.0030	0.91	1.06E-03	0.0592	1.06E-03	0.911	855.9	2.93
4	0.1005	8.42	2.65E-04	0.0026	0.91	1.07E-03					
5	0.1002	8.08	3.24E-04	0.0030	0.90	1.25E-03	0.0693	1.25E-03	0.904	725.8	2.86
6	0.0997	8.18	3.11E-04	0.0030	0.91	1.25E-03					
7	0.1018	8.33	3.39E-04	0.0037	0.92	1.42E-03	0.0792	1.42E-03	0.911	640.2	2.81
8	0.1014	8.44	3.39E-04	0.0033	0.91	1.43E-03					
9	0.1017	8.21	3.74E-04	0.0038	0.91	1.60E-03	0.0893	1.60E-03	0.915	570.3	2.76
10	0.0989	8.37	3.20E-04	0.0037	0.92	1.61E-03					
11	0.1014	8.32	2.84E-04	0.0044	0.94	1.69E-03	0.0937	1.68E-03	0.939	557.9	2.75
12	0.1006	8.45	3.03E-04	0.0047	0.94	1.68E-03					
13	0.0990	8.35	3.14E-04	0.0050	0.94	1.77E-03	0.0983	1.77E-03	0.938	531.0	2.73
14	0.0996	8.43	3.41E-04	0.0049	0.93	1.77E-03					
15	0.0991	8.33	3.65E-04	0.0052	0.93	1.95E-03	0.1081	1.94E-03	0.938	483.0	2.68
16	0.1005	8.38	3.64E-04	0.0059	0.94	1.94E-03					
17	0.1000	8.18	4.38E-04	0.0068	0.94	2.10E-03	0.1173	2.11E-03	0.942	447.2	2.65
18	0.1003	8.27	3.84E-04	0.0066	0.95	2.11E-03					
19	0.1025	8.35	3.68E-04	0.0067	0.95	2.20E-03	0.1223	2.20E-03	0.949	431.9	2.64
20	0.0991	8.19	3.78E-04	0.0071	0.95	2.19E-03					

Table B-26 Phenylethanol adsolubilization of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Phe	Surf_initial		Surf_equilibrium		Surf $_{(in\text{-}eq)}$	Phe_initial	Phe_equilibrium		Phe $_{(in\text{-}eq)}$
	(µl)	Area	Conc. (M)	Area	Conc. (M)	(M)	Conc. (M)	Area	Conc. (M)	(M)
1	100	784.4	6.95E-04	682.1	6.43E-04	5.12E-05	0.0207	5189.0	0.0187	0.0020
2	100	784.4	6.95E-04	686.9	6.46E-04	4.88E-05	0.0207	5204.3	0.0188	0.0019
3	100	784.4	6.95E-04	688.1	6.46E-04	4.82E-05	0.0207	5299.8	0.0192	0.0015
4	125	784.4	6.95E-04	666.7	6.36E-04	5.89E-05	0.0258	6467.5	0.0237	0.0021
5	125	784.4	6.95E-04	684.4	6.45E-04	5.00E-05	0.0258	6546.1	0.0240	0.0018
6	125	784.4	6.95E-04	648.8	6.27E-04	6.78E-05	0.0258	6484.2	0.0238	0.0020
7	150	784.4	6.95E-04	662.4	6.34E-04	6.10E-05	0.031	7818.8	0.0290	0.0020
8	150	784.4	6.95E-04	675.5	6.40E-04	5.44E-05	0.031	7756.9	0.0288	0.0022
9	150	784.4	6.95E-04	682.4	6.44E-04	5.10E-05	0.031	7846.7	0.0291	0.0019
10	200	784.4	6.95E-04	737.9	6.71E-04	2.33E-05	0.0413	10177.1	0.0382	0.0031
11	200	784.4	6.95E-04	721.5	6.63E-04	3.14E-05	0.0413	10148.9	0.0381	0.0032
12	200	784.4	6.95E-04	695.4	6.50E-04	4.45E-05	0.0413	10139.0	0.0380	0.0033
13	250	784.4	6.95E-04	690.0	6.47E-04	4.72E-05	0.0517	12728.5	0.0482	0.0035
14	250	784.4	6.95E-04	678.7	6.42E-04	5.29E-05	0.0517	12691.5	0.0480	0.0037
15	250	784.4	6.95E-04	691.7	6.48E-04	4.64E-05	0.0517	12692.6	0.0480	0.0037

Table B-26a Phenylethanol adsolubilization of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Phe	Surf_initial		Surf_equilibrium		Surf $_{\text{(in-eq)}}$	Phe_initial	Phe_equilibrium		Phe $_{\text{(in-eq)}}$
	(µl)	Area	Conc. (M)	Area	Conc. (M)	(M)	Conc. (M)	Area	Conc. (M)	(M)
16	300	784.4	6.95E-04	676.4	6.41E-04	5.40E-05	0.0620	15117.0	0.0575	0.0045
17	300	784.4	6.95E-04	685.6	6.45E-04	4.94E-05	0.0620	15276.4	0.0581	0.0039
18	300	784.4	6.95E-04	688.0	6.46E-04	4.82E-05	0.0620	15073.5	0.0573	0.0047
19	350	784.4	6.95E-04	686.1	6.45E-04	4.92E-05	0.0723	17692.6	0.0675	0.0048
20	350	784.4	6.95E-04	681.4	6.43E-04	5.15E-05	0.0723	17708.1	0.0676	0.0047
21	350	784.4	6.95E-04	673.7	6.39E-04	5.54E-05	0.0723	17661.5	0.0674	0.0049
22	400	784.4	6.95E-04	661.9	6.33E-04	6.13E-05	0.0827	20149.9	0.0771	0.0056
23	400	784.4	6.95E-04	665.0	6.35E-04	5.97E-05	0.0827	20158.9	0.0772	0.0055
24	450	784.4	6.95E-04	651.1	6.28E-04	6.67E-05	0.0930	22646.0	0.0869	0.0061
25	450	784.4	6.95E-04	665.2	6.35E-04	5.96E-05	0.0930	22578.4	0.0866	0.0064
26	475	784.4	6.95E-04	662.7	6.34E-04	6.09E-05	0.0982	23749.5	0.0912	0.0070
27	475	784.4	6.95E-04	660.5	6.33E-04	6.20E-05	0.0982	24076.6	0.0924	0.0058
28	500	784.4	6.95E-04	651.2	6.28E-04	6.66E-05	0.1033	25013.9	0.0961	0.0072
29	500	784.4	6.95E-04	640.3	6.23E-04	7.21E-05	0.1033	25082.5	0.0964	0.0069

Table B-26b Phenylethanol adsolubilization of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	pH (eq.)	Surf $_{(in-eq)}$ (M)	Phe $_{(in-eq)}$ (M)	X_{adm}	X_{aq}	Phe_equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	K_{adm}	log K_{adm}
1	0.0091	8.04	5.12E-05	0.0020	0.98	3.37E-04	0.0189	3.40E-04	0.973	2861.8	3.46
2	0.0095	8.09	4.88E-05	0.0019	0.97	3.38E-04					
3	0.0112	8.37	4.82E-05	0.0015	0.97	3.45E-04					
4	0.0092	8.47	5.89E-05	0.0021	0.97	4.27E-04	0.0238	4.29E-04	0.971	2263.3	3.35
5	0.0095	8.16	5.00E-05	0.0018	0.97	4.32E-04					
6	0.0113	8.45	6.78E-05	0.0020	0.97	4.28E-04					
7	0.0100	8.04	6.10E-05	0.0020	0.97	5.22E-04	0.0289	5.21E-04	0.973	1868.9	3.27
8	0.0097	8.18	5.44E-05	0.0022	0.98	5.17E-04					
9	0.0098	8.23	5.10E-05	0.0019	0.97	5.24E-04					
10	0.0103	8.06	2.33E-05	0.0031	0.99	6.87E-04	0.0381	6.86E-04	0.990	1443.8	3.16
11	0.0098	8.13	3.14E-05	0.0032	0.99	6.85E-04					
12	0.0098	8.00	4.45E-05	0.0033	0.99	6.84E-04					
13	0.0099	8.05	4.72E-05	0.0035	0.99	8.66E-04	0.0481	8.64E-04	0.987	1141.5	3.06
14	0.0104	8.18	5.29E-05	0.0037	0.99	8.64E-04					
15	0.0101	8.31	4.64E-05	0.0037	0.99	8.64E-04					

Table B-26c Phenylethanol adsolubilization of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	pH (eq.)	Surf $_{(in\text{-}eq)}$ (M)	Phe $_{(in\text{-}eq)}$ (M)	X_{adm}	X_{aq}	Phe_equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	K_{adm}	log K_{adm}
16	0.0105	8.23	5.40E-05	0.0045	0.99	1.03E-03	0.0576	1.04E-03	0.988	953.9	2.98
17	0.0096	8.11	4.94E-05	0.0039	0.99	1.04E-03					
18	0.0100	8.25	4.82E-05	0.0047	0.99	1.03E-03					
19	0.0096	8.35	4.92E-05	0.0048	0.99	1.21E-03	0.0675	1.21E-03	0.989	815.0	2.91
20	0.0098	8.12	5.15E-05	0.0047	0.99	1.22E-03					
21	0.0101	8.10	5.54E-05	0.0049	0.99	1.21E-03					
22	0.0105	8.14	6.13E-05	0.0056	0.99	1.39E-03	0.0771	1.39E-03	0.989	713.4	2.85
23	0.0095	8.04	5.97E-05	0.0055	0.99	1.39E-03					
24	0.0094	8.23	6.67E-05	0.0061	0.99	1.56E-03	0.0867	1.56E-03	0.990	635.1	2.80
25	0.0099	8.15	5.96E-05	0.0064	0.99	1.56E-03					
26	0.0094	8.24	6.09E-05	0.0070	0.99	1.64E-03	0.0918	1.65E-03	0.990	600.3	2.78
27	0.0099	8.01	6.20E-05	0.0058	0.99	1.66E-03					
28	0.0095	8.21	6.66E-05	0.0072	0.99	1.73E-03	0.0962	1.73E-03	0.990	572.6	2.76
29	0.0102	8.12	7.21E-05	0.0069	0.99	1.73E-03					

Table B-27 Phenylethanol adsolubilization of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

	Phe	Surf_initial		Surf_equilibrium		Surf $_{(in-eq)}$	Phe_initial	Phe_equilibrium		Phe $_{(in-eq)}$
Tube	(μl)	Area	Conc. (M)	Area	Conc. (M)	(M)	Conc. (M)	Area	Conc. (M)	(M)
1	100	467.0	5.98E-04	464.5	5.96E-04	1.25E-06	0.0207	5107.7	0.0184	0.0023
2	100	467.0	5.98E-04	454.6	5.91E-04	6.20E-06	0.0207	5093.3	0.0184	0.0023
3	100	467.0	5.98E-04	445.1	5.87E-04	1.10E-05	0.0207	5127.8	0.0185	0.0022
4	125	467.0	5.98E-04	441.8	5.85E-04	1.26E-05	0.0258	6377.8	0.0234	0.0024
5	125	467.0	5.98E-04	420.7	5.75E-04	2.32E-05	0.0258	6469.3	0.0237	0.0021
6	125	467.0	5.98E-04	425.6	5.77E-04	2.07E-05	0.0258	6417.2	0.0235	0.0023
7	150	467.0	5.98E-04	410.0	5.69E-04	2.85E-05	0.0310	7723.4	0.0286	0.0024
8	150	467.0	5.98E-04	409.6	5.69E-04	2.87E-05	0.0310	7665.0	0.0284	0.0026
9	150	467.0	5.98E-04	420.4	5.74E-04	2.33E-05	0.0310	7710.3	0.0286	0.0024
10	200	467.0	5.98E-04	425.1	5.77E-04	2.10E-05	0.0413	10246.7	0.0385	0.0028
11	200	467.0	5.98E-04	403.9	5.66E-04	3.16E-05	0.0413	10247.1	0.0385	0.0028
12	200	467.0	5.98E-04	399.8	5.64E-04	3.36E-05	0.0413	10095.2	0.0379	0.0034
13	250	467.0	5.98E-04	379.7	5.54E-04	4.37E-05	0.0517	12634.2	0.0478	0.0039
14	250	467.0	5.98E-04	393.4	5.61E-04	3.68E-05	0.0517	12741.4	0.0482	0.0035
15	250	467.0	5.98E-04	382.9	5.56E-04	4.21E-05	0.0517	12684.0	0.0480	0.0037

Table B-27a Phenylethanol adsolubilization of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Phe	Surf_initial		Surf_equilibrium		Surf $_{(in-eq)}$	Phe_initial	Phe_equilibrium		Phe $_{(in-eq)}$
	(µl)	Area	Conc. (M)	Area	Conc. (M)	(M)	Conc. (M)	Area	Conc. (M)	(M)
16	300	467.0	5.98E-04	400.5	5.64E-04	3.33E-05	0.0620	15190.9	0.0578	0.0042
17	300	467.0	5.98E-04	414.8	5.72E-04	2.61E-05	0.0620	15316.0	0.0583	0.0037
18	300	467.0	5.98E-04	410.6	5.69E-04	2.82E-05	0.0620	15233.6	0.0579	0.0041
19	325	467.0	5.98E-04	400.4	5.64E-04	3.33E-05	0.0672	16520.4	0.0630	0.0042
20	325	467.0	5.98E-04	398.8	5.64E-04	3.41E-05	0.0672	16525.0	0.0630	0.0042
21	350	467.0	5.98E-04	384.1	5.56E-04	4.15E-05	0.0723	17615.2	0.0672	0.0051
22	350	467.0	5.98E-04	400.3	5.64E-04	3.34E-05	0.0723	17728.6	0.0677	0.0046
23	400	467.0	5.98E-04	396.0	5.62E-04	3.55E-05	0.0827	20227.7	0.0774	0.0053
24	400	467.0	5.98E-04	405.2	5.67E-04	3.09E-05	0.0827	20216.5	0.0774	0.0053
25	450	467.0	5.98E-04	418.4	5.73E-04	2.43E-05	0.0930	22742.5	0.0872	0.0058
26	450	467.0	5.98E-04	414.3	5.71E-04	2.64E-05	0.0930	22759.1	0.0873	0.0057
27	475	467.0	5.98E-04	395.6	5.62E-04	3.57E-05	0.0982	23743.2	0.0911	0.0071
28	475	467.0	5.98E-04	403.1	5.66E-04	3.20E-05	0.0982	23829.9	0.0915	0.0067

Table B-27b Phenylethanol adsolubilization of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	pH (eq.)	Surf $_{\text{(in-eq)}}$ (M)	Phe $_{\text{(in-eq)}}$ (M)	X_{adm}	X_{aq}	Phe_equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	K_{adm}	log K_{adm}
1	0.0112	8.26	1.25E-06	0.0023	1.00	3.31E-04	0.0184	3.31E-04	0.997	3008.8	3.48
2	0.0114	8.21	6.20E-06	0.0023	1.00	3.30E-04					
3	0.0100	8.35	1.10E-05	0.0022	1.00	3.33E-04					
4	0.0102	8.16	1.26E-05	0.0024	0.99	4.20E-04	0.0235	4.24E-04	0.992	2341.3	3.37
5	0.0105	8.28	2.32E-05	0.0021	0.99	4.27E-04					
6	0.0099	8.29	2.07E-05	0.0023	0.99	4.23E-04					
7	0.0103	8.50	2.85E-05	0.0024	0.99	5.15E-04	0.0285	5.13E-04	0.989	1927.4	3.28
8	0.0109	8.19	2.87E-05	0.0026	0.99	5.11E-04					
9	0.0104	8.45	2.33E-05	0.0024	0.99	5.14E-04					
10	0.0105	8.34	2.10E-05	0.0028	0.99	6.92E-04	0.0383	6.88E-04	0.991	1438.8	3.16
11	0.0110	8.25	3.16E-05	0.0028	0.99	6.92E-04					
12	0.0109	8.26	3.36E-05	0.0034	0.99	6.81E-04					
13	0.0107	8.25	4.37E-05	0.0039	0.99	8.59E-04	0.048	8.63E-04	0.989	1145.9	3.06
14	0.0112	8.33	3.68E-05	0.0035	0.99	8.67E-04					
15	0.0104	8.23	4.21E-05	0.0037	0.99	8.63E-04					

Table B-27c Phenylethanol adsolubilization of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2^{o}C

Tube	Alumina (g)	pH (eq.)	Surf $_{(in-eq)}$ (M)	Phe $_{(in-eq)}$ (M)	X_{adm}	X_{aq}	Phe_equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	K_{adm}	log K_{adm}
16	0.0123	8.18	3.33E-05	0.0042	0.99	1.04E-03	0.058	1.04E-03	0.993	952.1	2.98
17	0.0104	8.19	2.61E-05	0.0037	0.99	1.05E-03					
18	0.0118	8.17	2.82E-05	0.0041	0.99	1.04E-03					
19	0.0109	8.22	3.33E-05	0.0042	0.99	1.13E-03	0.063	1.13E-03	0.992	876.3	2.94
20	0.0126	8.31	3.41E-05	0.0042	0.99	1.13E-03					
21	0.0114	8.20	4.15E-05	0.0051	0.99	1.21E-03	0.0674	1.21E-03	0.992	818.3	2.91
22	0.0101	8.33	3.34E-05	0.0046	0.99	1.22E-03					
23	0.0099	8.21	3.55E-05	0.0053	0.99	1.39E-03	0.0774	1.39E-03	0.994	714.2	2.85
24	0.0115	8.14	3.09E-05	0.0053	0.99	1.39E-03					
25	0.0100	8.15	2.43E-05	0.0058	1.00	1.57E-03	0.0873	1.57E-03	0.996	634.7	2.80
26	0.0107	8.10	2.64E-05	0.0057	1.00	1.57E-03					
27	0.0100	8.12	3.57E-05	0.0071	0.99	1.64E-03	0.0913	1.64E-03	0.995	606.4	2.78
28	0.0102	8.42	3.20E-05	0.0067	1.00	1.64E-03					

Table B-28 Phenylethanol adsolubilization of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Phe	Surf_initial		Surf_equilibrium		Surf $_{(in-eq)}$	Phe_initial	Phe_equilibrium		Phe $_{(in-eq)}$
	(μl)	Area	Conc. (M)	Area	Conc. (M)	(M)	Conc. (M)	Area	Conc. (M)	(M)
1	100	645.7	6.02E-04	640.3	5.99E-04	2.70E-06	0.0207	5426.3	0.0197	0.0010
2	100	645.7	6.02E-04	638.7	5.98E-04	3.50E-06	0.0207	5451.3	0.0198	0.0009
3	100	645.7	6.02E-04	629.2	5.93E-04	8.25E-06	0.0207	5464.3	0.0198	0.0009
4	150	645.7	6.02E-04	619.0	5.88E-04	1.34E-05	0.0310	8214.9	0.0305	0.0005
5	150	645.7	6.02E-04	620.4	5.89E-04	1.27E-05	0.0310	8176.8	0.0304	0.0006
6	150	645.7	6.02E-04	642.4	6.00E-04	1.65E-06	0.0310	8190.1	0.0304	0.0006
7	200	645.7	6.02E-04	621.5	5.90E-04	1.21E-05	0.0413	10915.6	0.0411	0.0002
8	200	645.7	6.02E-04	608.0	5.83E-04	1.89E-05	0.0413	10901.9	0.0410	0.0003
9	200	645.7	6.02E-04	616.2	5.87E-04	1.48E-05	0.0413	10922.5	0.0411	0.0002
10	250	645.7	6.02E-04	622.3	5.90E-04	1.17E-05	0.0517	13609.0	0.0516	0.0001
11	250	645.7	6.02E-04	605.2	5.81E-04	2.03E-05	0.0517	13600.3	0.0516	0.0001
12	250	645.7	6.02E-04	629.6	5.94E-04	8.05E-06	0.0517	13604.8	0.0516	0.0001
13	300	645.7	6.02E-04	635.0	5.96E-04	5.35E-06	0.0620	16213.2	0.0618	0.0002
14	300	645.7	6.02E-04	617.8	5.88E-04	1.40E-05	0.0620	16214.6	0.0618	0.0002
15	300	645.7	6.02E-04	636.0	5.97E-04	4.85E-06	0.0620	16208.5	0.0617	0.0003

Table B-28a Phenylethanol adsolubilization of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Phe	Surf_initial		Surf_equilibrium		Surf $_{\text{(in-eq)}}$	Phe_initial	Phe_equilibrium		Phe $_{\text{(in-eq)}}$
	(μl)	Area	Conc. (M)	Area	Conc. (M)	(M)	Conc. (M)	Area	Conc. (M)	(M)
16	350	645.7	6.02E-04	616.1	5.87E-04	1.48E-05	0.0723	18775.3	0.0718	0.0005
17	350	645.7	6.02E-04	611.4	5.85E-04	1.72E-05	0.0723	18751.2	0.0717	0.0006
18	350	645.7	6.02E-04	599.7	5.79E-04	2.30E-05	0.0723	18760.7	0.0717	0.0006
19	400	645.7	6.02E-04	598.5	5.78E-04	2.36E-05	0.0827	21538.2	0.0825	0.0002
20	400	645.7	6.02E-04	613.4	5.86E-04	1.62E-05	0.0827	21561.0	0.0826	0.0001
21	450	645.7	6.02E-04	614.0	5.86E-04	1.59E-05	0.0930	24048.1	0.0923	0.0007
22	450	645.7	6.02E-04	618.6	5.88E-04	1.36E-05	0.0930	24099.5	0.0925	0.0005
23	500	645.7	6.02E-04	571.2	5.64E-04	3.73E-05	0.1033	26546.0	0.1021	0.0012
24	500	645.7	6.02E-04	585.6	5.72E-04	3.01E-05	0.1033	26578.6	0.1022	0.0011
25	550	645.7	6.02E-04	587.8	5.73E-04	2.90E-05	0.1137	29034.2	0.1118	0.0019
26	550	645.7	6.02E-04	601.8	5.80E-04	2.20E-05	0.1137	29012.8	0.1117	0.0020
27	600	645.7	6.02E-04	582.5	5.70E-04	3.16E-05	0.1240	31341.9	0.1208	0.0032
28	600	645.7	6.02E-04	579.1	5.68E-04	3.33E-05	0.1240	31348.0	0.1208	0.0032

Table B-28b Phenylethanol adsolubilization of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	pH (eq.)	Surf $_{(in\text{-}eq)}$ (M)	Phe $_{(in\text{-}eq)}$ (M)	X_{adm}	X_{aq}	Phe_equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	K_{adm}	log K_{adm}
1	0.0100	8.12	2.70E-06	0.001	1.00	3.54E-04	0.0197	3.55E-04	0.99	2800.9	3.45
2	0.0103	8.09	3.50E-06	0.0009	1.00	3.55E-04					
3	0.0115	8.17	8.25E-06	0.0009	0.99	3.56E-04					
4	0.0121	8.11	1.34E-05	0.0005	0.97	5.49E-04	0.0305	5.48E-04	0.98	1794.8	3.25
5	0.0117	8.20	1.27E-05	0.0006	0.98	5.47E-04					
6	0.0104	8.12	1.65E-06	0.0006	1.00	5.48E-04					
7	0.0102	8.09	1.21E-05	0.0002	0.94	7.39E-04	0.0411	7.39E-04	0.94	1270.0	3.10
8	0.0116	8.13	1.89E-05	0.0003	0.94	7.38E-04					
9	0.0117	8.15	1.48E-05	0.0002	0.93	7.39E-04					
10	0.0102	8.14	1.17E-05	0.0001	0.90	9.28E-04	0.0516	9.28E-04	0.88	953.1	2.98
11	0.0105	8.17	2.03E-05	0.0001	0.83	9.27E-04					
12	0.0102	8.22	8.05E-06	0.0001	0.93	9.28E-04					
13	0.0114	8.13	5.35E-06	0.0002	0.97	1.11E-03	0.0617	1.11E-03	0.96	868.4	2.94
14	0.0106	8.10	1.40E-05	0.0002	0.93	1.11E-03					
15	0.0106	8.15	4.85E-06	0.0003	0.98	1.11E-03					

Table B-28c Phenylethanol adsolubilization of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	pH (eq.)	Surf $_{(in\text{-}eq)}$ (M)	Phe $_{(in\text{-}eq)}$ (M)	X_{adm}	X_{aq}	Phe_equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	K_{adm}	log K_{adm}
16	0.0107	8.27	1.48E-05	0.0005	0.97	1.29E-03	0.0717	1.29E-03	0.97	751.5	2.88
17	0.0108	8.07	1.72E-05	0.0006	0.97	1.29E-03					
18	0.0125	8.15	2.30E-05	0.0006	0.96	1.29E-03					
19	0.0104	8.18	2.36E-05	0.0002	0.89	1.48E-03	0.0826	1.48E-03	0.88	591.2	2.77
20	0.0116	8.05	1.62E-05	0.0001	0.86	1.49E-03					
21	0.0102	8.16	1.59E-05	0.0007	0.98	1.66E-03	0.0924	1.66E-03	0.98	587.3	2.77
22	0.0104	8.21	1.36E-05	0.0005	0.97	1.66E-03					
23	0.0115	8.17	3.73E-05	0.0012	0.97	1.83E-03	0.1021	1.84E-03	0.97	529.4	2.72
24	0.0114	8.23	3.01E-05	0.0011	0.97	1.84E-03					
25	0.0115	8.20	2.90E-05	0.0019	0.98	2.01E-03	0.1117	2.01E-03	0.99	491.6	2.69
26	0.0100	8.11	2.20E-05	0.002	0.99	2.01E-03					
27	0.0112	8.09	3.16E-05	0.0032	0.99	2.17E-03	0.1208	2.17E-03	0.99	456.2	2.66
28	0.0111	8.13	3.33E-05	0.0032	0.99	2.17E-03					

Table B-29 Ethylcyclohexane adsolubilization of C12S at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	ECH	Surf_initial		Surf_equilibrium		Surf $_{(in-eq)}$	ECH_initial	ECH_equilibrium		ECH $_{(in-eq)}$
	(μl)	Area	Conc. (M)	Area	Conc. (M)	(M)	Conc. (M)	Area	Conc. (M)	(M)
1	5	1047.7	1.63E-03	820.5	1.33E-03	3.02E-04	8.79E-04	0.85	1.30E-04	7.49E-04
2	5	1047.7	1.63E-03	815.1	1.33E-03	3.09E-04	8.79E-04	1.3	1.35E-04	7.44E-04
3	5	1047.7	1.63E-03	830.5	1.35E-03	2.89E-04	8.79E-04	1.1	1.33E-04	7.46E-04
4	6	1047.7	1.63E-03	825.6	1.34E-03	2.95E-04	1.05E-03	1.3	1.35E-04	9.15E-04
5	6	1047.7	1.63E-03	833.4	1.35E-03	2.85E-04	1.05E-03	1.3	1.35E-04	9.15E-04
6	6	1047.7	1.63E-03	840.1	1.36E-03	2.76E-04	1.05E-03	1.1	1.33E-04	9.17E-04
7	7	1047.7	1.63E-03	841.1	1.36E-03	2.75E-04	1.23E-03	1.3	1.35E-04	1.09E-03
8	7	1047.7	1.63E-03	828.5	1.34E-03	2.91E-04	1.23E-03	1.7	1.40E-04	1.09E-03
9	7	1047.7	1.63E-03	839.6	1.36E-03	2.77E-04	1.23E-03	1.4	1.37E-04	1.09E-03
10	8	1047.7	1.63E-03	802.8	1.31E-03	3.25E-04	1.41E-03	1.3	1.35E-04	1.27E-03
11	8	1047.7	1.63E-03	811.3	1.32E-03	3.14E-04	1.41E-03	1.6	1.39E-04	1.27E-03
12	8	1047.7	1.63E-03	801.7	1.31E-03	3.27E-04	1.41E-03	1.2	1.34E-04	1.28E-03
13	8.5	1047.7	1.63E-03	820.5	1.33E-03	3.02E-04	1.49E-03	1.2	1.34E-04	1.36E-03
14	8.5	1047.7	1.63E-03	814.1	1.32E-03	3.10E-04	1.49E-03	1.1	1.33E-04	1.36E-03
15	8.5	1047.7	1.63E-03	802.4	1.31E-03	3.26E-04	1.49E-03	1.2	1.34E-04	1.36E-03
16	9	1047.7	1.63E-03	828.2	1.34E-03	2.92E-04	1.58E-03	1.2	1.34E-04	1.45E-03
17	9	1047.7	1.63E-03	813.2	1.32E-03	3.12E-04	1.58E-03	1.6	1.39E-04	1.44E-03
18	9	1047.7	1.63E-03	809.7	1.32E-03	3.16E-04	1.58E-03	1.5	1.38E-04	1.44E-03
19	9.5	1047.7	1.63E-03	800.4	1.31E-03	3.29E-04	1.67E-03	1.1	1.33E-04	1.54E-03
20	9.5	1047.7	1.63E-03	798.6	1.30E-03	3.31E-04	1.67E-03	1.5	1.38E-04	1.53E-03
21	9.5	1047.7	1.63E-03	790.5	1.29E-03	3.42E-04	1.67E-03	1.3	1.35E-04	1.53E-03
22	10	1047.7	1.63E-03	768.3	1.26E-03	3.71E-04	1.76E-03	1.4	1.37E-04	1.62E-03
23	10	1047.7	1.63E-03	762.4	1.26E-03	3.79E-04	1.76E-03	1.2	1.34E-04	1.63E-03
24	10	1047.7	1.63E-03	771	1.27E-03	3.68E-04	1.76E-03	1.3	1.35E-04	1.62E-03

Table B-29a Ethylcyclohexane adsolubilization of C12S at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	pH (eq.)	Surf $_{\text{(in-eq)}}$ (M)	ECH $_{\text{(in-eq)}}$ (M)	X_{adm}	X_{aq}	ECH_equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	K_{adm}	log K_{adm}
1	0.1009	8.50	3.02E-04	7.49E-04	0.71	2.34E-06	1.33E-04	2.39E-06	0.71	297935	5.47
2	0.1004	8.50	3.09E-04	7.44E-04	0.71	2.44E-06					
3	0.1009	8.50	2.89E-04	7.46E-04	0.72	2.39E-06					
4	0.1003	8.50	2.95E-04	9.15E-04	0.76	2.44E-06	1.35E-04	2.43E-06	0.76	313735	5.50
5	0.1023	8.50	2.85E-04	9.15E-04	0.76	2.44E-06					
6	0.1003	8.50	2.76E-04	9.17E-04	0.77	2.39E-06					
7	0.1012	8.47	2.75E-04	1.09E-03	0.80	2.44E-06	1.37E-04	2.47E-06	0.80	322378	5.51
8	0.1080	8.40	2.91E-04	1.09E-03	0.79	2.53E-06					
9	0.1012	8.45	2.77E-04	1.09E-03	0.80	2.46E-06					
10	0.1044	8.50	3.25E-04	1.27E-03	0.80	2.44E-06	1.36E-04	2.45E-06	0.80	326020	5.51
11	0.1000	8.50	3.14E-04	1.27E-03	0.80	2.50E-06					
12	0.1040	8.50	3.27E-04	1.28E-03	0.80	2.41E-06					
13	0.1004	8.50	3.02E-04	1.36E-03	0.82	2.41E-06	1.34E-04	2.41E-06	0.81	337074	5.53
14	0.1020	8.48	3.10E-04	1.36E-03	0.81	2.39E-06					
15	0.1002	8.45	3.26E-04	1.36E-03	0.81	2.41E-06					
16	0.1011	8.41	2.92E-04	1.45E-03	0.83	2.41E-06	1.37E-04	2.47E-06	0.82	334428	5.52
17	0.1004	8.50	3.12E-04	1.44E-03	0.82	2.50E-06					
18	0.1009	8.40	3.16E-04	1.44E-03	0.82	2.48E-06					
19	0.1011	8.38	3.29E-04	1.54E-03	0.82	2.39E-06	1.35E-04	2.43E-06	0.82	337884	5.53
20	0.1013	8.50	3.31E-04	1.53E-03	0.82	2.48E-06					
21	0.1010	8.40	3.42E-04	1.53E-03	0.82	2.44E-06					
22	0.1001	8.38	3.71E-04	1.62E-03	0.81	2.46E-06	1.35E-04	2.43E-06	0.81	334659	5.52
23	0.1032	8.33	3.79E-04	1.63E-03	0.81	2.41E-06					
24	0.1001	8.36	3.68E-04	1.62E-03	0.81	2.44E-06					

Table B-30 Ethylcyclohexane adsolubilization of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	ECH	Surf_initial		Surf_equilibrium		Surf $_{(in-eq)}$	ECH_initial	ECH_equilibrium		ECH $_{(in-eq)}$
	(µl)	Area	Conc. (M)	Area	Conc. (M)	(M)	Conc. (M)	Area	Conc. (M)	(M)
1	5	801.8	7.03E-04	723.4	6.64E-04	3.92E-05	8.79E-04	47.8	5.34E-04	3.45E-04
2	5	801.8	7.03E-04	720.1	6.62E-04	4.08E-05	8.79E-04	51.4	5.91E-04	2.88E-04
3	5	801.8	7.03E-04	721.5	6.63E-04	4.01E-05	8.79E-04	41.0	4.26E-04	4.53E-04
4	6	801.8	7.03E-04	719.7	6.62E-04	4.10E-05	1.05E-03	43.1	4.59E-04	5.91E-04
5	6	801.8	7.03E-04	722.3	6.64E-04	3.98E-05	1.05E-03	51.0	5.85E-04	4.65E-04
6	6	801.8	7.03E-04	720.7	6.63E-04	4.06E-05	1.05E-03	39.0	3.94E-04	6.56E-04
7	7	801.8	7.03E-04	705.2	6.55E-04	4.83E-05	1.23E-03	57.0	6.80E-04	5.50E-04
8	7	801.8	7.03E-04	711.8	6.58E-04	4.50E-05	1.23E-03	60.6	7.38E-04	4.92E-04
9	7	801.8	7.03E-04	715.5	6.60E-04	4.31E-05	1.23E-03	74.0	9.51E-04	2.79E-04
10	8	801.8	7.03E-04	715.2	6.60E-04	4.33E-05	1.41E-03	72.7	9.30E-04	4.80E-04
11	8	801.8	7.03E-04	712.4	6.59E-04	4.47E-05	1.41E-03	77.8	1.01E-03	3.99E-04
12	8	801.8	7.03E-04	708.3	6.57E-04	4.68E-05	1.41E-03	76.3	9.87E-04	4.23E-04
13	9	801.8	7.03E-04	654.4	6.30E-04	7.37E-05	1.58E-03	76.7	9.94E-04	5.86E-04
14	9	801.8	7.03E-04	671.2	6.38E-04	6.53E-05	1.58E-03	90.7	1.22E-03	3.63E-04
15	9	801.8	7.03E-04	668.3	6.37E-04	6.68E-05	1.58E-03	85.6	1.14E-03	4.45E-04

Table B-30a Ethylcyclohexane adsolubilization of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	ECH (µl)	Surf_initial		Surf_equilibrium		Surf $_{(in-eq)}$ (M)	ECH_initial	ECH_equilibrium		ECH $_{(in-eq)}$ (M)
		Area	Conc. (M)	Area	Conc. (M)		Conc. (M)	Area	Conc. (M)	
16	10	801.8	7.03E-04	701.5	6.53E-04	5.01E-05	1.76E-03	105.3	1.45E-03	3.11E-04
17	10	801.8	7.03E-04	719.5	6.62E-04	4.11E-05	1.76E-03	106.1	1.46E-03	2.98E-04
18	10	801.8	7.03E-04	720.4	6.63E-04	4.07E-05	1.76E-03	103.7	1.42E-03	3.37E-04
19	11	801.8	7.03E-04	736.8	6.71E-04	3.25E-05	1.93E-03	117.5	1.64E-03	2.87E-04
20	11	801.8	7.03E-04	728.4	6.67E-04	3.67E-05	1.93E-03	109.4	1.51E-03	4.16E-04
21	11	801.8	7.03E-04	730.1	6.67E-04	3.58E-05	1.93E-03	102.1	1.40E-03	5.32E-04
22	12	801.8	7.03E-04	705.6	6.55E-04	4.81E-05	2.11E-03	110.6	1.53E-03	5.77E-04
23	12	801.8	7.03E-04	714.5	6.60E-04	4.36E-05	2.11E-03	109.7	1.52E-03	5.91E-04
24	12	801.8	7.03E-04	711.7	6.58E-04	4.50E-05	2.11E-03	106.4	1.47E-03	6.44E-04
25	13	801.8	7.03E-04	682.5	6.44E-04	5.96E-05	2.28E-03	112.1	1.56E-03	7.23E-04
26	13	801.8	7.03E-04	678.4	6.42E-04	6.17E-05	2.28E-03	119.0	1.67E-03	6.13E-04
27	13	801.8	7.03E-04	685.8	6.45E-04	5.80E-05	2.28E-03	113.6	1.58E-03	6.99E-04
28	14	801.8	7.03E-04	693.7	6.49E-04	5.40E-05	2.46E-03	119.1	1.67E-03	7.92E-04
29	14	801.8	7.03E-04	695.1	6.50E-04	5.34E-05	2.46E-03	116.4	1.63E-03	8.34E-04
30	14	801.8	7.03E-04	688.4	6.47E-04	5.67E-05	2.46E-03	119.0	1.67E-03	7.93E-04

Table B-30b Ethylcyclohexane adsolubilization of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	pH (eq.)	Surf $_{(in\text{-}eq)}$ (M)	ECH $_{(in\text{-}eq)}$ (M)	X_{adm}	X_{aq}	ECH_equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	K_{adm}	log K_{adm}
1	0.0102	8.07	3.92E-05	3.45E-04	0.90	9.61E-06	5.17E-04	9.31E-06	0.90	96447	4.98
2	0.0109	8.01	4.08E-05	2.88E-04	0.88	1.06E-05					
3	0.0101	8.05	4.01E-05	4.53E-04	0.92	7.66E-06					
4	0.0106	8.01	4.10E-05	5.91E-04	0.94	8.27E-06	4.79E-04	8.63E-06	0.93	108099	5.03
5	0.0118	8.04	3.98E-05	4.65E-04	0.92	1.05E-05					
6	0.0105	8.02	4.06E-05	6.56E-04	0.94	7.09E-06					
7	0.0111	8.06	4.83E-05	5.50E-04	0.92	1.22E-05	7.90E-04	1.42E-05	0.90	63358	4.80
8	0.0123	8.02	4.50E-05	4.92E-04	0.92	1.33E-05					
9	0.0110	8.05	4.31E-05	2.79E-04	0.87	1.71E-05					
10	0.0100	8.30	4.33E-05	4.80E-04	0.92	1.67E-05	9.76E-04	1.76E-05	0.91	51531	4.71
11	0.0106	8.01	4.47E-05	3.99E-04	0.90	1.82E-05					
12	0.0101	8.02	4.68E-05	4.23E-04	0.90	1.78E-05					
13	0.0118	8.00	7.37E-05	5.86E-04	0.89	1.79E-05	1.12E-03	2.01E-05	0.87	43257	4.64
14	0.0110	8.02	6.53E-05	3.63E-04	0.85	2.19E-05					
15	0.0117	8.01	6.68E-05	4.45E-04	0.87	2.04E-05					

Table B-30c Ethylcyclohexane adsolubilization of C16.5-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	pH (eq.)	Surf $_{(in\text{-}eq)}$ (M)	ECH $_{(in\text{-}eq)}$ (M)	X_{adm}	X_{aq}	ECH_equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	K_{adm}	log K_{adm}
16	0.0105	8.04	5.01E-05	3.11E-04	0.86	2.61E-05	1.44E-03	2.60E-05	0.88	33740	4.53
17	0.0101	8.03	4.11E-05	2.98E-04	0.88	2.63E-05					
18	0.0104	8.05	4.07E-05	3.37E-04	0.89	2.56E-05					
19	0.0105	8.07	3.25E-05	2.87E-04	0.90	2.96E-05	1.52E-03	2.73E-05	0.92	33588	4.53
20	0.0113	8.50	3.67E-05	4.16E-04	0.92	2.73E-05					
21	0.0105	8.02	3.58E-05	5.32E-04	0.94	2.52E-05					
22	0.0109	8.50	4.81E-05	5.77E-04	0.92	2.76E-05	1.51E-03	2.71E-05	0.93	34289	4.54
23	0.0117	8.49	4.36E-05	5.91E-04	0.93	2.73E-05					
24	0.0110	8.45	4.50E-05	6.44E-04	0.93	2.64E-05					
25	0.0106	8.20	5.96E-05	7.23E-04	0.92	2.80E-05	1.60E-03	2.88E-05	0.92	31860	4.50
26	0.0127	8.33	6.17E-05	6.13E-04	0.91	3.00E-05					
27	0.0105	8.35	5.80E-05	6.99E-04	0.92	2.85E-05					
28	0.0110	8.24	5.40E-05	7.92E-04	0.94	3.00E-05	1.65E-03	2.98E-05	0.94	31458	4.50
29	0.0108	8.01	5.34E-05	8.34E-04	0.94	2.93E-05					
30	0.0111	8.11	5.67E-05	7.93E-04	0.93	3.00E-05					

Table B-31 Ethylcyclohexane adsolubilization of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	ECH	Surf_initial		Surf_equilibrium		Surf $_{(in\text{-}eq)}$	ECH_initial	ECH_equilibrium		ECH $_{(in\text{-}eq)}$
	(µl)	Area	Conc. (M)	Area	Conc. (M)	(M)	Conc. (M)	Area	Conc. (M)	(M)
1	5	547.9	6.38E-04	468.5	5.98E-04	3.97E-05	8.79E-04	47.2	5.24E-04	3.55E-04
2	5	547.9	6.38E-04	465.2	5.97E-04	4.14E-05	8.79E-04	45.0	4.89E-04	3.90E-04
3	5	547.9	6.38E-04	458.7	5.94E-04	4.46E-05	8.79E-04	44.6	4.83E-04	3.96E-04
4	6	547.9	6.38E-04	462.1	5.95E-04	4.29E-05	1.05E-03	59.9	7.26E-04	3.24E-04
5	6	547.9	6.38E-04	465.8	5.97E-04	4.11E-05	1.05E-03	60.6	7.38E-04	3.12E-04
6	6	547.9	6.38E-04	460.1	5.94E-04	4.39E-05	1.05E-03	62.3	7.65E-04	2.85E-04
7	8	547.9	6.38E-04	471.9	6.00E-04	3.80E-05	1.41E-03	86.3	1.15E-03	2.63E-04
8	8	547.9	6.38E-04	469.3	5.99E-04	3.93E-05	1.41E-03	80.6	1.06E-03	3.54E-04
9	8	547.9	6.38E-04	468.5	5.98E-04	3.97E-05	1.41E-03	84.3	1.11E-03	2.95E-04
10	10	547.9	6.38E-04	466.7	5.98E-04	4.06E-05	1.76E-03	111.6	1.55E-03	2.11E-04
11	10	547.9	6.38E-04	472.5	6.00E-04	3.77E-05	1.76E-03	112.4	1.56E-03	1.98E-04
12	10	547.9	6.38E-04	475.4	6.02E-04	3.63E-05	1.76E-03	114.3	1.59E-03	1.68E-04
13	11	547.9	6.38E-04	487.1	6.08E-04	3.04E-05	1.93E-03	98.8	1.35E-03	5.85E-04
14	11	547.9	6.38E-04	477.6	6.03E-04	3.52E-05	1.93E-03	101.1	1.38E-03	5.48E-04
15	11	547.9	6.38E-04	481.0	6.05E-04	3.35E-05	1.93E-03	97.1	1.32E-03	6.12E-04

Table B-31a Ethylcyclohexane adsolubilization of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	ECH	Surf_initial		Surf_equilibrium		Surf $_{(in\text{-}eq)}$	ECH_initial	ECH_equilibrium		ECH $_{(in\text{-}eq)}$
	(µl)	Area	Conc. (M)	Area	Conc. (M)	(M)	Conc. (M)	Area	Conc. (M)	(M)
16	12	547.9	6.38E-04	470.2	5.99E-04	3.89E-05	2.11E-03	117.6	1.64E-03	4.65E-04
17	12	547.9	6.38E-04	466.5	5.97E-04	4.07E-05	2.11E-03	115.8	1.62E-03	4.94E-04
18	12	547.9	6.38E-04	465.5	5.97E-04	4.12E-05	2.11E-03	115.3	1.61E-03	5.02E-04
19	13	547.9	6.38E-04	449.1	5.89E-04	4.94E-05	2.28E-03	136.1	1.94E-03	3.41E-04
20	13	547.9	6.38E-04	450.3	5.89E-04	4.88E-05	2.28E-03	146.9	2.11E-03	1.69E-04
21	13	547.9	6.38E-04	451.8	5.90E-04	4.81E-05	2.28E-03	140.0	2.00E-03	2.79E-04
22	14	547.9	6.38E-04	451.7	5.90E-04	4.81E-05	2.46E-03	150.1	2.16E-03	2.98E-04
23	14	547.9	6.38E-04	449.3	5.89E-04	4.93E-05	2.46E-03	162.9	2.37E-03	9.45E-05
24	14	547.9	6.38E-04	450.6	5.89E-04	4.87E-05	2.46E-03	146.4	2.10E-03	3.57E-04
25	15	547.9	6.38E-04	462.3	5.95E-04	4.28E-05	2.64E-03	155.6	2.25E-03	3.91E-04
26	15	547.9	6.38E-04	458.7	5.94E-04	4.46E-05	2.64E-03	159.1	2.30E-03	3.35E-04
27	15	547.9	6.38E-04	460.5	5.94E-04	4.37E-05	2.64E-03	135.2	1.92E-03	7.15E-04
28	16	547.9	6.38E-04	455.5	5.92E-04	4.62E-05	2.81E-03	171.9	2.51E-03	3.01E-04
29	16	547.9	6.38E-04	451.2	5.90E-04	4.84E-05	2.81E-03	187.8	2.76E-03	4.83E-05
30	16	547.9	6.38E-04	450.7	5.90E-04	4.86E-05	2.81E-03	166.8	2.43E-03	3.82E-04

Table B-31b Ethylcyclohexane adsolubilization of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	pH (eq.)	Surf $_{(in-eq)}$ (M)	ECH $_{(in-eq)}$ (M)	X_{adm}	X_{aq}	ECH_equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	K_{adm}	log K_{adm}
1	0.0104	8.47	3.97E-05	3.55E-04	0.90	9.44E-06	4.99E-04	8.98E-06	0.90	100292	5.00
2	0.0102	8.01	4.14E-05	3.90E-04	0.90	8.81E-06					
3	0.0105	8.45	4.46E-05	3.96E-04	0.90	8.69E-06					
4	0.0113	8.24	4.29E-05	3.24E-04	0.88	1.31E-05	7.43E-04	1.34E-05	0.88	65633	4.82
5	0.0106	8.12	4.11E-05	3.12E-04	0.88	1.33E-05					
6	0.0110	8.15	4.39E-05	2.85E-04	0.87	1.38E-05					
7	0.0108	8.02	3.80E-05	2.63E-04	0.87	2.06E-05	1.11E-03	1.99E-05	0.89	44466	4.65
8	0.0114	8.10	3.93E-05	3.54E-04	0.90	1.90E-05					
9	0.0105	8.00	3.97E-05	2.95E-04	0.88	2.01E-05					
10	0.0102	8.04	4.06E-05	2.11E-04	0.84	2.79E-05	1.57E-03	2.82E-05	0.83	29541	4.47
11	0.0105	8.03	3.77E-05	1.98E-04	0.84	2.81E-05					
12	0.0101	8.10	3.63E-05	1.68E-04	0.82	2.87E-05					
13	0.0101	8.01	3.04E-05	5.85E-04	0.95	2.42E-05	1.35E-03	2.43E-05	0.95	38971	4.59
14	0.0102	8.05	3.52E-05	5.48E-04	0.94	2.49E-05					
15	0.0100	8.02	3.35E-05	6.12E-04	0.95	2.37E-05					

Table B-31c Ethylcyclohexane adsolubilization of C17-4PO5EOC at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	pH (eq.)	Surf $_{(in-eq)}$ (M)	ECH $_{(in-eq)}$ (M)	X_{adm}	X_{aq}	ECH_equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	K_{adm}	log K_{adm}
16	0.0103	8.04	3.89E-05	4.65E-04	0.92	2.96E-05	1.62E-03	2.92E-05	0.92	31616	4.50
17	0.0108	8.01	4.07E-05	4.94E-04	0.92	2.91E-05					
18	0.0102	8.15	4.12E-05	5.02E-04	0.92	2.89E-05					
19	0.0130	8.00	4.94E-05	3.41E-04	0.87	3.49E-05	2.02E-03	3.63E-05	0.83	22973	4.36
20	0.0107	8.02	4.88E-05	1.69E-04	0.78	3.80E-05					
21	0.0125	8.05	4.81E-05	2.79E-04	0.85	3.60E-05					
22	0.0112	8.05	4.81E-05	2.98E-04	0.86	3.89E-05	2.21E-03	3.98E-05	0.80	20093	4.30
23	0.0100	8.18	4.93E-05	9.45E-05	0.66	4.26E-05					
24	0.0110	8.02	4.87E-05	3.57E-04	0.88	3.79E-05					
25	0.0105	8.10	4.28E-05	3.91E-04	0.90	4.05E-05	2.16E-03	3.89E-05	0.91	23375	4.37
26	0.0131	8.05	4.46E-05	3.35E-04	0.88	4.15E-05					
27	0.0102	8.12	4.37E-05	7.15E-04	0.94	3.46E-05					
28	0.0111	8.06	4.62E-05	3.01E-04	0.87	4.52E-05	2.57E-03	4.62E-05	0.75	16263	4.21
29	0.0117	8.38	4.84E-05	4.83E-05	0.50	4.97E-05					
30	0.0110	8.11	4.86E-05	3.82E-04	0.89	4.37E-05					

Table B-32 Ethylcyclohexane adsolubilization of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	ECH	Surf_initial		Surf_equilibrium		Surf $_{(in\text{-}eq)}$	ECH_initial	ECH_equilibrium		ECH $_{(in\text{-}eq)}$
	(μl)	Area	Conc. (M)	Area	Conc. (M)	(M)	Conc. (M)	Area	Conc. (M)	(M)
1	5	658.2	6.08E-04	560.8	5.59E-04	4.87E-05	8.79E-04	28.4	6.41E-04	2.38E-04
2	5	658.2	6.08E-04	559.4	5.59E-04	4.94E-05	8.79E-04	35.4	7.34E-04	1.45E-04
3	5	658.2	6.08E-04	561.2	5.59E-04	4.85E-05	8.79E-04	34.0	7.15E-04	1.64E-04
4	6	658.2	6.08E-04	562.3	5.60E-04	4.80E-05	1.05E-03	42.7	8.30E-04	2.20E-04
5	6	658.2	6.08E-04	565.1	5.61E-04	4.66E-05	1.05E-03	45.0	8.60E-04	1.90E-04
6	6	658.2	6.08E-04	566.4	5.62E-04	4.59E-05	1.05E-03	41.3	8.11E-04	2.39E-04
7	7	658.2	6.08E-04	570.9	5.64E-04	4.37E-05	1.23E-03	52.6	9.60E-04	2.70E-04
8	7	658.2	6.08E-04	569.5	5.64E-04	4.44E-05	1.23E-03	43.3	8.38E-04	3.92E-04
9	7	658.2	6.08E-04	571.4	5.65E-04	4.34E-05	1.23E-03	48.8	9.10E-04	3.20E-04
10	8	658.2	6.08E-04	565.2	5.61E-04	4.65E-05	1.41E-03	66.2	1.14E-03	2.70E-04
11	8	658.2	6.08E-04	564.7	5.61E-04	4.68E-05	1.41E-03	65.2	1.13E-03	2.83E-04
12	8	658.2	6.08E-04	562.8	5.60E-04	4.77E-05	1.41E-03	66.5	1.14E-03	2.66E-04
13	9	658.2	6.08E-04	569.2	5.63E-04	4.45E-05	1.58E-03	84.3	1.38E-03	2.02E-04
14	9	658.2	6.08E-04	570.1	5.64E-04	4.41E-05	1.58E-03	71.8	1.21E-03	3.66E-04
15	9	658.2	6.08E-04	565.7	5.62E-04	4.63E-05	1.58E-03	81.9	1.35E-03	2.33E-04

Table B-32a Ethylcyclohexane adsolubilization of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

	ECH	Surf_initial		Surf_equilibrium		Surf $_{(in-eq)}$	ECH_initial	ECH_equilibrium		ECH $_{(in-eq)}$
Tube	(μl)	Area	Conc. (M)	Area	Conc. (M)	(M)	Conc. (M)	Area	Conc. (M)	(M)
16	10	658.2	6.08E-04	560.3	5.59E-04	4.90E-05	1.76E-03	80.7	1.33E-03	4.29E-04
17	10	658.2	6.08E-04	559.8	5.59E-04	4.92E-05	1.76E-03	96.9	1.54E-03	2.16E-04
18	10	658.2	6.08E-04	564.1	5.61E-04	4.71E-05	1.76E-03	92.5	1.49E-03	2.74E-04
19	11	658.2	6.08E-04	543.3	5.50E-04	5.75E-05	1.93E-03	73.6	1.24E-03	6.93E-04
20	11	658.2	6.08E-04	547.7	5.53E-04	5.53E-05	1.93E-03	110.2	1.72E-03	2.10E-04
21	11	658.2	6.08E-04	550.5	5.54E-04	5.39E-05	1.93E-03	90.0	1.45E-03	4.77E-04
22	13	658.2	6.08E-04	573.5	5.66E-04	4.24E-05	2.28E-03	100.4	1.59E-03	6.89E-04
23	13	658.2	6.08E-04	569.4	5.64E-04	4.44E-05	2.28E-03	103.9	1.64E-03	6.43E-04
24	13	658.2	6.08E-04	565.7	5.62E-04	4.63E-05	2.28E-03	93.0	1.49E-03	7.87E-04
25	14	658.2	6.08E-04	567.6	5.63E-04	4.53E-05	2.46E-03	120.6	1.86E-03	6.03E-04
26	14	658.2	6.08E-04	565.3	5.61E-04	4.65E-05	2.46E-03	120.1	1.85E-03	6.10E-04
27	14	658.2	6.08E-04	564.5	5.61E-04	4.69E-05	2.46E-03	121.6	1.87E-03	5.90E-04

Table B-32b Ethylcyclohexane adsolubilization of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	pH (eq.)	Surf $_{(in-eq)}$ (M)	ECH $_{(in-eq)}$ (M)	X_{adm}	X_{aq}	ECH_equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	K_{adm}	log K_{adm}
1	0.0107	8.25	4.87E-05	2.38E-04	0.83	1.15E-05	6.97E-04	1.25E-05	0.78	62397	4.80
2	0.0106	8.09	4.94E-05	1.45E-04	0.75	1.32E-05					
3	0.0105	8.20	4.85E-05	1.64E-04	0.77	1.29E-05					
4	0.0109	8.04	4.80E-05	2.20E-04	0.82	1.49E-05	8.34E-04	1.50E-05	0.82	54692	4.74
5	0.0105	8.02	4.66E-05	1.90E-04	0.80	1.55E-05					
6	0.0110	8.05	4.59E-05	2.39E-04	0.84	1.46E-05					
7	0.0115	8.18	4.37E-05	2.70E-04	0.86	1.73E-05	9.03E-04	1.63E-05	0.88	54136	4.73
8	0.0111	8.21	4.44E-05	3.92E-04	0.90	1.51E-05					
9	0.0112	8.15	4.34E-05	3.20E-04	0.88	1.64E-05					
10	0.0103	8.06	4.65E-05	2.70E-04	0.85	2.05E-05	1.14E-03	2.05E-05	0.85	41692	4.62
11	0.0128	8.04	4.68E-05	2.83E-04	0.86	2.03E-05					
12	0.0104	8.01	4.77E-05	2.66E-04	0.85	2.06E-05					
13	0.0103	8.11	4.45E-05	2.02E-04	0.82	2.48E-05	1.31E-03	2.36E-05	0.85	35913	4.56
14	0.0108	8.12	4.41E-05	3.66E-04	0.89	2.18E-05					
15	0.0102	8.15	4.63E-05	2.33E-04	0.83	2.42E-05					

Table B-32c Ethylcyclohexane adsolubilization of C16.5-4POS at 0.001 M NaCl, at pH 8.0-8.5, and at a temperature of 25±2°C

Tube	Alumina (g)	pH (eq.)	Surf $_{(in-eq)}$ (M)	ECH $_{(in-eq)}$ (M)	X_{adm}	X_{aq}	ECH_equilibrium (M)	Avg. X_{aq}	Avg. X_{adm}	K_{adm}	log K_{adm}
16	0.0116	8.00	4.90E-05	4.29E-04	0.90	2.40E-05	1.45E-03	2.62E-05	0.86	32672	4.51
17	0.0105	8.03	4.92E-05	2.16E-04	0.81	2.78E-05					
18	0.0115	8.00	4.71E-05	2.74E-04	0.85	2.68E-05					
19	0.0110	8.01	5.75E-05	6.93E-04	0.92	2.23E-05	1.47E-03	2.65E-05	0.87	32917	4.52
20	0.0103	8.05	5.53E-05	2.10E-04	0.79	3.10E-05					
21	0.0111	8.10	5.39E-05	4.77E-04	0.90	2.62E-05					
22	0.0102	8.14	4.24E-05	6.89E-04	0.94	2.86E-05	1.57E-03	2.83E-05	0.94	33210	4.52
23	0.0105	8.02	4.44E-05	6.43E-04	0.94	2.95E-05					
24	0.0101	8.11	4.63E-05	7.87E-04	0.94	2.69E-05					
25	0.0105	8.18	4.53E-05	6.03E-04	0.93	3.34E-05	1.86E-03	3.35E-05	0.93	27747	4.44
26	0.0123	8.20	4.65E-05	6.10E-04	0.93	3.33E-05					
27	0.0102	8.25	4.69E-05	5.90E-04	0.93	3.37E-05					

BIOGRAPHY

Name: Miss Jirapat Lewlomphaisan

Date of Birth: October 6, 1985

Place of Birth: Bangkok

Nationality: Thai

Education:

2003-2006 Bachelor's degree of science in environmental science, Faculty of science, Silpakorn University, Bangkok, Thailand

2008-2009 Master's degree of science in environmental management (international postgraduate programs), the national center of excellence for environmental and hazardous waste management (NCE-EHWM), Chulalongkorn University, Bangkok, Thailand

Presentation:

- Lewlomphaisan J., Charoensaeng A., Arpornpong N., Panswad D., Sabatini D. A., and Khaodhiar S. "Solubilization and Adsolubilization of Phenylethanol Using Anionic Ethoxy Carboxylate Extended Surfactants on Aluminum Oxide Surface". Proceeding of International Conference on Green and Sustainable Innovation 2009, Chiang Rai, Thailand, December 2 – 4, 2009.

- Lewlomphaisan J., Arpornpong N., Panswad D., Charoensaeng A., Sabatini D. A., and Khaodhiar S. "Adsolubilization of Phenylethanol into Anionic Carboxylate and Sulfate Extended Surfactants Modified Aluminum Oxide Surface". Proceeding of 2010 International Conference on Chemical Engineering and Applications (CCEA 2010), Singapore, February 26-28, 2010.